The mechanisms of crystallization and transformation of calcium carbonates

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Abstract:: The mechanisms of the formation and transformation of calcium carbonates and the inhibition by the phosphorus containing compounds were studied. Supersaturated solutions form the unstable polymorph, amorphous calcium carbonate, at first, followed by the transformation to the metastable polymorph which finally transforms to stable form, calcite. Transformation proceeds by a mechanism of recrystallization. The growth and transformation is strongly inhibited by a phosphorus containing compounds. Details of the adsorption mechanism were reported. The zeta potentials of calcium carbonates were determined at various solution conditions.
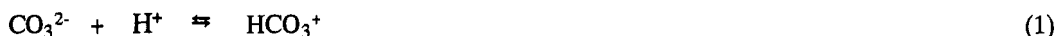
INTRODUCTION

In order to obtain reliable data of the solubility of solid in solution, it is quite important to study the mechanism of crystal growth by taking into consideration the solution equilibria of lattice ions. That is, the formation and transformation of crystals are often significantly retarded by a quite low amount of coexisting substances (inhibitors) in solution. If the transformation of an unstable form to the stable one is prohibited by inhibitors, the solution is saturated with unstable (more soluble) crystals even if the amount of these crystals is very small. The solubility experiments under these conditions lead to erroneous results. Consequently, it is quite important to understand the details of the mechanism of crystallization in order to obtain reliable solubility data. The present paper deals with the mechanism of crystal growth, transformation and the effect of phosphorus containing compounds, which are known as one of the strongest inhibitors, with respect to the most typical and well understood ionic crystal, calcium carbonate. The adsorption of these compounds on the crystal surface and the surface potential of the crystals were reported.

Calcium carbonate is one of the most common and widely dispersed minerals, occurring as limestone, chalk, and also biominerals. Because of harmless properties and inexpensiveness, it has been used for a variety of purposes such as neutralizing agent, filler, flux and cement. Furthermore, it is formed as undesirable precipitation such as scales on walls of heat exchangers and pipes. Thus, the problem of the crystal growth of calcium carbonate is situated not only at an important position in inoraganic chemistry, geochemistry and biomineralization, but also in the fields of chemical industries and water treatments. Practically crystalline $CaCO_3$ has three polymorphs (ref. 1): Calcite (solubility product: log K_{sp} = -8.48 at 25 °C) is the thermodynamically most stable form and most calcium carbonate occurs in the form of calcite in nature. Less stable form, aragonite (log K_{sp} = -8.34), is mainly found in the biosynthetic $CaCO_3$ such as shells and corals. The most unstable polymorph, vaterite (log K_{sp} = -7.91), rarely occurs in natural fields, but plays an important role in the calcium carbonate formation from solution. A huge number of studies have been carried out on the formation and transformations of $CaCO_3$ polymorphs. Coexisting substances in solution have significant effects on these reactions and equilibria, particularly the reactions in natural systems are quite complicated. The mechanistic studies of calcium carbonate precipitation is one of the most fundamental and typical subjects for elucidation of the formation of ionic crystals.

POLYMORPHIC TRANSFORMATION

Solution equilibria

Chemical equilibria of the calcium carbonate systems can be described in terms of the protonation of carbonate ion, dehydration of carboxylic acid and vapor pressure of carbon dioxide,

$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^+ \tag{1}$$

$$HCO_3^- + H^+ \rightleftharpoons H_2CO_3 \tag{2}$$

$$H_2CO_3 \rightleftharpoons CO_2 + H_2O \tag{3}$$

$$CO_2 \rightleftharpoons CO_2 \,(gas) \tag{4}$$

and the ion-par formation and hydrolysis of calcium ion:

$$Ca^{2+} + HCO_3^- \rightleftharpoons CaHCO_3^- \tag{5}$$

$$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3^0 \tag{6}$$

$$Ca^{2+} + OH^- \rightleftharpoons CaOH^+ \tag{7}$$

The solubility equilibrium of calcium carbonates is given by

$$CaCO_3 \,(solid) \rightleftharpoons Ca^{2+} + CO_3^{2-} \tag{8}$$

Activity coefficients of ionic species in the aqueous solution were calculated by using Davies equation. The reliable values of the thermodynamic (activity) equilibrium constants have been reported at various temperatures. (ref. 2) By using these equations, the activities of calcium ion $\{Ca^{2+}\}$ and carbonate ion $\{CO_3^{2-}\}$ were evaluated from the total concentrations of electrolytes and solution pH.

