Learning to Leap: Nanotechnology's Root in Soil Science

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Rediscovering Dr. Nil Ratan Dhar

A TRIBUTE

"The roots below the earth claim no rewards for making the branches fruitful".

-Rabindranath Tagore

Dhar's Vision

- He propounded importance of OM in soil fertility at a time when fertilizers were considered wonder material, and OM had been virtually discarded. Global Warming was unheard of at that time
- He advocated biological management of N, when world could not perceive GHG emission, nor assess its magnitude from farm fields.

What is NT?

- **Understanding and control of matter at dimensions of roughly 1-100 nm, where unique physical properties make novel applications possible**

(***EPA, 2007***)

❑ *What does it mean?*

Designing and building machines in which every atom and chemical bond is specified precisely

(Hall, 2006; p.21)

Where lies scope for soils?

"Like solid-state physics in the sense that it might tell us much of great interest about the strange phenomena that occur in complex situations" that "would have an enormous number of technical applications" and involved "the problem of manipulating and controlling things on a small scale".

- Richard Feynman, 1959

(There's plenty of room at the bottom)

3 Roots in Soil for burgeoning Nanotechnology

- Organic Matter
- Clay (nanoclay, nanocomposite, clay-polymer capsules)
- Soil System

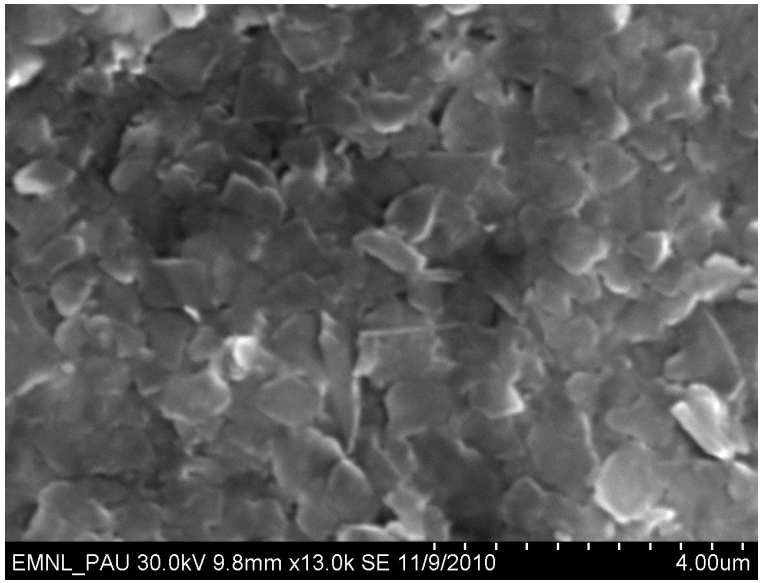
Let Us Perceive Soil System

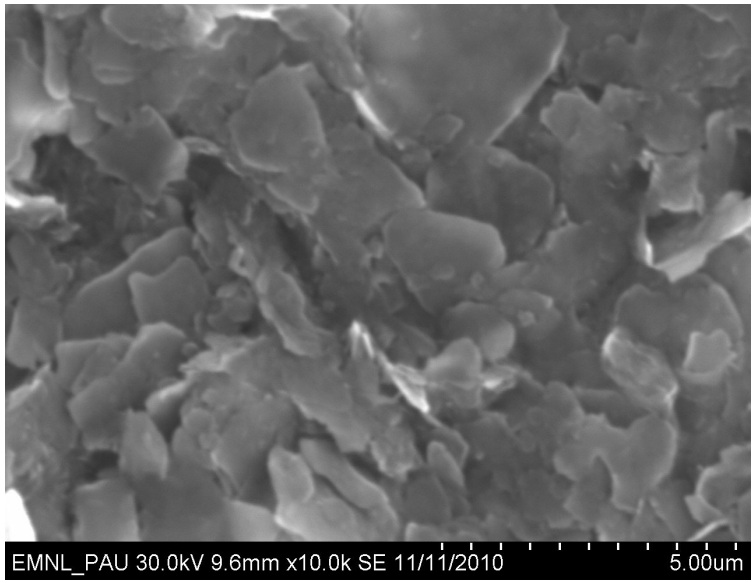
- **Soil could be perceived as a four dimensional system where a broad three dimensional structural fabric is filled by**
  - ***dynamic and reactive colloidal constituents***
  - **that *change with time.***

