Nanomaterial: Look at the Earth

Siddhartha S. Mukhopadhyay

Electron Microscopy and Nanoscience Laboratory,
Punjab Agricultural University
Ludhiana
Why clay?

- The unit cell dimensions of clay minerals are in nanometer scale in all three axes (x, y, and z)
advantages of clays

- their ordered arrangements,
- their large adsorption capacity,
- their shielding against sunlight (ultraviolet radiation),
- their ability to concentrate organic chemicals, and
- their ability to serve as polymerization templates.
Clay minerals and the genesis of life on earth

- Sir J.D. Bernal (1949) was first to suggest
- NASA offers an exclusive URL on the subject

(http://www.resanet/nasa/origins_life.htm)
Clay minerals and evolutionary diversification of Neoproterozoic life

- enhanced burial of organic carbon
- C got protected from reoxygenation
- allowed O$_2$ to accumulate in the environment
- Late Precambrian oxygenation led to the inception of ‘clay mineral factory’
Defining NANO...

- Environmental Protection Agency (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.
Nanotech involving soil minerals

- Nano-science (also nanotechnology) converges soil mineralogy with imaging techniques, artificial intelligence, and encompass bio molecules and polymers with microscopic atoms and molecules.

- Links macroscopic properties (thermodynamics) with microscopic properties (kinetics, wave theory, uncertainty principles, etc.).

- 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.
Industrial uses of clay

- Petroleum refinery
- Cement
- Soaps, detergents, shampoos, lipsticks
- Pesticide carrier
- Ceramics, pottery and sculpture
- Fertilizer conditioner
- Environmental clean up operations
- Pharmaceuticals and catalyst
Nanomaterials

- either newly-created through nanotechnology, or that exist in nature

- Example:
  - clays, zeolites, imogolite, Fe & Mn oxides

- Potential:
  - to manipulate structures or other particles at the nanoscale and to control and catalyze chemical reactions
nanomaterial

Applications:

- provide transparency, or increased strength with decreased weight
- Smart fabrics
- Controlled Environment Agriculture
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)
- nanoporous membranes
- Nanosorbents
- Nanocrystals of magnetite (< 12 nm)
- Nanosensors
- nanoscale precision farming
Basic Concepts involving Soil mineral structures
Ionic radius

- Ionic Radius, $r_{ion}$, is a measure of the size of an ion in a crystal lattice.
- Radius ratio of coordinating ions, and bond strength are critical components.
- The ionic radius is not a fixed property of a given ion, but varies with coordination number, spin state and other parameters.
\[ d = r (\text{cation}) + r (\text{anion}) \]
Radius ratio

- The ratio of the radius of a cation to the radius of anion; relative ionic radii are pertinent to crystal lattice structure, particularly the determination of coordination number.

Radius Ratio \( = \frac{R_{\text{cation}}}{R_{\text{anion}}} \)
# Relationship between radius ratio and coordination number in coordinating polyhedron system

<table>
<thead>
<tr>
<th>Radius Ratio</th>
<th>Arrange of Anions around the cation</th>
<th>Coordination Number (CN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15 - 0.22</td>
<td>Corners of equilateral triangle</td>
<td>3</td>
</tr>
<tr>
<td>0.22 - 0.41</td>
<td>Corners of a tetrahedron</td>
<td>4</td>
</tr>
<tr>
<td>0.41 - 0.73</td>
<td>Corners of an octahedron</td>
<td>6</td>
</tr>
<tr>
<td>0.73 - 1</td>
<td>corners of a cube</td>
<td>8</td>
</tr>
<tr>
<td>1</td>
<td>Midpoints of cube edges</td>
<td>12</td>
</tr>
</tbody>
</table>
Si-tetrahedron and Al-octahedron structure
Si tetrahedra and Al octahedra in clay minerals

The Mystery of Clays - Eytons' Earth
Coordination number

- **Coordination Number (CN) and Radius Ratio**

- In an ionic structure each cation tends to surround itself with anions; the number that can be grouped around it will depend on the relative size of the cations and anions.

