Adsorption of inorganic phosphates and organic polyphosphonate on calcite

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Adsorption of two inorganic phosphates (orthophosphate (P), tripolyphosphate (TPP)) and one organic polyphosphonate (EDTPH = ethylenediamine–N,N,N',N'-tetrakis(methylenephosphonic acid)) on the surface of well-developed and crushed calcite crystals has been investigated using radioactive isotopes as tracers at 25.0 °C, where inorganic phosphates (P, TPP) and EDTPH were labeled with ^{32}P and ^{14}C isotopes, respectively. The adsorbed amount of P and TPP systems on the calcite surface increases with an increase in their concentration in solution, whereas that of EDTPH was saturated at low concentration. The adsorbed amounts of P and TPP on the calcite surface also increase with an increase in Ca^{2+} activity in solution. This fact suggests that these phosphates are adsorbed in conjunction with the calcium ion. The adsorption of EDTPH, however, does not depend on the Ca^{2+} activity in solution. The adsorption of P and EDTPH were explained by Freundlich and Langmuir adsorption isotherms, respectively. On the other hand, TPP showed Freundlich adsorption isotherms on aged calcite but Langmuir adsorption isotherms on the crushed calcite. The adsorption of P, TPP and EDTPH on rough surfaces of calcite created by crushing the crystals, is much higher than on well-developed surfaces.

Introduction

Calcium carbonate is an important raw material in the chemical industry and 7% of the surface of the earth is composed of $CaCO_3$. It is also formed as undesirable precipitation such as scale on the wall of heat transfer and piping *etc*.[1–3] Calcium carbonate is commonly encountered in three polymorphic phases in nature, *i.e.*, calcite, aragonite and vaterite. Although calcite is thermodynamically the most stable polymorph among them, various polymorphs and morphologies of $CaCO_3$ are formed in solution as metastable phases depending upon the solution composition, the extent of the supersaturation, the temperature of the solution, *etc*.[4–6] In addition to the static effect, traces of organic and inorganic additives in solution can reduce the crystal growth rate by several orders of magnitude.[7,8] Particularly, phosphorus containing compounds (P-compounds) such as inorganic phosphates and organic polyphosphonates strongly inhibit the crystallization of calcium carbonate under a large variety of conditions.[9–15]

The effect of sodium triphosphate (TPP) on the crystal growth kinetics of calcite has been studied at low supersaturation.[16] The effect of polyphosphonates on the retardation of crystallization is much larger than that of orthophosphate (P),[10] and aminopolyphosphonates such as ethylenediamine–N,N,N',N'-tetrakis(methylenephosphonic acid) (EDTPH) and hydroxyethylene-1,1-diphosphonic acid (HEDPH) quench the crystal growth completely at very low concentration.[9–11,17] We have previously studied the inhibition effect of EDTPH on the formation and transformation of calcium carbonate from supersaturated solution.[18] The amount of inhibitor required to completely quench crystal growth is generally much smaller than that of the lattice ions in solution. As the amount of inhibitor is not enough to decrease the degree of supersaturation by complex formation with calcium ions in the solution, the inhibition effect has been explained by the adsorption of inhibitor on the calcium carbonate surface. Therefore, very high growth inhibition of P-compounds is explained by their large capacity to be adsorption and the selective poisoning of the active sites or growth sites.[9,13,19,20] Thus, it is quite important to study the adsorption phenomena as an initial step in the inhibition of crystal growth. In addition, the knowledge of the adsorption equilibria of P-compounds should give fund-

amental information for their applications in analytical (*e.g.*, contamination and co-precipitation of crystals, elimination of ions from solution) and industrial chemistry (*e.g.*, inhibition of scale on metal surface, removal of phosphate from waste water, desalination technology). The magnitude of the retardation effect depends on the polymorph of calcium carbonate, *i.e.* calcite, aragonite or vaterite.[17] We have previously investigated the detailed mechanism of the adsorption of phosphate on different polymorph (calcite and vaterite) surfaces by taking into consideration the detailed equilibria of phosphate in solution.[21,22]

The aim of this research is to investigate the adsorption of inorganic phosphates (orthophosphate (small molecule) and tripolyphosphate (relatively big molecule)) and organic polyphosphonate (EDTPH) on the calcite surface. The type of adsorption isotherm and the effects of calcium concentration and the surface roughness were studied.
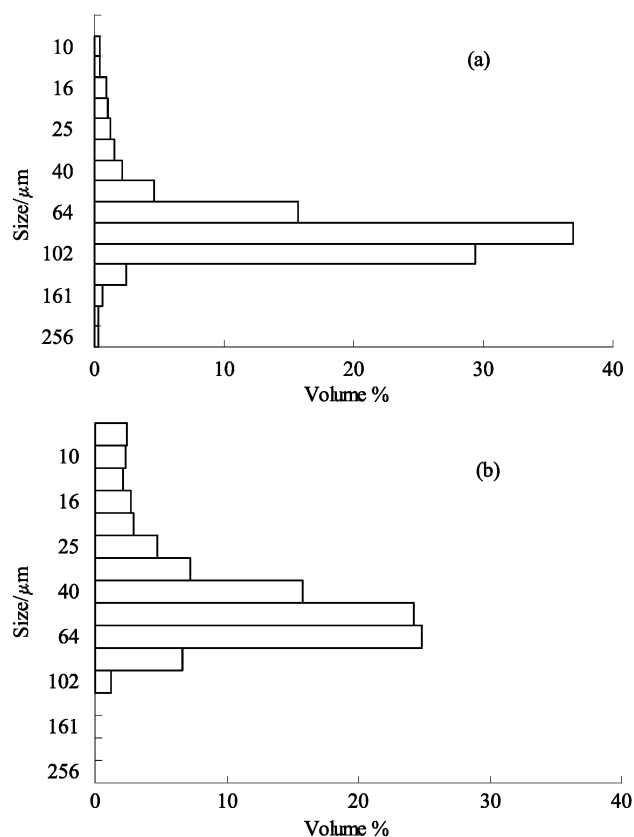
Experimental