Mechanism of transformation

A solution with a relatively high degree of supersaturation forms precipitates spontaneously (homogeneous precipitation). The detailed mechanism of the formation and transformation of calcium carbonate precipitated by mixing of calcium and carbonate ions was studied by monitoring the change of the solution composition and properties of crystals. (ref. 3) *The change in logarithmic ion activity product of calcium and carbonate, log IAP (IAP = $\{Ca^{2+}\}\{CO_3^{2-}\}$) at 25 °C is shown in Fig. 1 (a) as a function of time. The change in the polymorphic abundance of the precipitates of the suspension is shown in Fig. 1 (b).*

The log *IAP* curve consists of three regions, unstable (I), metastable (II) and stable (III) stages. An amorphous calcium carbonate (ACC) precipitated immediately after mixing of the calcium and carbonate solutions. The *IAP* remained at a very high value for several minutes and ACC gradually transforms to crystalline calcium carbonate, calcite and vaterite, during the unstable stage. The *IAP* value shows a steep decrease just after disappeance of the ACC. In the metastable stage the *IAP* value is almost constant and the ratio of the vaterite to calcite decreased with time, i.e. vaterite transforms to calcite.   The disappearance of vaterite leads to the *IAP* value to that of the stable stage. After crystals are transformed to pure calcite (stable stage, III), no more change in the *IAP* value or the polymorphic abundance was observed.

Fig. 1 (a) Change in log *IAP* with time at 25 °C.   I, unstable stage; II, metastable stage; III, stable stage. (b) Change in polymorphic abundance. Curve 1, amorphous; curve 2, vaterite; curve 3, calcite. Cited from reference 3.

These results indicates that both transformations, ACC to vaterite and vaterite to calcite, proceed by a recrystalization mechanism.   That is, during the transformation, the IAP value of the solution is kept at the solubility of the less stable polymorph and thus the solutions at the unstable and metastable stages were saturated with this polymorph present in the suspension.   The solution is supersaturated with respect to the more stable polymorphs. Consequently, dissolution of crystals should be much faster than
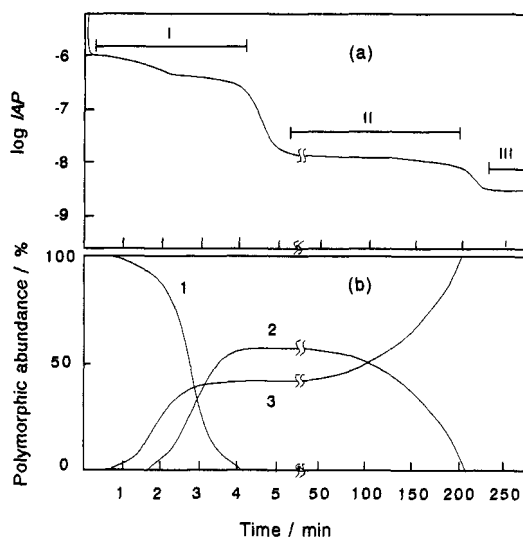
growth, that is, crystal growth is the rate determining step. The results of scanning electron micrograph and size distribution measurements support this recrystallizetion mechanism.

Effect of temperature

The polymorph abundance of calcium carbonate formed by the homogeneous precipitation strongly depends on temperature. (ref. 3,4) The abundance ratios of the calcium carbonate polymorphs in the early metastable stage are shown as a function of temperature in Fig. 2. (ref. 3) Calcite is the dominant polymorph at low temperature. With increasing temperature, the calcite abundance decreases. The predominant polymorph changes from calcite to vaterite and the formation of aragonite is observed at 40 °C. At high temperatures aragonite is the dominant species. All the crystals are finally transformed to calcite at any temperatures. The mechanism of transformation is essentially the same at any temperature. At high temperatures, the polymorphs formed in the metastable stage are aragonite and a small portion of calcite. The value of IAP of the metastable stage is kept at the solubility product of aragonite and the decrease in IAP at the end of the metastable stage is associated with the disappearance of aragonite. Thus, the transformation
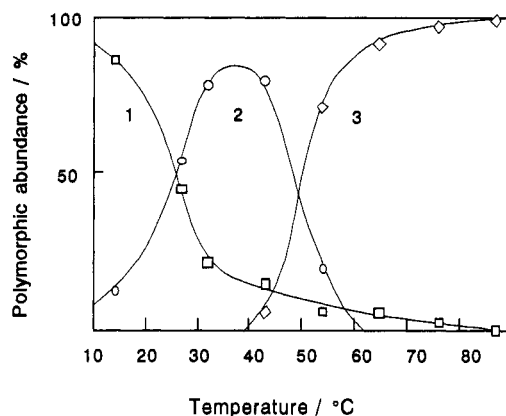

