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(54) Title: SLOW RELEASE FERTILIZER AND ACTIVE SYNTHETIC SOIL

(57) Abstract

A synthetic soil/fertilizer for horticultural application having all the agronomists essential for plant growth is disclosed. The soil comprises a synthetic apatite fertilizer having sulfur, magnesium and micronutrients dispersed in a calcium phosphate matrix, a zeolite cation exchange medium saturated with a charge of potassium and nitrogen cations, and an optional pH buffer. Moisture dissolves the apatite and mobilizes the nutrient elements from the apatite matrix and the zeolite charge sites.
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SLOW RELEASE FERTILIZER AND
ACTIVE SYNTHETIC SOIL

Origin of the Invention

The invention described herein may be manufactured and used by
or for the Government of the United States of America for governmental
purposes without the payment of any royalties thereon or therefor.

Field of the Invention

The present invention relates to an active synthetic soil for
horticulture. More particularly the present invention relates to an active
synthetic soil made from synthetic apatite and natural zeolite having a
complete spectrum of agronutrients necessary for plant growth.

Background of the Invention

Synthetic soils for horticulture (i. e., solid substrates for plant
support) include two general categories—inert and active. Inert
substrates are commonly used in nutriculture (e. g., hydroponics) and
are designed to provide mechanical support, proper root aeration and
drainage. Quartz sand is a good example of an inert soil. Plant
nutrients are added separately as, for example, liquid fertilizers such as
Hoagland's solution. Soils which are defined as "active" have the ability
to provide nutrient retention and release (i. e., incorporate fertilizing
capability) in addition to the other primary soil functions of the above
mentioned inert soils.

It is known that nutrient retaining activity in natural soils is due to
the presence of organic matter and clay components. Such components
have charge sites suitable for ion exchange. Prior to release, the
nutrient elements are held at the charge sites as "exchange ions."
Recent introduction of ion exchange media (that are not normally found
in natural soils) having a high exchange ion holding capacity have made
feasible the development of active synthetic soil-fertilizers which can
supply plant nutrients over a long period of time.

Mineral zeolites have been found to be a class of very useful ion
exchange media. Many natural species are prevalent and numerous
synthetic species have been made in the laboratory. Zeolites are
hydrated aluminosilicates of alkali and alkaline-earth cations that
possess infinite, three-dimensional crystal structures (i.e.,
tectosilicates). The primary building units of the zeolite crystal structure are (Al, Si)O₄ tetrahedra. When Al³⁺ and sometimes Fe³⁺ substitute for Si⁴⁺ in the central cation position of the tetrahedron, a net-negative charge is generated. This negative charge is counterbalanced primarily by monovalent and divalent "exchange cations." Zeolites have shown the ability to exchange most of their constituent exchange cations as well as hydrate/dehydrate without major changes in the structural framework. Most zeolites have large channels and/or cages that allow exchange cations easy access to charge sites and provide unique cation selectivity.

The use of zeolites as a major soil component has a relatively recent past. U. S. Patent 4,337,078 to Petrov et al. describes the use of a natural zeolite clinoptilolite with vermiculite and peat in a synthetic soil. The term zeaponics has been coined to describe synthetic soils containing zeolites in horticulture.

Agronomists and botanists have long recognized the vital function of sixteen nutrients needed by growing plants including the trace elements or micronutrients — zinc, chlorine, iron, manganese, copper, molybdenum and boron. It is also known that the optimal spectrum and concentration of micronutrients in a particular soil can vary depending on the plants being grown, soil properties, climate, and the stage of the plant growth cycle.

While most natural soils contain micronutrients at least to some extent and the overall need is small, depletion can occur with intensive agricultural activity. Even when the soil concentration is putatively adequate, other factors can prevent micronutrient uptake by the plant. Since micronutrients must be available as soluble ions, such ions can be immobilized in low solubility alkaline soils and/or can be trapped on clays or organic materials as insoluble complexes.

It has been common practice to supplement phosphorus-impoverished soil by using a mineral fertilizers such as rock phosphate or natural apatite. Such minerals, however, do not supply the required micronutrients and can contain toxic elements such as fluorine and cadmium.

Rock phosphate as mined is relatively insoluble in water. Therefore, the raw product is generally pretreated to enhance phosphate solubility prior to use. Such processes, however, are considered too
expensive for farmers in underdeveloped nations. Yet, fertilizer use is necessary to promote economic development.

Summary of the Invention

The present invention provides a synthetic soil and fertilizer composition for horticulture which contains an entire spectrum of nutrients essential for plant growth. The soil combines a cation exchange medium charged with ammonium and potassium exchange cations and a synthetic apatite composition comprising magnesium, sulfur and plant micronutrients. The synthetic apatite unlike natural varieties is essentially free of toxic elements. The presence of moisture mobilizes the plant nutrients at a slow, steady rate. In addition, the nutrient release rate can be closely tailored to the horticultural requirements. These features and others offer potential for use in lunar agriculture applications.

