Coprecipitation of Lead with Hydroxyapatite

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The distribution behavior of lead between aqueous phase and hydroxyapatite was investigated. Hydroxyapatite precipitates were prepared by dropping hydrogenphosphate ion extremely slowly to an aqueous solution containing calcium, lead, ethylenediamine and glycine at 80°C. The lead ion was coprecipitated in the apatite, obeying the Doerner and Hoskins logarithmic distribution law. Apparent distribution coefficient was roughly constant, though the stability constants at room temperature were used in calculating them. That the distribution coefficient of lead has a high value, approximately $10^{7.3}$, shows its high affinity for such apatite minerals as mineral bone.

INTRODUCTION

Hexagonal calcium hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, is the principal inorganic constituent of human bones and teeth, and also exists in nature as mineral hydroxyapatite. Trace elements in such apatite samples have been the subject of biological and geochemical investigations[1] especially since the increasing of an opportunity of taking poison metals and radioisotopes from atmosphere and foods.

Divalent ions such as strontium, barium and lead can be substituted for calcium in the apatite crystals to make solid solution. Among these substituted cations lead has attracted attention as the incorporation of lead in human skeletal system leads to lead–poisoning.[2] Previously, we have reported data on the coprecipitation of strontium,[3] copper,[4] and zinc[5] with hydroxyapatite by slow precipitation. In this paper, the coprecipitation of divalent lead with hydroxyapatite was investigated.

EXPERIMENTAL

Apparatus

Spectrophotometric measurements were made with a Hitachi Perkin-Elmer 139 UV-VIS spectrophotometer using 1.00 cm cells. A Hitachi-Horiba pH meter, model F–5, was used for the pH measurements.

Materials.

The lead and calcium stock solutions were prepared from their respective reagent–grade nitrates and were standardized by EDTA titration. The standard EDTA solution containing EDTA-magnesium chelate was standardized with the calcium solution which was prepared from dry calcium carbonate.

The other chemicals were reagent-grade materials.

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Coprecipitation Procedure

The procedure of the coprecipitation is essentially the same as those described in the previous papers.[3~5]   To a solution containing different amounts of solutions of lead nitrate and glycine in various proportions, add 20 ml of 0.5 M calcium nitrate and 10 ml of ethylenediamine in a reaction Erlenmeyer flask.   Adjust a desirable pH, dilute the solution to 500 ml and place it in a thermostatic bath regulated at 80°C.   Stir the solution continuously by a magnetic stirrer and pass the nitrogen gas in the flask.   Drop a 0.1 M diammonium hydrogenphosphate solution very slowly through a microfeeding pump.   Pipet an aliquot of the supernatant solution with the lapse of time.   After the centrifugalous separation, determine the lead content spectrophotometrically in the solution phase by extracting it with dithizone-chloroform and by measuring the absorbance at 510 nm.   Determine the calcium content by EDTA-titration using Eriochrome Black T.

RESULTS AND DISCUSSION

Composition of Hydroxyapatite in the Presence of Glycine.

The solid phase precipitates which deviates somewhat from hydroxyapatite in composition when the apatite precipitates from an aqueous solution.[6,7]   Previously, the ratio of calcium to phosphorus atom in the apatites precipitated from the solutions buffered by 0.25 M ethylenediamine was investigated in detail.[3,4]   In the present work, glycine was used as a chelating agent, as it has a moderate stability with lead ion.

The influence of the presence of glycine on the apatite composition was examined; the phosphate ion in the precipitates which were washed with water and dried at 110°C was measured spectrophotometrically with the molybdovanadophosphoric acid method[8] and calcium was determined by back-titrating an excess of EDTA with a magnesium standard solution.   As shown in Fig. 1, a little effect of glycine was observed, but each precipitate showed a typical X-ray pattern of apatite.   When the apatites were precipitated from the solution containing over 1.0 M of glycine, the Ca/P ratio became about
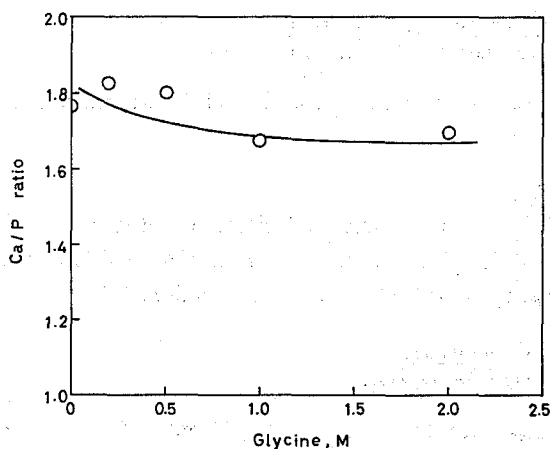

