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Lisa Ann Kessels

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THE DOLOMITE GROWTH MECHANISM IN THE CALCITE TO DOLOMITE TRANSFORMATION

By

Lisa Ann Kessels

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Geological Sciences

ABSTRACT

THE DOLOMITE GROWTH MECHANISM IN THE CALCITE TO DOLOMITE TRANSFORMATION

By

Lisa Ann Kessels

Dolomite precipitation at elevated temperatures is limited by the rate of nucleation and growth in the induction period. At 200° C in Ca-Mg Cl₂ solutions, dolomitization of calcite proceeds by three stages: (1) a period of no stable nucleation: (2) stable nucleation and slow replacement of the initial products; (3) the rapid precipitation of dolomite. SEM (Scanning Electron Microscopy) and AFM (Atomic Force Microscopy) analyses of the reactant surface revealed no products before the first 10 hours of the experiment. After 10 hours, Mg-carbonate phases were detected on calcite. Rapid replacement by dolomite occurs after 12 - 18 hours when only small amounts of dolomite (1-5%) are detected by XRD. Comparison of the microtopographic surfaces of products from the slow replacement of the induction period and the later rapid replacement period indicate the growth mechanism of the products is the same. Natural dolomite samples from the Seroe Domi Fm., Bonaire, N.A. (Miocene); San Pedros Island, Belize (Holocene); and the Davis Formation, Missouri (Cambrian), exhibited the same microtopographic surface features. No growth spirals were observed on any of the surfaces.

In memory of R. R. Kessels

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INTRODUCTION

Dolomite is the thermodynamically favored carbonate phase in seawater (Land 1985; Hardie 1987). The absence of dolomite in the majority of modern marine environments has been the subject of investigation for over 50 years. This phenomenon has been approached through the examination of experimentally-synthesized dolomite and naturally-occurring dolomites. The synthesis of dolomite in the laboratory has enabled the study of the reaction curve, chemical catalysts and inhibitors, and the growth mechanism (Katz and Matthews 1977; Gaines 1980; Baker and Kastner 1981; Sibley and Bartlett 1987; Sibley et al. 1987; Sibley 1990; Nordeng and Sibley 1994; Sibley et al. 1994). Naturally-occurring dolomites, the end-products of the reaction, have been petrographically examined to make inferences about the precipitation of dolomite in nature (Choquette and Steinen 1980; McKenzie 1981; Sibley 1982; Bullen and Sibley 1984; Gregg and Sibley 1984; Saller 1984; Middleburg et al. 1990; Fouke and Reeder 1992). Both approaches to the problem indicate the reaction initially proceeds slowly, followed by a period of rapid precipitation (Katz and Matthews 1977; Middleburg et al. 1990; Sibley et al. 1994).

In this study, three aspects of the process of dolomitization were studied. First, the initial slow stage of the reaction was studied to characterize the nature of initial precipitation. Second, the time interval representing the transition from slow to rapid

replacement was studied to determine if there is a change in growth mechanism to account for the rapid increase in products. Finally, the surface topography of natural dolomites was studied to determine if natural dolomite grows by the same mechanisms as experimentally-derived dolomite. The natural samples studied are dolomite from the Seroe Domi Fm., Bonaire, N.A. (Miocene); San Pedros Island, Belize (Holocene); and the Davis Formation, Missouri (Cambrian). The samples represent a diverse range of proposed dolomitization models and ages. The Seroe Domi Formation dolomite has been interpreted to represent dolomitization from mixed waters (Fouke 1994). The dolomite from Belize is interpreted as dolomitization in the shallow subtidal zone from seawater (Mazzullo *et. al* 1994). The Davis Formation dolomite is interpreted as burial dolomitization (Gregg 1985).

PREVIOUS WORK

The precipitation of most dolomite, $CaMg(CO_3)_2$, occurs through a replacement reaction in which a Ca-Mg carbonate precipitates at the expense of calcium carbonate. This transformation reaction has been divided into two distinct time intervals (Figure 1). During the first interval, referred to as the induction period, Ca-Mg carbonate phases nucleate and replacement of calcite is slow. The second interval is characterized by rapid replacement and is represented by a sharp change in slope on time-transformation curves (Sibley *et al.* 1987; Nordeng and Sibley 1994; Sibley *et al.* 1994). Experiments by Nordeng and Sibley (1994) indicate a series of metastable products precipitate before stoichiometric dolomite. Their results also indicate there is a progressive increase in the



Figure 1. Dolomite Transformation Curve



Figure 2. Spiral Growth Model (left) and Birth and Spread Model (right)

amount of Mg in the series of products. Examination of the reaction curve in previous studies (Sibley *et al.* 1987; Nordeng and Sibley 1994; Sibley *et al.* 1994) indicates the induction period is often the longest interval in the entire reaction.

Variables that catalyze and inhibit the reaction exhibit the greatest effect upon the length of the induction period. Sibley (1990) conducted experiments that demonstrated the length of the induction period decreased as the Mg/Ca ratio of the solution increased. Baker and Kastner (1981) found that sulfate in the dolomitizing solution slowed the rate of transformation. Katz and Matthews (1977) determined that an increase in the temperature significantly reduced the induction period. Their experiments also showed that the type of substrate affects the transformation. Aragonite transformed to dolomite faster than calcite at equal temperatures. Sibley and Bartlet (1987) showed that the duration of the induction period decreased with higher amounts of reactant surface area. Their experiments also showed that a very high Mg-calcite (VHMC, approximately 35 mole % $MgCO_3$) precipitated even when dolomite seeds were added. Gaines (1980) found an initial precipitate closer to the composition of dolomite when natural dolomite seeds were added to the reaction. However, in both of the studies, they report initial products first detected by XRD. In all of the previous work, however, no degree of alteration in the reaction conditions has removed the induction period.

CRYSTAL GROWTH MECHANISMS

Crystal formation can be divided into two-dimensional nucleation with planar growth, and three-dimensional growth (Burton *et al.* 1951; Nielsen 1964; Ohara and Reid

1973; Christian 1975). Three-dimensional growth, occurring at screw dislocations, is energetically easier because of the constant supply of energetically favorable sites provided by the spiral dislocations.

Two-dimensional nucleation models vary between two limiting conditions, mononuclear two-dimensional growth and polynuclear two-dimensional growth (Ohara and Reid 1973). In the mononuclear case, nucleation of a phase is considered the ratelimiting step. Once a phase nucleates, it spreads rapidly across the surface. The extreme case of polynuclear growth is where there is no lateral growth of the nuclei. The new phase covers the surface by accretion of nuclei. A model between these two extremes, referred to as the birth and spread model, involves nucleation and lateral spread across the surface at a finite rate (Figure 2). In this model, nuclei also develop on the newly generated surface of the precipitating phase and subsequently spread laterally across this surface at a finite rate.

The three-dimensional growth model (Burton *et al.* 1951; Nielsen 1964) explained why the crystal growth rate from near-equilibrium reactions was greater than predicted for the two-dimensional model. In the two-dimensional model, if each nucleus gave rise to only one layer of the new phase of the precipitating crystal, then the crystal growth observed for reactions at low saturation should not occur because once a layer is complete the surface energy required to nucleate a new growth unit on a flat layer would prevent further growth (Nielsen 1964). However, in the three-dimensional model, spiral growth around a defect has a center from which growth proceeds out laterally as well as rotating around the center of the defect. The growth proceeding around the center of the spiral is referred to as the arm of the growth spiral. The center is always

higher than the surrounding crystal and acts as the initiation point of the rotating arm (Figure 2). Thus, the precipitating mineral grows laterally as well as vertically without the need for a distinct and separate nucleation event for each layer of the precipitating mineral.

