

COMPOSITIONAL CHANGES IN TRIPLE SUPERPHOSPHATE FERTILIZER GRANULES

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Abstract

Optical microscopy, X-ray diffraction, scanning electron microscopy and X-ray microanalysis have been used to study the compositional changes in Triple Superphosphate fertilizer granules upon incubation. The granules were placed in tropical soils with high phosphate retention capacity, either in immediate contact with soil or separated from soil by a thin layer of cow dung or sewage sludge. Granules were incubated under field conditions for periods of 3 and 20 weeks. After incubation a part of the granules was powdered and crystalline compounds were identified with X-ray diffraction. Another part was impregnated with a polyester resin and polished into sections of about 0.35 mm thickness. Various crystalline compounds within an amorphous matrix were observed using optical microscopy. In the scanning electron microscope backscattered electron images they appeared as bright areas within a grayish matrix. X-ray microanalysis with a windowless energy-dispersive detector was used to determine the elemental composition of both crystalline and amorphous compounds. Crystals containing O, P and Ca were identified by comparing the P/Ca peak ratios with those of calcium phosphate standards. X-ray maps were recorded to visualize the distribution patterns of main elements. Line profiles through granules were analyzed to determine the radial distribution of P and Ca.

Fluorapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ), brushite ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ) and an amorphous phosphorus compound were detected in the incubated granules. It is assumed that fluorapatite formation has occurred during incubation. Brushite was concentrated at the periphery of the granules. Compositional changes in the granules were similar under all incubation conditions.

KEY WORDS: Fertilizer Residue, Triple Superphosphate, Tropical Soils, Phosphate Retention, Backscattered Electrons, X-ray Microanalysis, Quantitative Analysis, Optical Microscopy, X-ray Diffraction, Windowless ED-detector.

Introduction

Granulated triple superphosphate was used in soil fertility experiments in South West Kenya. This fertilizer was chosen because it is the most important phosphate source used in Kenya. The study aimed at a more efficient utilization of phosphate fertilizers. Special attention was given to soils with a low availability of native phosphate and a high retention capacity of fertilizer phosphate. Knowledge of the dissolution of phosphate fertilizers and the subsequent transport and precipitation of phosphate in the soil will be beneficial to the improvement of fertilizers and application methods.

This study tried to follow the compositional changes in triple superphosphate granules during incubation in tropical soils and manures under field conditions. Literature on this subject has been reviewed by Olsen & Flowerday (1971). Most previous studies were restricted to monocalcium phosphate monohydrate, the main component of triple superphosphate. Few concerned commercial triple superphosphate granules, which usually contained minor quantities of other compounds as well. When monocalcium phosphate monohydrate is applied to moist soils, this crystalline phosphate rapidly dissolves. According to Lawton & Vomocil (1954) most of the dissipation and eventual precipitation of phosphate outside the granules is completed within 24 hours. Lehr et al. (1959) found that about 30% of the phosphate remained in the granules as dicalcium phosphate, while Lindsay et al. (1962) found the rest of the phosphate to be retained in the surrounding soil. Commercial triple superphosphate behaved similarly (Lehr et al.), but is less hygroscopic (Lawton & Vomocil) and consequently will show lower reaction rates. The presence of other components may influence the amount of phosphate and the nature of the phosphate compounds that remain in the granules (Bouldin et al., 1960).

With optical microscopy and X-ray diffraction the specimens were investigated mineralogically,

while scanning electron microscopy and X-ray microanalysis were used for chemical identification of phosphate compounds and for studying distribution patterns of phosphorus and other elements in fertilizer granules. For a recent review of quantification in X-ray microanalysis, see Boekestein et al. (1980).

#### Materials and Methods

##### Incubation

Commercial triple superphosphate granules with a diameter of ca 3mm (composition as given by the manufacturer see Table 1),

Table 1. Composition of triple superphosphate.

|   | Weight % |
|---|----------|
| $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ | 67.5     |
| $\text{Ca}(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$           | 5.0      |
| $\text{Ca}_3(\text{PO}_4)_2$                                  | 3.0      |
| $\text{H}_3\text{PO}_4$                                       | 7.5      |
| $\text{H}_2\text{O}$  | 3.0      |
| $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$                     | 2.0      |
| $\text{CaF}_2$  | 3.0      |
| $(\text{Fe,Al})_x(\text{SO}_4, \text{PO}_4)_y$                | 4.0      |
| (Al,Mg)-silicates   | 3.0      |
| $\text{SiO}_2$ and Ca-silicofluoride                          | 2.0      |

