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Some Observations on the Formation of Wollastonite from Calcite and Quartz

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Mixtures of powdered calcite and quartz were reacted for various lengths of time at a total pressure of 2000 bars, 650 °C, in an H₂O-CO₂ fluid. Extent of formation of wollastonite was determined by partial chemical analysis of run products. Experimental scatter precludes detailed analysis of the reaction mechanism.

The data show that approximately 40% reaction takes place in the first 24 h, and that after this initial period the rate decreases. Examination of run products shows the calcite to be surrounded by radiating wollastonite crystals. This suggests that the wollastonite cover forms during the initial stages of reaction and, by shielding the calcite, suppresses the reaction.

Single cleavage flakes of calcite were packed in -325 mesh quartz and allowed to react under the same conditions as the powders. A scanning electron microscope was used to examine and photograph the fragment surfaces at the conclusion of the experiments.

Examination of the photographs shows the calcite to be completely covered with a thin layer of wollastonite crystals. Details of the morphology suggest that the wollastonite grew outward from nucleation centers and that the solution of calcite and quartz may have been accelerated near growing wollastonite. Although no details of the reaction mechanism can be deduced, the model favored here is that growth was most rapid near the calcite-wollastonite interface and the mantling effect slowed the reaction by preventing the transport of silica to the calcite surface.

Un mélange de calcite et de quartz broyé ont été soumis durant des périodes plus ou moins longues à une pression totale de 2000 bars, à 650 °C en milieu aqueux et dioxyde de carbone. La quantité de wollastonite formée a été déterminée par analyse chimique partielle des produits.

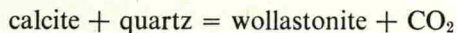
Les résultats d'expérience ne permettent pas une analyse détaillée du mécanisme de réaction.

L'observation montre qu'environ 40% de la réaction a lieu dans les premières 24 heures, et qu'après, le taux de réaction diminue. L'examen des produits expérimentaux montre que la calcite est entourée par des cristaux radiants de wollastonite. La wollastonite se formerait au début de la réaction, et faisant blindage autour de la calcite, arrêterait la réaction. De petits prismes de calcite mélangés à du quartz broyé à 325 mesh ont été soumis aux mêmes conditions que les poudres. Après expérience, les surfaces des fragments ont été examinées et photographiées à la microsonde. La calcite est alors complètement couverte d'une fine couche de cristaux de wollastonite. La morphologie suggère que la wollastonite s'est développée vers l'extérieur à partir de centres de nucléation et que la solution de calcite et de quartz était plus rapide près des cristaux de wollastonite en voie de développement.

Bien que l'on ne puisse tirer de conclusion quant au mécanisme de la réaction, il semble que la croissance soit plus rapide au contact calcite-wollastonite, et que le blindage ralentisse la réaction en empêchant le transport de silice vers la calcite.

Introduction

The detailed reconstruction of metamorphic events requires knowledge of the kinetics of the relevant metamorphic reactions. The objective of this study was to determine the mechanism of the reaction:



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under a particular set of physical conditions.

The results of the study elucidate to some extent the nature of the reaction, but they do not yield a rate equation. The conclusions may, however, be of use to experimentalists.

Experimental Technique

Starting Materials

Clear quartz from Alexander County, North Carolina, and Iceland spar calcite from the

collection of Princeton University were used in this study. The minerals were cleaned, crushed, and screened to separate the $-100 + 200$ mesh and $-200 + 325$ mesh fractions. Mixtures of calcite and quartz of the same size fractions were prepared by 10 min of careful hand mixing, followed by 30 s of oscillation in a Spex Mixer. A portion of each mix was annealed to 2000 bars P_{CO_2} and 700 °C for 48 h to remove surface strains and to recrystallize any extremely fine-grained starting material. For one series of experiments, starting materials were $1 \times 2 \times 4$ mm cleavage fragments of calcite packed in -325 mesh quartz.

The fluid phase in which reaction took place was composed of distilled water and Canadian Liquid Carbonic "Hi-Dry" CO_2 .

Apparatus and Control

The experiments were carried out in $\text{H}_2\text{O}-\text{CO}_2$ mixtures using the technique of Greenwood (1967a). Starting materials were supported in open platinum capsules in 25 cm Morey bombs. After the bombs were placed in the furnaces, sufficient CO_2 was pumped in to keep calcite and quartz stable until the bombs reached the desired temperature. The CO_2 pressure was then adjusted, and water pumped in to bring the fluid to the desired composition and pressure.

