

Kinetics of the Calcite \rightleftharpoons Aragonite Transformation¹

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Abstract. A beryllium pressure vessel mounted in an X-ray diffractometer has been used to study the rates of the transformation calcite \rightleftharpoons aragonite at temperatures to 500°C and pressures to 15 kb. The rates of transformation are shown to be both temperature and pressure dependent. It is proposed that the tail-off shown by all rate curves presented here results from a decrease in nucleation and loss of stored strain energy in the sample as the transformation progresses. In the vicinity of 400°C the rate of the calcite \rightarrow aragonite transformation at 15 ± 1 kb is similar to the reverse transformation at 1 bar. A decreasing-temperature extrapolation of the rate constant for the aragonite \rightarrow calcite transformation shows that this transformation at room temperature progresses at a negligible rate. The activation energy for this transformation at 1 bar is 106 kcal/mole. The use of the experimental rate data as well as calculated transformation times obtained from an empirical relationship describing the transformation has permitted the construction of curves of time for 99% transformation of aragonite \rightarrow calcite in the portion of the calcite stability field lying below 500°C.

INTRODUCTION

Some understanding of the structural properties of solids can be gained through a study of the speeds by which one polymorphic form will transform to another. Both the transformation velocities and the shapes of the rate curves can give information as to the type of transformation involved (i.e., whether reconstructive, displacive, etc.) and whether certain physical characteristics of the sample environment are speeding up, or retarding, the transformation. A classic example of this type of study is that carried out by *Bridgman* [1915] in which various solid-solid transformation rates were studied at constant volume.

A detailed study of the transformation rates for calcite \rightleftharpoons aragonite is presented here. Previous work includes that of *Chaudron* [1952], where the transformation at 1 atmosphere was followed continuously by a dilatometric method, and that of *Brown et al.* [1962], in which the rate curves were constructed from data of separate heating experiments also at 1 atmosphere. In both the above only the aragonite \rightarrow calcite

transformation was studied. Using ultrasonic pulse interferometry, *Ahrens and Katz* [1963] reported a minimum in longitudinal elastic wave velocity of 4.8 km/sec at room temperature and 8 kb in Solenhofen and Manlius limestones. They suggest that the minimum is due to a reversible transformation of calcite to aragonite. T. J. Ahrens (personal communication) proposes that the otherwise sluggish transformation was induced by shear stresses present in their apparatus.

EXPERIMENTAL METHOD

The experimental apparatus consists of a supported beryllium cylinder mounted on a X-ray diffractometer. Details of the apparatus and procedure have been described previously [*Davis and Adams*, 1964]. Several experiments were also carried out at 1 atmosphere using a heating stage designed by the M.R.C. Manufacturing Company.

The aragonite starting material was single-crystal aragonite from Kamsdorf bei Saalfeld, Saale (Germany), and a Franciscan metamorphic aragonite from Pacheco Pass, California. Only the former was used in the supported beryllium cylinder, but a comparison of the Kamsdorf and Pacheco Pass rates can be made from the experiments on the high-temperature stage. A finely precipitated synthetic CaCO₃ was used for the calcite starting material.

¹ Publication 387 of the Institute of Geophysics and Planetary Physics, University of California, Los Angeles.

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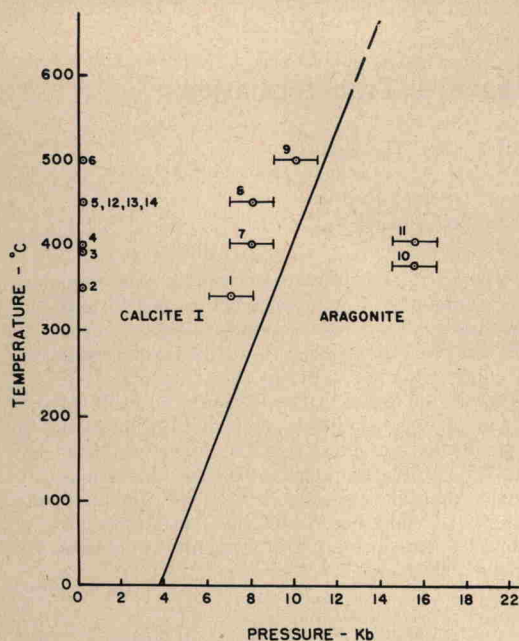


Fig. 1. Partial phase diagram of CaCO_3 showing known stability fields of calcite and aragonite and P - T coordinates of the experiments. The pressure uncertainty is indicated by the short horizontal lines.

The experiments are of four types:

(1) Aragonite \rightarrow calcite at temperatures from 300°C to 500°C, at atmospheric pressure, using the beryllium pressure vessel. Aragonite starting material was kept under pressure high enough to remain in the stability field of aragonite while the temperature was raised to the desired value. The pressure was then dropped to atmospheric and the rate recorded.

(2) Aragonite \rightarrow calcite at temperatures from 340°C to 500°C, at pressures near that of the equilibrium boundary (Figure 1), using the beryllium pressure vessel. As in (1) the aragonite starting material was kept in its equilibrium field until the desired temperature was reached, whereupon the pressure was dropped to just below that of the phase boundary into the calcite stability field.

(3) Calcite \rightarrow aragonite at 375°C and 405°C and at pressures considerably above the phase boundary. To obtain the pressure desired it was necessary to apply the pressure to the calcite starting material first and then to raise the temperature. Up to the two temperatures involved

the transformation rates were not great enough to convert more than 1 or 2% of calcite to aragonite before the temperature had reached the desired value. Any significant amount of transformation would, of course, be noted by the growth of aragonite peaks while the temperature was being elevated.

(4) Aragonite \rightarrow calcite at 450°C and at atmospheric pressure, using the M.R.C. heating stage. Here the temperature for the experiment was attained in about 5 seconds. Initial material was both Kamsdorf and Franciscan aragonite.

All rates were recorded by oscillating the goniometer about known peak localities for the product phase. The proportion of aragonite in the sample was determined from the ratio.

$$R = \frac{I_{104}^c}{I_{012}^a + I_{021}^a + I_{111}^a}$$

where I is the integrated intensity for the hkl reflection indicated. The superscripts a and c refer to aragonite and calcite, respectively. R was plotted against measured volume proportion of aragonite in calcite-aragonite aggregates. The several aragonite peaks were included in the ratio to help eliminate intensity anomalies due to preferred orientation on one or both of the two good aragonite cleavages. Calcite always becomes preferentially oriented on 104.

Figure 1 is a partial phase diagram of CaCO_3 [MacDonald, 1956; Jamieson, 1953; Clark, 1957] showing the P - T coordinates of the experiments. Pressures were determined from prior calibration of the vessel [Davis, 1964, p. 24]. The temperature uncertainty in the beryllium vessel is $\pm 2^\circ$, but the uncertainty for the M.R.C. high-temperature stage is probably between 10 and 20°.

RESULTS

Figures 2 to 4 present the observed rate curves in terms of per cent transformation versus time. Figure 4, *C* and *D*, contains three of the rate curves determined at atmospheric pressure using the M.R.C. high-temperature stage.

All rate curves, with the exception of that in Figure 4*D*, can be fitted to a general rate expression of the form

$$dx/dt = K(x_0 - x)^p \quad (1)$$

where x_0 and x are, respectively, the initial quan-