INTRODUCTION

Rhodochrosite, MnCO₃, 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 MnCO₃ 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 MnCO₃ 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 MnCO₃ was determined in diluted NaClO₄–HNO₃ solutions with an ionic strength of I = 0.05 at 25°C. 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 ± 2°C. The flasks were periodically (once a week) opened and intensely stirred in order to equalize CO₂ 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 ±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 NaClO₄⁻, NaNO₃⁻, MnClO₄⁻, and MnNO₃⁻, their occurrence in diluted NaClO₄–HNO₃ solution can be ignored. The same is true of NaHCO₃⁻, NaCO₃⁻, and MnHCO₃⁻, whose stability constants are 0.65, 7.9, and 6.3, respectively [7, 13]. The relatively stable MnCO₃⁻ complex with a stability constant of ~1.6×10⁵ [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

<table>
<thead>
<tr>
<th>Starting concentration, mM</th>
<th>Equilibrium value</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaClO₄</td>
<td>HNO₃</td>
</tr>
<tr>
<td>49.00</td>
<td>1.00</td>
</tr>
<tr>
<td>49.50</td>
<td>0.50</td>
</tr>
<tr>
<td>49.75</td>
<td>0.25</td>
</tr>
<tr>
<td>49.90</td>
<td>0.10</td>
</tr>
</tbody>
</table>
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:

$$\text{[ΣMn]} \approx \text{[Mn}^{2+}\rbrack$$  \quad (1)

and

$$\text{Alk} = \text{[HCO}_3^{-}\rbrack + 2\text{[CO}_3^{2-}\rbrack + 2\text{[MnCO}_3^{0}\rbrack,$$  \quad (2)

where [ΣMn] 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

$$\text{Alk} = a_{\text{CO}_3^{-}}\left(\frac{a_{H^+}}{K_2^0}\frac{2}{\gamma_{\text{CO}_3^{2-}}}\right) + 2\text{[MnCO}_3^{0}\rbrack,$$  \quad (3)

where $a_{\text{CO}_3^{-}}$ 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 $4.69 \times 10^{-11}$ at 25$^\circ$C [15]; $\gamma$ 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

$$K_{\text{MnCO}_3}^0 = \frac{a_{\text{MnCO}_3^{0}}}{a_{\text{Mn}^{2+}} a_{\text{CO}_3^{-}}}$$  \quad (4)

and

$$L_{\text{MnCO}_3}^0 = a_{\text{Mn}^{2+}} a_{\text{CO}_3^{-}},$$  \quad (5)

assuming that $\gamma_{\text{MnCO}_3^{0}} = 1$ for all electrically neutral species in the Debye–Hückel theory, we obtain

$$\text{[MnCO}_3^{0}\rbrack = a_{\text{MnCO}_3^{0}} = L_{\text{MnCO}_3}^0 K_{\text{MnCO}_3}^0,$$  \quad (6)

Expressing $a_{\text{CO}_3^{-}}$ through the solubility product of MnCO$_3$ and taking into account Eqs. (1) and (6), Eq. (3) can be transformed to

$$\text{Alk} = \frac{L_{\text{MnCO}_3}^0}{[\text{ΣMn}] \gamma_{\text{Mn}^{2+}}} \left(\frac{a_{H^+}}{K_2^0} \frac{2}{\gamma_{\text{CO}_3^{2-}}}\right)$$

$$+ 2L_{\text{MnCO}_3}^0 K_{\text{MnCO}_3}^0.$$  \quad (7)

Equation (7) contains the unknown quantities $L_{\text{MnCO}_3}^0$ and $K_{\text{MnCO}_3}^0$, which can be determined from the coefficients of the linear approximation

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

where $y = \text{Alk}$, $x = \frac{1}{[\text{ΣMn}] \gamma_{\text{Mn}^{2+}}} \left(\frac{a_{H^+}}{K_2^0} \frac{2}{\gamma_{\text{CO}_3^{2-}}}\right)$,

$$a = L_{\text{MnCO}_3}^0,$$ and $$b = 2L_{\text{MnCO}_3}^0 K_{\text{MnCO}_3}^0.$$