In one embodiment, the present invention provides a slow-release fertilizer. The fertilizer is made from a synthetic apatite comprising matrix of calcium phosphate having a dispersion of one or more agronutrients and a cationic exchange medium having a charge of one or more agronutrients. The apatite and cationic exchange medium are preferably essentially free of agrotoxins, such as, for example, fluorine, cadmium and sodium, in amounts detrimental to the growth of most plants. Agronutrients include, for example, potassium, ammonium-nitrogen, magnesium, sulfur, zinc, chlorine, iron, manganese, copper, molybdenum and/or boron. The fertilizer can further include a pH buffer to maintain a pH balance of from about 5.5 to about 7. The cationic exchange medium can comprise natural or synthetic zeolite, phyllosilicate or a combination thereof including clinoptilolite, chabazite, mordenite, phillipsite, Linde type A, Linde type X, vermiculite, smectite or a combination thereof. The cation exchange medium has a cation exchange capacity (CEC) of at least 50 cmolc/kg, preferably at least 100 cmolc/kg, and more preferably at least 150 cmolc/kg. The cation exchange medium preferably has a charge of ammonium and potassium ions at a weight ratio of from about 1 to about 5:1 of ammonium:potassium. The fertilizer preferably comprises from about 5 to about 100 parts by weight of the synthetic apatite per 100 parts by weight of the cationic exchange medium.
In another embodiment, the present invention provides a horticultural method. In one step, a botanical species is planted in a sufficient amount of the fertilizer composition described above. In another step, the fertilizer is contacted with moisture to mobilize the agronutrients.

In a further embodiment, the present invention provides a method of making an active synthetic fertilizer. In one step, a synthetic apatite is prepared by admixing in an aqueous medium from about 1.0 to about 1.6 moles per liter of a soluble ionic calcium compound and a solution mixture comprising from about 0.5 to about 0.8 moles per liter of a soluble ionic phosphate compound and an agronomic amount of, one or more soluble agronutrients selected from magnesium, zinc, sulfur, chlorine, iron, manganese, copper, molybdenum and boron to form a crystalline calcium phosphate precipitate having agronutrients dispersed therein. The precipitate is recovered, dried and suitably granulated. As another step, individual zeolite portions are charged with ammonium and potassium cations to displace native cations. The precipitate is blended with the charged zeolites at a proportion of from about 5 to about 100 parts by weight of the precipitate per 100 parts by weight of the ammonium and potassium charged zeolites. The weight ratio of ammonium charged zeolite to potassium charged zeolite is from about 1 to about 5:1. The zeolite is preferably clinoptilolite. The fertilizer blend preferably includes from 0 to about 10 parts by weight of a pH buffer per 100 parts by weight of the ammonium and potassium charged zeolites.

**Brief Description of the Figure**

The Figure shows diffractographs with peak spacing for three different synthetic apatite compositions of the present invention. The diffractographs indicate that the present synthetic apatite has a crystalline structure similar to naturally occurring hydroxyapatite and carbonate hydroxyapatite.

**Detailed Description of the Invention**

An entire spectrum of essential agronomic nutrients including nitrogen, potassium, magnesium, sulfur and micronutrients are incorporated into an active synthetic soil for horticulture. Upon contact by moisture, the nutrients are slowly released, as required, for plant use.
In addition, a fertilization rate can be controlled and the soil tailored to horticultural needs.

The major component of the synthetic soil composition is a synthetic apatite fertilizer. The apatite has a calcium phosphate matrix which is at least slightly soluble in water. Water solubility is necessary to give mobility to nutrient elements contained in the apatite matrix. Examples of suitable calcium phosphates include dicalcium orthophosphate (CaHPO₄), monocalcium orthophosphate (Ca(H₂PO₄)₂), tricalcium orthophosphate (Ca₃(PO₄)₂), hydrates thereof and calcium pyrophosphate pentahydrate (Ca₃P₂O₇·5H₂O). Preferably, from about 30 to about 50 parts by weight phosphorus are used per 100 parts calcium, and more preferably, from about 40 to about 45 parts by weight phosphorus per 100 parts calcium.

One or more essential agronomic nutrients besides calcium and phosphorus are dispersed within the crystal structure of the synthetic apatite. Essential agronomic nutrients (agronutrients) in addition to calcium and phosphorus, include potassium, nitrogen, magnesium, sulfur, zinc, chlorine, iron, manganese, copper, molybdenum and boron. The latter seven elements (zinc, chlorine, iron, manganese, copper, molybdenum and boron) are generally referred to as micronutrients and are needed by plants in lower amounts than the other essential agronutrients.

Agronutrients are provided in the present composition as water soluble inorganic (ionic) compounds. The inorganic compounds should not have acute toxicity (e.g. cyanide salts), or other undesirable properties and should be free of excessive amounts of agrotoxins including unwanted elements and organic toxins. Undesirable elements typically include most heavy metals such as lead, cadmium, mercury, and the like, and other elements such as fluorine, sodium, arsenic, antimony, selenium, tin, and the like. The synthetic apatite can, however, contain a relatively small amount of any of these toxins below a toxic level for plants and, where appropriate, grazing animals. For example, natural apatite contains about 6 percent fluorine and has only limited potential as a soil supplement because of the fluorine toxicity, particularly to grazing animals such as sheep which can ingest the fluorine, e.g. by licking the soil containing the supplement. Prior art phosphatic fertilizers, in contrast, can contain about 3000 ppm fluorine, whereas natural soils average about 300 ppm and plants typically
contain about 3 ppm fluorine. Thus, the present synthetic apatite composition should generally contain no more than 10 parts fluorine per 100 parts calcium, by weight, but preferably contains no more than 3000 ppm fluorine, more preferably no more than 300 ppm, and especially no more than 3 ppm. Tolerance levels of specific plants and animals for other agrotoxins can be found in the literature or determined empirically. The amount of agrotoxins in the synthetic apatite should be less than an amount which would result in release into the environment of the agrotoxins in excess of a given tolerance level.

