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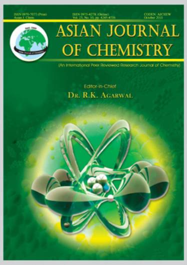

Calculation of $CaCO_3$ Solubility (Precipitability) in Natural Waters

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It is an important issue to calculate the $CaCO_3$ solubility (precipitability) in natural waters in karst geochemistry. This paper pointed out some serious problems in the existing methods dealing with this issue and put forward a new method to calculate the $CaCO_3$ solubility (precipitability) in natural waters. This new method is based on the calculation of $CaCO_3$ saturation index and takes the changes of pH values, activity coefficients and concentration changes of species into account and these factors are studied in open and closed systems, respectively. The results showed that if the above-mentioned changes were ignored, there would be significant errors in the calculated results.

Key Words: Natural waters, $CaCO_3$ solubility (precipitability), Calculation method, Saturation index.

INTRODUCTION

Calcium carbonate is a kind of usual compound in karst area forming the minerals of calcite and aragonite. The dissolution and precipitation of $CaCO_3$ play a significant role in karst hydrogeology. Study on the dissolution and precipitation of $CaCO_3$ can help us to understand the evolution of karst aquifers and to prevent karstic environmental hazards. Some work related to the dissolution and precipitation of $CaCO_3$ has been done recently[1-8]. For example, Cubillas *et al.*[1] studied the experimental dissolution rate of $CaCO_3$ at 25 ºC using a pH-4 HCl inlet solution. Another recent study conducted by Veress[4] investigated several factors on karstification and the results revealed that karren formation was more intense on slopes with *Pinus mugo* than on bare slopes and the dissolution process was controlled by wind.

Natural waters are usually in a non-equilibrium state with $CaCO_3$. The unsaturated water will dissolve $CaCO_3$, while oversaturated water will form $CaCO_3$ precipitation. For a given natural water, when it is unsaturated with $CaCO_3$, how much $CaCO_3$ will dissolve in it and when it is oversaturated with $CaCO_3$, how much $CaCO_3$ will precipitate from the water? This is a key question in the research of karst geochemistry. However, this question has not been properly answered and the literatures related are rare as well. Although a limited number of literatures have discussed this issue in detail, the methods used have some problems. For example, in a study conducted by the Karst Geology Research Institute of the Academy of Chinese Geological Sciences[9], the $CaCO_3$ solubility in natural water was calculated by formula (1).

$$\text{ACa} = \text{ECa} - \text{DCa} \qquad (1)$$

where, DCa is the Ca^{2+} concentration in water sample, ECa is the equilibrium concentration of Ca^{2+} under a given pressure of CO_2 (P_{CO_2}), which is calculated by the following formula:

$$\text{ECa} = \frac{K_C[H^+]^2 \times 40.08}{K_1 K_2 K_s \gamma_{Ca} P_{CO_2}} \qquad (2)$$

where, K_C is the solubility product of $CaCO_3$, K_s is Henry constant, K_1, K_2 are the first and second ionization constants of H_2CO_3, respectively, γ_{Ca} is the activity coefficient of Ca^{2+}, $[H^+]$ stands for the H^+ concentration in water. The formula (2) is derived based on the chemical reactions listed below:

$CO_2 + H_2O = H_2CO_3$	K_s
$H_2CO_3 = H^+ + HCO_3^-$	K_1
$HCO_3^- = H^+ + CO_3^{2-}$	K_2
$CaCO_3 = Ca^{2+} + CO_3^{2-}$	K_C

It must be noted that ECa calculated by formula (2) is the equilibrium concentration of Ca^{2+} in mg/L. ACa obtained by formula (1) stands for the solubility of $CaCO_3$ (in mg/L) denoted by Ca. The solubility of $CaCO_3$ (in mg/L) denoted by $CaCO_3$ can be calculated by:

$$\text{ACa}(CaCO_3) = \text{ACa}(Ca^{2+}) \times \frac{100.08}{40.08} \qquad (3)$$

