

土壤膠體之代換性鹽基對於磷酸固定量之影響

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(摘 要)

土壤中磷酸固定作用每受外界環境之影響而有很大差異，如粘土礦物的種類，土壤反應，代換性鹽基等，粘土礦物與土壤又應對於磷酸固定前，人已有較詳細之報告，本文特重視代換性鹽基之種類對於磷酸固定之關係。

本試驗以紫色土與黃壤為代表，均取於北碚。紫色土係發育於白堊紀自流井層紫色頁岩，屬中性而無石灰性反應， $\text{pH}=7.0$ ，黃壤係自侏羅紀灰色砂岩風化者，心土微紅， $\text{pH}=4.5-5.0$ ，為避免過高之有機質，均採取心土，按照 Stoke 氏定律提取 5 微米 (micron) 直徑之黏土粒，曬乾後，分別以 N NaCl ， N KCl ， $\text{N NH}_4\text{Cl}$ ， N MgCl_2 ， N BaCl_2 及 $\text{pH}=3 \text{ HCl}$ 處理，然後再以 90% 酒精洗滌至無氯為止，總之以不變更膠體之構造為原則，經處理之黏土，先分析其中之代換性鹽基以及鹽基代換總量，然後再測定其磷酸固定量，在酸性反應如 H^+ 黏土，其磷酸固定之主要因子為水化鐵及水化鋁，故再以 $\text{pH}=2$ 之鹽酸淋洗，除去其中遊離鐵鋁，再測定其磷酸固定量以資比較。

按分析結果，黃壤膠體 ($< 2 \text{ micron}$) 中之 $\frac{\text{SiO}_2}{\text{R}_2\text{O}_3}$ 為 2.19，紫色土為 2.56，前者鹽基代換總量每百克黏土粒 ($< 5 \text{ micron}$) 為 18m.e. 後者為 30m.e.，茲將試驗所得結果歸納如次：

1. 磷酸固定量每因土壤膠體之不同而有差異，由黃壤所提取之黏土其磷酸固定量亦較紫色土為高。

2. 土壤之磷酸固定量，非特因土壤膠體之不同而有差異，即或同一黏土，其磷酸固定量亦因其代換性鹽基之不同而有差異，概言之，鈉黏土之磷酸固定量為最小，鉀黏土次之，鋁、鎂黏土又次之，而以鈣黏土為最大，其磷酸固定次序為：

$\text{Ca-黏土} > \text{Mg-黏土} > \text{H-黏土} > \text{Ba-黏土} > \text{NH}_4\text{-黏土} > \text{K-黏土} > \text{Na 黏土}$

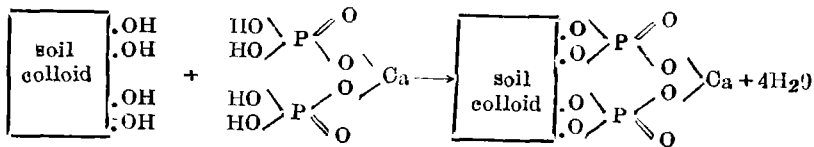
3. 各種不同代換性鹽基的黏土，加磷酸溶液後，其反應亦各不相同， H^+ 黏土之 pH 值為 3.2—4.5，因其酸度較高，溶液中之游離鐵與游離鋁含量較多，是故磷酸固定量亦較高，如以淡鹽酸 ($\text{pH}=2$) 洗滌，除去其中游離鐵鋁後，其磷酸固定量則大為減少， Na^+ 黏土與 K^+ 黏土之溶液中，因 OH^- 離子較多 ($\text{pH}=8.0-8.6$)，而磷酸鈉與磷酸鉀又為水溶性，故磷酸固定量為最少。 Ca^+ 黏土與 Mg^+ 黏土其反應屬中性至微鹼性， $\text{pH}=7.5-8.0$ ，因溶液中 Ca ， Mg 離子濃度較高，磷酸則為此 Ca ， Mg 離子所固定，故在中性土壤中，磷酸固定以 Ca 為其主要因子，酸性土壤則以水化鐵為其主要因子。

