

Coprecipitation of Cadmium with Calcite

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The distribution of cadmium between precipitates of calcite and saturated aqueous solution was measured at 25°C to understand the distribution of cadmium in the bivalves. Calcite was precipitated from calcium bicarbonate solution by the gradual release of carbon dioxide. The cadmium ions were coprecipitated in calcite, obeying the logarithmic distribution law. The apparent distribution coefficient was decreased as α , α' -dipyridyl increased, but the true distribution coefficient was found to be an almost constant value, 560. This value is fairly close to the ratio of solubility product constants $K_{\text{calcite}}/K_{\text{CdCO}_3}$, 890. This suggests that the deviation of the present solid solution from ideality is not very large.

INTRODUCTION

It has been known for many years that heavy metal contents are much higher in the marine biosphere than in the hydrosphere.¹⁾ More recent works have indicated an increasing interest in the biosphere, particularly in relation to trace-element uptake by such an organism as marine bivalves.^{2,3)} This also may elicit a considerable interest as to the impact of the marine environment on the heavy metal contents in the bivalve and as to the distribution behavior of the metal between shellfish and shell.

Though the shell is not a single chemical substance, there is evidence that it is essentially a calcium carbonate. And several metal ions can be coprecipitated with calcium carbonate by substituting for calcium in the solid phase.

There are several investigations dealing with the incorporation of such metal ions as strontium,^{4~6)} zinc,^{7~9)} uranium,¹⁰⁾ and copper⁹⁾ with calcite or aragonite because carbonate sediment is one of the most important materials to provide many geochemical informations.

Cadmium is one of the most insidiously toxic of the heavy metals to which man is exposed, and showed more enrichment in the shellfish, especially in the kidney and the organ of Keber than in the shell and in the marine environment. In this paper, the coprecipitation behavior of cadmium with calcite was investigated to understand the distribution of cadmium in the shell.

EXPERIMENTAL

Apparatus and Reagents

The radioactivity countings were made with a Packard Tricarb Liquid Scintilla-

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tion Spectrometer, Model 3320 and with a Metro NaI(Tl) (44.5 mm in dia. X 50.8 mm) well-type scintillation counter, Model PbW-6, connected with a Metro single channel pulse height analyser, Model SP-6F. The X-ray patterns of calcium carbonate were measured by using a Shimadzu X-ray Diffractometer, Model AZ-2A, with nickel filtered copper radiation.

Radioisotope, cadmium-115 m was supplied by New England Nuclear, Boston, Mass., U.S.A., as chloride in hydrochloric acid. This was diluted with dilute nitric acid to make the solution of about $1 \mu\text{Ci/ml}$. A calcium bicarbonate solution was freshly prepared by passing carbon dioxide into a calcium carbonate suspension in pure water for several hours, by allowing it to stand for a half hour and by filtering it. The filtrate was passed again with carbon dioxide for a half hour to make it ready for further procedure. A cadmium solution was prepared from reagent-grade nitrate. A standard EDTA solution containing EDTA-magnesium chelate was standardized with a calcium solution which has been prepared from dry calcium carbonate. A liquid scintillator for the measurement of the cadmium activity was prepared by dissolving 100 mg of 1,4-bis(5-phenyloxazolyl) benzene (POPOP), 4 g of 2,5-diphenyloxazole (DPO), and 75 g of naphthalene with dioxane and by diluting them to 1.00 l with the solvent.

All the other reagents were reagent-grade materials.

Procedure

The gradual release of carbon dioxide gas from the calcium bicarbonate solution was followed by the carbonate precipitation. This method was adopted as the coprecipitation procedure of cadmium with calcite. Ten hundred milliliters of the aqueous solution which contained 0.01 M of calcium bicarbonate solution, appropriate amounts of cadmium, cadmium 115 m, and α, α' -dipyridyl, were taken in a 1.0 l Erlenmeyer flask. The flask was sealed with a silicon rubber stopper fitted with a glass tube with 5.0 cm in length and a suitable size in diameter. The tube was open to the air.

