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**THE CHARACTERIZATION OF A PHOSPHATE REACTION PRODUCT  
IN A HYDROL HUMIC LATOSOL IN HAWAII**

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## ABSTRACT

Characterization of a phosphate reaction product in a Hydrol Humic Latosol in Hawaii has been carried out. The mineral taranakite ' $H_2K_3Al_3(PO_4)_3 \cdot 18H_2O$ ' was obtained in the reactions between Akaka soil and monopotassium phosphate solution ranging from 0.2 to 0.6 molar at pH values of the reacting system of 2.3 to 2.9. The reaction products were characterized in comparison with a synthetic taranakite by use of X-ray, chemical, optical, infra-red absorption and differential thermal techniques.

The taranakite was essentially a potassium aluminum phosphate complex. There was no indication of isomorphous substitution of iron for aluminum. The molar ratios of  $K/PO_4$  and  $Al/PO_4$  of the reaction product were found to be 0.37 and 0.72 respectively. The reaction product, taranakite, was thought to be formed by precipitating a soluble phospho-alumino complex anion with potassium ion. The soluble phospho-alumino anion resulted from the reaction of soluble soil aluminum with free phosphoric acid and  $H_2PO_4^-$  ion. Water was not a structural constituent.

The crystalline phospho-reaction products were colorless and pseudohexagonal in form. They were biaxial negative. The refractive indices were  $n_\alpha = 1.504$ ,  $n_\beta = 1.507$  and  $n_\gamma = 1.509$  respectively,  $n_\gamma - n_\alpha = 0.005$ .

The amount of taranakite produced increased with increasing concentration of phosphate solutions and increasing grams of soil used.

The degree of crystallinity of the taranakite, as evaluated by the half-peak breadth of the  $15.7 \text{ \AA}$  peak, increased with time.

The possibility of the formation of taranakite when soluble potassium and phosphate react with Akaka soil in the field is suggested. During the early stages of reaction, the reaction product is believed to be amorphous to X-ray.



## INTRODUCTION

There is evidence to indicate that large amounts of added phosphate in Hawaiian soils are rendered at least temporarily unavailable to plants. Davis (1935) attributed this phenomenon to an absorption effect of the soils. He found that for any given equilibrium phosphate concentration, the amount of phosphate fixed varies very much as the ratio of soil to solution. Chu and Sherman (1952) reported that in the presence of hydrated iron and aluminum, as much as 90 per cent of added soluble phosphate was fixed by the soils in a relatively short period of time. When the oxides were removed, less than 30 per cent of the applied phosphorus was fixed. The Hydrol Humic Latosols showed the highest phosphorus-fixing capacities, but Low Humic Latosols and Humic Latosols also fixed phosphorus to a considerable extent, due to the presence of kaolinite.

The manner in which phosphate is fixed in acid soils is as yet unknown, but in some instances it is likely to be of solution-precipitation nature. Kittrick and Jackson (1955) found by electron microscope observations the mechanism of solution-precipitation to be operative in the reaction of phosphate with colloidal iron oxide particles and thin aluminum hydroxide films at room temperature. Likewise they reported (1956) that the reaction mechanism of phosphate with kaolinite and greenalite at room temperature is also solution-precipitation. Taranakite was the reaction product in the potassium phosphate-kaolinite system.

Several workers have identified phosphate complexes which could occur as reaction products in hydrous colloidal sesquioxide systems (Nada, 1959; Birrell, 1961; Lindsay et al., 1962; Tamimi et al., 1963; Tamimi, 1964). These phospho-reaction products have been associated with the presence of calcium, ammonium and potassium cations in the system. The taranakite or similar complex potassic alumino-phosphate complex minerals appear to be the most likely reaction products to be identified in soils when potash and phosphate fertilizers are added together or over a short time interval. In this study a search was made for the presence of taranakite in an highly aluminous soil to which potash and phosphate fertilizers had been added.

## REVIEW OF LITERATURE

Records of naturally occurring taranakite are rare. Bannister and Hutchinson (1947) studied several native taranakite and pointed out that taranakite is usually found under damp conditions in localities where phosphate solutions from bird or bat guano react with rock or clay. Taranakite is massive, clay-like, pulverulent to compact. Its color is white; also gray or yellowish white. It is very soft and unctuous to the touch. It was first found on rocks which were used for bird colonies at Sugarloaves, Taranaki, New Zealand in 1868. Minerals minervite (France) and palmerite (Italy) have been found to be identical to taranakite. Chemical analysis of the taranakite occurring in Sugarloaves, Taranaki, New Zealand (Dana, 1981) is as follows:

	$K_2O$	$CaO$	$Al_2O_3$	$P_2O_5$	$H_2O$	Insol.	cl	$SO_3$	$FeO$
%	4.20	0.55	21.43	35.05	33.06	0.80	0.46	tr.	4.45

Murray and Dietrich (1969) also reported the occurrence of natural taranakite in a Virginia cave which was the home of a colony of bats. The taranakite was associated with brushite, a calcium phosphate mineral.

In artificial systems having soil constituents, crystalline phosphate products containing potassium and aluminum have been synthesized. Birrell (op. cit.) in New Zealand showed the addition of monopotassium phosphate to allophane produced a taranakite, the X-ray diffraction pattern of which agreed well with the value given by Murray and Dietrich (op. cit.) for a specimen of taranakite from Pig Hole

Cave, Virginia. Lindsay et al. (op. cit.) identified taranakite from Hartsells soil (from Tennessee) by the addition of monopotassium phosphate. Wada (op. cit.) reported the identification of a taranakite-like phosphate mineral resulting from the reaction of monoammonium phosphate with allophane and halloysite. Lindsay et al. (op. cit.) identified the reaction product of ammonium phosphate and Hartsells soil as ammonium taranakite. Tamimi et al. (op. cit.) were able to identify a taranakite by means of X-ray diffraction technique. In their study, the scanning speed of the X-ray machine was reduced to 1/4 degree 2 $\theta$  per minute. This taranakite was obtained by the reaction of three major Hawaiian agricultural soils, namely Akaka silty clay, Hilo silty clay loam and Pasohau silty clay loam, with ammonium chloride or diammonium phosphate in the presence of phosphoric acid. The reaction products were similar to the taranakite-like minerals obtained by Wada from Japanese allophane and halloysite. Tamimi (1964) postulated that taranakite could form at pH levels between 1.88 and 5.88, although no taranakite was actually identified. Work of synthesized taranakite of Haseman et al. (1961) also indicates that taranakite is stable at pHs from about 1.7 to 5.3. Kittrick and Jackson (1954) found that by the addition of molar potassium dihydrogen phosphate to kaolinite, taranakite can be formed at room temperature. Beaton et al. (1964) treated kaolinite with saturated monopotassium phosphate solution instead of one molar, however, found, that there was no evidence of taranakite formation. The probable reason these results do not seem to agree with each other is, because the phosphate solution

used in the latter case was so concentrated that the dissolution of aluminum from kaolinite was depressed.

In addition to chemical, optical and X-ray methods, Arledge et al. (1968) found that infra-red spectroscopy and differential thermal analysis were valuable auxiliaries to X-ray studies in the identification of tarenakite and compounds of similar nature. Infra-red spectroscopy, moreover, gave information on their structure and degree of crystallinity.

## MATERIALS

The soil selected for study was a subsoil of an Akaka silty clay taken from a steep road bank near the beginning of the forest reserve area on Kaiwiki Road approximately five miles west of the main Hilo-Ihukou Highway. Sampling depth was from 12 to 30 inches. This sample had a pH value of 5.3 and was a smecty clay. In addition to its prominent amorphous mineral, it contained small amount of crystalline gibbsite, goethite, magnetite, mica and quartz (Tanaka et al., 1963). The amorphous mineral colloid fraction is allophane-like, excepting that the silica to alumina ratio (Table I) is too low for the value of allophane approximated by Ross and Kerr (1934). The mineral is amorphous to X-ray, and differential thermal analysis indicates only a single low temperature endotherm at about 180° C (Figure 1). It resembles so-called stable allophane (Jackson, 1966) in that it is resistant to decomposition by dilute hydrochloric acid of pH 3.5 and 2 per cent sodium carbonate solution. Differential thermal analyses of amorphous oxides (Fieldes et al., 1962) such as silica, alumina, iron oxides and titanium oxides reveal that they either have more than one low temperature endotherm (silica and alumina) or an exotherm occurring at relatively low temperature (iron oxides and titanium oxides). This amorphous hydrated colloidal fraction apparently does not fit any of the above known criteria for amorphous mineral colloids of soils insofar as its differential thermal data is concerned. Table I shows the similarities of the allophane-like fraction of Akaka soil to several known amorphous materials present in soils. The relatively low ratio

TABLE I

CHARACTERISTICS OF THE ALLOPHANE-LIKE FRACTION OF AKAKA SOIL  
AS COMPARED WITH OTHER AMORPHOUS MINERAL COLLOIDS\* OF SOILS

Type of amorphous material	Differential thermal indication**		$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$	Solubility in dilute acid and alkali
	Endotherms °C	Exotherms °C		
Allophane, unstable	150	960	0.3-2.0	High
stable	150	960	2.0	Low
Silica	165-573	---	---	High
Alumina***	110-500	---	---	High
Iron oxides	160	350-450	---	High
Titanium oxides	195	465	---	Low
Allophane- like**** fraction of Akaka soil	180	---	0.8	Low

\* Jackson, M. L. (1956). Soil chemical analysis--advanced course, p. 528. University of Wisconsin.

