NANOSCIENCE AND NANO-TECHNOLOGY: CRACKING PRODIGAL FARMING [1]

Siddhartha S. Mukhopadhyay [2], V.R. Parshad [3], Inderpreet S. Gill [3]
[2] Department of Soils, and [3] Electron Microscopy and Nano-science Laboratory
Punjab Agricultural University, Ludhiana – 141004, India
[[1] e-mail siddhartha_soil@yahoo.co.in]

ABSTRACT

Nano-science coupled with nano-technology has emerged as possible cost-cutting measure to prodigal farming and environmental clean-up operations. It has ushered as a new interdisciplinary field by converging various science disciplines, and is highly relevant to agricultural and food systems. Environmental Protection Agency of USA defined nanotechnology as the understanding and control of matter at dimensions of roughly 1-100 nm, where unique physical properties make novel applications possible. By this definition all soil-clays, many chemicals derived from soil organic matter (SOM), several soil microorganisms fall into this category. Apart from native soil-materials, many new nanotech products are entering into soil system, some of which are used for agricultural production and some others for many other purposes.

Nano-science (also nanotechnology) has found applications in controlling release of nitrogen, characterization of soil minerals, studies of weathering of soil minerals and soil development, micro-morphology of soils, nature of soil rhizosphere, nutrient ion transport in soil-plant system, emission of dusts and aerosols from agricultural soil and their nature, zeoponics, and precision water farming. In its stride, nanotechnology converges soil mineralogy with imaging techniques, artificial intelligence, and encompass bio molecules and polymers with microscopic atoms and molecules, and macroscopic properties (thermodynamics) with microscopic properties (kinetics, wave theory, uncertainty principles, etc.), to name a few.

Some of the examples include clinoloptolite and other zeolite based substrates, and Fe-, Mn-, and Cu- substituted synthetic hydroxyapatites that have made it possible to grow crops in space stations and at Antarctica. This has eliminated costs of repeated launching of space crafts. A disturbing fact is that the fertilizer use efficiency is 20-50 percent for nitrogen, and 10-25 percent for phosphorus (<1% for rock phosphate in alkaline calcareous soils). With nano-fertilizers emerging as alternatives to conventional fertilizers, build ups of nutrients in soils and

thereby eutrophication and drinking water contamination may be eliminated. In fact, nano-technology has opened up new opportunities to improve nutrient use efficiency and minimize

[1] Paper presented at the International Symposium on Natural Resource Management held on 19-20 December 2008 at Jaipur, India (Accepted for publication by PROM Society)

costs of environmental protection. It has helped to divulge to recent findings that plant roots and microorganisms can directly lift nutrient ions from solid phase of minerals (that includes so-called susceptible (i.e., easily weatherable, as well as non-susceptible minerals).

1. Introduction

Nanoscience and its applied sphere that is known as nanotechnology have potential to bring the next revolutionary breakthrough in agricultural-biased natural resource management. It has ushered as a new interdisciplinary venture-field by converging science and engineering into agriculture and food systems (Abdul-Kalam, 2007, Lal, 2008). Electron microscopes are indispensable tools for this nascent discipline. Almost all electron microscopes [Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), and Atomic Force Microscope (AFM)], and their attachments [e.g., Energy Dispersive Spectroscope (EDS)] are used for soil study. Electron waves in SEM and TEM and laser beam in AFM are used for coalescing micrographs. Since the wavelength of electron under normal circumstances is 1 nm, viewing images of small materials under EMs are grossly termed as nanoscience/nanotechnology. Environmental Protection Agency of US has defined nanotechnology as the understanding and control of matter at dimensions of roughly 1-100 nm, where unique physical properties make novel applications possible (EPA, 2007). By this definition all soil-clays, many chemicals derived from soil organic matter (SOM), and several soil microorganisms fall into this category. Apart from native soil-materials, many new nanotech products are entering into soil system - some of which are used for agricultural production and some others for many other purposes. The advantages with EM are high resolution imaging, high magnification, and great depth of focus.

