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## The role of solution chemistry in calcite dissolution

*Discussion paper to “Evidence and potential implications of exponential tails to concentration versus time plots for the batch dissolution of calcite” by V. Truesdale*

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## Abstract

Chemical speciation calculations using Pitzer equations are used to assess the potential errors associated with the calcite dissolution kinetics reported by Truesdale (2015). While these errors are shown to be small, agreement between the measured saturation concentration of calcium and the thermodynamic solubility product of calcite is less good. Truesdale has derived an exponential equation for the increase of calcium concentration with time, and has proposed that the observed long tails of slow dissolution constitute a second, slower exponential decay. The exponential equation assumes that the back reaction has an order of one half in both calcium and carbonate, orders that do not represent a consensus in the calcite dissolution literature. An alternative exponential function, based on a back reaction that is first order in calcium and carbonate, is derived.

## Keywords

Calcite, dissolution, kinetics, chemical speciation

## 1. Introduction

Truesdale (2015) has studied the kinetics of calcite dissolution, with a particular focus on the behaviour at long timescales where he argues that the dissolution process exhibits a long exponential tail. He suggests that the integrated rate equation for the net dissolution process can be formulated as the sum of a fast exponential, representing the major part of the dissolution, and a slow exponential tail. The basis of this analysis is the Shrinking Object model developed by Truesdale, although the derivation of the double exponential function (Truesdale's Equation 8) assumes a constant surface area. Truesdale's analysis focuses essentially on the role of solution chemistry in the back (re-precipitation) reaction, and does not shed any light on the nature of the heterogeneous processes of dissolution and re-precipitation at the calcite surface.

Although each experiment was carried out at a constant pH, Truesdale has also measured initial rates at different pH values, showing a strong dependence on pH (his Figure 4). This implies that the proton plays a significant role in the dissolution reaction, although this is not consistent with the model of Plummer et al. (1978), in which attack by water is the rate-determining dissolution step under these conditions, as given in Truesdale's Equation 4. In his section 5.7.2, Truesdale argues that the pH dependence of the initial dissolution rate is an indirect effect caused by changing carbonate speciation. This appears to be inconsistent with use of initial rate measurements, whose aim is to characterise the forward reaction without interference from the back reaction: the solutions contained no calcium or carbonate before addition of calcite. While this does not affect the interpretation of the individual results at fixed pH values, I consider that this pH dependence should be investigated further.

While I am well aware that there are substantial complexities associated with the heterogeneous dissolution and precipitation reactions, I have chosen to discuss Truesdale's paper from a solution chemistry perspective. I have explored how state of the art equilibrium

thermodynamics (Pitzer equations) can contribute to the analysis of calcite dissolution kinetics, with a particular focus on Truesdale's results.

The extensive literature on studies of calcite dissolution kinetics relates the rate of dissolution (here represented by the increase of calcium concentration with time) to the degree of saturation  $\Omega$ , with the general equation of the form quoted by Truesdale as his Equation 1:

$$\frac{d[\text{Ca}]}{dt} = k(1 - \Omega^m)^n \quad (1)$$

where  $m$  and  $n$  are empirical fitted parameters. Many workers have used  $m=1$  with variable  $n$ , which has been termed the order of the reaction (Morse et al. 2007), although it is not a reaction order as defined in kinetics theory. Another variant was proposed by Sjöberg (1976), who concluded from his measurements that  $n=1$  and  $m=1/2$  provided a good fit, although it is unclear what mechanism could lie behind this value of  $m$ . There is thus significant uncertainty in the literature as to how the kinetics of calcite dissolution should best be represented.

Truesdale has approached this problem using a traditional chemical kinetics approach, with the aim of deriving rate equations for the net dissolution process at a constant pH. This is a promising approach, which I suggest should be combined with chemical speciation modelling in order to ensure that dissolved phase processes are described as accurately as possible, and also to assess how well measured saturation concentrations compare with the thermodynamic solubility product. In addition, I have derived the integrated rate equation for the case where the back reaction is first order in both calcium and carbonate. I suggest that it may be useful to assess experimental data using this equation.