Fig. 1.   The Ca/P ratio in the precipitates formed at various glycine concentrations.
　　　　　Dropping rate: 5.80 ml/hr.,　　pH: 8.30, Ca: 0.02 M,
　　　　　ethylenediamine: 0.25 M,　　temp.: 80°C

1.67 at pH 8.30; the ratio corresponded to the composition of hydroxyapatite. Then this pH value was essentially adopted in the present experiments.

Distribution Law in Coprecipitation System

The distribution of lead between the solution phase and the apatite precipitate is seen in the equation:

$$Ca_{cryst} + Pb_{soln} \rightleftarrows Pb_{cryst} + Ca_{soln} \tag{1}$$

The equilibrium constant, *i.e.*, the thermodynamic distribution coefficient, K_{Pb} for this reaction is:

$$K_{pb} = \frac{a_{Ca}^{soln} \cdot a_{PbPh}^{cryst}}{a_{Pb}^{soln} \cdot a_{CaPh}^{cryst}} \tag{2}$$

$$= \frac{m_{Ca} \cdot \gamma_{Ca}^{soln} \cdot m_{PbPh}^{cryst} \cdot \gamma_{PbPh}^{cryst}}{m_{Pb} \cdot \gamma_{Pb}^{soln} \cdot m_{CaPh}^{cryst} \cdot \gamma_{CaPh}^{cryst}} \tag{3}$$

where a^{cryst} and a^{soln} designate the activities of the chemical species in the crystal and solution phases, respectively. m_{CaPh}^{cryst} and m_{PbPh}^{cryst} are the mole fractions of calcium and lead in the apatite crystals; m_{Ca} and m_{Pb} are the molar concentrations of calcium and lead ions in the solution phase. γ_{CaPh}^{cryst} and γ_{PbPh}^{cryst} denote the activity coefficients in the crystals of calcium and lead phosphates; γ_{Ca}^{soln} and γ_{Pb}^{soln} denote those in the solutions of calcium and lead ions.

The apparent distribution coefficient, D, is defined:[9,10]

$$D = \frac{C_{Ca} \cdot m_{PbPh}^{cryst}}{C_{Pb} \cdot m_{CaPh}^{cryst}} \tag{4}$$

where C_{Ca} and C_{Pb} are the total concentrations of calcium and lead ions in the solution phase. This is called a homogeneous distribution law.

If the distribution equilibrium is attained between the crystal surface and the solution phase, the logarithmic distribution coefficient is expressed as follows:[11]

$$\lambda = \log \frac{C_{Pb,initial}}{C_{Pb,final}} \Big/ \log \frac{C_{Ca,initial}}{C_{Ca,final}} \tag{5}$$

The apparent distribution coefficients, D and λ, are calculated by using Eqs. (4) and (5).

Precipitation Rate

The non-equilibrium distribution coefficient, λ', of the microcomponent between precipitate and solution is related to the apparent distribution coefficient, λ, and to the degree of supersaturation, S, by the following equation.[12]

$$\lambda' = \frac{\delta_{micro}/\delta_{macro}}{\lambda(S-1) + \delta_{micro}/\delta_{macro}} \tag{6}$$

where δ_{micro} and δ_{macro} are the diffusion coefficients of the micro- and macro-components, respectively. In the equation (6), $S \rightarrow 1$, $\lambda' \rightarrow \lambda$, *i.e.* as the degree of supersaturation decreases, λ' approaches the value of the apparent logarithmic distribution coefficient. If both the elements are also of the same charge and nearly the same size, their diffusion
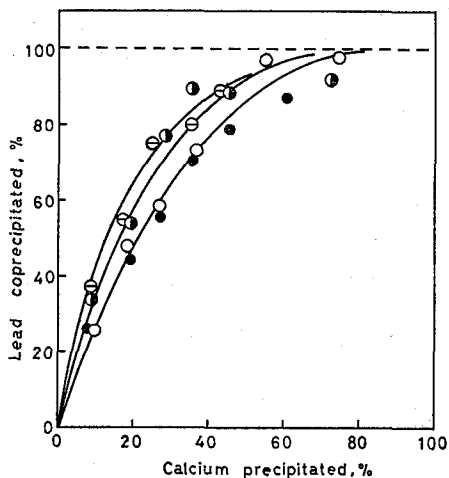
Fig. 2. The coprecipitation of lead with hydro-
xyapatite formed at various precipitation
rates.