An example is new emerging disciplines - nanopedology. This is a new off-shoot of pedology; a discipline that involves study of soil as a natural body. Nanopedology converges soil mineralogy with imaging techniques and artificial intelligence. Examples of impending opportunities are in the areas of establishing relationships between hereto vaguely-matched properties between bio molecules and polymer, and microscopic atoms and molecules, and establishing relationships between macroscopic properties (thermodynamics) and microscopic properties, where among others kinetics, wave theory, and uncertainty principles find place.

Nanoscience has been adorning glamour. But it is important to accept that science has always been idea driven, and it would remain so in the future. Therefore, one should have a clear idea of what to study and why to study. It can be illustrated from the fact that an object of 1 cm x 1 cm may have a magnified image of $3x10^{3}$ m by $3x10^{3}$ m in SEM that has magnification capacity of $3x10^{5}$. In this image, there are $9x10^{18}$ pixels of 1 mm^{2} size, and one has little opportunity to wonder between pixels!

2. Applications in soils studies

Some of the areas, where nanoscience and nanotechnology have found applications for the production of food and protection of environmental quality by managing natural resources (especially, soils) in the earth and extraterrestrial environments are:

i. Improving efficiency of native and applied nutrients in soils,
ii. Regulation of essential and toxic elements in pedosphere-hydrosphere continuum,
iii. Ion transport in soil-plant system, especially in the rhizosphere,
iv. Zeoponics: Controlled ecological life support system using zeolites, apatites, and similar materials,
v. Characterization of soil minerals,
vi. Weathering of soil minerals,
vii. Soil formation – history and micro-morphology,
viii. Dusts and aerosols and their nature, and
ix. Precision water farming.

Due to space constrains, the paper focuses on a few areas.

3. Improving efficiency of native and applied nutrients in soils

For the native nutrients, the basic processes whereby plants and soil-microorganisms directly influence the soil chemical environment is through the generation of weathering agents, biocycling of ions, and the production of biogenic minerals. For the applied nutrients, the basic processes remain the same, but applied nutrients force change in soil microbial diversity, alongside host of other processes by changing soil pH and composition of soil solution. We list some of our initiations along with a few other works in the following paragraphs:

Composition and electron micrograph of K-minerals in the soils of Punjab: The potassium dynamics is controlled exclusively by the solid phase in soils, and K availability is governed by both coarse and fine grains of soils. The phenomenon is most prominent in the soils that are rich in K-containing minerals (Brar et al., 2008; Mukhopadhyay and Brar, 2006, Mukhopadhyay and Dutta, 2001) The data on the elemental composition of alkali-feldspar and muscovite (Table 1) show remarkable similarities in the mineral grains in spite of the fact that the soils were drawn from different soil series of Punjab. There is little difference in the mineralogical make-up of the soils in these series. Therefore, it could be inferred that the differences in the response to applied potassium in these soils arise because of differences in the weathering state of the K-containing minerals, especially of micas, rather than from their elemental composition or, mineralogical make-up of soils. Secondly, the content of K in muscovite ranged from 7.99 to 8.88 percent (Brar et al., 2008), which is lower than the K content in the standard muscovite (10%). This implies a substantial loss of K from the interlayers of muscovite. It could happen only if layers open up, evidences of which can only be drawn by using nanoscience tools.

Table 1. Elemental composition of alkali-feldspar and muscovite in some soil series of Punjab [a]

Soil series	Chemical composition	
	Alkali-feldspar	Muscovite
Samana	$K_{0.93}Na_{0.06}Ca_{0.01}Al_{1.01}Si_{2.99}O_8$	$K_{8.88}Na_{0.17}Ca_{0.20}Al_{18.99}Fe^{3+}_{0.28}Mg_{0.49}Si_{22.03}O_{20}(OH)_4$
Bhundri	$K_{0.94}Na_{0.05}Ca_{0.02}Al_{1.03}Si_{2.97}O_8$	$K_{8.78}Na_{0.06}Ca_{0.20}Al_{12.93}Fe^{3+}_{0.42}Fe^{2+}_{0.28}Mg_{0.31}Si_{22.17}O_{20}(OH)_4$
Ghabdan	$K_{0.94}Na_{0.05}Ca_{0.02}Al_{1.01}Si_{2.99}O_8$	$K_{8.82}Na_{0.50}Ca_{0.10}Al_{17.50}Fe^{3+}_{0.43}Fe^{2+}_{0.28}Mg_{0.74}Si_{22.13}O_{20}(OH)_4$
Bains-Awans I		$K_{7.99}Na_{0.35}Ca_{0.20}Al_{17.40}Fe^{3+}_{1.45}Fe^{2+}_{0.08}Mg_{0.55}Si_{22.89}O_{20}(OH)_4$
	$K_{0.94}Na_{0.05}Ca_{0.02}Al_{1.01}Si_{2.99}O_8$	

[a] Sample of surface soils; Figures represent percent composition.

