

Manganese(II) partitioning during formation of MnCO_3 - CaCO_3 solid-solutions in suboxic aqueous solutions

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In anoxic sediments, the rhombohedral carbonates calcite (CaCO_3) and rhodochrosite (MnCO_3) form solid-solutions within a wide compositional range (e.g. Pedersen and Price, 1982) which have been suggested to be valuable indicators for the characterization of bottom-water redox conditions in the deeps of the Baltic Sea (Huckriede and Meischner, 1996). The formation of Ca-rhodochrosites seems to be related to oxygenation events (salt water inflows from the North Sea) followed by intense microbial activity at the sediment-water interface connecting the biogeochemical cycles of manganese, carbon, and sulphur (Huckriede and Meischner, 1996). The formation of mixed calcium-manganese(II) carbonates has been found in microbiological and inorganic precipitation experiments (e.g. Aller and Rude, 1988; Mucci, 1988). The exact formation conditions on a mechanistic and quantitative base, however, are still not fully understood. In the present study, the influence of precipitation conditions on $\text{Mn}^{2+}/\text{Ca}^{2+}$ partitioning during the formation of the complete rhodochrosite-calcite ($\text{Mn}_x\text{Ca}_{(1-x)}\text{CO}_3$) solid-solution ('RCSS') series from aqueous solutions is investigated at ambient temperature. Additionally, the possible effects of temperature (20–90°C) and dissolved magnesium are considered. The present study extends the investigated boundary conditions for the formation of rhodochrosite-calcite solid-solutions from aqueous solutions.

Experimental methods

Rhodochrosite-calcite solid-solutions ('RCSS') were prepared by three different methods. Conditions at 20°C were chosen to obtain different precipitation rates ($A \gg B > C$):

Method A: RCSS were precipitated at 20°C by the dropwise addition of 5 ml of an aqueous 2 M $(\text{Ca},\text{Mn},\text{Mg})(\text{NO}_3)_2$ or $(\text{Ca},\text{Mn})\text{Cl}_2$ solution to 100 ml of a vigorously agitated 0.5 M NH_4HCO_3 solution under N_2 gas (Böttcher, 1998). Method B: 100 ml of a 0.025 M NaHCO_3 solution was added to a 100 ml of a 2.5 M $(\text{Ca},\text{Mn})\text{Cl}_2$ solution at 20, 60 and 90°C. The unstirred resulting solution was allowed to slowly

degass CO_2 under a slow stream of N_2 passing leading to the precipitation of RCSS on the walls of a Duran glass bottle (Böttcher, 1998). Method C: Powdered aragonite was transformed into RCSS at 20°C in 2 M $(\text{Ca},\text{Mn})\text{Cl}_2$ solutions (Böttcher, 1997). Solid run products were characterized by AAS, powder XRD, and infrared and Raman spectroscopy. No other solid phases than anhydrous carbonates were observed. Aqueous solutions in the method C runs were analysed by AAS and ICP-AES. A partition coefficient D for manganese(II) partitioning between the aqueous solution ('aq') and the solid-solution ('ss') was calculated according to ($[]$ are molar concentrations):

$$D = ([\text{Mn}^{2+}]/[\text{Ca}^{2+}]_{\text{ss}})/([\text{Mn}^{2+}]/[\text{Ca}^{2+}]_{\text{aq}}) \quad (1)$$

Results and discussion

In both experimental series using method A and B, the precipitation of the complete rhodochrosite-

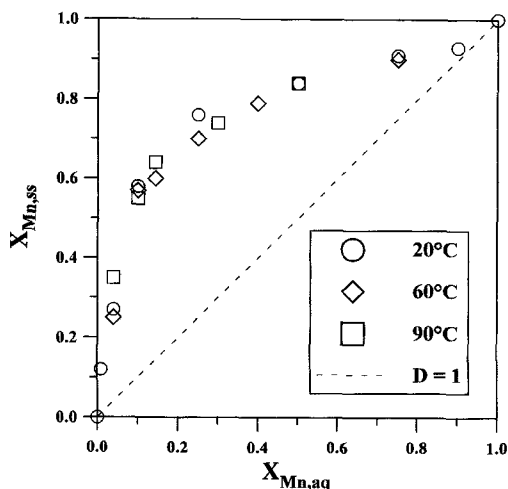


FIG. 1. The compositional relations between aqueous and solid-solutions during the precipitation of RCSS (Method B). $X_{\text{Mn,ss}}$, $X_{\text{Mn,aq}}$: Manganese mole fraction in the solid and liquid phase.

