

Chapter 2

Soil–Subsurface Interrelated Matrix

The soil–subsurface regime comprises two distinct, interacting phases which may be affected by anthropogenic chemicals: the *solid phase*, formed by mineral and organic constituents in various states of evolution, and the *liquid phase*, including the water retained in the soil–subsurface pores and in the aquifer. The impact of anthropogenic chemicals on the soil–subsurface system may lead to irreversible changes in the solid phase matrix and properties, as well as to alteration of the liquid phase chemical composition. In this chapter, we provide a basic overview of soil–subsurface system characteristics as formed under natural environmental conditions; the reader is referred to the literature for detailed information.

2.1 Soil and Subsurface Solid Phase

The soil and subsurface solid matrix consists generally of a heterogeneous, friable material with aggregates and fractures of various sizes exhibiting a large range of porosity. The soil solid matrix comprises a mineral phase originating directly from rock weathering and subsurface earth materials, as well as an organic matter phase obtained from the decomposition of earth vegetative cover or from microbial populations. Components of the soil organic phase may be transported into the subsurface as dissolved solutes, colloidal materials, or suspended particles in the leaching water coating the mineral phase or precipitating as minor organic deposits. The subsurface solid matrix contains a mineral phase resulting mainly from direct weathering processes of the local geological material, from wind- and alluvial-induced redeposition of earth materials originating from other geological systems, and/or from precipitation of salts and other inorganic components found in incoming waters.

2.1.1 The Mineral Phase

The minerals formed by inorganic processes are naturally occurring homogeneous solids with a definite chemical composition and ordered atomic arrangements. Minerals with the same chemical composition may have different crystal structure, and vice versa. The most common chemical elements in the earth's crust, together with their crustal average, mole fractions, ionic radius, and volume, are presented in Table 2.1.

Based on their dominant anion or anionic group, Hurlbut and Klein (1977) grouped the minerals into the following classes: native elements, sulfides, sulfosalts, oxides and hydroxides, halides, carbonates, nitrates, borates, phosphates, sulfates, tungstates, and silicates. The minerals in the soil and subsurface system may also be classified as primary or secondary minerals. Primary minerals originate at high temperature mainly from igneous or metamorphic rocks, and rarely from sedimentary rocks. Secondary minerals are formed at low-temperature reactions by weathering of sedimentary rocks (Jackson 1964). Below, we discuss specific matrix properties of these minerals, which control their potential interactions with anthropogenic chemical compounds.

2.1.1.1 Silicates

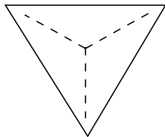
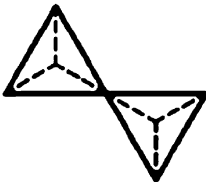
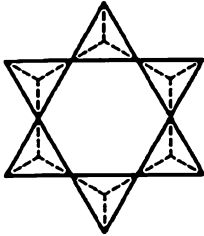
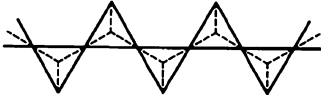
Silicates include a group forming about 90% of the earth's crust, comprising both primary and secondary minerals. The fundamental unit of the silicate tetrahedron consists of four O^{2-} ions coordinated to one Si^{4+} at the center. An O^{2-} ion is shared by individual tetrahedra to form various complex structures such as sorosilicates (double), cyclosilicates (ring), inosilicates (single or double chains), phyllosilicates (sheets), or tectosilicates (three dimensional). The various arrangements of silica minerals are presented in Table 2.2.

