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SHORT COMMUNICATIONS

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Solubility of Rhodochrosite and Speciation of Manganese(II) in Seawater

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INTRODUCTION

Rhodochrosite, $MnCO_3$, is the main mineral of sedimentary manganese carbonate ores [1]. It occurs in reduced layers of the bottom deposits of seas and oceans [2, 3] and was also repeatedly found in oxidizing environments as a relic of previous reducing processes [4]. Evidence on the physicochemical properties of rhodochrosite and, especially, its solubility is of prime importance for the determination of the conditions and mechanisms of formation of this mineral. Despite the fact that rhodochrosite solubility has been addressed in a number of publications, even the values of the thermodynamic solubility product of $MnCO_3$ recommended in handbooks are significantly different: 5.0×10^{-10} [5], 5.6×10^{-10} [6], and 1.8×10^{-11} [7]. The calculated estimates of species concentrations are even more controversial. In particular, the formation of complexes with inorganic ligands may result in an increase in the solubility of minerals of heavy metals by one–two orders of magnitude [8–10]. The goal of this study was to elucidate the physicochemical conditions of rhodochrosite formation in the ocean on the basis of experimental data on $MnCO_3$ solubility in seawater.

EXPERIMENTAL METHODS

Manganese carbonate with a distinct rhodochrosite crystal structure (determined by X-ray diffraction analysis) was synthesized by the method of [11] and used in our experiments.

In the first experimental series, the solubility of $MnCO_3$ was determined in diluted $NaClO_4$–HNO_3 solutions with an ionic strength of $I = 0.05$ and a nitrate content of 0.1–1.0 mM. The experimental pH value varied from 7.1 to 7.3. In the second experimental series, synthetic seawater was used with a salinity of 21–35‰ prepared by the procedure described by D.R. Kester. The pH value was monitored between 7.1 and 7.8 by adding seawater of a desired salinity in which 0.1 M NaCl was replaced by the equivalent amount of HCl. The solid phase to solution weight ratio was constant at 1 : 400 in both series. The experimental runs lasted eight months at a temperature of $25 \pm 2°C$. The flasks were periodically (once a week) opened and intensely stirred in order to equalize CO_2 partial pressures in the solutions and in the atmosphere.

Before analysis the samples were filtered through a fine paper filter ("blue band"), immediately after which pH value and carbonate alkalinity were measured in the filtrate by potentiometry and volume acidimetric titration, respectively, and the concentrations of dissolved manganese were measured in aliquots with added HCl by atomic absorption spectrometry on a Hitachi Z-8000 spectrophotometer with an air–acetylene flame. The relative uncertainties of the measurements were ± 0.005 pH and $\pm 2\%$ for alkalinity and manganese concentration. The experimental results are shown in Tables 1 and 2.

RESULTS AND DISCUSSION

Because of the low stability of the ionic pairs $NaClO_4^0$, $NaNO_3^0$, $MnClO_4^+$, and $MnNO_3^+$, their occurrence in diluted $NaClO_4$–HNO_3 solution can be ignored. The same is true of $NaHCO_3^0$, $NaCO_3^-$, and $MnHCO_3^+$, whose stability constants are 0.65, 7.9, and 6.3, respectively [7, 13]. The relatively stable $MnCO_3^0$ complex with a stability constant of $\sim 1.6 \times 10^5$ [14] yields a negligible contribution to the total manganese concentration at pH = 7.1–7.3, but its concentration may be more

Table 1. Solubility of rhodochrosite in diluted solutions with an ionic strength of $I = 0.05$ at $25°C$

Starting concentration, mM		Equilibrium value			
$NaClO_4$	HNO_3	pH	alkalinity Alk, mg-eq/l	concentration of ΣMn, µM	K_r^0/P_{CO_2} $\times 10^{10}$
49.00	1.00	7.11	0.12	397	2.92
49.50	0.50	7.16	0.19	231	2.14
49.75	0.25	7.23	0.23	159	2.03
49.90	0.10	7.31	0.25	114	2.10

than an order of magnitude higher than that of free CO_3^{2-} ions.

