TEMPERATURE CONTROLS ON ARAGONITE-CALCITE TRANSFORMATION IN AQUEOUS SOLUTION[1]

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Abstract

The fraction of aragonite transformed to calcite at 50–120°C is proportional to square of reaction time, indicating control by nucleation and growth of calcite. The rate constant decreases with temperature corresponding to an activation energy 57.4 kcal/mole, and can be interpreted in terms of a loosely hydrated calcium bicarbonate ion-pair. The activation energy agrees with earlier work by Taft and Metzger and Barnard, but the absolute rates are apparently a function of specific experimental conditions.

General Statement

The rate of transformation of aragonite to calcite in sedimentary environment is, among other variables, a function of temperature. The well-known sluggishness of the transformation in the dry state, and the persistence of aragonite in some Paleozoic fossils make it clear that in sedimentary environments transformation must take place via solution-reprecipitation process (Fyfe and Bischoff, 1965).

Previous studies of the kinetics of the transformation in aqueous solution by Brown *et al.* (1962) and Metzger and Barnard (1968) measured rates from 200 to 300°C, and Taft (1967) measured rates from 3°C to 70°C. Although their results were not interpreted quantitatively, it was implied that the measured rates were absolute, that is, having general geologic applicability.

This work reports on rates of transformation from 50°C to 120°C, with interpretation in terms of elementary rate theory. Emphasis is made on the high degree of specificity of such determined rates, and their causes are discussed.

Experimental Procedure

The method used is essentially that of an earlier study on the effects of various ions on the rate of the aragonite-calcite transformation (Bischoff and Fyfe, 1968).

Aragonite of about five micron length and containing less than 0.1 percent calcite was prepared by mixing concentrated solutions of calcium chloride and sodium carbonate near 100°C. The resulting precipitate was filtered, washed and dried.

A 0.001 molal $CaCl_2$ aqueous solution was equilibrated with excess aragonite and atmospheric CO_2 at room temperature prior to experimental runs. The procedure serves two purposes; to prevent a significant loss of total solid in the experimental run, and to prevent an unpredictable time lapse in the experiments as aragonite equilibrated. An excess of aragonite was placed in the solution and air bubbled through until equilibrium was reached, then

the solution was filtered. Equilibration of solution and aragonite at room temperature required approximately 2-1/2 hours, as indicated by pH measurements with time.

The crystallization of calcite from aragonite was carried out in sealed pyrex ampoules and required from 12 to 200 hours for completion, depending on the temperature.

Experimental runs were prepared as follows: 10 ml of equilibrated solution were added to 13 mm diameter pyrex ampoules containing 0.1500 g of aragonite, and the ampoule sealed by fusing, allowing a 4 ml gas phase above the solution. The tubes were then placed on a mechanical rotator, mounted within a constant temperature oven. Rotating the ampoules during the reaction served to normalize the effects of thermal gradients and diffusion. At set time intervals ampoules were removed and percent calcite determined. Usually eight to ten such runs were necessary to define the reaction curve for a particular temperature. Percent calcite was determined by an X-ray diffraction method adapted from Davies and Hooper (1963). Runs were made at 50°C, 62°C, 75°C, 90°C, 108°C, and 120°C.

EVALUATION OF THE RATE-CONTROLLING PROCESSES

Curves were constructed for each temperature relating percent calcite to time (Fig. 1).

The general shape of the curves, similar to those of Taft (1967) and Metzger and Barnard (1968), indicates that the reaction proceeds at a continually increasing rate, a pattern which has definite implications as to the rate controlling processes.

For any reaction, the overall reaction rate is determined by the slowest process within the reaction. The processes involved in the aragonite-cal-
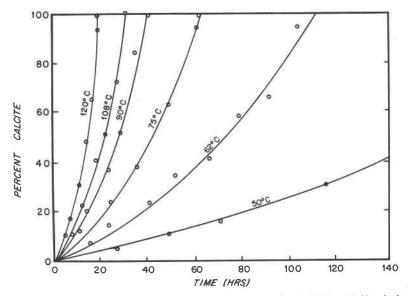

FIG. 1. Effect of temperature on aragonite-calcite transformation in 0.001 m CaCl$_2$ solution. Reaction expressed as percent calcite against time.

cite transformation in both the previously published recent studies and in this work are as follows:

1. Aragonite equilibrates with solution, and activities of calcium and carbonate ions are governed by the solubility product of aragonite.

2. The solution is supersaturated with respect to calcite, and nucleation of calcite begins.

3. Growth on the calcite nuclei takes place, and new nuclei form. Growth involves the following steps (Nancollas & Purdie, 1964):

    a. diffusion of ions to the crystal growth sites;
    b. absorption on the site;
    c. orientation of the ions onto the lattice;
    d. diffusion of waste products from the reaction site.

4. As the growing calcite takes up calcium and carbonate from the solution, additional amounts are provided by continuous equilibration of solution with aragonite, and diffusion of reactants to the growing calcite.

The process continues until all the aragonite is completely dissolved and the activity product of calcium and carbonate decreases to that of calcite.

If the slowest of the above processes were, 1. (aragonite solution) or 4. (reactant diffusion), the resultant reaction rates would, respectively, slow with time, or remain constant with time. Since this is not the case, these processes must be rapid with respect to the overall reaction. If 2. (nucleation) and 3. (growth) were slowest, the overall reaction rate would increase with time, since new nuclei are continuously added to the system as additional "reaction sites". Therefore, nucleation and growth of calcite must be the rate-controlling processes for both the previous and the present work on the aragonite-calcite transformation in aqueous solution.