● : 3.35 ml/hr, of 0.1 M phosphate,
○: 5.80 ml/hr.,　　◑: 10.2 ml/hr.,
⊖: 18.1 ml/hr.,　　Ca: 0.02 M,
Pb: 2×10^{-5} M,　　glycine: 1.0 M,
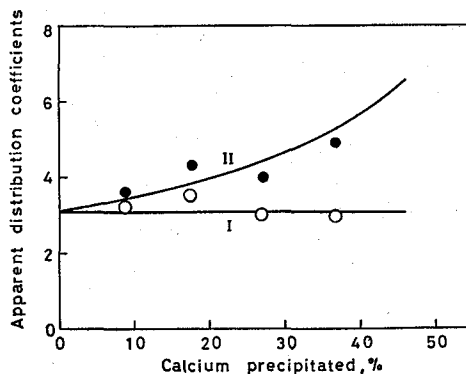ethylenediamine: 0.25 M,
pH: 8.30,　　　　temp.: 80°C

Fig. 3. Apparent logarithmic and homogeneous
distribution coefficients at each percentage
of precipitated calcium.

I: λ, II: D, dropping rate: 5.80 ml/hr.
Others are the same as in Fig. 2.

coefficients may be very nearly equal. In such cases, the Eq. (6) can be reduced to the following:

$$\lambda' = \frac{\lambda S}{\lambda(S-1)+1} \tag{7}$$

The degree of supersaturation is directly related to the rate of precipitation. Therefore, it is necessary to examine whether the distribution coefficient in the coprecipitation system of lead can be influenced by the precipitation rate of the apatite *i.e.* the dropping rate of hydrogenphosphate. In order to check the influence, the precipitation reaction was performed at the pumping velocities of 3.35, 5.80, 10.2, and 18.1 ml of the phosphate solution per hour; the concentrations of calcium, lead, ethylenediamine, and glycine were 2×10^{-2} M, 2×10^{-5} M, 0 25 M, and 1.0 M respectively; the thermostat was regulated at 80°C; pH was 8.30. The results were shown in Fig. 2; no significant change was observed at the dropping rate of 3.35 and 5.80 ml per hour, but the coprecipitation of lead tended to increase at more rapid dropping velocity.

The apparent homogeneous and logarithmic distribution coefficients were plotted in Fig. 3 against the percentage of the precipitated calcium. In the case of the slower addition of the phosphate, lead ion was coprecipitated obeying the logarithmic distribution law, while in the more rapid addition the logarithmic distribution coefficient decreased as calcium precipitated.

Glycine Concentration

Equation (7) shows that the non-equilibrium distribution coefficient approaches unity

as the degree of supersaturation increases. This indicates that the observed distribution coefficient becomes independent of the degree of supersaturation when the non-equilibrium or apparent distribution coefficient approaches unity by controlling the activity of trace metal ion in the solution phase using a suitable chelating agent.

When there exist complex-forming ions in the solution phase, the total ion concentrations of calcium, metal, and ligand are given by:

$$C_{Ca} = m_{Ca}\{1 + \sum \beta_i{}^{CaL_i} \cdot m_L{}^i\} \tag{8}$$

$$C_M = m_M\{1 + \sum \beta_i{}^{ML_i} m_L{}^i\} \tag{9}$$

$$C_L = m_L\{1 + \sum \beta_i{}^{LH_{n-i}}[H]^i\} + m_{Ca}\sum \beta_i{}^{CaL_i} m_L{}^i + m_M \sum \beta_i{}^{ML_i} m_L{}^i \tag{10}$$

where m_L is the molar concentration of ligand, and $\beta_i{}^{LH_{n-i}}$, $\beta_i{}^{CaL_i}$, and $\beta_i{}^{ML_i}$ denote the cumulative or gross stability constants of proton, calcium and metal complexes with the ligand, respectively. The values of m_{Ca} and m_M can be obtained by dissolving the simultaneous equations of Eqs. (8)~(10), and then the thermodynamic distribution coefficient, K_{Pb}, for the reaction of Eq. (1), is calculated, assuming that the all activity coefficients are equal to unity.