Source: Windmill laboratories, Vlaardingen, The Netherlands.

were placed at 7 cm below the soil surface, either in immediate contact with soil or separated from soil by a thin layer of cow dung or sewage sludge (composition)\*. Placement of the granules in the soil was done with a sharp-edged open fruit-juice can. The can was pushed in moist well-tilled soil. After lifting it up carefully, a column of soil remained in the can and a flat bottomed cylindrical hole was formed in the soil. Two grams of triple superphosphate granules were distributed over the bottom of this hole with a density of about 2 granules/cm<sup>2</sup>. Then the hole was filled up with soil. Either cow dung or sewage sludge was used in equal parts below and above the granules at a concentration of 100 cm<sup>3</sup>/hole. After the incubation the granules were excavated, collected, air-dried, sealed in plastic tubes and transported to the Netherlands.

Two kinds of soil\* were used in the experiments. One (Soil 1) was classified as a very fine clayey kaolinitic acid isothermic typic Paleudoll, and the other (Soil 2) as a fine clayey kaolinitic acid isohyperthermic typic Paleudoll (see Soil Taxonomy, 1975). Both soils differed in phosphate retention capacity and climatic conditions. Phosphate retention

\*For composition, see Discussion with Reviewers.

capacities were 27 and 14 mmol/kg dry soil for Soil 1 and Soil 2 respectively at a final phosphate concentration in the soil solution of 65  $\mu\text{mol/l}$ . The combinations with cow dung and sewage sludge were studied only in Soil 2. At Soil 1 the temperature at the level of the granules varied between 15°C and 25°C daily. During the incubation of 3 and 20 weeks rain fall was 110 mm and 900 mm respectively. At Soil 2 the temperature varied between 20°C and 30°C daily. During the incubation of 3 and 20 weeks rain fall was 160 mm and 850 mm respectively.

##### Optical Microscopy and X-ray Diffraction

Samples of fresh and incubated granules were impregnated with a polyester resin and polished into sections of 0.35 mm thickness. These sections, each with 10 and 15 granules, were scanned for crystalline compounds with a polarizing microscope. X-ray diffraction patterns of both fresh and incubated powdered granules were made with a Guinier camera and a Johansson monochromator using Co-K $\alpha$  radiation.

##### Scanning Electron Microscopy and X-ray Microanalysis.

Sections prepared as described above were mounted on aluminum stubs with carbon paste and coated with carbon to render the specimens conductive. Backscattered electron images were observed in the JEOL JSM-35 C scanning electron microscope at an accelerating voltage of 25 kV. The SEM was equipped with an energy-dispersive windowless X-ray detector (EDAX ECON) with an energy resolution of 152 eV and an elevation angle of approximately 10°. X-ray analysis was performed at 15 kV accelerating voltage and the specimen was tilted over 30° towards the detector. (Figs. 1-3)

The continuous background in the spectra was subtracted by a computer program of EDAX which calculated the shape of the background using a number of background points. The absorbed beam current was continuously monitored and proved to be highly constant. Semiquantitative information about the specimen composition was obtained by calculating the P K/Ca K $\alpha$  peak ratio on several areas along line profiles through the granules. These peak ratios were converted into molar ratios by comparing them with P K/Ca K $\alpha$  peak ratios of the following standards pressed into tablets:  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ,  $\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ,

Table 2. The P/Ca molar and peak ratio of a number of calcium-phosphate compounds.

| Compound   | P/Ca ratio |       |       |
|--|------------|-------|-------|
|  | molar      | peak  | S.D.  |
| $\text{Ca}_5(\text{PO}_4)_3\text{OH}$                          | 0.600      | 0.731 | 0.033 |
| $\text{Ca}_3(\text{PO}_4)_2$                                   | 0.667      | 0.790 | 0.007 |
| $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$                     | 1.000      | 1.244 | 0.010 |
| $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ | 2.000      | 2.279 | 0.034 |

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Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> · H<sub>2</sub>O. The P K/Ca Kα peak ratios and the <sup>32</sup>P/Ca molar ratios of the standards correlated highly (Correlation coefficient 0.9986, see Table 2).

Results

Optical Microscopy

The sections of both fresh and incubated granules, showed a colorless matrix with colorless fine-grained crystalline material and a number of larger colorless crystals (Table 3).

