STRAIN INDUCED CALCITE-ARAGONITE TRANSFORMATION IN CALCIUM CARBONATE

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ABSTRACT

The transformation of calcite to aragonite by grinding has been studied using *x*-ray diffraction methods and electron microscopy. Grinding at room temperature produced a partial transformation to aragonite. The transformation curve was characteristic of a nucleation and growth process. It is postulated that the nucleus is formed by atomic movements, produced by microstraining, which generated a small region having the new structure. Various stages have been identified in the deformation of the calcite particles.

INTRODUCTION

Calcium carbonate exists in three polymorphs: calcite, aragonite, and vaterite. Much work has been done on the calcite-aragonite phase transformations, since these minerals occur in large quantities in the earth's crust, and information on the phase equilibrium relationships can be of use in establishing the "history" of certain land masses.

Burns & Bredig (1956) were the first to report the partial transformation of calcite to aragonite by grinding. This change was subsequently confirmed by Goldsmith & Jamieson (1960) and Dachille & Roy (1960). These reports were only qualitative in nature, *i.e.*, the transformations have been reported, but few quantitative data showing the effect of mechanical deformation on the kinetics of the transformation could be found.

Work has also been done on the effect of deformation of the lattice, as measured by *x*-ray diffraction line broadening analysis. The only calcium carbonate polymorph for which data can be found in the literature is calcite (Rosenthal & Kaufman 1952, Paterson 1959, Gross 1965). These investigators all found that microstraining was the major cause of broadening.

However, no data were found which related lattice disturbances and the degree of transformation produced by mechanical deformation. A study was therefore made of the effect of mechanical deformation produced by ball milling on the calcite to aragonite phase transformation and

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on x-ray line broadening accompanying it. This type of analysis had proved to be very useful in the study of the strain-induced vaterite to calcite transformation (Northwood & Lewis 1968).

EXPERIMENTAL DETAILS

The calcite sample was optically pure iceland spar. The aragonite sample used for the preparation of standard mixtures came from the Aragon district in Spain, and was also optically pure. The materials were ground to minus 200 mesh (74 mμ) with a hand pestle and mortar before use in the ball mill.

The milling was done at ambient temperature with 1-gm samples, using steel grinding cylinders and balls in an M280 ball mill. This is a high speed grinding mill marketed by Glen Creston Limited. The material to be ground was placed in a grinding cylinder, 5 cm long and 2.2 cm in diameter, which was clamped in the adjustable jaws of a high speed shaking mechanism, and was shaken in a complex three-dimensional motion. One ball, 1.2 cm in diameter, was used. The sample was milled, examined on the x-ray powder diffractometer, and then returned to the mill for further grinding.

All the samples were examined on a Philips powder diffractometer. This consisted of a P.W. 1010 stabilized x-ray generator, a P.W. 1050 goniometer and proportional counter, and a P.W. 1051 scalar and recording panel. Nickel-filtered Cu $K\alpha$ radiation was used in every case. The profiles were chart recorded automatically using a scanning speed of 1/8° per minute in 2θ (or 1/4°/minute for extremely broad high angle peaks). A time constant of 1 sec. was employed in all cases except for very weak peaks where a time constant of 2 sec. was used. In certain cases, Debye-Scherrer powder diffraction photographs were also taken with a Philips 57.3 mm diameter camera. The percentage of each polymorph present after milling was determined by calibrating the intensity ratio $(10\bar{1}4)$ calcite/(111) aragonite with standard samples which were prepared containing 5, 10, 25, 50, 75, 90 and 95% by weight of aragonite in calcite.

The majority of the x-ray line broadening analysis was done using the quadratic integral breadth method (see Wagner & Aqua 1963). This method involves plotting $\beta^{*2}(\beta^2 \cos^2 \theta_0/\lambda^2)$ against $d^{*2}(4 \sin^2 \theta_0/\lambda^2)$. The intercept at $d^{*2} = 0$ yields directly $(1/D^{PF})^2$ and the slope is equal to $4\epsilon^2$, where D^{PF} is the effective crystallite size and ϵ is the microstrain, *i.e.*, random displacements from a perfect structure. Since multiple orders were not available because of overlapping of the reflections and loss of intensity at high Bragg angles, the best straight line was drawn through the available points, and an average microstrain and crystallite size were estimated from it. The x-ray diffraction line broadening due to instrumental effects was determined by using well-annealed calcite and aragonite samples which were assumed to be free from broadening effects (Jones 1938, Stokes 1948).