Fig. 2 Plot of abundance of crystalline calcium carbonates at the early metastable stage as a function of temperature. Curve 1, Calcite; curve 2, vaterite; curve 3, aragonite. Cited from reference 3.

of aragonite to calcite results from the dissolution of aragonite and the growth of calcite, and the latter process is the rate-determining step of the transformation. The mechanism of the transformation in the middle temperature range (40 and 50 °C) is rather complicated, because both of the less stable polymorphs, vaterite and aragonite, are formed in the metastable stage. Thus, the metastable stage consists of two steps, the step of transformation of vaterite followed by that of aragonite. Consequently, the log IAP curves with time in the metastable stage consist of two steps.

Rate of transformation

The rate and mechanism of polymorphic transformation have been directly studied for the systems of vaterite and aragonite to calcite. (ref. 5,6) A mixture of calcium carbonate crystals of a metastable polymorph (vaterite or aragonite) and stable one (calcite) were suspended in aqueous solution. The change in the abundance of vaterite, metastable (disappearing) polymorph, to calcite in the suspension is plotted as a function of time in Fig. 3. (ref. 5) The value of IAP of the solution is substantially maintained constant at the solubility product of the metastable polymorph during the transformation. As the growth of calcite is assumed to be the rate-determining step of the transformation, the rate of the transformation corresponds to the growth rate of calcite. Thus, the rate of transformation to calcite is given by

$$dA/dt = k_{tr} s f_x \qquad (9)$$

where A is the amount of calcite at time t and k_{tr} is the rate constant of transformation (correspond to calcite growth), f_x is the term concerned with the degree of the supersaturation with respect to calcite. As the degree of the supersaturation is kept constant, f_x is kept constant during the transformation. Consequently, the growth rate is directly proportional to the number of growth sites on the calcite surface, i.e., the surface area of calcite, s.

As the number of crystals does not change during the transformation, the increase in the rate of transformation with time (tangent of the plot of Fig.
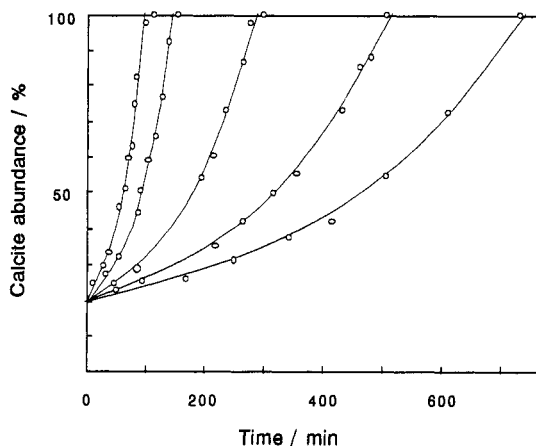

Fig. 3 Plots of calcite abundance as a function of time during the transformation of CaCO$_3$ crystal mixture. Initial ratio of CaCO$_3$ polymorphs: 80 % vaterite and 20 % calcite. (a) 25 °C, (b) 30 °C, (c) 40 °C, (d) 50 °C, (e) 60 °C. The solid lines are calculated curves with Eq 10. Cited from reference 5.

3) is explained by the increase in the surface area s. Thus, the amount of calcite, A, at time t is given by

$$A = (pt + q)^3 \qquad (10)$$

where q is an integration constant and the constant p is

$$p = (1/3) k_{tr} f_x A_0^{-2/3} s_0 \qquad (11)$$

s_0 and A_0 refer to the surface area and the amount of seed calcite at the beginning of transformation reaction, respectively. The values of p have been determined at various temperatures by the analysis of the results shown in Fig. 3. The curves calculated by these constants are given by solid lines in Fig. 3 and are in good agreement with the experimental results. Thus the increase in the transformation rate, i.e., slope of the plot, with time is explained in terms of the increase in the surface area of the growing calcite with the progress of the transformation reaction.

The supersaturation term, f_x, has bee formulated (ref. 7) as

$$f_x = (IAP^{1/2} - K_{sp}^{1/2})^2 \qquad (12)$$

and was evaluated from the IAP, which corresponds to the solubility product of vaterite or aragonite. By using the value of constant p, the rate constant, k_{tr}, has been calculated by Eq 11. The crystal growth rates of calcite, k_{gr}, have been determined directly by the calcite growth experiments. The values of k_{tr} are in good agreement with k_{gr}. These results corroborate the mechanism that the rates of transformations are essentially represented by the rate of calcite growth.