Table 3. The presence of crystalline compounds in sections of fresh and incubated triple super-phosphate granules after 3 and 20 weeks of incubation in soil, cow dung or sewage sludge. Bands, areas with new-formed lath-shaped crystals at the periphery of the granules.  $\Delta p/p \times 100$ , estimated mean fraction in % of the observed periphery covered with bands. Uniaxial crystals, crystals polished perpendicular to the c-axis. +) crystals are present. -) crystals are absent.

|                         | soil site 1 |          | soil site 2 |          | dung site 2 |          | sludge site 2 |          | fresh   |
|-------------------------|-------------|----------|-------------|----------|-------------|----------|---------------|----------|---------|
|                         | 3 weeks     | 20 weeks | 3 weeks     | 20 weeks | 3 weeks     | 20 weeks | 3 weeks       | 20 weeks | 0 weeks |
| granules in section     | 10          | 14       | 12          | 10       | 1           | 20       | 13            | 16       | 20      |
| granules with bands     | 4           | 1        | 1           | 1        | 1           | 10       | 7             | 1        | 0       |
| $\Delta p/p \times 100$ | 7.0         | 0.5      | 2.0         | 0.0      | 38.0        | 4.0      | 30.0          | 1.0      | 0       |
| uniaxial crystals       | +           | +        | +           | +        | +           | +        | +             | +        | +       |
| large lath crystals     | +           | -        | +           | -        | -           | +        | +             | +        | -       |
| tiny lath crystals      | +           | -        | +           | -        | -           | +        | +             | -        | -       |

In a number of cases the crystals were not properly orientated for optical analysis or were too small in size. In fresh and incubated granules, uniaxial negative, equant crystals, sometimes with hexagonal outlines were observed. They were up to 100 μm in size and were regularly distributed. Other crystals of variable shape and similar distribution pattern always showed birefringence and an oblique extinction.

At the periphery of some incubated granules new-formed lath-shaped crystals of 1 μm to 50 μm were observed. The crystals were grouped together in discontinuous small bands not wider than 100 μm (see Figure 3). Although this phenomenon was present in all incubated samples it was not observed in each granule. The estimated mean fraction of the observed periphery covered with bands is given in Table 3. The fraction decreased with prolonged incubation, and when in immediate contact with soil, bands were seen sporadically after 20 weeks. The occurrence of such crystals in bands was more pronounced in granules incubated in sewage sludge or cow dung. The crystals had a low birefringence, negative elongation and straight extinction. The axial angle could not be determined.

In a number of granules large lath-shaped

crystals with optical properties, similar to those of the new-formed crystals just described occurred as single crystals or small groups (see Figure 3). The crystals occupied not more than 15% of the observed area of a granule. After 3 weeks of incubation in both types of soil and in sewage sludge they were present in about 50% of the granules. The experiments with cow dung did not yield enough material for such an observation. After 20 weeks of incubation, they were present only in the granules which had been in contact with sewage sludge or cow dung. After 3 weeks of incubation in both types of soil, optically similar tiny lath-shaped crystals of about 20 μm were observed in some of the granules. After 20 weeks of incubation these crystals were observed in the experiment with cow dung only.

X-ray Diffraction

Monocalcium phosphate monohydrate was the only phosphate detected in samples of fresh granules. This compound was absent in samples of in-

cubated granules. From the intensities of the diffraction lines it followed that fluorapatite was one of the major compounds in samples of incubated granules.

Brushite (CaHPO<sub>4</sub> · 2 H<sub>2</sub>O) was detected in most samples of the incubated granules, but not in those of fresh granules. From the intensities of the diffraction lines it followed that the amount of brushite tended to decrease with prolonged incubation. After 20 weeks of incubation the brushite lines were rather weak. Incubation in soil, sewage sludge or cow dung did not produce obvious differences in the intensities.

Three non-phosphate minerals were observed in the X-ray diffractograms: anhydrite (γ CaSO<sub>4</sub>), gypsum (CaSO<sub>4</sub> · 2 H<sub>2</sub>O) and quartz (SiO<sub>2</sub>). Anhydrite and gypsum were seen as weak lines in samples of both fresh and incubated granules. Line intensities decreased with prolonged incubation and they were hardly visible after 20 weeks of incubation. Quartz was present in all samples and the apparent amount increased during incubation.

