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TECHNICAL REPORT

TOXIC CHEMICALS IN THE SOIL ENVIRONMENT

VOLUME 1. CHEMICAL PROPERTIES AND
CHARACTERIZATION OF SOILS

By

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Soil science embraces physical, chemical, biological, physiological, genetic-cartographical, and applied sciences. In order to define accurately the field of soil science, it is necessary to give an exact definition of what one means by "soil." Soil is a constantly changing, living earth cover, exposed to continual change due to the effect of insolation, precipitation, and living organisms. The formation and existence of soils depend upon special circumstances and factors that may be called collectively, soil-forming factors.		

20. Abstract (Cont'd)

These factors are characteristic of all soil types. Upon these soil-forming factors depend the peculiar structure of the soil and the physical, chemical, and biological properties that differentiate soils. This report deals with the above factors in the hope that such an evaluation would be beneficial to those who may be required, at some future time, to determine interactions of chemical warfare agents and soils.

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FOREWORD

This report was prepared by soil scientists at Oklahoma State University, Stillwater, Oklahoma, in conjunction with the Technical Analysis and Information Office, US Army Dugway Proving Ground, Dugway, Utah. The work was funded by EDTE Project 1M465710-D049, Joint Chemical and Biological (CB) Contact Point and Test (Project D049).

This work on the chemical properties and characterization of soils is volume 1 of a series of reports that were undertaken in response to a requirement to assess the hazard that may result from dust that has been contaminated by chemical warfare agents. Data regarding the interaction of chemical warfare agents and dust, that is, soils of which dust is composed, are few. The data that were found resulted from research that did not utilize important concepts of soil science; thus, the data were not useful for evaluating chemical warfare agent and soil interactions. For these reasons, an investigation of available information on the interaction of pesticides in soil, particularly those pesticides similar in composition to chemical warfare agents, was undertaken.

Because there was evidence of a lack of understanding of the basic concepts of soil science in the chemical weapons literature, information on this subject has been presented for the enlightenment of those chemists, and others, who may be required at some future time to determine the interactions of chemical warfare agents and soils. It should be evident to those who read this report that the chemistry of soils is complex. The discussion presented herein is primarily of mineral soils, low in organic matter content, as a prime source of dust.

The concepts presented are important to the study of many problems in chemical defense. Of primary interest is the fate of chemical agents in the soil. Since soil will be the location of the bulk of chemical agent that has been disseminated in any terrestrial environment, the ultimate fate of the agent should be studied. The decontaminating value of soil components, such as Fuller's Earth, has been demonstrated. The ultimate fate of the agent in the decontaminating soil or soil component under varying environmental conditions should be determined. The principles of soil chemistry should be recognized and utilized in these and any other study involving the interaction of soils and chemical agents and also biological agents.

The investigation of the interaction of some toxic chemicals, to include pesticide-type chemicals and also chemical warfare agents, and soils will be presented in volume 2, entitled, *Interactions of Some Toxic Chemicals/Chemical Warfare Agents and Soils*. An analysis and estimation of the hazard associated with dust that has been contaminated by chemical agents is reported in volume 3: *Possible CW Agent Hazard from Dust Storms*.

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SECTION 1. INTRODUCTION

1.1 BACKGROUND

Civilization, that is, a sedentary population probably began when man learned to plant seed, nurture food plants, and wait for the harvest. These early farmers were also the first soil chemists because they very quickly learned about productive and nonproductive soils. However, the application of the scientific method and development of soil science as a discipline in its own right is less than 150 years old.

To much of the lay public today, soil is still thought of in the context of the Greek word for soil or "pedo" meaning underfoot, that is, that on which we walk. To many physical and biological scientists, soil appears to be a bewildering mixture of inert mineral substances mixed with a trace to a few percent of amorphous organic debris, and probably not worthy of study.

Soil scientists have developed concepts that have caused the study of soil to be on a firm scientific base. The highest order of scientific expertise has been applied to the study of soil by skilled scientists from all parts of the world.

In the past 50 years, study of the ability of soil to absorb, detoxify, and otherwise cause the inactivation of a host of chemical compounds has been greatly intensified. The interaction of all types of soil with herbicides, insecticides, industrial and urban wastes, and natural products of the environment has been studied with the intent to use the soil as one of the cleansing agents of our civilization. Therefore, the study of the chemistry of this interaction merits a great deal of attention and support.

1.2 THE NATURE OF SOIL

Russell (1950) defines soil as a medium for plant growth and therefore as a medium for root development. He further divides the soil into four parts: (1) mineral matter derived from rocks, (2) calcium carbonate and phosphate, (3) residue of plants and microorganisms, and (4) soil water of the soil solution. Buol et al. (1973) defines soil genesis as that phase of soil science (pedology) that deals with the factors and processes of soil formation. Soils, therefore, are not geologic deposits but they are the upper portion of the earth's surface which has been invaded by organic matter and otherwise altered by processes caused by its position at the earth's surface. Thompson and Troeh (1978) point out that any definition of soil depends on the viewpoint of the person formulating the definition: an edaphologist would define soil as "a mixture of mineral and organic matter that is capable of supporting plant life" while a pedologist or a student of soil genesis would define

soil as "a natural product formed from weathered rock by the action of climate, slope, time, and living organisms." These two concepts have a common point of view, that is, life is required.

There are a number of concepts concerning the soil that should be addressed before an attempt is made to investigate the detailed chemistry of soil:

- (1) Local profile - the vertical exposure of the several horizons or layers of an individual soil or the superficial portion of the earth's crust which includes all layers that have been pedologically altered.
- (2) The solum - that part of the soil profile that is influenced by plant roots.
- (3) Soil horizon - a layer of soil approximately parallel to the soil surface with characteristics produced by soil forming processes.
- (4) Soil forming processes - these processes are essentially (a) additions to a soil body, (b) losses from a soil body, (c) translocation within a soil body, and (d) transformations within a soil body.

This very brief introduction to the nature of soil is not adequate for a student of soil science, but it may suffice to introduce some of the more detailed chemical processes within the soil. Therefore, we will proceed with a discussion of some of the chemical characteristics of the soil.

1.2.1 Cation Exchange

The cation exchange capacity (CEC) is the capacity of a soil to sorb or hold cations and to exchange those ions in reversible chemical reactions. The CEC has been expressed as milliequivalents/100 grams soil (meq/100 g). However, the nomenclature committee of the Soil Science Society of America has defined CEC as micromoles/gram ($\mu\text{m/g}$) and the ion is specified (usually calcium). CEC describes an experimental phenomenon with a number of analytical procedures for its determination. The most common procedures are:

- (1) Saturation at pH 7.0 with ammonium ion (leached with 1 molar ammonium acetate) and displacement of the ammonium ion, or
- (2) Saturation with calcium (Ca^{++}) and displacement with sodium (Na^+).

The summation method (sum of all exchangeable cations) is also commonly used, but must include exchangeable hydrogen and aluminum.

CEC of soils implies a source of negative charge in soil. The sources of charge are several and will be discussed in detail later. Some workers (Bohn et al., 1979) assume a clearcut boundary between the exchangeable cations held by the soil and the bulk solution. However, the concentration of ions around a negatively charged soil particle is probably distributed in an atmosphere around the particle variously described as the "diffuse-double-layer" where the soil particle (colloid) has an excess of cations near the particle surface and a deficit of anions. Calculations based on the Gouy-Chapman (1913) theory as reported by Van Olphen (1963) show that at a distance of 5 to 150 angstroms ($\text{\AA}$)¹ from the surface of a colloid clay particle, the concentration of cations in a dilute solution (0.01N) will be approaching 3N at the surface, and at 150 $\text{\AA}$, the concentration will be 0.01N. If the deficit of anions is also plotted, it can be shown that the surface of the negatively charged particle effectively excludes anions, but the concentration of anions increases with distance from the soil particle surface. "Double-layer" thickness decreases as the square root of the bulk solution salt concentration of the soil solution (N) and directly with increasing valence of the exchangeable cation.

Although cation exchange reactions are normally considered to be reversible and virtually instantaneous, there are exceptions where polyvalent heavy metals are sorbed irreversibly by organic matter in soils (discussed in a subsequent section). For the normal exchange reaction we can say that it is essentially stoichiometric. The cation exchange reaction as a simple electrostatic approach is defined by Coulomb's Law, but does not predict differences in selectivity of colloid surfaces for cations of the same valence. The selectivity or preference is related to the relative hydrated sizes and energies of hydration of the various cations, while ions of smaller dehydration radius have a greater density of charge per unit valence. The radius of highly hydrated ions like Na have a low density of charge and are more easily removed from charged soil particle surfaces, thus in normal temperate zone soils exchangeable Na is in the surface soil as a trace quantity and a larger amount may be present in the subsoil. Soil colloids (clay minerals) exhibit cation selectivity; e.g., clay minerals like vermiculite show a preference for magnesium (Mg), montmorillonite (smectite) tends to be selective for Na, while illite (hydrous mica) is selective for potassium (K).

There have been many attempts to develop mathematical models for the cation exchange reaction. However, due to the empirical nature of this reaction, no model developed to date has been completely satisfactory (Bohn et al., 1979; Bolt et al., 1976; and Kelley, 1948). Some authors suggest that application of the Capon equation (Bohn et al.,

¹One angstrom ($\text{\AA}$) = 10^{-10} m.

1979) which is a mass-action equation is useful although not rigorous over the entire range of ion concentration in a soil-salt solution system.

1.2.2 Anion Exchange

Anion exchange is not extensively discussed in the soil chemistry literature. Probably the identification of cation exchange as an electrostatic phenomenon of soil clay minerals causes discussion of anion exchange, which is not identified with some easily defined chemical phenomena, to be neglected. Therefore, many investigators neglect anion exchange or introduce the subject in much the same manner as Mott (1981) who states "One of the generalizations that can be made about soils is that the particles have a net negative charge" and he then continues, "There are exceptions."

Most anions are held much more strongly by the soil complex than we would at first surmise. Positively charged sites can exist on soil particles at a given pH and the quantity of anions sorbed can be quantitatively estimated.

The anions of strong mineral acids, e.g., anions of hydrochloric and nitric acid and also perchloric and hydrobromic acid, are nonspecifically sorbed by soil. The (ad)sorption is physical and there is no electron transfer or sharing of electrons between the anions and crystalline moieties. All other anions, including organic anions, are specifically sorbed by soil. The anions are sorbed at specific sites on soil particle surfaces and form chemical bonds. The "specific sorption" generally describes an anion bound as a ligand rather than an electrostatic bond. There are other anions which are attracted to a soil particle surface to a greater extent than would be inferred from the diffuse-double-layer anion exclusion theory.