Examples of suitable water soluble compounds of agronutrients used in the preparation of the synthetic apatite include potassium compounds such as potassium chloride, potassium nitrate, potassium nitrite, potassium sulfate, and potassium phosphate; magnesium compounds such as magnesium nitrate, magnesium chloride, magnesium nitrite, magnesium chlorate, magnesium perchlorate and hydrates thereof; sulfur compounds such as sodium sulfate, ammonium sulfate, potassium sulfate, and hydrates thereof; zinc compounds such as zinc chloride, zinc nitrate, zinc nitrite, zinc sulfate and hydrates thereof; chlorine compounds such as sodium chloride, potassium chloride, ammonium chloride; iron compounds such as ferric nitrate, ferrous nitrate, ferrous nitrite, ferric nitrite, ferric chloride, ferrous chloride, ferric sulfate, ferrous sulfate and hydrates thereof; manganese compounds such as manganese(II) nitrate, manganese(II) nitrite, manganese dichloride, manganese(II) sulfate and hydrates thereof; copper compounds such as copper(II) chloride, copper(III) chloride, copper(II) nitrate, copper(II) nitrite and hydrates thereof; molybdenum compounds such as ammonium paramolybdate, ammonium permolybdate, sodium trimolybdate, sodium tetramolybdate, sodium paramolybdate, sodium octamolybdate, potassium molybdate and hydrates thereof; and boron compounds such as sodium tetraborate, sodium metaborate, potassium tetraborate, potassium metaborate, ammonium tetraborate, hydrates thereof and orthoboric acid. The preferred, more preferred and optimum amounts of the agronomic nutrient elements per 100 parts calcium in the synthetic apatite, are set forth in Table 1.
The synthetic apatite composition can also comprise a silicon and/or carbonate solubility control agent dispersed in the apatite matrix.

The solubility control agent increases or decreases the water solubility and permits enhanced control over the rate at which nutrient elements are released. The effect of carbonate content on natural apatites is described in several publications including Caro, J., Journal of Agricultural Food Chemistry, 4:684-687, 1956; McClellan, G., American Mineralogist, 54:1374-1391, 1969; and Lehr R., National Fertilizer Development Center Bulletin, Y-43, Vol. 8 published by the Tennessee Valley Authority, Muscle Shoals, Alabama which are hereby incorporated herein by reference.

The solubility control agent is provided in the synthetic apatite composition as a water soluble inorganic or organic compound. Examples of suitable water soluble carbonate compounds include sodium carbonate, sodium bicarbonate, ammonium carbonate, ammonium bicarbonate, potassium carbonate and potassium bicarbonate. Examples of water soluble silicon compounds include inorganic silicates such as sodium silicate, sodium disilicate, sodium metasilicate, sodium orthosilicate, potassium disilicate, potassium metasilicate, potassium hydrogen disilicate, ammonium silicate, and hydrates thereof, and organic silicates such as ethyl orthosilicate and propyl orthosilicate.

A solubility control agent can comprise from 0 to about 15 parts by weight per 100 parts calcium. A carbonate agent is preferably used in an amount of 0 to about 15 parts by weight per 100 parts calcium,
more preferably from about 2 to about 10 parts by weight and optimally from about 4 to about 6 parts by weight. A silicon agent is preferably used in an amount of 0 to about 10 parts by weight per 100 parts calcium, more preferably from about 2 to about 6 parts by weight and optimally from about 3 to about 5 parts by weight.

The present synthetic apatite composition can optionally include a binder agent to assist processing of the calcium phosphate into pellet form. Examples of such processing aid binders include calcium-lignosulfonate, cellulose, and the like. The binder comprises from 0 to about 10 percent by weight or more of the synthetic apatite.

The present synthetic apatite composition is the precipitated product of a water soluble calcium compound and a water soluble phosphate mixture comprising a water soluble phosphate compound and one or more water soluble agronutrients. The resulting product has nutrient elements incorporated into the structure of the calcium phosphate matrix.

The second component of the present synthetic soil is a cationic exchange medium saturated with a charge of exchange cations of one or more agronutrients. Suitable cationic exchange media have a cation exchange capacity (CEC) greater than about 50 cmolc/kg. Cationic exchange media preferably have a CEC of at least about 100 cmolc/kg, but more preferably at least about 150 cmolc/kg. In addition, suitable cationic exchange media are substantially chemically inert, have low solubility in water and are essentially free of elements toxic to plant growth.

A most preferred class of suitable cationic exchange media are mineral zeolites. Zeolites as mentioned previously are hydrated aluminosilicates of alkali and alkaline-earth cations that possess infinite, three-dimensional crystal tetrahedral structures. Natural zeolites are a common mineral matter widely found in a relatively pure state. Synthetic zeolites have also been manufactured. Zeolites generally have a theoretical CEC of from about 200 cmolc/kg to about 600 cmolc/kg or more for some synthetically produced varieties.

Representative examples of common natural zeolites include clinoptilolite (Na₃,K₃)(Al₆Si₃₀O₇₂)·2₄H₂O, chabazite (Na₂,Ca)₆(Al₁₂Si₂₄O₇₂)·4₀H₂O, mordenite Na₈(Al₈Si₃₀O₉₆)·2₄H₂O, phillipsite (Na,K)₅(Al₅Si₁₁O₃₂)·2₀H₂O, and the like.
Representative examples of synthetic zeolites include Linde Type A \( \text{Na}_{96}\{\text{Al}_{96}\text{Si}_{96}\text{O}_{384}\}\cdot216\text{H}_2\text{O} \), Linde Type X \( \text{Na}_{88}\{\text{Al}_{86}\text{Si}_{106}\text{O}_{384}\}\cdot264\text{H}_2\text{O} \), and the like.