Reagents

Guaranteed-grade calcium chloride, sodium dihydrogen phosphate and disodium hydrogen phosphates (Wako) were recrystallized from doubly distilled water. Other reagents used were of guaranteed grade (Wako). Phosphoric acid labeled with radioactive isotope ^{32}P and ^{14}C labeled formaldehyde were obtained from Japan Radioisotope Association. Sodium triphosphate (TPP) labeled with ^{32}P was prepared as follows: a 0.5 cm³ solution of carrier free phosphoric acid (4×10^7 Bq) was added to 7.8 g (0.05 mole) of $NaH_2PO_4 \cdot 2H_2O$. After mixing, the crystals were dried at 90 °C. The crystals were mixed and homogenized with 14.2 g (0.1 mol) of Na_2HPO_4. The mixture was kept at 560 °C for 4 h. After dissolving in water, a 10^{-2} mol dm⁻³ stock solution was prepared. The ^{14}C labeled EDTPH was synthesized according to a method described elsewhere:[23,24] 30 g (0.5 mol) of ethylenediamine and 164 g (2.0 mol) of phosphorous acid were added to 500 cm³ of 5 mol dm⁻³ HCl and heated to reflux temperature. Then 320 cm³ of 40% formaldehyde ^{14}C labeled (4×10^7 Bq) was added dropwise to the mixture over the course of 1–2 h. After refluxing for 2 h and cooling, the acid form of EDTPH was precipitated by the addition of 200 cm³ of ethanol. The purity of $Na_5P_3O_{10}$ and EDTPH thus obtained were checked by ^{31}P-NMR spectroscopy and were determined as 88% and 85%, respectively.

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Calcite crystals, prepared by a method described elsewhere,[17] were grown to a large crystal size with a well-developed surface by recrystallization of vaterite on the calcite seed as follows: 5 g of well-developed calcite crystals were stirred with 200 g of vaterite in 5 cm³ water for 24 h. The same process was repeated three times resulting in 5 g of calcite crystals from the treatment with vaterite. The calcite crystals thus obtained "aged calcite" were checked by X-ray diffraction (Rigaku Denki, Japan) and confirmed as 100% calcite. In order to create a rough surface, a portion of the aged calcite was crushed using an agate mortar "crushed calcite".
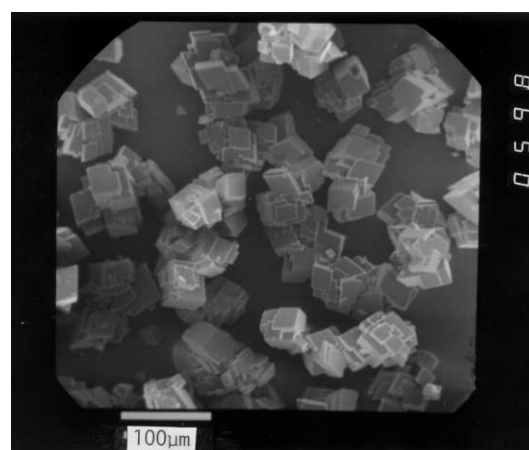
The size distribution diagrams (Coulter Counter Model TA-II, Coulter Electronics) and scanning electron microscope pictures (JEOL-JSM25) of the aged and crushed calcite crystals are shown in Figs.1 and 2. The mean particle sizes of the aged and crushed calcite were 80.6 and 50.8 μm respectively. The specific surface areas (SSA) of the aged and crushed calcite were determined by a single point BET gas adsorption method (Micrometrics 2205-2) as SSA = 0.14 and 0.24 m² g⁻¹, respectively.
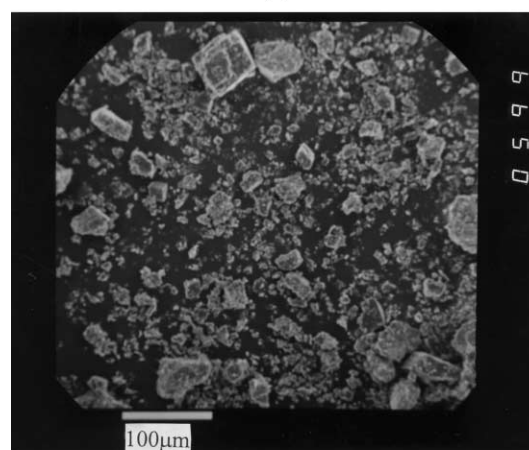

Fig. 1 The size distribution diagrams of the calcite crystals: (a) aged, (b) crushed.

Fig. 2 SEM pictures of the calcite crystals: (a) aged, (b) crushed.

