Journal of Crystal Growth 394 (2014) 137–144

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Calcite growth: Rate dependence on saturation, on ratios of dissolved calcium and (bi)carbonate and on their complexes

C.H. van der Weijden [a], R.D. van der Weijden [b,*]

[a] Faculty of Geosciences, Utrecht University, P.O. Box 80021, 3508 TA Utrecht, The Netherlands
[b] Environmental Technology, Wageningen University, P.O. Box 17, 6700 AA Wageningen, The Netherlands

ARTICLE INFO

Article history:
Received 12 August 2013
Received in revised form
23 February 2014
Accepted 25 February 2014
Communicated by K. Nakajima
Available online 3 March 2014

Keywords:
A1. Growth models
A1. Supersaturated solutions
A2. Seed crystals
A2. Growth from solutions
B1. Calcium compounds

ABSTRACT

The role of bicarbonate on the growth rate of calcite in thermo-, chemo- and pH-stated experiments was observed in a foregoing paper by Van der Weijden et al. (1997) [31]. The data are used here to explore especially the effect of bicarbonate on the calcite growth rate in more detail. The experimental range of pH is from 7.6 to 8.9, the initial seed concentrations are 165 ± 12 mg/L with an average surface area of $0.29\ m^2\ g^{-1}$. The median values of the molalities of Ca^{2+} and $CO_3{}^{2-}$ are, respectively, $6.7 \pm 2.4\ (\times 10^{-4})$ and $6.9 \pm 1.9\ (\times 10^{-4})$; the saturation values (Ω) are 2.1–4. In the pH-range of 7.6–8.9 the activity ratios of $HCO_3{}^-$ to $CO_3{}^{2-}$ decrease from 510 to 30. The effect of increasing bicarbonate on R_{lin} ($m\ s^{-1}$) is expressed in the apparent rate constant, k_{lin}, which decreases with a factor of 2.8 in the indicated pH-range. The contribution of bicarbonate to R_{lin} is also apparent in plots of R_{lin} versus the free dissolved calcium to carbonate ratios (r) for a selection of results with $\Omega = 2.7 \pm 0.7$ in the pH-range from 7.6 to 8.9. Where others found a dependence of R_{lin} with a maximum at $r \approx 1$, symmetrically decreasing on either side of this value, it is shown here that R_{lin} increases at $r > 1$ for higher values of free dissolved bicarbonate, in this case at pH 7.6. In the present paper a kinetic model relating the growth rate (R) to the activities of $CaCO_3{}^0$ and $CaHCO_3{}^+$ successfully describes the data with associated k-values for both species in a narrow Ω-range. Implicitly, these ion pairs represent the effect of Ca^{2+}, $CO_3{}^{2-}$ and $HCO_3{}^-$ on the growth rate.

1. Introduction

The effect of the ratio of the constituting ions on the growth rate of calcite has received renewed attention in the last decade [10,14,26,27,34,36,38]. The main findings of these studies are that growth and growth rate (R) of calcite not only depend on the saturation ratio ($\Omega = IAP/K_{sp}$, where IAP is the ion activity product and K_{sp} ($=10^{-8.39}$) is the solubility product of calcite), but also on the activity or concentration ratios, r, of Ca^{2+} and $CO_3{}^{2-}$. Nehrke et al. [14] state that this effect has been obscured in previous studies by simultaneous variation of Ω and r. For a given Ω (5 or 16 ± 2) and fixed pH (10.1 ± 0.1), they varied the ratio of the aqueous concentrations of Ca^{2+} and $CO_3{}^{2-}$ and obtained a bell-shaped curve with a maximum rate for $r \approx 1$. This is expected when the attachment rates of the calcite constituting ions are equal. In different experiments carried out within a pH-range of 7.5–12, Ruiz-Agudo et al. [24] used equal activities of Ca^{2+} and $CO_3{}^{2-}$ while maintaining a constant Ω ($=6.5$) and r ($=1$). They observed a decrease of R with increasing pH (7.5–10.25), which they attribute to a decrease of active surface sites ($>CaHCO_3{}^0$). Larsen et al. [10] and Stack and Grantham [26] observed that (at constant $\Omega = 2.5$) spiral growth at the $\{10\bar{1}4\}$ surface decreased with increasing r. The R's (nm/s), however, differ for acute and obtuse step velocities. For acute steps, a maximum velocity is reported for concentrations ratios ~0.6, whereas for obtuse steps the maximum velocity occurs at $r = \sim 4$ and is higher in magnitude [26]. The response of the growth rate of calcite to variations in r can also be studied based on the experimental design presented in Van der Weijden et al. [31]. In the present paper the interpretation of their results will be accentuated by concentrating on the effect of r on R as well as on the role of the pH-dependent $HCO_3{}^-$ concentration. Finally, kinetic models are tested to relate R with the concentrations of the ion pairs $CaHCO_3{}^+$ and $CaCO_3{}^0$, species that by their association constants depend on the activities of Ca^{2+}, $HCO_3{}^-$ and $CO_3{}^{2-}$.