Adapted from: Sidhu (1982) with some modification

For some soils of Punjab, electron micrographs of coarse sand size mica grains (biotite and muscovite) illustrate irregular boundary along with broken planes and itch pits that are produced through dissolution (Fig. 1). The macrocrystals were platy, often perturbed with foreign microcrystals. The grains were strained, and their edges were marked with cleavage opening (Mukhopadhyay et al., 2008; unpublished data). Earlier Sidhu and Gilkes (1977) opined that the mica grains of the surface soils of Punjab were regular in structure, and of fresh origin. The inconsistencies in these observations were perhaps because of our access to greater resolution and higher magnification than the former workers (Brar et al., 2008).

Some other works: Electron microscopy is a handy tool to understand flow path of nutrients in acid soils, where Al toxicity is a threat to plant growth. Adamo et al. (1998) analyzed root zone of winter oilseed rape (*Brassica napus*; cv. Rafal) using SEM in combination with EDS in back-scattered mode, and found that Al concentrated in the cell walls of immature roots and at the soil-root interface in the strongly acidic soils, while K, Ca, and P were associated with the external tissues of the central cylinder.

Atomic Force Microscopy has emerged as one of the major techniques for investigating mineral-surface heterogeneity and heterogeneous systems *in situ.* The advantage with AFM over SEM and TEM is that it can image nearly any surface in vacuum, in the air, or in a solution. Liu et al. (2003) observed that soil-clays of an Ultisols displayed distinct AFM surface features after different selective dissolution treatments (acid ammonium oxalate in the dark, and dithionite-citrate-bicarbonate). The images provide insight into the adsorption of plant nutrients on the surfaces of minerals.

During the third quarters of 20th Century, accessibility to electron microscope and sophisticated analytical instruments facilitated to see how weathering front advances, and how a mineral species give rise to another species. Mica received lime-light during the period. The reviews by Reichenbach (1972), Rich (1972), and Schroeder (1978) illustrate the electron micrographs, and the nature and factors of pedochemical weathering of micaceous minerals. It was proved that potassium slowly diffuses out of the interlayer spaces formed by cleavage planes between mica layers into the soil solution, which results in cleavage at the weathering edges of mica (Hensel and White, 1960 and Marel 1954; as cited by Jackson, 1964). Denison et al. (1929 - as cited by Jackson, 1964) showed that on weathering of biotite, there is a gain in Al, Si, and H_2O content, oxidation of Fe, and loss in Mg and K.