Procedure

The experiments were performed in a temperature-controlled vessel at 25.0 ± 0.1 °C. The pH of the calcium carbonate suspension was adjusted to 9.0 by addition of NaOH solution. The activity of the calcium ions in the solution, a_{Ca}, was adjusted to pCa = 2.3 and 3.3 by addition of calcium chloride, where pCa = −log a_{Ca}. The pH was measured with a glass-calomel combined electrode (Orion EA920) connected to an ion analyzer (EA 920, Orion). The calcium ion activity was measured using a calcium ion selective electrode (Orion 93-20) – a calomel electrode of a combined pH electrode pair. The electrode systems were standardized before and after each experiment with standard buffer solutions (N-bromosuccinimide) for the glass-calomel electrode and calcium chloride standard solutions for the calcium ion selective electrode. The CaCO₃ suspension was stirred for 30 min. The supernatant was separated from the crystals by centrifugation, and the crystals were discarded. A quantity of the supernatant liquid (20 cm³) was transferred into a 50 cm³ centrifuge tube with a stopper and 1 g of characterized calcite crystals was added. By using the reaction solution pre-equilibrated with calcium carbonate, the change in the surface condition of the working crystals of the calcite was minimized. After the solution was equilibrated with calcite for 30 min, a small amount of P-compound solution (P, TPP, EDTPH) labeled with ³²P or ¹⁴C, the pH and pCa of which were adjusted to the sample solution, was added. The suspension was shaken for 30 min and filtred through a cellulose nitrate membrane filter (Toyo Roshi, TM-4, pore size: 0.2 μm). It was confirmed by pre-experiments that 30 min stirring or shaking is enough to reach the solubility equilibrium of calcite and adsorption of P-compounds on calcite. After checking the pH and pCa, the radioactivity of the filtrate (concentration of P-compounds in solution) was measured using a scintillation counter (Aloka LSC-900, Japan). The radioactivity of the P-compounds adsorbed on the solid phase (calcite) was measured after dissolving in a suitable amount of hydrochloric acid. The recovery of the P-compounds, the ratio of the total amounts determined in solution and that adsorbed on the calcite compared to that initially added, is more than 95%.

Results

Influence of the concentration of the P-compound

The variuos concentrations of the P-compounds are defined as follows, T_p: the initial total concentration added to the solution (mol dm⁻³), C_p: the concentration in solution equilibrated with calcite (mol dm⁻³), $C_{p,s}$: the concentration of the P-compounds

adsorbed on the calcite surface (mol kg^{-1}). Orthophosphate is present in solution in various chemical forms such as PO_4^{3-}, protonated species and calcium-complex. The monohydrogen phosphates are predominate in solution under our experimental conditions (pH = 9 and pCa, 3.3 and 2.3), as will be mentioned later. The same applies to TPP and EDTPH.

The adsorption of P-compounds on the calcite were measured as a function of these concentrations under the conditions that the activities of hydrogen and calcium were kept constant at pH = 9 and pCa = 3.3. The plot of log $C_{p,s}$ as a function of log T_p is shown in Fig. 3. If we assume that all P-compounds are
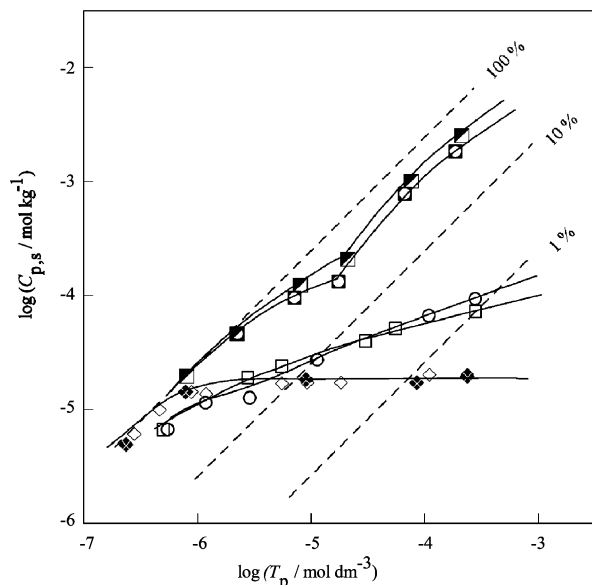
Fig. 3 Adsorption of P-compounds on the aged calcite at pH = 9.0. ○, P; □, TPP and ◇, EDTPH. Open symbols: pCa = 3.3. Partially filled symbols: pCa = 2.3.

adsorbed on the calcite surface, $C_{p,s}$ can be given by eqn. (1).

$$\log C_{p,s} = \log T_p + 1.30 \qquad (1)$$

The calculated adsorption percentages (1%, 10% and 100%) with respect to P-compounds are indicted by the dotted lines in Fig. 3. As can be seen, the adsorption curve of EDTPH is considerably different from those of P and TPP. The amount of EDTPH adsorbed on the surface, $C_{p,s}$, is almost the same as that added, *i.e.*, close to 100% adsorption, at low T_p (log T_p < −6.5). An increase in the concentration of EDTPH added to the solution has no effect on the adsorbed amount, ($C_{p,s}$) at high T_p, *i.e.*, adsorption is saturated. Thus, we can suggest that the adsorption of EDTPH is very strong and that it is completely adsorbed on the surface at low T_p, whereas the adsorption is saturated at low quantities ($C_{p,s}$).