In the laboratory, the growth model for carbonate reactions has been determined from surface microtopography using the Scanning Force Microscope (SFM), also referred to as the Atomic Force Microscope (AFM). Dove and Hochella (1992) observed the *in situ* formation of clusters (6 - 9 nm in height individually, combined clusters reached 31 nm in height) that grew laterally on the surface of calcite in contact with solutions saturated with respect to calcite in a square micron field of view. They interpreted the observations as the nucleation and lateral growth of calcite on a calcite substrate similar to the birth and spread model. In their study, they also observe that each new growth session of calcite is initiated by nucleation and layer growth. Spiral growth was not observed in their experiments until later in the reaction (2 hours). Gratz, Hillner, and Hansma (1993) observed sites of calcite initiation that followed a spiral pattern. These results were interpreted to represent the growth of single-arm and two-armed growth spirals. The two-armed growth spirals have centers less than 1 micrometer in size (estimated from their Figures 3a - 3f).

METHODS

Laboratory-derived dolomite was synthesized from 0.1 grams of Iceland Spar calcite $(160 - 200 \ \mu\text{m})$ placed in 23 ml Teflon-lined bombs with 15 ml of MgCl₂ and CaCl₂ solution with a Mg/Ca ratio of 1.2 heated to 200° Celsius. In each bomb, the solution contained 0.437 grams Mg²⁺ and 0.601 grams Ca²⁺. The CO₃²⁻ in solution is from the dissolution of the 0.1 grams calcite. Complete conversion of the Iceland Spar calcite to dolomite will yield a maximum of 0.092 grams stoichiometric dolomite. A solution with a Mg/Ca ratio of 1.0 was used during preliminary experiments. At specific times during the reaction, the bombs were removed, cooled to room temperature, and analyzed. Each point in the time of the transformation was studied with duplicate bomb experiments. The contents of each bomb were either kept in contact with the experimental solution and immediately studied with the fluid cell of the AFM or rinsed with distilled water and filtered.

Portions of the samples were powdered and X-rayed to determine the composition and amount of dolomite. An internal CaF₂ standard was used to calibrate the position of the d(104) peaks of calcite and dolomite. The calcite to dolomite ratio was determined by d(104) peak height ratios (Lumsden 1979). The composition of the dolomite was calculated by the position of the d(104) peak and the equation mole % $CaCO_3 = 333.33 d(104) - 911.99$ (Goldsmith and Graf 1958; Lumsden and Chimahusky 1980). Portions of the sample were also left intact and were prepared for SEM-EDS analysis. SEM-EDS analysis was used to determine the presence or absence of Mg. The term Mg-carbonate is used to describe the crystals smaller than the analytic resolution of

the instrument (5µm). Mg-carbonate crystals smaller than the field of analysis showed a Mg peak compared to the background calcite which did not show a Mg peak.

Preliminary work utilizing a solution with a Mg/Ca ratio of 1.0 yielded products with variable mole percent MgCO₃. The mole percent MgCO₃ increased with time, similar to the results of Nordeng and Sibley (1994). Two representative samples from the preliminary study which contain 89% and 97% weight percent dolomite are included in this study for comparison. These two samples were examined by atomic force microscopy to determine if the growth mechanism for this particular reaction is affected by a change in the Mg/Ca ratio. The samples chosen are from the rapid growth and final phase of the transformation of the preliminary work. Both samples are dolomite with a composition of Ca_{0.53}Mg_{0.47}CO₃.

Samples for AFM analyzes were adhered to a magnetic stub and observed under the AFM dry cell and wet cell using reactant solution and distilled water as the solution for the fluid cell. The reactant solution was used to maintain the sample initially as the surface was characterized. Distilled water was then allowed to flow through the fluid cell by gravity to determine the relative dissolution rates of different features on the surface. A record of the particular samples studied with the SEM and AFM is presented in Table 1. These samples are predominantly from the end of the induction period as determined by X-ray analysis. After this time interval of the transformation, the percent of dolomite product increases rapidly (Table 1). For samples studied with the AFM, the surfaces of five random grains were investigated in five square micron intervals.

Samples of natural dolomite were prepared for SEM and AFM analyses by treating their surfaces with dilute acid. The dolomite was rinsed three times with 0.5%

time	weight % products	AFM	SEM	initial wt.	final wt.
2.1	0.0	X		125.823	125.813
2.1	0.0	X		125.918	125.903
4.0	0.0			125.985	125.945
4.0	0.0			126.053	126.003
6.0	0.0	X		125.945	125.91
6.0	0.0	X		126.118	126.11
8.0	0.0			126.139	126.105
8.0	0.0			125.741	125.702
9.9	0.0	X	X	125.813	125.763
9.9	0.0	X	X	125.919	125.903
12.4	0.0	X		126.071	126.046
12.4	3.6			125.79	125.768
15.0	0.0	X	X	125.414	125.369
15.0	0.0	X	X	125.889	125.84
15.6	0.0	X	X	125.867	125.838
15.6	0.0	X	X	124.773	124.725
15.9	2.4		X	125.741	125.702
15.9	0.0	X	X	126.139	126.087
16.0	0.0	X	X	126.15	126.109
16.0	0.0	X	X	126.162	126.136
16.5	0.0	X	X	125.911	125.879
16.5	0.0	X	X	126.026	126.001
17.0	12.3	X	X	126.118	126.08
17.0	26.1		X	125.653	125.629
18.0	33.1		X	126.053	126.003
18.0	44.6		X	125.945	125.91
18.2	0.0	X	X	126.038	126.003
18.2	2.6	X	X	125.815	125.76
18.2	4.9	X	X	126.122	126.109
18.2	8.3	X	X	125.744	125.725
18.2	15.5	X	X	126.16	126.129
18.2	31.9		X	126.267	126.232
18.2	45.0		X	126.102	126.042
18.2	46.0		X	124.74	124.706
22.4	5.3		X	124.739	124.669
22.4	15.7		X	125.968	125.908
25.0	9.7		X	125.783	125.708
25.0	51.2		X	125.919	125.862
27.0	31.1		X	126.413	126.368
27.0	57.6		X	126.208	126.116
28.0	18.6		X	125.849	125.782
28.0	70.9		X	125.984	125.921
29.0	83.6			125.773	125.705

Table 1. XRD results and sample list

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time	%products	AFM	SEM	initial wt.	final wt.
29.0	82.1			125.909	125.86
30.0	100.0			125.919	125.833
30.0	100.0			124.855	124.793
38.7	64.1			126.225	126.209
38.7	80.4			125.945	125.928
44.0	96.6			125.847	125.77
44.0	95.2			126.148	126.091
64.3	98.6			125.985	125.777
64.3	100.0			125.849	125.709
69.7	100.0			126.358	126.248
69.7	100.0			126.024	125.957
72.8	100.0			125.923	125.808
72.8	100.0			125.881	125.72
80.0	100.0			125.806	125.679
80.0	100.0			124.883	124.759
92.9	96.0			126.005	125.658
92.9	100.0			126.336	125.969
92.9	100.0			126.01	125.948
92.9	100.0			124.912	124.766
94.3	100.0	X	X	126.18	126.008
94.3	100.0	X	X	124.763	124.61
167.9	100.0			125.929	125.879
167.9	100.0			126.14	126.056

Table 1 (cont'd).

hydrochloric acid in 15 ml portions and filtered using a millipore filter to remove more soluble phases and salts, and to etch the dolomite slightly to reveal in greater detail the surface structures. Samples were studied using the dry cell and fluid cell of the AFM. For image analysis in the fluid cell, distilled water was also allowed to flow across the surface as described for the synthetic samples.

