

# Time and Metamorphic Petrology: Calcite to Aragonite Experiments

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Although the equilibrium phase relations of many mineral systems are generally well established, the rates of transformations, particularly in polycrystalline rocks, are not. The results of experiments on the calcite to aragonite transformation in polycrystalline marble are different from those for earlier experiments on powdered and single-crystal calcite. The transformation in the polycrystalline samples occurs by different mechanisms, with a different temperature dependence, and at a markedly slower rate. This work demonstrates the importance of kinetic studies on fully dense polycrystalline aggregates for understanding mineralogic phase changes in nature. Extrapolation of these results to geological time scales suggests that transformation of calcite to aragonite does not occur in the absence of volatiles at temperatures below 200°C. Kinetic hindrance is likely to extend to higher temperatures in more complex transformations.

The occurrence of ultrahigh-pressure minerals that exist metastably at Earth's surface emphasizes our ignorance of the kinetics of geologic phase transformations. A good example is the discovery of diamond in regionally metamorphosed rocks (1). How is it possible that such unusual rocks survive slow transport to Earth's surface from depths of  $\geq 120$  km and temperatures  $\geq 800^\circ\text{C}$  without retrogression to graphite? Kinetic hindrance may also be important in altering the state of stress and seismic-failure processes in subducting lithosphere (2).

Currently, we cannot address such fundamental questions as where and under what conditions mineral reactions occur in nature because of the lack of experimental constraints on phase transformations in geologic materials in their natural polycrystalline form. Virtually every kinetic experiment on geologic materials has used single-crystal or powdered starting material—physical states that are quite different from those in the bulk of Earth. The results from these experiments are probably inapplicable to most natural situations for two reasons: (i) grinding introduces intracrystalline defects that affect the transformation and (ii) surface free energies, instead of grain-boundary or defect energies, can be a dominant factor in the driving potential for reactions in powders and single crystals (3).

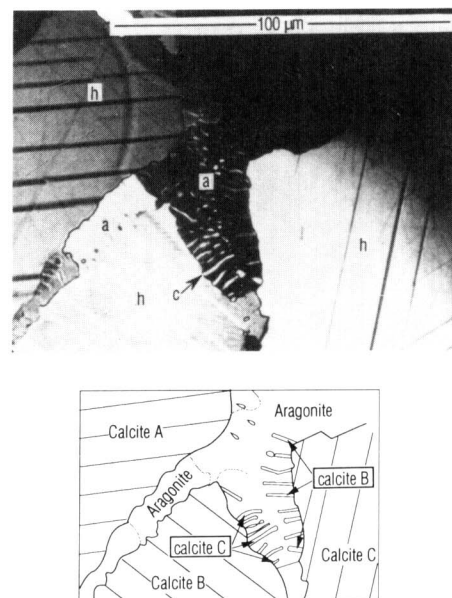
To expand our limited knowledge of phase changes in rocks, we have explored the kinetics and mechanisms of the calcite to aragonite transformation in marble. This transformation is a mineralogical archetype of a reconstructive change of state not involving changes in chemistry. Aragonite, the high-pressure orthorhombic polymorph, is about 7% denser than rhombohedral calcite.

We conducted experiments in a piston-cylinder apparatus, using NaCl as a confining medium (4). Cylindrical samples 6.4 mm in diameter by 6.4 mm high were drilled from a single block of Carrara marble (grain size, 115  $\mu\text{m}$ ), vacuum dried at 175°C, and welded inside silver capsules (5). There was no aragonite in the starting material. Experiments lasted from 15 min to 8 days at temperatures of 500° to 800°C and pressures of 1.78 to 2.49 GPa. The driving potential for the reaction was the reduction of the free energy of the sample, which is approximately the product of a pressure overstep and the volume change of  $-2.7 \text{ cm}^3 \text{ mol}^{-1}$  (6). The pressure oversteps varied from 0.1 to 1.0 GPa, resulting in volume free energies ( $\Delta G_{\text{rxn}}$ ) of about 300 to 2700  $\text{J mol}^{-1}$ . Afterward, the extent of reaction and the reaction microstructures were characterized by optical and universal-stage microscopy. The presence of aragonite was verified by x-ray diffraction and transmission electron microscopy.