The bonding of anions in soil may be due to sorption or exchange of hydroxyl (OH) with the solution anions (specifically sorbed anions). If titrations are carried out with a soil-solute salt mixture (in NaCl solutions from 1.0 to 0.001 molar), the resulting set of titration curves on the pH scale (abscissa) vs. microequivalents/gram ($\mu\text{eq/g}$) (ordinate) will cross at the same point, which is the point of zero charge (PZC). (This is also referred to as pH dependent charge.) The oxides of iron (Fe) and Al, or hydrated oxides are primarily responsible for this type of bonding. Therefore, goethite ($-\text{FeOOH}$) has a PZC between pH 8 and 8.5, which means that at this pH the positive and negative charges on the surface are balanced; however, to maintain this state the solution must contain 100 times more OH^- than H^+ while goethite holds protons (H^+) much more strongly than it holds water. If one considers the crystal structure of an oxide where surface cations like Fe^{+3} are not fully coordinated (for Fe the coordination number is 6) there will be a small residual charge on surface ligands. In aqueous solutions these sites will be hydroxylated and carry a net negative residual charge. The extent of charge, however, will be strongly dependent on which crystallographic planes are exposed to the soil environment. Specific anions have a strong affinity for hydroxylated

surfaces and displace the ligands to the cations. This illustrates ligand exchange and not electrostatic attraction.

These reactions are very often expressed with absorption isotherms, for example, Langmuir or Freundlich types. Although these absorption isotherms are empirical, they are useful for the investigation of anion exchange or sorption.

Ions that are electrostatically attracted to a charged surface are desorbed by approximately the same amount of energy as was released on sorption. However, with ligand exchange, this is not necessarily true because the ligand forms an "ionic-partly-covalent" bond with the surface, and the ligand is between the exchange lattice cation and the exchange anion. Usually there is selectivity in favor of the ligand anion. The implication of this is that desorption at constant pH will require more energy than sorption at the same conditions. This phenomenon is very well illustrated with phosphate sorbed on goethite (Hingston et al., 1974).

SECTION 2. SOIL MINERALOGY

Most mineral soils have features which relate them to the parent rocks from which they came. However, where the soil was formed from sediment (sedimentary rocks), which itself was formed from preexisting primary or igneous rocks, the relation between the parent rock and the soil might be quite remote. If a soil is formed directly from igneous rock, there may still be little resemblance between the soil and the parent rock due to weathering and the synthesis of secondary minerals.

If the minerals in igneous rocks are compared with the minerals found in soils, a wide difference in composition can be noted. For example, olivines, pyroxenes, amphiboles, and biotites are very easily weathered and, in most mineral soils, these minerals are present only in trace quantities while their presence in the parent rock may have been in excess of 50 percent. Most feldspars weather less readily; however, the Ca feldspars disappear early in the weathering process while the Na and K feldspars are much more stable and weather very slowly. Muscovite or K mica is quite persistent in soils and weathers at about the same rate as K feldspars. Quartz weathers very slowly and persists in soils after most of the metal-substituted Al silicates have been altered by weathering. Primary minerals from igneous rocks [e.g., anatase and rutile (TiO_2) and zircon (SiZrO_4)] weather so slowly in soils that they can be used for weathering indexes. The clay minerals vary in their resistance to weathering. Kaolinite and the hydrated oxides of Fe and Al are the most resistant to weathering of all of the clay minerals. Smectite, vermiculite, and the hydrous micas are less resistant to weathering. Therefore, soils found in high weathering intensity environments will have very low percentages of the smectite and micaceous minerals.

The clay minerals are all thought to be secondary minerals. Where rocks (sediments) and soils are weathered under free leaching conditions in tropical climates, the resulting soil is very high in gibbsite (hydrated Al_2O_3) and goethite. Where drainage is less free, there is a significant concentration of silicon (>2 ppm) in the soil solution and kaolinite is formed. When drainage is low and basic cations like Ca^{+2} , K^+ , Mg^{+2} , and Na^+ are present in the soil solutions, the 2:1 clay minerals, like hydrated mica (illite) and smectite (most montmorillonites, vermiculites, and chlorites), are present in the soil.

The clay component of soil is usually referred to as the "active fraction" because most properties of soil are related to sorption reactions on clay mineral surfaces. Clay minerals are an extremely difficult group of minerals to study because there are no "hand specimens." All of the clay minerals may be thought of as the "dwarf minerals" of the mineral kingdom. The upper limits for clay mineral size is approximately $2\text{ }\mu\text{m}$ or less in equivalent spherical diameter (ESD). Therefore, the specific surface areas for the clay minerals



range from $1 \text{ m}^2/\text{g}$ for very coarse grained ($2 \text{ }\mu\text{m}$) kaolinites, to an excess of $760 \text{ m}^2/\text{g}$ for the less than $0.02 \text{ }\mu\text{m}$ fraction of the smectites. The surfaces of many of these clay minerals carry a significant amount of electronic (negative) charge which is balanced by cations in the environment of the clay particle. The characteristics of each of these clay minerals are discussed in the succeeding paragraphs.

2.1 THE CLAY MINERALS IN SOILS

There are many outstanding references concerning the clay minerals found in soils. Van Olphen (1963) discusses the chemistry of the clay colloids, Brown et al. (1978) discuss these minerals in the Greenland and Hayes (1978) report, and Carroll (1970) has made an outstanding contribution to our understanding of the X-ray identification of these minerals. Dixon and Weed (1977) present an exposition of not only the soil clay minerals but other minerals in soils. Many other contributions too numerous to mention, including those by the authors of this report, will be cited either directly or indirectly.

The clay minerals are usually grouped by the silicon to aluminum ($\text{SiO}_2:\text{Al}$) ratio or potential charge per X-ray unit cell. The common clay minerals (as per Tables 1, 2, and 3) will be discussed here; the 1:1 minerals first and then the 2:1 minerals. These minerals are further divided into three series: (1) dioctahedral, (2) trioctahedral, and (3) tetrahedral.

The data in Table 1 show the empirical composition of the common clay minerals and their percentage composition. Tables 2 and 3 are attempts to classify the clay minerals usually encountered in clay mineralogy studies; Table 2 is a classification of minerals, by the Clay Minerals Section of the Mineralogy Society of Great Britain, based on molecular structure; and Table 3 is a classification, by the Nomenclature Committee of the American Clays and Clay Minerals Society, based on charge and structure.

Extensive literature on the chemistry and physics of clay mineralogy is available, with applications in agriculture, microelectronics, ceramics, catalyst-assisted chemical manufacture, oil well drilling, geochemical and geophysical petroleum exploration, commercial mining, and as sinks for disposal of hazardous chemicals. In essence, one could say that the basic chemistry of the land surface of the world is the chemistry of the clay minerals.

Anions are generally larger in ionic radii than cations and therefore form the framework of most silicate minerals. The data in Figure 1 show the relative size of the common ions found in the phyllosilicates (Greenland and Hayes, 1978, Figure 2.2). The two most common coordination structures found in clay minerals are the tetrahedron and the octahedron, as shown in Figures 2 and 3.

TABLE 1. CHEMICAL COMPOSITION OF THE COMMON CLAY MINERALS

CLAY MINERAL	COMPOSITION/COMMENTS
KAOLINITE	$(\text{OH})_3\text{Si}_2\text{Al}_2\text{O}_5$. The theoretical composition is SiO_2 , 46.54%; Al_2O_3 , 39.5%; and H_2O , 13.96%
HALLOYSITE	Dehydrated form: $(\text{OH})_3\text{Si}_2\text{Al}_2\text{O}_5$ Hydrated form: $(\text{OH})_3\text{Si}_2\text{Al}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$.
MONTMORILLONITE	$(\text{OH})_4\text{Si}_4\text{Al}_4\text{O}_{20} \cdot n\text{H}_2\text{O}$. Theoretical composition without an interlayer is SiO_2 , 56.7%; Al_2O_3 , 28.3%; and H_2O , 5.0% Actual analyses of montmorillonite minerals: Montmorillonite $\text{Na}_{0.56}(\text{OH})_4\text{Si}_8(\text{Al}_{3.34}\text{Mg}_{0.66})\text{O}_{20}$ Beidellite ^a $\text{Na}_{0.66}(\text{OH})_4(\text{Si}_{6.34}\text{Al}_{1.66}\text{Al}_{0.4})\text{O}_{20}$ Nontronite $\text{Na}_{0.66}(\text{OH})_4(\text{Si}_{6.34}\text{Al}_{1.66}\text{Fe}_{0.34})\text{O}_{20}$ Hectorite $\text{Na}_{0.66}(\text{OH})_4\text{Si}_8(\text{Mg}_{5.34}\text{Li}_{0.66})\text{O}_{20}$
MUSCOVITE	$(\text{OH})_4\text{K}_2(\text{Si}_6 \cdot \text{Al}_2)\text{Al}_4\text{O}_{10}$. This mineral is weathered to illite by K removal. Theoretical composition: K_2O , 11.8%; SiO_2 , 45.2%; Al_2O_3 , 38.5%; H_2O , 4.5%. (Not all of the K needs to be removed to form illite - more properly called hydrous mica)
BIOTITE	$(\text{OH})_4\text{K}_2(\text{Al}_6 \cdot \text{Al}_2)(\text{Mg} \cdot \text{Fe})_6\text{O}_{20}$. This mineral is weathered to vermiculite by K removal and addition of water. Theoretical composition varies widely.
CHLORITE	$(\text{OH})_4(\text{Si} \cdot \text{Al})_8(\text{Mg} \cdot \text{Fe})_6\text{O}_{20}$. Theoretical composition varies where the $\text{Si} \cdot \text{Al}$ varies from Si_2Al to Si_2Al_2 , and the $\text{Mg} \cdot \text{Al}$ varies from Mg_5Al to Mg_4Al_2 , with Fe and Mn partially replacing Mg, and Fe and Cr partially replacing Al.
VERMICULITE	$(\text{OH})_4(\text{Mg} \cdot \text{Ca})_x(\text{Si}_8 - x \cdot \text{Al}_x)(\text{Mg} \cdot \text{Fe})_6\text{O}_{20} \cdot Y\text{H}_2\text{O}$, with x varying from 1 to 1.4 and Y is about 8. The Mg and Ca are largely exchangeable ions, and Ca is not a part of the internal structure.
ATTAPULGITE	$(\text{OH})_4(\text{OH})_2\text{Mg}_5\text{Si}_8\text{O}_{20} \cdot 4\text{H}_2\text{O}$. However, a formula approaching $\text{H}_6\text{Mg}_5\text{Si}_{12}\text{O}_{30}(\text{OH}) \cdot \text{H}_2\text{O}$ may be more nearly the theoretical composition

^aMisra and Upchurch (1976) give the detailed chemical composition of beidellite as:

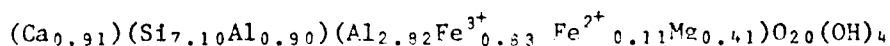


TABLE 2. CLASSIFICATION OF THE CLAY MINERALS BY THE MINERALOGICAL SOCIETY OF GREAT BRITAIN (Brown, 1955).