RESULTS

The course of the transformation is shown in Fig. 1. There is apparently a nucleation period of about $3\frac{1}{2}$ hours; then, aragonite begins to form, increases to a maximum of 78%, and decreases to 60% after 12 hours. The final product is a mixture of calcite and aragonite. The apparent increase and then decrease in the amount of aragonite formed was surprising but repeat runs confirmed the shape of the curve (each point of Fig. 1 is the average of at least two readings). The values for percentage transformation are reproducible to ±3%. The shape of the transformation curve suggested that it was probably a nucleation and growth transformation, so an attempt was made to fit the results to the Avrami (1939–1941) equation: $f = 1 - e^{-(kt)^n}$, where f = fraction transformed, k, n = constants and t = milling time. The results fit the equation quite well up to the time where the maximum amount of aragonite is

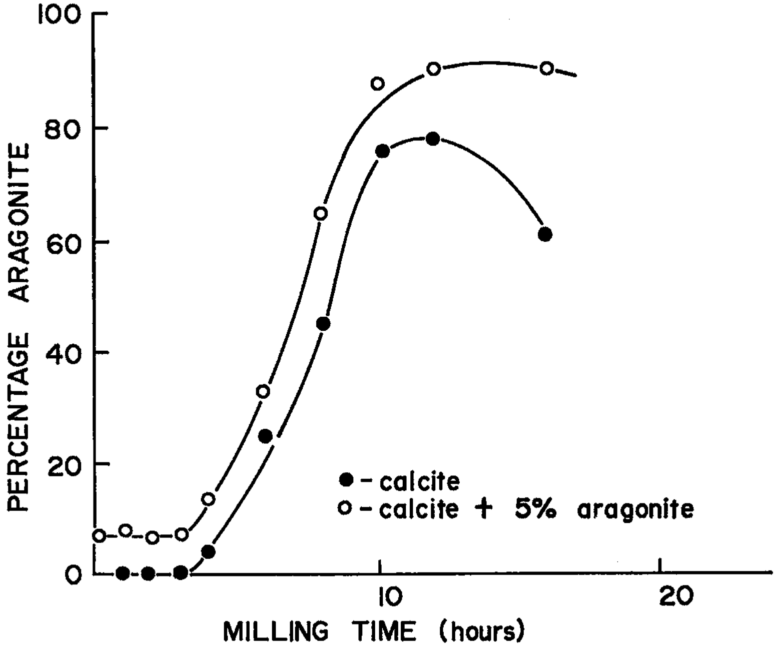

FIG. 1. Percentage aragonite vs. milling time for pure calcite and a calcite–5% aragonite mixture.

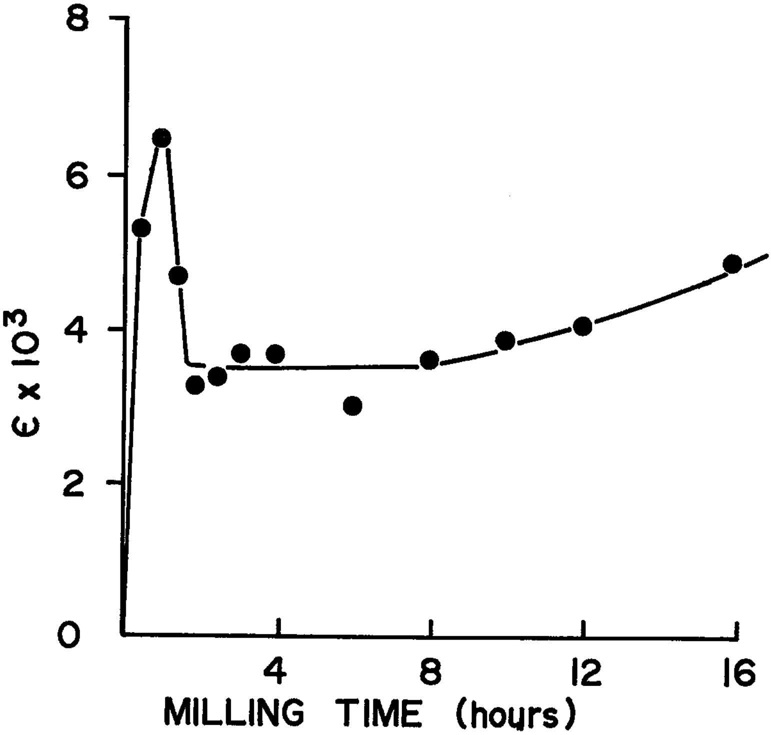

FIG. 2. Microstrain in ball-milled calcite.

formed, therefore the transformation would indeed appear to proceed by a nucleation and growth mechanism.