SEM and X-ray microanalysis

The X-ray maps of relevant elements, which were produced from the samples, did not show

distributions, in which an obvious radial pattern could be recognized. The distribution pattern thus obtained, was closely related to the distribution of the crystals (see Fig. 1 a-e). Incubation appeared not to have an influence on the element distributions. X-ray microanalysis showed that most of the crystals in the granules consisted of O, F, P and Ca. Crystals with O, S and Ca and crystals with O and Si were present in small amounts.

In order to investigate radial distribution patterns of P and Ca more precisely, the P and Ca peak intensities and the P/Ca peak ratio were followed along line profiles through the granules (Table 4). P and Ca peak intensities were considerably lower in the center of the granule, while the P/Ca peak ratio remained rather constant.

Table 4. The P K peak intensity, the Ca K $\alpha$  peak intensity and the P/Ca peak ratio along a line profile through a triple superphosphate granule incubated for 3 weeks.

| Location in the granule | peak intensity (cps) |               |       |
|-------------------------|----------------------|---------------|-------|
|                         | P K                  | Ca K $\alpha$ | P/Ca  |
| center                  | 70                   | 57            | 1.228 |
|                         | 131                  | 98            | 1.337 |
|                         | 131                  | 97            | 1.351 |
|                         | 136                  | 104           | 1.308 |
|                         | 132                  | 97            | 1.361 |
|                         | 149                  | 110           | 1.355 |
| periphery               | 268                  | 194           | 1.381 |

On the backscattered electron images of fresh and incubated granules (see Fig. 1 and 2) crystals of variable shape and size are visible. Few have a size of ca. 100  $\mu\text{m}$  with hexagonal outlines. These crystals consisted of O, F, P and Ca with the same P/Ca peak ratio as hydroxyapatite. The presence of F indicated that these crystals could be fluorapatite.

Crystals at the periphery of some granules of incubated samples were observed in the back-scattered images (see Fig. 3). In the X-ray spectra O, P and Ca were detected and the measured P/Ca peak ratio equalled the P/Ca peak ratio of the dicalcium phosphate standard. Identical P/Ca peak ratios were found for lath-shaped crystals in granules incubated for 3 weeks.

From the backscattered electron images it appeared that the crystals of both fresh and incubated granules were surrounded by an amorphous matrix. This amorphous matrix consisted of the major elements O, Al, P, Ca and Fe and the minor elements F, Na, Mg, Si, S and K. The peak intensities varied in the irregular matrix of fresh granules, but this variation diminished when incubation was prolonged for 20 weeks. Peak intensities of Na, Mg, S and K decreased and with prolonged incubation often no peaks were observed at all. In very homogeneous areas of the matrix of incubated granules peaks of O, F, Al, P, Ca and Fe were observed.

#### Discussion

Although brushite ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ), tricalcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ ) and fluorite ( $\text{CaF}_2$ )

were mentioned by the manufacturer as constituents of fresh triple superphosphate fertilizer granules (see Table 1), they were not found in the present study. Besides, fluorapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ), was found in small quantities in the fresh granules. As fluorapatite is the main component of Moroccan phosphate rock, the raw material for this triple superphosphate, its presence is probably a result of an incomplete acidulation.

Brushite was detected only in incubated granules and with SEM and optical microscopy it was found that brushite appeared as lath-shaped crystals both at the periphery and in the granules (Table 3). The disappearance of monocalciumphosphate monohydrate ( $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ ) as well as the formation of brushite ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ) during incubation are well known phenomena and are explained by Brown & Lehr (1959). With prolonged incubation brushite may dissolve and leach out of the granules. This probably explains the decreasing of brushite after 3 weeks of incubation.

Fluorapatite was found in both fresh and incubated granules as is evidenced by SEM and optical microscopy. X-ray diffraction analysis did not show fluorapatite in samples of fresh granules because the concentration was below the detection limit. Optical microscopy showed that fluorapatite appeared as uniaxial negative equant crystals or as crystals with similar sizes and an oblique extinction. The presence of a small amount of fluorapatite crystals in the fresh granules necessitates the hypothesis of a possible new-formation of fluorapatite during incubation. Fresh granules lose about 70 weight percent within 3 weeks of incubation. If fluorapatite is assumed to be insoluble, its amount in the residual granules is expected to increase about three-fold. The diffractograms of the fresh granules did not show lines of fluorapatite, whereas incubated granules showed very intense lines, so that we assume a new-formation of fluorapatite.