On the other hand, the adsorbed amount, log $C_{p,s}$, of inorganic phosphates (P and TPP) monotonically increases as log T_p increases. At low T_p, the degree of adsorption of P and TPP is much smaller than that of EDTPH. That is, the adsorption of P and TPP are much weaker than EDTPH. However, at high T_p, $C_{p,s}$ of orthophosphate and triphosphate exceeds that of EDTPH. The $C_{p,s}$ of P is slightly smaller than that of TPP at low T_p (log T_p < −5), whereas the opposite is observed at high T_p. The ratio of the amount adsorbed on the surface to that in solution decreases monotonically with the increase in log T_p.

Effect of calcium concentration

The adsorption of P-compounds was studied at high calcium concentration (pCa = 2.3) on aged calcite, which is shown by partially filled symbols in Fig. 3. Adsorption of P and TPP significantly increases with an increase in calcium concentration

in solution; the slopes are concave down to a certain concentration (log T_p = −4.7), followed by a rather steep increase. The amount of P adsorbed on the surface at high calcium concentration is higher than that of TPP and both of them are much higher than that of EDTPH at any T_p. At low T_p concentration, the ratio of P adsorbed on the surface is very high, *e.g.*, 70% of P is adsorbed on the surface at a break point (log T_p = −4.7), whereas less than 10% is adsorbed at log T_p = −4.7 under the condition of pCa = 3.3. The same adsorption trend is observed for TPP, while a break point is found at a little higher log T_p (−4.5). On the other hand, the adsorption curve of EDTPH is scarcely changed by the increase in calcium concentration.

Effect of surface roughness

The adsorption of P-compounds on the crushed calcite surface under the condition of pCa = 3.3 and pH = 9 is shown by filled symbols in Fig. 4 and compared with that of the aged crystals.
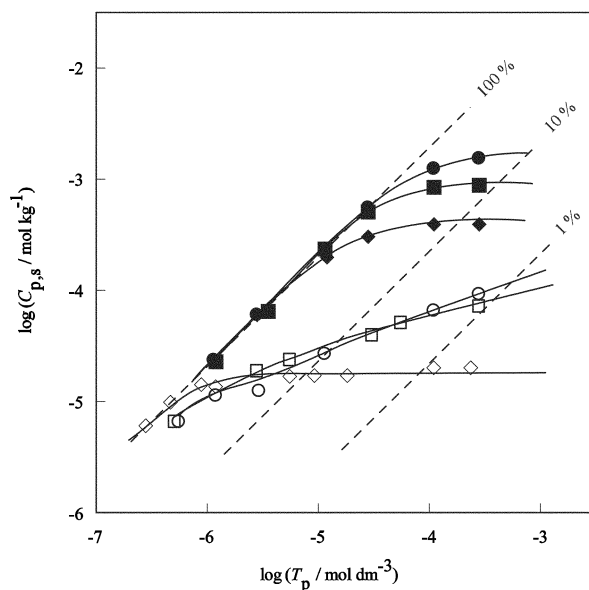
**Fig. 4** Effect of surface roughness on the adsorption of P-compounds at pCa = 3.3 and pH = 9. ○, P; □, TPP and ◇, EDTPH. Open symbols: aged calcite. Filled symbols: crushed calcite.

Generally, the adsorption on the rough surface is much higher than that on the aged surface. The adsorption behavior of organic polyphosphonate (EDTPH) on the crushed crystals is similar to that on the ripened crystals, when $C_{p,s}$ is quite high. That is, log $C_{p,s}$ in the saturated region is −3.4 on the crushed crystals whereas it was −4.8 on the aged crystal surface.

On the other hand, the adsorption behavior of inorganic P-compounds (P and TPP) on the crushed calcite surface is totally different from that on the ripened smooth crystals. The shapes of both adsorption curves are similar to that of EDTPH. Almost 100% of P and TPP are adsorbed on the crushed surface up to log T_p = −4.6, whereas log $C_{p,s}$ on the ripened crystals increases monotonically with the increase in log T_p. The adsorbed amount of P-compounds on the rough surface increases in the order EDTPH < TPP < P at any T_p.