In the method, the equilibrium concentration of Ca^{2+} calculated by formula (2) has the following problems: (1) The activity coefficients of Ca^{2+} and CO_3^{2-} will decrease with the dissolution of $CaCO_3$ in water, which will promote the dissolution of $CaCO_3$ and the dissolution of $CaCO_3$ will further make the activity coefficients of Ca^{2+} and CO_3^{2-} smaller. On the contrary, with the precipitation of $CaCO_3$, the activity coefficients of Ca^{2+} and CO_3^{2-} will increase. Therefore, the activity coefficient changes should be taken into account in the calculation of the $CaCO_3$ solubility and precipitability in natural waters. (2) With the dissolution or precipitation of $CaCO_3$, CO_3^{2-} will either enter into or precipitate from the solution. In both cases, the carbonate equilibrium in the solution will be re-adjusted, causing the pH value of the solution changed. In formula (2), pH value changes during the dissolution or precipitation process of $CaCO_3$ are not considered. (3) Ca^{2+} exists in water in several forms, in addition to the free Ca^{2+}, there are still $CaCO_3^0$, $CaSO_4^0$, $CaHCO_3^-$, $CaOH^+$, *etc*. The dissolution and precipitation of $CaCO_3$ will undoubtedly lead to the changes of their concentrations and these changes will in turn affect the dissolution or precipitation of $CaCO_3$. Therefore, the concentration changes of various forms of Ca^{2+} in water should be taken into account during the $CaCO_3$ solubility and precipitability calculation. (4) Even for the same solution, its ability to dissolve (precipitate) $CaCO_3$ is not the same due to the environmental conditions. In an open system, the solubility of $CaCO_3$ in water is significantly greater than that in a closed system because of a steady supply of additional CO_2. The situation of precipitation is just the opposite. When the $CaCO_3$ precipitates in an open system, CO_2 will escapes from the solution, which will cause the precipitation of $CaCO_3$ to be greater than that in a closed system.

It can be seen from the above analysis that the calculation of solubility and precipitability of $CaCO_3$ in natural waters should take these changes into account and the open system and closed system should be distinguished as well.

EXPERIMENTAL

Basic principle of the methods: The calculation of $CaCO_3$ solubility in natural waters is virtually the calculation of the amount of $CaCO_3$ needs to be dissolved in water to get an equilibrium state in unsaturated solution, and the calculation of $CaCO_3$ precipitability is virtually the calculation of the amount of $CaCO_3$ needs to be precipitated from water to get an equilibrium state in oversaturated solution. The indicator measuring the saturation state is called saturation index (SI), which is defined as:

$$SI = \frac{\{Ca^{2+}\}\{CO_3^{2-}\}}{K_C} \qquad (4)$$

In the formula (4), SI is the saturation index of water with respect to $CaCO_3$ (calcite), $\{Ca^{2+}\}$ and $\{CO_3^{2-}\}$ are respectively the activities of Ca^{2+} and CO_3^{2-} in the solution, K_C is the solubility product of calcite. When SI < 1, the solution is unsaturated with $CaCO_3$ and $CaCO_3$ will dissolve, when SI > 1, the solution is oversaturated with $CaCO_3$ and $CaCO_3$ will precipitate and when SI = 1, the solution is in equilibrium with $CaCO_3$ and no dissolution or precipitation will occur.

According to the definition of saturation index, when calculating the $CaCO_3$ solubility in natural waters, a preliminary dissolution amount of $CaCO_3$ named testing dissolution amount (TDA) can be given according to the water chemistry analysis results and calculated results of saturation index. Using testing dissolution amount, SI can be calculated by formula (4). If SI > 1, it shows the given testing dissolution amount is too large and it needs to be reduced, if SI < 1, it shows the given testing dissolution amount is too small and needs to be increased and when SI = 1, it shows the given testing dissolution amount is exactly the amount of $CaCO_3$ that the solution can dissolve. Whether SI > 1 or SI < 1, the $CaCO_3$ solubility can be obtained by reducing or increasing the testing dissolution amount. Similarly, when calculating the $CaCO_3$ precipitability of oversaturated solutions, a testing precipitation amount (TPA) can be given and SI is calculated by formula (4) using testing precipitation amount. If SI > 1, it shows the given testing precipitation amount is too small. If SI < 1, it shows the given testing precipitation amount is too large and if SI = 1, the given testing precipitation amount is equal to the amount of $CaCO_3$ that can be precipitated from the solution. Whether SI > 1 or SI < 1, the amount of $CaCO_3$ can be precipitated from the solution can be obtained by reducing or increasing the testing precipitation amount.