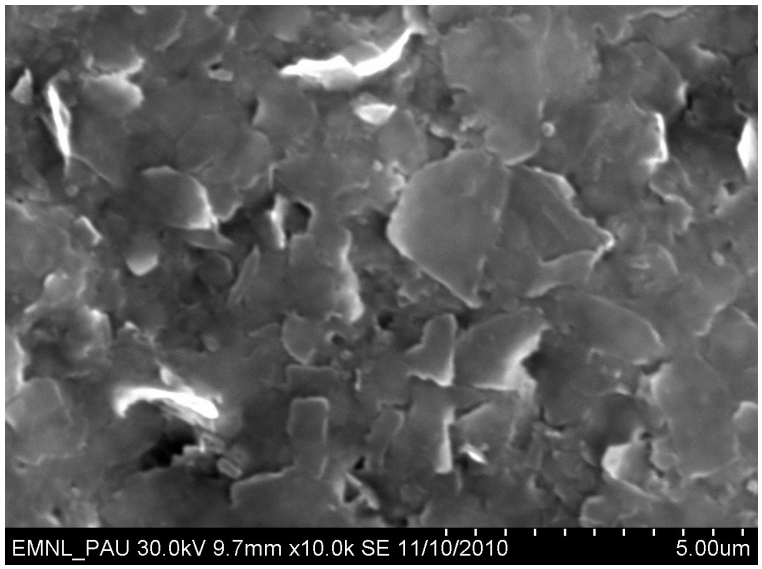
Humus Sorption on Clay

- Thermodynamically, both colloidal clays and colloidal organic matter (i.e., humus)would form complexes so as to attain stability (dG < 0).
- It is one of the natural phenomena that protect earth system.
- Humus occurs on clays on nanoscale.
- Clay bound humus can rejuvenate degraded ecosystems

Clay-Humus Complex in soils of Punjab







Top left: Mango orchard

Top right: Guava orchard

Left: Rice-Wheat field

Organic carbon (atom %) on soil-clays of Punjab (SEM-EDS data)

Land use	Humus Clay	Soil-Clay
Mango orchard	12.10	15.25
Guava orchard	15.60	18.90
Rice-Wheat field	9.78	11.69

The game people play: Is clay science a winner in NT game?

Clay science is not a winner,

but a conqueror

But, what is the scientific basis of the statement?

Clay minerals and Nanotechnology

The origins:

can be traced to clay mineralogy and crystallography when it was discovered that clay minerals were crystalline and of micrometer size

(Lower et al., 2001)

Advantages of clays

- The ever-growing application of clays in nanotechnology rests on fundamental principles of colloid chemistry
- They make soils as nature's great electrostatic chemical reactor
- The unit cell dimensions of clay minerals are in nanometer scale in all three axes (x, y, and z)

- ordered arrangements,
- large adsorption capacity,
- shielding against sunlight (UV radiation),
- ability to concentrate organic chemicals, and
- ability to serve as polymerization templates

Possible innovations

- nano-enhanced products
  (e.g. nanofertilizers and nanopesticides)
- nano-based smart delivery system
  (use of halloysite)
- Nanoporous materials
  (e.g. hydrogels and zeolites)
- Nanomaterials (sorbents of pollutants)

(Lal, 2009)