The average microstrain in the parent calcite as a function of the milling time is shown in Fig. 2. The microstrain increases rapidly up to one hour milling, and then drops suddenly. It then remains approximately constant until 12 hours milling when it again increases. Careful examination of a number of x-ray diffraction powder photographs showed that the decrease in microstrain after one hour was associated with the production of a very small amount of aragonite (probably less than 2%), which was not detected on the diffractometer. It would therefore seem that microstrain in the parent calcite particles can be relieved by a partial transformation to aragonite. A particularly interesting point arising from the x-ray line broadening study was that, for the sample that had been milled $\frac{1}{2}$ hour, the microstrain perpendicular to the $(10\bar{1}4)$ plane was smaller than that in the other directions. Analysis of the profile of the $(10\bar{1}4)$ reflection by the one-peak variance method of Langford & Wilson (1963) confirmed that the microstrain perpendicular to the $(10\bar{1}4)$ plane was very small for the ½ hour sample. As with the average microstrain, the microstrain perpendicular to the $(10\bar{1}4)$ plane increased up to one hour's milling, decreased, and then remained approximately constant. The results obtained by this method are summarized in Table 1.

TABLE 1. MICROSTRAINS AND CRYSTALLITE SIZES FOR CALCITE AS DETERMINED BY THE ONE PEAK VARIANCE METHOD

Milling time (hours)	Microstrain $\langle \epsilon^2_{(10\bar{1}4)} \rangle^{1/2}$	Crystallite Size $D^W_{(10\bar{1}4)}$
0.5	3.83×10^{-3}	300 Å
1.0	7.10×10^{-3}	280 A
1.5	5.83×10^{-3}	295 Å
2.0	5.35×10^{-3}	360 Å
4.0	6.43×10^{-3}	340 Å
6.0	5.83×10^{-3}	340 Å
8.0	6.70×10^{-3}	340 Å

The effect of milling on the average crystallite size is shown in Fig. 3. The crystallite size was quickly reduced to about 230 Å, and then decreased slowly. The decrease after six hours would seem to be associated with the transformation of some of the material to aragonite. These values are averages, like those for microstrain, because multiple orders were not available. These results were reproducible to ±10%. Warren-

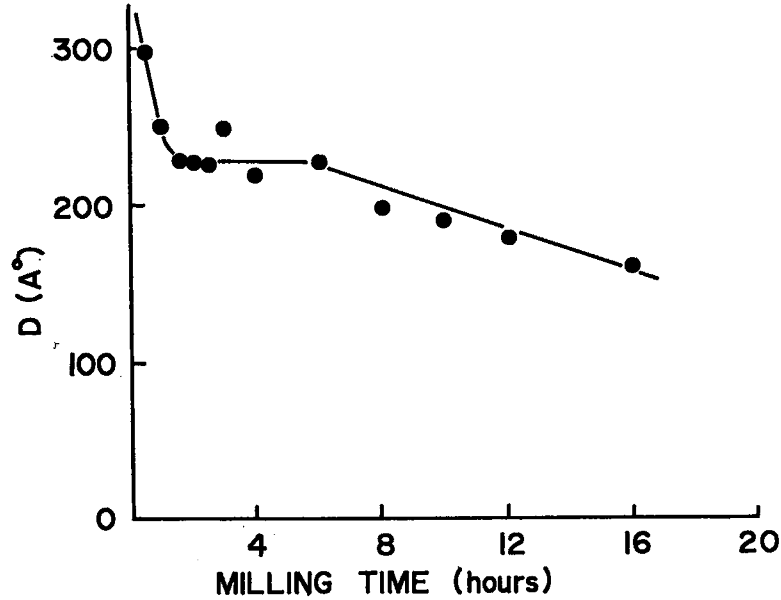

FIG. 3. Crystallite size of ball-milled calcite.

Averbach Fourier analysis (Warren 1959) was used to study the difference in crystallite size between the samples milled for $\frac{1}{2}$ hour and 1 hour. An average crystallite size was again obtained. The analysis showed that although the crystallite size was approximately the same for both samples, there was a wider distribution of crystallite sizes in the sample milled for $\frac{1}{2}$ hour, indicating that some large crystallites in the $\frac{1}{2}$ hour sample have not been broken down. These larger crystallites have more "weight" in the integral breadth method of analysis, which gives a 'size-average' dimension of the crystallite size, and therefore give a larger crystallite size than by the Fourier method, which gives a 'number-average' dimension.

The *x*-ray line broadening of calcite indicated, in agreement with the findings of previous workers, that considerable plastic deformation had taken place, producing a high degree of microstrain. In addition, there was also considerable *x*-ray diffraction line broadening due to small crystallite size, which was not found by the previous workers. Paterson (1959) and Gross (1965), used block samples, however, which are less likely to show *x*-ray diffraction line broadening due to a small crystallite size because there is no chance of mechanical attrition taking place.