4. 鈣黏土所固定之磷酸，如以 $0.002 \text{ N H}_2\text{SO}_4$ 提取，其所固定之磷酸復可溶解，是項固定之磷酸與 Heck 所稱「暫時固定磷酸」頗為相似。

The Influence of Exchangeable Cations on the Fixation of Phosphate by Colloidal Clays

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The fixation of phosphates by soils is one of the interesting problems of major importance in the realm of colloidal chemistry of soils. It was formerly believed that the fixation of phosphate in soils is a simple chemical reaction (chemical theory). The phosphates may be reacted with hydrated sesquioxides or with calcium carbonate in soils. Ghani (6) was able to show that the power of phosphate fixation of acid soils could be considerably reduced by deactivating iron and aluminum oxides in the soil with 8-hydroxyl quinoline. Sufficient evidences, however, have shown that the phosphate fixation was due to anionic adsorption. Davis, Ford, Ravikovitch and others (1, 3, 4, 5, 10, 11, 13) found that the amount of phosphates adsorbed by soil colloids mainly depends on its anion exchange capacity. The fixation is thus believed to be an exchange reaction between the phosphate ions of the solution and the OH group on the surface of the clay lattice. Phosphate may enter the clay lattice as an acidol constituent analogous to silicic acid (14). Monocalcium phosphate, for example, may be fixed by soil colloids in the manner represented by the following equation:



According to the mechanism suggested in the above equation, phosphate fixation will also bring an increase of base exchange capacity. The purpose of this paper is to study the degree of phosphate fixation in colloidal clay having saturated by different cations. The characteristics of fixed phosphate are also explained.

Experimental Methods

Samples for purple brown soil and yellow earth taken from Peipei, Chinking, were used in this study. Colloidal clays, having diameters less than 5 microns were isolated from each of the above soils by means of the Stokes' law. Sodium-, potassium-, calcium-, ammonium-, magnesium-, barium-, and hydrogen-clays were prepared by leaching 10-gram soil sample with 500 ml. normal chloride solution of the corresponding salt. A dilute HCl solution having a pH value of 3 was used for preparing the H-clay. The excess of free salt which was retained in the soil was washed out with 80% alcohol, until

the leachate was free from chloride. Analysis were then made for exchangeable hydrogen, exchangeable bases and total exchange capacity.

Determination of the phosphate fixation by the prepared clays were made by the following methods (2), (7).

(1) A 50 ml. solution of KH_2PO_4 containing 50 mgm. of phosphate was shaken with one gram of clay for 24 hours. The pH value of the mixed suspension was determined, and the clays were flocculated with 0.5 gm. NH_4Cl . The flocculated clay was then separated from the liquid portion by filtration. To insure that no phosphate ions other than those fixed by the colloidal clay were present in the flocculated residue, the flocculates were washed thoroughly with 70% alcohol on the filter paper. The amount of phosphate retained in the clay was taken as a measure of the extent of phosphate fixation. For H-clay, studies were also made on the effect of the removal of the free sesquioxides by repeatedly washing of the flocculated residue on the filter paper with dilute HCl (adjusted to a pH value of 2). It was generally believed that the operation made no destruction on the crystal lattice of the clay minerals. (1)

(2) 50 ml. of KH_2PO_4 solution, containing 400 p.p.m. phosphorus, to 0.5 gram of clay sample in a 500 c.c. Erlenmeyer flask was added. The flask was gently heated to dryness. To the dried residue 200 c.c. of 0.002 N. H_2SO_4 buffered to pH 3 were added. After shaking for 30 minutes, the phosphorus content in the filtrate was determined by Trong's method.

Chemical Composition of Soil Colloids

The chemical composition of the two clays isolated from purple brown and yellow earth are tabulated in table 1.

Table I. Chemical composition of soil colloids (<.002 mm.)

Soil group	Soil series	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	$\frac{\text{SiO}_2}{\text{R}_2\text{O}_3}$	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$	$\frac{\text{SiO}_2}{\text{Fe}_2\text{O}_3}$
Yellow earth	Hsi-san-ping clay loam	53.77	33.41	12.41	2.19	2.70	11.51
Purple brown earth	Hui-shang-fang silt clay loam	57.53	30.47	12.00	2.56	3.20	11.90

Exchangeable Bases and Base Exchange Capacity

The individual and total exchangeable bases, the exchangeable hydrogen, and the total exchange capacity are presented in table 2.

