## Soil Mineralogy: Recent Discoveries and Their Implications

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Many of the early investigations in soil mineralogy addressed identification of minerals in soils and weathered rocks throughout the world (Dixon and Weed 1977; 1989). I will pursue more the properties and reactions of soil minerals. The presentation will include a few phyllosilicate minerals, that are abundant in soils, sulfides, and oxides of iron and manganese that are important soil minerals. The clay-organic research area will only have brief mention as time permits.

The strength of soil mineralogy as a sub-discipline is predicated on a strong instrumental base. X-ray diffraction, scanning and transmission electron microscopy, infrared spectroscopy, and the various methods employed to quantify chemical elements, and electronic state of the elements in crystals e.g. x-ray photoelectron spectroscopy, etc. and new methods as they are developed (Rich and Kunze, 1964; Amonette and Zelazny, 1994).

The best opportunities in soil mineralogy continue with the ever-advancing theory and methodology from science and technology applied to very small particles i.e. colloids as they interact with water, natural organic matter and the numerous products, wastes, and other materials generated by man (Dixon and Schulze, 2002).

# Recent discoveries that have implications for future research or technological developments.

Sulfide minerals are familiar to earth scientists in the form of pyrite and marcasite, minerals that are frequently large particles or framboids of small particles. Colloidal sulfides are less common. In our research on growing shrimp in ponds we addressed the question of sulfide concentration because sulfides are toxic to marine organisms. We discovered a new colloidal sulfide precursor to mackinawite that has a layer structure with a high surface area and tendency to fold like smectite (Ritvo et al., 2000). We have called the new mineral dorite. Such colloidal sulfide is likely to be much more

chemically and physically reactive than pyrite and marcasite and may be a contributor to the control of sulfide ions in reducing environments such as those where shrimp are grown.

Iron oxides are known for their contribution of red, brown and yellow colors to soils and rocks. They also, are major contributors to the aggregation of soil particles and to anion retention. Goethite is one of the most common Fe oxides in soils and the crystals are usually sub-micron in size and frequently have numerous well-developed crystal faces (Dixon, 1999). These faces are likely sites of chemical reactivity.

Manganese (Mn) oxides (birnessite, todorokite, and lithiophorite) are important oxidants in soils. They have been the focus of much recent research because they are major oxidants of Cr(III) to the more toxic form Cr(VI). Our recent research on these minerals has shown that reference specimens have a higher surface area than expected and a complex open internal fabric that helps explain their effectiveness as oxidants in spite of their relative in frequency in soils (Kim et al., 2002).

Also, we found the Mn oxides to contain more trivalent Mn than normally stated in their formulas (Kim et al., 2002).

We recently discovered that halloysite has a particularly affinity for ferrihydrite Fe oxide

(Augustine et al., 2000). Previously we had noticed goethite aggregation with halloysite. These observations and the reported permanent charge of halloysite prompted us to hypothesize that the positive charge of the iron oxides due to their high zero point of charge causes them to aggregate with halloysite when they are less likely to aggregate kaolinite.

Also, we observed that halloysite compacts under centrifugation to lower bulk density clay plugs than kaolinite and that they have a higher hydraulic conductivity than kaolinite plugs produced by the same methods.

Smectite is well known for its forming thin sheets and for its high surface area and high cation exchange capacity (CEC). Recent investigations have shown that smectite tends to fold at the edges revealing lattice fringes indicating the number of layers in the particle.

Smectite CEC can be neutralized by treatment with the appropriate organic cation yet typically the treatment of smectite with large organic cations or other organic polymers only neutralizes a fraction of the CEC and the hydrophilic properties persist. The clayorganic reactions are amenable to study by several methods. Clay properties can be modified by selecting the organic molecule for its properties of charge, size and configuration as has been demonstrated by many investigators (Deng et al., in review; Dixon et al., 1970; Hwang and Dixon; 2000; Koh and Dixon, 2001)

The interstratification of smectite and illite (mica) have been better illuminated by sectioning of these minerals and viewing their lattice fringes (Woida and Thompson, 1993). These persist as relatively poorly understood phyllosilicate mineral associations in soils.

#### Questions that deserve research for scientific and practical reasons.

There is a widespread perception that ferrihydrite is a major chemical reactant in soils. Yet goethite, hematite and lepidocrocite are more commonly identified in soils by definitive methods. The kinetics of Fe oxide transformations in soils deserves research to help understand and predict soil behavior.

The intercalation of coarse kaolinite particles has been done by numerous researchers yet the reason for fine kaolinite resisting intercalation remains unexplained.

The flocculation of clays produced during mining operations to recover nodular phosphates persists as a major challenge deserving definitive research.

How do the interactions of clay particles influence soil aggregation, water movement and aeration?

How can the range of properties in each clay mineral group be quantitatively evaluated e.g. particle size, shape and crystal imperfection?

How does layer charge influence the interaction of different soil minerals e.g. silicates, oxides, etc.?

### **Conclusions**

Soil minerals occur in a wide range of particle sizes, shapes and compositions. Their reactions in soils need to be evaluated throughout the full range of properties to permit quantitative interpretation of their contribution to soil behavior.

Knowledge of mineral-to-mineral interactions should permit predicting and improving soil chemical, and even physical behavior, based on detailed soil mineral analysis.

Soil mineralogy is an interesting and rewarding field of study because of the great diversity of natural subjects and the many analytical instruments available to pursue it.

One of the challenging aspects of soil mineralogy is expressing the objectives of soil mineralogy research in terms that are clearly related to solving important problems.

Recent technological advances in microscopy and image processing make the acquisition and delivery of data more efficient and effective.

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