From Nanometer Aggregates to Micrometer Crystals: Insight into the Coarsening Mechanism of Calcite

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Supporting Information

ABSTRACT: Grain size increases when crystals respond to dynamic equilibrium in a saturated solution. The pathway to coarsening is generally thought to be driven by Ostwald ripening, that is, simultaneous dissolution and reprecipitation, but models to describe Ostwald ripening neglect solid–solid interactions and crystal shapes. Grain coarsening of calcite, CaCO₃, is relevant for biomineralization and commercial products and is an important process in diagenesis of sediments to rock during geological time. We investigated coarsening of pure, synthetic calcite powder of sub-micrometer diameter crystals and aged it in saturated solutions at 23, 100, and 200 °C for up to 261 days. Scanning electron microscopy (SEM) and Brunauer–Emmett–Teller (BET) surface area analysis showed rapid coarsening at 100 and 200 °C. Evidence of particle growth at 23 °C was not visible by SEM, but high resolution X-ray diffraction (XRD) data demonstrated steady growth of nanometer crystallites. The results can be described by theory where grains coarsen preferentially by aggregation at early times and high temperatures and by Ostwald ripening at later stages. Crystal form and dimension are influenced by the transition from one growth mechanism to the other. This has been poorly described by mean field coarsening models and offers predictive power to grain coarsening models.

INTRODUCTION

Grain coarsening, first described by Ostwald in 1896,1 is the tendency for crystals to coarsen during aging in a solution at equilibrium. Grain coarsening can be useful in industrial processes or a nuisance if the application requires constant surface area, particle dimension, or crystal form. When grains dissolve and reprecipitate in a geological formation, the recrystallized portion would have equilibrated with pore fluids, a process that is assumed to be negligible when isotope fractionation is used to make interpretations about paleo-temperature, dating, or the influx of fluids. In all cases where grains coarsen, a robust mechanistic model is central to being able to understand behavior in a crystal–fluid system and to predict its behavior.

Larger crystals are thermodynamically favored over smaller ones, so dynamic equilibrium promotes grain coarsening over time. Surface atoms have fewer solid bonds than those within the bulk, and there are more edge and corner atoms relative to surface atoms on a small crystal than a large one. As a consequence, the contribution of the average surface energy, or the average interfacial tension, γ, is higher for smaller crystals. The solubility near a small particle, Kₛ(A), is higher than the bulk fluid solubility, Kₛ(A=0), as described by a derivative of the Gibbs–Thomson equation (eq 1).2 This creates a driving force for net ion transport toward the larger particles, where surface area is lower:

\[
\log \left( \frac{Kₛ(A)}{Kₛ(A=0)} \right) = \frac{2γ}{3RTA}
\]

(1)

Grain coarsening is generally described as Ostwald ripening,3 that is, dissolution and reprecipitation. However, in systems where the ratio of solid to fluid is high, particles can also grow by aggregation, that is, the formation of larger particles from smaller particles through many possible mechanisms.

Calcite is the most stable form of CaCO₃ under most natural conditions. It is present in nearly all geological settings and is a very common industrial mineral. Calcite undergoes grain coarsening during diagenesis of sediments during burial. The degree of diagenesis in an oil-bearing rock is an indicator of porosity and permeability, two important parameters for determining the economic and technical feasibility for oil...
production, such as in the chalk of Northern Europe and Texas. Industries that produce paper, plastics, paint, aspirin tablets, toothpaste, and many other products use calcite as a fine powder, where parameters such as particle size and surface area play an important role in the quality of the product. Thus, better understanding of the controls on calcite crystal coarsening would improve predictive capabilities.

Temperature affects coarsening rates during both Ostwald ripening and growth by aggregation. For Ostwald ripening, the rates of dissolution and precipitation change by Arrhenius dependence and interparticle diffusion changes according to the Stokes–Einstein equation,\(^1\) that is, the diffusivity of the ions that leave and come to the surface is proportional to the ratio of temperature to viscosity. Interfacial tension is also influenced by temperature,\(^2\) thus affecting Ostwald ripening. Temperature affects the likelihood of particles attaching to each other, that is, aggregating, when they come into contact, which is described by Verwey and Overbeek\(^6\) as part of the Derjaguin, Landau, Verwey, Overbeek (DLVO) theory. Attachment is likely to enhance overgrowth when attached particles grow at different rates. If particles do not attach, a growing particle can exert a force on a neighboring particle, thus pushing it away and decreasing the likelihood of overgrowth or encapsulation.

