

Modelling calcite precipitation as affected by P_{CO_2} and organic ligands at 25°C

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The literature on modelling calcite precipitation is extensive. These studies are generally performed in clean systems and measure the effects of pH and P_{CO_2} on calcite precipitation at different temperatures for crystal growth. However, water soluble organic ligands and ions such as PO_4^{3-} have been known to act as precipitation inhibitors by blocking crystal growth sites. In a seeded crystal growth experiment Inskeep and Bloom (1986) found that the precipitation rate constant decreased to zero at $\omega = 8-9$ in the presence of 0.15 mM dissolved organic carbon (DOC) from a water-soil extract. Levels of DOC in natural environments are comparable to the levels found by Inskeep and Bloom (1986) to inhibit calcite precipitation. Lebron and Suarez (1996) incorporated the effect of the DOC in an equation to describe calcite precipitation. This model also includes a term for calcite precipitation by crystal growth and a term for calcite precipitation by heterogeneous nucleation. This is the only model in the literature that attempted to reproduce calcite precipitation in natural environments however, this model was developed only for atmospheric partial pressure of CO_2 . It is well known that concentrations of CO_2 in the root zone are 10–500 times higher than in the atmosphere. With that in mind, the objectives of the present study are: (1) To determine the effect of the DOC on crystal growth and heterogeneous nucleation of calcite at different levels of P_{CO_2} ; and (2) To quantify the effect of P_{CO_2} and DOC concentration in a precipitation rate model.

Precipitation rate of calcite as affected by P_{CO_2} in the presence of DOC

In the ω range of 2 to 20 we found an increase in the calcite precipitation rate with increasing P_{CO_2} , in qualitative agreement with the model of Plummer *et al.* (1978). However in the absence of DOC the model of Plummer under-predicts our measured precipitation rates. This disagreement may be due to the intrinsic assumption of Plummer's model, which is that crystal growth is the only mechanism

for calcite precipitation. In the absence of calcite crystals, precipitation occurs in supersaturated solutions far from equilibrium. Bacteria and particles in suspension may act as active sites for heterogeneous calcite nucleation.

We found that the DOC affects both crystal growth and heterogeneous nucleation at the three P_{CO_2} values studied. The precipitation rate of calcite in the range of $\omega = 2.5-20$ decreased when the DOC concentration increased for P_{CO_2} 0.035, 5, and 10 kPa, however higher DOC concentrations were needed to cause an equal reduction in the precipitation when the P_{CO_2} increased. Figure 1 shows the precipitation rate of calcite at P_{CO_2} 5 kPa and three concentrations of DOC. The fact that at constant ω a greater DOC concentration is required to block the active sites on the calcite crystals with increasing P_{CO_2} may be due to a combination of at least three different factors: (1) the increase in negative charge on the calcite surface with increasing P_{CO_2} ; (2) the decrease of the bonding capacity of the fulvic acid with decreasing pH of the solution; and (3) the decrease in the specific volume of the DOC due to increase in the ionic strength of the solutions.

The calcite precipitation rates measured at different P_{CO_2} and constant ω are shown in Fig. 2. As shown in Fig. 2, for constant $\omega = 5$, the precipitation of calcite increased linearly with increasing P_{CO_2} .

The increase of negative surface charge, together with the increase in the CaHCO_3^+ activity in solution may explain the increase in precipitation with increasing P_{CO_2} .

Precipitation equation

Calcite precipitation rate in the presence of fulvic acid and atmospheric P_{CO_2} has been represented by the following expression (Lebron and Suarez, 1996):

$$R_T = R_{\text{CG}} + R_{\text{HN}} \quad (1)$$

where R_T is the total precipitation rate of calcium carbonate (mM s^{-1}), R_{CG} is the calcite precipitation

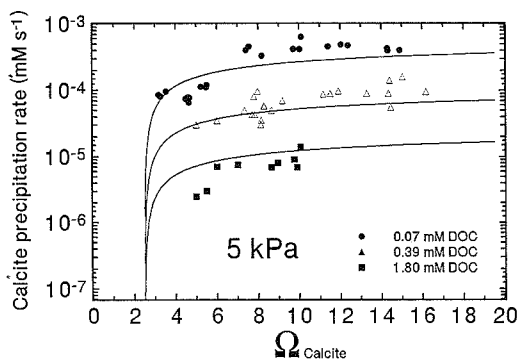


FIG. 1. Precipitation rate of calcite at P_{CO_2} 5 kPa and three concentrations of DOC.

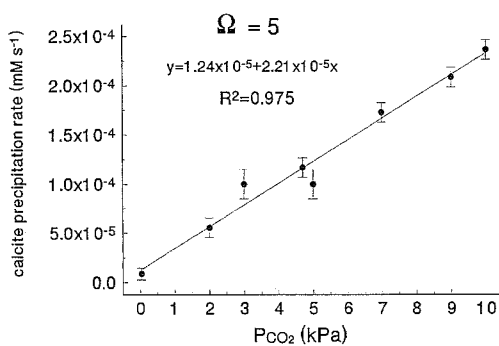


FIG. 2. Precipitation rate of calcite at constant ω at different P_{CO_2} .

rate due to crystal growth and R_{HN} is the precipitation rate due to heterogeneous nucleation. The final expression of the precipitation rate of calcite at various levels of P_{CO_2} and DOC is:

$$R_T = sk_{CG}([Ca^{2+}][CO_3^{2-}] - K_{sp}) + 8.57 \times 10^{-6} P_{CO_2} DOC^{(-3.05+0.793 \log(P_{CO_2}))} + k_{HN} f(SA) (\log(\Omega - 1.5)) 5.9 \times 10^{-3} P_{CO_2} DOC^{(-1.41+0.61 \log(P_{CO_2}))} \quad (2)$$

where s is the calcite surface area, k_{CG} is the precipitation constant for the crystal growth process, brackets represents activities, K_{SP} is the solubility constant for calcite at 25°C, and $f(SA)$ is the surface area factor which accounts for the particles in suspension. A more detailed explanation of the model is presented in Lebron and Suarez (1998).

The representation of Eqn 2 is shown in solid lines in Fig. 1. The model describes the precipitation rate of calcite, in excellent agreement with our experimental data in the range of P_{CO_2} 0.035 to 10 kPa and 0.02–3.5 mM DOC.

References

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