Discussion

In order to study the detailed mechanism of adsorption, the logarithmic concentrations of P-compounds adsorbed on a calcite surface, log $C_{p,s}$, are plotted as a function of logarithm of equilibrium concentration in solution, log C_p (Fig. 5 (a–c)). Fig. 5 (a) shows the adsorption of EDTPH on the aged and crushed calcite. The slopes of the plots are unity at low C_p,
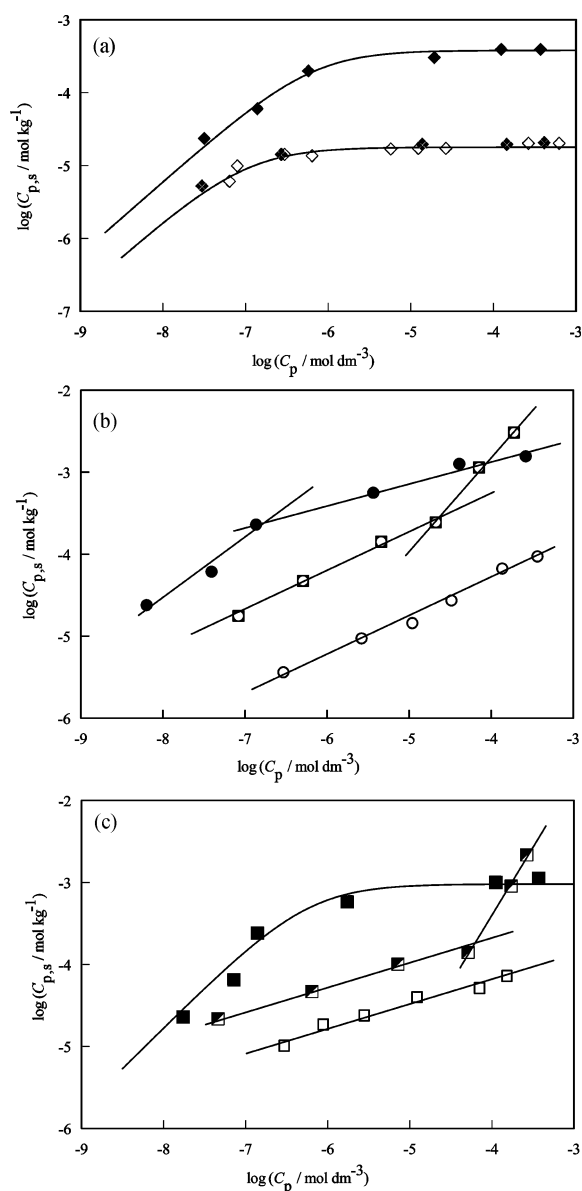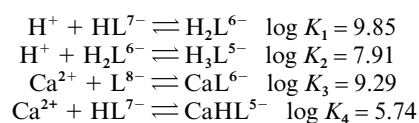
Fig. 5 Plots of $\log C_{p,s}$ as a function of $\log C_p$ in solution at pCa = 3.3 and 2.3 on aged calcite and pCa = 3.3 on crushed calcite. (a) EDTPH, (b) P and (c) TPP. Symbols: see Fig.3 and 4. The solid lines are the calculated values.

while at high C_p the values of $C_{p,s}$ are kept constant irrespective of C_p on both crystal surfaces, aged and crushed. These results suggest the Langmuir adsorption isotherm. The adsorption constant, K_{ads}, is given by the assumption of Langmuir adsorption:

$$K_{ads} = \frac{C_{p,s}}{C_p\left(C_{p,s}(\max) - C_{p,s}\right)} \qquad (2)$$

where $C_{p,s}(\max)$ refers to the EDTPH concentration of the maximum adsorption (*i.e.*, saturated region). The calculated curves obtained by this assumption are depicted by solid lines in Fig. 5 (a) and show a good agreement with the experimental results. Therefore, the adsorption of EDTPH can be explained by Langmuir adsorption isotherm for both crystals of well-developed and rough surfaces. The adsorption constants, K_{ads}, and the maximum concentrations of adsorption, $C_{p,s}(\max)$, are listed in Table 1. These values are not altered by the increase in calcium concentration. This result indicates that the chemical species of EDTPH adsorbed does not differ from that in solution.

The dominant equilibria of the protonation and complex formation of EDTPH in solution are:[25]

$$\begin{aligned} H^+ + HL^{7-} &\rightleftharpoons H_2L^{6-} &\log K_1 &= 9.85 \\ H^+ + H_2L^{6-} &\rightleftharpoons H_3L^{5-} &\log K_2 &= 7.91 \\ Ca^{2+} + L^{8-} &\rightleftharpoons CaL^{6-} &\log K_3 &= 9.29 \\ Ca^{2+} + HL^{7-} &\rightleftharpoons CaHL^{5-} &\log K_4 &= 5.74 \end{aligned}$$

where L is the EDTPH ligand and K_n are the equilibrium constants. Thus, the predominant species of EDTPH in solution (at pH = 9 and pCa = 2.3, 3.3) is the calcium complex of mono-protonated EDTPH as $CaHL^{5-}$. These results indicate that the main species of EDTPH adsorbed on the surface is the same as that in solution CaHL.

The plot of $\log C_{p,s}$ *versus* $\log C_p$ of P (Fig. 5 (b)) gives straight lines indicating the applicability of the classical adsorption isotherm to the adsorbate–adsorbent system. This result indicates that the adsorption of orthophosphate obeys Freundlich adsorption isotherm. The logarithmic form of Freundlich adsorption isotherm[26] is given by eqn. (3),

$$\log C_{p,s} = \log K_F + 1/n \log C_p \qquad (3)$$

where K_F and n are the Freundlich constant representing the adsorption capacity and the intensity of adsorption, respectively. The values of K_F and n obtained from the plots are listed in Table 1. A higher value for K_F indicates a higher affinity for adsorption and the values of n lie between 1 and 10 indicating favorable adsorption.[26]

Under the conditions of high calcium concentration in solution (pCa = 2.3), the plot of $\log C_{p,s}$ *versus* $\log C_p$ (Fig. 5 (b)) shows straight lines at low C_p ($\log C_p < -4.7$) with a slope almost the same as that at pCa = 3.3, whereas a steep increase in the slope is observed at higher C_p. On the other hand, in the adsorption of P on crushed calcite surfaces, the plot obeys Freundlich isotherm at high C_p, although the slope is relatively high at low C_p. The higher slope at low C_p might be attributed to the combination of Freundlich and Langmuir adsorption isotherms in this region.

