The Crystallization of Calcium Carbonate

I. Isotopic Exchange and Kinetics

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The kinetics of crystallization of calcium carbonate (calcite) at 25°C has been examined by following the changes in calcium and hydrogen ion concentration when stable supersaturated solutions are inoculated with calcite seed crystals. The calcite growth follows a rate equation second order with respect to concentration suggesting a surface-controlled process. Calcium ion concentration changes were followed using ^{45}Ca radiotracer and atomic absorption spectroscopy. Heterogeneous exchange of ^{45}Ca between a calcium carbonate solution and calcite seed crystals has also been examined (by a liquid scintillation counting technique) in order to analyze the crystal growth data.

INTRODUCTION

The mechanism of crystallization of calcium carbonate from supersaturated solutions is of importance in the desalination of water using evaporative techniques (1). Moreover, understanding of the calcium carbonate crystal growth mechanism has important consequences in geochemistry and oceanography (2, 3). Several experimental methods have been used to study crystal growth from solution. In the case of calcium carbonate, for example, measurement of the concentration changes accompanying spontaneous precipitation from supersaturated solution has been used as a measure of the extent of crystal growth (4, 5). In these experiments, however, it is not possible to determine whether nucleation and crystal growth occur simultaneously or consecutively and, in addition, there is a strong likelihood of complications caused by heterogeneous nucleation (6). Both diffusion and interfacially controlled rate processes have been proposed as the rate-determining steps for crystal growth (7).

In the present study the kinetics of growth of calcite crystals from supersaturated solu-tions has been examined. It is possible by careful control of experimental conditions to prepare supersaturated calcium carbonate solutions which are stable for days. At the start of a growth experiment aged calcite seed crystals are added to a stable super-saturated solution and the rate of growth is measured. This technique, yielding highly reproducible results, permits investigation not only of the mechanism of the calcite growth process but also of the effect of added substances on the rate of crystallization.

Calcium carbonate polymorphs and hy-drates existing at or near ambient condi-tions are (8) calcite, aragonite, vaterite, monohydrocalcite, trihydrocalcite, and hexa-hydrocalcite. The thermodynamically stable form of calcium carbonate under the experi-mental conditions of the present work (25°C; 1 atm pressure) is calcite (9) and this polymorph will precipitate from the super-saturated solutions of calcium carbonate used in this study (10).

MATERIALS AND METHODS

Analytical reagent grade chemicals, triply distilled water, and grade A glassware were

used throughout. Calcite seed crystals were prepared by slowly adding 0.2 M $CaCl_2$ solution to 0.2 M Na_2CO_3 solution at 25°C. Freshly precipitated seed crystals were aged overnight in mother liquor and were subsequently washed with distilled water several times each day for one week. A seed crystal suspension used in the growth experiments was prepared by adding washed seed crystals to a 0.02 M $NaHCO_3$ solution; it was aged for one month before use. The crystals consisted of well-formed, transparent rhombs with an average edge length of 10 μm. The surface area was estimated to be 0.3 m^2/gm.

Supersaturated calcium carbonate solutions were prepared by the drop-wise addition of 100 ml of sodium bicarbonate solution (0.0200 M) to 100 ml of calcium chloride solution(8×10^{-4} M) in the thermostated (25.00° $\pm$ .02°C) double-walled Pyrex glass vessel used for the growth experiments. The stability of the solutions was verified by the constancy of the pH for at least 1/2 hour before the start of each experiment.
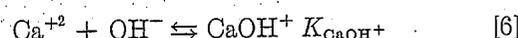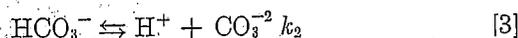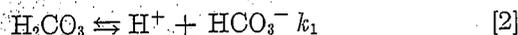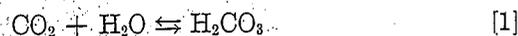
The pH changes accompanying calcite growth were followed using a Beckman Research Model pH meter ($\pm$ 0.1 mV) with a Beckman combination electrode. NBS standard buffer solutions, covering the pH range of interest, were used to calibrate the electrode system. The decrease in solution pH during calcite growth raises the pCO$_2$ of the supersaturated solution causing a net loss of CO_2 from the solution and concomitant significant changes in solution pH. The slow changes in pCO$_2$ make it difficult to attain an equilibrium calcium carbonate concentration at the conclusion of a kinetic experiment.