\*\* Fieldes et al. (1952).

\*\*\* Series of endotherms, Fieldes et al. (op. cit.).

\*\*\*\*  $\text{SiO}_2$ : 12%;  $\text{Al}_2\text{O}_3$ : 23%

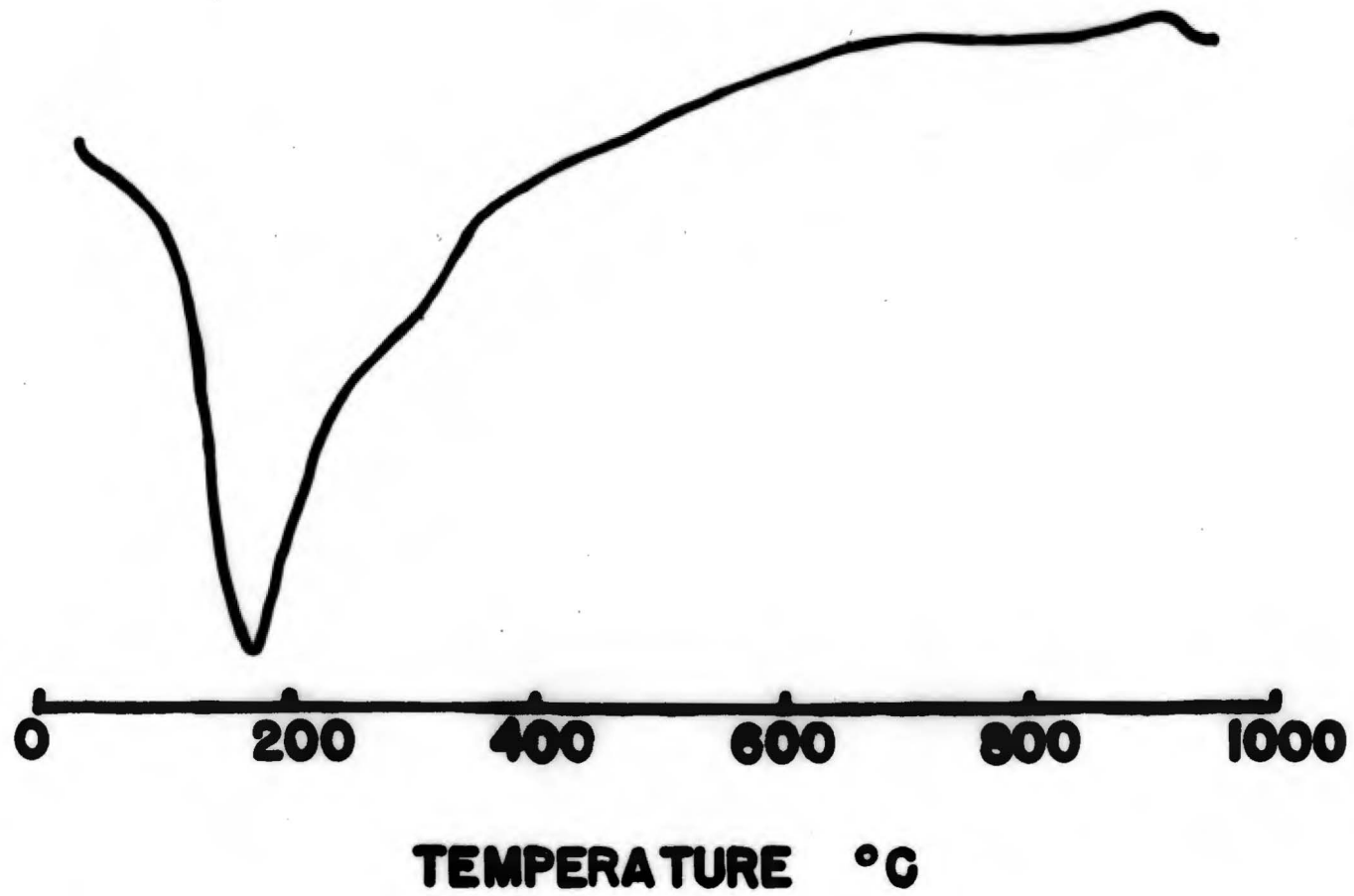


Figure 1

D. T. A. Curve of Clay Fraction, Akaka Soil



of silica to alumina (0.8) of the amorphous fraction suggests that part of the aluminum exists in the form of free amorphous aluminum hydroxide. Detmundrum and Chesters (1964) in their isolation and characterization of allophanes from Wisconsin soils also indicated the possible presence of amorphous aluminum hydroxide (or related polymers) in the allophanes.

The Akaka soil is a member of the Hydrol Humic Latosol Group. This soil was described by Cline et al. (1958). The Akaka soils were developed from volcanic ash, under a tropical rain forest with an average annual rainfall above 120 inches. They are highly hydrated in the natural state. The water content sometimes exceed 300 per cent. These Akaka soils have very low bulk densities ranging from 0.1 to 0.6. On dehydration they lose volume and exhibit an increase in particles of sand size. The dehydration is irreversible. The reason for the irreversible property of these soils was explained by Sherman (1957) when he reported that the process of dehydration caused the crystallization of the hydrous oxides to gibbsite, crystalline iron oxide minerals and alpha quartz.

The rapid weathering of the finely divided ash particles under a warm and very humid environment has produced rapid decomposition of the original minerals and an accompanying rapid leaching of bases and silica. This has favored the development of amorphous hydrated colloidal oxides and hydroxide gels. The heavy vegetative growth has contributed a high content of organic matter. The cation exchange capacity is high in the natural state, and may be 200 milli-equivalents per 100 grams. On dehydration they lose a substantial amount of their

cation exchange capacity (Kanehiro and Cheng, 1956; Kanehiro and Sherman, 1956). These soils are highly leached and have very low base saturation.

The nature of the hydrated colloidal fraction in these soils makes it an excellent selection for this study. King (1962) used this soil for a phosphate study and found it to be extremely reactive to phosphate in its moist condition. After dehydration its ability to fix phosphate was strikingly decreased. Because of the marked change in properties with dehydration, the soils were kept in the naturally moist condition by storing them in air-tight containers.

Monopotassium phosphate was used in the experiments. It is a product (reagent grade) of General Chemical Division, Allied Chemical Corporation, having the following maximum limit of impurities:

Insoluble, calcium and $\text{NH}_4\text{OH}$ precipitate . . . . .	0.010%
Loss on drying over $\text{H}_2\text{SO}_4$ . . . . .	0.20 %
pH of 0.2 M solution at 25° C . . . . .	4.3--4.5
Chloride (cl) . . . . .	0.001%
Nitrogen compounds (as N) . . . . .	0.001%
Sulfate ( $\text{SO}_4$ ) . . . . .	0.003%
Heavy metals (as Pb) . . . . .	0.001%
Iron (Fe) . . . . .	0.002%
Sodium (Na) . . . . . To pass test (limit abt. . .	0.02%

The pH of the phosphate solutions were adjusted by hydrochloric acid.

## PROCEDURES

1. Preparation of the Reaction Products for Characterization

The reaction products were prepared by the following procedure. Five to fifteen grams of wet Akaka soil were placed in a 200 ml. pyrex beaker or pyrex glass container of suitable size. One hundred ml. of potassium phosphate solution ranging from 0.05 molar to about 1 molar, with pH values varying from 2.0 to 4.0, were added. The glass container was wrapped in a plastic bag and kept at room temperature (about 25-30° C). The content of the glass container was then filtered after standing from 1 to 200 days, and the pH of filtrate was measured. The pH of the filtrate serves more or less as an indication of the pH of the reacting system, which in turn, predicts the possible species of ions that enter into reaction. The residue was washed successively with 60% methanol, 80% ethanol and 95% ethanol by decantation (Wada, 1959) to remove excess phosphate. The finer fractions of the solid phase were collected on the filter paper. The coarser fractions were left in the glass container. They were then air dried.

A taranakite sample was synthesized for comparison. The synthesized taranakite was prepared as follows: Twenty ml. of 65% phosphoric acid were mixed with an aluminum chloride solution containing 2.65 grams of aluminum chloride. The mixture of phosphoric acid and aluminum chloride was filtered and diluted to 50 ml., an aliquot of which was taken and neutralized with 10% potassium hydroxide to pH 3.4 to 3.9 in a pyrex beaker. The beaker

containing the flocculent precipitate was covered with a watch glass and kept in a 50° C water bath or at room temperature. The crystalline precipitates formed were separated by filtration and washed with distilled water. They were then air dried.