Favourable conditions for fluorapatite formation exist because of the presence of crystals, which may serve as nuclei for further crystal growth, and the occurrence of the necessary elements Ca, P, O and F in the amorphous dense matrix. However, the growth of already existing fluorapatite crystals is unlikely because of the similarity in size of the larger crystals in both fresh and incubated granules. New-formation of small crystals in the amorphous matrix is more likely as many of them could be detected in the incubated granules. Transformation of brushite into fluorapatite or in other basic calcium phosphates, such as  $\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{Ca}_3(\text{PO}_4)_2$  or  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  (Booth & Coates, 1961) probably did not occur, despite the high temperature, the humid conditions and the complete neutralization in the soil of acid produced in the dissolution and conversation of  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ , and in spite of the presence of F in the amorphous matrix of granules. There were indications that such transformations did not happen, as brushite remained throughout the entire incubation, the positions of brushite and fluorapatite crystals were not correlated, and no other basic calcium phosphates were found.

The amorphous matrix that remained as a

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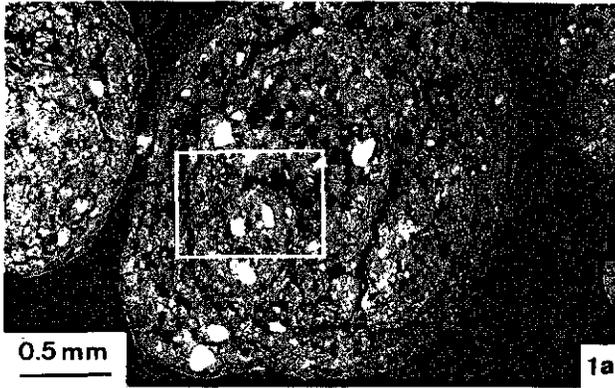


Fig. 1a. Backscattered electron image of a fresh granule.

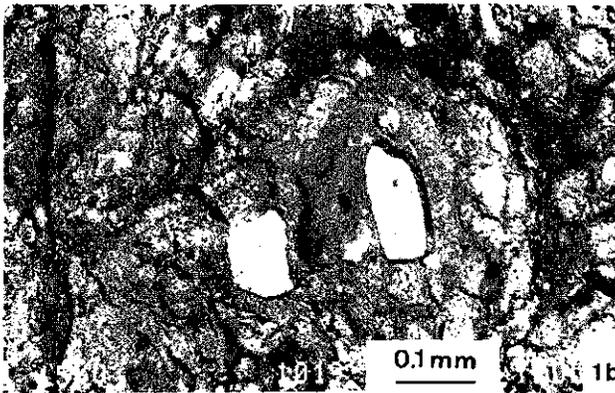


Fig. 1b. Backscattered electron image of a central area of a fresh granule (see Fig. 1a). The bright large crystal in the center (arrow) is a titanium oxide, a rare impurity in the granules.

Fig. 1c-1e. X-ray maps of Al, P and Ca of Fig. 1b are shown in Figures 1c, 1d and 1e.

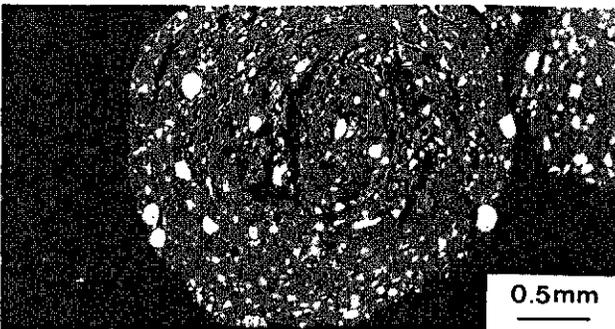
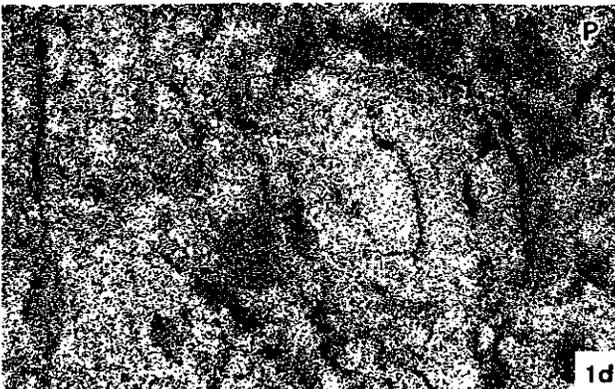
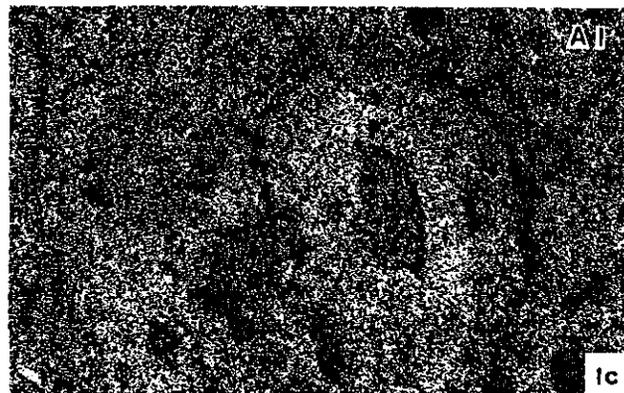