At the conclusion of a run the fluid was rapidly extracted through a two-stage cold trap into a known volume. Water content of the bomb was found by weighing the cold trap, and the other gases, principally CO_2 , were determined volumetrically. Gas chromatography was not used to analyze the gas phase in these experiments, but work done under similar conditions (Greenwood 1967a, 1967b; Gordon and Greenwood 1970) showed negligible CO or CH_4 .

Run up time in these experiments was usually about 4 h. Quench time was always less than 10 min and usually about 5 min.

All runs were at 2000 ± 30 bars, $650^\circ \pm 6^\circ\text{C}$, and $X_{\text{CO}_2} = 0.18 \pm 0.05$. Details of control and measurement may be found in Gordon and Greenwood 1970.

Extent of Reaction

Preliminary experiments indicated that the amount of silica in each capsule showed considerable variation from the beginning to the end of a run, while the amount of calcite remained constant. The extent of reaction was therefore meas-

ured by the ratio of the moles of wollastonite formed to the number of moles of calcite available for reaction. Determination of these quantities was made chemically. Remaining calcite was determined by measuring the CO_2 evolved by reacting the products with 1 M HCl, and the total calcite originally available was determined by measuring the total calcium in the products.

The CO_2 determination was made using essentially the gravimetric method outlined by Vogel (1961, p. 584). Total calcium was determined by atomic absorption spectrophotometry of the solution obtained by adding concentrated HCl to the products of the CO_2 determination, and boiling to completely gelatinize the wollastonite remaining.

The uncertainty in extent of reaction, based on five calibration determinations, is approximately 5% at 50% reaction.

Experimental Results

Run data are listed in Table 1 and plotted in Fig. 1.

The results from separate capsules in the same bomb differ by more than the expected analytical uncertainty only in runs 39, 40, 51, and 61. The scatter between different runs is much more pronounced.

The runs on non-annealed material generally have lower extents of reaction than runs of equivalent duration on annealed material. The scatter in each group is large enough that the groups overlap appreciably. It might be expected that annealing would reduce the reaction rate by decreasing the number of imperfections at the grain surfaces and hence reducing the most likely nucleation sites. In fact, the opposite is the case.

Some scatter could be eliminated by not considering runs in which the temperature or mol fraction of CO_2 differ by some arbitrary amount from their mean values for all experiments. Examination of the data shows, however, that the direction of deviation in the extent of reaction cannot be correlated with the direction of deviation of the experimental variables. All data points are therefore plotted in Fig. 1. Annealed and nonannealed starting material runs are shown with different symbols.

The data show that the initial 40% reaction takes place in less than 24 h and that after this initial period the rate decreases. Optical examination of some run products suggests a reason for