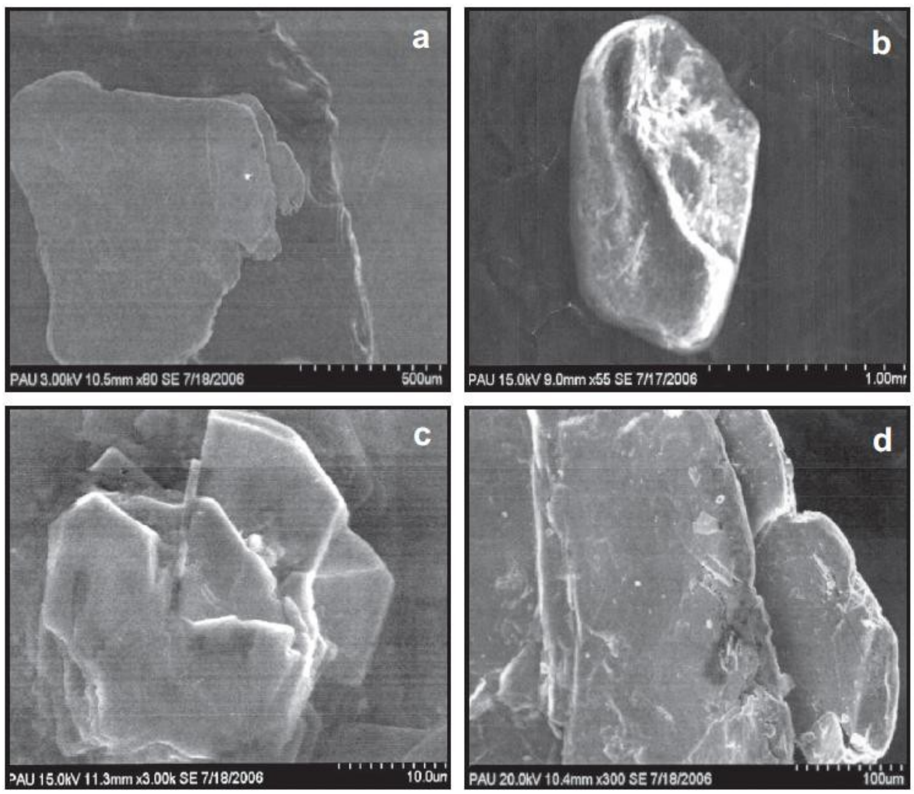

Fig. 1.

Secondary electron image of mica grains separated from very coarse sand in the Agro Ecological Sub-Region II of Punjab. (a) Muscovite. Note thin platy psedohexagonal nature of the grain. The grain boundary is more regular than biotite. (b) A biotite grain. (c) Biotite image at 15 kV accelerated current. Note: Broken boundary, and exfoliated nature. Growth of rod shaped psedocrystal is evident. (d) A closer look at high accelerated current. Note: Opening of cleavage plain. Dissolutions pits are evident.

4. Regulation of essential and toxic elements in pedosphere-hydrosphere continuum

Elemental balance: Elemental balance between pedosphere and hydrosphere is a central theme of safe drinking water and protection of life in water bodies, and to monitor continental weathering. Twenty percent of world's land falls into laterites that are essentially found in high precipitation zone. Laterization causes decreasing productivity of land, and these regions often turn into breeding ground of hostile political activity. Balan et al. (2007) used surface properties to establish relationship between theoretical modeling at microscopic (atomic structure) and at macroscopic (particle shape) length-scale.

5. Ion transport in soil-plant system, especially in the rhizosphere

Rhizosphere concept of nutrient availability: Recent research suggests that plant roots and microorganisms can directly lift nutrient ions from solid phase of minerals, which include so-called susceptible (easily weatherable) as well as non-susceptible minerals. There exists a close reciprocal relationship between plant root and soil microorganisms, and therefore all soil-plant nutrient transport systems are to be seen from this angle. Jongmans et al. (1997) have shown that feldspars and hornblends in eluvial (E) horizons of podzols contain abundant narrow tubular pores ranging in diameter from 3 to 10 µm. In field soils, these pores are sometimes occupied by fungal hyphae, and van Breemen et al. (2000) have suggested that these hyphae themselves are directly responsible for the spatially localized mining of the mineral grains. In a controlled environment experiment, van Hees et al. (2004) used some forest soils of U.K. (after screened through 6-mm sieve), and grew *Paxillus involutus*. Scanning electron micrographs of the experiment demonstrates that plant roots deeply penetrated into the grains of feldspars (Fig. 2). They had also shown that the mobilization of Fe and Si in the soil column was positively correlated with hyphal length, soil respiration and concentrations of oxalate in the soil solution; and mobilization of Al was strongly correlated with plant weight. Scanning electron microscopy revealed that most fungal hyphae were associated with mineral surfaces with little occupation of cracks and micropores within mineral grains. Kim et al. (2004) demonstrated that microorganisms can promote the smectite-to-illite reaction by dissolving smectite through reduction of structural Fe^{3+} at room temperature and 1 MPa pressure within 14 days. Trivalent iron bound in clay minerals can be an important electron accepter supporting the growth of bacteria in natural environments. It is essentially a K-capturing reaction. Glowa et al. (2003) demonstrated that Piloderma (a broad host range ectomycorrhizal fungal genus) can extract K^{+} and Mg^{2+} from biotite, microcline, and chlorite. These studies provide a new insight into nutrient management in soils.