## 2. Characterization of Phospho-reaction Products by X-ray Analysis

The reaction products were identified by X-ray diffraction, using a Norelco X-ray diffractometer with copper K $\alpha$  radiation. The X-ray diffraction patterns obtained throughout this study were of powder samples.

The effect of heating on both the crystalline substance resulting from the soil-phosphate system, and the synthesized taranakite was examined. Both were subject to different temperatures starting from 60° C up to 150° C or so. The products resulting from heat treatment were identified by X-ray diffraction.

## 3. Characterization of Phospho-reaction Products by Chemical Analysis

The evaluation of K/P $O_4$  and Al/P $O_4$  ratios for the reaction products was difficult because of unavoidable contamination of the reaction product by soil particles. A two-way experimental design (Snedecor, 1956) with four replications at three levels of soil was therefore prepared. Five, ten and fifteen grams of wet soil were used with a 0.4 molar potassium phosphate solution at pH 3. Phosphate was estimated by chlorostannous-reduced molybdophosphoric blue color method in hydrochloric acid system following fusion of the sample with sodium carbonate, then decomposition of the melt

with hydrochloric acid (Jackson, 1958). Potassium was determined by flame photometer method using a Model 21 Coleman Flame Photometer. Aluminum was analyzed by Chenery's colorimetric method, as modified by Moomaw et al. (1959). The whole experiment was repeated ten times. Homogeneity test was conducted using the M value as the criterion (Hartley, 1944). In its final form, the M-test involves computing

$$M = (n_1 + n_k) \log \frac{n_1 s_1^2 + \dots + n_k s_k^2}{n_1 + \dots + n_k} - (n_1 \log s_1^2 + n_k \log s_k^2)$$

where there are  $k$  samples,  $n_1, \dots, n_k$  are the respective degrees of freedom and  $s_1^2, \dots, s_k^2$  the respective estimates of variance. The homogeneity test showed that three of the ten experiments were not homogeneous with the others and they were therefore rejected. The M values, evaluated from the remaining seven experiments and their respective mean square of error, are presented in Table II. Data obtained from the seven experiments were combined. Analysis of variance with respect to the ratios of  $K/P_2O_5$  and  $Al/P_2O_5$  were carried out. The result of analysis of variance showed that there is no significant difference with respect either to  $K/P_2O_5$  or to  $Al/P_2O_5$  when the amount of soil used was varied.

The possibility of isomorphous substitution of iron for aluminum in the reaction product, under the conditions of investigation, was also examined. Relatively pure crystalline reaction products were selected and were ignited over the Meker

TABLE II

THE MEAN SQUARE OF ERROR OF THE SEVEN EXPERIMENTS  
 SELECTED FOR EVALUATING THE RATIOS OF  $K/P_2O_5$  AND  $Al/P_2O_5$   
 OF THE PHOSPHO-REACTION PRODUCTS PRODUCED  
 FROM AKAKA SOIL, AND THE RESULT OF  
 THEIR RESPECTIVE M-TESTS

Experiment ( $K/P_2O_5$ ) no.	Mean square of error	M-value	Experiment ( $Al/P_2O_5$ ) no.	Mean square of error	M-value
2	0.0000045		1	0.0000475	
3	.0000110		2	.0001310	
4	.0000031		4	.0002300	
5	.0000210	13.14	5	.0000750	10.10
6	.0000033		6	.0002700	
7	.0000075		9	.0000440	
8	.0000061		10	.0000290	

$$M \left( \frac{1.0}{.05}, 7 \right) = 13.27$$

burner. This approach is based primarily on the fact that iron-containing compounds give hematite upon ignition. If iron-substituted taranakite is present, the crystals should show a reddish color when ignited, but this did not occur.

#### 4. Characterization of Phospho-Reaction Products by Optical Methods

Optical analyses of the reaction products resulting from the soil-phosphate system, and the synthesized taranakite were conducted. The synthesized taranakite already described was used. In addition, a second synthetic preparation was prepared as follows: Ten ml. of 1.5 molar monopotassium phosphate solution were mixed with a solution containing 0.25 gram aluminum with vigorous stirring. The pH of this mixture was adjusted to 4.0 with 10% potassium hydroxide. The precipitates formed were kept in water at 50° C for a period of time. They were then filtered, washed with distilled water and air dried.

The crystalline substances subject to optical analyses were mounted in a suitable medium as described in the following two procedures: (a) mounted with immersion liquids for refractive index determination; (b) mounted as thin sections using Lakeside No. 70 Transparent Cement as the mounting medium.

#### 5. Characterization of Phospho-Reaction Products by Infra-red Analysis

Infra-red analyses of phospho-reaction product and synthesized taranakite were carried out. The phospho-reaction product produced from Akaka soil used was formed from 0.4 molar potassium phosphate

at pH 2, and 5 grams of the wet soil for 200 days. The synthesised taranakite used is described on page 11. Purification of the phospho-reaction products and taranakite samples were conducted by repeated reprecipitation in phosphoric acid solution with potassium hydroxide. The infra-red spectra of the samples (Figure 2) were obtained by pressed discs (with potassium bromide) using a Beckman infra-red spectrophotometer.

6. Characterization of Phospho-Reaction Products by Differential Thermal Analysis

Differential thermal analyses of phospho-reaction product and synthesised taranakite samples were conducted (Figure 3). The differential thermal setup is the same as the one described by Uehara and Sherman (1956). A differential thermocouple (two-headed thermocouple) was used as the heat sensitive device. One junction of the thermocouple was inserted in an inert material ( $Al_2O_3$ ) which does not undergo either exothermic or endothermic reactions through the temperature interval that was studied; the other junction was placed in the sample holder containing the sample that is to be tested. Both junctions are then heated in a furnace to a temperature of  $950^{\circ}C$  at a constant rate of 15 degrees per minute. A reflecting galvanometer was used as a measuring device for detecting any temperature difference between the sample and the aluminum oxide.