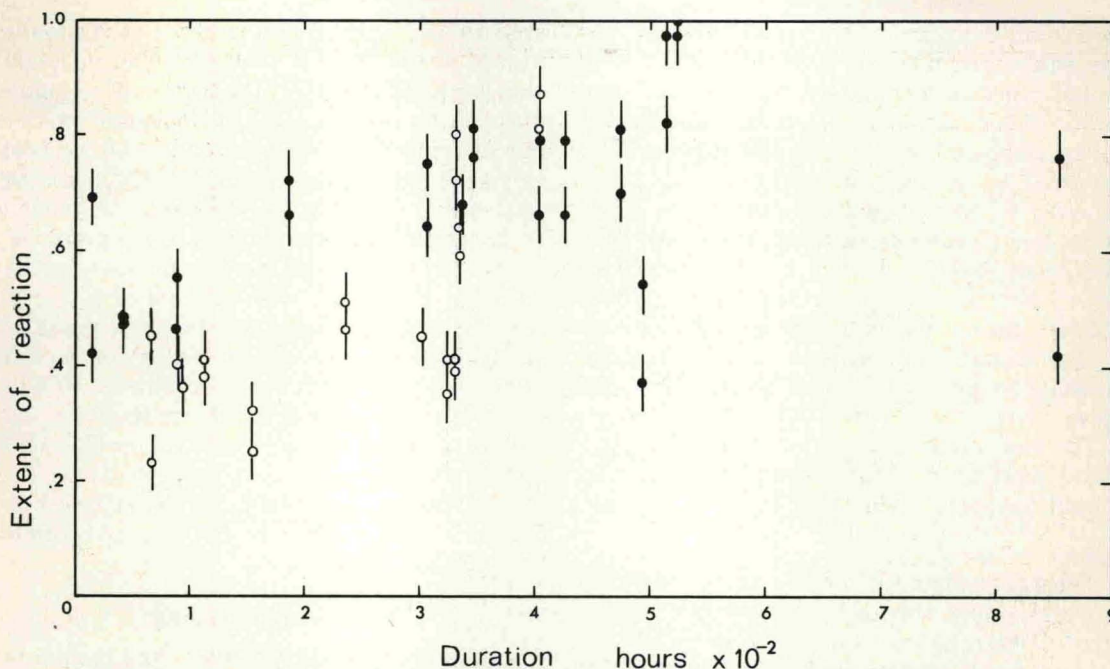


FIG. 1. Experimental results. Open symbols—starting material not annealed. Closed symbols—starting material annealed.

this phenomenon. Calcite grains are completely surrounded by radiating wollastonite needles ranging up to $.002 \times .25$ mm in size. Wollastonite also parallels the surface of calcite rhombs. This suggests that, under the experimental conditions, nucleation and rapid growth take place at or near the surface of the calcite, surrounding each grain with a wollastonite sheath. This armoring of the calcite suppresses the reaction, probably by interfering with the transport of reactant species. Additional evidence for this model follows.

Electron Microscope Examination

A Cambridge Instruments Steroscan II scanning electron microscope was used to examine the surface of single cleavage fragments of calcite that had been packed in -325 mesh quartz and reacted under the same conditions as the powders.

At the conclusion of each run the cleavage fragment was carefully removed from the powdered quartz and washed gently with acetone. Optical examinations showed that this did not disturb or remove any detectable wollastonite.

Each cleavage fragment was mounted on a holder and given a uniform gold coating (approximately 20 \AA) in a vacuum evaporator. No other preparation was necessary.

Cleavage fragments were scanned at a wide range of magnifications and photographs made of interesting features. No attempt was made to calibrate the magnification and hence magnifications and scale bars shown in Figs. 2, 3, and 4 have an uncertainty of $\pm 10\%$. Because of the geometry of the microscope, there is a slight distortion in photographed images, but this effect is not important for the purposes of the present study.

Not observable in photographs, but pertinent, are the facts that the wollastonite layer is only 3–5 crystals deep, and that no wollastonite was detected in the surrounding quartz powder.

