Coprecipitation of phosphate with calcite

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The mechanism of phosphate coprecipitation with calcite is proposed on the basis of homogeneous distribution of phosphate in the crystal at 20°C and pH 7.9-9.5. At a constant pH, phosphate content of calcite is proportional to total phosphate concentration in aqueous solution. PO₄³⁻ ions are uptaken into the calcite lattice, where 3 CO₃²⁻ ions are replaced by 2 PO₄³⁻ ions in aqueous solution, as described by the ion exchange equilibrium:

\[ 3(CO_3^{2-})_S + 2(PO_4^{3-})_L \rightleftharpoons 3(CO_3^{2-})_L + 2(PO_4^{3-})_S \]

where S and L represent calcite and aqueous solution, respectively.

INTRODUCTION

Phosphorus exchange between sediments and natural waters, and phosphate-calcium carbonate interaction have extensively been investigated (GULBRANDSEN, 1969; STUMM and MORGAN, 1970; MORSE and COOK, 1978). It has also been observed that dissolved phosphate ions are effectively coprecipitated with calcium carbonate (OTSUKI and WETZEL, 1972; KITANO et al., 1978). The explanations of these observations have mainly been focussed on surface phenomena including phosphate adsorption on calcium carbonate, formation of calcium phosphate, and inhibition of calcium carbonate crystallization (REDDY, 1977, BERNER et al., 1978; KANEL and MORSE, 1978).

The coprecipitation of divalent cations with calcium carbonate has widely been studied in terms of partition of trace elements between calcium carbonate and aqueous solution (HOLLAND et al., 1963; KITANO et al., 1968; KINSMAN and HOLLAND, 1969; KATZ, 1973; LORENS, 1981). The studies of the trace element partition have two aspects of interest: one is in the geological applications of partition coefficients (HOLLAND, 1956; KINSMAN, 1969; PINGITORE, 1978), the other in the crystallo-chemical control of the trace element partition. In the latter aspect, it has been suggested that partition coefficients of divalent ions have a parabolic relationship with respect to their ionic radii (ICHIKUNI, 1978; ONUMA et al., 1979; MASUDA and HIRANO, 1980).

On the other hand, little has been studied on the partition of ions having different valencies. The electrical neutrality of such ions must be maintained in their incorporation into a crystal. This restriction complicates the analysis of the partition mechanisms (MCINTIRE, 1963; WHITE, 1977). ICHIKUNI (1979) suggested an ion exchange model which indicates fluoride uptake by aragonite maintaining the charge balance between fluoride and carbonate ions. In this paper the ion exchange model is applied to the study of phosphate partition between calcite and aqueous solutions.

EXPERIMENTAL

In all the runs a 300ml glass beaker was used as a reaction vessel. The runs were executed at about 20°C. A varying amount (0.6-6.0mg) of PO₄³⁻ (as Na₃PO₄ solution), 20ml of 0.2M Na₂CO₃ solution, and 0.1M HCl (for pH control) were mixed in a beaker. The mixture was
diluted with distilled water to 180ml, and stirred with a magnetic stirrer at about 200rpm. Then 20ml of 0.1M CaCl₂ solution was added, drop by drop, over a period of 2-3 hours. Total volume of 200ml was thus obtained. After sealing the beaker with polyvinyliden chloride film, the solution was held at room temperature under continuous stirring until the equilibrium was reached (after about 30 hours). The contents of the beaker were filtered through a Millipore filter with pore size of 0.45µm. The precipitate was washed with distilled water and dried at 100°C. Ca²⁺ in the solution was determined by EDTA titration. PO₄³⁻ content of the filtrate and precipitate were analyzed colorimetrically by the molybdenum blue method. Na⁺ was determined by atomic absorption spectrophotometry.