The steep increase in $C_{p,s}$ at high T_p ($\log C_p > -4.7$, pCa = 2.3) is attributed to the precipitation of calcium phosphate. Under these solution conditions, the solution precipitates gelatinous calcium phosphate even in the absence of calcite crystals. This precipitate was identified by X-ray diffraction as a mixture of the metastable phases, octacalcium phosphate and tricalcium phosphate. This finding agrees with the results reported by Nancollas *et al.*[27,28] The precipitation of calcium phosphate was not observed for the solution at low phosphate concentration ($\log T_p < -4.8$ in Fig. 3 (b) *i.e.*, $\log C_p$ (-4.7 in Fig. 5 (b)).
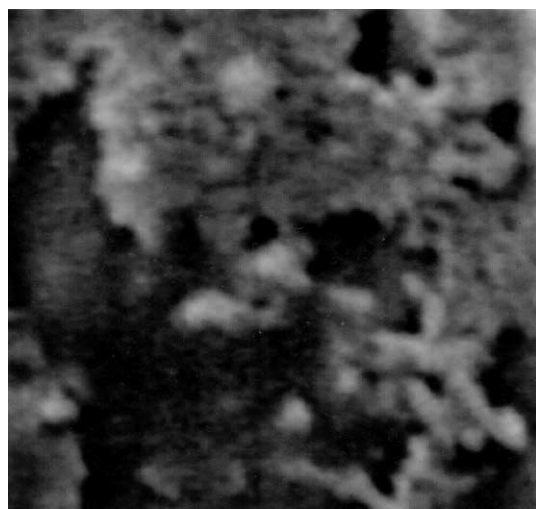
The scanning electron micrograph of the calcite surface equilibrated with P at $\log T_p = -3.6$ and pCa = 2.3 is shown in Fig. 6 (a). The attachment of gelatinous precipitate is observed. The picture of the phosphorus scanning map by electron probe microanalysis is depicted in Fig. 6 (b). The distribution of dots of the P-element corresponds to the precipitate in the SEM picture (Fig. 6 (a)). Thus, the attachment of the precipitation on the calcite surface was confirmed. It was confirmed by SEM measurements that the calcite surface does not change with the addition of a small amount of P.

As seen from Fig. 5 (c), the adsorption isotherms of TPP on aged calcite are similar to that of the P isotherms (Fig. 5 (b)). However, a steep increase in the slope of TPP (at pCa = 2.3) occurs at a slightly higher C_p compared with P. This steep increase in $C_{p,s}$ of TPP might be also ascribed to the formation of a homogeneous precipitation of calcium TPP. The relatively high values of K_F of orthophosphate compared with tri-phosphate (Table 1) indicate the higher adsorption affinity of P compared with TPP. However, the adsorption isotherm of

Table 1 Adsorption parameters of P-compounds on calcite

P-compounds	Crystals	pCa	Type of adsorption[a]	$\log K_{ads}$	n	r^b	$\log K_F$	$\log C_{p,s}^{*c}$	$\log C_{p,s}(max)$	$S_{m,o}^d$/Å²
P	Aged	3.3	F		2.3 ± 0.2	0.9817	−2.62 ± 0.06	−4.90 ± 0.04		
	Aged	2.3	F		2.1 ± 0.1	0.9970	−1.33 ± 0.03	−3.75 ± 0.02		
	Crushed	3.3	F + L		3.9 ± 0.4	0.9909	−1.84 ± 0.04	−3.16 ± 0.05		
TPP	Aged	3.3	F		3.5 ± 0.3	0.9942	−3.02 ± 0.05	−4.53 ± 0.05		
	Aged	2.3	F		3.7 ± 0.2	0.9857	−2.63 ± 0.06	−4.05 ± 0.06		
	Crushed	3.3	L	6.25 ± 0.04				−3.02 ± 0.05	−3.02 ± 0.05	−63 ± 8
EDTPH	Aged	3.3	L	7.01 ± 0.06				−4.75 ± 0.03	−4.75 ± 0.03	1310 ± 90
	Aged	2.3	L	7.03 ± 0.04				−4.77 ± 0.03	−4.77 ± 0.03	1370 ± 90
Crushed	3.3	L	6.20 ± 0.05				−3.42 ± 0.04	−3.42 ± 0.04	105 ± 10	

[a] F; Freundlich adsorption isotherm type, L; Langmuir adsorption isotherm type. [b] Correlation coefficient. [c] Concentration of P-compounds on the calcite surface at $\log C_p = 5$. [d] Average surface area covered with one molecule of P-compounds.
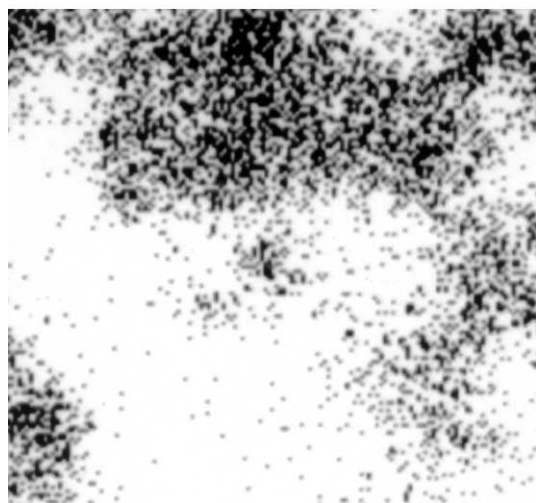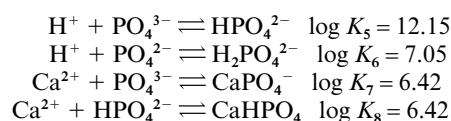

Fig. 6 (a) The scanning electron micrograph of the calcite surface equilibrated with orthophosphate at pCa = 2.3 and $\log T_p = -3.6$. (b) The scanning map of phosphorus by electron probe microanalysis.
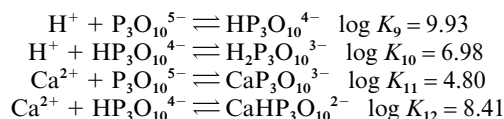
TPP on the crushed calcite surface is close to the Langmuir adsorption type.