Lifshitz and Slyozov\(^8\) and Wagner\(^9\) first described the mathematics of Ostwald ripening in 1961. Their conclusions, referred to as “LSW theory”, still form the cornerstone of our understanding. They determined that a unique and asymptotic particle size distribution is formed in a dilute system of coarsening particles. The predicted “LSW distribution”\(^3-5,9\) is skewed toward larger values and remains unchanged when normalized to the average radius (i.e., self-similar). Because the breadth of the particle size distribution shows the ensemble driving force for Ostwald ripening, a self-similar distribution allows for a mean field rate description, which can be generalized to any starting material. Once the LSW distribution is established \((t \geq 0)\), the average particle radius, \(\bar{R}\), grows by a power law dependence:

\[
\bar{R}(t) - \bar{R}(0) = k_{\text{OR}} t
\]

The rate constant, \(k_{\text{OR}}\), depends on many system parameters. The exponential factor, \(n\), is 3 for a diffusion limited system and 2 for a reaction limited system. Because very few experimentalists have collected data that fits an LSW distribution, many recent models have adjusted the parameters in \(k_{\text{OR}}\) to achieve a better fit. These models, described in reviews by Voorhees\(^10\) and Baldan,\(^9\) all assume self-similar particle size distributions (i.e., late stage coarsening), isometric particle shapes, and constant interfacial tension. These assumptions are reasonable for some materials, but they describe most real mineral systems poorly.

At high solid to solution ratios, the diffusive field becomes more complex, and one must also consider growth by particle aggregation. Smoluchowski\(^11\) proposed the first theory of rapid particle aggregation. This type of growth was recently observed by Huang et al.,\(^12\) as a precursor to Ostwald ripening in nanocrystalline ZnS. This transitional regime is particularly important for natural mineral systems because solid volume fractions are high and particle size distributions are more often skewed toward smaller values.\(^13\) A complete description of calcite coarsening ought to improve current models by incorporating crystal growth mechanisms, anisotropic crystal shapes and interfacial tension, higher volume fractions, and evolving particle size distributions.

Few, if any, laboratory studies have shown visible calcite coarsening because the rates are slow at low temperatures, especially when particles are large. In this paper, we present results from studies where we synthesized our own pure, sub-micrometer calcite that we aged in saturated solutions at 23, 100, and 200 °C (i) to observe grain coarsening and particle size distribution changes over time, (ii) to determine if a self-similar particle size distribution is achieved and Ostwald ripening models are applicable, and (iii) to compare the data to a theoretical temperature-dependence based on normal crystal growth and growth by aggregation.

## EXPERIMENTAL DETAILS

**Calcite Coarsening at High Temperature.** Calcite was synthesized by the method described by Schultz et al.,\(^14\) which produces pure material, with particles that are <1 μm in diameter, with surface area that is >10 m\(^2\)/g. This method was used because previous experiments (Supporting Figure S1, Supporting Information) showed that coarsening could not be observed using commercial calcite powder (Merck, 99.95 Suprapure) where crystal diameter was initially >10 μm, even at 200 °C.

The calcite-equilibrated aging solution was prepared with 0.1 M NaCl (to maintain constant ionic strength) and an excess (1 g/L) of calcite. After two weeks of stirring at room temperature, the solids were removed by three successive periods of centrifugation for 2 min at 1620g. The calcite-equilibrated supernatant was used for all experiments. This solution is henceforth referred to as the equilibrated solution, EQSOL.

We aged calcite samples at 23, 100, and 200 °C. For each sample, time, and temperature in the experiment matrix, 120 mg of calcite were placed into a 1.5 mL polytetrafluoroethylene centrifuge tube with 1 mL of EQSOL. The tubes were sealed and placed into a stainless steel high pressure/temperature reactor (Parr Instruments, model 4923EE), surrounded by EQSOL, and the vessel was heated to the target temperature. Periodically, for up to 261 days, samples were removed and centrifuged, and the solids were freeze-dried and then analyzed.