Measurement of total calcium ion concentration in solution during crystal growth was accomplished by using either a ^{45}Ca radioactive tracer with liquid scintillation counting (Packard Model Tri-Carb liquid scintillation spectrometer) [11] or atomic absorption spectroscopy (Perkin-Elmer Model 303). When ^{45}Ca radioactive tracer is used to follow calcite growth it is also necessary to consider the change of ^{45}Ca activity in solution due to the exchange of Ca^{+2} ions on the surface of the crystal with Ca^{+2} ions in the solution [12–14].

RESULTS AND DISCUSSION

The following equilibria must be taken into account in solutions of calcium carbonate.

$$CO_2 + H_2O \leftrightarrows H_2CO_3 \qquad [1]$$

$$H_2CO_3 \leftrightarrows H^+ + HCO_3^- \; k_1 \qquad [2]$$

$$HCO_3^- \leftrightarrows H^+ + CO_3^{-2} \; k_2 \qquad [3]$$

$$Ca^{+2} + HCO_3^- \leftrightarrows CaHCO_3^+ \; K_{CaHCO_3^+} \qquad [4]$$

$$Ca^{+2} + CO_3^{-2} \leftrightarrows CaCO_3^\circ \; K_{CaCO_3^\circ} \qquad [5]$$

$$Ca^{+2} + OH^- \leftrightarrows CaOH^+ \; K_{CaOH^+} \qquad [6]$$

$$Ca^{+2} + CO_3^{-2} \leftrightarrows \overline{CaCO_3} \; K_{SP} \qquad [7]$$

Values of the dissociation constants are $k_1 = 4.452 \times 10^{-7}$ mol l^{-1} [15] and $k_2 = 4.69 \times 10^{-11}$ mol l^{-1} [16]. Thermodynamic ion association constants have also been determined: $K_{CaHCO_3^+} = 1.94 \times 10^1$ l mol^{-1} [17], $K_{CaCO_3^\circ} = 1.59 \times 10^3$ l mol^{-1} [18], $K_{CaOH^+} = 2.5 \times 10^1$ l mol^{-1} [19], and the thermodynamic solubility product $K_{SP} = 4.01 \times 10^{-9}$ [9].

The concentrations of all the ionic species in the solutions were calculated from the experimental pH using expressions for mass balance by successive approximations for I, the ionic strength [20]. Activity coefficients f were obtained from the modification of the Debye-Hückel equation proposed by Davies [20].

$$\log f_z = -Az^2 \left(\frac{I^{1/2}}{1 + I^{1/2}} - 0.3I \right). \qquad [8]$$

Typical plots of calcium and carbonate concentration as a function of time are shown in Fig. 1 by the radiotracer technique and in Fig. 2 by atomic absorption spectroscopy.