2. Materials and methods

A detailed description of the materials and methods is given in Van der Weijden et al. [31]. A selection of the experimental data is listed in Appendix 1. In essence, the experimental design is

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* Corresponding author. Tel.: +31 317 483339.
E-mail address: renata.vanderweijden@wur.nl (R.D. van der Weijden).

http://dx.doi.org/10.1016/j.jcrysgro.2014.02.042
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characterized by a thermo-, chemo-, and pH-stated system during calcite growth in a suspension of healed calcite seeds. For all experimental pH regimes an almost equal initial mass of seeds of 165 ± 12 mg/L is used with an average surface area of 0.29 m^2/g and the mass outgrowth ($M_{end}/M_{initial} - 1$) during a single experimental run was 0.70 (70%). The surface area provided by the seeds (Appendix 2) as well as the outgrowth factor is high enough to neglect an initial surge or a contribution of surface nucleation to the growth rate [23,31]. A 0.7 M KCl solution is used as a supporting electrolyte, but the addition of the reagent solutions ($KHCO_3/K_2CO_3$ and $CaCl_2$) results, depending on the chosen pH, in slightly higher than 0.7 ionic strengths (I). Instead of the WateqX program used in the 1997 paper, PHREEQC (with Pitzer.dat) [19] is applied to determine speciation and saturation values (Ω) with respect to calcite. In view of the differences in I, the concentrations of the dissolved species are given in the molal scale, which is per kg H_2O instead of per liter solution. Weak ion associations of Ca^{2+} with Cl^-, and of K^+ with Cl^-, HCO_3^- and CO_3^{2-}, as in Inskeep and Bloom [7], are not considered in the applied PHREEQC.

3. Results

The experimental total molal concentrations of calcium and carbonates, as well as the calculated linear growth rates (R_{lin}), listed in Appendix 1, are based on data in Van der Weijden et al. [31]. The calculated R_{lin}'s of the seeds depend on the outgrowth factor and time to reach this outgrowth. For that reason, the results are standardized by only using data with outgrowth factors 0.70 ± 0.05. The molal concentrations and the activities of the key dissolved species as well as the ionic strength (I) and the saturation ratio (Ω) are given in Appendix 1. Molal concentrations [X] are preferentially used in the figures, but the related activities (X) are used for representation of thermodynamic and kinetic models. The pH-values for experiments D–F are abbreviated to 8.9, 8 and 7.6, respectively. For each pH-value, R_{lin} is approximately independent of almost constant CO_3^{2-} concentrations. To maintain supersaturation with respect to calcite at each pH, higher Ca^{2+} activities compensate lower CO_3^{2-} activities. As a consequence, R_{lin} depends on the Ca^{2+} activities. In the precipitation reaction $Ca^{2+} + CO_3^{2-} \rightarrow CaCO_{3s}$, the partial reaction orders for Ca^{2+} are about 2 at every pH, corroborating the kinetic dominance of the Ca^{2+} ions. R_{lin} can be plotted as a function of the saturation index $\sigma \equiv (\sqrt{\Omega}-1)$. As discussed in Van der Weijden et al. [31],