In order to compare the effect of calcium concentration on the adsorption process, the values of $\log C_{p,s}$ at $\log C_p = 5$, $\log C_{p,s}^*$, are listed in Table 1. The increase in $\log C_{p,s}^*$ with an increase in calcium ion concentration is about one unit for P, whereas it is 0.5 unit for TPP. Thus the adsorption of P on a calcite surface is accompanied by one calcium ion to give the predominant species in solution. However, the adsorption of

TPP is only partially accompanied by Ca^{2+} ions. Under the present experimental conditions, the dominant equilibria of protonation and complex formation of P [29,30] and TPP [31,32] in solution are:

$$H^+ + PO_4^{3-} \rightleftharpoons HPO_4^{2-} \quad \log K_5 = 12.15$$
$$H^+ + PO_4^{2-} \rightleftharpoons H_2PO_4^{2-} \quad \log K_6 = 7.05$$
$$Ca^{2+} + PO_4^{3-} \rightleftharpoons CaPO_4^- \quad \log K_7 = 6.42$$
$$Ca^{2+} + HPO_4^{2-} \rightleftharpoons CaHPO_4 \quad \log K_8 = 6.42$$

and

$$H^+ + P_3O_{10}^{5-} \rightleftharpoons HP_3O_{10}^{4-} \quad \log K_9 = 9.93$$
$$H^+ + HP_3O_{10}^{4-} \rightleftharpoons H_2P_3O_{10}^{3-} \quad \log K_{10} = 6.98$$
$$Ca^{2+} + P_3O_{10}^{5-} \rightleftharpoons CaP_3O_{10}^{3-} \quad \log K_{11} = 4.80$$
$$Ca^{2+} + HP_3O_{10}^{4-} \rightleftharpoons CaHP_3O_{10}^{2-} \quad \log K_{12} = 8.41$$

Accordingly, the predominant species of orthophosphate ions in solution are HPO_4^- and $CaHPO_4$, at pCa = 3.3 and $CaPO_4^-$ at pCa = 2.3. Therefore, the species adsorbed on the surface are estimated to be $CaHPO_4$ and $Ca_3(PO_4)_2$, which agree with the results reported in a previous paper.[21] On the other hand, the main chemical species of triphosphate in solution is $CaP_3O_{10}^{3-}$ at any pCa, thus the adsorbed species on the surface are suggested to be $CaP_3O_{10}^{3-}$ and $Ca_2P_3O_{10}^-$.

The increase in the specific surface area of the crushed calcite ($SSA = 0.24$ m² g⁻¹) is only 1.7 times compared with the aged calcite (0.14 m² g⁻¹). However, the adsorption of P-compounds on crushed calcite is much higher than that on the ripened crystals i.e., about 55 times for P, 30 for TPP and 20 times for EDTPH. These results suggest that the crushing of crystals not only causes an increase in the surface area, but also an increase in the affinity of the crystal surface for P-compounds by the appearance of fresh planes. That is, the new surface created by cracking is quite rough and active for adsorption.

The mean surface area occupied by one molecule of TPP and EDTPH, at saturated adsorption on aged or crushed calcite, $S_{m,o}$, can be calculated according to eqn. (4),[33]

$$S_{m,o} = \frac{SSA}{C_{p,s}(max) \times N_A} \quad (4)$$

and the results are listed in Table 1, where N_A is Avogadro constant. The values of $S_{m,o}$ of EDTPH on the aged calcite (listed in Table 1) are found to be independent of the calcium concentration and equal to 1340 Å² on average. This value for EDTPH substantially agrees with the value of minimum surface area covered by one molecule of polyphosphonate HEDPH that is required to completely stop crystal growth.[17]

The area of the crystal surface occupied by one molecule of P-compounds, $S_{m,c}$, was theoretically calculated using a molecular model of the P-compound with the help of the Chem 3D® program. The maximum area of the surface covered with a P-compound molecule was estimated as $S_{m,c} = 62$ Å² for EDTPH and 50 Å² for TPP.

Comparing $S_{m,o}$ with $S_{m,c}$ for EDTPH, $S_{m,o}$ is quite large, *i.e.*, less than 1/22 of the calcite surface is covered with EDTPH. This fact indicates that EDTPH on a well-developed surface is not adsorbed to cover the entire surface of the crystals, but is selectively attached to the kink or active site of the surface as predicted by the Kossel mechanism. Thus, the phosphonates effectively inhibit the crystal growth by the selective adsorption or poisoning of the active site of growth. However, in the case of phosphates, a high concentration is required for complete inhibition because of the weak and less selective adsorption. On the other hand, the surface area $S_{m,o}$ of EDTPH on crushed calcite (105 Å^2) is comparable to the calculated area $S_{m,c}$. This finding indicates that the surface of the crushed calcite is almost fully covered with EDTPH. For the adsorption of TPP on crushed calcite, the value of $S_{m,o}$ (63 Å^2) is close to $S_{m,c}$ (50 Å^2). Thus, the rough surface of crushed calcite might be fully covered with TPP.