It can be seen from the above discussion, the key point for calculating $CaCO_3$ solubility or precipitability in natural water is the calculation of SI after a certain amount of $CaCO_3$ is dissolved into or precipitated from the water, which in turn needs to calculate the activities of Ca^{2+} and CO_3^{2-} in solution.

Calculation of Ca^{2+} and CO_3^{2-} activities: Activity is obtained by multiplying the activity coefficient and the concentration. In natural waters, due to the complicated complexation of anions and cations, the water chemistry analysis results is unable to reflect the real forms of the species in the solution. Table-1 lists the water chemistry analysis results of 8 natural waters. In the solutions, Ca^{2+} can be joined by other anions, forming $CaSO_3^0$, $CaCO_3^0$, $CaHCO_3^+$ and $CaOH^+$. Similarly, other cations and anions can also be joined by the oppositely charged ions to form complex species. Table-2 lists the solution chemical model according to the water analysis results listed in Table-1 and the model contains a total of 26 species, including 9 basic components and 17 derived species. Since species are interacted by the chemical equilibrium in water, the

TABLE-1
CHEMICAL ANALYSIS RESULTS OF WATER SAMPLES (mg/L)

Sample No.	pH	t °C	Cl^-	SO_4^{2-}	CO_3^{2-}	HCO_3^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	SI
1	7.36	16.0	4.25	5.76	0.0	53.70	1.05	0.86	18.04	0.97	0.064
2	7.61	13.0	2.84	6.72	0.0	73.24	0.60	0.30	23.25	2.92	0.180
3	6.76	20.0	24.82	29.78	0.0	165.97	14.45	2.15	62.52	2.92	0.129
4	7.39	21.3	9.22	7.68	0.0	180.62	3.55	0.55	60.92	2.19	0.807
5	8.62	12.0	2.84	18.25	9.6	165.97	0.30	0.00	64.13	1.06	10.340
6	8.26	20.0	4.96	12.49	4.8	234.23	1.00	0.00	85.37	0.44	10.435
7	7.50	22.7	2.84	2.88	0.0	200.15	0.85	0.65	63.33	2.68	1.277
8	8.17	23.0	3.30	277.00	0.0	296.00	4.40	15.10	163.00	27.30	16.420

TABLE-2
CHEMICAL MODEL FOR THE STUDIED WATER

Basic components		Derived species		
No.	Constituents	No.	Constituents	Chemical reactions
1	Cl^-	1	$NaCl^0$	$Na^+ + Cl^- = NaCl^0$
2	SO_4^{2-}	2	KCl^0	$K^+ + Cl^- = KCl^0$
3	CO_3^{2-}	3	$H_2SO_4^0$	$2H^+ + SO_4^{2-} = H_2SO_4^0$
4	Na^+	4	HSO_4^-	$H^+ + SO_4^{2-} = HSO_4^-$
5	K^+	5	$NaSO_4^-$	$Na^+ + SO_4^{2-} = NaSO_4^-$
6	Ca^{2+}	6	KSO_4^-	$K^+ + SO_4^{2-} = KSO_4^-$
7	Mg^{2+}	7	$CaSO_4^0$	$Ca^{2+} + SO_4^{2-} = CaSO_4^0$
8	H^+	8	$MgSO_4^0$	$Mg^{2+} + SO_4^{2-} = MgSO_4^0$
9	OH^-	9	$H_2CO_3^0$	$2H^+ + CO_3^{2-} = H_2CO_3^0$
		10	HCO_3^-	$H^+ + CO_3^{2-} = HCO_3^-$
		11	$CaCO_3^0$	$Ca^{2+} + CO_3^{2-} = CaCO_3^0$
		12	$MgCO_3^0$	$Mg^{2+} + CO_3^{2-} = MgCO_3^0$
		13	$CaHCO_3^+$	$Ca^{2+} + H^+ + CO_3^{2-} = CaHCO_3^+$
		14	$MgHCO_3^+$	$Mg^{2+} + H^+ + CO_3^{2-} = MgHCO_3^+$
		15	$CaOH^+$	$Ca^{2+} + OH^- = CaOH^+$
		16	$MgOH^+$	$Mg^{2+} + OH^- = MgOH^+$
		17	H_2O	$H^+ + OH^- = H_2O$