RESULTS

When the initial solution was 1.2 Mg/Ca, the composition of initial products formed during the reaction was the same as the final products when the transformation had gone to completion. The weight percent of products formed relative to the weight percent of calcite reagent remaining and the initial and final weights of the bombs are reported in Table 1. The products were a dolomite with an average composition of $Ca_{0.51}Mg_{0.49}CO_3$. The composition ranged from 44 - 51 % mole MgCO₃ for the 45 out of 66 samples with dolomite detected by XRD. Thus, during the rapid growth interval and final phases of the transformation, the precipitating phase has the same composition when the reagant is exposed to fluid with a Mg/Ca ratio of 1.2 at 200° C. In the preliminary results with an initial solution of 1.0 Mg/Ca, the former scenario was not the case. The mole percent Mg of the first products detected by X-ray analysis (39 mole % MgCO₃, Sibley 1990) was lower than mole percent Mg of products formed later in the reaction (47 mole %MgCO₃).

SEM analysis verified a dramatic change in the amount of Mg-carbonate and

dolomite crystals from the slow replacement stage of the induction period to the rapid precipitation period as identified by the transformation curve (Figure 1). Figure 3 and 4 are of a sample that was at 200° Celsius for 15.0 hours and contains no detectable products by XRD analysis (sample from the induction period). Etch pits are present in the substrate calcite. A cluster of Mg-carbonate rhombs (1µm in diameter) are also present on the surface (Figure 3 and 4). Small product crystals ($0.5 - 2 \mu m$ in diameter) occur in small quantities (as few as two crystals have been found on an individual sample) on the crystal surface of samples with no detectable products by XRD analysis. The 15 hr sample has fewer crystals on the surface than samples reacted longer (Figure 5, 6, 7, and 8), which is indicative of a lower nucleation rate earlier in the reaction. Figure 5 and 6 are of a sample that was reacted for 18.2 hours and contains 3% dolomite by Xray analysis. Figure 5 shows dolomite crystals intergrew and coated the surface of the calcite substrate. Figure 6 shows the greatest abundance of crystals precipitated at the edges of the substrate, a feature of the reaction which will be discussed later. Figure 7 is a sample which reacted for 18.2 hours and contains 5% dolomite. The sample indicates that after the greater part of the calcite surface was covered with dolomite, dolomite continued to nucleate on itself as evidenced by the smaller crystals on dolomite precipitated earlier in the reaction. Figure 8 is of a sample that reacted for 94.3 hours and contains 100% dolomite by X-ray analysis. Dolomite crystals have completely replaced the substrate by continued nucleation and growth. The 94.3 hour sample exhibits crystal intergrowth as well as dolomite nucleation on previously-formed dolomite crystals. Thus, dolomite continued to nucleate in the final phase of the transformation.

Figure 3. Surface of a sample reacted for 15.0 hours. The sample represents the late induction period. Arrow points to a cluster of product crystals (Scale bar = 10μ m).



Figure 3

Figure 4. Closeup of Figure 2. Arrow point to cluster of product crystals (scale bar = $1\mu m$).



Figure 4

Figure 5. Surface of a sample reacted for 18.2 hours. The sample represents the early rapid replacement period (scale bar = $10\mu m$).

-



Figure 5

Figure 6. Surface of a sample reacted for 18.2 hours. The sample represents the early rapid replacement period. Note the increased number of product crystals on the edges of the calcite surface (scale bar = $10\mu m$).

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Figure 6

Figure 7. Surface of a sample reacted for 18.2 hours. The sample exhibits the nucleation of product crystals on previously precipitated product crystals (scale bar = $10 \mu m$).



Figure 7

Figure 8. Surface of a sample reacted for 94.3 hours. The sample has completely transformed to dolomite (scale bar = $10\mu m$).



Figure 8

The surface of the calcite reagant, as studied by the AFM, is a rough surface with pronounced etch pits at the near microtopographic scale $(1 - 5 \mu m \text{ in the x and y})$ directions) relative to the smoother surfaces of the precipitated dolomite. The calcite dissolution front did not have a rhombic outline whereas crystals of the product did have a rhombic outline. However, the steps on those product crystals were irregular, abruptly ending near the edge of the rhomb. Figure 9 is a microtopographic image of the 15.0 hour sample during the slow replacement stage, Figure 10 is the 18.2 hour sample and Figure 11 is the 94.3 hour sample. Figure 9 and Figure 10 show concentric growth layers on the dolomite. There are more centers of growth on the 18.2 hour sample than the 15.0 hour sample, indicating an accelerated rate of nucleation on the former. The sample of dolomite from the final phase of the reaction (94.3 hours) also has circular growth layers on the surface of the dolomite (Figure 11). No growth spirals were observed on any of the samples. Thus, the change from slow to rapid replacement during this time interval on the transformation curve is not the result of a change in growth mechanism from layer growth to spiral growth. Figures 12 and 13 are cross-plots of the 15.0 hour and 18.2 hour samples. Steps on the surface are interpreted as growth layers on the forming crystal. These layers consist of growth units which are multiples of the dspacing parallel to the d(104), or 2.886 angstroms (Goldsmith and Graf 1958; Lumsden and Chimahusky 1980) for ideal dolomite ($Ca_{0.50}Mg_{0.50}CO_3$). The height of individual steps on these samples range from 4.4 to 17.6 angstroms. The steps are interpreted as multiple growth units where a single growth unit is the unit cell. The height of the individual steps on the 94.3 hour sample range from 15.6 to 24.5 angstroms (Figure 14). These steps are also interpreted as multiple growth units.
Figure 9. Microtopographic surface of product crystals from a 15.0 hour sample.



Figure 10. Microtopographic surface of product crystals from an 18.2 hour sample.

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Figure 11. Microtopographic surface of product crystals from a 94.3 hour sample.



Figure 12. Cross-plot of 15.0 hour sample surface (Figure 9).



Figure 13. Cross-plot of 18.2 hour sample surface (Figure 10).



Figure 14. Cross-plot of 94.3 hour sample surface (Figure 11).

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35.156 nm nan µm DC 102 nm 29.297 DM .348 4.69 35.155 nm 2.791 de4 0.149 nm 1.714 nm 0.004 hm 0.596 ualid L RMS IC Ra(Ic) RMa)(RZ Rz Cnt u loriz distance Horiz distance Jert distance Vert distance Spectral and Angle Angle Section Analysis Min Spectrum 0.75 1.00 1.25 g 0.50 0.25 ž 0 I O nez

Figure 14

A sample reacted for 9.9 hours contained no detectable dolomite or other products as determined by X-ray analysis. AFM analysis of the precipitate on the reactant surface shows the same microtopographic surface structures (Figure 15 - 18) as seen in the previous samples. When distilled water was drawn across the surface by gravity, the individual layers on the surface of the substrate calcite retreated, but layers on the precipitate did not retreat within the two hour time frame of the fluid cell experiment. Thus, the precipitate is a Ca-Mg carbonate of unknown composition. Early carbonate phases in similar experiments are Ca-rich dolomites and very high Mg-calcites (Sibley *et al.* 1994).

Examination of samples from the onset of nucleation in the induction period (Figures 15 -18), the slow growth stage in the induction period (Figure 9 and 12), the beginning of the rapid replacement period (Figure 10 and 13), and the end of the reaction (Figure 11 and 14) all exhibit the same microtopographic surface features. Hillocks on the surface consist of concentric layers which form terraces of irregular polygons. Smaller hillocks comprised of concentric layers are randomly located on broad terraces forming the larger hillocks. A hillock is interpreted as the result of the formation of nuclei and lateral growth similar to the birth and spread model, or nucleation and twodimensional lateral growth model (Burton *et al.* 1951; Ohara and Reid 1973; Sunagawa 1984,1986). Thus, the entire reaction is characterized by the birth and spread model.