Due to desirable sand-like mechanical properties, a high degree of internal tunneling for favorable nutrient retention capacity and relative abundance in nature, a most preferred natural zeolite is clinoptilolite which is widely found in a relatively pure state. Clinoptilolite has been found to have good drainage and water holding characteristics, and a high theoretical cation exchange capacity of about 200 cmol/\(\text{kg}\). Clinoptilolite also has a high affinity for \(\text{NH}_4^+\) and the ability to hold the ion internally away from nitrifying bacteria. Hence nitrification rates are slow and the amount of leached N is low. Clinoptilolite is commercially available as sand-sized particles.

While zeolites are preferred cationic exchange media, other types can be used. Examples of other natural mineral exchange media are phyllosilicate clays such as vermiculite and smectite. Ion exchange resins can also be used though more expensive. For convenience of illustration, the cationic exchange medium will be referred to hereinbelow as the preferred but non-limiting zeolite embodiment.

The zeolite in the present synthetic soil is wholly or partially saturated with a charge of exchange cations of one or more agronomic nutrients so that existing native cations such as \(\text{Na}^+\) are replaced with the desired agronutrient cations. Applicable agronutrients which can be charged on the zeolite generally include potassium, ammonium, manganese(II), zinc, iron(II), copper(II), calcium and magnesium.

Selectivity (i.e. retention capacity) of exchange cations can vary depending on the type and variety of the cation exchange medium in question. However, as a rule of thumb, the adsorption selectivity in clinoptilolite favors monovalent exchange cations over divalent cations and among these, ion selectivity generally decreases with increasing ion hydration radius. For a clinoptilolite sample mined in the Wyoming region, selectivity for agronutrients and sodium was determined as follows: potassium > ammonium > sodium > manganese(II) = copper(II) = iron(II) > zinc > calcium > magnesium.

In the practice of the present invention, the zeolite is preferably saturated with ammonium and potassium cations (totally replacing native cations) at a weight ratio of from about 1 to about 5:1 of ammonium:potassium. As used herein, agronomic nutrients saturated
on the zeolite will be referred to by the preferred but non-limiting potassium and ammonium embodiment.

The present soil comprises from about 5 to about 100 parts of the synthetic apatite per 100 parts by weight of the K⁺, NH₄⁺ saturated zeolite.

A third optional but preferred component of the present soil composition is a pH buffer to maintain a soil pH in the range of from about 5.5 to about 7. Examples of suitable pH buffers include weak acids (e.g., humic acid). The pH buffer is used at from about 0 to about 10 parts per 100 parts by weight of the K⁺, NH₄⁺ saturated zeolite.

The synthetic apatite is conveniently made, for example, by preparing two or more aqueous stock solutions containing the appropriate compounds and mixing the stock solutions together. An inorganic replacement reaction occurs in the solution mixture to produce a precipitate. The precipitate can be recovered, e.g., by filtration, and dried.

A first stock solution is made by dissolving a suitable quantity of the water soluble calcium compound in a neutral or basic aqueous medium. Examples of suitable calcium compounds include calcium nitrate, calcium nitrite, calcium chloride, calcium chlorate, hydrates thereof, and the like. Calcium nitrate tetrahydrate is a preferred compound. The first solution preferably includes the calcium compound in an amount of from about 1.0 to about 1.6 moles per liter.

A second stock solution is prepared by dissolving a suitable quantity of the soluble phosphate compound and suitable quantities of the soluble anionic nutrient compound(s) in a neutral or basic aqueous medium. Examples of suitable soluble phosphate compounds include ammonium orthophosphate-mono-H, ammonium orthophosphate-di-H, ammonium orthophosphate, ammonium hypophosphatate and the like. The second solution preferably includes the phosphate compound in an amount of from about 0.5 to about 0.8 moles per liter. The amount of anionic nutrient compound(s) in the second solution will depend on the desired concentration in the synthetic apatite end product which, in turn, will depend on the agronomic application. Generally, the second stock solution can include one or more anionic nutrient compounds each in an amount of from about 0.002 to about 0.4 moles per liter.

A third stock solution is prepared, where appropriate, by dissolving a suitable quantity of the soluble cationic nutrient
compound(s) in a neutral or basic aqueous medium. The quantity of the
cationic nutrient compound(s) in the third solution will again depend on
the desired concentration in the synthetic apatite end product which, in
turn, will depend on the agronomic application. Generally, the third
solution includes one or more cationic nutrient compounds, each in an
amount of from about 0.05 to about 5 moles per liter.

The optional silicon and/or carbonate solubility control agent can
be added to the second (anionic) stock solution in an amount of from
about 0.002 to about 0.4 moles per liter.

When preparing the above stock solutions, it is desirable to avoid
mixing salts together which can undergo unwanted inorganic
replacement reactions in the stock solutions. Therefore, ionic
compounds having a desired component element in the anion are held in
solution separately from ionic compounds having a desired
component element in the cation. Liquid organic compounds (e. g. ethyl
orthosilicate), however, can be added to any of the stock solutions or
added separately before or after the stock solutions are mixed together.

A preferred basic aqueous medium comprises a solution of from
about 18 to about 30 percent by weight of ammonium hydroxide in
deonized water. A preferred neutral aqueous medium comprises
deonized water.

Typically, the third stock solution is mixed with the second stock
solution and the combined solution is then mixed with the first stock
solution. The resulting mixture is then maintained at ordinary
temperature and pressure for a sufficient time period for the crystalline
precipitate to form.

The precipitate is recovered by ordinary means, such as, for
example, by decanting the supernatant and filtering in a Büchner funnel.
The precipitate is preferably washed with deionized water.