In the present system, glycine which shows a moderate stability with lead was used as a chelating agent. The coprecipitation of lead was performed with the solutions containing 0.20, 0.35, 0.50, 1.0, 1.5, and 2.0 M of glycine. The results were shown in Fig. 4, where the coprecipitation of lead considerably decreased as glycine concentration increased. This was shown in Fig. 5, where the apparent distribution coefficient was plotted against the concentration of glycine.

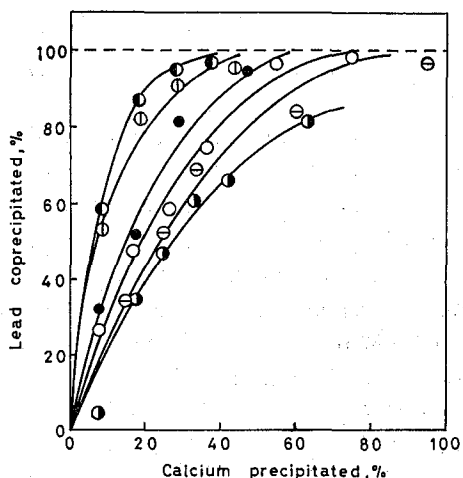The thermodynamic distribution coefficient in the lead coprecipitation system, K_{Pb},

Fig. 4. The effect of glycine concentration.
The total concentration of glycine
◖: 0.20 M, ◐: 0.35 M, ●: 0.50 M,
○: 1.0 M, ⊖: 1.50 M, ◑: 2.0 M,
dropping rate: 5.80 ml/hr.,
Ca: 0.02 M, Pb: 2×10^{-5} M,
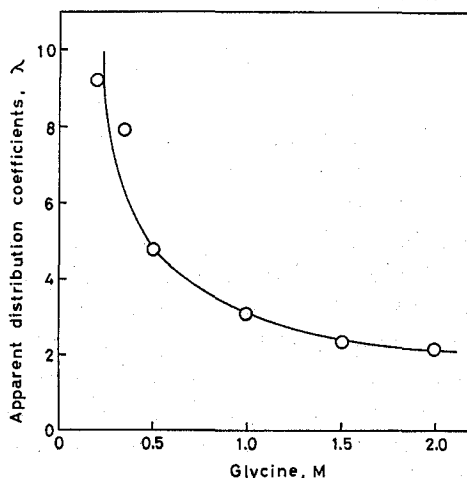ethylenediamine: 0.25 M,
pH: 8.30, temp.: 80°C

Fig. 5. The apparent distribution coefficient at various glycine concentrations.

Table I. Apparent and Thermodynamic Distribution Coefficients at Various
Glycine Concentrations

Total glycine M	Logarithmic Coefficient	
	K'_{Pb}	$\log K_{Pb}$
0.20	9.25	6.87 (7.03)
0.30	7.88	7.15 (7.20)
0.50	4.77	7.01 (7.10)
1.00	3.11	7.30
1.50	2.42	7.40
2.00	2.16	7.52

Ca: 0.02 M, Pb: 2×10^{-5} M, pH: 8.30, Temp.: 80°C

was calculated from the constants at room temperature, as the equilibrium constants of
glycine with calcium and lead ions at 80°C were not yet measured. The results were
shown in Table I; lead ion was coprecipitated in a logarithmic manner, having a nearly
constant value of the distribution coefficient, about $10^{7.3}$. The value of $\log K_{Pb}$ tended
to increase with the ligand concentration. This may have occurred because the stability
constants utilized in calculating K_{Pb} values were not those at 80°C, but at room temper-
ature. Another possible reason is the imperfectness of the solid solution as seen in Fig. 8.
The values in parentheses in Table I were obtained by correcting the K_{Pb} value with the
decreasing parts in Fig. 8. However, the corrected values were still slightly off from the
constant.

pH Effect

The coprecipitation behavior of lead at pH 7.60, 7.80, 8.00, 8.30, 8.65, and 9.05 was
shown in Figs. 6 and 7; glycine concentration was 1.0 M and dropping velocity, 5.80 ml/hr.
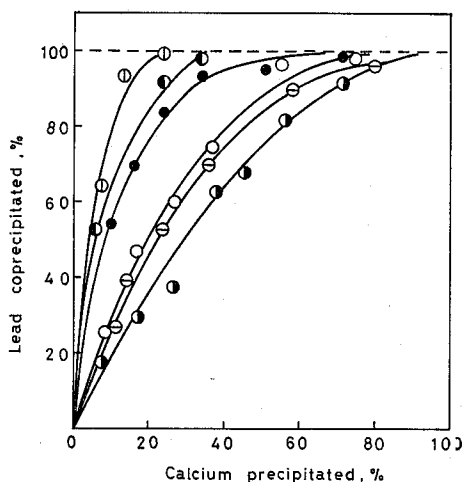

