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Precipitation of Calcite and Aragonite

BY JOHN L. WRAY AND FARRINGTON DANIELS

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The two common polymorphs of calcium carbonate, calcite and aragonite, have been precipitated by mixing soluble carbonate solutions with solutions of calcium ions under conditions of controlled temperature, concentration and aging. Results from these experiments have provided new information regarding the factors affecting the formation of these two crystalline varieties.

Introduction

Although the preparation of calcium carbonate has been described many times in the chemical and geological literature, the products usually have not been well defined and they have varied considerably with the experimental conditions. Among the important early workers who have attempted to determine the factors controlling the formation of the various crystalline varieties of calcium carbonate are Credner,¹ and Johnson, Merwin and Williamson.² A comprehensive summary of much of the early work was compiled by Mellor.³ More recently, studies of artificial calcium carbonate have been made by deKeyser and Dugueldre.⁴ Calcium carbonate can be precipitated in the laboratory in different crystalline forms as calcite, aragonite or vaterite, although calcite is the only thermodynamically stable form of pure CaCO_3 at room temperature and atmospheric pressure. The factors which are involved in the formation of the polymorphs of CaCO_3 apply then to the kinetics of metastable forms, rather than to equilibrium conditions.

The purpose of this investigation was to determine the conditions necessary to precipitate pure calcite, pure aragonite, or specific mixtures of the two. There is practical significance also for such a study. Calcium carbonate is finding extensive

use in chromatography and the efficiency in such work depends not only on the size of the particles, but also on the calcite-aragonite ratio. Again, calcite and aragonite are found in nature and their origin is important in the interpretation of geologic phenomena.

Experimental

Calcium carbonate was precipitated in 500-ml. round-bottom flasks by mixing soluble carbonate solutions with solutions of calcium ions with rapid mixing by a motor-driven stirrer. Reagent grade calcium nitrate manufactured by Merck and Co. was used. Spectrographic analysis of selected impurities in this material given in parts per million are as follows: MgO , 80; Fe_2O_3 , 20; MnO , 3; SrO , 30; Pb <3; and BaO <3. Sodium carbonate manufactured by the Baker Chemical Co. gave MgO <10, Fe_2O_3 <10, MnO <3, SrO <3, Pb <5, and BaO <3. The experiments were carried out at temperatures from 30 to $70 \pm 1^\circ$ and the precipitates were aged for periods from 6 minutes to 18 hours. The solutions were mixed to give precipitates of calcium carbonate as shown in Table I.

TABLE I
CONCENTRATIONS OF SOLUTIONS USED IN PRECIPITATING
 CaCO_3

Expt. series	Soln. added	Addn. rate, ml./min.	Soln. in flask
1	20 ml. 1.0 M $\text{Ca}(\text{NO}_3)_2$	5	200 ml. 0.1 M Na_2CO_3
2	20 ml. 1.0 M Na_2CO_3	5	200 ml. 0.1 M $\text{Ca}(\text{NO}_3)_2$

Additional experiments were performed in which 1.0 M $\text{Ca}(\text{NO}_3)_2$ and 1.0 M Na_2CO_3 were mixed. At selected temperatures and aging periods, calcium chloride was substituted for calcium nitrate in experiment series 1 and 2.

The pH of each solution was determined with a glass electrode. At the end of each aging period the precipitate was filtered immediately through a Büchner filter, thoroughly washed with distilled water, and dried at room temperature.

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- (3) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 3, Longmans, Green and Co., London, 1923.
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The per cent. of calcite, aragonite and vaterite in the precipitates was determined by X-ray diffraction measurements and by examination with a petrographic microscope, in which the relative areas of rhombs of calcite, needles of aragonite, and spherulitic growths of vaterite were estimated with the aid of a linear scale. The limits of error in these determinations, both by X-ray diffractometer and petrographic microscope, may be as great as $\pm 15\%$.

Results

Table II gives the results of experiment series 1.