Several conclusions may be drawn from examination of Figs. 2, 3, and 4.

It appears that nucleation and growth of wollastonite took place primarily on the calcite surface and that growth resulted in a rosette pattern in the wollastonite. Growth was most rapid parallel to the calcite surface, resulting in a thin but complete wollastonite sheath around the calcite fragment. After this initial period, growth of wollastonite was effectively stopped. Wollastonite crystals from the 473 h run are essentially the same size as those in 41 h run.

The indentation of quartz and calcite near wollastonite crystals suggests either that local

TABLE 1. Experimental results

Run	$T^{\circ}\text{C}$	X_{CO_2}	Time (h)	Initial quartz: calcite	Extent of reaction
Runs with -100 +200 starting material					
20A	649 \pm 7	.210	67	1:1	.45
21A	649 \pm 3	.153	90	1:1	.40
23A	649 \pm 3	.2 \pm .05	94	1:1	.36
24A	645 \pm 4	.195	301	1:1	.45
26A	644 \pm 4	.229	113	1:1	.38
B					.41
27A	648 \pm 3	.203	156	1:1	.25
B					.32
28A	650 \pm 4	.169	330	1:1	.39
B					.41
29A	649 \pm 3	.165	324	1:1	.35
B					.41
31A	652 \pm 4	.2 \pm .05	235	1:1*	.51
B					.46
32B	650 \pm 4	.2 \pm .05	68	1:1*	.23
37A	649 \pm 3	.133	426	1:1*	.79
B					.66
38A	650 \pm 3	.245	345	1:1*	.76
B					.81
39A	650 \pm 3	.150	512	1:1*	.97
B					.82
40A	655 \pm 3	.166	493	1:1*	.37
B					.54
42A	645 \pm 6	.187	186	1:1*	.72
B					.66
43A	645 \pm 4	.143	336	1:1*	.68
48B	646 \pm 2	.192	851	1:1*	.42
49A	642 \pm 6	.187	851	1:1*	.76
B					.76
50A	647 \pm 4	.265	521	1:1*	.97
B					1.00
51A	651 \pm 2	.203	403	1:1†	.79
B					.66
52A	648 \pm 2	.189	403	1*1‡	.81
B					.85
53A	649 \pm 2	.203	334	3:1	.59
B					.59
C					.64
Runs with -200 +325 starting material					
58A	660 \pm 11	.231	330	2:1	.80
B				4:1	.72
60A	650 \pm 5	.183	306	2:1†	.75
B				4:1†	.64
61A	650 \pm 3	.202	16	2:1†	.42
B				4:1†	.69
62A	650 \pm 3	.177	89	2:1†	.55
B				4:1†	.46
63A	650 \pm 4	.181	473	2:1†	.70
B				4:1†	.81
64A	650 \pm 2	.165	41	2:1†	.48
B				2:1†	.47