Table 2. Exchangeable hydrogen, individual and total exchangeable bases in various prepared clays

Kinds of clay	Exchangeable- m. e. per 100 gms.						Exchangeable capacity m. e./100 gms.	Exchangeable cation Exchangeable capacity x 100
	Ca	Mg	Na	K	Ba	NH ₄ II		
Yellow earth	Ca-clay	13.6 ⁵					18.04	76.22
	Mg-clay		87.8				18.01	48.75
	Na-clay			15.40			17.87	86.17
	K-clay				13.05		18.05	72.30
	Ba-clay					15.31	18.31	83.69
	NH ₄ -clay						12.87	69.95
	H-clay						16.21	92.80
Purple brown earth	Ca-clay	26.77					29.11	81.09
	Mg-clay		12.04				29.00	41.52
	Na-clay			22.10			29.19	75.92
	K-clay				19.10		29.33	65.12
	Ba-clay					27.12	29.12	93.13
	NH ₄ -clay						25.02	86.24
	H-clay						25.17	87.45

Results and Discussion

The data from Table (3) and Fig. (1) indicate that the clay from yellow earth which has a lower SiO₂/R₂O₃ ratio fixed more phosphate than that from the purple brown soil. It was formerly found (9) that the phosphate fixation power of soils varies inversely with the ratio of SiO₂/R₂O₃ of the soil colloids. For clays with the same SiO₂/R₂O₃ ratio, the degree of fixation of phosphate varies with the characteristics of exchangeable bases. In present experiment, the degree of phosphate fixation in various clays follows the following order:

Ca-clay > Mg-clay > H-clay > Ba-clay > NH₄-clay > K-clay > Na-clay

Table 3. The fixation of phosphate by colloidal clay as affected by the exchangeable bases (First method)

Kinds of clay	Yellow earth				Purple brown soil			
	PO ₄ in solution mgm.	Fixed PO ₄ mg n./g n clay	Fixed PO ₄ mgm. per 100 gm. clay	pH	PO ₄ in solution mgm.	Fixed PO ₄ mgm./gm. clay	Fixed PO ₄ mgm. per 100 gm. Clay	pH
Ca-clay	47.58	2.42	242	7.50	47.74	2.26	226	7.72
Mg-clay	48.04	1.96	196	8.01	48.61	1.29	129	7.78
Na-clay	49.22	0.73	78	8.42	49.34	0.66	66	8.60
K-clay	48.95	1.05	105	8.00	49.21	0.79	79	8.12
Ba-clay	48.60	1.50	150	7.85	48.65	1.35	135	7.91
NH ₄ -clay	48.90	1.10	110	7.80	48.98	1.02	102	7.85
H-clay	48.02	1.98	198	3.21	48.90	1.10	110	4.1
*H-clay	49.65	0.35	35	2.33	49.55	0.45	45	2.98