Nanotechnology and clay

Ionic character (%) of a bond is determined by the difference between the electronegativities of the two atoms concern, and can be expressed by using Pauling's equation:

$$p = 16|x_A - x_B| + 3.5\,|x_A - x_B|^2$$

Si-O bond ~ 33.8% ionic,

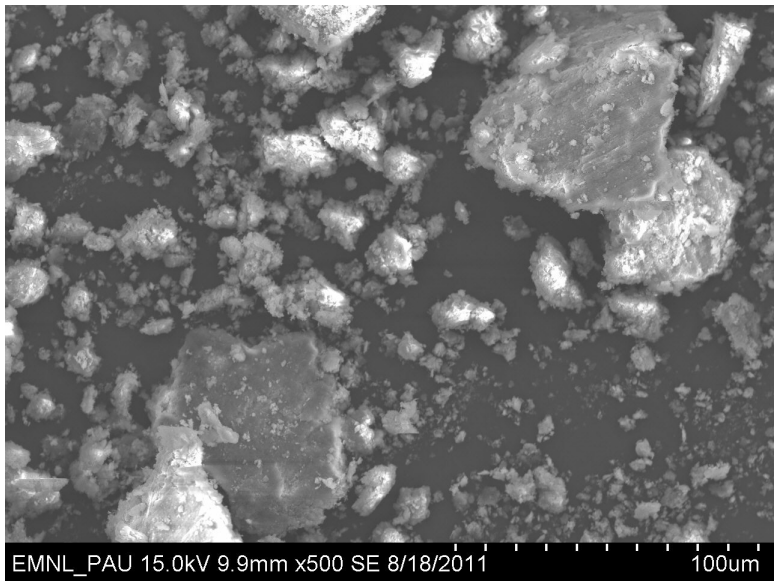
Al-O bond ~ 46.0% ionic

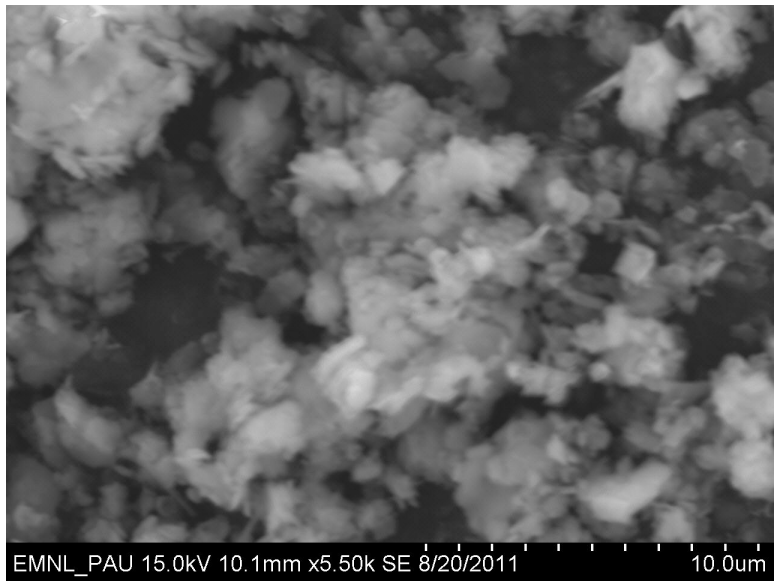
Manufacturing bonds in clays?

