

## NOTE

## ADSORPTION OF PHOSPHATE ON IMOGOLITE

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Imogolite is a hydrous aluminum silicate which has been found in many volcanic ash soils. Electron microscopy has shown that the mineral consists of bundles of tubes with a length of about 1  $\mu\text{m}$ . The bundles have a diameter of 10.0–30.0 nm with individual tubes having external and internal diameters of 2.0 and 1.0 nm respectively.

The structure of the external surface of the tubes is similar to the gibbsite (001) face. The internal surface has silica tetrahedra above vacant octahedral sites so that SiOH groups are protruding from the surface (Cradwick *et al.*, 1972).

Since volcanic ash soils are capable of fixing large amounts of phosphate, particularly if aluminum rich allophane is present, the adsorption of phosphate on imogolite has been studied as a model system (Cloos *et al.*, 1968).

Imogolite was separated from macroscopic gel film collected from the Kitakami pumice bed. Extractable oxides were removed by treating 100 mg of imogolite with 0.5 M  $\text{NaHCO}_3$  and 0.5 g  $\text{Na}_2\text{S}_2\text{O}_4$  at 80°C (15 min), centrifuging and washing with 50 ml 0.05 M HCl (15 min) followed by further washes with water. After removal of organic matter with 6%  $\text{H}_2\text{O}_2$  the imogolite was washed several times with distilled water, centrifuged and freeze dried.

Ten mg of imogolite were placed in a polythene centrifuge tube, 5 ml  $10^{-2}$  M KCl, 5 ml of a known  $\text{KH}_2\text{PO}_4$  solution (from 1.3 to 65  $\mu\text{moles}$ ) added, the pH adjusted by the addition of either dilute HCl or NaOH, and allowed to stand at room temperature (27°C) for 2 days. Longer reaction times did not give detectable changes in the amount of adsorption. Similar but less reproducible results were obtained when tubes were shaken during the reaction period. The equilibrium pH was then measured, the suspension centrifuged, and a suitable aliquot (1 or 2 ml) taken for determination

of the equilibrium phosphate concentration by the method of Boltz and Mellon (1947).

The adsorption isotherm of phosphate on imogolite at pH 4.0 is given in Fig. 1. The plateau for adsorption at pH 4.0 occurs at 280  $\mu\text{mole}$  phosphate per g imogolite. The isotherm is similar to those of Muljadi *et al.* (1966) for the adsorption of phosphate on gibbsite. Maximum adsorption is observed at low pH and adsorption falls from 280  $\mu\text{mole}$  at pH 4 to 190  $\mu\text{mole}$  phosphate per g imogolite at pH 8.

The experimental data could be recalculated very satisfactorily by an equation of the same form as that used by Muljadi, Posner and Quirk (1966),

$$A = A_1 + \frac{A_2 K [P]}{1 + K [P]}$$

Here  $A$ , the amount adsorbed at pH 4, is recalculated from  $A_1$ , a high affinity region amounting to 60  $\mu\text{mole/g}$ , and a Langmuir type term which describes a lower affinity region 60–310  $\mu\text{mole/g}$  (i.e.  $A_2 = 250 \mu\text{mole/g}$ ).  $[P]$  is the phosphate concentration. The value of the Langmuir constant,  $K = 0.22 \text{ mmolar}^{-1}$ , is somewhat smaller than the  $K$  values for gibbsite ( $K = 1.1 \text{ mmolar}^{-1}$  at pH 3; 0.78 at pH 5) (Muljadi *et al.*, 1966). However, the physical significance of the comparison is uncertain, because the value of  $K$  for imogolite is sensitive to the choice of values for other parameters and the introduction of additional parameters. Within the concentration range studied here we did not observe adsorption behavior corresponding to Region III postulated by Muljadi *et al.* (1966).