The flask was supported in a water bath at 25°C whose temperature was controlled by a immersion heating coil regulated by a mercury thermoregulator, and was stirred with a magnetic Tefloncoated bar which was driven by a magnetic stirring motor placed under the bath. At appropriate intervals of time, an aliquot of the supernatant solution was pipetted out. After the centrifugalous separation of the solid phase, cadmium activities in the solution phase were counted with a NaI(Tl) well type scintillator, or with a liquid scintillation spectrometer after 2 ml of 0.1 M hydrochloric acid and 15 ml of liquid scintillator had been added to 2 ml of the sample solution. Calcium was determined by EDTA titration using Eriochrome Black T. The presence of α, α' -dipyridyl and cadmium showed no interference for the determination of calcium. The apparent distribution coefficients were calculated from the equation (1) or (2) as shown later. After having been filtered off, washed with pure water and dried in an air bath, the formed precipitates of the carbonate were used for the identification of the crystal form by X-ray diffraction.

RESULTS AND DISCUSSION

As a crystal grows from an aqueous solution, microcomponents distribute between the two phases in two characteristic manners. One is called the homogeneous distribution law, and the macro- and microcomponents distribute to obey the following equation, which was introduced by Chlopin¹¹⁾ and by Henderson and Kracek:¹²⁾

$$D = \frac{C_{Ca} \cdot M_{CdCO_3}}{C_{Cd} \cdot M_{CaCO_3}} \quad (1)$$

where C_{Ca} and C_{Cd} are the total concentrations of calcium and cadmium ions in the solution phase. M_{CaCO_3} and M_{CdCO_3} are the mole fractions of calcium and cadmium in the carbonate phase.

The other is called the logarithmic distribution law¹³⁾ and expressed as follows:

$$\lambda = \log \frac{C_{Cd, initial}}{C_{Cd, final}} / \log \frac{C_{Ca, initial}}{C_{Ca, final}} \quad (2)$$

Whether the partition of a micro-component follows the homogeneous distribution law or the logarithmic law depends on the conditions of crystallization. In general, it is found that the precipitation from homogeneous solution is followed by the logarithmic distribution law.

McIntire¹⁴⁾ gave a comprehensive review of theory and experimental data relative to the distribution coefficients of trace elements in geology. It is notable in his review that the nonequilibrium logarithmic distribution coefficient, λ' , of micro-component between precipitate and solution phases is related to the apparent distribution coefficient, λ and to the degree of supersaturation, S by the following equation, if the diffusion coefficients of micro- and macro-components are very nearly equal:

$$\lambda' = \frac{\lambda S}{\lambda(S-1)+1} \quad (3)$$

From the equation above, the following tests are required to obtain more accurate true distribution coefficients in the coprecipitation system obeying the logarithmic distribution law. Firstly, the distribution coefficients should be measured in different precipitation rates because the precipitation rate is related to the degree of supersaturation. Secondly, the logarithmic distribution coefficient in a state of non-equilibrium approaches unity as the degree of supersaturation increases. Inversely this indicates that the distribution coefficient becomes scarcely affected by the degree of supersaturation if the apparent distribution coefficient can approach unity by decreasing the activity of metal ions in the solution phase with a chelating agent.

To investigate the coprecipitation behavior of cadmium with calcite, cadmium was coprecipitated from the simplest parent solution system that the solution contained only calcium, bicarbonate and cadmium. Because the precipitation rate of calcite depended upon the diameter of the glass tube through which carbon dioxide was released, the precipitation reaction was performed with changing the diameter

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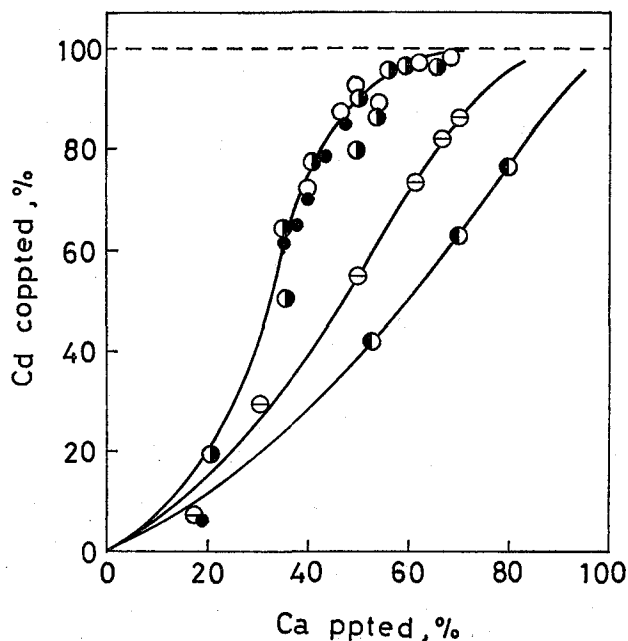