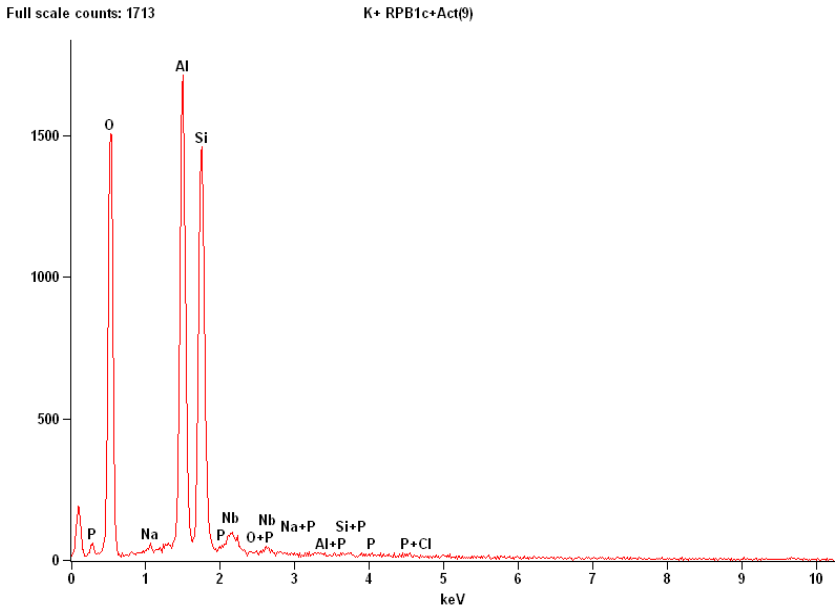
- Si replaced by Al - increase of 12.2% ionic character in silicon tetrahedron
- If Si is replaced by Al in zeolite framework structure, the tunnel diameter changes
- Organic materials can bridge different bonds

Nanofabrication of P on kaolinite (PAU Work)

- SEM micrograph and EDS spectrum of nano-kaolinite with phosphorus adsorbed on positively charged face of kaolinite