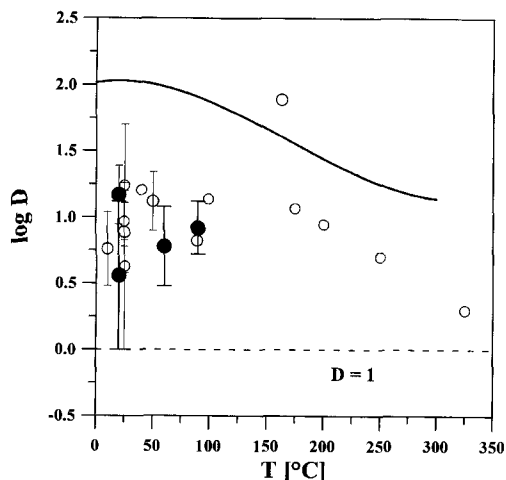


FIG. 2. Range of experimentally determined D values as a function of temperature. Closed symbols: This study (Böttcher 1997, 1998); open symbols: literature data (compiled by Böttcher, 1998). Solid line: Theoretical exchange equilibrium distribution coefficient.

calcite solid-solution series was observed and no indication for the presence of miscibility gaps was found (e.g. Fig. 1). At very high precipitation rates (Method A), no fractionation of the cations between aqueous solution and solid-solution was observed (\equiv partition coefficient (D) of 1). These results were not influenced by the presence of dissolved magnesium. Mg^{2+} , however, coprecipitating with Ca^{2+} and Mn^{2+} in a multicomponent carbonate solid-solution ($Mn_xCa_yMg_zCO_3$) was generally depleted with respect to the liquid. The range of magnesium contents of ternary solid-solutions which were produced in different types of precipitation experiments at ambient temperature was surprisingly small and in good agreement with the compositions of authigenic carbonates in sediments of the Baltic Deep. From the combined experimental results of this study and Mucci (1988) it can be concluded that formation of $Mn_xCa_{(1-x-y)}Mg_yCO_3$ solid-solutions with significantly more than about 10 mol% $MgCO_3$ would require unusual high dissolved $Mg/(Mn+Ca)$ ratios. In the microbiological study of Aller and Rude (1988) a possible involvement of bacteria may have

led to slightly higher magnesium contents in some of the precipitated carbonates.

At lower precipitation rates (Method B), Mn^{2+} was generally enriched in the solid compared to the aqueous solution. Corresponding partition coefficients ranged between 1.5 and 13.3 (20°C), 3.0 and 11.9 (60°C), and 5.3 and 12.9 (90°C). The D-values decreased with increasing Mn^{2+}/Ca^{2+} ratios of the aqueous or solid-solutions, indicating the influence of precipitation kinetics and/or varying activity coefficients of the solid components (e.g. Lorens, 1981; Mucci, 1988; Böttcher, 1998). Results comparable to this study were obtained during the experimental formation of mixed $MnCa(Mg)$ -carbonates (Aller and Rude, 1988) resulting from the oxidation of solid phase sulphides by manganese oxides and bacteria at 25°C (D values between about 1 and 22). Method C led to the formation of calcian rhodochrosites and the highest D values. An increase in $X_{Mn, aq}$ resulted in an acceleration of the transformation rates (Böttcher, 1997).

A comparison of the present results with previous precipitation experiments leads to the suggestion that manganese(II) partitioning during formation of rhodochrosite-calcite solid-solutions below 100°C is essentially controlled by precipitation kinetics with a limiting value for D of 1 (Fig. 2). None of the experimental investigations at low temperatures reached the theoretical exchange equilibrium distribution coefficient (91 at 20°C). Whereas no evidence was found between 20 and 90°C for the formation of the intermediate ordered compound $CaMn(CO_3)_2$ (kutnahorite), several solid-solutions of intermediate composition (so-called 'pseudo-kutnahorite') were precipitated.

References

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