The change in ^{45}Ca activity in a supersaturated solution inoculated with seed crystals of calcite results both from crystal growth and exchange of calcium ions be-
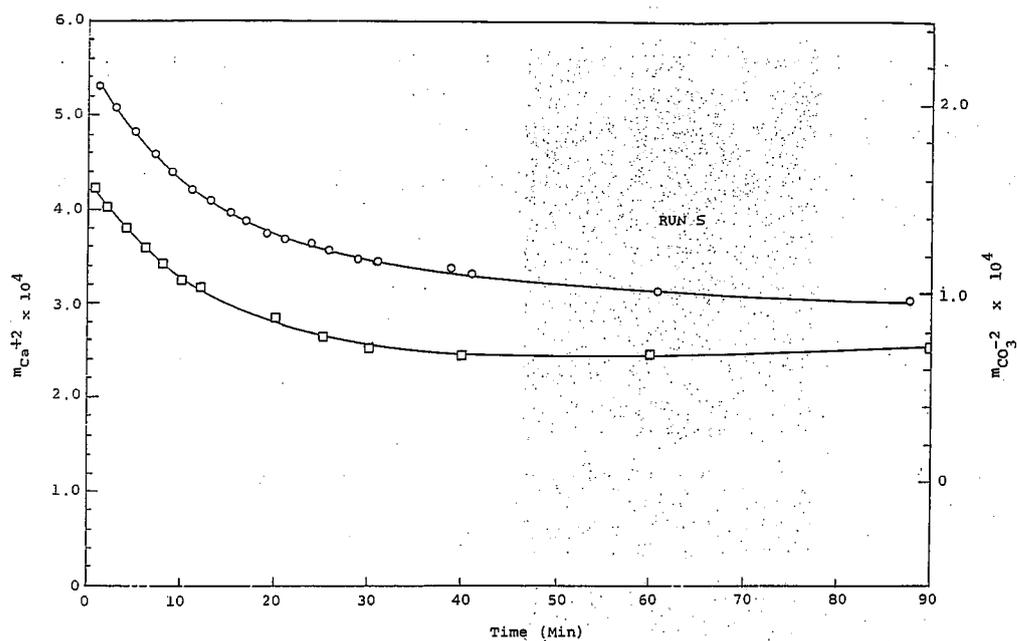
FIG. 1. Plots of calcium ($\square$) and carbonate ($\bigcirc$) concentrations in run 5 against time for calcite growth followed using ^{45}Ca radiotracer. Initial concentrations $m_{Ca}{}^{+2} = 4.352 \times 10^{-4}$, $m_{CO_3}{}^{-2} = 2.160 \times 10^{-4}$, $m_{HCO_3^-} = 1.013 \times 10^{-2}$, pH = 8.520, calcite seed concentration = 31.5 mg/100 ml.
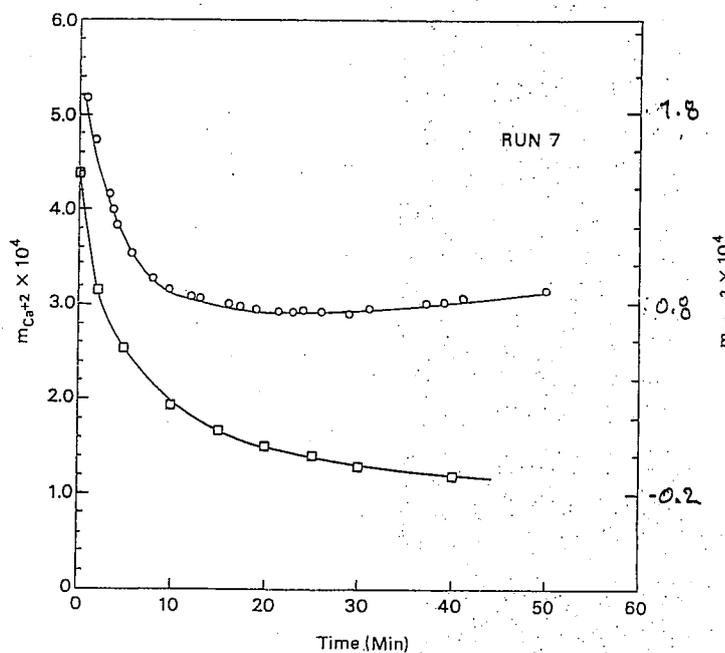

FIG. 2. Plots of calcium ($\square$) and carbonate ($\bigcirc$) concentrations in run 7 against time for calcite growth followed using atomic absorption spectroscopy. Initial concentrations $m_{Ca}{}^{+2} = 4.402 \times 10^{-4}$, $m_{CO_3}{}^{-2} = 1.833 \times 10^{-4}$, $m_{HCO_3^-} = 1.015 \times 10^{-2}$, pH = 8.455, calcite seed concentration = 230. mg/100 ml.

tween the solid and solution. The resultant change may be expressed by Eq. [9].

$$-\frac{d\ ^{45}Ca}{dt} = k_G\ sF[A_{sol}(m - m_0)]$$

$$+ k_{EX}\ s(A_{sol} - A_{crystal}),$$ [9]

where $d\ ^{45}Ca/dt$ is the change in ^{45}Ca count rate in solution in (cpm/gm of sol)/min, s the surface area of the crystals, k_G the rate constant of crystal growth, k_{EX} the rate constant of heterogeneous exchange, m the molar concentration of calcium carbonate in the supersaturated solution, m_0 the equilibrium concentration of calcium carbonate, and A_{sol} and $A_{crystal}$ the specific activities (^{45}Ca cpm/mole of Ca^{+2}) in the solution and crystal phases, respectively. The function $F[A_{sol}(m - m_0)]$ is proportional to the rate of crystal growth.