-
- I. Amorphous (noncrystalline clays)
 - Allophane (example, Ando soils of Japan)
 - II. Crystalline Minerals
 - A. Two-layer type (sheet structures composed of units of one layer of silica tetrahedra and one layer of alumina octahedra.
 - 1. Equidimensional: Kaolinite group - kaolinite, macrite, dickite
 - 2. Elongate: Halloysite group
 - B. Three-layer types (sheet structure composed of one central dioctahedral layer between two silica tetrahedra, or three trioctahedral layers).
 - 1. Expanding lattice
 - a. Equidimensional: (1) Montmorillonite group (montmorillonite, sauconite); (2) Vermiculite
 - 2. Nonexpanding lattice: Illite group - hydrous micas
 - C. Regular mixed layer types (ordered stacking of alternate layers of different types).
 - Chlorite group
 - D. Chain structure types (rotablende-like chains of silica tetrahedra linked together by octahedral groups of oxygens and hydroxyls containing Al and Mg atoms).
 - Attapulgite, sepiolite, palygorskite (these three minerals are often lumped together as the same mineral).
-

NOTE: The classification scheme for clay minerals was reviewed again in 1969 however, there has been little change to date. International meetings of mineralogists may have some changes, but it is hoped that the nomenclature will be close to Tables 2 and 3.

TABLE 3. CLASSIFICATION SCHEME AS PROPOSED BY THE JOURNAL OF THE CLAY MINERALS SOCIETY^a

Type	Charge ^b (x=charge)	Group	Subgroup	Species in Subgroup
1:1	x=0	Kaolinite/ Serpentine	Kaolinites Serpentines	Kaolinite, Halloysite Chrysotile, Lizardite, Antigorite
	x=0	Pyrophyllite/ Talc	Pyrophyllites Talcs	Pyrophyllite Talc
	x=0.25 to 0.60	Smectite or Montmorillonite	Diocahedral Montmorillonites	Montmorillonite, Beidellite, Nontronite
2:1	x=0.60	Vermiculite	Diocahedral Vermiculites	Vermiculite
	x=1	Mica	Diocahedral Micas	Muscovite, Paragonite
			Triocahedral Micas	Biotite, Phlogopite
	x=2	Brittle Mica	Diocahedral Triocahedral	Margarite Clintonite
2:1:1	Vari- able	Chlorite	Diocahedral (4-5 Oct. cations per formula)	
			Triocahedral (5-6 Oct. cations per formula)	Pennine, Clinocllore, Prochlorite

^aFrom Brindley et al., 1968. Further recommendations were that the term "lattice" refer to a uniform distribution of points in space and that the term not be used synonymously with structure. Therefore, the term "clay mineral lattice" should be "clay mineral structure." The term "plane" refers to a plane of atoms, and the term "sheet" refers to terms like "tetrahedral sheet" and not "tetrahedral plane." "Layers" would refer to two or more sheets and "interlayers" would refer to the sheets between the layers.

^bGroup charge per formula unit.

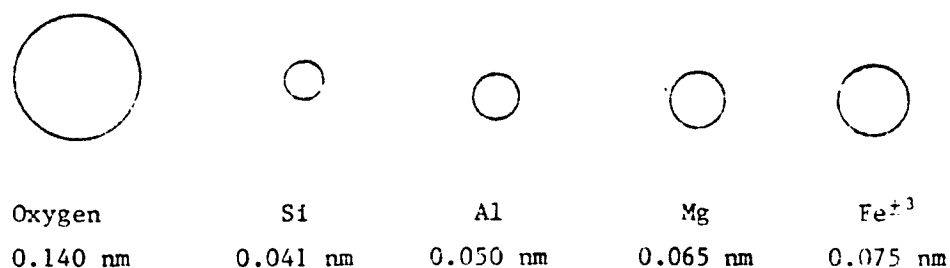


Figure 1. Ionic radii and relative sizes of ions commonly occurring in phyllosilicates (from Whittaker and Munkus, 1970).

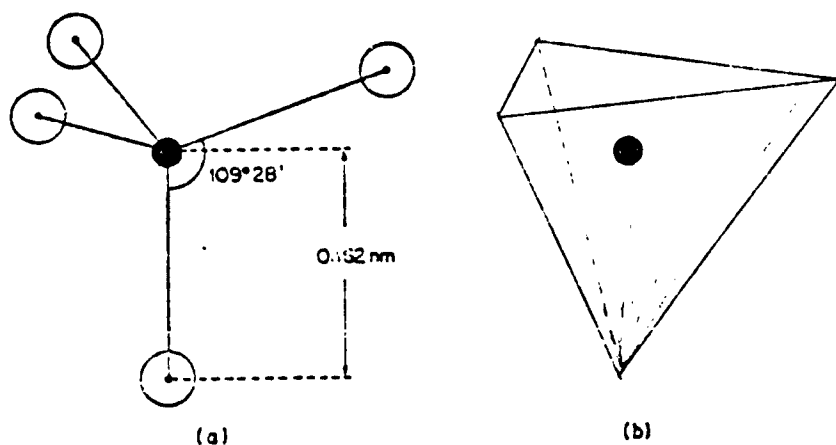


Figure 2. The tetrahedron formed by coordination of Si by four oxygens: (a) bond lengths and angle, (b) isometric representation (from Greenland and Hayes, 1978).

The linking of octahedra and tetrahedra in the clay minerals is shown in Figures 4 to 7. It is obvious that the major volume of the clay minerals are assigned to oxygen (O), and that bonds are shared between O and the metals or silicon (Si).

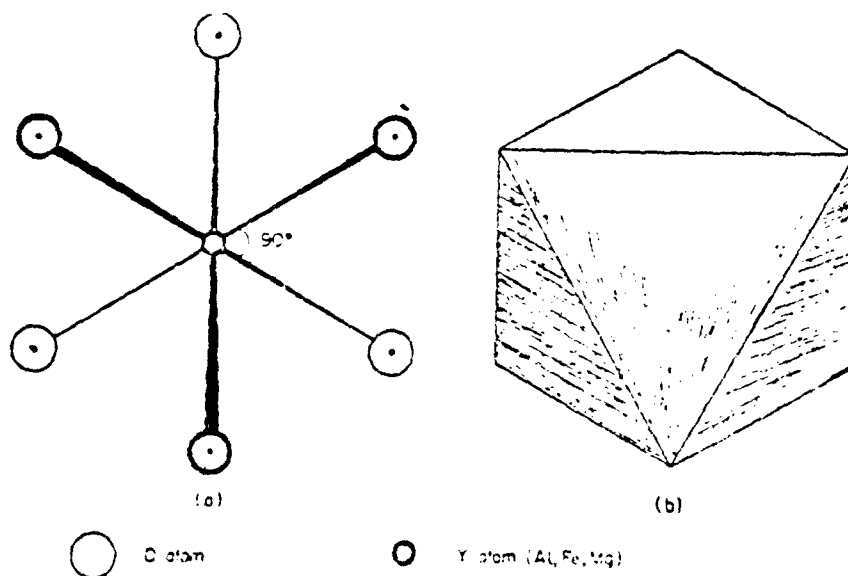


Figure 3. The octahedron formed by coordination of a cation (such as Al) by six oxygens. (a) as a "ball and spoke" model, and (b) an isometric representation (from Greenland and Hayes, 1978).

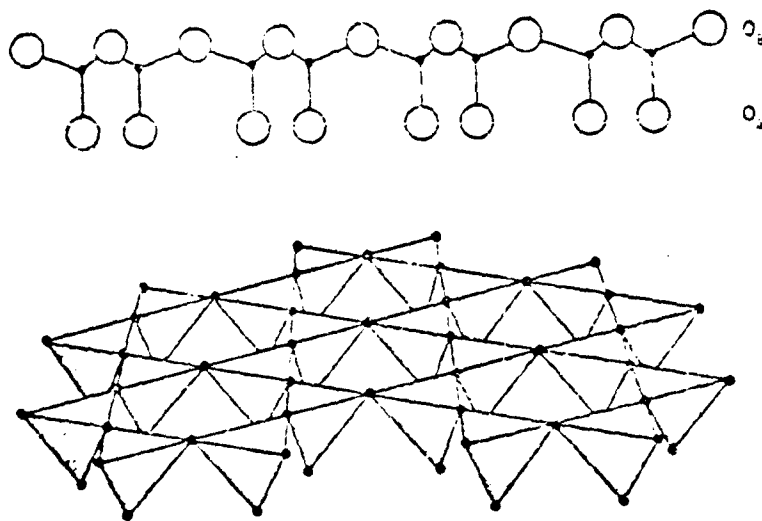


Figure 4. Linked Si_5O_6 rings in 1:1 and 2:1 layer silicates (from Greenland and Hayes, 1978).

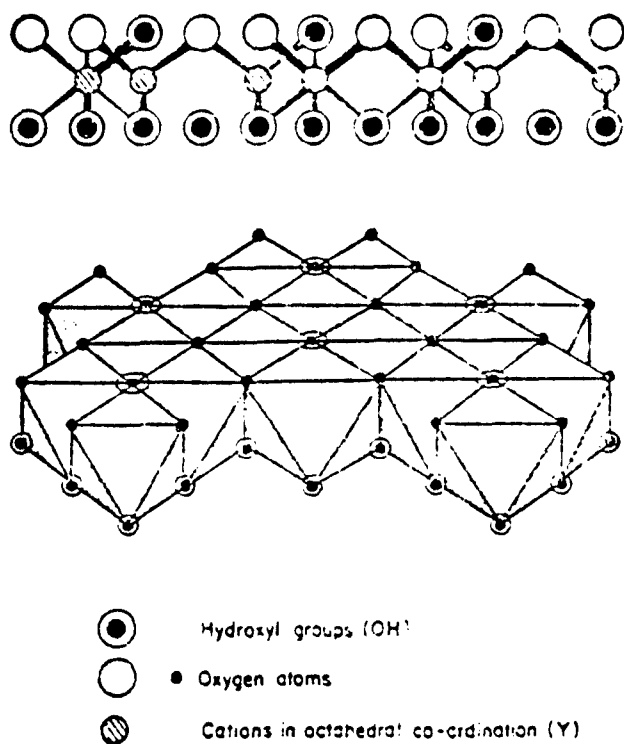


Figure 5. An ideal structure for a dioctahedral sheet in kaolinite (from Greenland and Hayes, 1978).

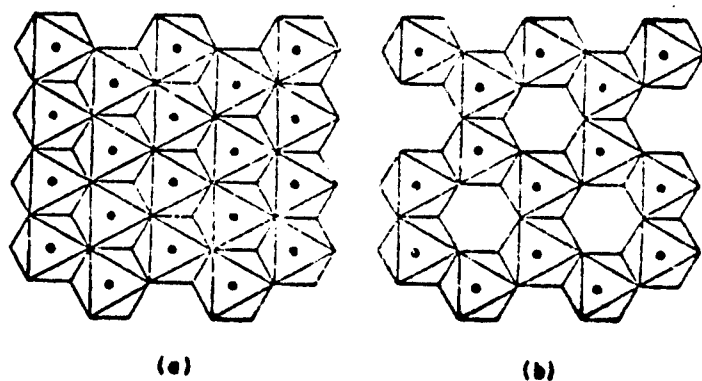


Figure 6. Types of octahedral sheets: (a) trioctahedral, and (b) dioctahedral.

2.1.1 Kaolin

The general chemical composition of kaolin or kaolinite is shown in Table 2. Kaolinite is often the dominant clay mineral in highly weathered tropical soils and is usually present as a few percent in all soils. It is composed of a tetrahedral sheet of Si and O and an octahedral sheet of Al, O, and OH. The tetrahedral sheet shows a thickness of approximately 2.1 Å, and the octahedral sheets, 5.01 Å.