Nucleation of the aragonite crystals occurred predominantly on grain boundaries; less than 1% of the nuclei formed on intragrain defects such as dislocations and twins. Nucleation occurred nearly simultaneously on the boundaries of all grains before any significant grain growth. Consequently, the transformation rate was dominated by the rate of grain-boundary migration. The restriction of nuclei to grain boundaries is expected, because grain-boundary free energies are larger than free energies of intragranular defects (7). Moreover, the relatively small values of  $\Delta G_{\text{rxn}}$  in this study mean that there was only sufficient driving potential for nuclei to form at sites with the least free energy cost. Intersections of twins with grain boundaries were common nucleation sites. The grain-boundary nucleation rate at 600° to 750°C was approximately  $10^7$  nuclei per square meter per second, as determined by a count

of grain densities in the shortest experiments. Aragonite crystals were randomly oriented with respect to adjacent calcite crystals, indicating that the nuclei formed incoherent interfaces with their host calcite crystals. The lack of topotaxy suggests that the interfacial free energy cost of creating aragonite nuclei (which can be minimized in topotactic relations) is small relative to the strain free energy cost caused by the approximately 7% volume difference between the two phases.

At temperatures of 600° to 750°C, growing aragonite crystals are shaped like gloves that fit over needlelike fingers of calcite (Fig. 1). The calcite fingers are about 1  $\mu\text{m}$  wide, and their long axes are orthogonal to the original calcite grain boundaries. Most aragonite grains contain two or more sets of these calcite fingers divided by an interface that marks the fossil calcite-calcite grain boundary along which aragonite nucleated. The calcite fingers in a given set do not share the orientation of the immediately adjacent original calcite crystal, and in many instances they have the same orientation as the original calcite crystal on the opposite side of the aragonite crystal (Fig. 1). Thus, the fingers must be composed of recrystallized calcite (8). The calcite fingers may be stabilized by the partitioning of an impurity that cannot be accommodated in the aragonite. The shape of the fingers may

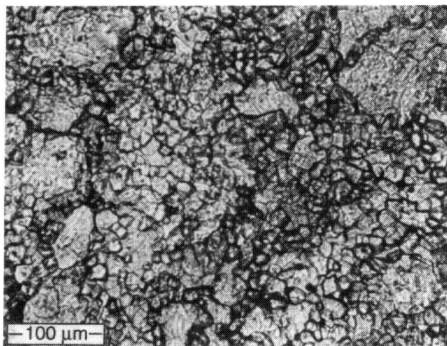


**Fig. 1.** Optical photomicrograph with cross-polarized light and line drawing showing the morphology of glovelike aragonite and calcite fingers formed in 48 hours at a pressure of 2.0 GPa and a temperature of 600°C; h, host calcite crystals; a, aragonite; c, neoblastic calcite fingers. Calcite fingers in boxes labeled "calcite B" and "calcite C" share the same crystallographic orientation as host calcite crystals "Calcite B" and "Calcite C."

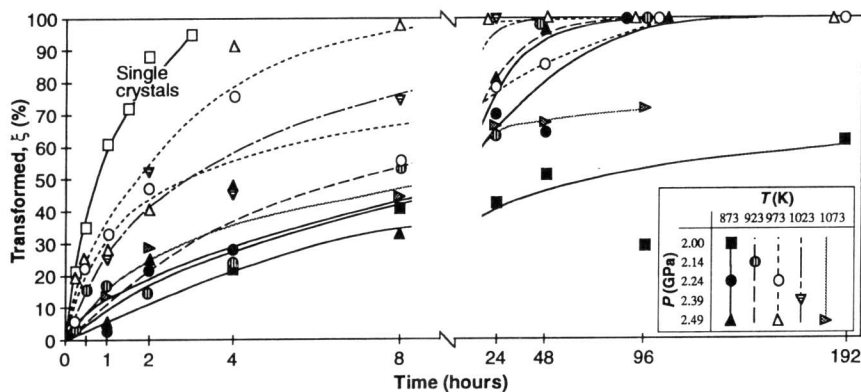
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require a smaller strain free energy contribution during formation of the calcite-aragonite interfaces because a needle has less strain free energy for a given volume than a sphere (9). The glove-and-finger texture persists even when the host calcite crystals have been completely consumed. The growth rate of the aragonite gloves is linear and ranges from  $\approx 1 \times 10^{-10} \text{ m s}^{-1}$  at  $600^\circ\text{C}$  to  $\approx 10 \times 10^{-10} \text{ m s}^{-1}$  at  $750^\circ\text{C}$  (10).