Taking into account these considerations, the following relations hold for the experiments with diluted sodium perchlorate solutions:

$$[\Sigma Mn] \approx [Mn^{2+}] \qquad (1)$$

and

$$Alk = [HCO_3^-] + 2[CO_3^{2-}] + 2[MnCO_3^0], \qquad (2)$$

where $[\Sigma Mn]$ and $[Mn^{2+}]$ are the total (analytical) manganese concentration and the concentration of free Mn^{2+} ions in the solution, respectively; Alk is the carbonate alkalinity; $[HCO_3^-]$, $[CO_3^{2-}]$, and $[MnCO_3^0]$ are the concentrations of free HCO_3^-, CO_3^{2-}, and $MnCO_3^0$ species, respectively. Equation (2) can be recast as

$$Alk = a_{CO_3^{2-}}\left(\frac{a_{H^+}}{K_2^0\gamma_{HCO_3^-}} + \frac{2}{\gamma_{CO_3^{2-}}}\right) + 2[MnCO_3^0], \qquad (3)$$

where $a_{CO_3^{2-}}$ and a_{H^+} are the activities of CO_3^{2-} and H^+; K_2^0 is the thermodynamic constant of the second-stage dissociation of carbonic acid, which equals 4.69×10^{-11} at 25°C [15]; γ is the activity coefficient of free ions, which can be calculated with an adequate accuracy by the third-approximation Debye–Hückel equation modified by Davies [16].

Since the thermodynamic stability constant of the $MnCO_3^0$ species and the thermodynamic solubility product of $MnCO_3$ are, respectively

$$K_{MnCO_3^0}^0 = \frac{a_{MnCO_3^0}}{a_{Mn^{2+}}a_{CO_3^{2-}}} \qquad (4)$$

and

$$L_{MnCO_3}^0 = a_{Mn^{2+}}a_{CO_3^{2-}}, \qquad (5)$$

assuming that $\gamma_{MnCO_3^0} = 1$ for all electrically neutral species in the Debye–Hückel theory, we obtain

$$[MnCO_3^0] \approx a_{MnCO_3^0} = L_{MnCO_3}^0 K_{MnCO_3^0}^0. \qquad (6)$$

Table 2. Solubility of rhodochrosite in seawater with salinities of 21 and 35‰ at 25°C

| Ionic strength I | Equilibrium value | | | $\gamma^*_{Mn^{2+}}$ |
	pH	alkalinity Alk, mg-eq/l	concentration of ΣMn, μM	
Seawater with a salinity of 21‰				
0.4	7.84	1.20	16.7	0.261
0.4	7.83	1.15	18.7	0.245
0.4	7.81	1.13	22.2	0.226
0.4	7.81	1.08	23.7	0.212
0.4	7.75	0.95	27.8	0.238
0.4	7.69	0.82	37.8	0.230
0.4	7.62	0.70	53.0	0.227
0.4	7.52	0.60	79.0	0.241
0.4	7.19	0.28	386	0.226
			Average:	0.234 ± 0.014
Seawater with a salinity of 35‰				
0.7	7.75	1.05	28.4	0.233
0.7	7.74	1.00	31.3	0.221
0.7	7.70	0.91	33.8	0.246
0.7	7.69	0.87	38.8	0.225
0.7	7.65	0.82	51.0	0.205
0.7	7.60	0.71	63.0	0.209
0.7	7.50	0.56	103	0.203
0.7	7.25	0.32	289	0.229
0.7	7.07	0.21	684	0.221
			Average:	0.221 ± 0.014