TABLE II
CRYSTAL PHASES PRODUCED BY ADDING 1 M $\text{Ca}(\text{NO}_3)_2$ TO
0.1 M Na_2CO_3

Temp., °C.	Digestion time, hr.	Crystal phase (%)		
		Aragonite	Calcite	Vaterite
30	0.1	..	5	95
	0.5	..	10	90
	3.0	..	20	80
	10.0	..	20	80
	18.0	..	100	..
40	0.1	5	95	..
	0.5	..	100	..
	3.0	..	100	..
	10.0	..	100	..
	18.0	..	100	..
45	0.1	70	30	..
	0.5	30	70	..
	3.0	2	98	..
	10.0	..	100	..
	18.0	..	100	..
50	0.1	100
	0.5	100
	3.0	95	5	..
	10.0	85	15	..
	18.0	70	30	..
70	0.1	100
	0.5	100
	3.0	100
	10.0	100
	18.0	100

The pH of the initial sodium carbonate solution was 10.9 at 30° and after complete precipitation with calcium nitrate it was 9.1. The sizes of the CaCO_3 particles ranged from about 10 to 15 μ .

The aragonite-calcite components of this series after various periods of aging, which are given in Table II between 40 and 50°, are shown graphically in Fig. 1.

Table III gives the results of experiment series 2.

The pH of the 0.1 M $\text{Ca}(\text{NO}_3)_2$ was 6.3 at 30° and increased to 9.1 with the addition of the 1 M Na_2CO_3 . The grain size varied from about 10 to 20 μ .

The effect of increasing the concentrations of the reagents, using 1 M solutions of both $\text{Ca}(\text{NO}_3)_2$ and Na_2CO_3 , was to give a finer grained precipitate (5–10 μ) and products that contain a much greater proportion of calcite and vaterite than aragonite when precipitated at high temperatures and allowed to age only for brief periods. For example, a precipitate containing 70% calcite, 20% vaterite and 10% aragonite was obtained at 70° after 6 minutes aging when 100 ml. of 1 M Na_2CO_3 was added to 100 ml. of 1 M $\text{Ca}(\text{NO}_3)_2$.

TABLE III

CRYSTAL PHASES PRODUCED BY ADDING 1 M Na_2CO_3 TO
0.1 M $\text{Ca}(\text{NO}_3)_2$

Temp., °C.	Digestion time, hr.	Crystal phase (%)		
		Aragonite	Calcite	Vaterite
30	0.1	..	5	95
	0.5	..	5	95
	3.0	..	5	95
	18.0	..	25	75

40	0.1	..	15	85
	0.5	5	45	50
	3.0	5	95	..
	18.0	..	100	..

50	0.1	30	70	..
	0.5	25	75	..
	3.0	20	80	..
	10.0	10	90	..
	18.0	..	100	..
60	0.1	95	5	..
	0.5	95	5	..
	3.0	90	10	..
	10.0	50	50	..
	18.0	..	100	..
70	0.1	100
	0.5	100
	3.0	100
	10.0	..	100	..
	18.0	..	100	..

Essentially the same results, as shown in Tables II and III, were obtained when calcium chloride was substituted for calcium nitrate. This reagent grade material was manufactured by Mallinckrodt Chemical Works and analyzed (in p.p.m.): MgO, 25; Fe_2O_3 , 25; MnO < 3; SrO, 60; Pb < 3; BaO < 3.

Many of the precipitations in experiment series 1 and 2 were repeated with reagent grade calcium nitrate manufactured by the General Chemical Company. This material analyzed (in p.p.m.): MgO, 25; Fe_2O_3 , 35; MnO, 3; SrO, 40; Pb < 3; BaO < 3. These results were within $\pm 15\%$ of the products obtained with the Merck calcium nitrate shown in Tables II and III.

Discussion

It is evident from the results of this investigation that it is easy to control temperature, pH and time so as to get either calcite or aragonite. It is surprising to find, as shown in Fig. 1, that the temperature range is so small and so critical. At 40° the precipitate is nearly pure calcite. At 45° it is 30% calcite and 70% aragonite, but changes during two hours digestion to more than 90% calcite. At 50° the precipitate is mostly aragonite. At temperatures between 45 and 50°, with suitable periods of digestion, one can obtain practically any ratio of calcite to aragonite. Although the precipitate suspended in solution may go rather rapidly to the more stable calcite, this change is stopped by filtering and drying the material. The rate of change in the dry state is indefinitely slow in the laboratory.

The temperature at which dry aragonite changes spontaneously into calcite at atmospheric pressure is quite high (usually above 400°). At very high pressures, aragonite is thermodynamically stable

at lower temperatures, even at room temperature. The phase equilibrium diagram for the different crystalline varieties of calcium carbonate has been fully worked out.⁵

There is much geological and laboratory evidence to show that the aragonite crystal structure is favored by the inclusion in its lattice of cations as impurities which are larger than the calcium ion such as strontium, barium, and lead.^{6,7}

The ionic radii of the cations of the calcite and aragonite groups are given in Table IV.