Fig. 1 Coprecipitation of cadmium with calcite formed at various precipitation rates.
 Ca^{2+} , 0.01 M; Cd^{2+} , 5×10^{-6} M; α , α' -dipyridyl, 1×10^{-3} M;
 $t_{1/2}$, \odot , 1.6 hrs; \ominus , 3.3 hrs; \bullet , 1 day; \circ , 4 days; \bullet , 14 days; temp., 25°C.

from 1.5 to 9.0 mm: the concentrations of calcium, cadmium, and α , α' -dipyridyl were 1×10^{-2} M, 5×10^{-6} M, and 1×10^{-3} M, respectively; the thermostat was regulated at 25°C; the time required to precipitate 50 per cent of the calcium ions from the beginning of calcite precipitation, $t_{1/2}$ was about 1.6 hrs, 3.3 hrs, 1 day, 4 days, and 14 days when the diameter of the glass tube was 9.0, 7.0, 5.0, 2.5, and 1.5 mm, respectively. All precipitates showed X-ray patterns typical of calcite. The results are shown in Fig. 1, in which the percentages of the coprecipitated cadmium are plotted against the fraction of precipitated calcium. The figure shows that cadmium coprecipitation with calcite is little influenced by the precipitation rate in the slower range than $t_{1/2} = 1$ day, and gradually decreased in the faster range. The apparent distribution coefficients, D and λ were calculated from Eqs. (1) and (2).

In the present system, α , α' -dipyridyl was used to decrease the cadmium activity, while this scarcely reacted with calcium ions. The formation of the cadmium chelates gave a profound effect on the apparent distribution coefficient.

Generally, the total concentrations of calcium, cadmium, and ligand, C_{Ca} , C_{Cd} , and C_{L} are represented in the following equations if there exists the ligand in the solution phase:

$$C_{\text{Ca}} = m_{\text{Ca}} \{1 + \sum \beta_i^{\text{CaL}} m_{\text{L}}^i\} \quad (4)$$

$$C_{\text{Cd}} = m_{\text{Cd}} \{1 + \sum \beta_i^{\text{CdL}} m_{\text{L}}^i\} \quad (5)$$

$$C_{\text{L}} = m_{\text{L}} \{1 + \sum \beta_i^{\text{LH}} [\text{H}]^i\} + m_{\text{Ca}} \sum \beta_i^{\text{CaL}} m_{\text{L}}^i + m_{\text{Cd}} \sum \beta_i^{\text{CdL}} m_{\text{L}}^i \quad (6)$$

where m_{Ca} , m_{Cd} , and m_{L} are the molar concentrations of calcium, cadmium, and ligand, and β_i^{LH} , β_i^{CdL} , and β_i^{CaL} denote the cumulative or gross stability constants of proton, calcium and cadmium complexes with the ligand, respectively.

In the present system, as calcium ion scarcely reacts with α, α' -dipyridyl, and C_{Ca} is negligible compared with C_{L} , Eqs. (4), (5), and (6) are abbreviated to the following equations:

$$m_{\text{Cd}} = C_{\text{Cd}} / \{1 + \sum \beta_i^{\text{CdL}} m_{\text{L}}^i\} \quad (7)$$

$$m_{\text{Ca}} = C_{\text{Ca}} \quad (8)$$

$$m_{\text{L}} = C_{\text{L}} / \{1 + \sum \beta_i^{\text{LH}} [\text{H}]^i\} \approx C_{\text{L}} \quad (9)$$

The true distribution coefficient, λ^0 for the present system can be calculated from the ratio of C_{Cd} to m_{Cd} and Eq. (2). The following values were used as the equilibrium constants of proton and cadmium with α, α' -dipyridyl at 25°C:^{15,16)}

$$\beta_1^{\text{CdL}} = 10^{4.5}, \quad \beta_2^{\text{CdL}} = 10^{8.0}, \quad \beta_3^{\text{CdL}} = 10^{10.5}, \quad K_1^{\text{LH}} = 10^{4.44}$$

Figure 2 shows the relationships between the true distribution coefficients and the per cent of calcium precipitated. As shown in the figure, the distribution of cadmium on calcite obeyed the logarithmic distribution law and the true distribution coefficient gave nearly a constant $10^{2.75}$ when $t_{1/2}$ was longer than 1 day.