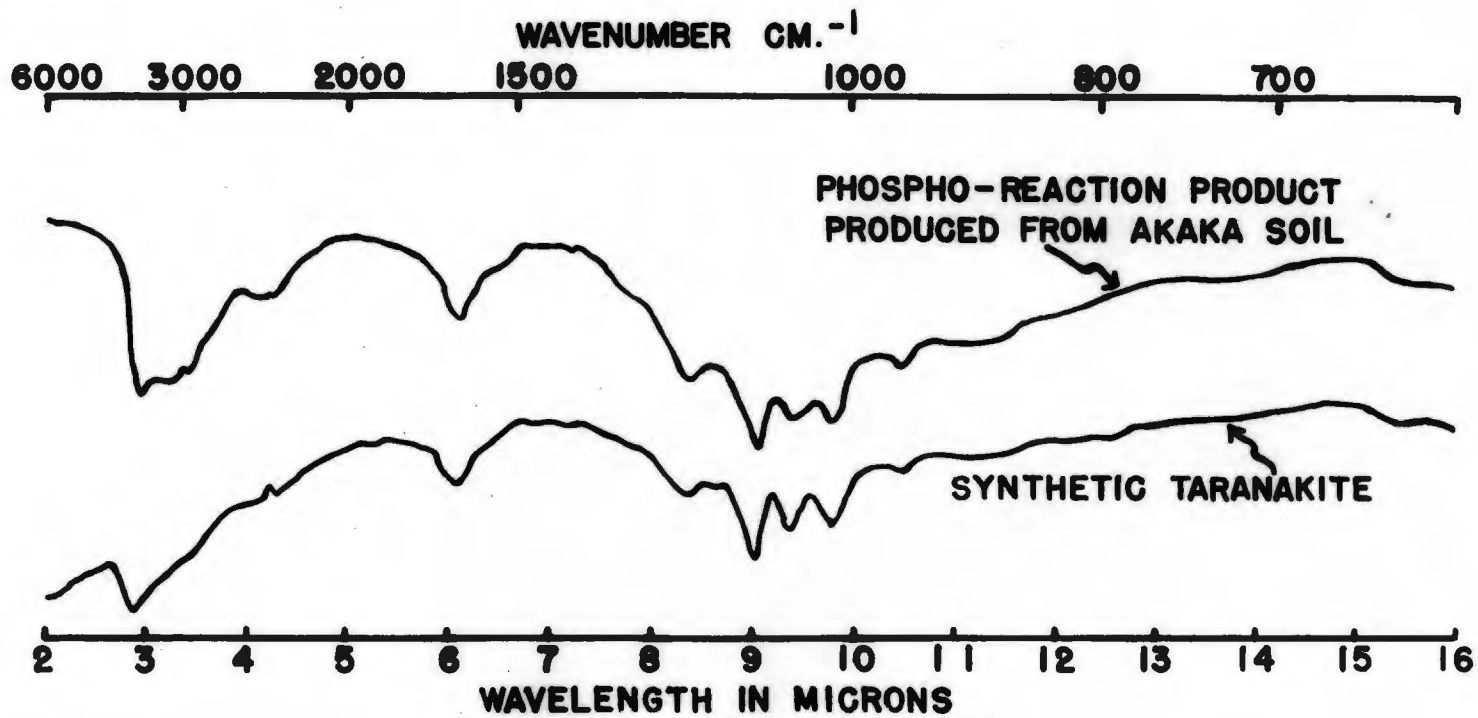


Figure 2

Infra-red Absorption Spectra of Phospho-Soil Product and Synthetic Taranakite

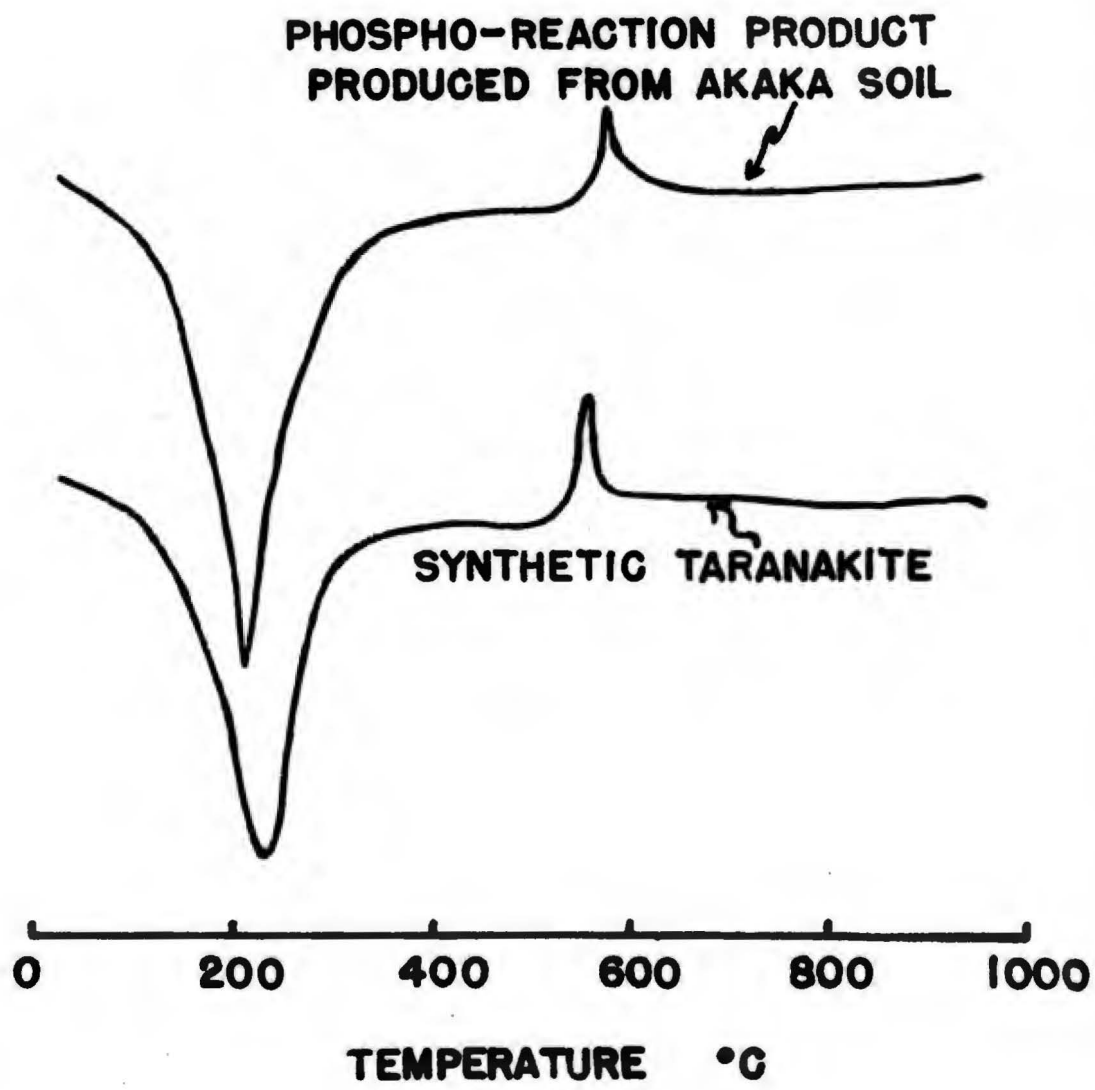


Figure 3

D. T. A. Curves of Phospho-Reaction Product Produced from Akaka Soil and Synthetic Taranakite

7. The Effect of pH on the Reaction of Potassium Phosphate and the Akaka Soil Samples

Five- to fifteen-gram portions of wet Akaka soil were treated with 100 ml. of potassium phosphate solutions at pH 2.0, 2.5, 3.0, and 4.0. The phospho-soil systems were allowed to stand from 2 to 200 days. The pH values of the filtrates were measured after 2 days standing and at the date of sampling. The reaction product was identified by X-ray diffraction. The method of collecting samples for conducting X-ray analysis was the same as described under "Characterization of Phospho-Reaction Products by X-ray Analysis."

8. The Effect of Concentration on the Reaction of Potassium Phosphate and the Akaka Soil Samples

Five, ten and fifteen-gram portions of the wet Akaka soil were treated with 0.2, 0.5, and 0.6 molar potassium phosphate solutions at pH 2. The phospho-soil systems were allowed to stand for six days. The relative amounts of the crystalline reaction products formed were estimated visually.

9. The Effect of Time on the Degree of Crystallinity of the Phospho-Reaction Product Produced from the Akaka Soil

Five-gram portions of the wet Akaka soil were treated with:  
(a) 0.4 molar potassium phosphate at pH 2 and the reaction system was left to stand for 5, 54 and 200 days. The finer fraction of the solid phase was filtered, washed and dried as usual. X-ray diffraction analyses were conducted. The half-peak breadths of the

15.7 Å peaks were measured. The half-peak breadths (log scale) were plotted against time. (b) 0.5 molar potassium phosphate at pH 2 for 6, 10 and 15 days. X-ray analyses were carried out. The half-peak breadths of the 15.7 Å peaks (log scale) versus time were plotted.

## RESULTS AND DISCUSSION

1. Characterization of Phospho-Reaction Products by X-ray Analysis

X-ray diffraction patterns of the phospho-reaction products produced by the treatment of Akaka soil with solutions containing potassium phosphate ranging from 0.05 to 1 molar at pH 2.0 to 4.0 were obtained. Crystalline products were obtained only for the concentration range 0.2 to 0.6 molar and when the potassium phosphate solution had an initial pH value of 2. These crystalline products were identified by X-ray analysis to be taranakite. Table III shows the data of reaction products resulting from 0.4 molar potassium phosphate at pH 2 and 5 grams of wet Akaka soil for 5 days, 54 days and 200 days standing respectively. For comparison, that of the synthesized taranakite, the taranakite from Sugarloaves, Taranaki, New Zealand, the taranakite found in Pig Hole, Giles County, Virginia, the synthesized taranakite studied by Haseman et al. and the taranakite formed from Tirau ash clay fraction in New Zealand are included. The data presented in Table III clearly show the similarity of the X-ray diffraction patterns obtained from the reaction products produced from Akaka soil, and that obtained by other workers on synthesized and natural taranakites. The prominent peaks of natural taranakites of Sugarloaves, Taranaki, New Zealand, and Pig Hole Cave, Giles County, Virginia are at 16.2 Å, 7.6 Å, 3.82 Å and 15.49 Å, 7.82 Å, 3.79 Å, 3.12 Å respectively. The 16.2 Å and 15.49 Å peaks are the strongest. The synthesized taranakite produced in this experiment,

TABLE III

POWDER X-RAY DIFFRACTION DATA OF THE REACTION PRODUCTS, SYNTHESIZED TARMAKITE, TARMAKITE FROM SUGARLOAVES, TARMAKI, NEW ZEALAND, TARMAKITE FOUND IN PIG HOLE CAVE, GILES COUNTY, VIRGINIA, SYNTHESIZED TARMAKITE OBTAINED BY HASEMAN ET AL. AND THE TARMAKITE FORMED FROM TIRAU ASH CLAY FRACTION IN NEW ZEALAND