Table 2.1 The 12 most common elements in the earth's crust (after Hurlbut and Klein 1977)

Element	Crustal average ($G\ kg^{-1}$)	Mole fraction	Ionic radius (Nm)	Volume (%)
O^{2-}	466.0	0.6057	0.140	89.84
Si^{4+}	277.2	0.2052	0.039	2.37
Al^{3+}	81.3	0.0627	0.051	1.24
Fe^{2+}	50.0	0.0186	0.074	0.79
Mg^{2+}	20.9	0.0179	0.066	0.60
Ca^{2+}	36.3	0.0188	0.099	1.39
Na^{+}	28.3	0.0256	0.097	1.84
K^{+}	25.9	0.0138	0.133	1.84
Ti^{++}	4.4	0.0019	0.068	0.08
H^{+}	1.4	0.0288	†	†
Mn^{4+}	0.9	0.0003	0.060	0.01
P^{5+}	1.0	0.0007	0.035	0.01

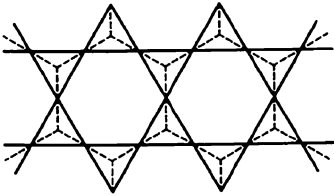
†undetermined

Table 2.2 Classification of silicate minerals (after Schulze 1989; Allen and Fanning 1983; Hurlbut and Klein 1977)

Silicate class	Unit composition and arrangement of SiO_4 tetrahedra	Mineral	Ideal formula
Nesosilicates $(\text{SiO}_4)^{4-}$		Olivine	$(\text{Mg, Fe})_2\text{SiO}_4$
		Forsterite	Mg_2SiO_4
		Fayalite	Fe_2SiO_4
		Zircon	ZrSiO_4
		Sphene	$\text{CaTiO}(\text{SiO}_4)$
		Topaz	$\text{Al}_2\text{SiO}_4(\text{F, OH})_2$
		Garnets	$\text{X}_3\text{Y}_2(\text{SiO}_4)_3$ where X = Ca, Mg, Fe ²⁺ , Mn ²⁺ Y = Al, Fe ³⁺ , Cr ³⁺
		Andalusite	Al_2SiO_5
		Silimanite	Al_2SiO_5
		Kyanite	$\text{Fe}_2\text{Al}_9\text{O}_6(\text{SiO}_4)_4$ (O, OH) ₂
Sorosilicates $(\text{Si}_2\text{O}_7)^{6-}$		Staurolite	$\text{Ca}_2(\text{Al, Fe})\text{Al}_2\text{O}$ $(\text{SiO}_4)(\text{Si}_2\text{O}_7)$ (OH)
		Epidote	$\text{Ca}_2(\text{Al, Fe})\text{Al}_2\text{O}$ $(\text{SiO}_4)(\text{Si}_2\text{O}_7)$ (OH)
Cyclosilicates $(\text{Si}_6\text{O}_{18})^{12-}$		Beryl Tourmaline	$\text{Be}_3\text{Al}_2(\text{Si}_6\text{O}_{18})$ $(\text{Na, Ca})(\text{Li, Mg, Al})$ $(\text{Al, Fe, Mn})_6$ $(\text{BO}_3)_3(\text{Si}_6\text{O}_{18})$ (OH)
Inosilicates (single chains) $(\text{SiO}_3)^{2-}$		Pyroxenes Augite	$(\text{Ca, Na})(\text{Mg, Fe, Al})$ $(\text{Si, Al})_2\text{O}_6$
		Enstatite	MgSiO_3
		Hypersthene	$(\text{Mg, Fe})\text{SiO}_3$
		Diopside	$\text{CaMgSi}_2\text{O}_6$
		Hedenbergit	$\text{CaFeSi}_2\text{O}_6$
		Pyroxenoids	
		Wollastonite	MnSiO_3
		Rhodonite	MnSiO_3

(continued)

Table 2.2 (continued)

Silicate class	Unit composition and arrangement of SiO ₄ tetrahedra	Mineral	Ideal formula
Inosilicates (double chains) (Si ₄ O ₁₁) ^{6−}		Amphiboles	
		Hornblende	(Ca,Na) _{2–3} (Mg,Fe,Al) ₅ Si ₆ (Si,Al) ₂ O ₂₂ (OH) ₂
		Tremolite	Ca ₂ Mg ₅ Si ₈ O ₂₂ (OH) ₂
		Actinolite	Ca ₂ (Mg,Fe) ₅ Si ₈ O ₂₂ (OH) ₂
		Cummingtonite	(Mg,Fe) ₇ Si ₈ O ₂₂ (OH) ₂
		Grunerite	Fe ₇ Si ₈ O ₂₂ (OH) ₂