*Mix previously annealed at 700°C, 2000 bars P_{CO_2} for 48 h.

†Annealed mix. Top of capsule packed with extra quartz.

‡Not annealed. Top of capsule packed with extra quartz.

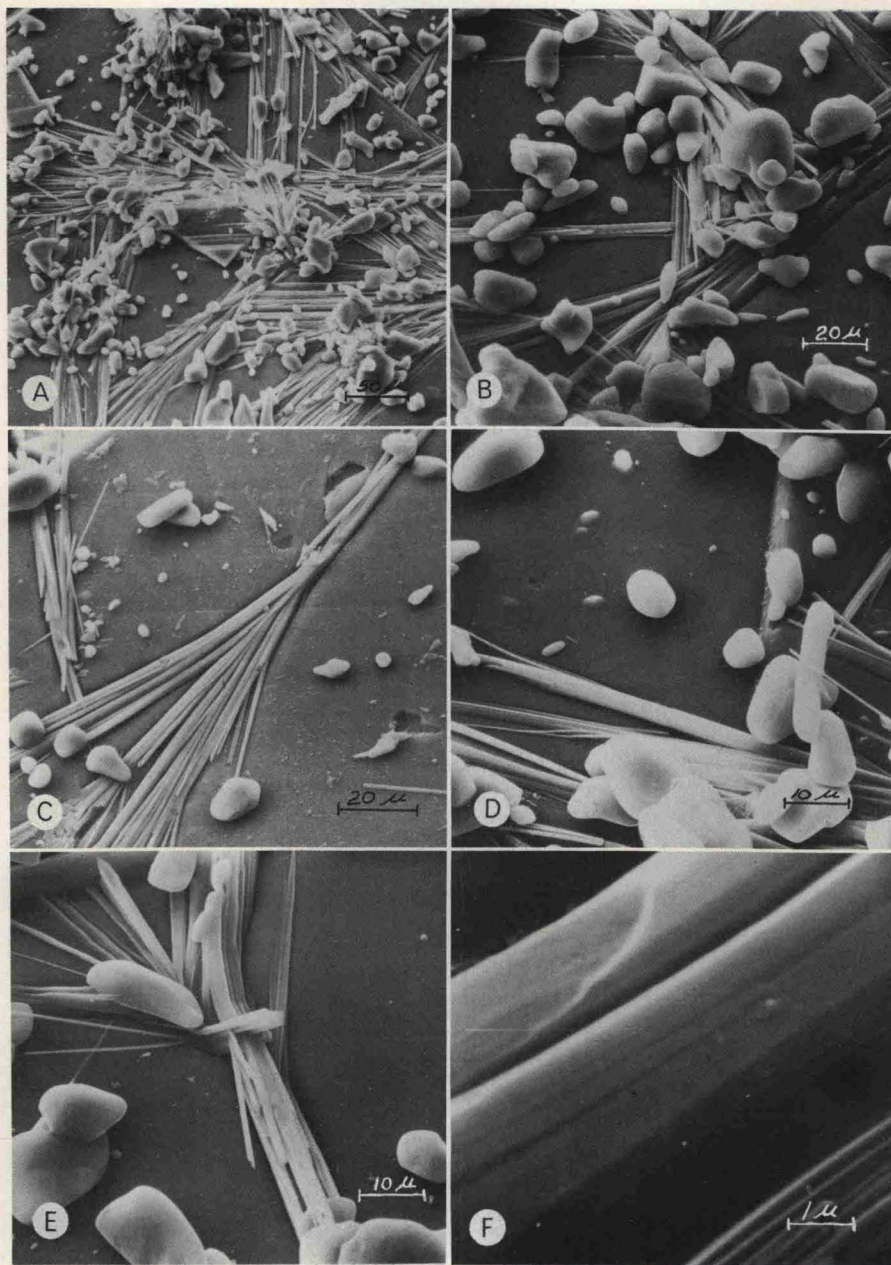


FIG. 2. Run W-67 2000 bars, $646^{\circ} \pm 2^{\circ}\text{C}$, $X_{\text{CO}_2} = 0.175$, $T = 19$ h.

A) General view of specimen surface. Wollastonite appears to have nucleated at specific centers and grown parallel to calcite surface. Calcite substrate, rounded quartz, wollastonite needles. $\times 180$.

B) Closer view of surface. What appears to be a crystallization center at top center is obscured by quartz grains. $\times 450$.

C) Surface view. Apparent indentation of calcite surface near wollastonite may be a result of sample coating technique, but this, and next two photographs, suggest the indentation is real. $\times 420$.

D) Detail showing cleavage step in calcite surface and indentation of calcite near wollastonite crystals. $\times 900$.

E) Detail of crystallization center. Wollastonite crystal perpendicular to surface may have been broken in sample preparation. Calcite appears indented near wollastonite. $\times 900$.

F) Detail of wollastonite crystal showing "steps" on surface. $\times 8400$.