Conclusions

The adsorption of P-compounds on a calcite surface was studied using radioactive isotopes as tracers. The adsorption of phosphonate, EDTPH, is much stronger than both orthophosphate and triphosphates. P-compounds are adsorbed accompanied by calcium ions. EDTPH adsorbed on well-developed calcite is explained by the Langmuir isotherm, while orthophosphate and tripolyphosphate are explained by the Freundlich isotherm. The adsorption of EDTPH on a well-developed calcite surface is saturated at low concentration, where 1/22 of the surface is covered with EDTPH. The amounts of P-compounds adsorbed on the rough calcite surface are much higher than that on the smooth surface. The rough surface of the crushed calcite is almost fully covered with EDTPH and TPP under the conditions of saturated adsorption.

References

1 L. Legrand and P. Leroy, *Prevention of corrosion and scaling in water supply systems*, Ellis Horwood Series in Water and Waste Technology, New York, 1990.
2 L. Legrand, G. Poirier and P. Leroy, *Les équilibres carboniques et l'équilibre calcocarbonique dans les eaux naturelles*, Eyrolles, Paris 1981.
3 J. C. Cowan and D. J. Weintritt, *Water-Formed Scale Deposits*, Gulf Publishing Co., Houston, TX, 1976, pp. 255–290.
4 L. N. Plummer and E. Busenberg, *Geochim. Cosmochim. Acta*, 1982, **46**, 1011.
5 T. Sabbides, E. K. Giannimaras and P. G. Koutsoukos, *Environ. Technol.*, 1992, **13**, 73.
6 E. K. Giannimaras and P. G. Koutsoukos, *Langmuir*, 1988, **4**, 855.
7 H. J. Meyer, *J. Crystal Growth*, 1984, **66**, 639.
8 P. Cailleau, C. Jacquin, D. Dragone, A. Girou, H. Roques and L. Hubert, *Rev. Inst. Fr. Pet.*, 1979, **34**((1)), 83.
9 M. M. Reddy and G. H. Nancollas, *Desalination*, 1973, **12**, 61.
10 G. Koutsoukos and C. G. Kontoyannis, *J. Crystal Growth*, 1984, **69**, 367.
11 G. H. Nancollas, T. K. Kazmierczak and E. Schuttringer, *Corrosion/ 1980*, Natl. Assoc. Corrosion, Chicago, 1980, paper no. 226.
12 O. J. Vetter and D. A. Campbell, *Report for 1979*, Lawrence Berkeley Laboratory, Berkeley, CA, 1979.
13 L. J. Plant and W. A. House, *Colloids Surf., A*, 2002, **203**, 143.
14 S. L. Woodruff, W. A. House, M. E. Callow and B. S. C. Leadbeater, *Int. Rev. Hydrobiol.*, 1999, **84**, 509.
15 A. M. Hartely, W. A. House, M. E. Callow and B. S. C. Leadbeater, *Water Res.*, 1997, **31**, 2261.
16 A. M. Kavanagh, T. Rayment and T. J. Price, *J. Chem. Soc. Faraday Trans.*, 1990, **86**, 965.
17 G. H. Nancollas and K. Sawada, *J. Pet. Technol.*, 1982, **34**, 645.
18 T. Ogino, N. Tsunashima, T. Suzuki, M. Sakaguchi and K. Sawada, *Nippon Kagaku Kaishi*, 1988, 899.
19 M. M. Reddy, *J. Crystal Growth*, 1977, **41**, 287.
20 W. A. House and L. Donaldson, *J. Colloid Interface Sci.*, 1986, **112**, 309.
21 T. Suzuki, S. Inomata and K. Sawada, *J. Chem. Soc., Faraday Trans.*, 1986, **82**, 1733.
22 K. Sawada, S. Yoshida and T. Suzuki, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 2227.
23 K. Moedritzer and R. R. Irani, *J. Org. Chem.*, 1966, **31**, 1603.
24 T. Ichikawa and K. Sawada, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 829.
25 K. Sawada, T. Araki and T. Suzuki, *Inorg. Chem.*, 1987, **26**, 1199.
26 W. Stumm and J. Morgan, *Aquatic chemistry: Chemical Equilibria and Rates in Natural Waters*, 3rd edn., John Wiley and Sons, New York, 1996, pp. 521–526.
27 G. H. Nancollas and B. Tomazic, *J. Phys. Chem.*, 1974, **78**, 2218.
28 P. Koutsoukos, Z. Amjad, M. B. Tomson and G. H. Nancollas, *J. Am. Chem. Soc.*, 1980, **102**, 1553.
29 P. Salomaa, R. Hakala, S. Vesala and T. Aalto, *Acta Chim. Scand.*, 1969, **23**, 2116.
30 A. Chughtai, R. Harshall and G. H. Nancollas, *J. Phys. Chem.*, 1968, **72**, 208.
31 H. Waki and M. Hatano, *Polyhedron*, 1982, **1**, 69.
32 M. M. T. Khan and P. R. Reddy, *J. Inorg. Nucl. Chem.*, 1973, **35**, 179.
33 S. J. Gregg and K. S. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, London and New York, 1982.