$$R_{lin} = k_{lin}\sigma_n \tag{1}$$

where k_{lin} is a rate constant and n is the empirical reaction order which depends on the growth mechanism. It has to be realized that k_{lin} not only includes the value of $\sqrt{K_{sp}}$, but also a surface area factor, so the k_{lin}-values have no general application. The value of the surface area used to calculate R_{lin} is an average value of the mixture of seeds of various sizes, therefore k_{lin} is an apparent rate constant. The log–log plot of R_{lin} versus σ (Fig. 1A) shows that the dependence of R_{lin} with the saturation index is different for experiments D, E and F (Appendix 1). Values of k_{lin} and n can be derived from this plot. The log k_{lin}-values are equal to the value of log R_{lin} at log $\sigma = 0$, the n-values are equal to slopes of linear fits of the data. For experiments D, E and F, the k_{lin}-values (in 10^{-10} $m \cdot s^{-1}$) are respectively 2.19, 4.11 and 5.32, and the experimental n-values 2.14, 1.77 and 1.68 (Fig. 1A). The k_{lin}-values differ from those reported in Van der Weijden et al. [31], but in the present case only experimental results with an outgrowth factor of 0.70 ± 0.05 are considered and the applied speciation models in their and this study are different. The k_{lin}-values obtained for experiments D–F have a linear relationship with $(HCO_3^-)/(CO_3^{2-})$ as a function of pH as shown in [31]. The relation between the k_{lin}'s and this ratio is given by

$$k_{lin} = 2.1 \times 10^{-10} + 8.26 \times 10^{-13} \times 10^{-pH}/10^{-10.36} = 10^{-9.68} + 10^{-(1.89+pH)} \tag{2}$$

So, for each pH, a k_{lin}-value can be calculated. The equation

$$\log R_{lin} - \log k_{lin} = n \log \sigma \tag{3}$$

is plotted in Fig. 1B and results in a linear relationship with slope n.

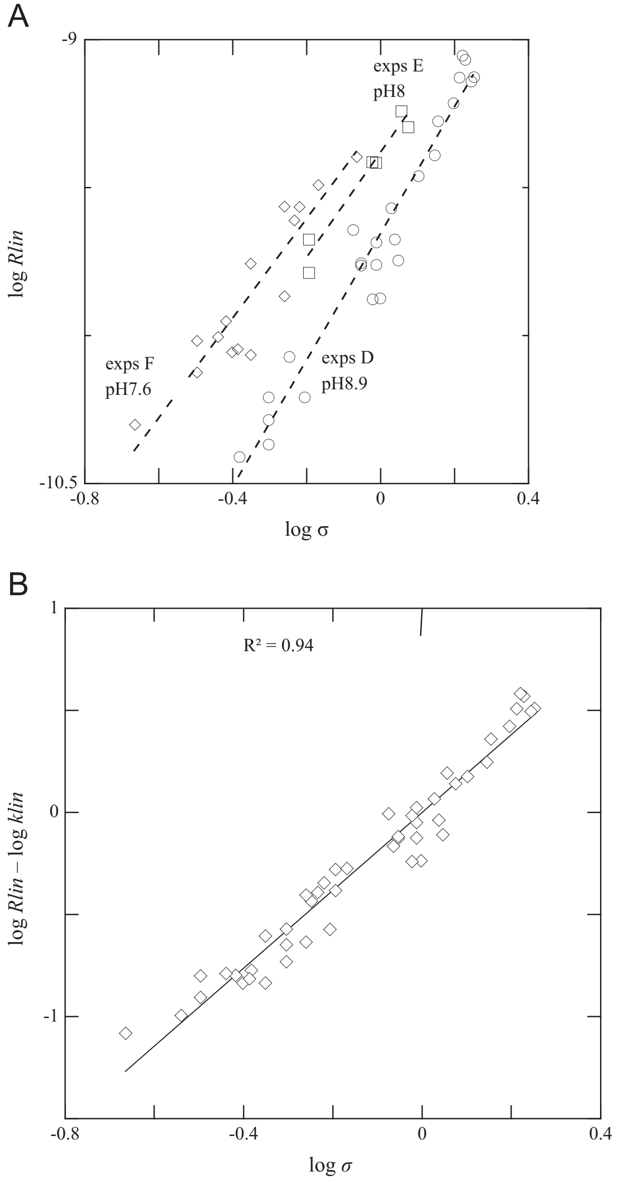

Fig. 1. The figures are based on the dataset presented in Appendix 1. (A) Log–log plot of linear growth rates (R_{lin}) versus saturation index $\sigma(\equiv\sqrt{\Omega}-1)$ with $\Omega = IAP/K_{sp}$; (B) log–log plot of R_{lin}'s minus rate constants k_{lin} versus σ.

4. Discussion

The conditions and methods, described in full in Van der Weijden et al. [30,31] and summarized above, guarantee that during each single experiment the ionic strength, the concentration and activity of the dissolved species, and the saturation value of the suspension remains constant (Table 1). In this respect, comparison can be made with other studies applying similar conditions [10,14]. However, Van der Weijden et al. [31] studied