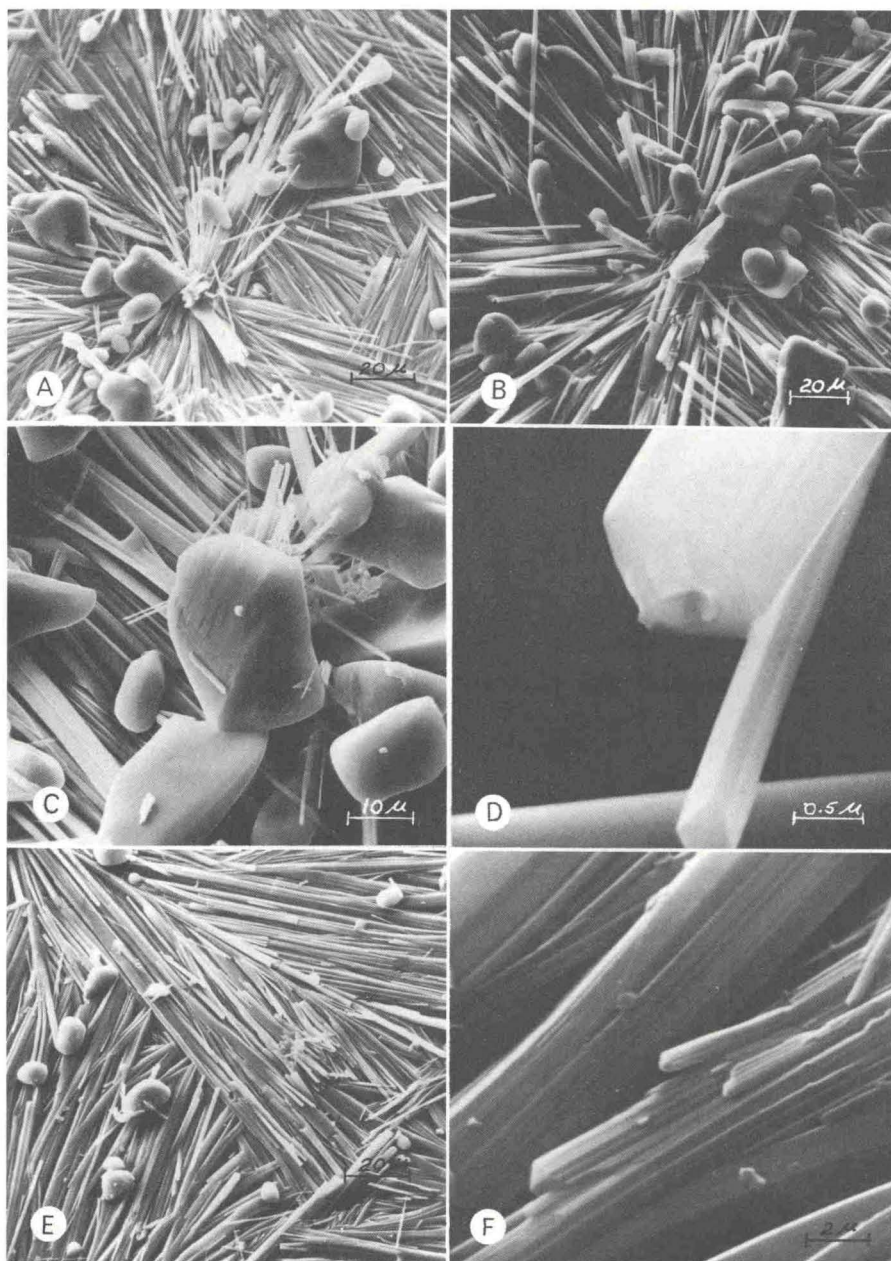


FIG. 3. A) Run W-64 2000 bars, $650^{\circ} \pm 2^{\circ}\text{C}$, $X_{\text{CO}_2} = 0.165$, $T = 41$ h.
 B), C), D) Run W-65 2000 bars, $646^{\circ} \pm 3^{\circ}\text{C}$, $X_{\text{CO}_2} = 0.211$, $T = 68$ h.
 E), F) Run W-62 2000 bars, $650^{\circ} \pm 3^{\circ}\text{C}$, $X_{\text{CO}_2} = 0.177$, $T = 89$ h.
 A) General surface view. There is an apparent center of crystallization in lower center of photograph. $\times 420$.
 B) Crystals of wollastonite have a slight tendency to radiate away from calcite surface but are still principally parallel to cleavage face. $\times 425$.
 C) Rounded quartz grains. Wollastonite possibly growing on opposite side of central grain. $\times 865$.
 D) Detail of end of wollastonite crystal. Note striated surface and branching crystal. $\times 17250$.
 E) Surface detail. Wollastonite crystals have random orientation. $\times 425$.
 F) Detail of wollastonite. Striated surfaces are characteristic of crystals grown in these runs. $\times 4090$.