The effect of surface exchange on the ^{45}Ca activity in solution during a labeled growth experiment was examined by adding labeled calcite seed crystals to: (1) a saturated calcite solution and (2) a supersaturated calcite solution. The results, shown in Fig. 3,
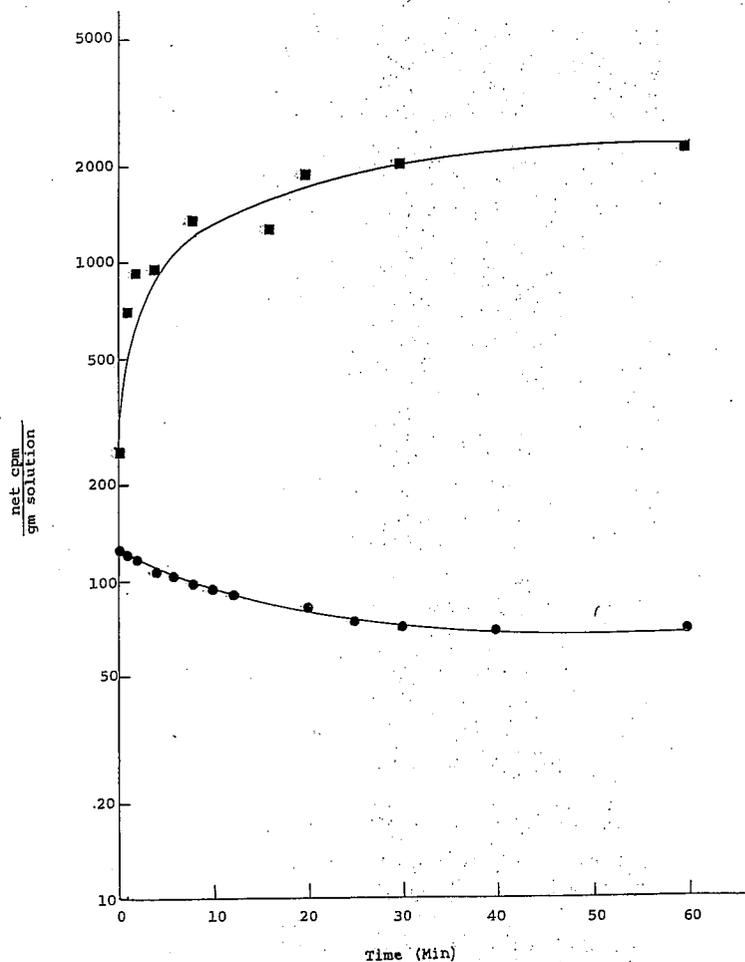

FIG. 3. Plots of ^{45}Ca count rate in solution against time: ^{45}Ca labeled calcite seed suspension added to saturated solution (■), added to supersaturated solution (●). Initial concentrations in the saturated solution $m_{Ca^{+2}} = 2.625 \times 10^{-5}$, $m_{CO_3^{-2}} = 5.10 \times 10^{-4}$, $m_{HCO_3^-} = 2.00 \times 10^{-2}$, pH = 8.538, labeled calcite seed concentration = 33.0 mg/100 ml, and in the supersaturated solution $m_{Ca^{+2}} = 4.352 \times 10^{-4}$, $m_{CO_3^{-2}} = 2.160 \times 10^{-4}$, $m_{HCO_3^-} = 1.013 \times 10^{-2}$, pH = 8.520, labeled calcite seed concentration = 31.5 mg/100 ml.

indicate that when a labeled seed suspension is added to a saturated solution the solution count rate increases owing to isotopic exchange. The lower curve in Fig. 3 shows that when the same suspension is added to a supersaturated solution the solution count rate decreases reflecting the growth of calcite from the supersaturated solution. Moreover, this change in calcium concentration parallels within 10 % the concentration changes measured in the atomic absorption experiments which are not affected by the exchange reaction. It is seen that under the conditions of this experiment calcite crystal growth commences immediately upon the addition of seed crystal. There appears to be little or no exchange of ^{45}Ca between the crystal surface and the supersaturated solu-