We did not rinse the solid because we did not want to risk changing it. From its porosity (~30%), we estimated that <50 μL of EQSOL remained in the solid pellet after centrifugation. When the water evaporated, this amount would produce 0.29 mg of NaCl, that would add <0.25% to the solid mass after drying, which is negligible. The reactor pressure was the vapor pressure of EQSOL, that is, ~16 bar for experiments at 200 °C and ~1 bar for those at 100 °C. We assumed that the effect of pressure on coarsening in an incompressible fluid is negligible compared to the effect of temperature. Also, as temperature increases, the solubility of calcite decreases because of the decreased solubility of CO\(_2\) that is, decreased activity of the carbonate species.\(^15\) Thus, heating EQSOL from laboratory temperature, 23 °C, to 200 °C could result in a maximum of 2.3 μg of calcite precipitated, or <0.002% of the sample mass, which is also negligible.

**Particle Analyses.** Dried samples were mounted on aluminum sample stubs, coated with ~10 nm of gold and imaged with scanning electron microscopy (SEM; FEI Quanta 3D). To measure particle size distribution at each sample time, we selected a representative SEM image containing at least 150 particles. A polygon selection tool in the ImageJ software\(^16\) was used to outline the two-dimensional projection of each particle. The cross sectional area was quantified, and the diameter for each particle was estimated by assuming a spherical shape. For the equant rhombohedral crystal form of calcite, this is a reasonable assumption.

We used the Brunauer–Emmett–Teller method (BET)\(^17\) to measure the specific surface area of the dried calcite samples (Quantachrome, Nova 2000). X-ray diffraction (XRD) was used to confirm calcite purity and to observe changes in crystal size that could not be resolved with SEM or BET. XRD was done using a Bruker Advanced diffractometer (Discover D8) with Cu radiation with K\(_{\alpha1}\) (λ = 1.5406 Å) and K\(_{\alpha2}\) (λ = 1.5445 Å) over the 2θ range from 5° to 90°. The fwhm broadening of the Bragg peaks, when calibrated and
compared with a LaB₆ standard, provides crystallite dimension from
the Scherrer formula.\textsuperscript{18} Phase identification and fwhm determination
were made using the TOPAS 4.2 software package.

\section*{RESULTS AND DISCUSSION}

\textbf{Surface Area and Crystal Size.} The surface area of the
calcite used for all of the experiments was initially 11.8 m\textsuperscript{2}/g.
Figure 1 shows a clear decrease in surface area with time during
reaction at 100 and 200 °C. At room temperature, there is no
change within BET analytical uncertainty (10%).

![Graph showing evolution of calcite surface area over time.](image)

Table 1. Crystallite Dimensions\textsuperscript{a} over Time, for Samples
Aged at 23 °C, for the Major Calcite Crystal Faces

| crystal face | {01.2} | {10.4} | {11.0} | {11.3} | {20.2} |
|-------------|--------|--------|--------|--------|--------|
| 0 days      | 217    | 157    | 84     | 80     | 76     |
| 60 days     | 264    | 205    | 131    | 103    | 113    |
| 112 days    | 465    | 304    | 158    | 129    | 163    |

\textsuperscript{a}In nanometers.

XRD of the starting material confirmed that calcite was the
only solid phase present (Supporting Figure S2, Supporting
Information). Although no changes were observed with SEM or
BET for the samples aged at 23 °C, Rietveld refinement of the
XRD patterns showed that crystallite dimensions on each face
grew steadily (Table 1). The specific numbers recorded in the
table cannot be assumed to represent the absolute particle size
because the Sherrer equation is only applicable for nanometer-
size crystals. However, the trends in the data indicate
crystallite growth. For the sample at 210 days, and for all the
samples aged at 100 and 200 °C, the crystallite diameters were
too large for effective application of the Rietveld method. XRD
data have been averaged for the entire particle volume but
growth would have occurred near the reactive interface.
Therefore, growth would decrease the interfacial tension by
removing surface defects and indicate coarsening.