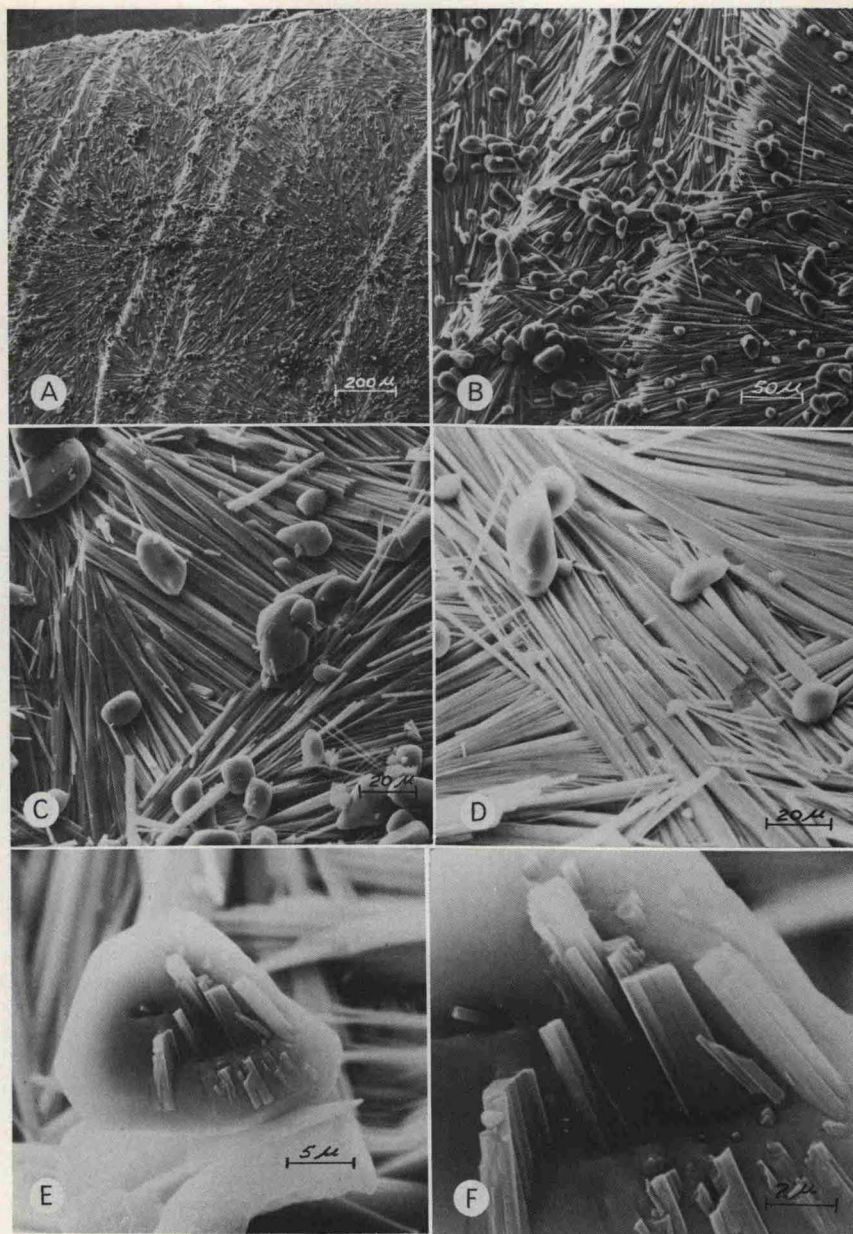


FIG. 4. A), B), C) Run W-60 2000 bars, $650^{\circ} \pm 5^{\circ}\text{C}$, $X_{\text{CO}_2} = 0.183$, $T = 306$ h.

D), E), F) Run W-63 2000 bars, $650^{\circ} \pm 5^{\circ}\text{C}$, $X_{\text{CO}_2} = 0.181$, $T = 473$ h.

A) Low magnification view of surface of cleavage fragment. Wollastonite has grown parallel to cleavage surface but otherwise in random orientation. "Steps" are due to original calcite configuration. Note "rosette" texture. $\times 38$.

B) View at higher magnification. Apparent jagged edges on wollastonite needles are a result of photographic process. $\times 150$.

C) Surface detail. Wollastonite crystals have a wide range of sizes. Calcite surface is completely covered. Examination of intentionally scratched surface showed that wollastonite layer is only 1-5 crystals deep. $\times 400$.

D) General view. Although this run had the longest duration of any studied with the electron microscope, the wollastonite crystals are not noticeably larger than those from shorter runs. $\times 460$.

E) One of the rare instances where apparently wollastonite has grown on the surface of a quartz grain. $\times 1850$.

F) Detail of figure above. Substrate is embayed near euhedral crystals. $\times 4600$.

composition gradients controlled the decomposition of the reactants, or, that growth took place most readily in regions where the reactant minerals were intrinsically more soluble.

The model favored here is that local imperfections or impurities on the calcite surface acted as nucleation centers.² Growth was most rapid at the calcite-wollastonite interface. Solution of calcite was accelerated by the local composition gradients set up near growing wollastonite crystals. After the calcite was sheathed in wollastonite growth continued, but the transport of silica to the highly reactive calcite surface was slowed. Growth rate then became dependent either on the transport of Ca through the wollastonite to the wollastonite-fluid interface, and/or the transport of silica to the calcite-wollastonite interface.

Alternatively, it could be argued that, at the beginning of a run, the fluid phase becomes rapidly supersaturated with respect to wollastonite. This supersaturation is restricted to the calcite surface because of the differing rates of solution of calcite and quartz. When the fluid and calcite are separated by the wollastonite layer, the fluid reaches equilibrium with wollastonite and the reaction stops.

Conclusions

The interpretations offered suggest that specific surface area of calcite is of critical importance to the rate of reaction. Experimentalists have long known that reducing the grain size of reactants increases the rate of reaction. This is normally attributed to increase in the rate of

²Note added in proof: A recent study by Kridelbaugh (1971) shows that, in the presence of pure CO₂, wollastonite nucleates and grows on quartz. This is in marked contrast with the results of this study and indicates that the composition of the fluid phase plays a major role in determining the nature of the reaction mechanism.

solution. This study shows that the accelerating effects may be due equally to increase in number of nucleation and growth sites.

It is further suggested that some reactions may be self-arresting due to effects analagous to the mantling phenomena in these experiments.

Acknowledgments

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