The surfaces of the two preliminary samples from a solution with a Mg/Ca ratio of 1.0 also show concentric layers indicative of nucleation and two-dimensional growth (Figure 19 - 20). Both samples represent the rapid replacement period. Thus, a change in the Mg/Ca ratio from 1.0 to 1.2 does not change the growth mechanism from layer

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Figure 15. Microtopographic surface of a sample reacted for 9.9 hours.

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Figure 16. Closeup of 9.9 hour sample surface (Figure 15).

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Figure 17. Closeup of hillocks on 9.9 hour sample (Figure 16).



Figure 18. Block diagram of 9.9 hour sample surface (Figure 15).



Figure 19. Microtopographic surface of a sample from the preliminary study (Mg/Ca = 1.0) which consists of 89 wt. % dolomite.

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Figure 20. Microtopographic surface of a sample from the preliminary study (Mg/Ca = 1.0) which consists of 97 wt. % dolomite.



growth to spiral growth at the transition from the induction period to the rapid replacement period.

The microtopographic surfaces of natural dolomite samples from the Seroe Domi Fm., Bonaire, N.A. (Sibley 1980); San Pedros, Belize; and the Davis Formation, Missouri are also characterized by multiple hillocks and steps with irregular boundaries. Figure 21 is the microtopographic surface structure picture of Pliocene dolomite from the Seroe Domi Fm., Bonaire, N.A. (Sibley 1980). The surface shows concentric growth layers consistent with the birth and spread model. Figure 22 and 23 are the microtopographic surface structure pictures of dolomite crystals from San Pedros, Belize and the Davis Formation, Missouri. Both surfaces exhibit concentric growth layers and are also consistent with the birth and spread model. The height of individual steps from all three natural samples fell in the range of 5.0 - 32.1 angstroms, or presumably growth layers consisting of multiple growth units. Thus, the examined natural dolomites have surface structures consistent with the experimental surface structures and growth mechanisms.

DISCUSSION AND MODELLING OF RESULTS

Surface structure microtopographs indicate the Ca-Mg carbonate phases grow by a birth and spread mechanism during and after the induction period. Nucleation occurs on the calcite as well as on earlier formed Ca-Mg carbonate precipitates. SEM results indicate the dominate face is the $(10\overline{14})$ face. Thus, microtopographs represent the $(10\overline{14})$ face. Growth spirals have been found with the TEM on the $(10\overline{11})$ face of early natural crystals with the aide of cathodluminesence (Fouke and Reeder 1992). However,

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Figure 21. Microtopographic surface of dolomite crystals from the Seroe Domi Fm., Bonaire, N.A.



Figure 22. Microtopographic surface of dolomite crystals from San Pedros, Belize.



Figure 23. Microtopographic surface of dolomite crystals from the Davis Formation, Missouri.



in that study screw dislocations were not observed on the $(10\overline{14})$ face.

In modelling the growth of dolomites and high Mg-calcites, previous researchers have determined from modified Arrhenius plots that aqueous diffusion is not the ratelimiting step (Kunzler and Goodell 1970; Katz and Matthews 1977). Thus, a surfacelimited approach to the precipitation kinetics of dolomitization was utilized. Dolomite preferentially precipitates at the edges and corners of calcite (Figure 6), generally thought as energetically more difficult precipitation sites, but presumably areas of higher carbonate ion concentration due to enhanced dissolution of calcite at edges and corners. However, Ca-Mg carbonate precipitation also occurred at the center of calcite faces along lines parallel to the crystal edge. A possible reason for the observation of precipitate concentrated at corners and edges of the calcite and generally areas of higher dissolution of calcite, is the fact these areas would have a high concentration of steps. The inside edge of a step would offer another source of bonding and reduce the surface energy of the new nuclei. However, since the calcite is highly rounded and etched almost immediately after the reaction begins and well before the precipitation of Ca-Mg carbonate phases begin, the availability of these preferential sites is not the rate-limiting step for the growth of Ca-Mg carbonate. The rate-limiting step for the dissolution of calcite for these particular reaction conditions is inconclusive from SEM results.

The transition from the induction period to the rapid replacement period is not a result of a change in growth mechanism nor a change in the surface of the dissolving substrate calcite. Thus, the two main factors left which can accommodate this transition are the growth rate and the nucleation rate. Since the number of new crystals on a given

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surface was observed to increase with reaction time, the nucleation rate is increasing with reaction time. Factors affecting the nucleation rate include the type of substrate available which varies in this reaction from a calcium carbonate to stoichiometric dolomite. A substrate closer to the composition of stoichiometric dolomite will be an energetically easier site for nucleation. Thus, the development of surface area composed of a mineral of composition close to stoichiometric dolomite, increases the nucleation rate. The precipitation of mineral of this composition will propagate its own precipitation by continually providing new substrate and enhances the reaction rate as demonstrated by the following model.

The transformation data (Table 1) was modelled with the Avrami isothermal time-transformation curves (Avrami 1939; Christian 1975; Carlson 1983; Sibley 1990). A growth rate of 1.1 X 10⁻⁸ cm/sec was used as determined previously for the transformation of calcite to dolomite (Sibley 1990). The nucleation rate, nuclei/cm³sec (see Appendix I), was raised to correspond with the increasing number of product crystals at longer reaction times as observed by SEM analysis.

The modelled volume of products was calculated from the following equation:

$$V = 1 - \exp(-kt^{n})$$
 (Avrami 1939; Christian 1975)

where n is the exponential factor of time and k is the product of a shape factor, the growth rate cubed, and the nucleation rate. For equations and terms for each of the three models see Table 2. Figure 24 is a plot of the raw data and the amount of theoretical

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Table 2. Model Equations and Constants

Model	k	Shape Constants
n = 4	(411/3) G ³ Nt ⁴	
n = 3	(II/3) dG ² Nt ³	d = 2.886 angstroms
n = 2	a GNt²	a = 8.344 square angstroms

-



Figure 24. Model Transformation Curve (n=4)
product calculated from the model with n=4. Figure 25 and Figure 26 are the same plots of raw data and modelled data with n=3 and n=2 respectively. The power n to which time, t, is raised, has been correlated to nucleation and growth mechanisms (Avrami 1939: Christian 1975; Carlson 1983). A value of n between 2 and 3 correlates to the dominance of lateral growth away from the nuclei on the surface, and a value between 3 and 4 correlates to a model where nucleation is not superseded by lateral growth, or, essentially continuous growth in three dimensions. The latter is represented by two cases (Avrami 1939; Christian 1975). The first case is a spiral growth mechanism where growth occurs in all three dimensions. The second is the case of birth and spread where the rate of nucleation is roughly equivalent to the rate of lateral growth. Avrami (1939) and Christian (1975) both discuss the case where there are a very limited number of nucleation sites, or germ nuclei. However, in this experiment, there are multiple phases precipitating. Each phase will have nucleation sites available. As noted earlier in the discussion of the SEM data, Ca-Mg carbonate phases precipitated on previously precipitated Ca-Mg carbonate phases and the calcite substrate. Figure 27, 28, and 29 are the respective best linear fit plots of the actual data versus the theoretical data as calculated from each model. Figure 28, corresponding to a model with n=3, yields the best results with an r-squared value of 0.896. However, a model with n=3 requires a higher nucleation rate to fit the data than a model with n=4 (see Appendix I). The model with n=4 yields an r-squared value of 0.874. Thus, the data fit a model of n=3 and n=4, but not a model of n=2 which represents planar growth.