Examination of the milled samples in the electron microscope indicated that the deformation of the particles took place in various stages. Up to $\frac{1}{2}$ hour the particles were broken down into smaller crystallites, some of which were gradually rounded off, *i.e.*, the place faces and sharp corners were replaced by more rounded surfaces. The particles then became still more rounded and lost their obvious crystal form. The particles then collected into irregular-shaped "cauliflower-like" aggregates, which appeared to be severely deformed. As the ball milling was continued the surfaces wrinkled still further. These observations can also explain the very low value for the microstrain perpendicular to the $(10\bar{1}4)$ plane, after $\frac{1}{2}$ hour's milling. During this time considerable cleavage along the $(10\bar{1}4)$ planes is taking place, which would have the effect of relieving the microstrains perpendicular to the $(10\bar{1}4)$ plane.

Jamieson (1957) in his paper on high pressure polymorphism by *x*-ray diffraction suggested that a polymorph calcite II could be formed, and that it was an anion disordered phase. He found that the production of this phase resulted in the virtual extinction of the $(11\bar{2}3)$ reflection. However, no abnormal decrease in the intensity of the $(11\bar{2}3)$ reflection was found. Therefore it does not seem possible that an anion disordered phase is formed in ball milled calcite, although it would appear that an anion disordered phase could be a possible intermediate product in the calcite to aragonite transformation.

The aragonite that is formed from the calcite by grinding is itself in a highly deformed state. The results for the average microstrain and crystallite size of the aragonite are summarized in Table 2. As the transformation proceeds, the microstrains in the aragonite increase slightly, and there is a decrease in the crystallite size, presumably because it is being formed from calcite of a smaller crystallite size. A similar behaviour has been noted in the case of strain-induced transformations in lead monoxide (Lewis, Northwood & Reeve 1969).

TABLE 2. MICROSTRAINS AND CRYSTALLITE SIZES OF ARAGONITE FORMED BY MILLING CALCITE

Milling time (hours)	Microstrain ϵ_I	Crystallite Size D_I^{PF}
8	3.57×10^{-3}	390 Å
10	4.18×10^{-3}	280 Å
12	4.62×10^{-3}	235 Å
16	4.12×10^{-3}	180 Å

Previous work on the thermally-induced aragonite to calcite transformation had shown that adding a small amount of calcite to the aragonite reduced the nucleation period for the aragonite to calcite transformation (Subba Rao & Yoganarasimham 1965). It was therefore decided to add approximately 5% aragonite to the calcite to see if it would act as nuclei in the strain-induced transformation. The effect is shown in Fig. 1. The aragonite has not reduced the nucleation period for the transformation; rather, the curve for the calcite-aragonite mixture was merely moved up the *y*-axis by about 5%. The aragonite particles were therefore not in a suitable form to act as nuclei for the strain-induced transformation. It is our opinion, now, that each small calcite particle requires a nucleus to be formed within the particle before transformation will take place. The only way to form this nucleus is by atomic movement, produced by microstraining which generates a small region having the new structure.

DISCUSSION

The study shows that calcite can be converted to aragonite at room temperature by grinding. The conversion is associated with the presence of lattice strain in both calcite and aragonite. Thus, when interpreting the history of regions in the earth's crust from evidence concerned with the presence of calcite and aragonite, care must be taken when using the phase diagram of calcium carbonate because transformation may have occurred due to severe mechanical deformation of the calcite, produced perhaps by shear at high pressure. More information may be obtained by the examination of polycrystalline blocks of the calcite and aragonite to see if lattice microstrains are present, as these might indicate that some strain-induced phase transformations occurred at temperatures other than those to be expected from the equilibrium phase diagrams alone. Further evidence could be obtained from crystal size measurements.

CONCLUSIONS

1. Grinding of calcite at room temperature caused a partial transformation to aragonite. The transformation curve was characteristic of a nucleation and growth process.
2. Pronounced microstraining of calcite was produced by ball milling. Transformation of the calcite to aragonite partially relieved the condition. Aragonite was also highly strained.
3. Adding a small amount of aragonite to act as a nucleating agent did not reduce the nucleation period. This suggests that seeding is ineffective; and that a nucleus must form within each small calcite particle. We consider this nucleus is formed by atomic movements, induced by microstraining.
4. Various stages have been identified in the deformation of calcite particles. First there was a cleaving down of the particles to produce smaller crystals, some of which were rounded off; then, particles became more rounded and lost their obvious crystalline appearance; and finally these particles collected into cauliflower-like aggregates. Microstraining tended to increase as the crystallite size decreased.

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