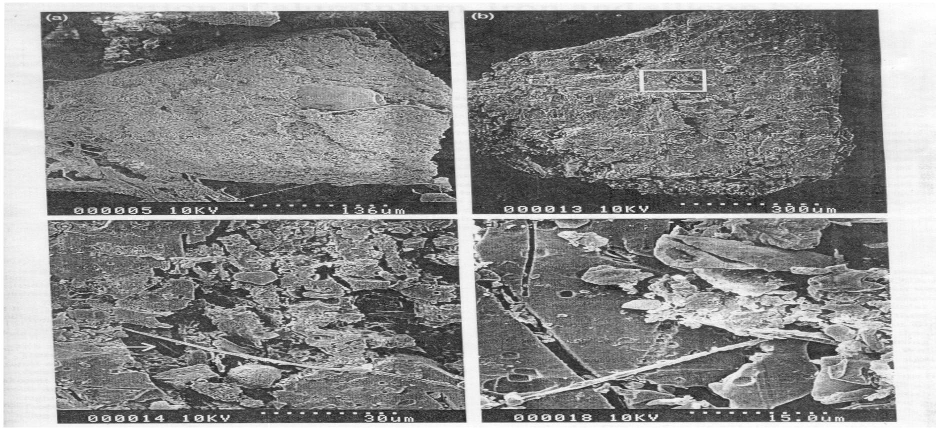

Fig. Scanning electron micrograph of soil with plant and Paxillus involutus (Adapted from Van Hees, 2004)

Fig. 2. Scanning electron micrograph of soil with plant and *Paxillus involutus (M-)*: (a) Na (Ca) feldspar grain with hyphae on the surface; (b) Ca (Na) feldspar (with inclusions of Na and K feldspars) grain with hyphae entering a crack; (c) magnification of rectangle in (b), arrow points at possible interior hypha; (d) possible trace of hypha on mineral surface of Ca (Na) feldspar (Adapted from van Hees et al., 2004).

Soil microorganisms colonize around the exposed mineral surfaces of the colloidal soil minerals (clays), coat them with extracellular polymers, and physically disrupt the grains in their attempt to gain access to nutrients and energy. They create a complex microenvironment at the mineral-water interface, where metabolically catalyzed redox reactions and the generation of acids and complexing agents lead to pH and concentration gradients markedly different from the bulk solution. This often promotes a state of thermodynamic disequilibrium that fosters faster rates of weathering (Konhauser, 2007).

Both biotic and abiotic interaction with soil minerals, to a great extent, is unexplored. Trivalent iron bound in clay minerals can be an important electron accepter supporting the growth of bacteria in natural environments. Some clay minerals significantly affect microbial life by modifying the physicochemical characteristics of microbial habitat, and through direct surface interaction. The ability of microorganisms to weather soil minerals, degrade organic matter, and transform nutrients and pollutants may be substantially influenced by interactions with mineral colloids. Therefore, attention should be paid to the role of clay minerals in mediating toxicity of a wide spectrum of organic and inorganic agents, both of abiotic and biotic origin (Huang and Bollag, 1998).

The central problem posed by the link between microbial diversity and soil function is to understand the relations between genetic diversity and community structure and between community structure and function. A better understanding of the relations between microbial diversity and soil functions requires not only the use of more accurate assays for taxonomically and functionally characterizing DNA and RNA extracted from soil, but also high-resolution imaging to detect inactive and active microbial cells in the soil matrix. The holistic approach, based on the division of the systems in pools and the measurement of fluxes linking composition of microbial communities with quantification of nutrient transformations these pools, is the most efficient (Nannipieri et al., 2003).

6. Zeoponics

Zeoponics; a system founded on the concept of interconnected nature of all life-forms and life-support-forms; relies on recycling and operation of system-components. It opened new vistas in the traditional fields of agriculture and forestry by demonstrating that a system can be made self-supporting, and can supply nutrients to plants for a long time, if a balance is struck between loss and gain of nutrients. The system provides a framework where impetus and response are almost equal. This implies that the first law of thermodynamics can be translated to near implementation level in an open system. This is the only means of survival in the extraterrestrial planets, space stations, and in the Antarctica. It supplies nutrients needed for plants, sorbes gases and converts bio-waste into useful materials. It recycles production-consumption-waste system without contaminating immediate environment. It can be used as a nutrient-controller (for P and micronutrients) or release rate limiter (for N).