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

<table>
<thead>
<tr>
<th>Ionic strength</th>
<th>Equilibrium value</th>
<th>Concentration of ΣMn, µM</th>
<th>$\gamma_\text{Mn}^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>pH</td>
<td>Alk, mg-eq/l</td>
<td></td>
</tr>
<tr>
<td>Seawater with a salinity of 21‰</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>7.84</td>
<td>1.20</td>
<td>16.7</td>
</tr>
<tr>
<td>0.4</td>
<td>7.83</td>
<td>1.15</td>
<td>18.7</td>
</tr>
<tr>
<td>0.4</td>
<td>7.81</td>
<td>1.13</td>
<td>22.2</td>
</tr>
<tr>
<td>0.4</td>
<td>7.81</td>
<td>1.08</td>
<td>23.7</td>
</tr>
<tr>
<td>0.4</td>
<td>7.75</td>
<td>0.95</td>
<td>27.8</td>
</tr>
<tr>
<td>0.4</td>
<td>7.69</td>
<td>0.82</td>
<td>37.8</td>
</tr>
<tr>
<td>0.4</td>
<td>7.62</td>
<td>0.70</td>
<td>53.0</td>
</tr>
<tr>
<td>0.4</td>
<td>7.52</td>
<td>0.60</td>
<td>79.0</td>
</tr>
<tr>
<td>0.4</td>
<td>7.19</td>
<td>0.28</td>
<td>386</td>
</tr>
<tr>
<td>Average: 0.234 ± 0.014</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Seawater with a salinity of 35‰</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.7</td>
<td>7.75</td>
<td>1.05</td>
<td>28.4</td>
</tr>
<tr>
<td>0.7</td>
<td>7.74</td>
<td>1.00</td>
<td>31.3</td>
</tr>
<tr>
<td>0.7</td>
<td>7.70</td>
<td>0.91</td>
<td>33.8</td>
</tr>
<tr>
<td>0.7</td>
<td>7.69</td>
<td>0.87</td>
<td>38.8</td>
</tr>
<tr>
<td>0.7</td>
<td>7.65</td>
<td>0.82</td>
<td>51.0</td>
</tr>
<tr>
<td>0.7</td>
<td>7.60</td>
<td>0.71</td>
<td>63.0</td>
</tr>
<tr>
<td>0.7</td>
<td>7.50</td>
<td>0.56</td>
<td>103</td>
</tr>
<tr>
<td>0.7</td>
<td>7.25</td>
<td>0.32</td>
<td>289</td>
</tr>
<tr>
<td>0.7</td>
<td>7.07</td>
<td>0.21</td>
<td>684</td>
</tr>
<tr>
<td>Average: 0.221 ± 0.014</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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 $L_{\text{MnCO}_3}^0 = a = 9.52 \times 10^{-12}$ and $K_{\text{MnCO}_3}^0 = b/2a = 7.82 \times 10^5$. The obtained thermodynamic solubility product of rhodochrosite is lower than the estimates of [5, 6] ($5.0 \times 10^{-10}$ and $5.6 \times 10^{-10}$) and close to a value of $1.8 \times 10^{-11}$ reported in [7]. Our $K_{\text{MnCO}_3}^0$ value is of the same order of magnitude as the estimate of [14] ($1.6 \times 10^5$) 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

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

corresponds to the reaction

$$\text{MnCO}_3 + 2\text{H}^+ = \text{Mn}^{2+} + \text{H}_2\text{O} + \text{CO}_2 \quad (10)$$

with the thermodynamic equilibrium constant

$$K_r^0 = \frac{a_{\text{Mn}^{2+}}P_{\text{CO}_2}}{a_{\text{H}^+}^2}, \quad (11)$$

where $P_{\text{CO}_2}$ is the partial pressure of CO$_2$. Since

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

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

$$\gamma_{\text{Mn}^{2+}}^* = \frac{K_r^0a_{\text{H}^+}^2}{a_{\text{H}^+}^2P_{\text{CO}_2}[\Sigma\text{Mn}]} \Rightarrow (13)$$

In the case of equilibrium between the solution and atmospheric air, which was achieved by periodic stirring of samples in open flasks, equal $K_r^0/P_{\text{CO}_2}$ values must be obtained in the experiments with diluted sodium perchlorate solutions and seawater of different salinity. For diluted solutions, $\gamma_{\text{Mn}^{2+}}^* = \gamma_{\text{Mn}^{2+}}^*$. Therefore, using the Davis equation to calculate the activity coefficient of free Mn$^{2+}$ ($\gamma_{\text{Mn}^{2+}}^* = 0.443$ for an ion strength of 0.05), we can determine $K_r^0/P_{\text{CO}_2}$ as

$$\frac{K_r^0}{P_{\text{CO}_2}} = \frac{[\Sigma\text{Mn}]\gamma_{\text{Mn}^{2+}}^*}{a_{\text{H}^+}^2}. \quad (14)$$

As can be seen from Table 1, the last three points cluster near the value $K_r^0/P_{\text{CO}_2} = 2.09 \times 10^{10}$, which was used for subsequent calculations (the value $2.92 \times 10^{10}$ in the sample with pH = 7.11 does not strongly change the average $K_r^0/P_{\text{CO}_2}$ value, but deviates significantly from other points).

Given the $K_r^0/P_{\text{CO}_2}$ value, the bulk activity coefficient of Mn$^{2+}$ in seawater can be estimated by Eq. (13). According to the calculations (Table 2), $\gamma_{\text{Mn}^{2+}}^*$ is $0.234 \pm 0.014$ and $0.221 \pm 0.014$ 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-
dissociation of carbonic acid (0.031, 0.03, 0.029) and concentration constants of the first and second stages of rhodochrosite at pH = 7.4–7.8 and 7.68, respectively. These estimates are identical within the analytical uncertainty to the activity coefficients of free Mn2+ ions (γMn2+) calculated using the third-approximation equation of the Debye–Hückel theory modified by Davies.

The solubility of MnCO3 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.

ACKNOWLEDGMENTS

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