The washed precipitate can be dried at room temperature.
Preferably, however the precipitate is dried at a temperature ranging
from about 200°C to about 600°C for a time period of from about 2 to
about 20 hours in drying equipment such as an oven, wherein the
temperature is preferably boosted in steps of 200°C after 2 hour
intervals. The drying procedure can simultaneously dry the precipitate
and dehydrate or partially dehydrate the calcium phosphate endproduct.
Solubility is also partially dependent on the degree of hydration of the
calcium phosphate crystals, i. e., crystal size and degree of crystallinity.
Since solubility is reduced by dehydration, the drying procedure specified can be used to adjust the solubility of the final product. The actual drying procedure used is not particularly critical so long as care is exercised in obtaining the desired degree of dehydration. The dried precipitate is preferably cooled in a low humidity environment.

The precipitate can be crushed, granulated or pelletized by conventional means to produce a suitable particle size for use in soil treatment. Binding agents can be used to assist the formation of a relatively consistent granulation particle size and avoid the production of fines. Preferably, non-reactive binders are used.

As indicated above, the type of nutrient elements incorporated into the calcium phosphate crystal structure can vary from a single nutrient element to all seven micronutrients as well as potassium, sulfur, and magnesium. The quantity of each nutrient element incorporated can be specified based on the agronomic factors involved.

Prior to use, native cations of the zeolite exchange medium are replaced with cations of agronutrients, preferably NH$_4^+$, K$^+$ as mentioned above. Various methods can be employed. Generally, zeolite particles having a size from about 50 mm to about 1000 mm are preferably divided into individual portions for each agronutrient used. Each portion is then preferably individually charged with the desired agronutrient until saturation. The agronutrient charge is conveniently provided by a sufficiently concentrated (e.g., 1 M) aqueous solution of an ionic compound such as a chloride, nitrate, sulfate, and the like of the agronutrient. Typically, the zeolite and nutrient solution are contacted at a suitable weight ratio, such as, for example, from about 1:2 to about 1:5 zeolite:nutrient solution. To ensure that the exchange sites of the zeolite are saturated with the agronutrient, the mixture is preferably agitated in a suitable vessel for a period of time such as 24 hours, the solution is decanted, and the zeolite is washed an additional two times with the appropriate solution. Afterward, the supernatant is decanted and the zeolite is washed with deionized water to remove excess nutrient solution. The wash supernatant can be tested with an indicator compound to determine the presence of excess solution in the zeolite.

Silver nitrate, for example, is a good indicator for chloride ions.

After each portion of the zeolite is saturated with the desired agronutrient charge and excess solution is removed, the saturated zeolites are dried in an oven, for example, at a temperature on the order
of 105°C for a time period on the order of 24 hours. Once dried, the synthetic apatite and various saturated zeolite components can be dry blended in suitable equipment at a desired ratio.

When the instant synthetic soil comes in contact with moisture, nutrient elements become mobilized as the apatite is dissolved. As a first step, nutrients dispersed in the apatite matrix (magnesium, sulfur and micronutrients in addition to phosphorus and calcium) are slowly released as dissolution proceeds. Calcium ion production is adsorbed by the zeolite which acts as a Ca$^{2+}$ sink. Removal of Ca$^{2+}$ from the solution phase shifts the equilibrium towards increased apatite dissolution and phosphate fertilization in the soil. Adsorbed calcium ions compete with the K$^{+}$ and NH$_4^+$ ion charge at zeolite exchange sites causing the release of K$^{+}$ and NH$_4^+$ into the soil. The pH buffer maintains a mildly acidic soil pH to further assist the rate of apatite dissolution and nutrient release.

Desired apatite solubility and nutrient release rate are usually determined empirically based on type of plant being grown, growth cycle requirements, and the like agronomic factors.

The present fertilizing soil can be used in conventional agronomic applications by direct addition by conventional means to a suitably prepared field but is preferably used in horticultural applications such as zeponics and hydroponics.

The present synthetic soil has potential for lunar applications since zeolite synthesis from minerals found on the moon is thought to be feasible. Furthermore, plant-essential elements occur in trace quantities in lunar rock and can be extracted.

To conduct a zeponics culture, for example, a suitable greenhouse or culture environment has the present synthetic soil and fertilizer appropriately blended and spread to a sufficient depth to support the root structure of seedlings planted therein. The soil is kept moist to fertilize the plants.

The present invention is further illustrated by the following examples:

**Examples 1-3**

Three synthetic apatite compositions having nutrient elements incorporated into the crystalline structure were synthesized by an inorganic replacement reaction to simulate a naturally occurring
hydroxyapatite mineral. Initially, three stock solutions (A, B and C) were prepared using laboratory reagent grade chemicals. Each reaction was run using 500 ml of stock solutions A and B and 20 ml of stock solution C. The composition of the solutions is shown in Table 2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solution A (0.5 liters 20 wt % NH₄OH in deionized water)</th>
<th>Solution B (0.5 liters 20 wt % NH₄OH in deionized water)</th>
<th>Solution C (20 ml deionized water)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Example 1</td>
<td>Example 2</td>
<td>Example 3</td>
</tr>
<tr>
<td>Calcium nitrate tetrahydrate</td>
<td>141.52</td>
<td>141.52</td>
<td>141.52</td>
</tr>
<tr>
<td>(Ca(NO₃)₂·4H₂O)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5 After stock solutions A, B and C were prepared, solution C was quickly added to solution B and vigorously mixed for several seconds. This combined solution (B and C) was then added to solution A. In Example 2, the ethyl orthosilicate liquid was also added to solution A concurrently with solutions B and C. In all the examples the final mixture was vigorously stirred for 5 minutes and then allowed to stand for 18
hours to precipitate the calcium phosphate product. The clear supernatant was decanted and disposed of. The precipitate was washed 4 times with 3 liters of deionized water each washing. The precipitate was filtered using a Büchner funnel and Whatman #41 filter paper, and washed again with an additional 500 ml of deionized water. The precipitate was removed from the filter paper and placed into a glass beaker for drying. The precipitate was dried in an oven at 200°C for 17 hours, lightly crushed in an agate mortar and stored in a desiccator.