At a temperature of  $800^\circ\text{C}$ , equant aragonite crystals (Fig. 2) nucleate at a rate of about  $5 \times 10^4$  nuclei per square meter of

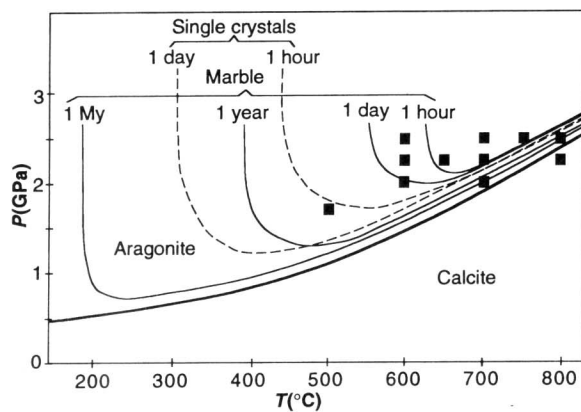


**Fig. 2.** Growth of equant aragonite crystals at temperatures  $\geq 800^\circ\text{C}$ .



**Fig. 3.** Transformation versus time at various temperatures and pressures (see inset for key). Note the lack of an incubation period and the marked difference in transformation rate at  $600^\circ\text{C}$  and 2.0 GPa between single crystals (open squares) and marble (filled squares). The measurement uncertainties are smaller than the symbol size.

**Fig. 4.** Observed and extrapolated times required for the transformation of calcite to 50% aragonite (17). The heavy line divides the calcite and aragonite stability fields (18). Thin lines show the time required for 50% transformation in marble for periods of 1 hour, 1 day, 1 year, and 1 million years (My). Dashed lines are for single-crystal experiments. The uncertainty of the predicted curves below  $500^\circ\text{C}$  is of the order of  $\pm 100^\circ\text{C}$ . Conditions of the present experiments are shown as filled squares.



grain boundary per second and grow at a rate that depends exponentially on time. The change from needles to spheres with temperature may reflect a change in the relative importance of volume-related free energies relative to free energies that scale with area.

The progress of the reaction (displayed as transformation versus time curves in Fig. 3) for our marble data (11) was much slower than the transformation rate of calcite single crystals in earlier studies (open squares) (12). As expected, the reaction proceeds more rapidly at higher temperatures and at higher values of  $\Delta G_{\text{rxn}}$  (that is, at higher pressures at a given temperature). The activation energy is approximately  $141 \text{ kJ mol}^{-1}$  as determined by the relation between inverse temperature and the time required to reach a given amount of transformation, normalized by the magnitude of the reaction free energy.

There are large differences between calcite to aragonite experiments on marble and corresponding experiments on single crystals and powders. The activation energy for aragonite growth in Carrara marble is approximately  $141 \text{ kJ mol}^{-1}$ , significantly more than the activation enthalpy of about  $90 \text{ kJ mol}^{-1}$  for transformation of calcite

single crystals to aragonite (3, 12). Several critical aspects of the phase transformation can only be observed in nonporous material and can never be realized from experiments on powders. The change in aragonite growth morphology from glovelike at temperatures  $\leq 750^\circ\text{C}$  to equant neoblasts at  $800^\circ\text{C}$  occurs only because calcite-calcite grain boundaries are initially present in the marble but not in powder or single crystals. Aragonite crystals grown in marble show no crystallographic relation to their host calcite crystals. This is in direct contrast to studies of calcite powders and single crystals, which typically show topotactic growth of aragonite (13). The lack of topotaxy suggests that the strain free energy cost of nucleating aragonite overrides the effect of minimizing the interfacial free energy. For experimental time scales, the transformation rate for marble is about 1/100 to 1/10,000 times as fast as the calcite to aragonite transformation in single crystals (12). The discrepancy would be greater for time scales of natural metamorphism, as illustrated in Fig. 4 (14).