Fig. 2. Backscattered electron image of a granule incubated for 20 weeks in soil. To the right of the top of the granule a soil aggregate is present on the outside.

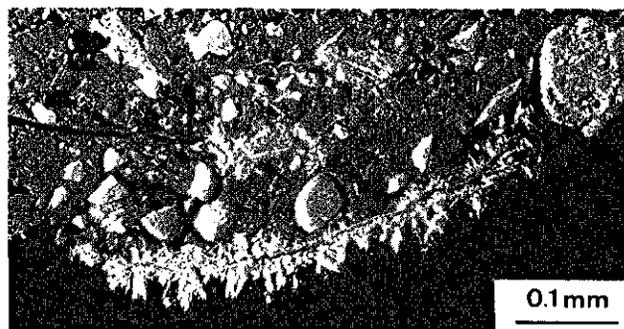


Fig. 3. Backscattered electron image of a peripheral area of a granule incubated for 3 weeks in soil.

major substance in the granules after incubation, consisted of elements that were already present in the fresh granules in comparable quantities. Therefore it is unlikely that these elements, especially Fe and Al were supplied by the surrounding materials. No obvious differences in chemical composition of the amorphous matrices were observed, when the granules were incubated in soil, sludge or cow dung for the same period. This assumes that the materials in which and the site where the granules were incubated, are of minor importance for the final composition of the amorphous matrix. The increase of P and Ca peak intensities towards the periphery of the granules can be partly explained by a decrease in porosity. Since P and Ca are present in both the crystalline and amorphous compounds, the concentrations of P and Ca will increase towards the periphery. Another reason is that brushite is concentrated at this periphery.

The presence of fluorapatite, brushite and amorphous matrices with similar phosphorus compounds in the incubated granules was not affected by the material in which and the site where they were incubated. Therefore we assume that the compositional changes in triple superphosphate granules are predominantly controlled by the intrinsic chemical properties of the fertilizer.

The phenomenon that part of the phosphorus remains in the granule after applying triple superphosphate in tropical soils with high phosphate retention capacities may be important for phosphorus fertilizer application practice. Since the residual granule is highly porous, favourable physical conditions are present in the granules for development of root hairs and for uptake of phosphorus directly from the granule. The conversion of easy soluble monocalcium phosphate monohydrate into less soluble phosphate compounds within 3 weeks of incubation, together with the good crop responses that were obtained with this readily convertible triple superphosphate fertilizer, make it worth studying the response and the benefit of directly applied Moroccan phosphate rock.

#### Acknowledgements

The authors would like to thank Mr. J. van Doesburg of the Department of Soil Science and Geology, Agricultural University, Wageningen, Netherlands, for performing the X-ray diffraction analyses and for interpreting the diffractograms, and Mr. C. J. van de Waal of the same department for the preparation of the polished samples. Mr. W. G. Wielemaker of the Subdepartment of Tropical Soil Science, Agricultural University, Wageningen, Netherlands, is gratefully acknowledged for the classification of the soils.

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#### Discussion with Reviewers

R.L. Fox: I would have liked to have seen the X-ray maps of Al, P and Ca from the granules incubated for 3 and 20 weeks in soil.

Authors: X-ray maps representing the elemental distribution of Al, P and Ca in the fresh and incubated granules were recorded initially and it appeared hard to distinguish between maps of incubated or fresh granules. Therefore we did not rely on X-ray mapping in the determination of differences in the distribution of elements in the granules.