The three synthetic materials were characterized by powder x-ray diffraction and by electron microprobe analysis. The Figure shows diffractographs of the compositions. The peaks (d-spacing) correspond to peaks for natural hydroxyapatites. Peak width was narrow suggesting that individual crystals have a width of from about 200-500 angstroms.

The chemical analysis of the composition is shown in Table 3.

<table>
<thead>
<tr>
<th>Component</th>
<th>Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Example 1</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0</td>
</tr>
<tr>
<td>K₂O</td>
<td>0</td>
</tr>
<tr>
<td>SO₄</td>
<td>0.439</td>
</tr>
<tr>
<td>CaO</td>
<td>46.165</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>33.461</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.001</td>
</tr>
<tr>
<td>MgO</td>
<td>2.839</td>
</tr>
<tr>
<td>SiO₂</td>
<td>-</td>
</tr>
<tr>
<td>OH</td>
<td>3.163</td>
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<tr>
<td>CO₃</td>
<td>6.7</td>
</tr>
<tr>
<td>Mn</td>
<td>2028 ppm</td>
</tr>
<tr>
<td>Cu</td>
<td>38 ppm</td>
</tr>
<tr>
<td>Cl</td>
<td>350 ppm</td>
</tr>
<tr>
<td>Zn</td>
<td>303 ppm</td>
</tr>
<tr>
<td>MoO₃</td>
<td>4 ppm</td>
</tr>
<tr>
<td>BO₃</td>
<td>1237 ppm</td>
</tr>
</tbody>
</table>

Examples 4-12

In the following examples, the apatite compositions prepared in Examples 1-3 were contacted with deionized water to determine the equilibrium ion concentration after dissolution. At the end of each run, pH and the ion concentrations of the various elements were measured. Concentrations of manganese, iron, copper and zinc ions were determined using DTPA chelating agent (pH=7.3). The procedure
The synthetic apatite composition consisted of placing a 0.5 g sample of the synthetic apatite composition in a covered glass bottle containing 80 ml of deionized water. The bottles and samples were placed in an environmentally controlled reciprocal shaker at a setting of 100 rpm and shaken for 96 hours. The temperature was held at 25°C. Results are given in Table 4.

### Table 4

<table>
<thead>
<tr>
<th>Ex. No.</th>
<th>Sample</th>
<th>pH</th>
<th>Element Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>mg/l</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ca</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>8.70</td>
<td>1.33</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>8.70</td>
<td>1.30</td>
</tr>
<tr>
<td>6</td>
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</tr>
<tr>
<td>7</td>
<td>2</td>
<td>8.13</td>
<td>0.17</td>
</tr>
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<td>8</td>
<td>2</td>
<td>8.16</td>
<td>0.22</td>
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<td>9</td>
<td>2</td>
<td>8.16</td>
<td>0.17</td>
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<tr>
<td>10</td>
<td>3</td>
<td>7.00</td>
<td>2.95</td>
</tr>
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<td>11</td>
<td>3</td>
<td>6.95</td>
<td>3.80</td>
</tr>
<tr>
<td>12</td>
<td>3</td>
<td>7.12</td>
<td>3.45</td>
</tr>
</tbody>
</table>

* DTPA extractable, pH=7.3.