In modelling the nucleation rate, or the number of nuclei on the surface at a specific point in time, nucleation is broken down into its representative physical



Figure 25. Model Transformation Curve (n=3)



Figure 26. Model Transformation Curve (n=2)

Lan and service



Figure 27. Actual Data vs. Model Data (n=4)



Figure 28. Actual Data vs. Model Data (n=3)



Figure 29. Actual Data vs. Model Data (n=2)

components:

 $N^* = N \exp(-\delta G^*/k_bT)$ (Nielsen 1964; Steefel and Van Cappellen 1990)

where N* is the surface density of critical nuclei at a particular point in time (simply N in the Avrami models), N (in this equation) is the density of units of the precipitating phase in the adsorption layer available to accumulate and form a critical-sized radius, δG^* is the free energy required for a critical-sized nucleus to form, k_b is the Boltzmann's constant, and T is temperature. A critical-sized nucleus is a stable nucleus that is adding more molecules of the precipitating mineral than molecules that are leaving the surface. Assuming the reaction is surface limited, N should be a constant near infinity relative to N*, or the units of the precipitating phase in the adsorption layer should be much larger than the units of the precipitating phase actually on the surface forming a critical sized nucleus (Nielsen 1964; Steefel and Van Cappellen 1990; Nordeng and Sibley 1994). Since all the other terms can be considered as constants in this experiment, N* varies only with δG^* . The free energy required to form a critical size nucleus can be defined as follows:

$$\delta G^* = \pi v^3 \sigma^3 / 3 (K_b T \ln \Omega)^2$$
 (Nielsen 1964; Steefel and Van Cappellen

1990; Nordeng and Sibley 1994)

where Ω is the saturation state, v is the molar volume, and σ is the surface free energy

term. Thus, δG^* varies with saturation, molar volume, and the surface free energy term. The saturation state of the interval of the transformation curve of interest, the induction period and the transition period from slow replacement to rapid replacement, is approximately constant because the amount of product formed is too small to change the solution composition (Sibley 1990). Thus, δG^* , and indirectly N^{*}, varies only with the molar volume and the surface free energy term. A smaller molar volume requires a smaller activation energy. From the previous equations, as δG^* decreases, N*, the number of critical nuclei, increases. Thus, as more Mg-rich phases (Nordeng and Sibley 1994) with smaller molar volumes are precipitated, the number of nuclei able to precipitate on the newly generated surface should increase. Since the products detected by XRD analysis have the same molar composition, the molar volume and surface free energy term associated with the precipitate during the rapid growth and final phase of the transformation should be constant and should not change N^{*}. However, later in the transformation, the saturation state will decrease, decreasing N*. Thus, an increase in the Mg content of each new precipitate enhances the nucleation rate because the new crystals serve as a nucleation site with a lower surface free energy for Ca-Mg carbonates. The fact that the observations of the final products does not support a decrease in the nucleation rate indicates the decrease in the Mg/Ca ratio from 1.2 to 1.13, a 5.8% decrease in the molar ratio, does not stop dolomite nucleation. The lack of a change in dolomite nucleation is likely due to the large amount of solution relative to the reagant.

As demonstrated earlier, an increase in nucleation up to the end of the induction period fits the curve of the raw data (Figure 1). Since the end of the induction period

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also corresponds to the onset of precipitation of dolomite with the final composition for this experiment, the rate-limiting step is the nucleation and slow replacement of each separate phase of the different Mg-carbonate products as the Mg content increases up to the end of the induction period. Researchers (Katz and Matthews 1977; Mucci and Morse 1983) have shown calcium carbonate with a composition less than 35 mole % Mg (composition of first metastable precursor detected in experimental dolomitization) and greater than 21 mole % Mg (Mg/Ca ratios up to 10.3 were required for Mg incorporation into calcite to obtain high concentrations) are difficult to form and usually do not precipitate at all. Thus, if the first phase contains 35 mole % Mg, it would be energetically difficult to nucleate on the reagent, Iceland Spar calcite, as discussed previously. This energetic barrier would result in the long period with no stable nucleation.

Sibley *et al.* (1987) suggested thermodynamically-favorable environments such as seawater in contact with calcium carbonate, where no detectable dolomite is forming, represent the induction period. However, they did not determine when, in the induction period, stable nucleation first occurs. This study demonstrates that there is not only slow replacement by Ca-Mg carbonate phases in the induction period, but an initial time interval in which no stable nucleation occurs. Based on the results of this study we expect to find some carbonate sediments in contact with seawater in which: 1) no dolomite nuclei have formed, 2) dolomite nuclei have formed but have grown too slowly to be detectable by XRD analysis, and 3) detectable amounts of dolomite are present. To date, no studies have been done to test statements 1 and 2.

The study also verifies that the mechanism by which dolomite precipitates for the

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observed recent and ancient dolomite is the same as the growth mechanism for the experimentally-derived dolomite. Although the natural samples were rinsed with a 0.5% HCl, this is not believed to have greatly affected the surface because of the slow rate of dissolution of dolomite (Busenburg and Plummer 1982). However, it is likely the Seroe Domi and Davis formation dolomites have undergone some dissolution after dolomite precipitation in their natural environments. Dissolution of crystal surfaces can expose growth layers. Therefore, it is likely the hillocks observed on these natural dolomites have been exposed to dissolution. Given all the dissimilarities between the three natural dolomites and the natural versus laboratory conditions, the results suggest that the birth and spread mechanisms may be very common.

CONCLUSIONS

A rhombic phase which dissolves slower than calcite precipitated before detectable amounts of product can be verified by X-ray analysis. The surface microtopographic structure of the Ca-Mg carbonate precipitated during slow replacement and the dolomite precipitated during the rapid growth and final phases of the transformation are the same and both indicate growth similar to the Birth and Spread Model (Burton *et al.* 1951; Ohara and Reid 1973; Sunagawa 1984, 1986). A slight decrease in saturation from a Mg/Ca ratio of 1.2 to 1.0 does not affect the surface and growth mechanism interpretations. Naturally occurring dolomite shows a structure indicative of the same growth mechanism as the experimentally-derived dolomite.

From the Avrami time-transformation models and raw data, the number of nuclei

increase as the Mg content of each new precipitate increases towards stoichiometric dolomite. AFM analyses show a period of ten hours before any stable nucleation occurs indicating the first phase is the most difficult to nucleate.

The calcite to dolomite transformation has been characterized by the nature of the induction period and the rapid replacement period. In this study, the following is concluded:

1) The induction period consists of two stages. The first stage is characterized by no stable nucleation. The second stage is characterized by the nucleation and slow replacement of Ca-Mg carbonate phases.

2) The transition from the induction period to the rapid replacement period is not the result of a change in growth mechanism.

3) Precipitate from the induction period and the rapid replacement period, as well as the final products, have microtopographic surfaces interpreted as growth by a mechanism similar to the Birth and Spread Model.

4) Samples of naturally-forming dolomites exhibit the same microtopographic features as the experimentally-derived dolomite and consequently, are interpreted to grow by the same mechanism.

Thus, the lack of dolomite in thermodynamically-favorable environments is interpreted as the result of a long induction period in which little to no precipitate forms. The length of the induction period in natural environments will vary considerably due to fluctuation in conditions, such as saturation state, temperature, and available substrate, since the length of time in which favorable conditions persist will greatly affect the induction period. Furthermore, the history of the mineralizing environment determines whether dolomite will form.

