INHIBITION OF APATITE DISSOLUTION DUE TO FORMATION OF CALCIUM OXALATE COATING

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Abstract The amount of apatite dissolution increased with decreasing final pH when two apatite samples (0.2-0.04 mm) were treated with 10 mmol L⁻¹ of citric acid or 4.0 mmol L⁻¹ HCl. However, when they were treated with 10 mmol L⁻¹ of oxalic acid, the amount of dissolution was much smaller than the treatment with the same concentration of citric acid at around pH 4. According to the X-ray diffraction (XRD), scanning electron microscope (SEM) observation and energy dispersive X-ray analysis (EDX) of the oxalic acid-treated apatite, a coating of calcium oxalate was formed on the surface of the apatite particles which inhibited the dissolution of apatite under the experimental conditions.

INTRODUCTION

One of the research goals for the direct application of phosphate rocks to agricultural lands is to find an effective combination of soil, climate, crop and management¹⁾. Among the soil factors, soil pH primarily affects the dissolution of apatite¹⁾. With a decrease in soil pH, the amount of apatite dissolution increases¹⁾.

In the weakly acidic to neutral soil pH range, the solubility of apatite is not very high and the effect of organic acids having a chelating ability may be an important plant factor¹⁾. It is well-known that some crops exude chelating organic acids from their roots. For example, citric and malic acids are exuded by chick pea (*Cicer arietinum* L.)^{2,3)} and P-deficient rape plants (*Brassica napus* L.)¹⁾ and piscidic acid by pigeon pea (*Cajanus cajan* Millsp.). Oxalic acid was found in soil solutions of forest and cultivated soils at a concentration of 60 - 1043 μ mol L⁻¹^{4,5,6)}.

Fresh rhyoritic to andesitic volcanic ash commonly include 1 - 3 g P₂O₅ kg⁻¹ of apatite^{7,8)} and this may be useful as a phosphorus (P) source for revegetation and restoration of agriculture especially in the area where soluble P fertilizers are not easily available. Hence, we examined the reactions of various soil components and apatite contained in fresh Mt. Pinatubo volcanic ash, Philippines, to seek an effective soil management method to utilize the apatite for crop production.

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During this study, we found that the dissolution of P with oxalic acid treatment showed a different pH dependence from that with dilute HCl or citric acid treatment. The amount of P dissolved with the oxalic acid treatment remained small even at a pH of 3 - 4 while it increased with decreasing pH during the treatment with the other materials. As it was impossible to isolate apatite particles from the volcanic ash, the reason for the low P dissolution by oxalic acid treatment was not elucidated. The objective of the present study was to confirm the mechanism of P dissolution inhibition by the oxalic acid treatment using high purity apatite particles.

EXPERIMENTAL

Two particulate apatite samples from Florida, U.S.A. (Florida apatite)⁹⁾ and Makatea Island, France (Makatea apatite)¹⁰⁾ were used. The analytical P, Ca and F¹¹⁾ contents were 141, 373 and 33 g kg⁻¹ for the Florida apatite and 161, 406 and 28 g kg⁻¹ for the Makatea apatite on an air-dried basis, respectively. Because F content of these apatite samples were intermediate between those of fluorapatite and hydroxyapatite, solubility isotherms of these samples seem to lie between the two pure minerals¹²⁾. The major mineral of these samples was confirmed to be apatite by XRD. Florida apatite contained a small amount of quartz, which is not likely to affect solubility of the apatite due to its scattered occurrence in the apatite particle as small discrete mineral grains. A particle-size fraction of 0.2 - 0.04 mm, which was used for the dilute HCl, oxalic acid and citric acid treatments, was prepared using sieves.

To 20 mg of the apatite samples, 100 mL of various acid solutions was added. The acid solutions were 10 mmol L⁻¹ oxalic acid aqueous solution adjusted to pH 3.0, 4.0, 5.0 or 6.0 using NaOH, 10 mmol L⁻¹ citric acid aqueous solution adjusted to pH 3.0, 4.0, 5.1 or 6.1 using NaOH and 4, 2, 1, 0.5, 0.2 and 0 mmol L⁻¹ of HCl. The mixtures were shaken for 16 h at 25°C. After measuring the final pH, the supernatant solutions were separated from the apatite particles by centrifugation and filtration. P and Ca in the supernatant solutions were determined by the molybdenum blue colorimetric method¹³⁾ and atomic absorption method, respectively. The treated apatite particles were used for XRD after washing with distilled water, air-drying, and grinding.

To about 10 mg of Florida apatite particles having a diameter near 1 mm, 25 mL of 10 mmol L⁻¹ oxalic acid solution adjusted to pH 4 by NaOH was added and shaken for 16 h at 25°C. After separation of the apatite particles, washing with distilled water and air-drying, an apatite particle was cut with scissors under an optical microscope to conduct EDX elemental analysis of the surface and section of the oxalic acid-treated apatite particle. The sample particles were held by double-sided

adhesive tape on a carbon sample holder and were coated with vacuum-evaporated carbon. The SEM observations were conducted using a HITACHI S4200 operated at 15 kV. The EDX analysis was carried out using a Kevex X-ray microprobe equipped with the SEM.