- In most of SM, the **Coordination Number (CN)** is defined as the number of anions that can fit around a cation.
This number increases as the radius ratio increases. The number of anions that can ‘fit’ around a cation is related to the relative size difference between the ions, and this size difference can be described using the radius ratio, which is given by:

\[ \frac{r_{\text{cation}}}{r_{\text{anion}}} \].

When this number is small, then only a few anions can fit around a cation. When this number is large, then more anions can fit around a cation. When CN is 4, it is known as tetrahedral coordination; when it is 6, it is octahedral; and when it is 8, it is known as cubic coordination.
Pauling’s Rules in coordinating polyhedra

- **Pauling's rules:**
  Five rules published by Linus Pauling in 1929 for determining the crystal structures of complex ionic crystals
A coordinated polyhedron of anions is formed about each cation, the cation-anion distance determined by the sum of ionic radii and the coordination number (C.N.) by the radius ratio.
- Tetrahedron is formed when $RR > 0.22$ and $< 0.41$

- Octahedron may form with a $RR \geq 0.414$

- When $RR > 0.732$, a cubic conformation becomes more stable.
2) An ionic structure will be stable to the extent that the sum of the strengths of the electrostatic bonds that reach an anion equal the charge on that anion.
3) The sharing of edges and particularly faces by two anion polyhedra decreases the stability of an ionic structure. Sharing of corners does not decrease stability as much, so (for example) octahedra may share corners with one another.

Effect is largest for cations with high charge and low C.N. (especially when $r+/r-$ approaches the lower limit of the polyhedral stability).
In a crystal containing different cations, those of high valency and small coordination number tend not to share polyhedron elements with one another.

The number of essentially different kinds of constituents in a crystal tends to be small. The repeating units will tend to be identical because each atom in the structure is most stable in a specific environment. There may be two or three types of polyhedra, such as tetrahedra or octahedra, but there will not be many different types.
Structure of kaolinite (China clay)
Structure of Montmorillonite

Montmorillonite

\[(\text{Al}_{3.2}\text{Mg}_{0.8})(\text{Si}_{8}\text{O}_{20}\text{OH})_{4}X_{0.8}\]

\[\begin{array}{c}
\text{Na}^{+}/\text{Ca}^{++}
\end{array}\]

**Tetrahedral**

4 Si, 6 O

**Octahedral**

4 O + 2 OH
3.2 Al^{3+} + 0.8 Mg^{2+}
4 O + 2 OH

**Tetrahedral**

4 Si, 6 O
Tectosilicates: Zeolite
TEM of a zeolite
Replacement criteria of different atoms

- **Isomorphous substitution:**
  
The process by which one element fills a position usually filled by another of similar size.

- **Criterion:**
  
  Isomorphous substitution between two similarly (not same) charged ions can occur provided the difference between their size is within the limit of $\pm 15\%$. 

Examples:

- $O^{2-}$ is replaced by $OH^{-}$ and $F^{-}$
- $Si^{4+}$ is replaced by $Al^{3+}$ and $As^{5+}$
- $Al^{3+}$ is replaced by $Be^{2+}$, $Ca^{2+}$, $Fe^{2+}$, $Fe^{3+}$, $Mg^{2+}$, $Mn^{2+}$, $Zn^{2+}$, etc.
Exception: 

Al$^{2+}$ replaces Si$^{4+}$, although their radii differ by 28% because of

1. Lithogenesis
2. Same co-ordination: Al:O radius ratio of 0.36 is close to critical value of 0.3 for transition from 6- to 4- coordination
Soild Solution:

- Many pairs of elements or chemical compounds are capable of replacing each other through Isomorphous substitution, thereby forming crystals with widely varying composition.

- Thus it is possible to grow homogenous crystals of any composition between the two extremes, eg. Feldspars \{Albite; Na(AlSi$_3$)O$_8$ and anorthite; Ca(Al$_2$Si$_2$)O$_8}\}
Birth of semiconductivity
Nanotechnology in agriculture is like a game of Quidditch that Harry Potter and other pupils played in the School of Magic. No matter what’s the score, if the seeker catches snitch, his team wins.
Thank you!