INHIBITION OF CRYSTAL GROWTH

Crystal growth inhibition by phosphonates

Many kinds of inorganic and organic ions such as metal ions, low molecular wight (soluble) polyelectro-lyte, phosphates, aminopolyphosphonates strongly retard crystal growth. Among them phosphorus containing compounds show a very strong inhibitor effect. The effect of aminopolyphosphonates on the crystal growth of calcium carbonate has been studied. (ref. 8) Figure 4 shows the effect of EDTMP [ethylenediaminetetrakis(methylenephosphonic acid)] on the formation and transformation of calcium carbonate under the conditions given in Fig. 1. (M = mol dm^{-3}) Various concentrations of EDTMP were added just after the mixing of calcium and carbonate ion solutions (indicated by an arrow in Fig. 4) Although the addition of 10^{-6} M EDTMP doesn't change the mechanism of the transformation, it strongly retards the transformation of calcium carbonate polymorphs (Fig 4 (b)). The addition of more than $10^{-5.5}$ M EDTMP prohibits the transformation of vaterite to calcite (Fig. 4 (c)). As shown in Fig. 5, the polymorphic ratio of metastable polymorph vaterite is unchanged at least several days in the presence of 10^{-5} M EDTMP. The log IAP curve at the unstable region shows a complicated change by the formation of vaterite. A peculiar behavior was observed for the transformation at $10^{-4.7}$ M EDTMP (Fig. 6). Small portion of the
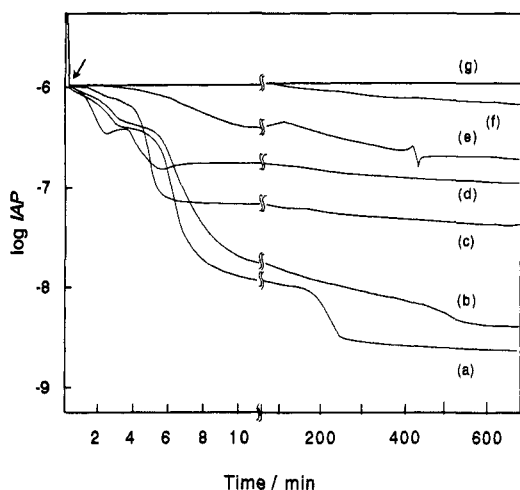

Fig. 4 The effect of EDTMP on the log IAP change at 25 °C. Arrow indicates the addition of EDTMP. Concentration of EDTMP, c_{EDTMP}: (a), free; (b), $10^{-6.0}$; (c), $10^{-5.5}$; (d), $10^{-5.0}$; (e), $10^{-4.7}$; (f), $10^{-4.5}$; (g), $10^{-4.0}$ M. Cited from reference 8.
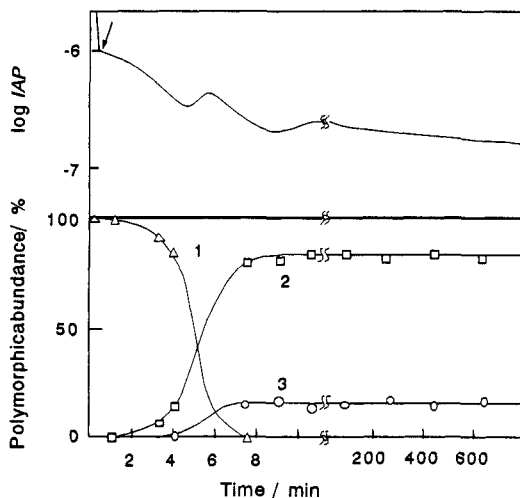
Fig.5 The change in log IAP, polymorphic abundance with time in the presence of 10^{-5} M EDTMP. Curve 1, amorphous; curve 2, vaterite; curve 3, calcite. Cited from reference 8.

ACC transforms to calcite within several minutes and the further transformation is stopped for a long time. At a certain time (about 300 min), the ACC transforms to vaterite within a very short time accompanied by the complicated change of IAP. EDTMP adsorbed on the solid is released to solution during this transformation. In the presence of more than 10^{-4} M EDTMP the amorphous calcium carbonate (ACC) shows no more change and crystalline polymorphs are never formed. The ACC solids thus obtained are quite stable and show no transformation to crystalline calcium carbonates at least several days even if it is dried at 100 °C after filtration.