Extrapolation of our experimental transformation rates also shows that the transformation becomes impossibly sluggish for geological time scales at temperatures below about  $200^\circ\text{C}$  in the absence of volatiles (Fig. 4) (14, 15). This kinetic hindrance and considerable textural complexity occur even though transformation to aragonite involves no change in chemistry and hence no intracrystalline diffusion. Most metamorphic reactions involve multiple reactants and products and hence require diffusive transport of chemical components. This should introduce even more textural complexity and may extend kinetic hindrance to higher temperatures (16).

## REFERENCES AND NOTES

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5. This does not mean that the samples were absolutely dry. Trace  $\text{H}_2\text{O}$  was undoubtedly present, and a  $\text{CO}_2$  vapor phase must also have formed from breakdown of the solid carbonate.
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8. These grain-boundary microstructures resemble

- cellular or discontinuous precipitation features, but we have been unable to determine whether a trace element is unequally partitioned between the neoblastic aragonite and calcite.
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  10. We determined the growth rate by measuring the length of neoblastic calcite fingers that were sub-parallel to 30- $\mu\text{m}$  sections prepared from the experimental sample. There is no marked dependence of growth rate on host crystal orientation.
  11. We determined the transformation rate by counting aragonite and calcite grains in 30- $\mu\text{m}$  sections, using an automated point-counting stage.
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  14. J. W. Cahn [*Acta Metall.* **4**, 449 (1956)], following M. Avrami [*J. Chem. Phys.* **7**, 1103 (1939); *ibid.* **8**, 212 (1940)], showed that a transformation with instantaneous grain-boundary nucleation can be described as:
 
$$\xi = 1 - \exp[-6.7/d\dot{\xi}t]$$
 where  $\xi$  is the fractional amount of transformation,  $d$  is grain size,  $\dot{\xi}$  is the growth rate [see (17)], and  $t$  is time. The extrapolation assumes that the reaction mechanism and rate observed in the laboratory also occur in nature—and this has not been proven. The extrapolation also applies only to natural situations with trace amounts of volatiles [see (5)].
  15. M. Madon and Ph. Gillet [*Earth Planet. Sci. Lett.* **67**, 400 (1984)] made a similar prediction by fitting Brar and Schloessin's (12) kinetic data to a theoretical model in which the transformation was assumed to occur by glide of partial dislocations. The agreement between their calculations and ours is fortuitous.
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  17. We modeled the growth rate with an equation of the form:
 
$$\dot{\xi} = b(kT/h)\{\exp(-\Delta G^*/RT) / [1 - \exp(-\Delta G_{\text{xn}}/RT)]\}$$
 where  $b$  is an empirical constant,  $k$  is Boltzmann's constant,  $h$  is Planck's constant,  $\Delta G^*$  is the activation energy for growth,  $\Delta G_{\text{xn}}$  is the volume free energy,  $R$  is the universal gas constant, and  $T$  is temperature [D. Turnbull, *Solid State Phys.* **3**, 225 (1956)]. We find that  $\Delta G^* \approx 141 \text{ kJ mol}^{-1}$  and  $b \approx 1 \times 10^{-14} \text{ m}$ ; note that  $b$  is several orders of magnitude smaller than the interplanar spacings in carbonate structures, a value that is not expected on the basis of this simple theory.
  18. The equilibrium boundary below 600°C is from W. Johannes and D. Puhan [*Contrib. Mineral. Petrol.* **31**, 28 (1971)]; that above 500°C is from B. R. Hacker and S. R. Bohlen (unpublished work).
  19. We thank B. Hankins and J. Pinkston for laboratory assistance; we thank G. Ernst, R. Fournier, J. G. Liou, J. Mosenfelder, G. Nord, D. C. Rubie, and two anonymous reviewers for comments. This work was supported by the Department of Energy and the U.S. Geological Survey.

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