Expressing $a_{CO_3^{2-}}$ through the solubility product of $MnCO_3$ and taking into account Eqs. (1) and (6), Eq. (3) can be transformed to

$$Alk = \frac{L_{MnCO_3}^0}{[\Sigma Mn]\gamma_{Mn^{2+}}}\left(\frac{a_{H^+}}{K_2^0\gamma_{HCO_3^-}} + \frac{2}{\gamma_{CO_3^{2-}}}\right) + 2L_{MnCO_3}^0 K_{MnCO_3^0}^0. \qquad (7)$$

Equation (7) contains the unknown quantities $L_{MnCO_3}^0$ and $K_{MnCO_3^0}^0$, which can be determined from the coefficients of the linear approximation

$$y = ax + b, \qquad (8)$$

where $y = Alk$, $x = \dfrac{1}{[\Sigma Mn]\gamma_{Mn^{2+}}}\left(\dfrac{a_{H^+}}{K_2^0\gamma_{HCO_3^-}} + \dfrac{2}{\gamma_{CO_3^{2-}}}\right)$, $a = L_{MnCO_3}^0$, and $b = 2L_{MnCO_3}^0 K_{MnCO_3^0}^0$.

Alk, mg-eq/l
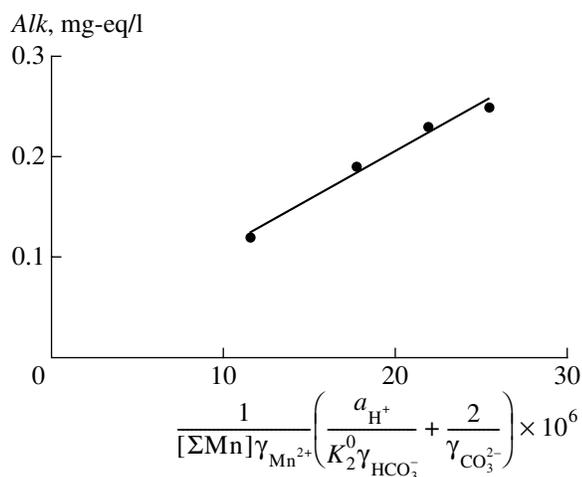
Fig. 1. Relationships between alkalinity and $\dfrac{1}{[\Sigma Mn]\gamma_{Mn^{2+}}}\left(\dfrac{a_{H^+}}{K_2^0\gamma_{HCO_3^-}}+\dfrac{2}{\gamma_{CO_3^{2-}}}\right)$ in experiments on the solubility of rhodochrosite in diluted solutions.

log[ΣMn], M
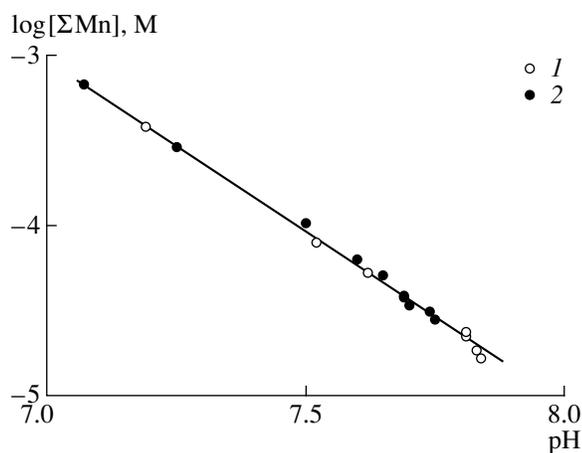
Fig. 2. Concentration of manganese (II) in equilibrium with rhodochrosite as a function of the pH value of seawater with a salinity of (*1*) 21 and (*2*) 35‰.

The coefficients of Eq. (8) were estimated by the analysis of experimental data on the solubility of $MnCO_3$ in diluted solutions (Fig. 1): $a = 9.52 \times 10^{-12}$ and $b = 1.49 \times 10^{-5}$, with a correlation coefficient of $r = 0.992$. These values give $L^0_{MnCO_3} = a = 9.52 \times 10^{-12}$ and $K^0_{MnCO_3^0} = b/2a = 7.82 \times 10^5$. The obtained thermodynamic solubility product of rhodochrosite is lower than the estimates of [5, 6] (5.0×10^{-10} and 5.6×10^{-10}) and close to a value of 1.8×10^{-11} reported in [7]. Our $K^0_{MnCO_3^0}$ value is of the same order of magnitude as the

estimate of [14] (1.6×10^5) obtained by the method of comparative calculation.