concentration of each species must be calculated simultaneously to determine the concentrations of Ca^{2+} and CO_3^{2-}. The following non-linear programming problems were summarized in a previous study[10].

$$\begin{cases} \min|ZI| = \left|\sum_{k=1}^{m} a_k z_k + \sum_{j=1}^{n} c_j z_j - ZI_0\right| & (5) \\ a_k + \sum_{j=1}^{n} P_{k,j} c_j = T_k \qquad k=1,2.....,m & (6) \\ c_j = K_j F_j^{-1} \prod_{k-1}^{m} a_k^{P_{k,j}} \qquad j=1,2,.......n & (7) \end{cases}$$

where, a_k is the concentration of the k′th basic components, z_k is the electric charge of the k′th basic components, m is the number of the basic components, c_j is the concentration of the j′th derived species, z_j is the electric charge of the j′th derived species, n is the number of derived species, ZI_0 is the charge balance difference caused by water quality analysis error, $P_{k,j}$ is the stoichiometric number, F_j^{-1} is the correction factor for activity coefficient, T_k is the total concentration of all components containing the k′th basic component in water.

The non-linear programming problems can be solved by the Newton-Raphson iteration method combined with Golden Section method[10-12]. After the calculation, the activity coefficients and the concentrations of all species in water can be obtained and of course, Ca^{2+} and CO_3^{2-} are included.

Environmental conditions: Because of the CO_2-H_2O equilibrium, the calculations of $CaCO_3$ solubility and precipitability are different in different environmental conditions.

In a closed system, there is no further recharge of CO_2. For the calculation of $CaCO_3$ solubility and precipitability, all we have to do is simply adjust the testing dissolution (precipitation) amount of $CaCO_3$ and solve the non-linear programming problems of (5), (6) and (7) repeatedly until SI = 1. When SI = 1, the testing dissolution (precipitation) is equal to the amount of $CaCO_3$ that can be dissolved into or precipitated from water in a closed system. When a testing dissolution (precipitation) amount is added, the total concentrations of species containing Ca^{2+} and CO_3^{2-} in the solution will change according to the following relations:

$$T_{Ca} = T^0_{Ca} + \Delta T \tag{8}$$

$$T_C = T^0_C + \Delta T \tag{9}$$

where, T_{Ca} and T_C are the total concentrations of species containing Ca^{2+} and CO_3^{2-} respectively after a given amount of testing dissolution (precipitation) is added, T^0_{Ca} and T^0_C are respectively the total concentrations of species containing Ca^{2+} and CO_3^{2-} in the original solution, and ΔT is the testing dissolution (precipitation) amount of $CaCO_3$.