IMPLICATIONS FOR NATURAL DOLOMITIZATION

This study of the growth mechanism by which dolomite precipitates demonstrates the applicability of experimental high-temperature dolomite studies to dolomite forming in natural environments. The series of studies (Land 1967; Gaines 1974; Katz and Matthews 1977; Gaines 1980; Baker and Kastner 1981; Gregg 1983; Bullen and Sibley 1984; Sibley and Bartlett 1987; Morrow and Rickets 1988; Sibley 1990; Zempolich and Baker 1993; Nordeng and Sibley 1994; Sibley *et al.* 1994) including this study, all of which involved dolomitization of calcium carbonate, have been based on the assumption that experimentally-derived dolomite and naturally-occurring dolomite grow by the same mechanism. This study provides direct evidence for similar microtopography, and subsequently similar growth mechanisms, between natural and experimental samples despite the stark differences between laboratory synthesis and natural precipitation.

The Atomic Force Microscopy analyses of experimentally-derived and natural sample surfaces provide three new insights into the process of dolomitization: 1) the growth mechanism of three different natural dolomites and the experimentally-derived dolomite in this study is the same, 2) there is no evidence for a change in growth mechanism during the transition from the induction period to the rapid replacement period, and 3) characterization of the early stages of nucleation show there is a lack of stable product formed during approximately the first half of the induction period. This allows the kinetic results from previous studies to be applied with greater confidence to

events occurring in natural dolomite environments. While this study does not preclude the existence of metastable phases during the beginning of the induction period, it demonstrates there is a hiatus after mineral-solution contact and before the formation of stable nuclei of Ca-Mg carbonates which dissolve slower than calcite.

Observations of natural dolomites which support the inferences made from experimental modelling range from the scale of a thin section to the outcrop. In nature, fine-grained calcium carbonate is preferentially dolomitized over coarse-grained calcium carbonate (Murray and Lucia 1967). Experimental studies show an increase in the rate of dolomitization with a decrease in calcium carbonate reactant size (Bartlett 1984). Cathodoluminescence and light microscopy of natural dolomite crystals reveal inclusions and a mottled appearance at the center of the crystals (Sibley et al. 1994). This is consistent with observations of dolomite precipitate coating the surface of the calcite reactant and engulfing the partially dissolved calcite reactant. Similar observations were made in studies where VHMC precipitated at the expense of calcite and the VHMC was later replaced by stoichiometric dolomite (Sibley et al. 1994). The textures of experimentally-derived dolomite and natural dolomites are also similar (Sibley 1990; Sibley et al. 1994). The mineral phases VHMC and Ca-rich dolomite are common mineral assemblages only in modern environments (Kocurko 1986; Wenk et al. 1993; Sibley et al. 1994). These mineral phases precipitate prior to stoichiometric dolomite in experimental studies (Nordeng and Sibley 1994; Sibley et al. 1994). Solution modelling of natural dolomites indicates a correlation between Mg/Ca ratio of natural dolomites and the Mg/Ca cation ratio in solution (Sass and Katz 1982; Sass and Bein 1988). In experimental studies, a similar correlation exists (Sibley et al. 1994). Another

important correlation is the increase in stoichiometry with the increase in percent dolomite in natural dolomites (Schmidt 1965; Langbein et al. 1984). This supports the transition from VHMC to stoichiometric dolomite (an increasing Mg content) found in laboratory studies (Nordeng and Sibley 1994). Outcrops of partially dolomitized beds have abrupt contacts between the limestone and the dolomitized section (Sibley et al. 1994). This observation is consistent with the model of laboratory dolomitization. In the laboratory, dolomite is characterized by a rapid replacement period after the induction period indicating once nucleation and growth of dolomite begins (1-5% dolomite produced from calcite reagant), the reaction usually goes to completion (Sibley 1990). Thus, abrupt contacts between limestone and dolomite in natural partially-dolomitized limestones represents a solution front where the dolomitized side of the front had a residence time in the solution long enough to reach the rapid replacement period. Therefore, fluctuations in the solution front do not produce dolomite of smaller crystal size with less time exposure to the dolomitizing solution. Past a threshold residence time, dolomitization goes to completion on one side of the solution contact and does not on the other side. Lumsden (1988) observed the persistence of nonstoichiometric dolomite in sea water over millions of years. Nordeng and Sibley (1994) demonstrated the suppression of stoichiometric dolomite nucleation by fluctuating one of the factors that catalyze the dolomitization reaction, temperature. Their results produced VHMC and increased the time until stoichiometric dolomite was first detected by XRD (also referred to as the length of the induction period for that particular phase, stoichiometric dolomite). Thus, natural observations support the experimentally-determined time dependence of dolomitization.

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Based on these findings, natural environments which thermodynamically favor the precipitation of dolomite but lack any products, such as sea water, are expected to be in a period of unstable nuclei formation of Ca-Mg carbonates, or to contain calcium carbonate surfaces with hillocks of a Ca-Mg carbonate phase which dissolve slower than calcite precipitated on the surface, not previously detectable by conventional methods. It is also expected that the length of the induction period for dolomite in these environments will vary due to the time dependence of the reaction. APPENDIX

Appendix 1.

Table 3. Model Transformation Data (n=4)

	wainht %	VOLUMA &				Nucleation	Model volume	Model volume
time	products	products	time^4	shape	growth ^{°3}	rate	products	% products
2.08	0	0	18.72	4.19	6.2E-14	100000	4.86639E-07	4.86639E-05
2.08	0	0	18.72	4.19	6.2E-14	100000	4.86639E-07	4.86639E-05
4	0	0	256	4.19	6.2E-14	100000	6.65568E-06	0.000665568
4	0	0	256	4.19	6.2E-14	100000	6.65568E-06	0.000665568
9	0	0	1296	4.19	6.2E-14	100000	3.36939E-05	0.003369393
9	0	0	1296	4.19	6.2E-14	100000	3,36939E-05	0.003369393
∞	0	0	4096	4.19	6.2E-14	100000	0.000106486	0.010648557
8	0	0	4096	4.19	6.2E-14	100000	0.000106486	0.010648557
9.9	0	0	9606	4.19	6.2E-14	100000	0.000249713	0.024971262
6.6	0	0	9606	4.19	6.2E-14	100000	0.000249713	0.02497126
12.4	0	0	23872	4.19	6.2E-14	100000	0.000620446	0.062044611
12.4	3.61	3.42715	23872	4.19	6.2E-14	1000000	0.006187167	0.618716681
15	0	0	50625	4.19	6.2E-14	1000000	0.013075682	1.307568249
15	0	0	50625	4.19	6.2E-14	1000000	0.013075682	1.307568249
15.6	0	0	58468	4.19	6.2E-14	1000000	0.015086175	1.508617502
15.6	0	0	58468	4.19	6.2E-14	1000000	0.015086175	1.508617502
15.9	2.38	2.25799	63113	4.19	6.2E-14	1000000	0.016274705	1.62747051
15.9	0	0	63113	4.19	6.2E-14	1000000	0.016274705	1.62747051
16	0	0	66029	4.19	6.2E-14	1000000	0.017020252	1.702025167
16	0	0	66029	4.19	6.2E-14	1000000	0.017020252	1.702025167
16.5	0	0	74120	4.19	6.2E-14	1000000	0.019085883	1.908588309