Silica minerals may be altered by physical weathering, forming secondary or altered primary minerals which form clay materials. As a consequence, the two predominant minerals in soils and subsurface are quartz (a silica mineral) and clay. The ratio (wt./wt.) of these two minerals defines the physical and surface properties of the earth materials. Below we present briefly the characteristics of these two major minerals that define the matrix and properties of the soil–subsurface system.

2.1.1.2 Quartz

Quartz, a silicate mineral, is one of the most abundant minerals in the soil–subsurface solid phase. In the soil and subsurface environment, quartz is found generally in sand and silt fractions, the amount of silicate mineral being determined by the parent material and the degree of weathering. Quartz is a primary mineral when crystallized from magma, and a secondary mineral (neoformed quartz) created in situ under specific temperature and pressure.

Common trace elements in quartz are Al, Ti, Fe, Na, Li, K, Mg, and Ca. Aluminum tends to be the most frequent element in quartz, substituting for Si in the crystal structure (Dennen 1966). In soil and subsurface systems, quartz may be altered in situ by chemicals and by physical weathering. Quartz is generally found in these systems in the form of anhedral grains (Fig. 2.1a), exhibiting also a variety of granular forms (Fig. 2.1b, c) and rarely prismatic forms, with the prism terminated by a set of rhombohedral faces (Fig. 2.1d). Quartz yields a characteristic X-ray pattern with well-defined peaks exhibiting a d-spacing ranging between 0.426 and 1.181 nm (Dress et al. 1989). The infrared (IR) absorption band is at 692 cm^{−1}, with two strong doublets at 798 and 780 cm^{−1}, as well as at 390 and 370 cm^{−1} (Chester and Green 1968).

The silica tetrahedron in quartz is almost symmetrical and has a Si–O distance of 0.16 nm. Quartz has a spiral network structure consisting of silica tetrahedra around z-axis (Wilding et al. 1989). Each tetrahedron is repeated in the network by a rotation of 120° and a translation of c/3 (Fig. 2.2). The dense packing of the crystal structure and the high activation energy required to alter the Si–O–Si bond contribute to the high stability of quartz (Stober 1967). The specific gravity of quartz

Fig. 2.1 Scanning electron microscope images of various quartz grains (after Drees et al. 1989). Copyright 1989, Soil Science Society of America. Reprinted with permission

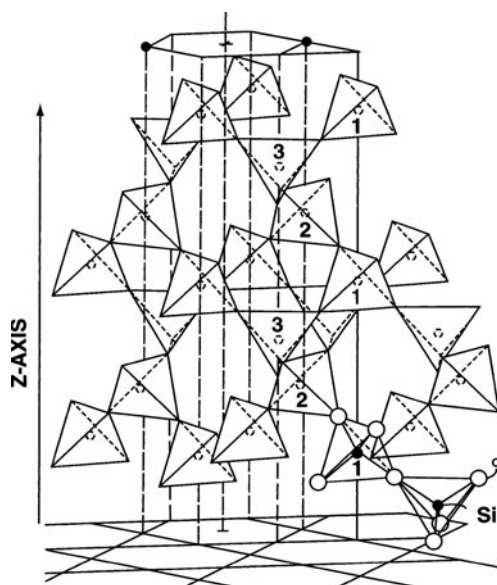
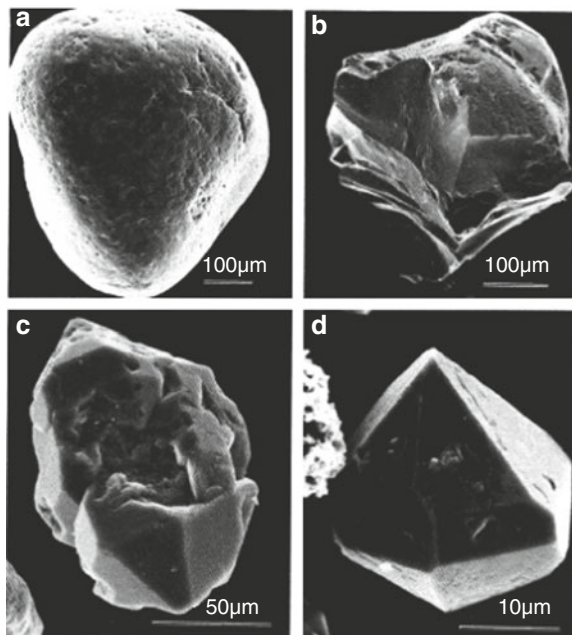