Reaction products obtained from potassium phosphate on Akaka soil, days of standing			Synthesized tarmakite		Tarmakite (Sugarloaves, Taranaki, New Zealand)		Tarmakite (Pig Hole Cave, Giles County, Virginia)		Synthesized tarmakite studied by Haseman et al.		Tarmakite from Tirau ash clay fraction studied by Birrell			
5	54	200												
d	d	I <sup>a</sup>	d	I	d	I	d	I	d	I	d	I	d	I
15.7	15.7	VS	15.7	VS	15.7	VS	16.2	VS	15.49	3250	15.7	1.00	15.60	1.00
7.43	7.89	M	7.89	M	7.89	S	7.6	S	7.82	750	7.88	.85	7.82	.20
5.90	7.43	M	7.43	M	7.43	M	5.8	M	7.43	570	7.35	.68	7.40	.32
4.33	5.90	M	5.94	M	5.90	M	5.1	MW	7.19	190	5.81	.29	5.88	.40
3.83	5.64	M	5.27	W	5.03	W	4.39	M	5.82	420	5.03	.13	4.31	.40
3.60	4.33	M	5.06	W	4.67	W	3.82	S	5.61	140	4.60	.08	4.02	.10
3.35	4.02	W	4.49	W	4.31	M	3.58	M	4.62	110	4.30	.87	3.81	.90
3.14	3.81	S	4.33	M	4.02	W	3.34	MW	4.27	390	4.14	.11	3.36	.25
2.93	3.60	M	4.04	W	3.81	S	3.15	S	4.15	60	3.99	.09	3.15	.80
2.83	3.36	M	3.81	S	3.75	M	2.84	S	4.00	110	3.79	.71	2.82	.50
2.62	3.30	M	3.75	M	3.57	M	2.73	WV	3.79	800	3.55	.44	2.62	.40
	3.14	S	3.59	M	3.35	M	2.63	MS	3.72	550	3.34	.22		
	2.95	W	3.36	M	3.29	M			3.57	500	3.27	.25		
	2.94	W	3.31	M	3.13	S			3.34	300	3.13	.65		
	2.82	M	3.14	S	2.94	W			3.27	320	2.93	.16		
	2.73	W	2.96	W	2.93	W			3.16	300	2.81	.48		
	2.62	M	2.94	W	2.84	M			3.12	620	2.72	.34		
			2.93	W	2.81	M			3.06	30	2.61	.40		
			2.85	M	2.73	M			2.94	140				
			2.74	W	2.62	M			2.83	390				
			2.62	M					2.81	400				
									2.73	250				
									2.79	80				

<sup>a</sup> Observed intensities estimated visually in decreasing order of strength VS, S, M, and W.

and those of Haseman et al., showed strongest peak at 15.7 Å and strong peaks at 7.89 Å, 3.81 Å, 3.14 Å and 7.55 Å, 3.79 Å, 3.13 Å respectively. Excepting the 7.89 Å peak given by the phospho-reaction product produced from Akaka soil, the prominent peaks of natural and synthesized taranakite are similar to the reaction products obtained from the Akaka soil. Birrell (op. cit.) identified a taranakite by treating Tirau ash clay fraction from New Zealand with potassium phosphate solution. The X-ray diffraction of the taranakite studied by Birrell showed prominent peaks at 15.60 Å, 3.81 Å, and 3.13 Å, which is very similar to the phospho-reaction products obtained from the Akaka soil.

The reaction products resulting from soil-phosphate systems, and the synthesized taranakite, were heated to different temperatures in order to examine the dehydration products, as well as the effect of heating on crystallinity. The dehydration products resulting from the soil-phosphate systems and the synthesized taranakite were of similar nature. Powder X-ray diffraction pattern showed characteristic d-spacings of 13.4 Å, 6.8 Å, 5.5 Å, and 3.4 Å upon heating. This substance is a Product B-like compound as synthesized by Haseman et al. Both the reaction product resulting from soil-phosphate systems and the synthesized taranakite became amorphous above 130° C. Table IV shows X-ray diffraction patterns of the heated reaction products, as compared with the synthesized taranakite and Product B synthesized by Haseman et al.

TABLE IV

POWDER X-RAY DIFFRACTION PATTERNS OF THE HEAT TREATED REACTION PRODUCTS, SYNTHESIZED TARAMAKITE  
AND PRODUCT B OF HASEMAN ET AL. (1950)

Phospho-Reaction Products Produced from Akaha Soil, Days of Standing																
5			24				200									
70° C :		120° C :	90° C :		105° C :		90° C :		105° C :		110° C :		120° C :		135° C	
d	d	Ch.I*	d	Ch.I	d	I	d	I	d	Ch.I	d	Ch.I	d	Ch.I	d	Ch.I
7.43	<u>13.6</u>		15.7	↓	<u>13.6</u>	S	<u>13.6</u>	S	<u>13.6</u>		<u>13.6</u>	↑	<u>13.6</u>	↑	<u>13.6</u>	↓
5.53	<u>7.43</u>	↓	<u>13.6</u>		<u>7.37</u>	N	<u>7.43</u>	S	<u>7.43</u>	↓	<u>7.43</u>	↓	<u>7.43</u>	↓	<u>7.43</u>	↓
<u>4.29</u>	<u>5.53</u>	↓	<u>7.37</u>		<u>6.86</u>	N	<u>7.08</u>	W	<u>7.08</u>	↓	<u>7.08</u>	↓	<u>7.08</u>	↓	<u>6.86</u>	↓
<u>3.40</u>	<u>4.33</u>		<u>5.55</u>		<u>5.55</u>	N	<u>6.86</u>	W	<u>6.86</u>	↑	<u>6.86</u>	↑	<u>6.86</u>	↑	<u>5.57</u>	↓
<u>3.33</u>	<u>4.15</u>		<u>4.29</u>	↑	<u>4.33</u>	N	<u>5.57</u>	N	<u>5.57</u>	↑	<u>5.57</u>	↓	<u>5.57</u>		<u>3.40</u>	↓
<u>3.03</u>	<u>3.40</u>	↑	<u>4.15</u>		<u>4.15</u>	N	<u>4.35</u>	N	<u>4.29</u>		<u>4.31</u>	↑	<u>4.31</u>	↑		
<u>2.81</u>	<u>3.33</u>	↓	<u>3.40</u>		<u>3.66</u>	W	<u>4.31</u>	N	<u>4.15</u>		<u>4.15</u>		<u>4.15</u>	↑		
			<u>3.15</u>		<u>3.61</u>	W	<u>4.15</u>	N	<u>3.66</u>		<u>3.67</u>		<u>3.69</u>	↓		
			<u>2.91</u>		<u>3.40</u>	S	<u>3.69</u>	W	<u>3.40</u>	↑	<u>3.54</u>	↓	<u>3.54</u>	↓		
			<u>2.81</u>	↓	<u>3.15</u>	N	<u>3.40</u>	S	<u>3.15</u>		<u>3.40</u>	↑	<u>3.40</u>	↓		
					<u>3.02</u>	W	<u>3.15</u>	W	<u>3.03</u>		<u>3.15</u>		<u>3.15</u>			
					<u>2.90</u>	W	<u>3.03</u>	N	<u>2.91</u>	↑	<u>3.13</u>		<u>3.03</u>	↑		
					<u>2.77</u>	W	<u>2.91</u>	N	<u>2.81</u>	↑	<u>2.91</u>	↑	<u>2.91</u>	↑		
							<u>2.80</u>	N	<u>2.77</u>		<u>2.81</u>		<u>2.77</u>			
							<u>2.77</u>	N					<u>2.69</u>			
													<u>2.66</u>			

\* Change in intensity: ↑ represents increase in intensity.  
↓ represents decrease in intensity.



TABLE IV (CONT'D)

POWDER X-RAY DIFFRACTION PATTERNS OF THE HEAT TREATED REACTION PRODUCTS, SYNTHESIZED TARMAKITE AND PRODUCT B OF HASEMAN ET AL. (1950)

Synthesized Taramakite										: Product B of : Haseman et al.	
70° C		80° C		90° C		100° C		120° C			
d	Ch.I	d	Ch.I	d	Ch.I	d	I	d	Ch.I	d	I/I <sub>1</sub> **
15.7	↓	15.7	↓	15.7	↓	13.6	S	13.6	↓	13.8	1.00
7.89	↓	13.8		13.6	↑	7.37	N	7.37	↓	7.35	.68
7.43		7.89	↓	7.43	↑	6.80	N	6.80	↑	6.79	.51
5.86	↓	7.43	↑	5.53	↑	5.53	N	5.53		6.05	.15
4.31		5.81	↓	4.29	↑	4.29	N	4.29	↓	5.46	.68
4.14		5.57		4.13	↑	4.13	N	4.13	↓	4.26	.40
3.80	↓	4.31		3.57		3.66	W	3.66	↓	4.14	.51
3.73		4.13	↑	3.40	↑	3.53	W	3.40	↓	3.89	.04
3.72		3.80	↓	3.13		3.40	S	3.14	↓	3.64	.24
3.57	↓	3.73	↓	2.91	↑	3.14	N	3.03	↓	3.50	.16
3.40		3.72	↓	2.84		3.03	N	2.91		3.89	1.00
3.35	↓	3.57	↓	2.81		2.91	N	2.81	↓	3.13	.49
3.29	↓	3.40	↑			2.81	N	2.77	↓	3.01	.40
3.13	↓	3.13				2.77	N			2.90	.64
2.84		2.91								2.84	.11
2.81	↓	2.84								2.79	.38
2.73	↓	2.81	↓							2.76	.40
2.62	↓									2.74	.25
										2.68	.16
										2.64	.24
										2.56	.09

\*\* Represents visual estimates of peak intensities.