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Model volume	% products	1.908588309	19.64227141	19.64227424	23.97748689	23.97748689	24.95969319	24.95969319	24.95969319	24.95969319	24.95969319	24.95969319	24.95969319	24.95969319	47.85051549	47.85051549	63.48621071	63.48621071	74.88452269	74.88452269	79.90894098	79.90894098	84.09998003	84.09998003	87.82648492	87.82648492
Model volume	products	0.019085883	0.196422714	0.196422742	0.239774869	0.239774869	0.249596932	0.249596932	0.249596932	0.249596932	0.249596932	0.249596932	0.249596932	0.249596932	0.478505155	0.478505155	0.634862107	0.634862107	0.748845227	0.748845227	0.79908941	0.79908941	0.8409998	0.8409998	0.878264849	0.878264849
Nucleation	rate	1000000	10000000	10000000	10000000	10000000	10000001	10000000	10000000	10000000	10000000	10000000	10000000	10000000	10000000	10000000	10000000	10000000	10000000	10000000	10000000	10000000	10000000	10000000	10000000	10000000
	growth ^{°3}	6.2E-14																								
	shape	4.19	4.19	4.19	4.19	4.19	4.19	4.19	4.19	4.19	4.19	4.19	4.19	4.19	4.19	4.19	4.19	4.19	4.19	4.19	4.19	4.19	4.19	4.19	4.19	4.19
	time^4	74120	84112	84112	1E+05	3E+05	3E+05	4E+05	4E+05	5E+05	5E+05	6E+05	6E+05	7E+05	7E+05	8E+05	8E+05									
volume %	products	0	11.7402	25.0646	31.8985	43.2532	0	2.49551	4.67402	7.92775	14.7978	30.7118	43.6705	44.6948	5.06461	14.9905	9.2574	49.8534	29.9673	56.2591	17.7594	69.7863	82.8583	81.2428	100	100
weight %	products	0	12.31	26.09	33.08	44.58	0	2.63	4.92	8.33	15.49	31.87	45	46.03	5.33	15.69	9.72	51.2	31.11	57.58	18.56	70.91	83.61	82.05	100	100
	time	16.5	17	17	18	18	18.2	18.2	18.2	18.2	18.2	18.2	18.2	18.2	22.4	22.4	25	25	27	27	28	28	29	29	30	30

	weight %	volume %				Nucleation	Model volume	Model volume
time	products	products	time^4	shape	growth [°] 3	rate	products	% products
38.7	64.08	62.8308	2E+06	4.19	6.2E-14	10000000	0.996977469	99.69774692
44	96.55	96.366	4E+06	4.19	6.2E-14	10000000	0.999941391	99.9941391
44	95.24	94.9897	4E+06	4.19	6.2E-14	10000000	0.999941391	99.9941391
64.3	98.61	98.5342	2E+07	4.19	6.2E-14	10000000	1	100
64.3	100	100	2E+07	4.19	6.2E-14	10000000	1	100
69.7	100	100	2E+07	4.19	6.2E-14	10000000	1	100
69.7	100	100	2E+07	4.19	6.2E-14	10000000	1	100
72.8	100	100	3E+07	4.19	6.2E-14	10000000	1	100
72.8	100	100	3E+07	4.19	6.2E-14	10000000	1	100
80	100	100	4E+07	4.19	6.2E-14	10000000	1	100
80	100	100	4E+07	4.19	6.2E-14	10000000	1	100
92.9	96	95.7879	7E+07	4.19	6.2E-14	10000000	1	100
92.9	100	100	7E+07	4.19	6.2E-14	10000000	1	100
92.9	100	100	7E+07	4.19	6.2E-14	10000000	1	100
92.9	100	100	7E+07	4.19	6.2E-14	10000000	1	100
94.3	100	100	8E+07	4.19	6.2E-14	10000000	1	100
94.3	100	100	8E+07	4.19	6.2E-14	10000000	1	100
168	100	100	8E+08	4.19	6.2E-14	10000000	1	100
168	100	100	8E+08	4.19	6.2E-14	10000000		100

Table 3 (cont'd).

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(n=3)
Data
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Model
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Table

	weight %	volume %				Nucleation	Model volume	Model volume
time	products	products	time^3	shape	growth [°] 2	rate	products	% products
2.08	0	0	8.999	0	1.6E-09	1E+11	4.26645E-05	0.004266452
2.08	0	0	8.999	0	1.6E-09	1E+11	4.26645E-05	0.004266452
4	0	0	64	0	1.6E-09	1E+11	0.000303389	0.03033893
4	0	0	64	0	1.6E-09	1E+11	0.000303389	0.03033893
9	0	0	216	0	1.6E-09	1E+11	0.00102357	0.102357003
و	0	0	216	0	1.6E-09	1E+11	0.00102357	0.102357003
8	0	0	512	0	1.6E-09	1E+11	0.002424539	0.242453869
œ	0	0	512	0	1.6E-09	1E+11	0.002424539	0.242453869
9.9	0	0	970.3	0	1.6E-09	1E+11	0.004589794	0.458979389
9.9	0	0	970.3	0	1.6E-09	1E+11	0.004589793	0.458979336
12.4	0	0	1920	0	1.6E-09	1E+11	0.009064083	0.906408303
12.4	3.61	3.427153	1920	0	1.6E-09	1E+11	0.009064083	0.906408303
15	0	0	3375	0	1.6E-09	1E+11	0.015874129	1.587412906
15	0	0	3375	0	1.6E-09	1E+11	0.015874129	1.587412906
15.6	0	0	3760	0	1.6E-09	1E+11	0.017669002	1.76690023
15.6	0	0	3760	0	1.6E-09	1E+11	0.017669002	1.76690023
15.9	2.38	2.257993	3982	0	1.6E-09	1E+11	0.018701694	1.870169396
15.9	0	0	3982	0	1.6E-09	1E+11	0.018701694	1.870169396
16	0	0	4119	0	1.6E-09	1E+11	0.019339841	1.933984132
16	0	0	4119	0	1.6E-09	1E+11	0.019339841	1.933984132
16.5	0	0	4492	0	1.6E-09	1E+11	0.02107276	2.107275994
16.5	0	0	4492	0	1.6E-09	1E+11	0.02107276	2.107275994
17	12.31	11.74017	4939	0	1.6E-09	1E+12	0.208772218	20.87722179
17	26.09	25.06462	4939	0	1 .6E-09	1E+12	0.20877224	20.87722403
18	33.08	31.89846	5851	0	1.6E-09	1E+12	0.242270013	24.22700135
18	44.58	43.2532	5851	0	1.6E-09	1E+12	0.242270013	24.22700135

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Model volume	% products	24.96689977	24.96689977	24.96689977	24.96689977	24.96689977	24.96689977	24.96689977	24.96689977	41.18321283	41.18321283	52.11524548	52.11524548	60.67091544	60.67091544	64.80028569	64.80028569	68.53598478	68.53598478	72.19954502	72.19954502	93.52601054	93.52600844	98.23800632	98.23800632	99.99965828	99.99965828
Model volume	products	0.249668998	0.249668998	0.249668998	0.249668998	0.249668998	0.249668998	0.249668998	0.249668998	0.411832128	0.411832128	0.521152455	0.521152455	0.606709154	0.606709154	0.648002857	0.648002857	0.685359848	0.685359848	0.72199545	0.72199545	0.935260105	0.935260084	0.982380063	0.982380063	0.999996583	0.999996583
Nucleation	rate	1E+12	1E+12	1E+12	1E+12	1E+12	1E+12	1E+12	1E+12	1E+12	1E+12	1E+12	1E+12	1E+12	1E+12	1E+12	1E+12	1E+12	1E+12	1E+12	1E+12	1E+12	1E+12	1E+12	1E+12	1E+12	1E+12
	growth [~] 2	1.6E-09	1.6E-09	1.6E-09	1 .6E-09	1.6E-09	1.6E-09	1.6E-09	1 .6E-09	1.6E-09	1.6E-09	1.6E-09	1.6E-09	1.6E-09	1.6E-09	1.6E-09	1.6E-09	1.6E-09	1.6E-09	1.6E-09	1.6E-09	1.6E-09	1.6E-09	1.6E-09	1.6E-09	1.6E-09	1.6E-09
	shape	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
-	time 3	6058	6058	6058	6058	6058	6058	6058	6058	11194	11194	15531	15531	19683	19683	22023	22023	24389	24389	27000	27000	57736	57736	85184	85184	3E+05	3E+05
volume %	products	0	2.495505	4.674019	7.927747	14.79781	30.71185	43.67055	44.69484	5.064612	14.99045	9.257403	49.85341	29.96732	56.25906	17.75945	69.78634	82.85831	81.24282	100	100	62.8308	79.49581	96.36598	94.98973	98.53419	100
weight %	products	0	2.63	4.92	8,33	15.49	31.87	45	46.03	5.33	15.69	9.72	51.2	31.11	57.58	18.56	70.91	83.61	82.05	100	100	64.08	80.36	96.55	95.24	98.61	100
	time	18.2	18.2	18.2	18.2	18.2	18.2	18.2	18.2	22.4	22.4	25	25	27	27	28	28	29	29	30	30	38.7	38.7	44	44	64.3	64.3