tion during the first 60 min of calcite growth. In this experiment the new solid phase appears to be in isotopic equilibrium with the solution from which it has grown, rather than with the underlying seed crystal. Doerner and Hoskins (21) have examined this type of distribution and have derived a logarithmic law based on the assumption that the supersaturated solution is in equilibrium with the surface layer of the growing crystal but not with the crystal as a whole. Later workers have demonstrated that a number of precipitation reactions follow this logarithmic distribution law (22). Labeled calcite growth may thus be interpreted as an isotope dilution experiment and the ion concentrations can be calculated
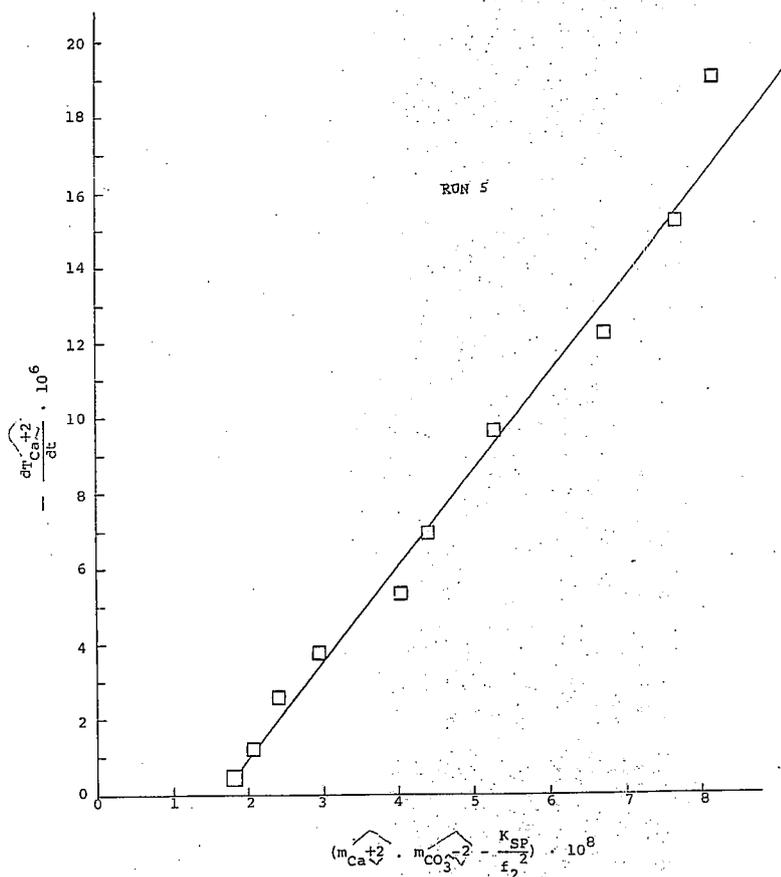

FIG. 4. Plot of $dT_{Ca}{}^{+2}/dt$ against $(m_{Ca}{}^{+2} \cdot m_{CO_3}{}^{-2} - K_{SP}/f_2{}^2)$ for run 5.

using the ^{45}Ca solution count rate measurement and the solution pH.

The data represented in Figs. 1 and 2 follow a rate expression of the form

$$dT_{Ca^{+2}}/dt = -k_G \; s(m_{Ca^{+2}}m_{CO_3^{-2}} - K_{SP}/f_2^2), \quad [10]$$

where $T_{Ca^{+2}}$ is the total calcium ion concentration in solution, t is time in minutes, and $m_{Ca^{+2}}$ and $m_{CO_3^{-2}}$ are the ionic concentrations. Plots of the rate of crystal growth against $(m_{Ca^{+2}} \; m_{CO_3^{-2}} - K_{SP}/f_2^2)$ in Figs. 4 and 5 show that Eq. [10] satisfactorily represents the data. The line joining the data points from the tracer experiment in Fig. 4 does not pass exactly through the origin. This may be due to slow exchange of ^{45}Ca activity in the bulk crystal with Ca^{+2} ions