Fig. 6. The effect of pH.
pH; ◖: 7.60, ⊖: 7.80, ○: 8.00,
●: 8.30, ◑: 8.65, ⦶: 9.05
glycine: 1.0 M, Ca: 0.02 M,
Pb: 2×10^{-5}M, ethylenediamine: 0.25 M,
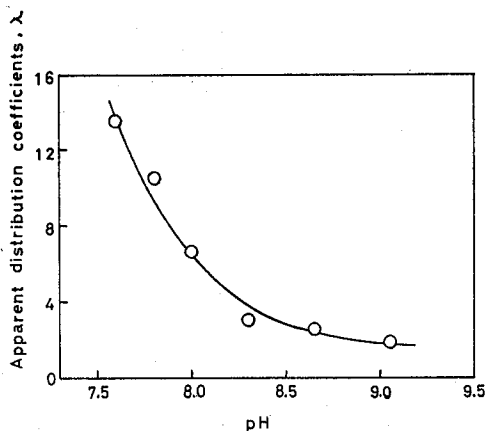dropping rate: 5.80 ml/hr., temp.: 80°C

Fig. 7. The apparent distribution coefficient at
various pH values.

Table II. Apparent and Thermodynamic Distribution Coefficients at Various pH Values

pH	Logarithmic Coefficient K'_{Pb}	log K_{Pb}
7.80	10.5	7.05 (7.15)
8.00	6.59	7.22
8.30	3.11	7.30
8.65	2.62	7.60
9.05	1.91	7.70

Ca: 0.02 M, Pb: 2×10^{-5} M, Glycine: 1.0 M   Temp.: 80°C

These diagrams show that the extent of lead coprecipitated increased as the pH value rose. The change of the apparent distribution coefficient by the pH value is mainly caused by the variety of the ligand concentration of glycine. The thermodynamic distribution coefficient calculated in a similar manner to the case of glycine concentration, was shown in Table II. The value of log K_{Pb} also increased slightly as the pH value rose. The other possible reason to explain this inconstancy, in addition to the causes described in the effect of glycine concentration, is that the apatite composition changes with the pH value.

Lead Concentration

In principle, the distribution coefficient should be independent of the initial relative concentrations, *i.e.*, molar ratio of two components for such systems forming the isomorphous mixed crystals as lead-calcium and strontium-calcium apatite systems. However, it was observed in the strontium-calcium apatite system that the distribution coefficient decreased at the higher concentrations of strontium.[3]

To investigate the effect of molar ratio between lead and calcium apatites, the precipitation reaction was performed in the range of lead from 1.0×10^{-2} to 2.0×10^{-5} M, *i.e.*, of the molar ratio of calcium to lead from 2 to 10^3. The results were shown in Fig. 8. The apparent distribution coefficient began decreasing at the higher concentration than 10^{-4} M of lead. Like the strontium-calcium system, it was noticed that considerable
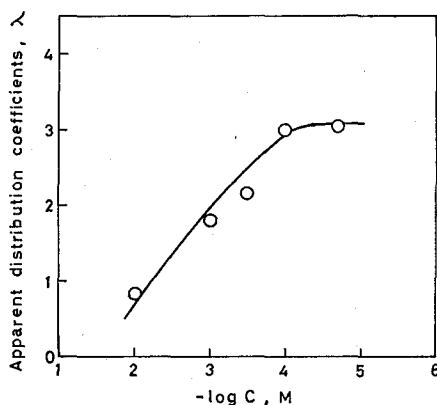

Fig. 8. The effect of lead concentration.
Ca: 0.02 M, glycine: 1.0 M, ethylenediamine: 0.25 M,
pH: 8.30, dropping rate: 5.80 ml/hr.

poor precipitates crystallized from X-ray diffraction pattern and therefore the isomorphous solid solution crystallized more slowly than the pure apatite crystals.

The distribution coefficient between lead and calcium apatites was measured in a neutral or weakly basic solution at 80°C. The application of these results to a process occurring in the biological system of vast different temperature is not yet possible. However, nothing has been brought out in this work that would indicate that considerable accumuration of lead in mineral bone is impossible.

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