\textbf{SEM Image Analysis.} No visible changes could be seen in
the SEM images for samples aged at 23 °C (Supporting Figure
S3, Supporting Information), but clear changes were seen for
samples aged at 100 and 200 °C. Calcite particles coarsened
after only one day at 200 °C, and many grew to diameters of 2 µm
or more after 2 days (Figure 2). The larger particles grew
rapidly for the first 15 days, and the smaller particles either
dissolved or were engulfed by larger, growing crystals. The
engulfing process is most evident in the image at 2 days, where
small windows in the large crystal allow the engulfed particles
to be seen. At this stage in the experiment, coarsening rates
were fast, and sub-micrometer particles remained in close
proximity to the larger, growing crystals.

![SEM images of calcite coarsening at 200 °C.](image)

Figure 3. Average diameter of particles that coarsened at 100 and 200
°C. Error bars show the 95\% confidence interval of the mean estimates
based on counting over 150 particles for each sampling time.

After 1 day, the particle size distribution was skewed, with an
abundance of small particles (Figure 4, top). Over time, the size
distribution evolved to a more symmetric form. The size
distribution can also be represented as a cumulative count from
the smallest to largest (Figure 4, bottom), which shows a
shifting profile that favors larger particles, a growing median
diameter, and a larger spread in particle size. The exact images
used for the measurements are provided in Supporting Figure
S4, Supporting Information.

Compared to data at 200 °C, coarsening at 100 °C was much
slower, but effects were evident even after only 1 day of
reaction (Figure 5). After 261 days at 100 °C, the average
diameter was 1.6 μm, compared with 3 μm at 200 °C (Figure 3). Crystal form was generally rhombohedral.

For the samples aged at 100 °C, the particle size distribution (Figure 6) evolved in the same way but at a slower rate. The exact images used for the measurements are provided in Supporting Figure S5, Supporting Information. The particle size distributions at both temperatures demonstrated that neither the LSW distribution nor a self-similar distribution had yet been achieved, and thus the mean field models that assume such profiles (i.e., in the form of eq 2) are not valid.

After 261 days at 100 °C, the distribution is still skewed toward smaller values. The distribution resembles the shape and average radius that was measured after 6 days for samples aged at 200 °C, but the crystal form is much more rhombohedral. This observation is quite interesting because it suggests a different growth mechanism. Behavior could be explained by a difference in surface nucleation and growth or by the influence of aggregation.

At low saturation state, where homogeneous nucleation is highly unlikely, crystals grow mass by spiral growth, adding material at dislocations and building terraces that expand outward, one by one. Growth rates are controlled by saturation state, solution composition, and interfacial tension. Particles were initially rhombohedral, showing exposed \{10.4\} faces, so if Ostwald ripening (i.e., surface growth) is responsible, the ratio of the velocity perpendicular to the \{10.4\} face, \(v_1\), to the velocity parallel, \(v_2\), would have to be higher at 200 °C in order to create other exposed faces that did not exist before. Figure 7 shows the similar particle size distributions.

Figure 8 describes how growth rates during spiral growth, \(v_1\) and \(v_2\), could influence which face is expressed. If crystal face growth explains the difference in crystal form, the final particle size could be determined primarily by the ratio of \(v_1\) to \(v_2\), and thus temperature. This highlights a behavior unique to mineral systems that current Ostwald ripening models do not consider but that could have important effects on long-term prediction of particle coarsening at different temperatures.

Comparison of Experimental Rates with Theoretical Estimates at 100 and 200 °C. In this section, we estimate the theoretical ratio between calcite growth rate \((dr/dt)\) at 200 and 100 °C. In the first case, we assume that growth occurs by Ostwald ripening, that is, normal crystal growth. In the second case, we assume that particles grow by aggregation. It is likely that both mechanisms contribute to total coarsening in the experimental systems. The purpose of the theoretical estimates is (i) to see if we should expect more growth by aggregation, relative to Ostwald ripening, at 200 °C, which could explain why the particle shapes are different and there is more encapsulation at 200 °C in Figure 7, and (ii) to see if the temporal change in experimental growth rate ratios (i.e., Figure 3) suggests that the mechanism changes over time.