The mineral is most easily recognized by its X-ray diffraction-reflection (spacings) based on 001 of 7.15 Å and 002 of 3.57 Å. However, in any mixture of minerals (soil), the 003 and 004 reflections are so weak as to be of little help in identification. Different metals may be present in the tetrahedral and octahedral structures, which radically alter the chemistry of the clay minerals. For example, two-thirds of the octahedra in kaolinite contain an Al ion, and the remaining octahedra of O and OH is vacant. When all octahedra contain a metal other than Al, usually divalent metals (e.g., Mg), the mineral belongs to the general class of serpentines.

Ideally, kaolinite has a structure where all negative and positive sites are equal with no substitution and therefore no charge on the crystal X-ray unit cell. Each unit cell contains a layer of six OH ions, a layer of four Al ions, a layer of four O and two OH ions, a layer of four Si ions, and finally a layer of six O ions. The ideal structural formula is $\text{Si}_4\text{Al}_4\text{O}_{10}(\text{OH})_2$. Detailed analysis and quantification in mixed mineral soils has been carried out by many authors (Townsend and Reed, 1971).

The chemistry of kaolinite and the associated group of minerals is primarily due to exposed crystal edges and corners of the mineral. The charge on the individual unit cell is essentially zero; therefore, exposed edges and corners will have a small charge due to the broken bonds, as shown in Figure 7 (Dixon, 1977). These broken bonds are thought to be a complex cation $[\text{Al}_4(\text{OH})_{10}]^{+6}$ sorbed on the planar sites of the mineral. When exposed to acidic conditions, the edge of the mineral further accepts protons. Although these two ideas appear to be in conflict, each concept explains the positive charge on kaolin in an acid environment. The CED ranges from 0 to 10 meq/100 g. This small charge (permanent charge) may be due to a very small amount of isomorphous substitution or a very small amount of hydrous mica impurity in the sample. The exchange properties of kaolin are probably more closely related to a pH dependent charge than any other factor.

2.1.2 Halloysite and Other 1:1 Minerals

Halloysites are essentially the same mineral as kaolinite except they contain additional water, which is removed at temperatures of ca. 110° C. The mineral is usually thought to be fibrous rather than platy, contrasted to kaolin. Hydrated halloysite forms complexes with many organic compounds, particularly the diols. It is suggested by some investigators that this is a unique property of the halloysite minerals.

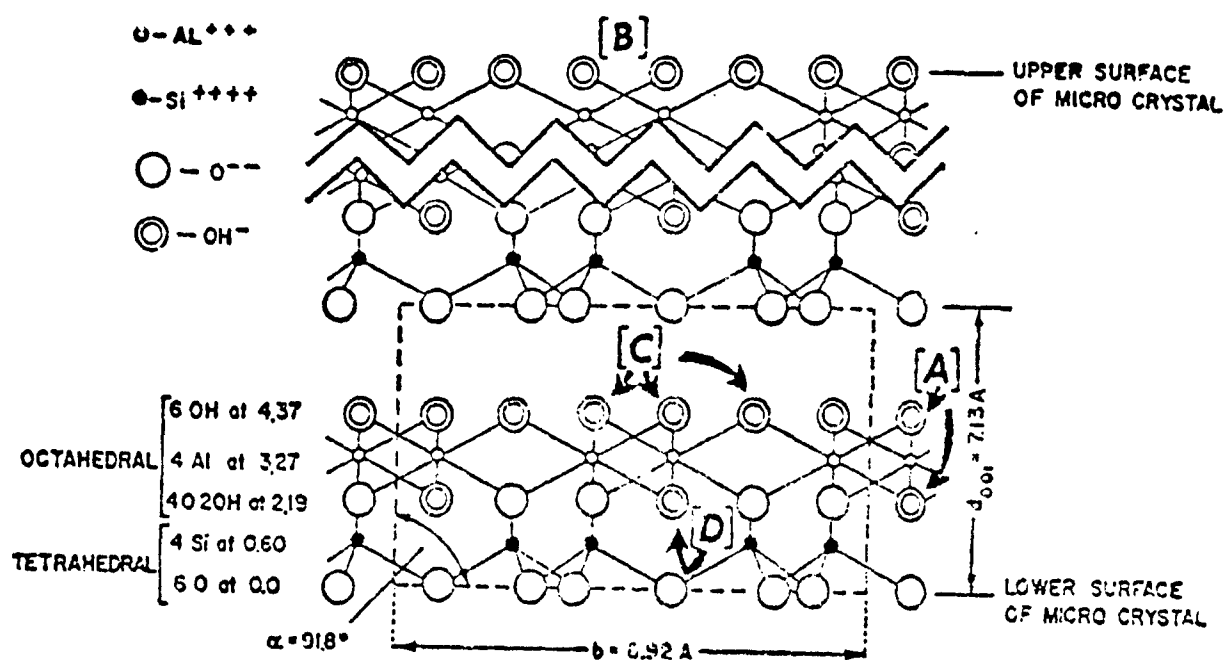


Figure 7. Projection of the structure of kaolinite on the (100) plane showing the stacking of successive layers in a micro crystal. A and B indicate "outer hydroxyls," C designates "inner-surface hydroxyls," and D indicates "inner-hydroxyls" (from Dixon, 1977).

Other minerals in this group are dickite and nacrite which are quite rare in soils. Serpentine are also included in this group by many investigators; however, serpentines are also quite rare in soils. Serpentine are found as weathering products of ultrabasic rocks and are found in temperate and tropical zones with rainfall in excess of 150 mm annually. They will rapidly weather to smectite.

2.1.3 The Micas

The micas are widely distributed in rocks and soils. They have a wide range of chemical composition and vary in isomorphic substitution from none to the maximum. The mica minerals most commonly found in soils are known as hydrous mica (illite). The hydrous mica clay particle is not a simple crystal of a single compound but often is a complex partially weathered crystal with frayed edges that are capable of sorbing water and cations. These minerals are often intimately associated with interlayers of other minerals like smectite (montmorillonite) with different activities for sorbing cations and water as shown in Figure 9 (Greenland and Hayes, 1978). In hydrous mica, the charge balance between cations and anions is incomplete with a deficit of two units of negative charge per X-ray unit cell.

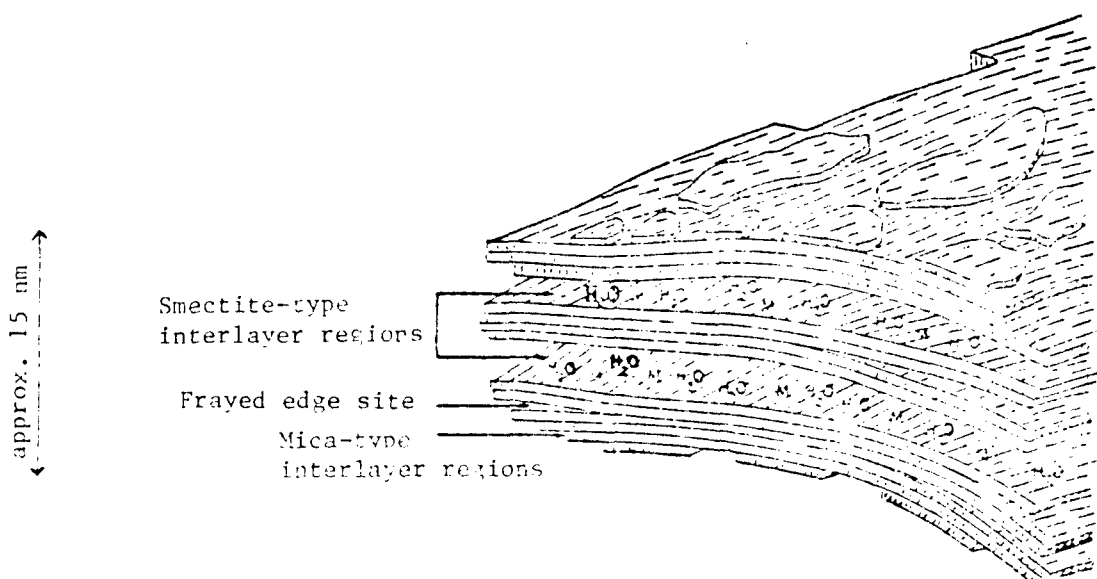


Figure 8. Schematic illustration of "illite" particle in a soil clay, with two smectite-type layers interstratified with mica-type layers. The crystal is shown to be flexed deliberately, as the thin crystals of illites and smectites in soil clays are unlikely to be rigid (from Greenland and Hayes, 1978).

The most common micaceous minerals in soils are the muscovites and altered muscovite minerals. These minerals have isomorphically substituted cations in the octahedral layer, and this charge is normally satisfied with the K ion. Hydrous mica contains less K and more SiO_2 and H_2O than muscovite. Usually, the layer charge in mica is due to isomorphic substitution of Al for one-fourth of the Si ions. These minerals are composed of an octahedral sheet of Al cations surrounded by six anions (four O and two OH), which is "sandwiched" between two sheets of Si tetrahedra. The muscovite micas have, in the octahedral layer, two-thirds of all possible cation positions occupied and the third position unoccupied. The biotite micas have all positions occupied in the octahedral position; therefore, the octahedra contain divalent elements such as Mg, Fe, etc. Very rarely will any of the alkaline earths other than Mg be found in the structure of the micas. Only the muscovite micas (partially K stripped, hydrous mica) occur in soils. Soil mineralogists measure the hydrous mica content of soil clays, identified by powder X-ray diffraction, by multiplying the percent K_2O of the whole clay fraction sample by 10.

Clay minerals that show strong tendency for bonding organic cations as well as inorganic cations are shown in Figure 9 (Greenland and Hayes, 1978).