	Mg	Fe	Zn	Mn	Cd	Ca	Sr	Pb	Ba
Calcite type	0.78	0.83	0.83	0.91	1.03	1.06
Aragonite type	1.06	1.27	1.32	1.43

In this Laboratory, it was found⁹ that aragonite generally has a higher content of strontium than calcite, and that the formation of aragonite is induced by adding strontium, barium or lead under conditions, namely, high pH, such that they will be co-precipitated with the calcium carbonate. Only in case these ions are incorporated into the lattice would they be expected to produce the aragonite. It was pointed out that the presence of these larger ions under the proper conditions tends to produce the aragonite, rather than that the aragonite is produced from other causes and takes up the strontium, barium, or lead which happen to be in solution.

In studying the aging process, it is important to distinguish three different stages¹⁰ in the mechanics of crystallization: (a) an aggregation velocity in which the ions are brought together and precipitated; (b) an orientation velocity in which the ions in colloidal or amorphous material of the precipitated particles form crystals; and (c) a rate of recrystallization.

In the present work the aggregation velocity is considered to be infinitely rapid, the orientation is probably complete in a few seconds or minutes, and the recrystallization takes place in minutes, hours or days, and longer depending on conditions.

With the facts and generalizations discussed here, it is possible to explain the experimental results and to point out the factors which affect the production of calcite or aragonite.

The formation of the unstable aragonite having a larger crystal structure than calcite is favored by the incorporation of larger-sized cations, Sr⁺⁺, Ba⁺⁺ or Pb⁺⁺, into the CaCO₃ lattice. The concentration of these ions may be very low, because once a seed crystal of aragonite or calcite is formed, the rest of the crystal growth tends to follow the same crystal pattern.

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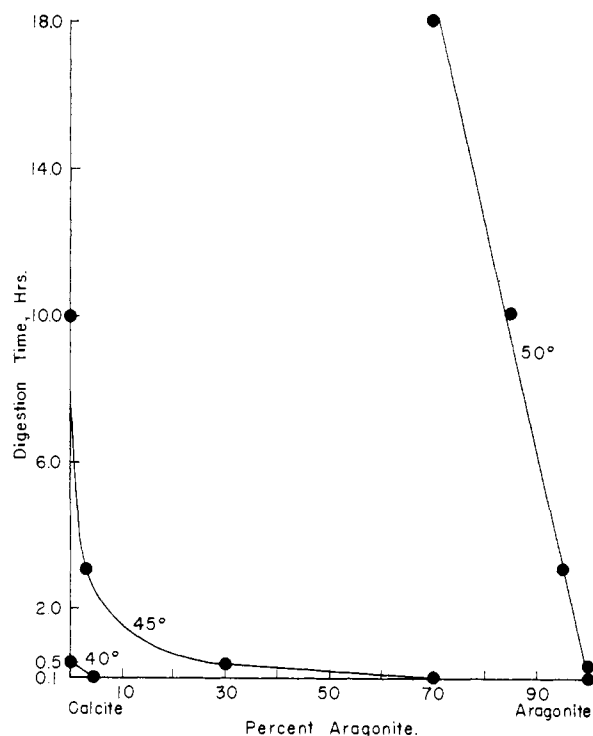


Fig. 1.—Influence of temperature and aging on the crystal form of precipitated calcium carbonate.

At low pH values, strontium, barium and lead carbonates do not precipitate, and the first colloidal particles of calcium carbonate to form do not contain these larger ions. Calcite is precipitated under these conditions. At higher pH values, however, these larger ions are co-precipitated with the calcium carbonate and there is a tendency to form aragonite.

At the instant of precipitation, the strontium ions as well as the calcium ions are brought from a large volume of solution into the small volume of the first colloid particles to form, thus giving in these aggregates a high concentration. In a matter of seconds or minutes, the colloid aggregate undergoes orientation leading to crystal formation. If there is sufficient time between precipitation and crystallization, the strontium (and barium and lead) ions can diffuse out of the colloidal particles into the strontium-depleted solution which surrounds them. Factors which tend to shorten this time for escape of strontium ions tend to produce aragonite, and those which lengthen the time before crystallization give more opportunity for the escape of strontium ions and thus tend to produce calcite.