### Example 40

In the following examples, the apatite compositions prepared in Examples 1-3 were contacted with an aqueous medium wherein the pH was varied between 5 and 7 to determine the equilibrium ion concentration after dissolution. The procedure was similar to Examples 4-12 except that a 0.5 M sodium acetate solutions buffered with acetic acid to the desired pH were used instead of deionized water. Results are given in Table 5. As expected, the synthetic apatite dissolved to a greater extent in a more acidic medium.
<table>
<thead>
<tr>
<th>Ex. No.</th>
<th>Sample</th>
<th>pH</th>
<th>Ca</th>
<th>Mg</th>
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<td>314.7</td>
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<td>18</td>
<td>1</td>
<td>6.31</td>
<td>310.5</td>
<td>66.0</td>
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<td>19</td>
<td>1</td>
<td>5.08</td>
<td>1216</td>
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</tr>
<tr>
<td>20</td>
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<td>5.08</td>
<td>1384</td>
<td>82.6</td>
</tr>
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<td>5.08</td>
<td>1244</td>
<td>84.6</td>
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<td>15.8</td>
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<tr>
<td>28</td>
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<td>5.07</td>
<td>1098</td>
<td>20.7</td>
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<td>20.5</td>
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<td>2</td>
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<td>1098</td>
<td>20.6</td>
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<td>7.56</td>
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<td>35.6</td>
</tr>
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<td>7.55</td>
<td>37.9</td>
<td>37.9</td>
</tr>
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<td>6.15</td>
<td>189.5</td>
<td>53.8</td>
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<td>54.2</td>
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</tr>
<tr>
<td>39</td>
<td>3</td>
<td>5.05</td>
<td>975</td>
<td>74.6</td>
</tr>
</tbody>
</table>
Claims:
1. A fertilizer, comprising:
   one or more agronutrients dispersed in a matrix of calcium
   phosphate essentially free of agrotoxins; admixed with
   one or more agronutrients exchanged onto a cationic exchange
   medium.
2. The fertilizer of claim 1, further comprising a pH buffer.
3. The fertilizer of claim 1, wherein the cationic exchange medium
   comprises natural or synthetic zeolite, phyllosilicate or a
   combination thereof.
4. The fertilizer of claim 1, wherein the cationic exchange medium is
   selected from clinoptilolite, chabazite, mordenite, phillipsite, Linde
   type A, Linde type X, vermiculite, smectite or a combination
   thereof.
5. The fertilizer of claim 1, wherein said cationic exchange medium
   has a cation exchange capacity of at least 50 cmolc/kg.
6. The fertilizer of claim 1, wherein said cationic exchange medium
   has a cation exchange capacity of at least 100 cmolc/kg.
7. The fertilizer of claim 1, wherein said cationic exchange medium
   has a cation exchange capacity of at least 150 cmolc/kg.
8. The fertilizer of claim 1, wherein the agronutrients in the cation
   exchange medium comprise ammonium and potassium at a
   weight ratio of from about 1 to about 5:1 of ammonium:potassium.
9. The fertilizer of claim 1, comprising from about 5 to about 100
   parts by weight of the calcium phosphate per 100 parts by weight
   of the cationic exchange medium.
10. The fertilizer of claim 2, wherein said buffer maintains a soil pH of
    from about 5.5 to about 7.
11. The fertilizer of claim 1, wherein the agronutrients are selected
    from potassium, ammonium-nitrogen, magnesium, sulfur, zinc,
    chlorine, iron, manganese, copper, molybdenum, boron or a
    combination thereof.
12. The fertilizer of claim 1, wherein the calcium phosphate matrix
    comprises from about 30 to about 50 parts phosphorus per 100
    parts calcium by weight.
13. The fertilizer of claim 1, comprising not more than 10 parts
    fluorine per 100 parts calcium.
14. The fertilizer of claim 1, wherein the calcium phosphate matrix
comprises a synthetic apatite.

15. The fertilizer of claim 1, comprising (a) from about 5 to about 100
parts by weight of the calcium phosphate matrix, wherein said
matrix comprises synthetic apatite matrix having dispersed
therein, per 100 parts calcium, up to about 5 parts magnesium, up
to about 4 parts sulfur, up to about 0.4 parts zinc, up to about 1.25
parts chlorine, up to about 4 parts iron, up to about 1.2 parts
manganese, up to about 0.12 parts copper, up to about 0.0025
parts molybdenum, up to about 0.05 parts boron, and less than
about 10 parts fluorine; admixed with (b) 100 parts by weight of
zeolite saturated with a charge of potassium and ammonium at a
weight ratio of from about 1 to about 5:1 of ammonium:potassium.

16. The fertilizer of claim 15, further including from 0 to about 10 parts
by weight of a pH buffer per 100 parts by weight of the ammonium
and potassium charged zeolite.

17. A horticultural method, comprising the steps of:
planting a botanical species in a sufficient amount of a fertilizer
composition comprising one or more agronutrients
dispersed in a matrix of calcium phosphate essentially free
of agrotoxins and admixed with one or more agronutrients
charged in a cationic exchange medium; and
contacting the fertilizer with moisture to mobilize the agronutrients.

18. A method of making an active synthetic fertilizer, comprising the
steps of:
admixing an aqueous calcium solution and a solution mixture
comprising a soluble phosphate and one or more soluble
agronutrients selected from magnesium, zinc, sulfur,
chlorine, iron, manganese, copper, molybdenum and boron
to form a crystalline calcium phosphate precipitate having
agronutrients dispersed therein;
recovering and drying the precipitate;
charging zeolite with ammonium and potassium cations; and
blending from about 5 to about 100 parts by weight of the
precipitate with 100 parts by weight of the charged zeolite.

19. The method of claim 18, wherein the charging step comprises
contacting a first particulated zeolite portion with said ammonium
cations, and contacting a second particulated zeolite portion with
said potassium cations, and further comprising mixing said first and second zeolite portions to form a zeolite mixture having a weight ratio of ammonium charged zeolite to potassium charged zeolite from about 1:1 to about 5:1.

20. The method of claim 18, further comprising blending from 0 to about 10 parts by weight of a pH buffer with said zeolite and precipitate.

21. A slow-release fertilizer, comprising:
one or more agronutrients structurally dispersed in a matrix of calcium phosphate essentially free of agROTOXINS.

22. The fertilizer of claim 21, wherein the agronutrients comprise potassium, magnesium, sulfur, zinc, chlorine, iron, manganese, copper, molybdenum, boron or a combination thereof.

23. The fertilizer of claim 21, comprising:
from about 30 parts to about 50 parts phosphorous per 100 parts calcium by weight;
magnesium up to about 5 parts per 100 parts calcium by weight;
sulfur up to about 4 parts per 100 parts calcium by weight;
zinc up to about 0.4 parts per 100 parts calcium by weight;
chlorine up to about 1.25 parts per 100 parts calcium by weight;
iron up to about 4 parts per 100 parts calcium by weight;
manganese up to about 1.2 parts per 100 parts calcium by weight;
copper up to about 0.12 parts per 100 parts calcium by weight;
molybdenum up to about 0.0025 parts per 100 parts calcium by weight; and
boron up to about 0.05 parts per 100 parts calcium by weight.