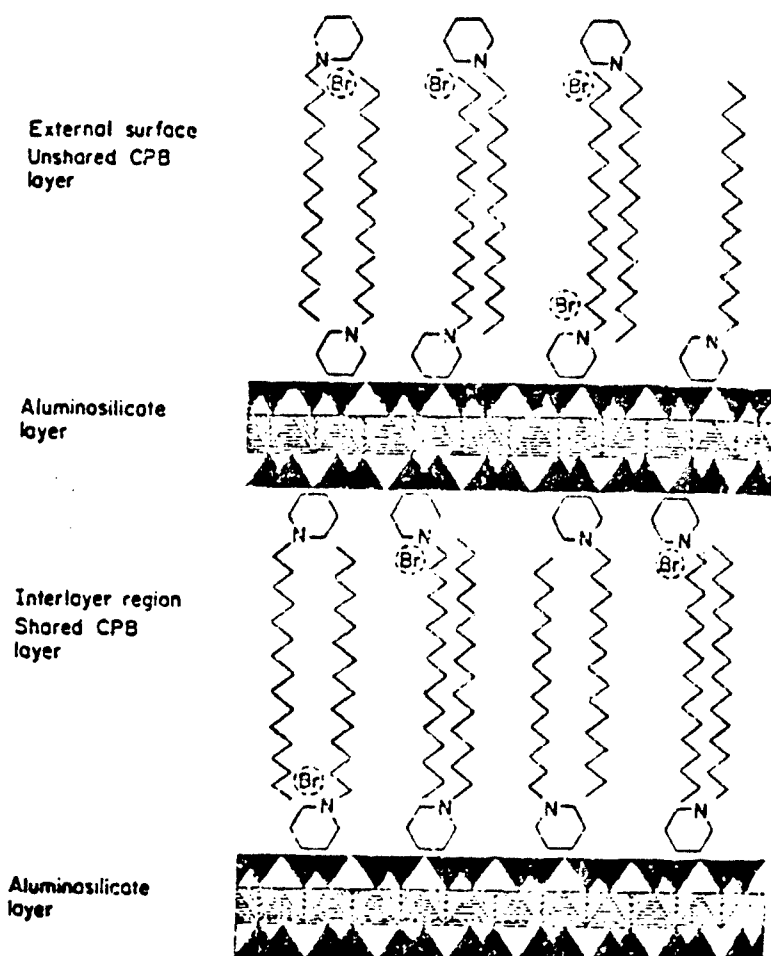


Figure 9. Cetyl pyridinium bromide (CPB) adsorption on the internal and external surfaces of a smectite clay at maximum adsorption. The unshared layer on external surfaces leads to a mean surface coverage of 0.27 nm^2 per cetyl pyridinium group, whereas the interlayer region of each adsorbed pyridinium group requires its projected area of 0.54 nm^2 . The $d(001)$ value for the montmorillonite-CPB complex is 4.2 nm , which, allowing for the aluminosilicate layer thickness of 1.0 nm , gives 3.2 nm for the CPB layer, corresponding closely with the known dimensions of CPB ions (from Greenland and Hayes, 1978).

The structure of the fibrous clay minerals departs dramatically from that of the smectites and kaolinites. Palygorskite (or attapulgite) is a lathe-shaped, fibrous mineral, and it is found in many areas of the world, particularly in desert regions or in areas where it has been buried by other sediments. In the mineral's structure, there may be a significant substitution of Mg for Al in the octahedral layer but little substitution in the tetrahedral layer (Zelasny and Calhoun, 1977). For example, palygorskite contains channels with a cross section of $3.8 \times 6.3 \text{ \AA}$, and sepiolite has channels of $3.8 \times 9.4 \text{ \AA}$. These channels contain cations and water, and the mineral could be used as a molecular sieve. The behavior of palygorskite somewhat resembles that of zeolite.

2.1.4 Smectites (Montmorillonites)

For the purpose of this report, the smectites will include vermiculite and other minerals that some investigators prefer to place with the micas and minor mineral groups. Most of the CEC of temperate zone, fine-to-medium textured soils is due to the smectites. Smectite absorbs and releases large quantities of water and organic compounds, and this mineral is probably responsible for most of the shrink-swell characteristics of soils.

The crystal structure of smectite is similar to that of mica, in that it is composed of two silica tetrahedral sheets with a central Al-octahedral sheet where O ions are shared between the tetrahedral and octahedral sheets. The charge on these minerals is due to isomorphic substitution in both the octahedral and tetrahedral sheets. Most soil smectites are dioctahedral; that is, for each three vacancies in a nest of O and OH ions, two are filled and one is vacant. The metal ion most commonly found in the octahedral sheet is Al, and the most common substitutions are Mg and Fe, with less common substitutions of manganese (Mn), copper (Cu), zinc (Zn), lithium (Li), silver (Ag), and chromium (Cr). The only substitution found in the silica tetrahedral sheet is Al for Si.

Most of the smectite minerals are easily identified by X-ray diffraction. Special preparation of the clay separate from the soil is required for accurate X-ray diffraction identification (Jackson, 1954; Rich and Earnhiser, 1977). Substitution in these minerals is responsible for their charge, with about 5 meq/100 g of clay due to broken bonds on the edges and corners. Maximum substitution per X-ray unit cell is one-sixth charge for Al substitution for Si ($\text{Si}_{1.5}\text{Al}_{0.5}$), and one-fourth charge for Mg substitution for Al ($\text{Al}_{1.5}\text{Mg}_{0.5}$). The CEC due to maximum substitution in these minerals varies between 117 and 135.5 meq/100 g of clay. The minerals of the smectite group are montmorillonite, beidellite, and nontronite.

Laboratory examination techniques for these minerals, in addition to X-ray diffraction, are transmission electron microscopy (TEM), scanning electron microscopy (SEM), thermal analysis (thermogravimetric, differential thermal), infrared (IR) spectroscopy, elemental analysis, and selective dissolution analysis (Sawhney and Jackson, 1958; Grim and Kulbicki, 1961; Farmer and Russell, 1967).

Another aspect of the smectites is that because of their pH-dependent charge due to "broken bonds," below neutrality they attract hydronium (H_3O^+) ions rather than other cations, at pH values above seven, other cations take part in the exchange reactions; thus, as the pH increases, the CEC increases. However, OH-Al complexes found in soils, soil organic matter, and noncrystalline minerals may exhibit substantial pH-dependent charge. Many smectite minerals exhibit "K fixation"; that is, mica-like areas in the mineral flakes preferentially sorb K as an exchange ion in a 12-coordination structure.

The suite of exchangeable cations found on the exchange complex is held by the smectite minerals by varying charge densities, where the larger cations (including hydration volumes) of monovalent charge (Na, Li) are held with much less energy than the polyvalent cations of lesser hydration (Ca, Ba, Al, etc.) volume. Anion exchange in these minerals is limited to the pH-dependent charge fraction of the total charge.

Soils high in smectites are most obviously identified by very large shrink-swell properties (Brown, 1977). Soils with substantial quantities of smectites are difficult to stabilize for engineering purposes and for agricultural manipulation. Many workers have proposed that there are from two to 50 water layers between adjacent basal plane layers of these clays. However, most smectites are chemically and physically stable in neutral, poorly drained environments and in highly saline environments. As these environments change, smectites may become unstable.

The structures of some smectite minerals are shown in Figure 10 (Barchardt, 1977). It is noted that each of these minerals has essentially the same structure, but there are highly significant differences. In beidellite, the major source of charge is due to isomorphic substitution of Al for Si on the tetrahedral sheet; therefore, the charge (-) is near the planar surface of the mineral. Montmorillonite shows a significant charge (-) deficit on the octahedral sheet and is at least four times weaker than the bond observed in the beidellite. Because of these differences in source of charge, the montmorillonite clay is much more susceptible to swelling and, as shown in Figure 10, may be found with basal spacings of 10 to 20 Å, or more.

Nontronite is quite rare in soils because distortion due to significant amounts of iron in the octahedral layer cause distortion and weaken the bonds holding the mineral together, and cause it to be susceptible to hydrolysis. However, nontronite does have many of the same properties found in beidellite; that is, very strong bonding of exchange cations, particularly the polyvalent cations.

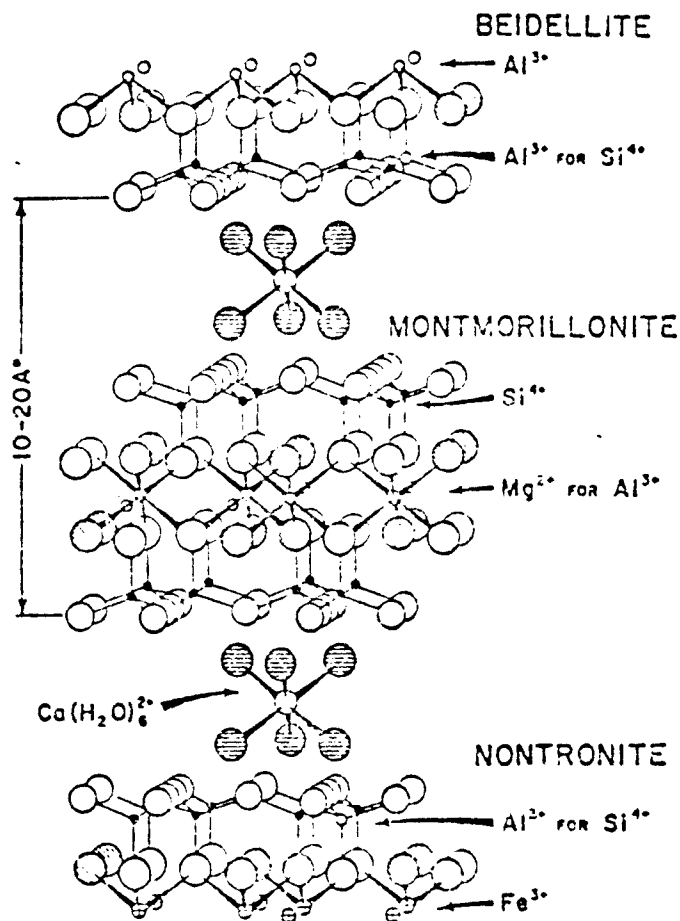


Figure 10. The crystal structure of smectites, illustrating three common types of substitution (from Barchardt, 1977)

2.1.5 Chlorites and Vermiculites

True chlorites are relatively rare in soils; however, Al or Fe-OH interlayered (hydroxy-hydronium polymers of metals) micaceous clay minerals are very similar to chlorites and have been called "soil chlorite." Because of their X-ray diffraction patterns, they may be mistaken for other minerals (kaolinite, etc.) but relatively simple procedures are available for positive identification. The layer structure of chlorite is a four-layered structure with two tetrahedral silica sheets and one octahedral alumina sheet, as in mica and smectite; however, the remaining portion is a brucitic $[\text{Mg}_3(\text{OH})_6]$ or gibbsitic $[\text{Al}_2(\text{OH})_6]$ layer fitted between two tetrahedral sheets which binds the structure together in a 2:2 (silica:alumina) structure. These hydroxy interlayered minerals in soils are probably the norm and not the exception. Probably the interlayer

material (particularly the gibbsitic material) is a polymer composed of six-membered rings of $\text{Al}_6(\text{OH})_{12}^{+6}$, and higher order, up to 54 Al ions, as shown in Figure 11 (Barnhisel, 1977).