At the higher temperatures, the rate of crystallization is accelerated rapidly and the strontium ions do not have time to escape and thus they are incorporated into the CaCO₃ lattice giving the larger structure—aragonite. In series 1, calcite is formed at temperatures below 40° and aragonite is formed at temperatures above 50°. At temperatures between these limits, the incorporation of strontium in the lattice is intermediate and a mixture of aragonite and calcite is formed.

The greater the concentration of precipitating

ions the greater the tendency to form colloidal precipitates and the longer the time available for expulsion of strontium ions before crystallization. Accordingly, when all other conditions are the same, an increase in concentration tends to favor calcite formation rather than aragonite, as was found when 1 molar solutions were mixed.

Thus far only the first two stages have been discussed—the formation of aggregates and the orientation or first crystallization. The work of de Keyser and Dugueudre⁴ was concerned only with these first two steps, but extensive changes from aragonite to calcite can take place by further contact with the solution from which the precipitates were formed. The transformation of the solid aragonite to solid calcite all in the same crystal is an exceedingly slow process at room temperature, but if these crystals are in contact with water, the more soluble aragonite goes into solution and recrystallizes as the less soluble calcite. Moreover, the redissolved calcium carbonate produced by the solution of the aragonite brings its strontium into solution where it is diluted so that it is less likely to produce aragonite.

Spectrographic analyses showed a higher per cent. of strontium (80 p.p.m.) in the 70% aragonite precipitated at 45° (Fig. 1) than in the recrystallized calcite (25 p.p.m. strontium) after 10 hours of standing in the solution.

The removal of strontium ions from aragonite which is undergoing recrystallization is believed responsible for the formation of calcite. This hypothesis was confirmed with additional experiments. Pure aragonite precipitated at 50° and its surrounding solution was divided equally and placed in two separate flasks and maintained at 50°. To one of these was added 100 ml. of 0.1

M Sr(NO₃)₂. In this flask there was no trace of calcite formation after 20 hours, whereas in the flask to which strontium nitrate had not been added, about 50% of the aragonite had changed to calcite in the same period of time.

The fact that similar results were obtained with calcium nitrate of two different manufacturers probably indicates that after a certain minimum concentration of strontium and other critical impurities are reached, higher concentrations have but little further effect.

At first sight, it would be expected that the recrystallization from aragonite to calcite would go faster at high temperatures, but an examination of Fig. 1 shows that at 40° the 95% calcite changes to 100% calcite in half an hour, at 45° it changes from 30 to 100% in about 10 hours, and at 50° it changes only from zero to about 35% in 18 hours. The number of calcite crystals to act as nuclei for further growth is much less in the precipitates formed at the higher temperatures. The slowness to go from aragonite to calcite at the higher temperatures is thus explained as due to the relative absence of calcite seed crystals. This hypothesis was checked by taking out a precipitate of 50% aragonite and 50% calcite slowly changing at 45°. When this precipitate in its solution was heated to 70° the change to calcite was complete in two hours, whereas at 45° it required ten hours. If sufficient seed crystals are present, the higher temperature does give a faster rate of transformation to the stable calcite, as would be expected.

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[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY, CHEMISTRY DIVISION, OAK RIDGE, TENN.]

Equilibrium Ultracentrifugations of Acidic Hg(I), Hg(II), In(III), and Au(III) Solutions¹

BY JAMES S. JOHNSON AND KURT A. KRAUS

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Equilibrium ultracentrifugations confirm that In(III) in HBr and Au(III) in HCl exist as mononuclear complexes. The results contradict recent suggestions based on solvent extraction data that dimers of In(III) and Au(III) exist in the aqueous phase. The method was checked by comparing apparent molecular weights of Hg(I) and Hg(II) in nitrate solutions.

In recent years the extractability of several metal ions from aqueous into organic phases has been reported to increase with decreasing concentration of the metal. For example, from 3.7 *M* HCl, the extraction coefficient of Ga(III) into bis-2-chloroethyl ether increases manyfold as the aqueous Ga(III) concentration is decreased from 10⁻² *M* to 10⁻⁸ *M*.² Similar changes in extractability have been observed for Au(III) in HCl, In(III) in HBr and Tl(III) in HCl.³ It has been

suggested² that such results could be explained by the formation of unextractable dimers of the metal ion species in the aqueous phase at the higher metal concentrations, but alternate explanations have also been advanced.⁴⁻⁶ Recently Irving and Rossotti have attributed this change in extractability for In(III) from HBr solutions to dimerization.⁷

We have attempted to decide between alternate explanations by molecular weight measurements with the equilibrium ultracentrifuge.

(1) This document is based on work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory.

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