Fractional leaching of the precipitates was executed to confirm the homogeneous distribution of phosphate in calcite. About 80mg of a product was suspended in distilled water under vigorous stirring. An appropriate amount of 0.1M HCl was dropwise added to the suspension. The total volume of the solution was adjusted to 60ml after the addition of HCl solution. After the filtration, Ca²⁺ and PO₄³⁻ concentrations of the filtrate were determined as described above.

**RESULTS AND DISCUSSION**

*Inhibition of vaterite nucleation by phosphate*

Calcite precipitates were prepared from phosphate containing Na₂CO₃ solutions by slow addition of CaCl₂ solutions. In the absence of phosphate ions, this method is known as the synthetic procedure of vaterite (McCAULEY and Roy, 1974). However, vaterite was not obtained in the solutions containing more than 4 × 10⁻⁵M phosphate ions, and the precipitates showed only calcite peaks in the X-ray diffractometry. Since phosphate ions act as a poison to the crystal growth of calcium carbonate (REDDY, 1977), nucleation of thermodynamically unstable vaterite may be inhibited by phosphate ions. Any precipitates which contained detectable amounts of vaterite are excluded from the following discussion.

*Effect of aging*

The recrystallization of the precipitates was observed during the time of aging. Figure 1 shows the scanning electron micrographs of the calcite precipitates. Added amounts of phosphate and 0.1M HCl were fixed at 1.1mg and 15ml, respectively. The initial precipitates formed by the rapid precipitation consisted of spheric calcite (Fig.1-a). These precipitates recrystallized to rhombohedral calcite crystals as a result of aging (Fig. 1-b).

Figure 2 shows the phosphate compositions of the precipitates and aqueous solutions as a function of aging time. The aqueous Ca²⁺ concentrations are also depicted. The data were obtained from the different runs, where the

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**Fig. 1-a**

*Fig. 1*. Effect of aging on morphology of calcite precipitates at 20°C and pH 9.6. The time of aging: (a) 15hrs.; (b) 96hrs. Bar length: 10µm.

**Fig. 1-b**
amounts of phosphate and 0.1 M HCl added were fixed at 1.1 mg and 20 ml, respectively. After 30 hours, the aging did not actually influence the liquid and solid compositions. It can be assumed that the equilibrium partition of phosphate ions is almost established through the solution and recrystallization of the rapidly precipitated calcite.

Homogeneous distribution of phosphate in calcite If crystals of homogeneous composition are in equilibrium with an aqueous solution, the partition of a trace ion is treated as Nernst-type partition. The homogeneous distribution was examined by the fractional leaching of calcite which was held under aging. If PO$_4^{3-}$ ions are uniformly distributed in the crystals, the percentage of dissolved PO$_4^{3-}$ ions is equal to that of dissolved Ca$^{2+}$ ions. Figure 3 shows the result of the leaching experiment. The homogeneous distribution was almost established in the calcite precipitates.

Figure 4 shows the relationship between coprecipitated amount of phosphate and total phosphate concentrations in aqueous solutions.

$$[\text{PO}_4^{3-}]_S \text{ (mol/kg)} = 1.74 \times 10^3 [\text{PO}_4^{3-}]_L \text{ (mol/l)} \quad (1)$$

where the subscripts S and L represent calcite and aqueous solution, respectively. Beyond these values, the phosphate content of calcite deviated from the linearity. The slope of this linear relationship depended on the pH of aqueous solutions. The quantitative relationship of phosphate between calcite and aqueous solutions will be considered in the following section.

Mechanism of phosphate partition The incorporation of an impurity ion having different charge is constrained by the maintenance of electrical neutrality in a crystal. With the substitution of such an ion for a lattice ion, the maintenance of electrical neutrality will require one of the followings: the substitution of a second impurity ion elsewhere in the lattice, the addition of a second impurity ion at an inter-
stitial site, the formation of vacancy elsewhere in the lattice, or any combination of these processes (McIntire, 1963).