ADSORPTION AND SURFACE POTENTIAL

The amount of inhibitor required for complete quenching of the crystal growth is generally much smaller than that of lattice ions. The amount of inhibitor is not enough to decrease the degree of supersaturation by the complex formation with calcium ion in the solution phase. Consequently, the inhibition effect is explained by the adsorption of inhibitor on the calcium carbonate surface. In order to understand the mechanism of the inhibition of the formation and transformation of crystals, it is important to elucidate the detailed mechanism of adsorption of inhibitors on the crystal surface.

Adsorption of phosphorus containing compounds

Adsorption isotherms of phosphates (orthophosphate and tripolyphosphate) and phosphonate (EDTMP) were studied by using P-31 and C-14 labeled compounds, respectively. The labeled compound was added to a calcite suspension and equilibrated. After the filtration the amount of the compounds in the solid and aqueous phases were determined. Logarithmic concentration of phosphorus compound on the calcite surface, $\log c_{p,s}$, is plotted as a function of logarithmic initial concentration of the compound in solution (added in solution), $\log T_p$ in Fig. 7. The solid concentration of suspension used for the experiments depicted Fig. 7 is as crystal amount : solution volume = 1 g : 20 cm^3. Thus, if all the phosphorus compound is adsorbed on the calcite, $\log T_p = \log c_{p,s} + 1.30$. The 100 %, 10 % and 1 % adsorption lines are shown by broken lines in Fig. 7.

Results of adsorption on the ripened calcite are shown by open symbols. Adsorption of EDTMP is much stronger than phosphates and obeys Langmuir (monolayer) isotherm. The surface concentration of EDTMP on the calcite is saturated at $c_{p,s} = 10^{-4.8}$ mol kg^{-1}. Adsorption curves of phosphate and triphosphate are considerably different from that of EDTMP and obey a Freundlich isotherm. That is, the concentration of phosphates on the surface increases by increasing in those in solution even in the high T_p region. Adsorption of phosphates
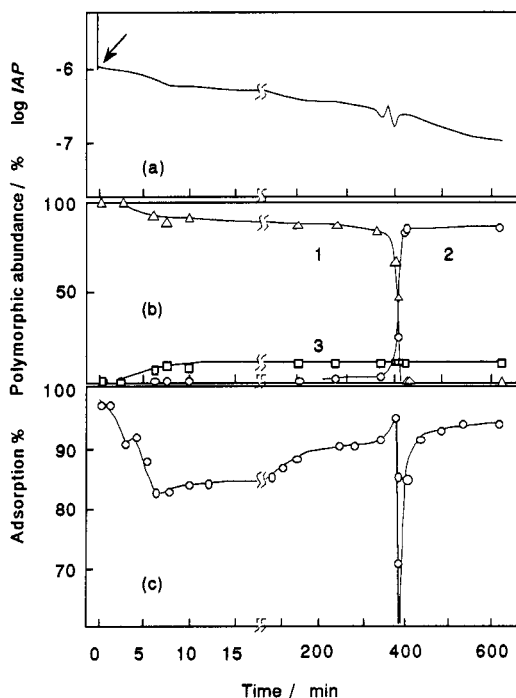

Fig. 6 The changes in Log *IAP*, polymorphic abundance and adsorption percentage of EDTMP in the presence of $10^{-4.7}$ M EDTMP. Curve 1, amorphous; curve 2, vaterite; curve 3, calcite. Cited from reference 8.
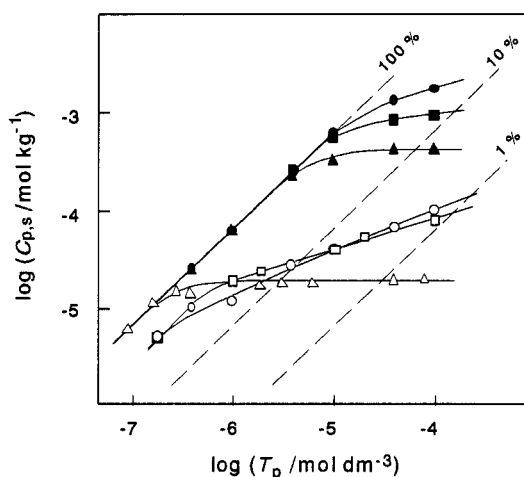
Fig. 7 Adsorption of phosphorus-containing com-pounds on calcite. $c_{p,s}$: Concentration of compound on the solid. T_p: Total concentration initially added in solution. PH = 9.0. {Ca^{2+}} = $10^{-3.0}$ M. ○, orthophosphate; □, triphosphate; △, EDTMP. Open symbols: Aged calcite. Filled symbols: Crushed calcite.
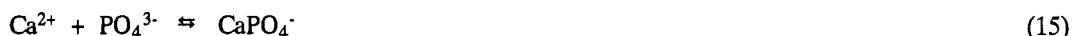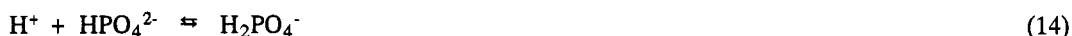
significantly increases by the increase in calcium concentration in solution. Whereas the adsorption curve of EDTMP is scarcely changed by the change in calcium concentration.