24. The fertilizer of claim 21, further comprising a silicon and/or carbonate solubility control agent.

25. The fertilizer of claim 24, comprising from about 0 to about 10 parts silicon agent per 100 parts calcium.

26. The fertilizer of claim 1, comprising from about 0 to about 15 parts carbonate agent per 100 parts calcium.

27. The fertilizer of claim 1, wherein the matrix comprises synthetic apatite.

28. The fertilizer of claim 1, comprising not more than 10 parts fluorine per 100 parts calcium by weight.

29. The fertilizer of claim 3, comprising not more than 3000 ppm fluorine.
30. A method for preparing a synthetic apatite composition, comprising the steps of:

mixing in an aqueous medium:

(1) a water soluble ionic calcium compound;
(2) a water soluble ionic phosphate compound; and
(3) one or more water soluble agronutrient compounds of potassium, magnesium, sulfur, zinc, chlorine, iron, manganese, copper, molybdenum and boron, or combinations thereof;

precipitating calcium phosphate crystals; and recovering and drying the precipitate.

31. The method of claim 30, wherein the calcium compound comprises calcium nitrate, calcium nitrite, calcium chloride, calcium chlorate or a hydrate thereof and the phosphate compound comprises ammonium orthophosphate-mono-H, ammonium orthophosphate-di-H, ammonium orthophosphate, ammonium hypophosphate, hydrazine orthophosphate or hydrazine hypophosphate.

32. The method of claim 30, wherein the magnesium compound is selected from magnesium nitrate, magnesium chloride, magnesium nitrite, magnesium chlorate, magnesium perchlorate and hydrates thereof; the sulfur compound is selected from sodium sulfate, ammonium sulfate, potassium sulfate, ammonium bisulfate, ammonium sulfite, ammonium bisulfite and hydrates thereof; the zinc compound is selected from zinc chloride, zinc nitrate, zinc nitrite, zinc sulfate and hydrates thereof; the chlorine compound is selected from sodium chloride, potassium chloride, ammonium chloride, ammonium chlorate and ammonium perchlorate; the iron compound is selected from ferric nitrate, ferrous nitrate, ferrous nitrite, ferric nitrite, ferric chloride, ferrous chloride, ferric sulfate, ferrous sulfate and hydrates thereof; the manganese compound is selected from potassium permanganate, potassium manganate, manganese(II) nitrate, manganese(II) nitrite, manganese dichloride, manganese(II) sulfate and hydrates thereof; the copper compound is selected from copper(II) chloride, copper(III) chloride, copper(II) nitrate, copper(II) nitrite and hydrates thereof; the molybdenum compound is selected from ammonium paramolybdate, ammonium permolybdate, sodium
trimolybdate, sodium tetramolybdate, sodium paramolybdate, sodium octamolybdate, potassium molybdate and hydrates thereof; and the boron compound is selected from sodium tetraborate, sodium metaborate, potassium tetraborate, potassium metaborate, ammonium tetraborate, ammonium peroxyborate, hydrates thereof and orthoboric acid.

33. The method of claim 32, wherein the mixture further comprises at least one water soluble solubility control agent selected from silicon and carbonate.

34. The method of claim 33, wherein the carbonate compound is selected from sodium carbonate, sodium bicarbonate, ammonium carbonate, ammonium bicarbonate, potassium carbonate and potassium bicarbonate; and the silicon compound is selected from sodium silicate, sodium disilicate, sodium metasilicate, sodium orthosilicate, potassium disilicate, potassium metasilicate, potassium hydrogen disilicate, ammonium silicate, hydrates thereof and ethyl orthosilicate.

35. A method of preparing a synthetic apatite composition, comprising the steps of:

admixing in an aqueous medium from about 1.0 to about 1.6 moles per liter of a soluble ionic calcium compound and a solution mixture comprising from about 0.5 to about 0.8 moles per liter of a soluble ionic phosphate compound and an agronomic amount of, one or more soluble agronutrients selected from magnesium, zinc, sulfur, chlorine, iron, manganese, copper, molybdenum and boron to form a crystalline calcium phosphate precipitate having agronutrients dispersed therein; and recovering and drying the precipitate.

36. A method for supplying nutrient elements in an agronomical process, comprising the steps of:

placing a fertilizing amount of the synthetic apatite composition of claim 1 adjacent a plant root system; and contacting the synthetic apatite with moisture to release the agronutrients.
A. CLASSIFICATION OF SUBJECT MATTER
   IPC(S) : CO1B 25/16; COSB 7/00; COSC 5/00
   US CL : 71/1, 27, 33, 34, 64, 13, 903, 904, 423/308, 311
   According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
   Minimum documentation searched (classification system followed by classification symbols)
   U.S. : 71/1, 27, 33, 34, 64, 13, 903, 904; 423/308, 311
   Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
   Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
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<tbody>
<tr>
<td>Y</td>
<td>US, A, 4,139,599 (Tomlinson et al) 13 February 1979, see entire document.</td>
<td>1-36</td>
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<td>Y</td>
<td>US, A, 4,402,725 (Heller et al) 06 September 1983, see entire document.</td>
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<td>Y</td>
<td>US, A, 5,037,470 (Matzen et al) 06 August 1991, see entire document.</td>
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<td>US, A, 5,106,405 (Goto) 21 April 1992, see entire document.</td>
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</table>

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
   "A" document defining the general state of the art which is not considered to be part of particular relevance
   "E" earlier document published on or after the international filing date
   "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
   "O" document referring to an oral disclosure, use, exhibition or other means
   "P" document published prior to the international filing date but later than the priority date claimed
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"Z" document member of the same patent family

Date of the actual completion of the international search 06 JANUARY 1994
Date of mailing of the international search report 04 FEB 1994

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