In an open system, in addition to the dissolution and precipitation of $CaCO_3$, the dissolution and escape of CO_2 must also be taken into account for the calculation of $CaCO_3$ solubility (precipitability) in natural waters. This is because the atmospheric CO_2 and water have a close contact in an open system. For a given open system, the partial pressure of atmospheric CO_2 is constant. Therefore, the concentration of $H_2CO_3^0$ in water should be kept constant in accordance with the Henry's law:

$$[H_2CO_3^0] = K_s P_{CO_2}$$

When $CaCO_3$ dissolves into or precipitates from water, the carbonate equilibrium will readjust. In order to maintain the equilibrium, the atmospheric CO_2 will dissolve into the water or the soluble CO_2 will escape from water. Therefore, in an open system, for a given testing dissolution (precipitation) amount, the total concentrations of species containing CO_3^{2-} should be calculated as follows:

$$T_C = T^0_C + \Delta T + \Delta C \tag{10}$$

where, ΔC is the amount of CO_2 dissolved into or escaped from water in order to maintain the equilibrium between the atmospheric CO_2 and water, ΔT is the testing dissolution (precipitation) amount of $CaCO_3$. For the calculation of ΔC, the non-linear programming problem of (5), (6) and (7) is also needed to be solved. After the testing dissolution (precipitation) amount is added, if the concentration of $H_2CO_3^0$ in water increases, then CO_2 will escape from the water. The ΔC is negative, then adjust ΔC repeatedly and solve the nonlinear programming problem, when the concentration of $H_2CO_3^0$ equals to that in the original solution, ΔC is the escaped amount of CO_2 corresponding to ΔT. If the concentration of $H_2CO_3^0$ in water reduces after the testing dissolution (precipitation) amount is added, then the atmospheric CO_2 will dissolves into the water. At this moment, ΔC is positive, the dissolution amount of CO_2 corresponding to ΔT can be get by adjusting ΔC and solving the nonlinear programming problem repeatedly. The solubility (precipitability) of $CaCO_3$ in natural waters in an open system is the testing dissolution (precipitation) amount when SI = 1 after adding ΔT and ΔC at the same time.

RESULTS AND DISCUSSION

Validation of the calculation methods: The solubility of calcite and aragonite at 25 ºC in pure water was calculated with the methods above to verify the calculation method. The parameters used in the calculation are listed in Table-3. The calculated results were compared with the results reported in literatures[13-15]. The solubility of calcite given by Yuan and Cai[13] and Karst Research Group of the Institute of Geology of the Chinese Academy of Sciences (KRGIGCAS)[14] is 14 mg/L, while the calcite solubility given by Ren and Liu[15] is 14.3 mg/L. The aragonite solubility given by the previous reports is the same, being 15.3 mg/L. Using the above method, the calculated solubilities of calcite and aragonite at 25 ºC in pure water are 14.02 and 15.84 mg/L, respectively. It can be seen that the calculated solubilities of calcite and aragonite in pure water at 25 ºC have good agreement with the reported results, which indicates that the methods developed here can be successfully used to calculate the solubility of $CaCO_3$ in natural water.

TABLE-3
REACTION AMONG SPECIES IN WATER AND THEIR EQUILIBRIUM CONSTANTS

Reactions	Equilibrium constants at 25 ºC
$2H^+ + CO_3^{2-} = H_2CO_3^0$	$10^{-16.69}$
$H^+ + CO_3^{2-} = HCO_3^-$	$10^{-10.33}$
$Ca^{2+} + CO_3^{2-} = CaCO_3^0$	$10^{-3.15}$
$Ca^{2+} + H^+ + CO_3^{2-} = CaHCO_3^+$	$10^{-11.32}$
$Ca^{2+} + OH^- = CaOH^+$	$10^{-2.20}$
$H^+ + OH^- = H_2O$	$10^{-13.999}$
Calcite $CaCO_3(s) = Ca^{2+} + CO_3^{2-}$	$10^{-8.34}$
Aragonite $CaCO_3(s) = Ca^{2+} + CO_3^{2-}$	$10^{-8.22}$

The calculated solubility (precipitability) for the water samples (Table-1) are listed in Table-4. The column named formula (1) is the calculated results by formula (1). In the calculated results, the positive values denote the dissolution amount and the negative values denote precipitation amount.