## 2. Chemical speciation modelling

I have calculated the chemical speciation during Truesdale's dissolution experiments using Pitzer equations for activity coefficients. The Pitzer coefficients used are those derived for use in seawater (Waters and Millero 2013) together with those for Tris (Millero 2009). The maximum amount of concentrated hydrochloric acid used was 26 mL in 1.3 L, which gives a concentration of  $0.2 \text{ mol L}^{-1}$  assuming the hydrochloric acid concentration to be approximately  $10 \text{ mol L}^{-1}$ . I have therefore assumed an ionic strength of  $0.2 \text{ mol L}^{-1}$ , with the hydrochloric acid replaced with sodium chloride to achieve different pH values as described in Truesdale's section 3.3. No details were given of the pH scale used or of pH measurement method: I have assumed that pH was measured using glass electrodes calibrated with NIST buffers. The pH scale used in the speciation modelling was the free hydrogen ion concentration scale,  $\text{pH} = -\log_{10}[\text{H}^+]$ , which should be reasonably close to this NIST scale at this relatively low ionic strength. In support of this assumption, the calculated pH on the free hydrogen ion concentration scale at  $20^\circ\text{C}$  with no substitution of hydrochloric acid with sodium chloride is 7.93, which agrees well with the reported pH values ranging between 7.94 and 7.98 for the lowest pH measurements (Truesdale's Tables 2-4).

### 2.1 Comparison of the measured saturation constants with the thermodynamic solubility product

The thermodynamic solubility product for calcite,  $K_{SP} = a_{\text{Ca}^{2+}}a_{\text{CO}_3^{2-}}$  is given by the equation

$$\log_{10}K_{SP} = -171.9065 - 0.0077993T + 2839.319/T + 71.595 \log_{10}T \quad (2)$$

where  $T$  is the temperature in Kelvin (Millero 1995), giving a value of  $\log_{10}K_{SP} = -8.45$  at  $20^\circ\text{C}$ . This value, together with the speciation model, can be used to calculate total  $\text{Ca}^{2+}$  concentrations at saturation. The calculated total calcium concentrations at saturation  $c_{sat}$  are  $0.0018 \text{ mol L}^{-1}$  at pH 7.98, and  $0.0006 \text{ mol L}^{-1}$  at pH 9.15. These concentrations are significantly lower than those reported in Truesdale's Table 3. Uncertainty in the saturation concentration may also lie behind the results shown in Truesdale's Figure 3a(i), where the dissolution appears to stop well short of the dashed line representing the saturation concentration. Uncertainty in the value of  $c_{sat}$  may also affect the interpretation of the plots of  $\ln(1-c/c_{sat})$  versus time.

## 2.2 The calcium carbonate complex in solution

For a solution chemist, the kinetics of calcium carbonate dissolution and precipitation have an interesting parallel in the dissolved phase, since calcium and carbonate ions can interact not only through the formation of solid phases, principally calcite and aragonite, but also through the formation of the dissolved complex  $\text{CaCO}_3^0$ . This has a stability constant  $\log_{10}K = 3.15$  at zero ionic strength and  $25^\circ\text{C}$  (Smith and Martell 1976), and is sufficiently strong that it is included as a separate dissolved species in ion interaction models of seawater using Pitzer equations. The formation and dissociation of the  $\text{CaCO}_3^0$  complex thus provides a direct dissolved phase analogue to the precipitation and dissolution of calcite. For compatibility with the treatment of the calcite dissolution reaction, we will define the dissociation equilibrium constant  $K$ :

$$K = \frac{a_{\text{Ca}^{2+}}a_{\text{CO}_3^{2-}}}{a_{\text{CaCO}_3^0}} \quad (3)$$