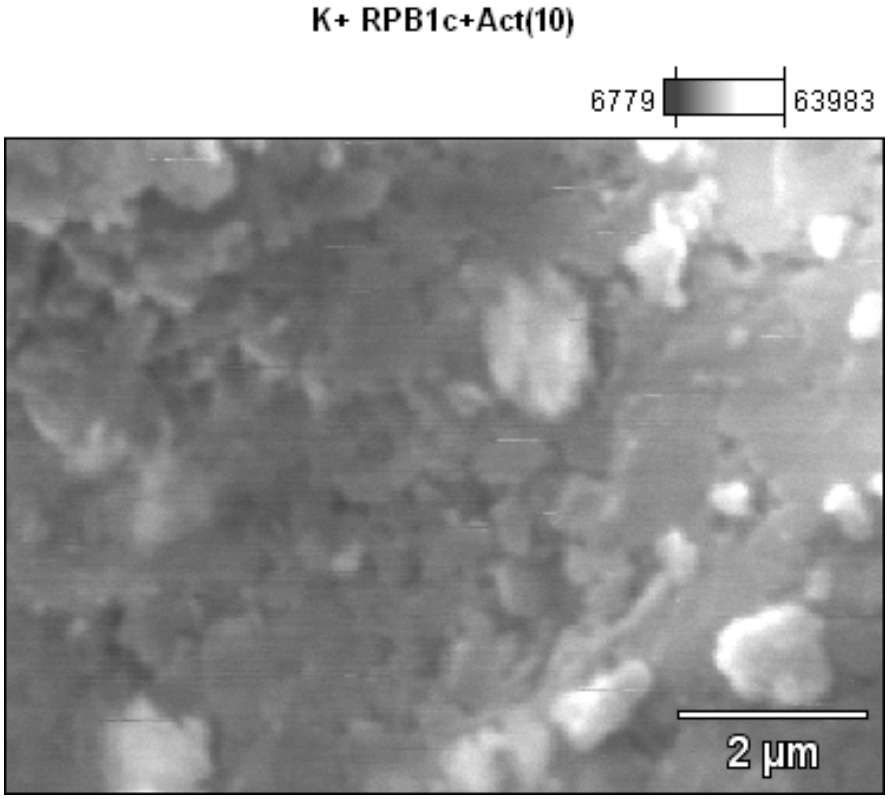


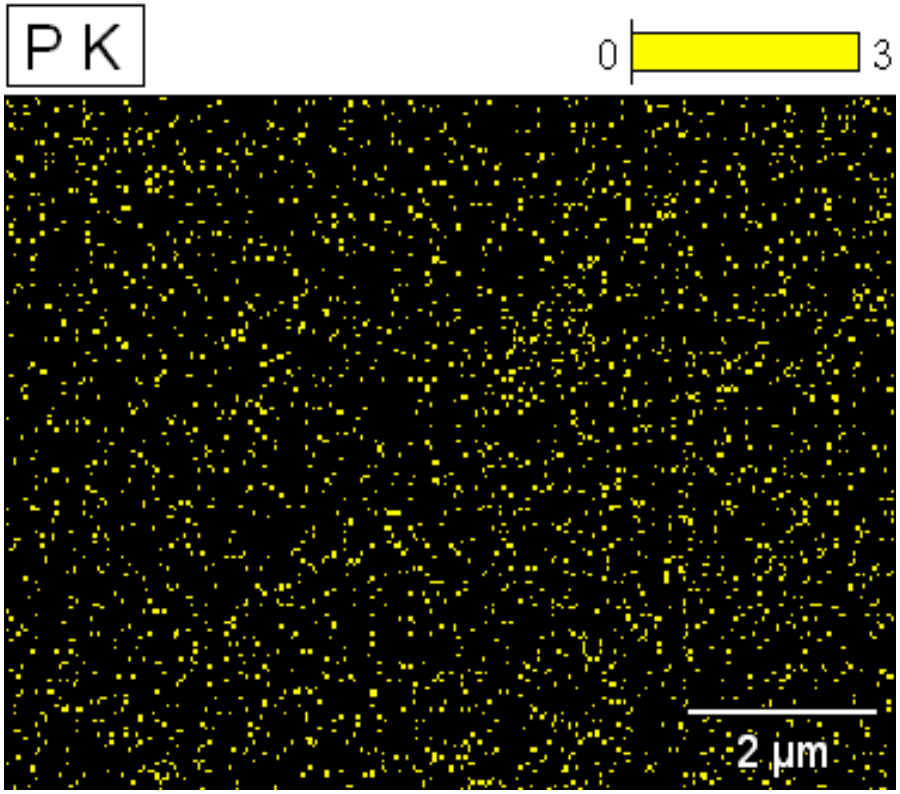




Element	*Atom %*
O	65.43
Na	0.34
Al	16.06
Si	16.75
P	0.43
Nb	0.99
Total	100.00

Contd…..





Why is clay based NT a distinct field?

- Depart from traditional NT (e.g., nanoelectronics, nanomaterials)
- Depart from conventional appl. fields (e.g., cell phone, computer, sensors)
- Clay – an interface of physical and biological worlds
- Soil is the central domain of GBAH-spheres

Nanofrabication with clay: Methods

- Methods followed in industry (like melting materials at a high temp. to segregate atoms / ions at plasma state) cannot be copied
- Stability of mineral in soil environment is important

Is that a hindrance?

No, because system obeys the laws of ion exchange, adsorption-desorption, aggregation - dispersion, solubility-dissolution etc.

Most vital yardstick is

that the system has to be capable of releasing nutrient ions in plant-available forms

"Clay-Plant nutrient nanofactory"

Control of clay based NT

- does not promise a control system that we experience in electrical machines, or in satellites, or in chemical reactors.

It has to be knowledge based passive system

Clay-NT Dream

- ***Let it create millions of rhizos-pheres in an acre of land to support the growth of millions of plants of a crop***

a breakthrough to place agriculture into new millennium

Calling All Nanotechnologists: Learning Lessons from Soil System

- Dynamic equilibrium
- Ion transport in soil-plant-atmosphere continuum
- Solubility – dissolution reactions
- pH buffering
- Ion exchange

Domain of uncertainty

- Positional uncertainty
- Command structure
- Transport uncertainty
  (e.g., preferential flow; groundwater contamination)
- Self regulatory behavior
- Surface energy

But, nanotechnology is rooted in soil

If

Nanotechnology in agriculture is a castle in the air

Nanotechnology in agriculture is a castle in the air

Just put foundation beneath it

Before my Alma-mater
Before the teachings of my mentors
And before this august gatherings
“I, being poor, have only my dreams;
I have spread my dreams beneath
your feet;
Tread softly because you tread on my
dreams...”

- William Butler Yeats

Thank you