The coprecipitation of cadmium was performed from the solutions having $1.0 \times 10^{-3} \text{ M}$, $1.5 \times 10^{-3} \text{ M}$, and $2.0 \times 10^{-3} \text{ M}$ of α, α' -dipyridyl in order to examine the

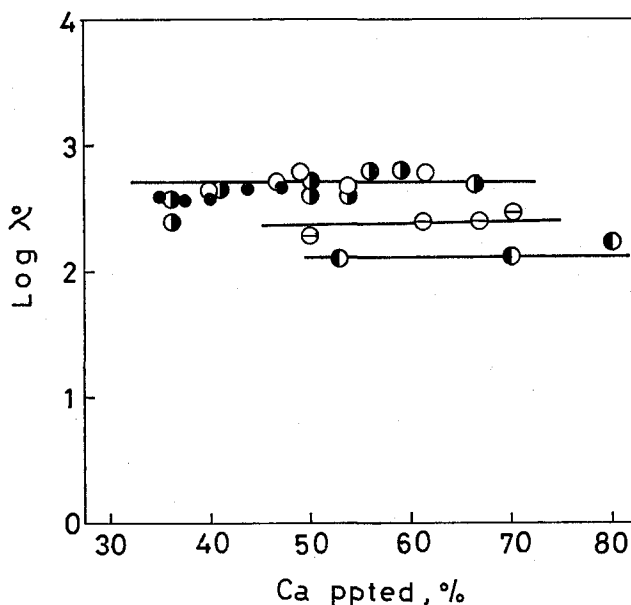


Fig. 2 The true distribution coefficients at each percentage of precipitated calcium.

$t_{1/2}$: ●, 1.6 hrs; ○, 3.3 hrs; ◐, 1 day; ○, 4 days; ●, 14 days.

Others are the same as in Fig. 1.

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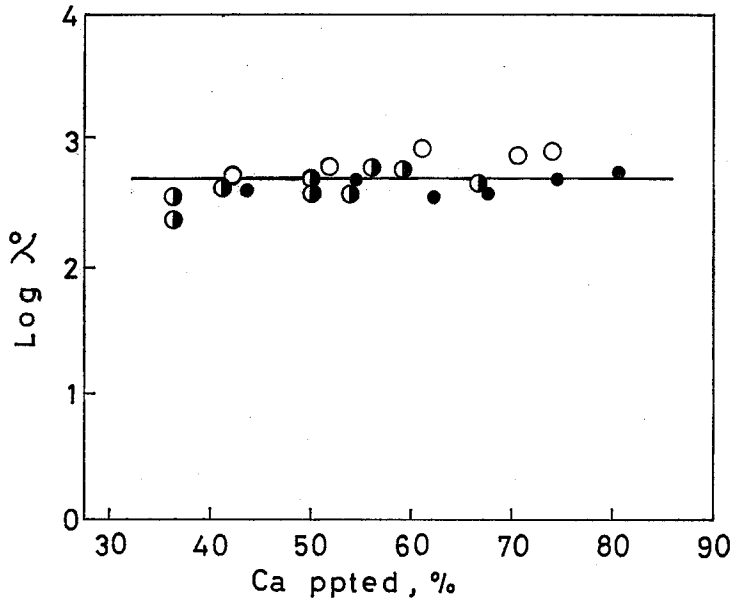


Fig. 3 The true distribution coefficients at various α, α' -dipyridyl concentrations. α, α' -dipyridyl, \circ , $1.0 \times 10^{-3} \text{ M}$; \circ , $1.5 \times 10^{-3} \text{ M}$; \bullet , $2.0 \times 10^{-3} \text{ M}$; $t_{1/2}$, 1 day.

effect of cadmium activity on the apparent and true distribution coefficients. The apparent coefficient decreased from 3.0 to 0.7 as α, α' -dipyridyl increased from 1.0×10^{-3} to $2.0 \times 10^{-3} \text{ M}$, but the true coefficient showed an almost constant value as shown in Fig. 3. This indicates that the degree of supersaturation, S in Eq. (3) is close to unity in the present system.

Principally, the true distribution coefficient should be independent of where the molar ratio between calcium and cadmium ions in the system the isomorphous solid solution is formed. In order to examine the molar ratio, the calcite was precipitated from the calcium bicarbonate solutions having cadmium ranging from $5 \times 10^{-5} \text{ M}$ to 3×10^{-7} when the other circumstances were kept identical. The results are shown in Figs. 4 and 5; no significant change was observed in the true distribution coefficient of cadmium.