It can be seen from Table-4, the errors of $CaCO_3$ solubility (precipitability) calculated by formula (1) are significant. For example, the calculated result by formula (1) is 652.171 mg/L for water sample 1, whereas using the method developed in this paper, the calculated result of $CaCO_3$ solubility in open system is 67.31 mg/L and in closed system the result is only 9.49 mg/L. The result of formula (1) is about 10 times of that calculated in an open system and more than 65 times of that in a closed system. Let's take water sample 7 for another example. The precipitability calculated by formula (1) is 39.214 mg/L, but using the method developed in this paper, the calculated precipitabilities in open system and in closed system are, respectively, 13.14 and 4.34 mg/L, which are only 1/3 and 1/9 of the result by formula (1). Similar situations also exist in the other water samples. In short, whether the calculation of solubility or precipitability, the results of formula (1) are too large.

TABLE-4
CALCULATED AMOUNTS OF DISSOLVED (PRECIPITATED) $CaCO_3$ FOR THE WATER SAMPLES

Sample No.	Formula (1)	Open system			Closed system	
	$CaCO_3$	$CaCO_3$	CO_2	pH	$CaCO_3$	pH
1	652.171	67.31	29.22	7.778	9.49	8.402
2	259.165	47.25	20.43	7.866	6.85	8.271
3	1010.26	119.74	52.41	7.099	50.7	7.367
4	29.686	11.35	4.94	7.423	3.66	7.464
5	-145.906	-87.47	-35.07	8.264	-20.39	7.687
6	-194.475	-117.01	-48.37	7.899	-35.37	7.368
7	-39.214	-13.14	-5.69	7.463	-4.34	7.415
8	-386.685	-173.49	-71.03	7.665	-64.5	7.121

In addition, it can also be seen from Table-4 that the $CaCO_3$ solubility in open system is greater than that in closed system and the $CaCO_3$ precipitability in open system is also greater than that in closed system. The reason for this is that in an open system, with the dissolution of $CaCO_3$, the atmospheric CO_2 will dissolve into water and CO_2 will escape from the water with the precipitation of $CaCO_3$. For example, for water sample 3, when 119.74 mg/L of $CaCO_3$ dissolved into water in an open system, 52.41 mg/L of CO_2 dissolved into water along with. But in a closed system, there is no CO_2 dissolution, so the amount of dissolved $CaCO_3$ was only 50.70 mg/L. For water sample 5, when 87.47 mg/L of $CaCO_3$ precipitated in open system, 35.07 mg/L of CO_2 escaped from the water. But in closed system, there is no CO_2 escaped, so the amount of precipitated $CaCO_3$ is only 20.39 mg/L. And because of this, the pH value of water in open system is lower than that in closed system when dissolution equilibrium is reached, and the pH value of water in open system is higher than that in closed system when precipitation equilibrium is reached.

In order to study the other factors impacting $CaCO_3$ dissolution (precipitation) in natural waters, Table-5 lists some parameters including activity coefficients of Ca^{2+} and CO_3^{2-} before and after the dissolution of $CaCO_3$, the concentrations of species containing Ca^{2+} and the calculation results of pH values.

It can be concluded from Table 5 that: (1) For unsaturated solution, the activity coefficients of Ca^{2+} and CO_3^{2-} at equilibrium state, both in open system or closed system, are smaller than those in the original solution. But for oversaturated solution, the activity coefficients of Ca^{2+} and CO_3^{2-} at equilibrium in open system and closed system are larger than those in the original solution; (2) For water unsaturated with $CaCO_3$, when it reaches the equilibrium state in open system or closed system, the concentrations of $CaSO_3^0$, $CaCO_3^0$, $CaHCO_3^+$ and $CaOH^+$ in water will increase. But for water