The effect of pH on the concentration of dissolved Mn(II) in seawater in equilibrium with rhodochrosite appeared to be indistinguishable for salinities of 21 and 35‰ (Fig. 2), and the slope of the dependency

$$\log[\Sigma Mn] = -2.03pH + 11.21, \quad r = 0.998 \quad (9)$$

corresponds to the reaction

$$MnCO_3 + 2H^+ = Mn^{2+} + H_2O + CO_2 \quad (10)$$
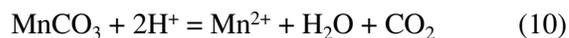
with the thermodynamic equilibrium constant

$$K_r^0 = \frac{a_{Mn^{2+}}P_{CO_2}}{a_{H^+}^2}, \quad (11)$$

where P_{CO_2} is the partial pressure of CO_2. Since

$$a_{Mn^{2+}} = [\Sigma Mn]\gamma^*_{Mn^{2+}}, \quad (12)$$

where $\gamma^*_{Mn^{2+}}$ is the bulk activity coefficient of Mn^{2+}, then

$$\gamma^*_{Mn^{2+}} = \frac{K_r^0 a_{H^+}^2}{P_{CO_2}[\Sigma Mn]}. \quad (13)$$

In the case of equilibrium between the solution and atmospheric air, which was achieved by periodic stirring of samples in open flasks, equal K_r^0/P_{CO_2} values must be obtained in the experiments with diluted sodium perchlorate solutions and seawater of different salinity. For diluted solutions, $\gamma^*_{Mn^{2+}} \approx \gamma_{Mn^{2+}}$. Therefore, using the Davis equation to calculate the activity coefficient of free Mn^{2+} ($\gamma_{Mn^{2+}} = 0.443$ for an ion strength of 0.05), we can determine K_r^0/P_{CO_2} as

$$\frac{K_r^0}{P_{CO_2}} = \frac{[\Sigma Mn]\gamma_{Mn^{2+}}}{a_{H^+}^2}. \quad (14)$$

As can be seen from Table 1, the last three points cluster near the value $K_r^0/P_{CO_2} = 2.09 \times 10^{10}$, which was used for subsequent calculations (the value 2.92×10^{10} in the sample with pH = 7.11 does not strongly change the average K_r^0/P_{CO_2} value, but deviates significantly from other points).

Given the K_r^0/P_{CO_2} value, the bulk activity coefficient of Mn^{2+} in seawater can be estimated by Eq. (13). According to the calculations (Table 2), $\gamma^*_{Mn^{2+}}$ is 0.234 ± 0.014 and 0.221 ± 0.014 for seawater with salinities of 21 and 35‰, respectively. These values are identical within the analytical accuracy to the activity coefficients of free Mn^{2+} calculated by the Davies equa-

log[ΣMn], M
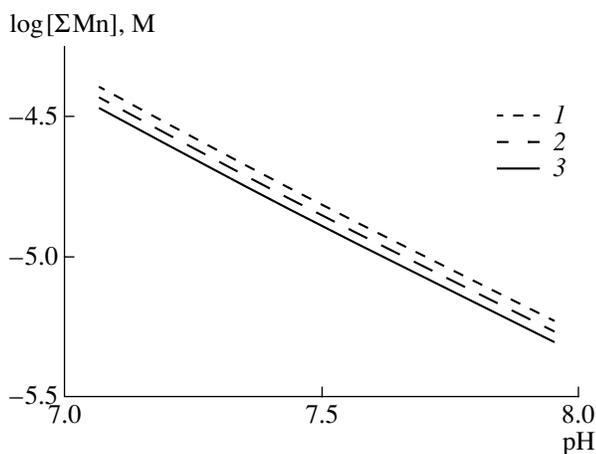
Fig. 3. Solubility of rhodochrosite in seawater with a salinity of 35‰ at various pH and carbonate alkalinity values: (*1*) *Alk* = 2.0 mg-eq/l, (*2*) *Alk* = 2.2 mg-eq/l, and (*3*) *Alk* = 2.4 mg-eq/l.