Adsorption curves on the crushed calcite prepared by grinding of the ripened crystals are shown by filled symbols in Fig. 7. Although the increase in the specific surface area of the crushed calcite (specific surface area, SSA = 0.24 m^2 g^{-1}) is about twice compared with the ripened (SSA = 0.14 m^2 g^{-1}), the adsorption of phosphorus compounds on crushed crystals is about 25 times higher than that on ripened. These compounds are completely adsorbed on the surface in the region of log $c_{p,s}$ < -3.8. Consequently the new surface created by cracking is quite rough and active for adsorption .

Surface area occupied one molecule of EDTMP obtained from surface concentration at saturated adsorption is calculated as 1500 and 50 $Å^2$ molecule^{-1} for well-developed surface and rough surface created by crush, respectively. These results indicate that in the case of well developed surface the phosphorus compounds are not adsorbed to cover the whole surface of the crystals, but selectively attach to the kink or active site of the surface. Very high ability of growth inhibition of phosphorus-containing compounds is interpreted in terms of the very high adsorption ability and the selective poisoning of the active sites or growth sites. (ref. 7, 9-11)
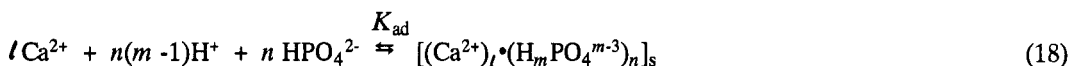
Adsorption of phosphate ion

As an example of the strict treatment of the adsorption equilibria, the adsorptionf orthophosphate on the calcite (ref. 12) and vaterite (ref. 13) was studied under various solution conditions. The side reactions of the phosphate ion to be considered in the neutral to alkaline solution are protonation of the phosphate ion and the ion pair formation with the calcium ion,

$$H^+ + PO_4^{3-} \leftrightarrows HPO_4^{2-} \tag{13}$$

$$H^+ + HPO_4^{2-} \leftrightarrows H_2PO_4^{-} \tag{14}$$

$$Ca^{2+} + PO_4^{3-} \leftrightarrows CaPO_4^{-} \tag{15}$$

$$Ca^{2+} + HPO_4^{2-} \leftrightarrows CaHPO_4 \tag{16}$$

Thus the total concentration of phosphate in the aqueous phase is given by:

$$c_p = [PO_4^{3-}] + [HPO_4^{2-}] + [H_2PO_4^{-}] + [CaPO_4^{-}] + [CaHPO_4] \tag{17}$$

The adsorption ratio of phosphate ions increases with the increase in the calcium ion concentration in solution. This fact indicates that the phosphate ion adsorbs on the calcium carbonate surface accompanying Ca^{2+}. Thus, the chemical species adsorbed is given by a chemical species, $[(Ca^{2+})_l \bullet (H_m PO_4^{m-3})_n]_s$ as a general form and the adsorption equilibrium is written by Eq 18 by using HPO_4^{2-}, which is the predominant species of the phosphate ion in the solution under the usual experimental conditions.

$$l Ca^{2+} + n(m-1)H^+ + n HPO_4^{2-} \overset{K_{ad}}{\leftrightarrows} [(Ca^{2+})_l \bullet (H_m PO_4^{m-3})_n]_s \tag{18}$$

The adsorption constant of Eq 18 is defined as:

$$K_{ad} = \frac{[(Ca^{2+})_l \bullet (H_m PO_4^{m-3})_n]_s}{[Ca]^l [H^+]^{n(m-1)} [HPO_4^{2-}]^n} \tag{19}$$