Reviewer I: There are no chemical analysis data given on the cow dung or sewage sludge, or the amount of chemicals leachable from these materials. This data would be useful in evaluating the effect they had on the superphosphate.

Authors: ----- See Table 5.

Reviewer I: Could not a positive optical identification of the crystalline components in the granules be made by crushing the fertilizer pellets?

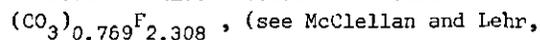
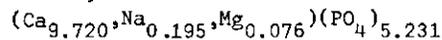
Authors: Optical identification will not improve by crushing the fertilizer pellets for the following reasons:

1. The size of the crystallites of the fertilizer pellets is such, that the determination of the optical axial angle is not possible.
2. The brushite crystals show elongation along the c-axis; a negative elongation with straight extinction.
3. A few fluorapatite crystals have hexagonal outlines and are large enough to determine the negative axial angle.

Reviewer I: The speculation based on X-ray diffraction, that there was an increase in the amount of apatite, should be backed up by more than increases in peak intensity. Was an internal standard used to quantify the X-ray analysis?

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Francolite, a variety of apatite, is the main phosphate in Moroccan phosphate rock, not fluorapatite. The distinction should be made between the two varieties since fluorapatite,  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ , is much less soluble than the francolite,



(see McClellan and Lehr, *American Mineralogist*, 1969) used in the production of the authors' triple superphosphate.

**Authors:** There was no internal standard used in the X-ray diffraction, but the analytical conditions were carefully controlled and remained constant. In future experiments we will certainly use an internal standard.

As can be concluded from a representative spectrum of a fluorapatite crystal, peaks of Na, Mg, Al, Si, K and Fe are present. The peaks are, however, very small in comparison with the peaks of O, F, P and Ca. The peaks of these trace-elements have not been quantified yet. The nomenclature of apatites is rather complex and has been controversial for a long time. It has often been found, that  $\text{Ca}^{2+}$ ,  $\text{P}^{5+}$ ,  $\text{O}_2^-$  and  $\text{F}^-$  have been substituted by ions of other elements. As many substituting elements are known and as the degree of substitution varies, apatites vary in chemical composition accordingly. Consequently, pure fluorapatite  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$  occurs rarely in nature. In this study, the fluorine containing apatites were called fluorapatites in order to distinguish them from hydroxy- and chlorapatites. The authors did not aim a further identification of the crystals. If, however, fluorapatite should be considered to be composed of Ca, PO, and F only and may not contain any trace of Na, Mg, Al, Si, K and Fe, then these fluorine containing apatite crystals should be named differently. To name them Francolite, a fluorapatite in which  $\text{Ca}^{2+}$  has been substituted by  $\text{Na}^+$  and  $\text{Mg}^{2+}$ , and  $\text{PO}_4^{3-}$  by  $\text{CO}_3^{2-}$  and  $\text{F}^-$ , is questionable either. Al, Si, K and Fe were identified in the fluorine containing apatite crystals, whereas these elements are considered to be absent in Francolite. Furthermore, the concentration of Na and Mg has not been determined yet, so it is unknown whether it lies between the defined limits for Francolite.

**F. Habashi:** This paper draws attention to the possible formation of fluorapatite during the application of triple superphosphate in the soil.

Fluorapatite was detected by SEM and optical microscopy in small amounts in the original sample but could not be identified by X-ray diffraction only because its concentration was below the detection limit. However, after application to the soil, intense X-ray diffraction lines due to fluorapatite appeared. The sample loses 70% of its weight when applied to the soil because of its water solubility. If fluorapatite was present in the original sample, its concentration in the residue should therefore increase three fold because of its insolubility in water, and this may be the reason that it could be detected by X-rays after application to the soil.

**Authors:** When the sample loses 70% of its weight during incubation, 30% of its weight remains as a residue. The intensity of the diffraction lines

then increases with a factor 100/30 due to the concentration effect. However, the increase in intensity was much more than 100/30 and therefore new-formation of fluorapatite is assumed.

**F. Habashi:** It is not clear why the authors think that more fluorapatite formed during incubation. In fact a simple but crucial test could answer the question: extract the sample with water and examine the residue by X-rays. Will an intense diffraction pattern of fluorapatite appear? If yes, then it is due to concentration effect. If no, then the soil plays a role in its formation.