TABLE-5
COMPARISON OF SEVERAL PARAMETERS BEFORE AND AFTER THE DISSOLUTION OF $CaCO_3$

Conditions	Sample No.	$\gamma_{CO_3^{2-}}$	γ_{Ca}	Ca^{2+} (mmol/L)	$CaSO_4^0$ (μmol/L)	$CaCO_3^0$ (μmol/L)	$CaHCO_3^+$ (μmol/L)	$CaOH^+$ (μmol/L)	pH
Original solution	1	0.839	0.842	0.447	1.762	0.268	2.367	0.001	7.360
	2	0.818	0.821	0.574	2.410	0.733	3.839	0.001	7.610
	3	0.730	0.738	1.520	23.242	0.563	19.298	0.001	6.760
	4	0.742	0.749	1.485	6.136	3.552	27.932	0.004	7.390
	5	0.743	0.749	1.526	13.798	41.613	22.147	0.026	8.620
	6	0.714	0.723	2.027	12.311	45.461	49.530	0.031	8.260
	7	0.740	0.747	1.541	2.395	5.682	34.063	0.005	7.500
	8	0.599	0.615	3.578	325.878	73.313	98.222	0.052	8.170
Open system	1	0.774	0.779	1.102	3.592	4.201	14.432	0.004	7.778
	2	0.776	0.781	1.034	3.834	4.070	11.972	0.004	7.866
	3	0.677	0.687	2.653	33.745	4.356	69.671	0.003	7.099
	4	0.736	0.743	1.593	6.442	4.403	32.155	0.004	7.423
	5	0.805	0.809	0.712	7.795	4.025	4.767	0.006	8.264
	6	0.786	0.791	0.942	7.196	4.357	10.661	0.007	7.899
	7	0.748	0.754	1.416	2.258	4.451	28.966	0.005	7.463
	8	0.639	0.652	2.094	222.982	4.464	18.843	0.010	7.665
Closed system	1	0.828	0.831	0.536	2.048	4.200	3.378	0.009	8.402
	2	0.811	0.814	0.638	2.627	4.070	4.662	0.006	8.271
	3	0.705	0.714	2.000	28.105	4.356	37.223	0.004	7.367
	4	0.740	0.747	1.520	6.234	4.404	29.231	0.004	7.464
	5	0.753	0.760	1.364	12.769	4.025	18.318	0.003	7.687
	6	0.731	0.739	1.728	11.097	4.358	36.848	0.003	7.368
	7	0.742	0.749	1.501	2.351	4.448	32.391	0.004	7.415
	8	0.612	0.627	3.065	293.554	4.466	66.683	0.004	7.121

oversaturated by $CaCO_3$, when it reaches the equilibrium state, the contents of the above-mentioned species in water will decrease to different degrees; (3) Both in open and closed systems, pH values of water will increase with the dissolution of $CaCO_3$ and will decrease with the precipitation of $CaCO_3$.

The activity coefficients of species, the concentrations of Ca^{2+} complex and the changes of pH values are interrelated and indivisible and they all have great influences on the calculated results of $CaCO_3$ solubility (precipitability) in natural waters. Therefore, in the calculation of $CaCO_3$ solubility (precipitability) in natural waters, the above changes must be handled simultaneously.

Conclusion:

(1) The calculation of $CaCO_3$ solubility (precipitability) in natural waters must be based on the calculation of equilibrium distribution of species, the open system and closed system should be distinguished and at the same time, the changes of the pH values and activity of species with the $CaCO_3$ dissolution (precipitation) should be taken into account. (2) The essence of $CaCO_3$ solubility (precipitability) calculation in natural waters is to calculate the amount of $CaCO_3$ that can dissolve into or precipitate from water when a dissolution and precipitation balance of $CaCO_3$ is reached. The key issue is to calculate the activity of Ca^{2+} and CO_3^{2-} in water. (3) Without considering the activity coefficients, the concentrations of Ca^{2+} complex and the changes of pH values in water, the error of $CaCO_3$ solubility (precipitability) calculation is significant and the calculated results will greatly exceed the actual dissolution (precipitation) ability. (4) The $CaCO_3$ dissolution of unsaturated water in open system is larger than that in closed system and the $CaCO_3$ precipitation of oversaturated water in open system is larger than that in closed system. The reason for this is that in open system, the atmospheric CO_2 will dissolve into water with the dissolution of $CaCO_3$ and the soluble CO_2 will escape from water with the precipitation of $CaCO_3$.

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