The total concentrations of adsorbate (phosphate) on the crystal surface ($c_{p,s}$) and in the aqueous solution (c_p) are measured under various solution conditions. In order to take into consideration the equilibria of phosphate in solution (Eqs. 13-16), we defined a corrected distribution ratio, D^*:

$$D^* = c_{p,s} / [HPO_4^{2-}] \tag{20}$$

where $c_{p,s}$ is the total concentration of phosphate on the surface (= $n[(Ca^{2+})_l \bullet (H_m PO_4^{m-3})_n]_s$). Substitution of Eq 19 into Eq 20 leads to

$$\log D^* = \log K_{ad} + l \log [Ca^{2+}] - n(m-1)pH + (n-1) \log [HPO_4^{2-}] + \log n \tag{21}$$

Consequently, the slopes of the plots of log D^* vs log $[Ca^{2+}]$, pH and log $[HPO_4^{2-}]$ represent the numbers of l, $-n(m-1)$ and $(n-1)$, respectively.

The results of phosphate adsorption on vaterite, log D^*, are plotted as a function of logarithmic activity of calcium ion, log $\{Ca^{2+}\}$, in Fig. 8 as an example, where the concentrations of other components are kept constant. The slope of the plot of log D^* vs. log $\{Ca^{2+}\}$ is unity (l=1), thus the number of calcium ions accompanying the phosphate adsorption is one. In the same manner, the number of the m and n were obtained and the chemical species adsorbed on the calcite and vaterite were determined. The chemical

species adsorbed on the vaterite surface is negatively charged one:

$[Ca^{2+} \cdot PO_4^{-3}]$.
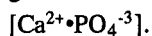
The chemical species adsorbed on the calcite surface are electrically neutral one:

Low phosphate concentrations: $[(Ca^{2+})_3(PO_4^{3-})_2]$

High phosphate concentrations: $[(Ca^{2+})(HPO_4^{-2})]$
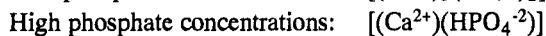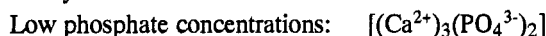
Surface charge

The chemical species adsorbed are entirely different between vaterite and calcite, that is, negatively charged species on vaterite, and non-charged species on calcite. This difference is predominantly caused by the difference of the surface charge of the crystals. Surface charge of the calcium carbonates were determined by a streaming potential method. The zeta potentials of calcite and vaterite in solution are plotted as a function of the logarithmic activity of calcium ion, log $\{Ca^{2+}\}$, in Fig. 9. As the solution is equilibrated with crystals, the concentration of carbonate ions is correlated to log $\{CO_3^{2-}\}$ = log K_{sp} - log $\{Ca^{2+}\}$. The surface charge of the crystals shifts to the positive side with the increase in the calcium ion activity in both systems. The zeta potential curves are totally different between calcite and vaterite. Under the usual experimental conditions (the order of Ca^{2+} concentration is 10^{-3} mol dm^{-3}), the surface of calcite is negatively charged. Consequently, calcite requires the adsorption of electrically neutralized species. On the other hand, the

Fig. 8 Plots of log D^* of phosphate ion on vaterite as a function of log $\{Ca^{2+}\}$. pH = 9.5 for curves 1 and 2 (log T_p: 1, -3.0; 2, -6.0). log T_p = -6.0 for curves 3 and 4 (pH: 3, 10.4; 4, 8.6). The slopes of the solid lines are unity. Cited from reference 13.

vaterite surface is positive and thus the adsorption of negatively charged species is reasonably explained.

As shown in Fig. 10, the surface charge of calcium carbonates is scarcely changed by the change in pH under the conditions that the activity of CO_3^{2-} or Ca^{2+} is kept constant. Consequently, the hydrogen ion is not the surface charge controlling ion. It has been reported that the surface charge of the calcium carbonate shifts to positive side with the decrease in pH. These experiments were conducted under the conditions that the equilibrium concentrations of lattice ions are not kept constant. Thus the change in the potential is the result of the decrease in the
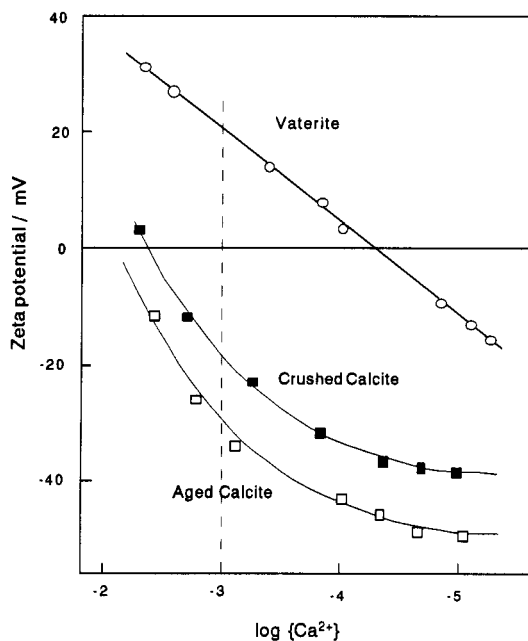