Until recently, vermiculite was not thought to be a clay mineral common in soils; however, vermiculites have been reported in all of the great soil groups from the polar regions to the tropics (Douglas, 1977). The vermiculites are generally thought to be alteration products of the

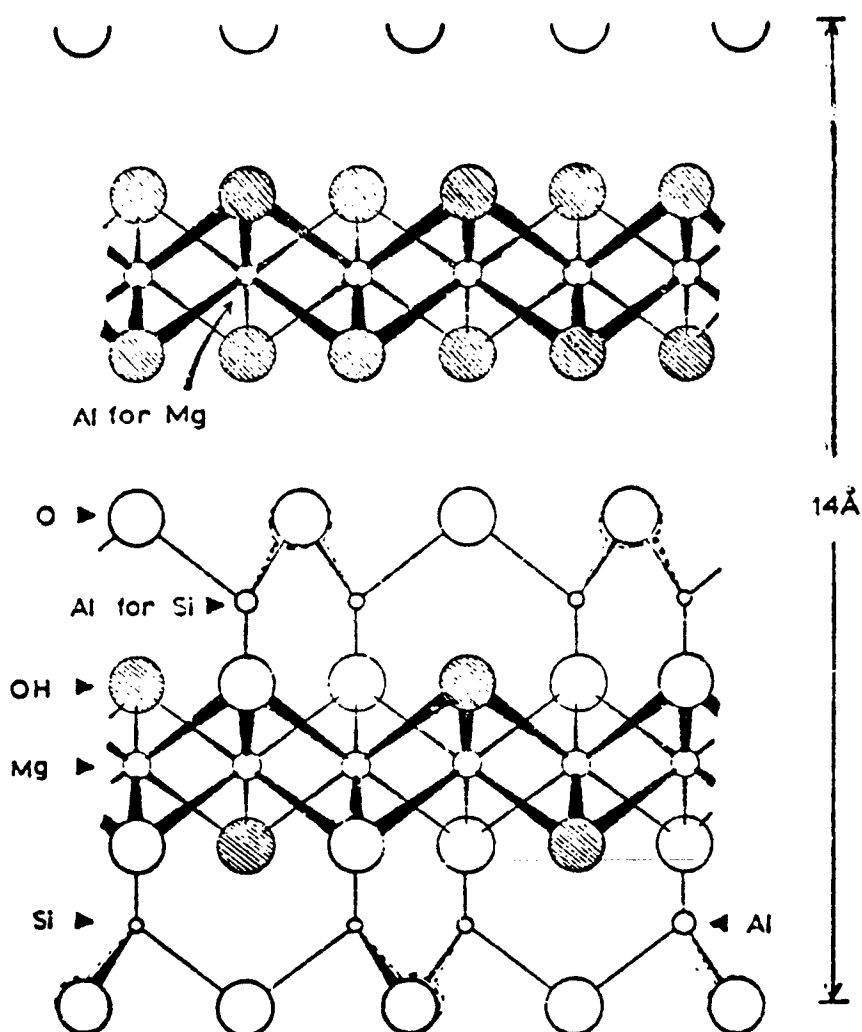


Figure 11. The idealized crystal structure of trioctahedral chlorite (from Barnhisel, 1977, which was modified from Brindley et al., 1950, and Jackson, 1954).

micas (biotite, muscovite, etc.). These minerals are somewhat different from other soil clay minerals in that they may be found in the sand and clay fraction of the soil. The octahedral sheet of vermiculite carries a positive charge and the tetrahedral sheet, a negative charge. The balance of charge results in a residual negative charge of 0.5 to 1.0 per X-ray unit cell, as shown in Figure 12. The charge deficiency is balanced by exchange cations with a preference for K; however, most vermiculites have the major amount of charge balanced with Mg, with lesser amounts of Ca.

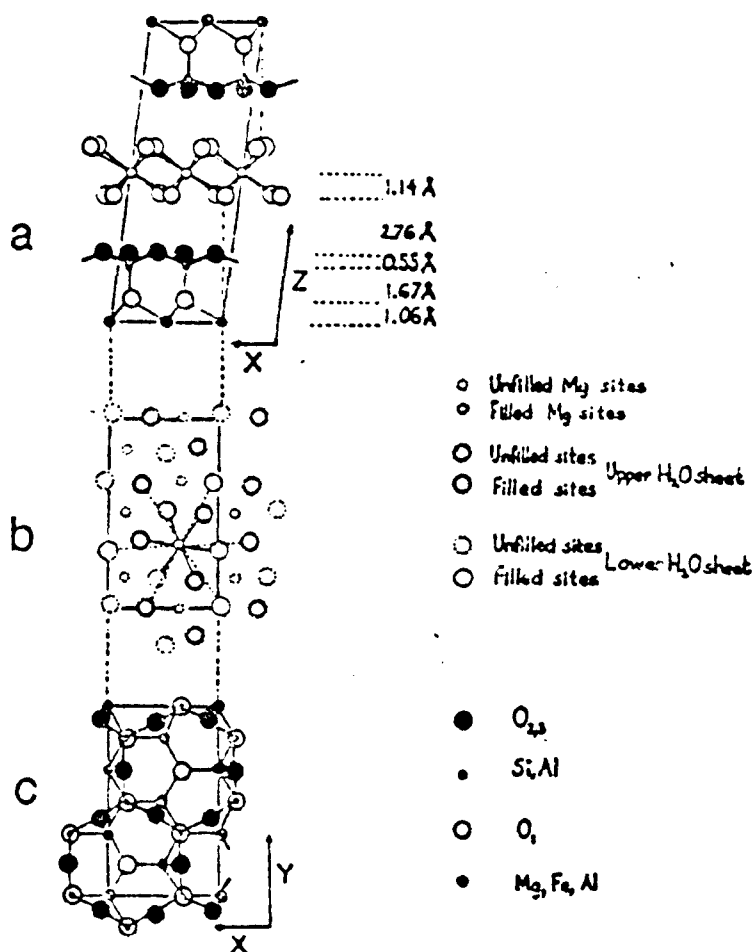


Figure 12. The crystal structure of Mg-vermiculite: (a) projection on the X-Z plane, (b) projection of the interlayer region showing interlayer water, normal to the X-Y plane, (c) projection of the silicate layer normal to the X-Y plane (from Douglas, 1977).

Vermiculite, like soil chlorite, is usually found to be interlayered with hydroxy Al and Fe polymers in soil. Vermiculite that has been extensively interlayered is quite resistant to chemical weathering and therefore will often be found in significant amounts in tropical soils that have been exposed to an intensive mineral weathering environment. Most of this vermiculite is dioctahedral.

Trioctahedral vermiculite is the most common vermiculite of commerce and has been used for a variety of purposes. The presence of a trioctahedral vermiculite in soil has been questioned by several investigations; however, a mineral with some dioctahedral and some trioctahedral components has been identified in many soils.

There is a marked difference in the chemistry of the di and trioctahedral vermiculites. The finest fraction of vermiculites is most probably that found in soil, and has been shown to be, in most instances, dioctahedral vermiculite. However, the chemistry of the clay fraction of soils with vermiculitic minerals is probably the chemistry of the dioctahedral mineral, which has a high CEC and is usually interlayered. Trioctahedral vermiculites may have a charge equal to as much as 160 meq/100 g CEC, while the dioctahedral minerals may have a charge in excess of 200 meq/100 g, and theoretically expanded vermiculite could have a charge of 250 meq/100 g for the dioctahedral mineral.

The micaceous minerals (smectite, chlorite, vermiculite, etc.) show profound changes in chemical and physical properties when interlayered extensively. For example, extensively interlayered minerals (Kidder and Reed, 1972) were shown to have zero CEC and zero shrink-swell. When the interlayer was removed, CEC increased to 130 meq/100 g for smectite, and swelling increased from 0 to >30 in volume.

Clay minerals in soil environments are exposed to weathering stress and when one considers isomorphic substitution and the strain placed on the structure of these minerals due to substitution of different sized ions, it is not at once obvious why these minerals persist. In the process of weathering, Al ions are usually most easily removed from the octahedral layer of the clay mineral. Aluminum, because of its charge and its amphoteric character, complexes water, hydronium and hydroxyls to give a complex charge polymer, as shown in Figure 13 (Kidder and Reed, 1972). The sorption of the resultant compounds cause the bonding within the clay crystal to become much stronger and, for all practical purposes, resistant to further weathering. Further weathering may occur, but only if the environment changes drastically.

2.2 NON-CLAY SOIL MINERALS

2.2.1 Silica

Quartz is an ubiquitous material in nature and is found in almost all soils. However, silica includes many more compounds than quartz and these compounds have widely varying properties depending on crystallinity or lack of crystallinity, and particle size. Quartz is generally

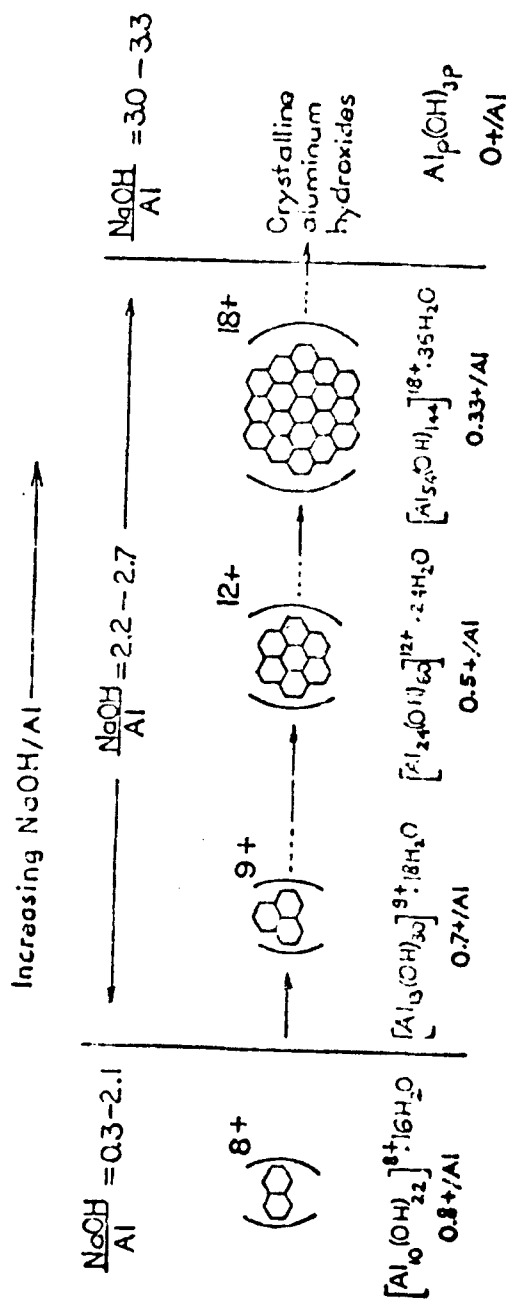


Figure 13. Development of aluminum hydroxide, as proposed by Hsu and Bates (1964a). This figure shows a series of compounds, the first of which is $[\text{Al}_6(\text{OH})_{12}]^{8+}$ or the first hydrolysis product of base/Al; ratio of 2:1 or less. This large cation readily migrates to the basal plane of the clay mineral and is sorbed more or less permanently as a cation not subject to exchange (from Kidder and Reed, 1972).

considered to be SiO_2 ; however, isomorphic substitution is possible and is known to occur. Aluminum is the most common substitution, with less frequent substitutions of Fe, Li, and other elements of similar charge and size and having a coordination number of four. Many elements may be found in quartz which are bound interstitially, with Na and Li being the most common and K, Fe, Mn, Mg, and Ca less often reported. The presence of these elements in quartz and the other silica minerals is responsible for some electrical (electrostatic) charge on quartz grains. Although quartz may have a slight charge due to these impurities, it is of very little consequence unless the mineral is very finely divided.

Cristobalite and tridymite are silica minerals that have a much more open crystalline framework than quartz. Tridymite is probably a solid solution component between the silica and nonsilica phases. These non-silica phases (impurities) are elements other than Si and water. For example, opal is a hydrated silica whose water content commonly varies between 4 and 9 percent and may be as high as 30 percent. Plant opal may contain cytoplasmic material from plants and occluded water that is lost on ignition, but reported as 100 percent water loss. Plant opal is somewhat reversible on dehydration-rehydration. The open framework of plant opal allows water to enter and is essentially nonvolatile at temperatures of 100°C . Water entering this open structure may dislodge small organic molecules held on these silica surfaces by van der Waals-London forces. Diatoms and sponge spicules derived from marine sources are also common in soils. These silica compounds are also a part of the opal family of substances. In general, the crystallinity of quartz and other silica minerals varies from very crystalline for β -quartz, to X-ray amorphous for opal, with cristobalite and tridymite intermediate in crystallinity.