in the solution. Experimental data from atomic absorption measurements in Fig. 5 lie on a straight line which passes through the origin in good agreement with Eq. [10]. The solubility value for calcite could not be obtained from crystal growth experiments because of the difficulty in reaching carbon dioxide equilibrium between the solution and gas phases. Equilibrium concentrations of calcium carbonate were calculated using the best available estimate of the calcite solubility product at 25°C, $K_{SP} = 4.01 \times 10^{-9}$, taken from the survey of Langmuir (9). In the present work, the calcite crystal growth rate has been found to be a linear function of the weight of seed crystal used to initiate growth. The average value of the crystal growth rate constant, $k_G = 2.90$
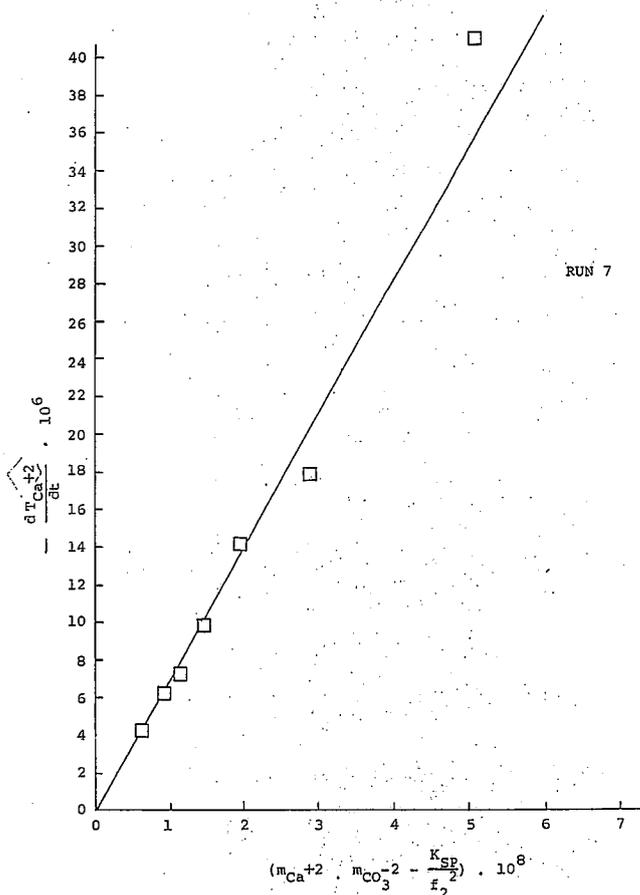

FIG. 5. Plot of $dT_{Ca^{+2}}/dt$ against $(m_{Ca^{+2}} m_{CO_3^{-2}} - K_{SP}/f_2^2)$ for run 7.

$min^{-1} M^{-1}$ (mg seed/100 ml sol)$^{-1}$, was independent of the stirring rate in the solution. This points against diffusion as the rate-controlling mechanism.

If the growth of calcite crystals involves the incorporation of lattice ions directly into the crystal at the growth site, the flux of solute, J_G, onto the crystal surface, $J_G = k_G \ s \ m_{Ca^{+2}} m_{CO_3^{-2}}$. The diffusional flux of solute away J_k from the surface of the crystal, $J_k = k's$. In a saturated solution these rates are equal:

$$J_G = J_k = k's = k_G \ s(m_{Ca^{+2}} \ m_{CO_3^{-2}})_0; \quad [11]$$

$$k's = k_G \ s(K_{SP}/f_2^2). \quad [12]$$

Assuming that the diffusion step is not rate determining, the rate of growth in a supersaturated solution is given by

$$\frac{-dT_{Ca^{+2}}}{dt} = J_G - J_k$$

$$= k_G \ s(m_{Ca^{+2}} \ m_{CO_3^{-2}} \quad [13]$$

$$- K_{SP}/f_2^2).$$

Equation [13] is identical with Eq. [10], which has been shown to represent the experimental data. The proposed second-order surface-controlled process is consistent with the observed lack of dependence of k_G on stirring rate and also with the inhibition of calcite growth from supersaturated solutions by extremely small amounts of polyphosphates (23). A quantitative study of the inhibition of calcite growth using the seeded growth technique is planned under simulated boiler conditions.

SUMMARY

Experimental results obtained in this study indicate that the surface of a calcite seed crystal growing in a labeled supersaturated solution is in isotopic equilibrium with the solution from which it grows, and than an isotope dilution method is feasible for the study of the growth of calcite crystals. Interpretation of results obtained by both radiotracer and atomic absorption methods shows that the growth of calcite from a

supersaturated solution is a second-order surface-controlled reaction.

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