If we consider only the first four points at 200 °C, where the final particle sizes after 6 days are similar to the final particle sizes at 100 °C after 261 days, we see that the ratio, \((dr/dt)_{200}/(dr/dt)_{100}\), is approximately 27 (plots are presented in Supporting Figure S6, Supporting Information). In the same data range, the ratio of \((dr^2/dt)\) is 42, which is more convenient for comparison with the theoretical model for growth by aggregation. The ratio, \((dr/dt)_{200}/(dr/dt)_{100}\), decreases over time.
Growth by Ostwald Ripening. If Ostwald ripening dominates and if we assume equal molar concentrations (i.e., $C = [Ca^{2+}] = [CO_3^{2-}]$), normal calcite growth can be described by eq 3, where $r$ represents the radius, $\beta$ represents the kinetic coefficient, $K_s$ is the solubility of calcite ($10^{-9.27}$ at 100 °C and $10^{-11.29}$ at 200 °C), and $f_2$ is the divalent ion activity coefficient:19

$$\frac{dr}{dt} = \beta \left( C - \frac{K_s^{1/2}}{f_2} \right)$$

Equation 3 can be rewritten using the Gibbs−Thompson equation, relating concentration, $C$, to molar volume, $V_m$, interfacial tension, $\gamma$, and radius, $r$:

$$\frac{dr}{dt} = \beta \left( \frac{K_s^{1/2} 2\gamma V_m}{rRT} \right)$$

To relate $\beta$ to $T$, an apparent activation energy of ~46 kJ/mol has been estimated by several researchers.23−26 One higher value (155 kJ/mol) was estimated by Koutsoukos and Kontoyannis,27 who were the only ones to study crystals immediately after nucleation. Using 46 kJ/mol, we estimate that the ratio, $\beta_{200}/\beta_{100}$, is 23 based on Arrhenius dependence; that is, $\beta \propto \exp(E_a/RT)$. A reasonable $\gamma$ for calcite in aqueous NaCl solution is 98 mJ/m², determined by Sohnel.5 Nothing is known about the temperature dependence of $\gamma$ for calcite, but we can relate $\gamma$ to the equilibrium concentration, $C_{200}$ (from $K_s$ at 100 and 200 °C)15 by an empirical correlation:28

$$\gamma = -18.3 \log C_0 + 34.5$$

From this we estimate that $\gamma_{200} = 138$ mJ/m² and $\gamma_{100} = 119$ mJ/m². Finally, we can estimate $f_2$ using the Davis equation: For calcite in 0.1 M NaCl, $f_2 = 0.33$ at 100 °C and $f_2 = 0.23$ at 200 °C. Going back to eq 4, we can now estimate that for Ostwald ripening, $(dr/dt)_{200°C}/(dr/dt)_{100°C} \approx 3.3$.

This estimate is an order of magnitude smaller than the data for the first four time points, that is, when most coarsening occurred, but is closer to the total growth at the end points of the experiment, namely, 1.9.

Growth by Aggregation. For an estimate, we use the theory of rapid aggregation by Smoluchowski.39 From this, it can be shown that particle growth is estimated by29,30

$$r_t^2 - r_0^2 = \frac{1}{3 \eta \gamma W_r} \frac{n_i \alpha_m RT}{t}$$

Figure 6. Particle size distributions of calcite exposed to 100 °C.

Figure 7. Cumulative distribution after 261 days at 100 °C and 6 days at 200 °C, showing similarity in size and distribution in spite of a difference in crystal form (inset images).
where \( n_\text{m} \) is the bulk concentration of the subparticles, \( r_1 \) is the radius of the primary particle, \( r_2 \) is the radius of the primary particle at \( t = 0 \), \( r_3 \) is the radius of the subparticle, \( A \) is Avogadro’s number, \( \eta \) is the medium viscosity (0.25 cP at 100 °C and 0.05 cP at 200 °C),\(^3\) and \( W \) is the stability (or Fuchs) factor. If \( W = 1 \), then every time two particles collide, they remain attached. If we assume that the particles attach side by side, we can assume that they approach each other as parallel plates\(^32\) and estimate \( W \) by

\[
W = \frac{1}{2kd} \exp \left( \frac{E_m}{RT} \right) \tag{7}
\]

where \( \kappa^{-1} \) represents the Debye length and \( d \) is the half distance between plates. \( E_m \) can be estimated with DLVO theory\(^6\) as the maximum of the interparticle potential function \( V = V_R + V_A \), where \( V_R \) and \( V_A \) represent the repulsive and attractive potentials, given by

\[
V_A = \frac{AO}{48\pi d^2} \tag{8}
\]

\[
V_R = \frac{2000}{RT} \kappa^{-1} \left( \frac{\eta \psi}{RT} \right) (1 - \tanh \kappa dd) \tag{9}
\]