RESULTS AND DISCUSSION

The dissolution of two apatite samples was dependent on the final pH when they were treated with 10 mmol L⁻¹ of citric acid or dilute HCl (FIGURE 1). The amount of P dissolved from the two apatite samples increased with decreasing final pH values and was larger after the citric acid treatment than after the dilute HCl treatment especially in the pH range between 5 and 6. This is possibly due to chelation of Ca and donation of H⁺ by the citric acid.

In contrast, when the two apatite samples were treated with 10 mmol L⁻¹ oxalic acid, the amount of dissolved P was much smaller than those treated with citric acid or HCl in the final pH ranging between 3.4 and 4.3 (FIGURE 1). When the final pH was about 3 due to the treatment with citric acid or dilute HCl, the amount of P dissolved was more than 96% of the original P content of the samples. When the final pH was 3.4 due to the treatment with oxalic acid, the amount of P dissolved was only about 10% of the original P content and was not much different from those at the final pH of 5 to 7. The low P dissolution with oxalic acid treatment compared with citric acid and HCl treatment was close to the result using the Pinatubo volcanic ash.

FIGURE 1 Relationship between final pH and the amount of P dissolved from Florida and Makatea apatites with 10 mmol L⁻¹ oxalic acid, 10 mmol L⁻¹ citric acid, or 4.0 mmol L⁻¹ HCl treatment. Vertical bars indicate standard deviation.

FIGURE 2 Relationship between final pH and the amount of Ca dissolved from Florida and Makatea apatites with 10 mmol L⁻¹ oxalic acid, 10 mmol L⁻¹ citric acid, or 4.0 mmol L⁻¹ HCl treatment. Vertical bars indicate standard deviation.

FIGURE 3 X-ray diffraction patterns of untreated Florida apatite (a), Florida apatite treated with 10 mmol L^{-1} oxalic acid (b: final pH=3.4, c: final pH=4.3, d: final pH=5.2, e: final pH=6.9), and guaranteed grade $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (f).

A similar inhibiting effect by oxalic acid treatment was also observed upon Ca dissolution from the two apatite samples (FIGURE 2). The amount of Ca dissolved increased with decreasing final pH values when the apatite samples were treated with citric acid or dilute HCl. A higher Ca dissolution due to citric acid treatment than dilute HCl treatment was also observed in the final pH ranging from 5.6 to 6.1, possibly due to chelating or the H^+ donating effect of citric acid. However, the amount of Ca dissolved by oxalic acid treatment was remained low and less than 4.2% of the original content of the apatite samples in the final pH range between 3.4 and 7. The dissolution of Ca was lower than that of P if one assumes congruent dissolution of an ideal apatite that has an atomic Ca/P ratio of 1.67. This consideration suggests that the net exchange of P with oxalic acid took place in the solid phase.

The formation of calcium oxalate from the oxalic acid treatment of the Florida apatite was

FIGURE 4 SEM image (i), EDX spectra of selected areas (ii), and X-ray element maps of P(iii) and Ca (iv) of the oxalic acid-treated (10 mmol L^{-1}) Florida apatite. Spectra a and b in (ii) were obtained from the analysis of selected square areas a (surface) and b (section) in (i), respectively. Line graphs in (iii) and (iv) show the abundance of P and Ca along the horizontal straight lines, respectively

revealed by XRD (FIGURE 3). Similar results were also obtained for the Makatea apatite. Four small diffraction peaks at 0.591, 0.364, 0.296 and 0.235 nm appeared in the XRD patterns of the Florida apatite after oxalic acid treatment in the final pH range between 3.4 and 7. These four XRD peaks are identical to the four strongest powder XRD peaks for $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$. The solubility of calcium oxalate is very low except under strongly acidic conditions. This result indicate that the calcium oxalate formed due to the reaction of oxalic acid and apatite.

The distribution of calcium oxalate after the oxalic acid treatment of the apatite samples was

elucidated by an SEM-EDX analysis. FIGURE 4-i shows an SEM image of the surface (right-hand side) and the section (left-hand side) of an oxalic acid-treated Florida apatite particle at pH 4.

According to the selected area analysis, the peak intensity for P-K α on the surface of the particle was much weaker than that of the section (FIGURE 4-ii). The element maps and traces of electron microprobe line scans for P (FIGURE 4-iii) and Ca (FIGURE 4-iv) further illustrates the difference in the P and Ca distributions between the surface and the section. The abundance of P is high and almost constant inside the particle and it gradually decreases toward the surface due to formation of the calcium oxalate coating (FIGURE 4-iii). The thickness of the calcium oxalate coating was estimated to be less than 2 μ m based on the results from the line scan for P. A similar result was also observed in the line scan for Ca (FIGURE 4-iv) although the difference in Ca content was small between the surface and the section. Thus, it was confirmed that calcium oxalate was formed by oxalic acid treatment of the apatites as a surface coating material and the calcium oxalate coating inhibited further dissolution of apatite.

According to the results obtained here, the existence of oxalic acid in soil may not be necessarily profitable for utilization of apatite although oxalic acid is effective for avoiding Al toxicity in acid soils⁶⁾. When powdery apatite of less than 0.04 mm was used, however, the inhibitory effect on the apatite dissolution was smaller than that for the apatite having a particle size of 0.2-0.04 mm. Thus, the extent of the inhibitory effect of the calcium oxalate coating was dependent on the particle size of the apatites used in this experiment.

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