Fig. 9 Plot of zeta potential of calcium carbonates in aqueous solution as a function of logarithmic activity of calcium ion.
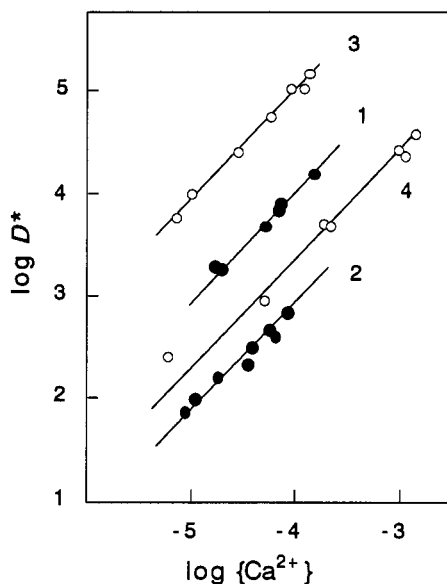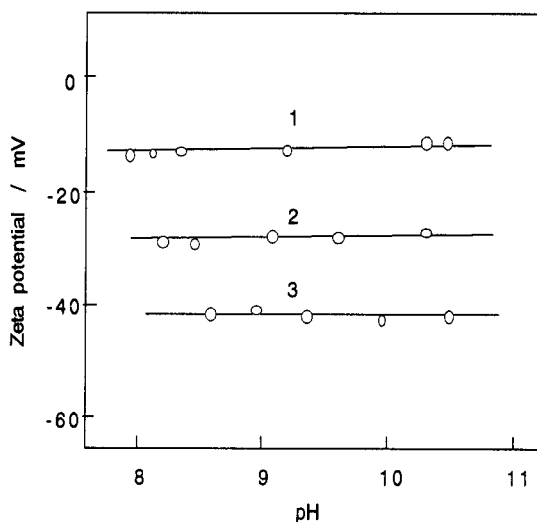

Fig. 10 Plot of zeta potential of aged calcite in aqueous solution as a function pH. Log $\{Ca^{2+}\}$: 1, -3.0; 2, -3.8; 3, -4.7.

carbonate ion concentration, $[CO_3^{2-}]$, caused by its protonation, i. e., the increase in the Ca^{2+} concentration.

The surface properties of crystals are significantly altered by the conditions of the way of preparation and history of the crystals. Particularly, the crystal surface created by crush is very rough and active e.g., Figs. 7 and 9. The rate of crystal growth on rough surface is much higher than that on the smooth surface and that surface is more favorable for adsorption. Consequently, attention is called for the comparison of the thermodynamic and kinetic data between the crystals from different origins and treatment even if they have the same polymorph.

EXPERIMENTAL

Potentiometric measurements

The activities of hydrogen ion and calcium ion were measured by a glass electrode and a calcium ion selective electrode, respectively, in a thermostated vessel at a given temperature.

Polymorphic ratio and crystal properties

An aliquot of the suspension was filtered by 0.2 μm membrane filter. The calcium carbonate precipitate was dried and characterized by X-ray powder diffraction . In the case of unstable polymorphs, EDTMP was added to each aliquot of suspension in order to prevent the further transformation of the calcium carbonate polymorphs. The polymorphic ratio of the calcium carbonate was determined from the areas of the characteristic peaks of each polymorph. The calcium carbonates precipitates were also characterized by means of electron microscopy, electron proved microanalyzer, specific surface area and size distribution determination.

Adsorption isotherm of phosphorus containing compounds

Phosphorus containing compounds labeled with radio active P-32 and C-14 was synthesized. After filtration of suspension, the radio activities of both of the sold phase and filtrate aqueous phase were measured by an liquid scintillation counter. The amount of metal ions were determined by means of atomic absorption spectroscopy.

Surface charge of calcium carbonates

Zeta potential of the calcium carbonates surface was measured by means of streaming potential and was analyzed by using a Helmholtz-Smolcowski equation.

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