\( A \) is the Hamaker constant (10\(^{-20}\) J for calcite),\(^33\) \( O \) represents the area of surface interaction (9 \( \times 10^{-13} \) m\(^2\)), which we estimated to be the square of the initial particle radius obtained from the measured surface area. \( I \) represents ionic strength (0.1 M), \( F \) is the Faraday constant, and \( \psi \) is the diffuse layer potential, which is assumed to be the \( \zeta \)-potential. Calcite data for \( \zeta \)-potential are numerous and controversial\(^34\) because the value depends on pH, pCO\(_2\), pCa, ionic strength, and saturation state. For estimating, we assumed 25 mV, which is estimated to be the square of the initial particle radius obtained\(^\text{ff} \) from BET or SEM, but estimates of crystal face dimensions using Rietveld refinement of high resolution XRD data provide clear evidence that crystallites grew steadily from 0.4 to 2.2 nm/day along each crystal axis. This demonstrates that even at slow rates and at a temperature with a high energy barrier for aggregation, the surfaces continue to rearrange and grow. This is Ostwald ripening, and the process affects average interfacial tension by eliminating kinks and steps.

For 25 °C, the interparticle potential function, \( V_i \), is calculated to be 100 (in kT units). At 100 °C, \( V = 3 \) and at 200 °C, there is no maximum. This is important because it implies that at 25 °C, the potential barrier for aggregation is high so the suspension is stable and the particles are more likely to coarsen by Ostwald ripening.

\[ W \text{ cannot be proven by data from BET or SEM, but estimates of crystal face dimensions using Rietveld refinement of high resolution XRD data provide clear evidence that crystallites grew steadily from 0.4 to 2.2 nm/day along each crystal axis. This demonstrates that even at slow rates and at a temperature with a high energy barrier for aggregation, the surfaces continue to rearrange and grow. This is Ostwald ripening, and the process affects average interfacial tension by eliminating kinks and steps.}

### CONCLUSIONS

This study demonstrates that grain coarsening of calcite at 100 and 200 °C is characterized in the early stages by fast growth of particles by aggregation. As time proceeds, less stable faces are eliminated, and the thermodynamically favored rhombohedral form returns. Temperature influenced not only the rates but also the mechanism of growth. This conclusion is supported by a theoretical comparison of rates, which highlights a strong temperature dependence of the stability factor \( W \). When combined with the observation of encapsulation at early stages, and most notably in the experiments at 200 °C, this provides strong evidence that the early stages grew by aggregation, and the late stages were dominated by Ostwald ripening. A similar observation, where ZnS nanoparticles coarsened by oriented attachment, followed by Ostwald ripening, was reported by Huang et al.\(^{12}\) Our results suggest that a similar transition occurs with the slower coarsening rates of calcite if particles are small and temperature is high.

Grain coarsening at 23 °C could not be proven by data from BET or SEM, but estimates of crystal face dimensions using Rietveld refinement of high resolution XRD data provide clear evidence that crystallites grew steadily from 0.4 to 2.2 nm/day along each crystal axis. This demonstrates that even at slow rates and at a temperature with a high energy barrier for aggregation, the surfaces continue to rearrange and grow. This is Ostwald ripening, and the process affects average interfacial tension by eliminating kinks and steps.

Traditional mean-field Ostwald ripening models poorly describe behavior in systems with high solid to fluid ratios, evolving particle size distributions, and particle aggregation, but these qualities are very relevant in real systems. For example, diagenesis in sedimentary basins and coarsening in industrial pastes occur at high solid to liquid ratios, and the particle size distributions are most commonly skewed to the right.\(^{13}\) Thus in summary, our results demonstrate that for systems at elevated temperatures or high solid to fluid ratios, including the effects of particle aggregation and a dynamic and anisotropic interfacial tension results in a more realistic model to describe grain coarsening.

### ASSOCIATED CONTENT

\* Supporting Information

Six additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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