The net rate of dissociation of  $\text{CaCO}_3^0$  is given by

$$-\frac{d[\text{CaCO}_3^0]}{dt} = k_f a_{\text{CaCO}_3^0} - k_b a_{\text{Ca}^{2+}}a_{\text{CO}_3^{2-}} \quad (4)$$

where  $k_f$  and  $k_b$  are the rate constants for the forward and backward reactions respectively. Since  $K = k_f/k_b$ , we can write

$$-\frac{d[\text{CaCO}_3^0]}{dt} = \frac{d[\text{Ca}^{2+}]}{dt} = k_f a_{\text{CaCO}_3^0} - \frac{k_f}{K} a_{\text{Ca}^{2+}}a_{\text{CO}_3^{2-}} \quad (5)$$

$$\frac{d[\text{Ca}^{2+}]}{dt} = k_f \left( a_{\text{CaCO}_3^0} - \frac{a_{\text{Ca}^{2+}}a_{\text{CO}_3^{2-}}}{K} \right) \quad (6)$$

## 3. Extension of the solution chemistry equations to calcite dissolution

While the precipitation and dissolution of calcite cannot necessarily be expected to follow the same rate equations as those for the formation and dissociation of the dissolved complex

$\text{CaCO}_3^0$ , we can use these same equations as a starting point for the discussion of calcite kinetics from a solution chemistry perspective. If we now consider the corresponding reactions for calcite,  $\text{CaCO}_3(\text{s})$ , with a solubility product  $K_{SP}$ , and recalling that the activity of a solid phase is unity, we obtain the equation

$$\frac{d[\text{Ca}^{2+}]}{dt} = k_f \left( 1 - \frac{a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}}}{K_{SP}} \right) = k_f (1 - \Omega) \quad (7)$$

where the increase in dissolved  $\text{Ca}^{2+}$  concentration is used as a measure of the dissolution rate. In order to simplify the equations, I have not included the surface area  $A$  and volume  $V$  of the dissolving calcite as parameters in this equation: they are implicitly included in  $k_f$ . This is justified since  $A$  and  $V$  are in effect considered to be constant in Truesdale's analysis. Equation 7 is equivalent to Equation 1 with  $n=1$  and  $m=1$ .

#### 4.1. Does the use of total Ca concentrations introduce significant errors?

Integration of Equation 7 requires account to be taken of the changes of both  $[\text{Ca}^{2+}]$  and  $[\text{CO}_3^{2-}]$  with time. The experiments reported in Truesdale's paper were carried out at constant pH: although the dissolved carbonate will be partly protonated to bicarbonate, the ratio between free and total carbonate will be essentially constant. Truesdale uses the symbol  $\xi$  for this ratio:  $[\text{CO}_3^{2-}]_{\text{TOT}} = \xi [\text{CO}_3^{2-}]$ . Since the solution contains neither calcium nor carbonate before the dissolution starts, then  $[\text{Ca}^{2+}]_{\text{TOT}} = [\text{CO}_3^{2-}]_{\text{TOT}}$  at all times. The experiments described by Truesdale follow the change in total dissolved calcium concentration, using this concentration as a proxy for free carbonate concentration assuming that  $\xi$  has a constant value. Truesdale thus estimates the experimental degree of saturation  $\Omega_{\text{exp}}$  as

$$\Omega_{\text{exp}} = \frac{\xi [\text{Ca}^{2+}]_{\text{TOT}}^2}{\xi_{\text{eq}} [\text{Ca}^{2+}]_{\text{TOT,eq}}^2} \quad (8)$$