Na$^+$ ions are simultaneously coprecipitated with calcite (Table 1), but Na$^+$ content has no distinct relation with PO$_4^{3-}$ content of the solids. Thus it is concluded that Na$^+$ ions, as second impurity ions, do not contribute to the electrical neutralization of PO$_4^{3-}$ ions in calcite.

If the charge balance is maintained between CO$_3^{2-}$ and PO$_4^{3-}$ ions, the following ion exchange equilibrium is assumed:

$$3(CO_3^{2-})_S + 2(PO_4^{3-})_L = 3(CO_3^{2-})_L + 2(PO_4^{3-})_S \tag{2}$$

Then the equilibrium constant $K$ for eq. (2) is defined using the activities of these ions as:

$$K = \frac{(a^{L}_{CO_3^{2-}})^3 (a^{S}_{PO_4^{3-}})^2}{(a^{S}_{CO_3^{2-}})^3 (a^{L}_{PO_4^{3-}})^2} \tag{3}$$

As the calcite precipitates are in equilibrium with the aqueous solutions (Fig. 2), solubility product $K_{SP}$ (4) can be written as:

$$K_{SP} = a^{L}_{Ca^{2+}} \cdot a^{S}_{CO_3^{2-}} \tag{4}$$

From eqs. (3) and (4), eq. (5) is obtained:

$$\log \frac{a^{S}_{PO_4^{3-}}}{a^{L}_{PO_4^{3-}}} = 1.5 \log \frac{a^{L}_{Ca^{2+}}}{a^{S}_{PO_4^{3-}}} + 0.5 \log \frac{K_{SP}}{K_3} \tag{5}$$

The second term of the right hand side in eq. (5) can be regarded as a constant, because $a^{S}_{CO_3^{2-}}$ is nearly constant.

To prove the validity of the ion exchange equilibrium, $\log [PO_4^{3-}]_S/a^{L}_{PO_4^{3-}}$ was plotted.

Table 1. Partition of phosphate ions between calcite and aqueous solutions at 20°C. Added amount of phosphate ions was constantly fixed at 1.0mg
against $\log a_{\text{Ca}^{2+}}$ in Fig. 5. The $\text{PO}_4^{3-}$ activities of the solids are expressed in mol/kg. The used data are listed in Table 1. The observed relationship was formulized by the least square fit as:

$$
\log \frac{[\text{PO}_4^{3-}]_S}{a_{\text{PO}_4^{3-}}} = 1.50 \log a_{\text{Ca}^{2+}} + 13.53 \quad (6)
$$

The slope of experimental eq. (6) is in agreement with that of theoretical eq. (5).

The ion activity products $(a_{\text{Ca}^{2+}}^2 \cdot a_{\text{PO}_4^{3-}})$ of the solutions were all below the solubility product of tricalcium phosphate $K_{SP} = 1.20 \times 10^{-29}$ (GREGORY et al., 1974). Thus the regulation of aqueous $\text{PO}_4^{3-}$ concentrations by the formation of tricalcium phosphate is neglected in this discussion.

$\text{HPO}_4^{2-}$ ions were major species of phosphate in the aqueous solutions. It was examined using the similar ion exchange model whether $\text{PO}_4^{3-}$ were incorporated as $\text{HPO}_4^{2-}$ in calcite or not. However, no reasonable result was obtained.

In the above mechanism, 3 $\text{CO}_3^{2-}$ ions in calcite are replaced by 2 $\text{PO}_4^{3-}$ ions. This substitution means implicitly the formation of a $\text{CO}_3^{2-}$ vacant site in the lattice. Vacancy formation is generally ascertained in alkali halides containing divalent cations (KITTEL, 1976). Vacant sites in calcite can be also assumed in the substitution of $\text{PO}_4^{3-}$ ions which have different charge compared to $\text{CO}_3^{2-}$. Although the vacancy formation in calcite is not well known, it is assumed that the partition of foreign ions having different charges between the crystal and aqueous solution is controlled by the nature of the defects.

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REFERENCES