Soil minerals, like hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] are successfully used for this system. Similarly, exchange of NH_4^+ and K^+ are regulated effectively through substituted clinoptilolite (Allen et al., 1995; Ming et al., 1995; Sutter et al., 2002; Sutter et al., 2003). Others like zirconium complexes containing cyclopentadienyl ligands allow direct observation of N-H bond formation from N_2 and H_2. Subsequent warming of the complex cleaves the N-N bond at 45^0 C, and continued hydrogenation at 85^0 C results in complete fixation to ammonia (Pool et al., 2004). This observation may aid the design of new stoichiometric and catalytic nitrogen fixation processes. Sutter et al. (2003) used TEM images to decipher Fe-, Mn-, and Cu- substituted synthetic hydroxy apatite. Their TEM-EDS images show how core apatite changes when ions of Fe, Mn, or Cu substitute H^+.

To comprehend nutrient dynamics, soil-plant system must be treated holistically, and sub-divided into components, each with realistic independent system-variables coupled with the processes, which tie these system variables. Structure and function of every component and their time hierarchy and interactions with the environment must also be taken into account (Karpinets and Greenwood, 2003; Mukhopadhyay and Brar, 2006; Mukhopadhyay and Datta, 2003). In such ventures high resolution imaging not only provides evidence of the changes that occur in various phases, but also an indispensable tool to understand how dynamic systems operate.

7. Epilogue: Let's shoot up agronomic production - knock down input use – jut out prodigal farming

Future agricultural research must be kind to nature, and in harmony to the mutually beneficial man-nature relationship. In such endeavors, the nutrients (also water) must be measured in terms of plants' requirements. This eliminates nutrient build up in soils and water bodies, and eventually increases profits of the farmers. Nanoscience exactly aims for it.

Environmental concern: Our expanding ability to synthesize nanoparticles for use in electronics, biomedical, ceramics, pharmaceutical, cosmetic, energy, environmental, catalytic, material etc. has alarmed concern for these particles role in environmental safety. You can guess the situation from the fact that in 2004, 2000 tons of engineered materials were used, which is expected to increase to 58 000 tons in 2011-2020 (Nowack and Bucheli, 2007). All these materials eventually land on soil. To be useful to the society, nanoscience efforts must adhere to environmental ethos.

References

Abdul-Kalam, A.P.J., 2007. Innovate to Empower Agriculture and Convergence of Technologies. Address and Interaction with the Students, Faculty Members and Staff of the G.B. Pant University of Agriculture and Technology Pantnagar, Uttarakhand on 11 August 2007 (Website <www.gbpuat.ac.in>).

Adamo, P., McHardy, W.J., Edwards, A.C., 1998. SEM observations in the back-scattered mode of the soil-root zone of *Brassica napus* (cv. Rafal) plants grown at a range of soil pH values. Geoderma 85, 357-370.

Allen, E.R., Ming, D.W., Hossner, L.R., Henninger, D.L., Galindo, C., 1995. Growth and nutrient uptake of wheat in clinoptilolite-phosphate rock substrates. Agron. J. 87, 1052-1059.

Balan, E., Lazzeri, M., Mauri, F., Calas, G., 2007. Structure, reactivity and spectroscopic properties of minerals from lateritic soils: Insights from *ab initio* calculations. European J. Soil Sci. 58, 870-881.

Brar, M.S., Mukhopadhyay, S. S., Dhillon, N. S., Sharma, P., Singh, A., 2008. Potassium: Mineralogy and Status in Soils, and Crop Response in Punjab, India. International Potash Institute, Horgen, Switzerland. 69 pp.

EPA, 2007. Nanotechnology White Paper. U.S. Environmental Protection Agency Report EPA 100/B-07/001, Washington DC 20460, USA.

Glowa,K.R., Arocena, J.M., Massicotle, H.B., 2003. Extraction of potassium and/or magnesium from selective soil minerals by *Piloderma*. Geomicrob. J. 20, 99-111.

Huang, P.M., Bollag, J.M., 1998. Minerals-Organics-microorganisms interactions in soil environment. *In* Huang, P.M., Sensei, N., Buffle, J. (Eds.) Structure and Surface Reactions of Soil Particles. John Wiley, New York. pp. 3-39.

