Mineralogical Character of Some Iron and Aluminum Phosphates Containing Potassium and Ammonium

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The mechanisms through which phosphate is fixed in the soil are poorly understood, despite the many studies of the subject. In particular, more information is needed on the mineral combinations of fixed phosphate, especially combinations with iron and aluminum. Crystallographic and chemical data on iron and aluminum phosphates that might be expected in soils should facilitate the identification of soil phosphates. An indication of some of the types of phosphate minerals that may occur in soils can be obtained from fixation experiments in the laboratory and from a study of precipitated phosphates of iron and aluminum.

Cole and Jackson (4) precipitated crystalline dihydroxy dihydrogen phosphates of aluminum and iron by adding sodium hydroxide to acidic solutions of the metal chlorides that contained an excess of phosphate as the potassium or sodium salt. They concluded that the aluminum phosphate precipitates contained variscite and strengite, that the iron phosphate precipitates contained strengite, and that these minerals may result from the fixation of phosphate in the soil. The compound identified by Cole and Jackson as strengite, \( [\text{Al(OH)}_2]_2 \cdot \text{HPO}_4 \cdot \text{H}_2\text{PO}_4 \), gave an X-ray diffraction pattern corresponding to that of potassium aluminum phosphate \( \text{H} \) in the present work.

Haseman, Brown, and Whitt (8) obtained minerals related to tetrakite (2) [palmerite, \( \text{K}_2\text{Al}_3(\text{PO}_4)_3 \cdot 7\text{H}_2\text{O} \), (5)] by treating clays and hydroxides of iron and aluminum with acidic solutions of sodium, ammonium, and potassium phosphates. They also produced minerals of the variscite-barrandite-strengite isomorphic series by reacting clays and hydroxides of iron and aluminum with acidic solutions of calcium and magnesium phosphates. Minerals similar to tetrakite, variscite, and strengite were also obtained as precipitates by adding alkali and alkaline-earth hydroxides to strongly acidic solutions of aluminum phosphate and iron phosphate. It was concluded that tetrakite-like minerals, as well as variscite and strengite, may form in the soil when phosphate is fixed.

Several investigators have obtained results which indicate that tetrakite-like minerals form when aluminum and iron phosphates are precipitated or digested in the presence of sodium, potassium, or ammonium phosphate. Joffe and Kolodny (9) repeatedly wetted and dried iron and aluminum phosphates in the presence of potassium chloride and found that a large part of the potassium was fixed in a nonexchangeable form. Stout (12) treated halloysite with potassium phosphate and obtained a product that gave an X-ray diffraction pattern similar to tetrakite. Stout did not identify the compound. Ensminger (6) produced crystalline ammonium aluminum phosphates by treating clays and aluminum oxide with ammonium phosphate and by mixing solutions of aluminum chloride with solutions of ammonium phosphate. Cohen (3) added diammomium phosphate to ferric and aluminum chloride solutions and obtained double phosphates with the compositions \( \text{NH}_2\text{H}_2\text{PO}_4 \cdot \text{FePO}_4 \) and \( \text{NH}_2\text{H}_2\text{PO}_4 \cdot \text{AlPO}_4 \). Bannister and Hutchinson (2) studied several native tetrakites and stated that soil conditions

The present paper presents crystallographic and chemical information about some iron and aluminum phosphate minerals that may occur in the soil. Relatively crystalline iron and aluminum phosphates were prepared by precipitation and prolonged digestion, their composition and some of their mineralogical properties were determined, and the compounds were classified. Emphasis was placed upon the group of phosphates containing potassium or ammonium to iron or aluminum.

**PREPARATION OF THE PHOSPHATES**

Into 2 liters of a cool solution containing 10 g of hydrogen or aluminum chloride and 20 g of phosphate, there was slowly stirred a concentrated suspension of the hydroxide of potassium, ammonium, or magnesium; or the carbonate of lithium or cesium, until the pH was lowered to 3. The resultant precipitates were dispersed in 2 liters of distilled water, and remained in 100 or 200 ml of a phosphate salt solution of the alkaline-earth cation that was used in the precipitation. The precipitate was collected, dispersed in 2 liters of distilled water, and remaining 5 to 20 grams of the moist, washed precipitates were treated with mixed solutions of the alkali or alkaline-earth cation to standard solutions of orthophosphoric acid. In a few experiments, the precipitates were treated with mixtures of potassium phosphate and potassium fluoride.

The dispersion of the precipitate was sealed in Pyrex glass and digested from 1 to 54 days at a constant temperature. Treatments were made at several temperatures between 145° C. The dispersions were shaken occasionally.

The digested products were washed repeatedly with water and once with 80% ethyl alcohol. They were evacuated and then keto over calcium chloride at room temperature.

Each of the 150 preparations was examined under a microscope, and the optical properties of the crystals were determined. Most of the samples contained essentially one mineral phase. The crystallographic data were obtained by analysis of powder X-ray diffraction patterns. The density of some of the preparations was determined by the pycnometr method.

**CHARACTERIZATION OF THE PHOSPHATES**

Most of the products were well crystallized. The aluminum phosphate preparations generally contained one mineral species, whereas some of the iron phosphate preparations contained two or more types of minerals. Each crystal phase was easily recognized by its optical properties. When significant amounts of more than one phase were present in a preparation, a relative sample of the major phase usually could be removed on gleyation.