## 2. Characterization of Phospho-Reaction Products by Chemical Analysis

The average values of  $K/PO_4$  and  $Al/PO_4$ , obtained from the seven experiments, were considered to be taken from a representative sample because the M-test proved to be insignificant (Table II). The molar ratios of  $K/PO_4$  and  $Al/PO_4$  for the reaction products were 0.37 and 0.72 respectively (Table V). Those for the synthesized taranakite were as follows: 0.37 for  $K/PO_4$  and 0.60 for  $Al/PO_4$  as shown in Table VI. These values are very close to the ones calculated from the formula of taranakite established by Smith and Brown (1959) which is 0.38 for  $K/PO_4$  and 0.63 for  $Al/PO_4$ . The reason the molar ratio  $Al/PO_4$  of the reaction products estimated is somewhat higher is because most of the crystalline substances that were separated from the reacting system were contaminated with soil particles.

Ignition of the crystalline substance obtained from the soil-phosphate systems, showed that the crystals, as a whole, are white in color with a few minute adherent particles of hematite, presumably derived from the contamination with soil particles. That is, this hematite is formed by the crystallization of hydrated iron oxide in the soil. This shows that the active constituent reacting with phosphate in Akaka soil is aluminum rather than iron for the conditions of the present investigation. Recent work on the precipitation of phosphate in acid soils by Taylor et al. (1964) also revealed that aluminum hydroxide is the principal

TABLE V  
 CHEMICAL ANALYSIS AND THE K/PO<sub>4</sub> AND Al/PO<sub>4</sub> VALUES  
 OF THE REACTION PRODUCTS

Expt. no.	Soil gm.	Repetition no.	K%	Al%	PO <sub>4</sub> %	K/PO <sub>4</sub>	Al/PO <sub>4</sub>
1	5	1	5.70	7.46	36.88		.712
1	10	1	5.70	7.88	36.88		.752
1	15	1	5.90	8.10	38.56		.738
1	5	2	6.20	7.90	40.00		.698
1	10	2	5.00	6.76	32.72		.730
1	15	2	4.80	6.48	31.44		.726
1	5	3	3.60	5.01	24.16		.730
1	10	3	3.80	5.26	25.52		.724
1	15	3	5.70	7.46	36.72		.714
1	5	4	7.60	10.22	48.72		.738
1	10	4	5.60	7.26	36.48		.700
1	15	4	5.90	8.26	38.56		.754
2	5	1	5.90	7.85	38.56	.374	.717
2	10	1	5.90	7.70	38.56	.374	.701
2	15	1	5.90	7.96	38.56	.374	.727
2	5	2	5.90	7.95	38.56	.374	.725
2	10	2	6.20	8.38	40.00	.375	.738
2	15	2	5.00	6.72	32.56	.370	.725
2	5	3	6.20	8.10	40.00	.375	.712
2	10	3	5.00	6.66	32.56	.370	.720

TABLE V (CONT'D)  
 CHEMICAL ANALYSIS AND THE K/PO<sub>4</sub> AND Al/PO<sub>4</sub> VALUES  
 OF THE REACTION PRODUCTS

Expt. no.	Soil gm.	Repetition no.	K%	Al%	PO <sub>4</sub> %	K/PO <sub>4</sub>	Al/PO <sub>4</sub>
2	15	3	6.20	8.20	40.00	.375	.722
2	5	4	6.90	8.94	44.47	.376	.708
2	10	4	5.90	8.11	38.56	.374	.740
2	15	4	5.90	7.98	38.56	.374	.728
3	5	1	5.60		36.48	.372	
3	10	1	5.90		38.56	.374	
3	15	1	7.60		48.72	.378	
3	5	2	6.90		44.47	.376	
3	10	2	6.90		44.47	.376	
3	15	2	5.00		32.72	.369	
3	5	3	6.90		44.24	.377	
3	10	3	5.70		36.88	.373	
3	15	3	5.00		32.56	.370	
3	5	4	5.70		36.88	.373	
3	10	4	6.20		40.00	.375	
3	15	4	5.90		38.56	.374	
4	5	1	5.90	7.71	38.56	.374	.703
4	10	1	5.70	7.64	36.88	.373	.730
4	15	1	5.90	8.08	38.56	.374	.735

TABLE V (CONT'D)  
 CHEMICAL ANALYSIS AND THE K/PO<sub>4</sub> AND Al/PO<sub>4</sub> VALUES  
 OF THE REACTION PRODUCTS

Expt. no.	Soil gm.	Repetition no.	K%	Al%	PO <sub>4</sub> %	K/PO <sub>4</sub>	Al/PO <sub>4</sub>
4	5	2	7.40	7.94	38.08	.377	.734
4	10	2	6.60	8.61	42.54	.375	.713
4	15	2	5.90	7.76	38.56	.374	.710
4	5	3	6.60	8.66	42.56	.375	.716
4	10	3	5.90	8.04	38.56	.374	.734
4	15	3	4.80	6.64	31.44	.368	.743
4	5	4	5.90	8.00	38.56	.374	.729
4	10	4	6.60	8.58	42.56	.375	.710
4	15	4	5.70	7.57	36.88	.373	.723
5	5	1	6.60	8.74	42.56	.375	.723
5	10	1	5.60	7.52	36.48	.372	.727
5	15	1	5.90	7.80	38.56	.374	.712
5	5	2	5.70	7.52	36.88	.373	.720
5	10	2	4.00	5.34	26.24	.365	.718
5	15	2	5.60	7.62	36.48	.372	.735
5	5	3	5.00	6.73	32.56	.370	.727
5	10	3	5.70	7.70	36.88	.373	.736
5	15	3	6.60	8.82	42.56	.375	.730
5	5	4	5.00	6.63	32.56	.370	.722
5	10	4	7.40	9.32	48.72	.378	.710

TABLE V (CONT'D)  
 CHEMICAL ANALYSIS AND THE K/PO<sub>4</sub> AND Al/PO<sub>4</sub> VALUES  
 OF THE REACTION PRODUCTS

Expt. no.	Soil gm.	Repetition no.	K%	Al%	PO <sub>4</sub> %	K/PO <sub>4</sub>	Al/PO <sub>4</sub>
5	15	4	5.70	7.60	36.88	.373	.726
6	5	1	5.90	7.70	38.56	.374	.702
6	10	1	5.70	7.80	36.88	.373	.744
6	15	1	5.60	7.44	36.48	.372	.720
6	5	2	5.60	7.60	36.48	.372	.733
6	10	2	4.10	5.38	26.96	.366	.702
6	15	2	5.20	6.94	33.76	.371	.724
6	5	3	4.80	6.42	31.44	.368	.720
6	10	3	5.90	8.05	38.56	.374	.735
6	15	3	4.80	6.53	31.44	.368	.730
6	5	4	5.90	7.96	38.56	.374	.726
6	10	4	5.00	6.57	32.56	.370	.710
6	15	4	5.90	7.90	38.56	.374	.722
7	5	1	6.60		42.56	.375	
7	10	1	5.30		33.76	.371	
7	15	1	5.60		36.48	.372	
7	5	2	5.60		36.48	.372	
7	10	2	4.30		28.08	.367	
7	15	2	6.60		42.56	.375	

TABLE V (CONT'D)  
 CHEMICAL ANALYSIS AND THE K/PO<sub>4</sub> AND Al/PO<sub>4</sub> VALUES  
 OF THE REACTION PRODUCTS

Expt. no.	Soil gm.	Repetition no.	K%	Al%	PO <sub>4</sub> %	K/PO <sub>4</sub>	Al/PO <sub>4</sub>
7	5	3	5.00		32.56	.370	
7	10	3	5.60		36.48	.372	
7	15	3	5.00		32.56	.370	
7	5	4	4.80		31.44	.368	
7	10	4	5.00		32.56	.370	
7	15	4	5.70		36.88	.373	
8	5	1	5.70		36.88	.373	
8	10	1	5.60		36.48	.372	
8	15	1	6.60		42.56	.375	
8	5	2	5.70		36.88	.373	
8	10	2	4.80		31.44	.368	
8	15	2	4.80		31.44	.368	
8	5	3	4.80		31.36	.369	
8	10	3	5.60		36.48	.372	
8	15	3	4.30		28.08	.367	
8	5	4	5.70		36.88	.373	
8	10	4	5.60		36.48	.372	
8	15	4	6.60		42.56	.375	
9	5	1		7.64	36.88		.729

TABLE V (CONT'D)  
 CHEMICAL ANALYSIS AND THE K/PO<sub>4</sub> AND Al/PO<sub>4</sub> VALUES  
 OF THE REACTION PRODUCTS

Expt. no.	Soil gm.	Repetition no.	K%	Al%	PO <sub>4</sub> %	K/PO <sub>4</sub>	Al/PO <sub>4</sub>
9	10	1		6.79	32.72		.731
9	15	1		6.66	32.56		.720
9	5	2		6.68	32.56		.722
9	10	2		7.54	36.48		.728
9	15	2		8.90	42.56		.736
9	5	3		6.44	31.56		.723
9	10	3		8.89	42.56		.735
9	15	3		8.05	38.56		.735
9	5	4		7.52	36.88		.720
9	10	4		6.73	32.56		.725
9	15	4		7.64	36.48		.737
10	5	1		8.90	42.56		.736
10	10	1		7.54	36.48		.730
10	15	1		8.75	42.56		.724
10	5	2		7.54	36.48		.728
10	10	2		7.66	36.88		.732
10	15	2		8.89	42.56		.735
10	5	3		7.93	38.56		.725
10	10	3		6.42	31.44		.720
10	15	3		7.64	36.88		.729