*The free iron and aluminum oxides were removed

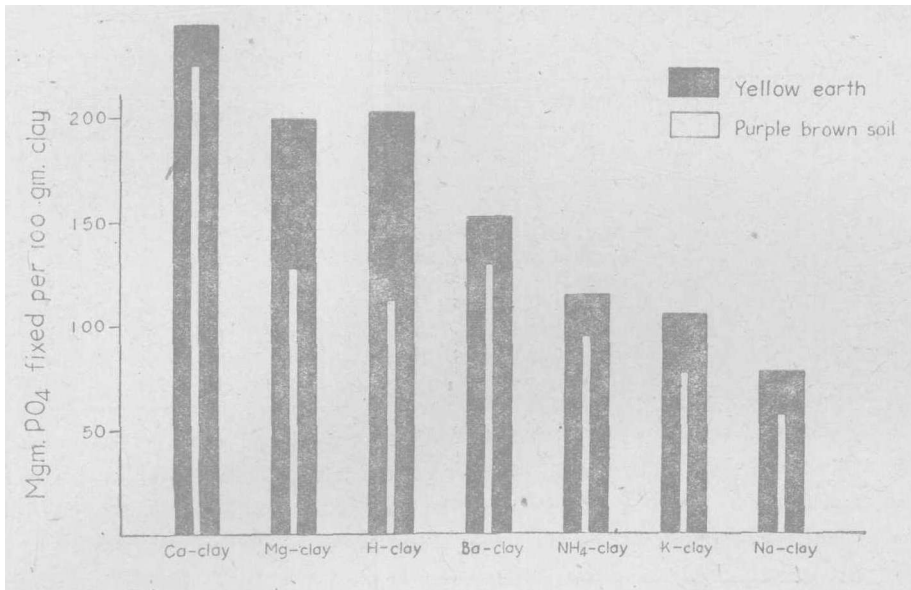


Fig 1. Fixation of PO_4 by Various Clays

Ca-clay and Mg-clay showed the highest fixation power of phosphate, the next was H-clay, while the K-clay fixed the least.

As the KH_2PO_4 solution was mixed with the colloidal clay, a part of the cations originally adsorbed on the colloidal clay was liberated as a result of the base exchange reaction. In Ca- and Mg-clay systems, the liberated cations were Ca and Mg, at equilibrium such systems had pH values ranging from 7.50 to 8.01. According to McGeorge (12), little $H_2PO_4^-$ will exist in soils at such a pH range. Most of the phosphate ions are in the form of $HPO_4^{=}$ which forms insoluble compounds with calcium and magnesium.

In the case of Na- and K-clay systems, fixation of phosphate is at minimum level, because of the greater solubilities of the Na- and K-salts with phosphate. The high pH value in the equilibrium solution indicates the predominance of OH ions. These OH ions in the solution may induce anion exchange with phosphate ions in case the latter were adsorbed on the colloidal surface. If the OH ions exceed the PO_4 ions, little phosphate or none of it can be fixed.

In H-clay, because of the strong acidity of the solution, free iron and aluminum oxides are present in rather high concentration. The phosphate fixation under such conditions was believed primarily due to the chemical combination of the oxides and phosphates. Removal of the free sesquioxide oxides therefore markedly reduced the phosphate fixation.

Table 4. The fixation of phosphate of different clays (Second method)
(50 c.c. KH_2PO_4 solution, containing 400 ppm. P. shaken with 0.5gm. clay)

Kinds of clay	Yellow earth		Purple brown soil	
	Fixed P p.p.m.	Available P p.p.m.	Fixed P p.p.m.	Available P p.p.m.
Ca-clay	43.5	336.5	38.7	361.3
Mg-clay	57.3	342.4	41.5	358.5
Na-clay	39.0	361.0	32.9	377.1
K-clay	47.3	352.7	36.2	363.8
Ba-clay	43.4	346.6	40.1	359.9
NH_4 -clay	34.5	365.5	45.1	354.9
H-clay	113.4	286.6	87.4	312.6

The amount of phosphate fixed in the difficultly available form by yellow earth was more than that of purple brown soils as shown in Table 4. The greatest amount of phosphate fixation was found in H-clay, while phosphate fixed by Ca-clay was much less and might be reliberated by treating with dilute acid (0.002N H_2SO_4). It indicated that the combination of phosphate on soil colloidal complex and the exchangeable calcium was unstable, and it only represents a form of temporarily fixed phosphate analogous in the nature to Heck's "readily available fixed phosphate". (8)

Summary

1. Homo-ionic colloidal clays (<5 micron) isolated from purple brown soil and yellow earth taken from Poipei (北碚) were used to study the effect of exchangeable cations on the phosphate fixation by soil colloids.

2. The degree of phosphate fixation by colloidal clays having different exchangeable cations varies according to following order:

$\text{Ca-clay} > \text{Mg-clay} > \text{H-clay} > \text{Ba-clay} > \text{NH}_4\text{-clay} > \text{K-clay} > \text{Na-clay}$.

3. The colloidal clays from yellow earth having lower $\text{SiO}_2/\text{R}_2\text{O}_3$ ratios fix more phosphate than that from purple brown soil.

4. The phosphate fixation power of H-clay is markedly reduced after the removal of free iron and aluminum oxides.

5. In Ca-clay, the fixed phosphate was unstable. The association of phosphate with the exchangeable calcium is easily liberated by a very dilute acid solution.

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