The surface of quartz and other silica minerals contains a very thin layer (0.03 μm) of an amorphous or disrupted layer of hydrated $\text{SiO}_2 \cdot n\text{H}_2\text{O}$. Some organic molecules have been shown to react with this thin layer of amorphous silica and then dissolve in the soil solution (Evans, 1965, Crook, 1958) carrying some SiO_2 away with the soil solution. Data on the role of organic materials reacting with hydrated silica leads to conflicting conclusions. Cleary and Conally (1972) concluded that organic root exudates cause dissolution of silica, but Wilding and Pries (1974) concluded that organic molecules shielded silica from dissolution. Organic molecules bound by weak van der Waals-London forces to the surface of quartz-silica grains in soils are probably released from the quartz grains by water due to the greater affinity of water for quartz surfaces than for most organic molecules.

Sand is generally considered to consist of particles more than 0.05 mm in diameter, but the very finest sand can be airborne and carried great distances by the wind. Kuenen (1960) discusses sand and sand formation, and reported that sand is formed from the chemical and mechanical disintegration of rock. When running water moves the products of weathering, the finest material tends to be moved the farthest from the source; therefore, sand, silt, and clay are separated from the boulders. Where chemical weathering of the parent rock is strong, the end product,

sand, is largely quartz and other resistant minerals. Where mechanical weathering is strong (e.g., deserts and alpine areas), the sand grains will often be rich in feldspar in addition to quartz. When rock fragments are weathered by the action of wind, the grains are constantly abraded and ground down to a size of approximately 0.05 mm, which is about the smallest size of dune (desert) sand. Loess, however, which is considered to be in the silt size, does not show the wind abrasion or "frosted" characteristics of sand found in regions where the wind is a dominant erosion factor. Loess, then, must be the fine material resulting from the chemical and mechanical disintegration of fine-grained or felsitic rocks, or from the "rock flour" produced by glaciers.

2.2.2 Minerals With Exchange Character (Zeolites)

Zeolites are members of a group of minerals which sometimes have ion exchange properties as well as water sorption. Zelazny and Calhoun (1977) discuss some of the properties of zeolites in soil environments, and Eitel (1954) discusses some of the chemical reactions of these materials. Zeolites have X-ray diffraction data that do not coincide with other soil minerals, and they show substantial substitution of Al for Si as found in the clay minerals. The structure consists of a linked tetrahedral network or framework in three dimensions. The tetrahedra consist of a central ion (Si or Al) surrounded by four O ions with each O shared by two tetrahedra and with no mobile anions present. The resulting structure has a net negative charge which is usually countered by alkali metals and alkaline earth cations. In addition, the relatively open framework of tetrahedra includes the presence of water molecules within the structural channels. Although the water is bound to the surfaces of channels, the binding is loose or weak, and water and cations can be removed without disrupting framework bonds. The structural channels of zeolites are formed by linked tetrahedral rings, double rings, and large symmetrical polyhedral units. Each ring is composed of tetrahedra with specific combinations within a given zeolite providing for channels or restrictions of known size. Larger numbers of tetrahedra form wider channels. Zeolites with 8- and 12-member rings have channels large enough for admission of organic molecules as well as water and cations. Thus zeolites can act as molecular or ionic sieves; ionic or molecular diffusion into these channels is dependent on the water content of the system. Permutite is a synthetic (natural) substance which is sodium saturated and is used in many commercial water softeners or ion exchangers.

Zeolites have a reported CEC from 100 to 300 meq/100 g, but the criterion for exchange is dependent on channel width, diffusion of ions or molecules, water content, and hydration. Water absorption by zeolites is high, but the amount of absorbed water is dependent on the zeolite species as well as the cation in the channel. Water is removed from zeolites below temperatures of 200° and the water can be replaced volume for volume by substances of quite different properties.

In general, it can be concluded that zeolites are quite rare in the soil environment. They are generally restricted to soils of high pH where acidic weathering has been restricted. Known commercial deposits of zeolite occur in old saline-lake environments of Tertiary age in the western United States and in bedded volcanic tuffs of northern Japan. These minerals apparently formed from vitric volcanic materials reacting with waters of saline-alkaline lakes. A high pH appears to be necessary for zeolite formation in order to sustain a high concentration of Si and Al at the time of synthesis.

Zeolites have been used as molecular sieves and are finding ever increasing use in engineering processes as catalysts (Gould, 1971). Zeolites have been synthesized for use as molecular sieves to absorb cyclohexane, n-hexane, alkylammonium compounds, acetaldehyde, acetone, phenol, methanol, etc. The diameter of the channels in zeolites depends on whether the mineral is natural or synthetic. Some minerals have channels as small as 2.6 Å in diameter, as in the mineral analcime, and some are as large as 7.5 Å in a synthetic erionite.

Saline-alkali lakes are found in Wyoming and other western states where the silica content of the water is in excess of 1000 ppm, which would suggest the formation of zeolites in the lake bottom (Mariner and Surdam, 1970). The main deterrent for the formation of zeolite gels in these alkaline environments is the absence of Al. When this element is present in low concentrations the gels do not form. However, weathering of feldspar with adequate amounts of Si and Al will hasten the formation of zeolites in a saline-alkaline environment.

2.3 CHEMISTRY OF ORGANIC SOIL COLLOIDS

The organic matter found in soils is made up of live organisms and their decomposed and undecomposed remains. Soil organic matter is more commonly thought to be a heterogeneous mixture composed of the products resulting from biochemical and nonbiochemical transformations of organic debris. These transformed products are referred to by most investigators as humified products. Probably one can identify soil organic matter as consisting of two materials:

1. Amorphous polymeric brown-colored substances which can be differentiated based on solubility, and
2. Recognizable classes of compounds such as polysaccharides, polypeptides, lignins, and altered lignin products, etc. (Hayes and Swift, 1978).

The classification of soil organic matter is shown in Figure 14.

Many soil chemists who specialize in the study of soil organic matter identify humic acid as an alkali soluble fraction, fulvic acid as an acid soluble fraction, and humin as a fraction insoluble in alkali and mineral acids. The major portion of most organic matter in soils is

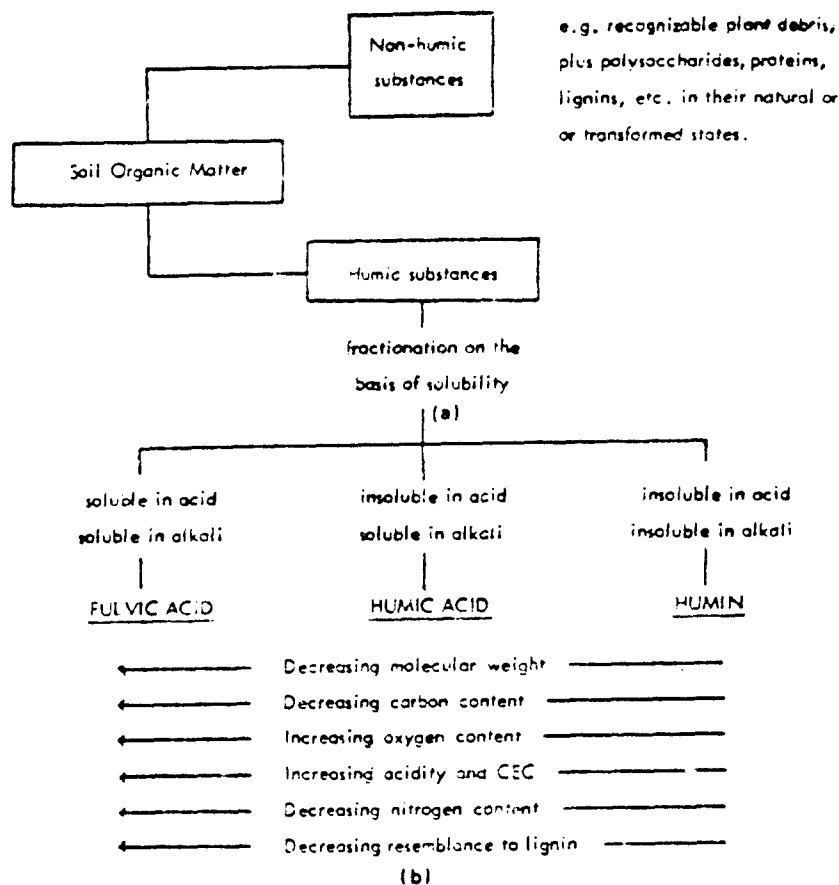


Figure 14. Fractionation of soil organic matter and humic substances (a): showing how some properties vary in the fulvic acid-humin range (b).

the humic acid. In general, soil organic matter is approximately 55-60 percent carbon (C), 35-50 percent O, 2-6 percent H, and 4-5 percent N. The functional chemical groups of these complex organic substances are carboxyl, phenolic hydroxyl, alcoholic hydroxyl, carbonyl, quinone and methoxyl groups. The carboxyl group is the major contributor to the CEC properties of soil organic matter. Most soil chemists suggest the CEC of the soil organic matter fraction to be between 100 and 400 meq/100 g of organic matter. Hayes and Swift (1978) give an excellent review of the methodology for the investigation of the functional groups of the several fractions of the soil organic matter.

When soil organic matter is digested with KMnO_4 , a great number of compounds can be separated from the digest. Whether or not all of these

compounds actually exist as such in the soil organic matter or are artifacts due to the digestion has often been debated. However, the very complexity of the mixture indicates that the soil organic matter itself consists of a complex mixture of aliphatic and aromatic compounds (Greenland and Hayes, 1978).

2.4 INTERACTION OF ORGANIC AND MINERAL COMPONENTS OF SOIL

The chemical groups of soil organic matter must react with the active nonorganic or mineral components of soil (Harter, 1977; Schnitzer and Kodama, 1977). Techniques for investigating the absorbance of organic molecules by the mineral (clay) fraction of the soil are many, and some success has been had with the application of X-ray diffractometry and IR spectroscopy. With X-ray diffractometry it is possible to determine the orientation of organic molecules between the layers (intercalation) of the clay minerals and therefore also measure the size of the organic molecule. If the mineral is sufficiently well crystallized, one-dimensional electron density maps of the organic molecule can be drawn with identification of electronic bonding. IR spectroscopy of clay-organic complexes has also been used successfully to identify organic molecules and the bonding of the molecules on the clay mineral surfaces (Farmer, 1974). IR spectroscopy of clay-organic complexes identifies the location of bonds responsible for bonding of the organic molecule on the mineral surface. However, IR must operate in a water-free environment and is only applicable to small molecules. It should also be pointed out that IR spectroscopy is not extremely sensitive and requires loading of the system for good resolution.