TABLE V (CONT'D)  
 CHEMICAL ANALYSIS AND THE K/PO<sub>4</sub> AND Al/PO<sub>4</sub> VALUES  
 OF THE REACTION PRODUCTS

Expt. no.	Soil ga.	Repe- tition no.	K%	Al%	PO <sub>4</sub> %	K/PO <sub>4</sub>	Al/PO <sub>4</sub>
10	5	4		6.49	31.44		.726
10	10	4		8.00	38.56		.729
10	15	4		7.64	36.43		.737
Mean :						.37	.72
Standard error :						.00	.01

TABLE VI  
K/PO<sub>4</sub> AND Al/PO<sub>4</sub> VALUES OF THE PHOSPHO-REACTION PRODUCT,  
SYNTHESIZED TARNAKITE AND TARNAKITE  
STUDIED BY SMITH AND BROWN

	Reaction Product Produced from Akaka Soil	Synthesized Tarnakite	Tarnakite Studied by Smith and Brown
K/PO <sub>4</sub>	0.37	0.37	0.38
Al/PO <sub>4</sub>	0.72	0.60	0.63

reagent in the precipitation of phosphate from fertilizers in acid soils.

### 3. Characterization of Phospho-Reaction Products by Optical Methods

Both the reaction products obtained from the soil-phosphate systems and the synthesized taranakite, when examined under the polarizing microscope showed that they were biaxial negative with a very small value of  $2V$ . The interference figures obtained from crystals immersed in liquids for refractive index determination were generally much better than those from thin section preparations. The refractive indices determined for the phospho-reaction product were  $n_{\alpha} = 1.504$ ,  $n_{\beta} = 1.507$ ,  $n_{\gamma} = 1.509$  and  $n_{\gamma} - n_{\alpha} = 0.005$ . Those for the synthesized taranakite were:  $n_{\alpha} = 1.503$ ,  $n_{\beta} = 1.505$  and  $n_{\gamma} = 1.506$ ,  $n_{\gamma} - n_{\alpha} = 0.003$ . These values are in reasonable agreement with those obtained by Haseman et al. (op. cit.). The crystals are colorless and occur as tiny columnar aggregates. Two aggregates of crystals tend to grow together perpendicular to each other to form a twin-like crystal in a rosette pattern. This results in a pseudohexagonal outline.

Smith and Brown (1959) re-examined the synthesized taranakite prepared by Haseman et al. and considered that the taranakite was hexagonal and uniaxial negative. In the original report of Haseman et al., they described their synthesized product as pseudohexagonal and biaxial negative. It seems that taranakite might exist dimorphously between hexagonal and pseudohexagonal with  $2V$  values

ranging from zero to about twenty degrees. In this particular respect, further crystallographic study on the phospho-reaction product and the synthesized taranakite is necessary.

#### 4. Characterization of Phospho-Reaction Products by Infra-red Analysis

The infra-red spectra of the phospho-reaction product produced from Akaka soil and synthesized taranakite in pressed KBr discs were in good correspondence with each other. Absorption peaks near  $3400\text{-cm.}^{-1}$  and  $1624\text{-cm.}^{-1}$  showed the presence of water of crystallization. Corbridge et al. (1954) reported that all hydrated salts absorb in the  $3300\text{-cm.}^{-1}$  and  $1640\text{-cm.}^{-1}$  regions which presumably correspond to O-H stretching and O-H bending respectively. Complex phosphate absorption bands between  $1200\text{-}$  and  $670\text{-cm.}^{-1}$  and P-OH linkages near  $2500\text{-cm.}^{-1}$  indicated the presence of  $\text{PO}_4^{3-}$  and acidic phosphate ions respectively (Corbridge et al., 1956). These results are very close to the infra-red absorption spectrum for taranakite obtained by Arlidge et al. (op. cit.).

#### 5. Characterization of Phospho-Reaction Products by Differential Thermal Analysis

The differential thermal curves show that both the phospho-reaction product produced from the Akaka soil and the synthesized taranakite undergo endothermic reactions at about  $230^\circ\text{C}$  and exothermic reactions between  $500$  and  $600^\circ\text{C}$ . These d. t. a. curves indicate that the phospho-reaction product produced from Akaka soil and synthesized taranakite lose their water of crystallization in one stage as evidenced by the endotherm at

230° C. Work of Arlidge et al. (op. cit.) on samples supplied by the Tennessee Valley Authority also showed the same phenomenon. Natural taranakite from Pig Hole Cave and the taranakite prepared by Arlidge et al., however, lose their water of crystallization in two stages (Arlidge et al., op. cit.). This variation is thought to be associated with variations in degree of crystallinity of particle size. The exothermic peak between 500 and 600° C represents probably the recrystallization of the mineral after it has been dehydrated as suggested by Murray and Dietrich (op. cit.). The differential thermal gravimetric curves for taranakite as obtained by Arlidge et al. (op. cit.) also reveal that there is no weight change during the process of exothermic reaction indicating the possibility of recrystallization.

The fact that all the taranakite samples studied in this experiment are amorphous to X-ray when they are heated above 130° C shows that the recrystallized products from dehydrated taranakite are too small or too poorly-ordered to be identified by X-ray diffraction.

6. The Effect of pH on the Reaction of Potassium Phosphate and Alumin Soil Samples

Crystalline phospho-reaction products were detectable only when the pH of the reacting system was 2.3 to 3.9. This clearly indicates that the pH of the reaction system plays an important role in connection with the crystallization of taranakite. There was very little change in pH values of the filtrates of the

phospho-soil system during the experiment (Table VII and VIII). The formation of taranakite in an environment having pH values of 2.3 to 2.9 suggests that the phosphate is in the form of free phosphoric acid and  $H_2PO_4^-$  and aluminum as  $Al(H_2O)_3(OH)_2^+$  or related forms entering into the reaction

Time required to detect the presence of crystalline taranakite in the soil-phosphate system, under the conditions specified in this experiment, is approximately a week or less. It is evident from phosphate fixation studies that the fixation occurs readily and abundantly. In experiments in which potassium phosphate solutions of similar strength as the ones in this experiment were used, with pH values of 3 and 4, no crystalline substance was detected when standing over a period of months. This is presumably because both the free phosphoric acid and  $Al(H_2O)_3(OH)_2^+$  are not as abundant as when the system is at lower pH values. The taranakite formed is therefore either in an amorphous state or the amount produced is so small that it is not able to be detected by X-ray diffraction within a relatively short period of time.

The fact that crystalline taranakite can be synthesized at room temperature at pH 5 suggests that phosphate might be fixed by Akaka soil in amorphous form at the beginning, and then become crystalline as time goes on. In addition, whenever potassium fixation occurs in acid soils, it is possible that fixation is due to the formation of taranakite.

TABLE VII

AVERAGE pH VALUES OF THE FILTRATES OF PHOSPHO-SOIL  
 REACTION SYSTEMS FOR POTASSIUM PHOSPHATE  
 CONCENTRATION OF 0.25 M

pH value of phosphate solution	Days of standing	2	4	5	6	7	10
	2.0		2.3	2.3	2.3	2.3	2.3
2.5		2.6	2.6	2.6	2.7	2.7	2.6
3.0		4.1	4.1	4.1	4.2	4.1	4.1
3.5		4.6	4.6	4.6	4.6	4.6	4.6
4.0		5.1	5.1	5.1	5.1	5.0	5.1

TABLE VIII

pH VALUES OF THE FILTRATES OF PHOSPHO-SOIL  
REACTION SYSTEMS FOR POTASSIUM PHOSPHATE AT pH 2.0

Concentration of phosphate solution, molar	Days of standing					
	2	4	5	6	7	10
0.23	2.3	2.3	2.3	2.5	2.5	2.3
0.43	2.4	2.4	2.4	2.4	2.4	2.4
0.63	2.2	2.2	2.3	2.5	2.5	2.3



7. The Effect of Concentration on the Reaction of Potassium Phosphate and Alaska Soil Samples

Visual observations were made over a six day period of the relative amounts of crystalline taranakite formed with varying amounts of soil material and varying concentrations of phosphate solution. Table IX revealed that the amount of crystalline taranakite formed increased as the concentration of the phosphate solutions and the grams of soil material used increased. This phenomenon was observed only when phosphate solutions at pH 2 was used.