EVALUATION OF TEMPERATURE EFFECT

Reaction rates commonly vary with temperature according to the Arrhenius equation,

$$K = A \exp(-E_a/RT)$$

where K is the rate constant, A a temperature insensitive expression, E_a the activation energy, R the perfect gas constant, and T absolute temperature (see Glasstone, Laidler, and Eyering, 1941).

Absolute rate theory attempts to understand the meaning of A and E_a. The theory proposes the existence of an activated complex, a configuration of the reactants corresponding to a state of maximum energy prior to forming the product. The energy of the activated state is often thought of as an energy barrier over which the reaction must pass. The rate of

reaction, according to this theory, is proportional to the concentration of the activated complex.

In the case of the aragonite-calcite transition, the activated complex may be a loosely hydrated calcium bicarbonate ion-pair on the surface of the growing calcite nucleus or crystal (Bischoff and Fyfe, 1968). In evaluating E_a, an approximation is made that calcite crystallization obeys the rate law,

$$dC/dt = K_T a_{Ca^{2+}} a_{HCO_3^-}$$

where K_T is the temperature-dependent rate constant, and $a_{Ca^{2+}} a_{HCO_3^-}$ is the activity product of calcium and bicarbonate, and is proportional to the activity of the calcium bicarbonate ion pair (see Bischoff and Fyfe, 1968).

The extent of experimental reactions appears to be linearly proportional to the square of time (Fig. 2). Therefore, the rate constant for the experimental conditions is taken as

$$K_T = S/a_{Ca^{2+}} a_{HCO_3^-}$$

where S is the first derivative of the time-squared plots of Figure 2. Calculation of $a_{Ca^{2+}}$ and $a_{HCO_3^-}$ was accomplished by

a. analysis of final solution for Ca^{2+}
b. estimate of activity coefficients by the Debye-Huckel theory (Garrels and Christ, 1965, p. 61)
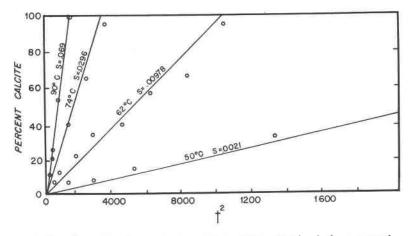c. use of relevant ionic equilibria constants at the working tempera-

Fig. 2. Transformation of aragonite to calcite in 0.001 m CaCl₂ solution expressed as percent calcite against time squared. S refers to slope values.

tures, taken from the data of Ryzhenko (1963), Harned and Owen (1958), Miller (1952), Ellis (1959), and Garrels and Christ (1965).

An Arrhenius plot of log K_T against $1/T$ (Fig. 3) is a fairly straight line excepting the point for 50°C. The apparent activation energy for the linear portion of the curve calculated from the slope is

$$E_a = 57.4 \text{ kcal/mole}.$$

The fact that the 50° point does not plot on the line may indicate a change in the activation energy, and therefore, a different mechanism or
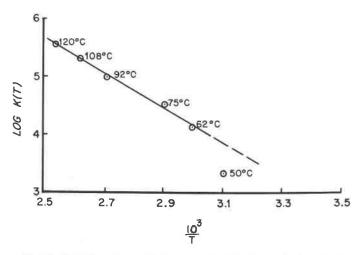

FIG. 3. Plot of logarithm of the approximated rate constant against the reciprocal of the absolute temperature.

rate controlling process at lower temperatures. Alternatively, the determination of the calcium-bicarbonate activity product may be in error for this point, a conclusion suggested by the smooth fit of all the points in figure 4—(see below).

COMPARISON WITH PREVIOUS DATA

The reaction curves of Taft (1967) and Metzger and Barnard (1968) display approximately the same time-squared relationship as this present work. Unfortunately, the rate constants, as used in Figure 3, cannot be calculated and compared because information is lacking on the calcium-bicarbonate activity product for their solutions. It is possible, however, to calculate values for S, as was done with this present data, and to compare plots of log S against $10^3/T$ (Figure 4). It is immediately apparent
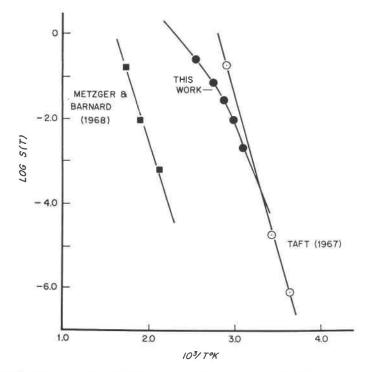
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Fig. 4. Plot of logarithm of S (slopes of reaction curves when plotted as percent calcite vs. time square) against reciprocal of absolute temperature for this work, and for data of previous workers.

that data from the individual workers plot on well-defined curves. However, the curves themselves, although somewhat parallel, are not coincident, indicating that specific experimental conditions must govern the absolute rates.

Earlier work (Bishoff and Fyfe, 1968) indicated that calcite nucleation during the aragonite-calcite transformation took place on the aragonite surfaces, and that aragonite of differing origins and grain sizes gave significantly differing absolute rates. Also, the control of the transformation rate by specific solution chemistry is very marked (Fyfe & Bischoff, 1965). Thus differences in solution chemistry and in the nature of the aragonite make generalizations of absolute transformation rates of any given temperature rather meaningless.

Assuming no great changes in the concentration of the activated complex with temperature within each set of experimental conditions, the slopes of the curves in Figure 4 are approximately proportional to the activation energy. The activation energy, therefore, of the transformation

for the various investigations must be rather similar as indicated by the pronounced parallelism of the plots in Figure 4.

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