**Authors:** The suggested test was carried out by the authors. Triple superphosphate was percolated continuously with water during 4 days in a previous experiment. In the X-ray diffraction pattern of the residue intense lines of fluorapatite appeared. The suggested test will always yield intense diffraction lines as a residual increase as well as a residual increase in combination with a new-formation will cause accumulation of fluorapatite. So the test will not discriminate between the two possibilities unless a very accurate quantification is carried out.

**M.L. Jackson:** The proposal for the direct application of Moroccan phosphate rock is only valid for acid soils.

**Authors:** The study of the response and benefit of directly applied Moroccan phosphate rock is meant not only for acid soils but for neutral and alkaline soils as well, because plants may alter some soil properties in the rhizosphere. If plants take up more equivalents of cations than anions, the pH in the soil solution will decrease. Consequently the P concentration in the soil solution will increase and  $\text{HPO}_4^{2-}$  will be transformed into  $\text{H}_2\text{PO}_4^-$  which is considered to be taken up more readily by plant roots. In addition, if plants utilize both Ca and P from phosphate rock, dissolution of calcium phosphates continues and if Ca and P are taken up in molar Ca/P ratios which are higher than those in the calcium phosphates, the P concentration in the soil solution will also increase.

Table 5. Composition of soils in terms of dry matter at 105°C, and composition of cow dung and sewage sludge at time of application in terms of dry matter at 70°C. CEC-Cation Exchange Capacity with ammonium acetate at pH 7.0. Ca, Al, Fe extractable with ammonium acetate/acetic acid at pH 4.8.

|                      | soil site 1 | soil site 2 | dung site 2 | sludge site 2 |
|----------------------|-------------|-------------|-------------|---------------|
| moisture wt%         |             |             | 156         | 15            |
| organic matter wt%   |             |             | 22          | 46            |
| C(organic) wt%       | 4.8         | 2.6         |             |               |
| P(total) mmol/kg     | 34          | 22          | 126         | 313           |
| P(water) mmol/kg     | 0.07        | 0.06        | 11          | 3             |
| P(Olsen) mmol/kg     | 0.10        | 0.10        |             |               |
| Ca(total) mmol/kg    | 71          | 54          | 168         | 367           |
| Ca(extract.) mmol/kg | 39          | 29          |             |               |
| Al(total) mmol/kg    | 3.8         | 2.8         |             |               |
| Al(extract.) mmol/kg | 2.8         | 1.1         |             |               |
| Fe(total) mmol/kg    | 1.7         | 1.5         | 1.5         | 0.5           |
| Fe(extract.) mmol/kg | <0.02       | 0.02        |             |               |
| CEC meq/kg           | 262         | 160         |             |               |
| pH(H <sub>2</sub> O) | 5.5         | 5.2         | 7.8         | 6.0           |
| pH(KCl 1 mol/l)      | 4.4         | 4.5         |             |               |

G.H. McClellan: The apatite in Moroccan phosphate rock is cryptocrystalline and can only be seen at high magnification in a SEM and usually is not visible in an optical microscope.

Authors: We did not study Moroccan phosphate rock. We suppose that during acidulation the fine crystalline material, which is referred to as cryptocrystalline apatite, is transformed completely. However, the few large apatite crystals with sizes up to 100  $\mu\text{m}$  which were found in fresh fertilizer granules, remained during the production of triple superphosphate.

G.H. McClellan: What is the source of fluorine to form fluorapatite.

A calculation of the data in table 1 shows that only about 1% to 1.5% F is in this sample and an equally low amount of S. I would like to see the spectra of these analyses since they represent a significant analytical accomplishment in a difficult and complicated system.

Authors: The source of F is the fertilizer granule itself. The presence of F is illustrated in figure 4.

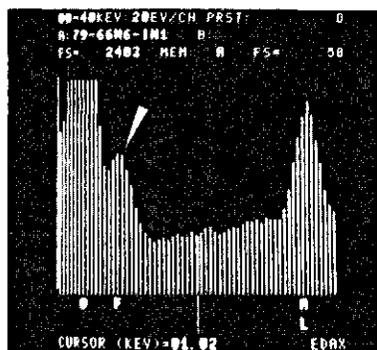


Fig. 4.

G.H. McClellan: How does a BSE image distinguish between crystalline and non-crystalline areas?

Authors: With a BSE image of flat specimen surfaces as used in this study only a discrimination is obtained between relatively high mean atomic number areas and relatively low mean atomic number areas. However, we used our crystallographic results obtained with optical microscopy in interpreting the BSE image.