tion (0.232 and 0.223). This implies that dissolved manganese (II) is strongly dominated by free ions. The published estimates of the speciation of divalent manganese in seawater are strongly variable: the fraction of free Mn^{2+} ions was estimated as 23 [17], 58 [18], and 72% [19]. Although the analysis of our experimental data on $MnCO_3$ solubility suggested a weak complexation of manganese (II) in seawater, this conclusion is not indisputable, because the activity coefficients of transitional metal ions can be very different from the values calculated by the Davies equation.

Given the average value of CO_2 partial pressure in the atmosphere (3.2×10^{-4}), the thermodynamic equilibrium constant of reaction (10), K_r^0, is calculated as 6.69×10^6. P_{CO_2} can be expressed from the values of carbonate alkalinity and activity of hydrogen ions:

$$P_{CO_2} = \frac{Alk \, a_{H^+}^2}{K_h' K_1' (a_{H^+} + 2K_2')}, \quad (15)$$

where K_h', K_1', and K_2' are the Henry constant and concentration constants of the first and second stages of dissociation of carbonic acid (0.031, 9.99×10^{-7}, and 7.68×10^{-10}, respectively) for seawater with a salinity of 35‰ at 25°C [12, 20, 21]. Taking into account Eq. (15), Eq. (13) can be recast to obtain an expression for the calculation of $MnCO_3$ solubility in seawater with a salinity of 35‰ as a function of pH and carbonate alkalinity:

$$[\Sigma Mn] = \frac{K_r^0 K_h' K_1' (a_{H^+} + 2K_2')}{\gamma_{Mn^{2+}}^* Alk}. \quad (16)$$

As can be seen in Fig. 3, the solubility of rhodochrosite at pH = 7.4–7.8 and *Alk* = 2.4 mg-eq/l is 7–

16 μM, which is more than three orders of magnitude higher than the average concentration of manganese (II) in oceanic water (0.002 μM [22–25]) and several times higher than the manganese content in the pore solutions of oxidized pelagic sediments (usually no higher than 1 μM [26]), where dissolved manganese species may be dominated by manganese (IV) hydroxo complexes, $MnO(OH)_2^0$ [17]. This leads us to the conclusion that rhodochrosite can be formed only in reduced bottom sediments where the concentration of manganese (II) is as high as 200–500 μM [27].

CONCLUSIONS

The thermodynamic solubility product of rhodochrosite, $MnCO_3$, and the thermodynamic stability constant of the $MnCO_3^0$ complex were determined at 25°C as 9.52×10^{-12} and 7.82×10^5, respectively.

The experimental values of the bulk activity coefficient of Mn^{2+} ($\gamma_{Mn^{2+}}^*$) in seawater with salinities of 21 and 35‰ are 0.234 and 0.221, respectively. These estimates are identical within the analytical uncertainty to the activity coefficients of free Mn^{2+} ions ($\gamma_{Mn^{2+}}$) calculated using the third-approximation equation of the Debye–Hückel theory modified by Davies.

The solubility of $MnCO_3$ in seawater increases by two orders of magnitude in response to a decrease in pH by one: from ~10 μM at pH = 8 to 1000 μM at pH = 7. The data obtained here allow us to conclude that conditions favorable for rhodochrosite formation can be generated only in bottom deposits with reducing conditions, where the concentration of manganese (II) is as high as 200–500 μM.

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