Interaction of clay minerals with organic molecules is dependent on the origin of that charge in the clay mineral. Clays with a substantial amount of charge on the tetrahedral sheet react much more strongly with weak organic bases than those whose charge is primarily on the octahedral sheet. When clays, whose charge originates in the tetrahedral sheet are saturated with ammonium (amine) or butylammonium salts, the ammonium ion keys into the ditrigonal interlayer cavity of the clay basal plane (oxygen layer); the resulting compound is very stable with very slow degradation of the butyl component. The localization of charge in the tetrahedral sheet contributes to the preferential absorption of many organic compounds by clay minerals. Clay minerals saturated with Li, Na, or Mg are susceptible to strong swelling pressures due to the hydration of the metallic cation. Therefore, clay minerals susceptible to swelling may sorb organic molecules which may penetrate between the basal planes and be sorbed and held on the surface by electrostatic and van der Waals-London forces.

Organic compounds bound by clay minerals in soils, however, must have certain characteristics that are compatible with bond formation. Organic molecules carry an intrinsic charge which may be very weak but generally anionic in character. Certain molecules, however, may be positively charged, particularly those which may contain nitrogen. The herbicides paraquat (1,1'-dimethyl-4,4'-bipyridylium dichloride) and diquat [1,1'-ethylene-2,2'-bipyridylium dichloride (I or Br)] are

organic cations and are bound by clay minerals very strongly to the full extent of the CEC of the mineral in question, particularly smectite. When these minerals sorb cationic herbicides, the X-ray basal spacings change, which gives conclusive evidence to the organic cation moving into the interlayer space (Esfandiari, 1971).

Organic molecules with lone-pair electrons [N, O, sulfur (S), and phosphorus (P)] appear to have particular importance in reaction with minerals. However, S and P are rarely involved. Oxygen and N may form coordination bonds with clay minerals, and in aqueous solution these lone-pair electrons are active Brønsted acids forming a positively charged molecule or a cation. For compounds whose $\text{pH} = \text{pK}_a \rightarrow 1$, the chances for protonation increase to $\text{pH} = \text{pK}_a \rightarrow 2 = 100$ percent, and the molecule will react as an organic acid cation. Thus the probability for sorption by clays is high when the pH of the compound's environment is above its pK_a . The acid form of this type compound would be an undissociated carboxylic acid and the H bonds could form between the organic molecule and the clay mineral surface.

Many organic compounds have both acidic and basic functional groups in the molecule. The isoelectric point (IP) for these molecules is the pH at which the molecule has zero (0) electric charge. At pH values above this point the molecule has a net negative charge, and at pH values below this the molecule has a net positive charge. At pH values below this IP, then, the organic molecule could be sorbed by the electrostatic charge on the clay mineral.

Uncharged organic molecules often are sorbed by soil minerals as a result of differences in electron density within the organic molecule, that is, a polarity effect. Organic molecules may have a permanent dipole moment or polarity, or this may be induced by the charge field around the clay particles. As a result of this polarity, organic molecules may be sorbed by the mineral.

The complexity of the interaction of organic compounds with soil clay minerals is obvious when one considers steric hindrance of organic molecules reacting with clay minerals. The ability of a clay mineral to react with an organic molecule will depend on whether the individual organic molecule can fit a clay sorption site. In soils where buffering salts are present, the induction of polarity in organic molecules is reduced, that is, the electric-double-layer around the mineral particle is reduced in volume and the polarity of the organic molecule is the same as that in bulk solution. Therefore, in systems buffered against pH change, sorption usually occurs within one pH unit of the IP or pH_a , and with departure from this point the molecule becomes progressively less protonated.

Any increase in solution ionic strength will alter the electric field near a soil-particle-charged surface by decreasing the thickness of the electric-double-layer and thereby decreasing the sorption of the weakly ionized organic molecule. Substituted urea herbicides are readily sorbed by protonated clay mineral surfaces, and when the solution

ionic strength increases or the surfaces become more saturated with metallic cations, sorption of the herbicide is drastically reduced.

There are many bonding mechanisms in soils, as pointed out previously, among which are ion-exchange, H bonding, protonation at the mineral surface, and bonding where organic molecules are linked to cations on the clay mineral basal planes and on the edges of the mineral (e.g., Al bonding for phosphate). Bonding of organic molecules through cations on the mineral surface is particularly important in low water content systems. This type of bond formation is between the hydronium of the water molecule and the lone-pair electrons of the organic molecule. Conversely, when a system described above is hydrated thus decreasing the average polarization of the water molecules, the organic molecule is released. In addition to this mechanism, the exposed hydroxyl groups of clay minerals, particularly those with little or no electrostatic charge, will react with some organic molecules. For example, it has been shown that acetate ions will react with edge OH^- to form H^+ bonds with the mineral.

The van der Waals-London forces are probably formed from oscillating charges producing dipoles which attract each other. The forces are very small, but if one is dealing with a poly-atomic molecule the forces are additive and may assume substantial importance. These forces therefore may play a role in the bonding of organic molecules on mineral surfaces.

Many organic molecules can form coordination complexes (complex formed by the combination of metal cations with organic molecules having lone-pair electrons). Here the organic molecule competes with water for cation sites in a dehydrated system, that is, these molecules form coordination complexes in the absence of water, but are displaced upon rehydration of the system (Yariv et al., 1966). Coordination is one of the few mechanisms for bonding organic molecules to mineral surfaces, however, the bond is usually between carbonyls and metal ions. When Ca is the metal ion the bond is quite strong. This phenomenon probably explains why montmorillonite (smectite) clays sorb two layers of ethylene glycol when solvated as compared to Na-saturated clays where only one layer of ethylene glycol is bound.

Greenland (1965) reports that 50 to 100 percent of the organic compounds in soils are associated with the clay fraction of the soil. Humic substances, the major organic component of soils, contain per unit weight relatively large numbers of "O"-containing groups (carboxyl, phenolic, and carbonyl) and these humic compounds are natural polyelectrolytes. Humic substances are readily absorbed on the surfaces of soil mineral particles. The surface absorption, in addition to metal complexing, may also involve the formation of H bonding between the carboxyl, carbonyl, and hydroxyl groups in the humic substances and between the hydroxyl groups and O of the minerals. The main reactions governing the interlayer sorption of the low molecular weight humic substances by clay minerals appears to be the ability of undissociated humic materials to displace water from the interlayers of the clay mineral.

2.5 WATER ON SOIL SURFACES

Bulk water in soils has always been of profound interest to farmers, agronomists, and soil scientists. Water is essential for plant growth and is the medium through which soil-borne elements reach the plant. However, the first molecular layer of water on the soil particle surface has not drawn the attention it deserves and the properties of this water are much different from that in the bulk (Farmer, 1978). Water held on clay mineral basal planes (siloxane surfaces) is the major water holding reservoir in air dry soil and this water is held much too strongly for plants to extract (removed at 150-200°C). Each clay mineral sheet is interleaved with one or more layers of water between each two sheets. Within these layers of water molecules the exchangeable cations are found which are necessary to balance the negative charge due to isomorphic substitution in the clay mineral structure. Therefore, the role of water on these mineral surfaces is very close to that of water in crystalline salts or hydrates. For example, completely dry (heated, 550°C) smectite minerals usually give an X-ray diffraction spacing of 10 Å but under most laboratory conditions a spacing of 4.4 ± 1 Å is obtained, which means each sheet has two layers of water molecules on the basal plane. Vermiculite, when allowed to freely imbibe water, will expand from 10 Å to approximately 14-15 Å, while smectites with most of the layer charge located octahedrally will commonly give X-ray diffraction spacing of 19 Å or more, indicating as many as four layers of water molecules (close packed). When water enters anhydrous clays a strong exothermic reaction is noted, and the coordination of water around exchangeable cations and an O (siloxane) basal planes reacts in much the same way as the addition of water to anhydrous CaCl_2 , that is, very strongly exothermic. This phenomenon is particularly applicable to clays saturated with monovalent alkali metals and divalent alkaline earth metals.

It is generally recognized that hydration and dehydration of soil minerals by water includes interaction of the exchange cations and the surface O of the basal planes. X-ray diffraction studies show that water molecules are sorbed at ambient conditions to give spacings of 11.5 to 12 Å for single water sheets for vermiculite and spacings of 14 to 15 Å for smectites. Electron paramagnetic resonance (EPR) spectra of Cu ions form a single layer complex in smectite with a 12.8 Å spacing, and the EPR spectra show Cu forming a square planar coordination complex of four water molecules parallel to the basal plane and two weak bonds directed perpendicularly toward the basal mineral oxygen plane. These bonds interact with two or three adjacent O instead of one. According to EPR studies, each of the several clay minerals shows different configurations of the Cu ion and water between the clay mineral layers.

Of all the several methods available for studying the interaction of soil minerals and water, IR spectroscopy is far superior to any other method (Farmer, 1974). For example, at 50 percent relative humidity and 25°C, Mg ions on clays form a hexahydrate and may absorb four to 18 more water molecules if space is available, forming a double sheet of water molecules. In these water sheets there are two families of H bonds, the

stronger bonds lie parallel to the water sheets while the weaker bonds are directed toward the O basal planes of the clay mineral. The strong bonds are from 2.83 to 2.88 Å in length while the weaker bonds are from 2.82 to 3.0 Å in length. Water in layer silicates can be displaced by polar molecules and can donate protons to bases in the interlayer spaces. Conversely, water can displace fewer polar molecules from the interlayer spaces.

In soils the layer silicates are often imperfectly crystallized and contain islands of hexahydroxyalumina polymers (Figure 13) (Hsu, 1977), islands of humin polymers, and complex hydroxides of Fe. These factors profoundly affect the hydration-dehydration characteristics of clay minerals and their interactions with a given environment. Therefore, under these conditions water may be held to much higher temperatures and conversely much more heat is released on wetting the anhydrous system. Hydrous oxides (Fe and Al) are quite common in soils with water coordinated to structural cations. Most of these minerals, that is, the oxides and poorly crystallized layer silicates, easily sorb organic matter (humic acid), phosphates, arsenates, and silica. Similarly hydrated silica is common in soils and readily coordinates with water, and this silica is usually contaminated with Al to form allophane and imogolite and similar soil minerals. Allophane and imogolite are gel-like aluminosilicates with highly porous structures and a large surface area (500-700 m²/g). These structures are very highly hydrated or hygroscopic, and water may constitute 55-60 percent of their volume. However, when these compounds are oven dried the dehydration is not reversible (Wada, 1977).

When organic substances are sorbed onto mineral surfaces the surface may become strongly hydrophobic and, if these minerals are found in soils to any marked extent, they impart some very unfavorable characteristics to the soil. If they are found under conditions of heavy rainfall, their water repellency causes severe erosion. Generally coarse textured soils are more apt to be water repellent than fine textured soils. Water repellency is also much more common under warm low-rainfall climates. Water repellency is apparently caused by monomolecular coatings (or a few layers) of fatty acids, fatty alcohols, alkanes, and ketones on hydroxylated silica and layer silicate minerals. These surfaces are not only water repellent but will dissolve (or sorb) other organic molecules. The sorbed molecules, if slightly to strongly polarized, may react with the strongly polarized water molecule and be released when the system is hydrated.

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