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del volume	products	.99998934	.999988934	.999999888	.999999888	100	100	100	100	100	100	100	100	100	100
мo	%	99	99	66	66										
Model volume	products	0.999999893	0.999999893	0.999999989	0.999999989	1	1	1	1	1	1	1	1	1	1
Nucleation	rate	1E+12	1E+12	1E+12	1E+12	1E+12	1E+12	1E+12	1E+12	1E+12	1E+12	1E+12	1E+12	1E+12	1E+12
	growth [°] 2	1.6E-09	1.6E-09	1.6E-09	1.6E-09	1.6E-09	1.6E-09	1.6E-09	1.6E-09	1.6E-09	1.6E-09	1.6E-09	1 .6E-09	1.6E-09	1.6E-09
	shape	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	time^3	3E+05	3E+05	4E+05	4E+05	5E+05	5E+05	8E+05	8E+05	8E+05	8E+05	8E+05	8E+05	5E+06	5E+06
volume %	products	100	100	100	100	100	100	95.78792	100	100	100	100	100	100	100
weight %	products	100	100	100	100	100	100	96	100	100	100	100	100	100	100
	time	69.7	69.7	72.8	72.8	80	80	92.9	92.9	92.9	92.9	94.3	94.3	168	168

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ne Model volume	% products	7 0.014268671	7 0.014268671	5 0.052758596	5 0.052758596	7 0.118667701	7 0.118667701	4 0.210867436	4 0.210867436	7 0.322742722	7 0.322742697	5 0.508304558	5 0.508304558	7 0.73936668	7 0.73936668	1 0.794361078	1 0.794361078	3 0.825179304	3 0.825179304	2 0.843948211	2 0.843948211	8 0.893937791	8 0.893937791	3 9.122440319	1 9.12244102	
Model Volun	products	0.00014268	0.00014268	0.00052758	0.000527586	0.00118667	0.00118667	0.002108674	0.002108674	0.00322742	0.00322742	0.005083040	0.00508304	0.00739366	0.00739366	0.00794361:	0.00794361	0.008251793	0.008251793	0.00843948	0.00843948	0.008939378	0.008939378	0.09122440	0.0912244	
Nucleation	rate	1E+15	1E+15	1E+15	1E+15	1E+15	1E+15	1E+15	1E+15	1E+15	1E+15	1E+15	1E+16	1E+16	18.16											
	growth	4E-05	4E-05	4E-05	4E-05	4E-05	4E-05	4E - 05	4E-05	4E-05	4E-05	4E-05	4E-05	4E-05												
	shape	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	c
	time^2	4.326	4.326	16	16	36	36	64	64	98.01	98.01	154.5	154.5	225	225	241.8	241.8	251.2	251.2	257	257	272.3	272.3	290	290	2 4 55
volume %	products	0	0	0	0	0	0	0	0	0	0	0	3.42715	0	0	0	0	2.25799	0	0	0	0	0	11.7402	25.0646	31 8985
weight %	products	0	0	0	0	0	0	0	0	0	0	0	3.61	0	0	0	0	2.38	0	0	0	0	0	12.31	26.09	33 08
	time	2.08	2.08	4	4	9	9	8	8	9.9	9.9	12.4	12.4	15	15	15.6	15.6	15.9	15.9	16	16	16.5	16.5	17	17	18

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Table 5 (cont'd).

пT																			_	-						
MODEL VOLUME	% products	10.15659396	10.38189091	10.38189091	10.38189091	10.38189091	10.38189091	10.38189091	10.38189091	10.38189091	15.21500788	15.21500788	18.56124475	18.56124475	21.37219439	21.37219439	22.82848413	22.82848413	24.22377154	24.22377154	25.68411171	25.68411171	38.90284521	38.90284283	47.19411144	47.19411144
Model Volume	products	0.10156594	0.103818909	0.103818909	0.103818909	0.103818909	0.103818909	0.103818909	0.103818909	0.103818909	0.152150079	0.152150079	0.185612447	0.185612447	0.213721944	0.213721944	0.228284841	0.228284841	0.242237715	0.242237715	0.256841117	0.256841117	0.389028452	0.389028428	0.471941114	0.471941114
Nucleation	rate	1E+16	1E+16	1E+16	1E+16																					
	growin	4E - 05	4E-05	4E - 05	4E - 05	4E-05	4E-05	4E-05	4E-05	4 E-05	4E-05	4E-05	4E-05													
-	snape	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	time z	324.7	332.3	332.3	332.3	332.3	332.3	332.3	332.3	332.3	500.4	500.4	622.5	622.5	729	729	785.7	785.7	841	841	900	900	1494	1494	1936	1936
volume %	products	43.2532	0	2.49551	4.67402	7.92775	14.7978	30.7118	43.6705	44.6948	5.06461	14.9905	9.2574	49.8534	29.9673	56.2591	17.7594	69.7863	82.8583	81.2428	100	100	62.8308	79.4958	96.366	94.9897
weight %	products	44.58	0	2.63	4.92	8.33	15.49	31.87	45	46.03	5.33	15.69	9.72	51.2	31.11	57.58	18.56	70.91	83.61	82.05	100	100	64.08	80.36	96.55	95.24
	tıme	18	18.2	18.2	18.2	18.2	18.2	18.2	18.2	18.2	22.4	22.4	25	25	27	27	28	28	29	29	30	30	38.7	38.7	44	44

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Model volume	% products	74.39542767	74.39542767	79.8574389	79.8574389	82.60517582	82.60517582	87.8871189	87.8871189	94.21335608	94.21335608	94.21335608	94.21335608	94.66963401	94.66963401	99.99085948	99.99085948
Model Volume	products	0.743954277	0.743954277	0.798574389	0.798574389	0.826051758	0.826051758	0.878871189	0.878871189	0.942133561	0.942133561	0.942133561	0.942133561	0.94669634	0.94669634	0.999908595	0.999908595
Nucleation	rate	1E+16															
	growth	4E-05	4E - 05	4E-05													
	shape	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	time^2	4131	4131	4858	4858	5303	5303	6400	6400	8640	8640	8640	8640	8889	8889	28197	28197
volume %	products	98.5342	100	100	100	100	100	100	100	95.7879	100	100	100	100	100	100	100
weight %	products	98.61	100	100	100	100	100	100	100	96	100	100	100	100	100	100	100
	time	64.3	64.3	69.7	69.7	72.8	72.8	80	80	92.9	92.9	92.9	92.9	94.3	94.3	168	168

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