Chlopin's distribution coefficient, D was derived by Ratner¹⁷⁾ and Vaslow and Boyd¹⁸⁾ on the basis of thermodynamics.

$$D = \frac{K_{\text{CaCO}_3}(\gamma_{\text{Cd}})}{K_{\text{CdCO}_3}(\gamma_{\text{Ca}})} \exp\left(\frac{-\Delta\mu}{RT}\right) \quad (10)$$

where K_{CaCO_3} and K_{CdCO_3} denote the thermodynamic solubility product constants for CaCO_3 and CdCO_3 , γ_{Ca} , and γ_{Cd} stand for molal activity coefficients of calcium and cadmium in the solution phase, and $\Delta\mu$, the excess free energy, is the partial molar free energy involved in transferring one mole of cadmium ions from a large quantity of ideal solid solution to the real solid solution at the same mole fraction.

The distribution coefficient, D in Eq. (10) is composed of a product of three

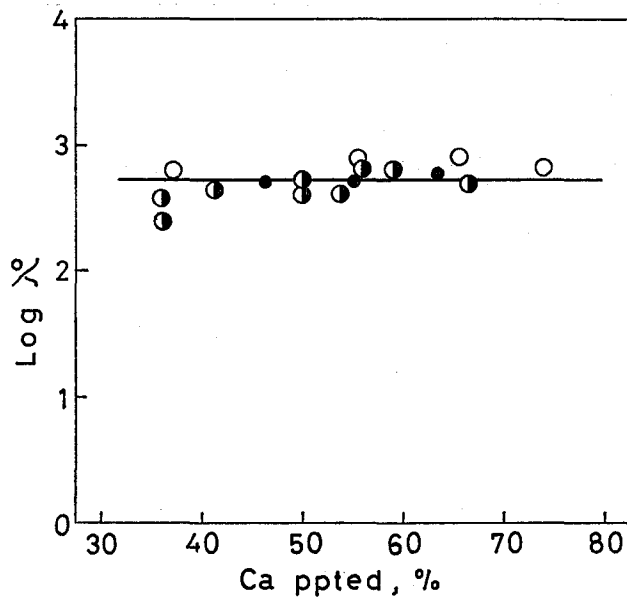


Fig. 4 The true distribution coefficients at various cadmium concentrations.

Cadmium concentration, ●, 3×10^{-7} M; ○, 5×10^{-6} M; ○, 5×10^{-5} M; $t_{1/2}$, 1 days.

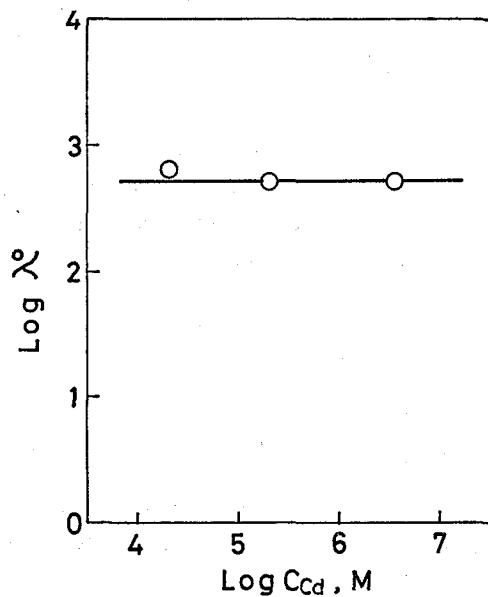


Fig. 5 The effect of cadmium concentration on the true distribution coefficients.

factors; the first factor is the ratio of the solubility product constants, the second expresses the effect of the composition of the solution phase, and the third shows the nature of the solid solution. If the solid solution is ideal, D is expressed as $K_{\text{CaCO}_3}/K_{\text{CdCO}_3}$ because the other two factors in Eq. (10) closely approach unity.

Solubility product constants for calcite and hexagonal cadmium carbonate are -8.34 and -11.29 of $\log K_{\text{MCO}_3}$.⁸⁾ And the ratio of the solubility product of cadmium carbonate to that of calcite as zero'th order approximation to a distribution coefficient is 890. This value is approximately close to the distribution coefficient observed in the present experiment, about 560. From this the following is suggested; as the ionic radii of calcium and cadmium are very similar (Ca^{2+} ; 0.99\AA , Cd^{2+} ; 0.97\AA), the magnitude of $\Delta\mu$ is fairly small and the deviation of the present solid solution from ideality is not so large.

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