This is an approximation whose accuracy can be tested by comparing  $\Omega_{\text{exp}}$  with the calculated value  $\Omega_{\text{calc}}$ , which uses the Pitzer model to take account of the variation of activity coefficients (and thus also  $\xi$ ) during the experiments, and also the formation of  $\text{CaCO}_3^0$ :

$$\Omega_{\text{calc}} = \frac{[\text{Ca}^{2+}] \gamma_{\text{Ca}^{2+}} [\text{CO}_3^{2-}] \gamma_{\text{CO}_3^{2-}}}{[\text{Ca}^{2+}]_{\text{eq}} \gamma_{\text{eq,Ca}^{2+}} [\text{CO}_3^{2-}]_{\text{eq}} \gamma_{\text{eq,CO}_3^{2-}}} \quad (9)$$

Calculations show that the maximum difference between  $\Omega_{\text{exp}}$  and  $\Omega_{\text{calc}}$  is 2.4% at pH 7.98 and 1.9% at pH 9.15. These maximum differences occur at the very beginning of the dissolution process and diminish towards zero at equilibrium. These errors should not be significant in the context of this set of experiments. However, I consider it important that the potential sources of error arising from simplifications in the treatment of solution chemistry be assessed in experiments of this type.

#### 4.2 Integration of the rate equation

Using  $\Omega_{\text{exp}}$ , and assuming that  $\xi = \xi_{\text{eq}}$ , equation 7 can be written

$$\frac{d[Ca^{2+}]}{dt} = k_f \left( 1 - \frac{[Ca^{2+}]_{TOT}^2}{[Ca^{2+}]_{TOT,eq}^2} \right) \quad (10)$$

Or, in the notation used by Truesdale

$$\frac{dc}{dt} = k_f \left( 1 - \frac{c^2}{c_{sat}^2} \right) \quad (11)$$

Truesdale has, however, used without further discussion used the equation

$$\frac{dc}{dt} = k_f \left( 1 - \frac{c}{c_{sat}} \right) \quad (12)$$

This equation can be shown to follow the conclusions of Sjöberg (1976), who proposed values of  $m = 1/2$  and  $n = 1$  in Equation 1. This is, however, just one of the variants of Equation 1 that has been reported in the literature. If the back reaction is instead assumed to be first order with respect to calcium and carbonate (always the simplest assumption), the rate equation can be written:

$$\frac{dc}{dt} = \frac{k_f}{c_{sat}^2} (c_{sat}^2 - c^2) \quad (13)$$

This integrates to

$$\frac{1}{2c_{sat}} \ln \left| \frac{c+c_{sat}}{c-c_{sat}} \right| = \frac{k_f t}{c_{sat}^2} + const \quad (14)$$

Since  $c < c_{sat}$  during the dissolution process, the modulus can be removed giving

$$\frac{1}{2c_{sat}} \ln \frac{c_{sat}+c}{c_{sat}-c} = \frac{k_f t}{c_{sat}^2} + const \quad (15)$$

At  $t = 0$ ,  $c = 0$  and thus  $const = 0$ . Thus

$$\ln \frac{c_{sat}-c}{c_{sat}+c} = -\frac{2k_f t}{c_{sat}} \quad (16)$$

With further rearrangement:

$$c = \frac{c_{sat} \left( 1 - \exp(-2k_f t / c_{sat}) \right)}{\left( 1 + \exp(-2k_f t / c_{sat}) \right)} \quad (17)$$

This equation gives a steeper approach to saturation than the simple exponential function (Figure 1). It would be interesting to explore whether this equation, based on simple first order kinetics for the back reaction, is more appropriate for analysis of the observed dissolution kinetics.

## 5. Conclusions

This short discussion paper has shown how state of the art chemical speciation modelling can contribute to studies of dissolution kinetics. Ensuring that the solution chemistry and the relevant solubility product are described as accurately as possible will provide a sound basis for the derivation of rate equations, and for identifying heterogeneous effects that cannot be explained by solution chemistry. The integrated rate equation for a back reaction at constant pH, which is linear in both calcium and carbonate, has been derived.

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## Figure legend

**Fig. 1** Approach to saturation using a simple exponential decay, and the function shown in Equation 17