The imogolite has four different types of surfaces. The following estimates of surface area were made by assuming the length of the fibers to be 1  $\mu\text{m}$ , the diameter of the bundle to be 20 nm, the internal and external diameter of a fiber to be 1.0 and 2.0 nm respectively and the density to be  $2.6 \text{ g cm}^{-3}$ . This gives: (1) ends of tubes  $1 \text{ m}^2 \text{ g}^{-1}$ ; (2) outside surface of bundles  $100 \text{ m}^2 \text{ g}^{-1}$ ; (3) outside surface of tubes within bundles  $900 \text{ m}^2 \text{ g}^{-1}$ ; (4) inside surface of tubes  $500 \text{ m}^2 \text{ g}^{-1}$ .

By analogy with gibbsite the most likely site for adsorption is on the ends of the tubes where Al is coordinated to both  $\text{OH}^-$  and  $\text{H}_2\text{O}$  (Muljadi *et al.*, 1966). If one assumes one phosphate ion covers about  $30 \times 10^{-20} \text{ m}^2$  of surface (Visser, 1968) then the total surface covered by 280  $\mu\text{mole}$  phosphate is  $50 \text{ m}^2 \text{ g}^{-1}$ . Therefore the main part of phosphate adsorption must be at other sites.

The outside surface of bundles of tubes with a surface area of  $100 \text{ m}^2 \text{ g}^{-1}$  has a structure similar to the gibbsite (001) face except that it will be distorted due to the curvature of the surface. Muljadi *et al.* (1966) thought that the gibbsite (001) face could not absorb phosphate but Parfitt *et al.* (personal communication) found that organic acids were

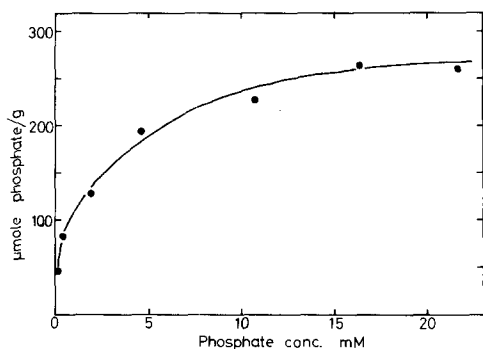


Fig. 1. Phosphate adsorption,  $\mu\text{mole/g}$  imogolite, in  $5 \times 10^{-3}$  M KCl at pH 4.0.

adsorbed on this gibbsite surface. Since Muljadi *et al.* (1966) found that phosphate was adsorbed in large amounts on gibbsite, and in excess of the available edge sites, it seems possible that adsorption of phosphate can also take place on the (001) face.

If the phosphate ion is adsorbed on this surface then half the surface will be covered and one ion will occur on  $60 \times 10^{-20} \text{m}^2$  of surface or 1.2 unit cells where the area of the unit cell is approximately  $50 \times 10^{-20} \text{m}^2$  on the outside surface using gibbsite *a*- and *b*-dimensions for imogolite  $2\pi/n$  and *c*-directions (Cradwick *et al.*, 1972).

Imogolite which had been heated to 250°C prior to reaction with phosphate adsorbed more (400  $\mu\text{mole phosphate/g}$  at pH 4.0) than untreated imogolite. Heating to 250°C removed water from between the tubes causing the structure to partly collapse. This surface is then less available for adsorption (Wada and Hermi, 1972). Since there was an increase in phosphate adsorption after heating and not a decrease it is not likely that phosphate adsorbs between the tubes. In fact the increased adsorption suggests that more external Al—OH sites become available due to distortion of the fibers.

It is unlikely that phosphate adsorbs inside the tubes since this surface has silanol groups and is silica rich. Silica rich allophanes probably have a similar structure and they are less likely to adsorb phosphate (Saunders, 1965; Cloos *et al.*, 1968).

The adsorption of phosphate by imogolite probably results in coordination of phosphate oxygen atoms by  $\text{Al}^{3+}$  ions. This mechanism, a ligand exchange reaction, in which phosphate displaces  $\text{OH}^-$  or  $\text{H}_2\text{O}$  from coordination shells of  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$  has been proposed for some oxide and hydroxide minerals and layer lattice silicates containing iron or aluminum in edge sites (Hingston *et al.*, 1972; Atkinson *et al.*, 1972).

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