8. The Effect of Time on the Degree of Crystallinity of the Phospho-  
Reaction Product Produced from the Alaska Soil

It is generally known that Bragg's law,  $\lambda = 2d \sin \theta$ , was deduced by finding the conditions under which the waves reflected from all of one set of the planes in a crystal are in phase with each other. An appreciable amount of radiation will be scattered if there is incomplete reinforcement of the waves reflected by successive lattice planes. The possible deviation from Bragg's law is greater the smaller the crystal. For small crystals the deviations may be quite large, and the reflections which appear over a range of angles are said to be broadened (Henry, Lipscomb and Weester).

An attempt was made to relate the half-peak breadth of the  $15.7 \text{ \AA}$  peak with respect to time. Figure 4 shows that an inverse

TABLE IX

VISUAL COMPARISON OF THE RELATIVE AMOUNT\* OF  
TARANAKITE FORMED AS EFFECTED BY THE GRAMS OF  
SOIL AND THE CONCENTRATION OF PHOSPHATE  
SOLUTION AT pH 2, WHEN REACTED FOR SIX DAYS

Phosphate solution, molar	grams of soil		
	5	10	15
0.20			+
0.50	+	++	++
0.60	+	++	+++

\* (+) small; (++) moderate; (+++) abundant

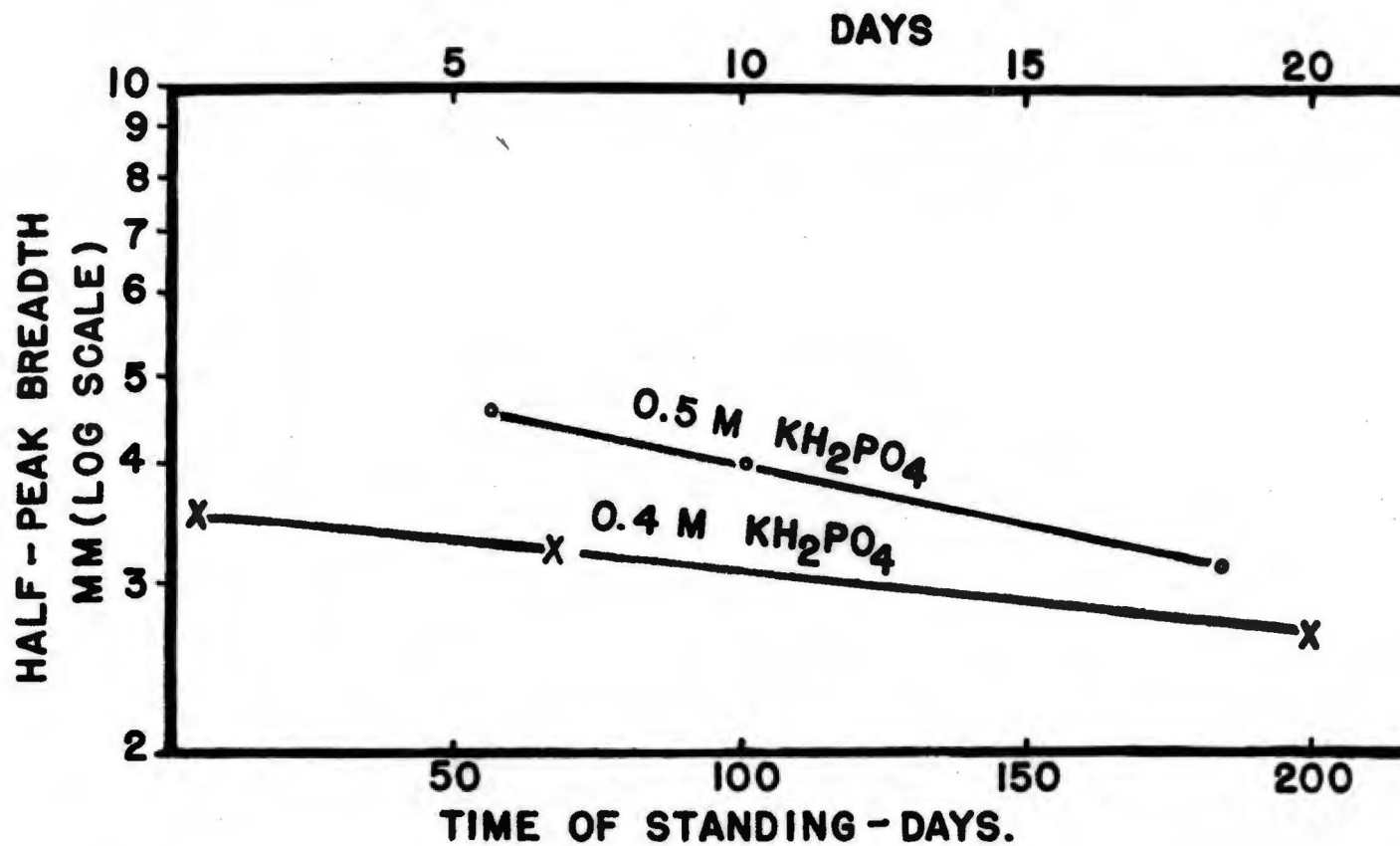


Figure 4

The Relationship of Half-peak Breadth with Respect to Time

relationship exists when the half-peak breadth (log scale) was plotted against time, indicating the growth of the crystalline size of the taranakite with time.

## SUMMARY AND CONCLUSIONS

Reaction products resulting from the addition of solutions of potassium phosphate at various pHs and concentrations to a Hydrol Humic Latosol in Hawaii were characterized. Characterizations were made by X-ray, chemical and optical methods, infra-red and differential thermal analysis in comparison with a synthesized taranakite.

1. Crystalline taranakite formed when the Akaka soil was treated with potassium phosphate solutions ranging from 0.2 to 0.6 molar and a pH value of 2.3 to 2.9 of the reacting system. On heating, the phosphate reaction products and synthesized taranakite gave similar dehydration products. Their X-ray diffraction patterns showed characteristic d-spacings of 12.6, 6.8, 5.8 and 3.4. The dehydration products were similar to the Product B synthesized by Haesman, J. P., Lehr, J. R. and Smith, J. P. (1980). Above 130° C, the taranakite became amorphous.
2. The taranakite was essentially a potassium aluminum phosphate complex. There was no indication of isomorphous substitution of iron for aluminum. The molar ratios of  $K/PO_4$  and  $Al/PO_4$  of the reaction product was estimated to be 0.37 and 0.72 respectively. These values agreed fairly well with the synthesized taranakite obtained in this study, and the one obtained by Smith and Brown (1989).

3. Optical analysis showed that the taranakite crystals were colorless and pseudohexagonal in form. They were biaxial negative. The refractive indices were  $n_{\alpha} = 1.504$ ,  $n_{\beta} = 1.507$  and  $n_{\gamma} = 1.509$  respectively,  $n_{\gamma} - n_{\alpha} = 0.005$ .
4. Structural diagnosis by means of infra-red spectroscopy of this potassium aluminum phosphate complex revealed that  $\text{PO}_4^{3-}$  (absorption bands between 1200 and 870- $\text{cm}^{-1}$ ), P-OH linkages (absorption near 2500- $\text{cm}^{-1}$ ) and water of crystallisation were present (absorption near 3400 and 1634- $\text{cm}^{-1}$ ). The infra-red spectra of the phospho-reaction product produced from Akala soil and synthesized taranakite were in good correspondence with that obtained by Arlidge, E. J., Farmer, V. G., Mitchell, B. D. and Mitchell, W. A. (1963) for taranakite.
5. Differential thermal data showed that both the phospho-reaction product and synthesized taranakite underwent endothermic reaction at about 230° C and exothermic reaction between 500 and 600° C which agreed well with the results obtained by Arlidge et al. (1963).
6. The pH value of the reacting system exerted a strong influence on the crystallisation of the phospho-reaction products. The fact that a pH value of 2.3 to 2.9 for the reacting system enhanced crystallisation of taranakite suggests that a soluble complex anion is formed by the reaction of free phosphoric acid and  $\text{H}_2\text{PO}_4^-$  ions with octahedral aluminum. This complex anion is

precipitated by potassium ion at a suitable pH value. In addition, the water can be driven off at a relatively low temperature. This indicates that the water molecules do not occupy any of the octahedral positions of the complex anion as the structural constituent.

7. Visual comparison of the relative amount of the crystalline reaction product formed during a six day period, showed that within the range of 0.2 to 0.5 molar potassium phosphate at pH 2, and for 5 to 15 grams of the wet Akaka soil, at room temperature, the amount of the crystalline product produced increased with increasing concentration of phosphate solutions and increasing grams of soil used.
8. There was evidence indicating that the logarithms of the half-peak breadth of the 15.7 Å peak of the phospho-reaction products were inversely related to reaction time. This shows that the degree of crystallinity of the reaction products increased with time.

In view of the results of X-ray, chemical, infra-red, differential thermal and optical analyses of the reaction product obtained from the soil-phosphate system, it is obvious that at the appropriate pH values, soil aluminum is rendered soluble. The soluble aluminum then reacts with phosphate and potassium in solution, and precipitates to form taranakite. It is suggested that taranakite can also be the final form when soluble potassium and phosphate react with Akaka soil in the field.

It is further believed that during the early stages of reaction, the reaction product is amorphous to X-rays.



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