Jackson, M.L., 1964. Chemical composition of soils. *In* Bear, F.E. (Ed.) Chemistry of the Soil. Oxford & IBH, New Delhi, pp. 71-141.

Jongmans, A.G., van Breemen, N., Lundstrom,U., Finlay, R.D., van Hess, P.A.W. *et al.* 1997. Rock eating fungi. Nature 389, 662-683.

Kim, J., Dong, H., Seabaugh, J., Newell, S.W., Eberl, D.D., 2004. Role of microbes in the smectite-to-illite reaction. Science. 303, 830-832.

Konhauser, K., 2007. Introduction to Geomicrobiology. Blackwell, Maldan. 436 pp.

Lal, R., 2008. Soils and India's food security. J. Indian Soc. Soil Sci. 56, 129-138.

Liu, C., Li, X., Xu, F., Huang, P.M., 2003. Atomic Force Microscopy of soil organic colloids. Soil Sci. Plant Nutr. 49, 17-23.

Ming, D.W., Barta, D.J., Golden, D.C., Galindo Jr., C., Henninger, D.L., 1995. Zeoponic plant growth substrates for space applications. *In* Ming, D.W., Mumpto, F.A. (Ed.) Natural Zeolites '93: Occurrence, properties, and use. International Committee on Natural Zeolites, New York, pp. 505-515.

Mukhopadhyay, S.S., Brar, M.S., 2006. Mineralogy and management of soils rich in potassium containing minerals. *In* Benbi, D.K., Brar, M.S., Bansal, S.K., (Ed.) International Symposium on Balanced Fertilization, Proceedings, Volume 1. International Potash Institute, Horgen. p. 95-114.

Mukhopadhyay, S.S., Datta, S.C., 2001. Potassium availability in relation to mineralogy in the Indo-Gangetic Plains. *In* Importance of Potassium in Nutrient Management for Sustainable Crop Production in India. International Potash Institute, Horgen. pp.33-44.

Nannipieri, P., Ascher, J., Ceccherini, M. T., Landi, L., Pietramellara, G., Renella, G., 2003. Microbial diversity and soil function. European J. Soil Sci. 54, 655–670.

Reichenbach, H.G., 1972. Factors of mica transformation. *In* Potassium in Soil. International Potash Institute, Berne, pp. 33-42.

Rich, C.I.., 1968. Mineralogy of soil potassium. *In* Kilmer, V.J., Younts, S.E., Brady, N.C., (Ed.) The Role of Potassium in Agriculture. American Society of Agronomy, Madison, pp. 79-108.

Sidhu, P.S., 1982. Mineralogy of potassium in soils of Punjab, Haryana, Himachal Pradesh, and Jammu and Kashmir. *In* Mineralogy of Soil Potassium. Potash Research Institute of India, Gurgaon, India. pp. 6-14.

Sidhu, P.S., Gilkes, R.J., 1977. Mineralogy of soils developed on alluvium in the Indo-Gangetic Plain (India). Soil Sci. Soc. Am. J. 41, 1194-1201.

Schroeder, D., 1978. Structure and weathering of potassium containing minerals. *In* Potassium Research – Review and Trends. International Potash Institute, Berne, pp. 43-64.

Sutter, B., Ming, D.W., Clearfield, A., Hossner, L.R., 2003. Mineralogical and chemical characterization of iron-, manganese-, and copper-containing synthetic hydroxyapatites. Soil Sci. Soc. Am. J. 67, 1935-1942.

Sutter, B., Wasowicz, T., Howard, T., Hossner, L.R., Ming, D.W., 2002. Characterization of iron, manganese, and copper synthetic hydroxyapatites by electron paramagnetic resonance spectroscopy. Soil Sci. Soc. Am. J. 66, 1359-1366.

van Breemen, N., Lundstrom, U.S., Jongmans, A.G., 2000. Do plants drive podzolization via rock eating fungi? Geoderma 94, 167-171.

van Hees, P.A.W., Jones, D.L., Jentschke, G., Godbold, D.L., 2004. Mobilization of aluminium, iron and silicon by *Picea abies* and ectomycorrhizas in a forest soils. European J. Soil Sci. 55, 101-111.