Fig. 2.2 The structure of quartz (Drees et al. 1989). Copyright 1989, Soil Science Society of America. Reprinted with permission

ranges between 2.65 g mL^{-1} in macrocrystalline varieties and 2.60 g mL^{-1} in cryptocrystalline varieties (Fron del 1962; Katz et al. 1970). Substitution of Al by Si in quartz leads to a decrease in its specific gravity. Quartz minerals may exhibit

cleavage parallel to lattice planes, especially along planes where Si–O bonds are broken (Margolis and Krinsley 1974).

2.1.1.3 Clay Minerals

Clay minerals are the major natural nanomaterials in the soil–subsurface system, which interact with almost all of the contaminants introduced into the environment by humans. While the fraction of clay minerals in the soil–subsurface system is often relatively low, even small percentages of clay have a critical effect on the transport and fate of chemical contaminants, due to large active surface areas which substantially exceed those of other components.

Most soil and subsurface clays are a mixture of one or more aluminosilicate clays with minute amounts of iron oxides and hydroxides, quartz and feldspar, oxides and hydroxides of aluminum and manganese, and carbonates (especially calcite). Many clay minerals have a layer structure in which the atoms within layers are strongly bonded to each other; the bonding between layers is weaker. The layers in different kinds of clays are structurally similar. However, different layers can fit together to form stable structures common among interstratified clay minerals. Bailey et al. (1971) define layer silicates as continuous, two-dimensional tetrahedral sheets of composition Z_2O_5 in which individual tetrahedra are linked to neighboring tetrahedra by sharing three corners each when Z is the tetrahedrally coordinating cation of Si^{4+} or Al^{3+} . Tetrahedral sheets are linked in the unit structure to octahedral sheets, groups of coordinated cations or individual cations. As a function of their external or internal surface characteristics, clays interact differently with organic or inorganic contaminants.

The clay solid phase is characterized by a net charge on the solid phase that is in contact with the liquid or gaseous phase. These charged surfaces usually are faced by one or more layers of counter ions having a net charge separate from the surface charge. The adsorption of charged solute on the mineral solid phase surface is subject to both chemical binding forces and an electric field at the interface, and is controlled by electrochemical properties.

We focus our discussion below on the characterization of two major groups of clay minerals: *kaolinite*, with a 1:1 layered structured aluminosilicate and a surface area ranging from 6 to 36 m² g^{−1}, and *smectites*, with a 2:1 silicate layer and a total (internal and external) surface area of about 800 m² g^{−1} (Schofield and Samson 1954; Borchard 1989).

Kaolinite is composed of unit layers, each consisting of one silica tetrahedral sheet and one alumina octahedral sheet bound together in a common sheet with shared oxygens (Grim 1962). The units are stacked one above the other in the *c*-axis direction. The classical schematic diagram (Gruner 1932) of a kaolinite unit layer is reproduced in Fig. 2.3. Refinements of the kaolinite structural diagram were developed later (e.g., Brindley and MacEvan 1953; Dixon 1989), but we consider the original Gruner representation to remain valid for didactic purposes.

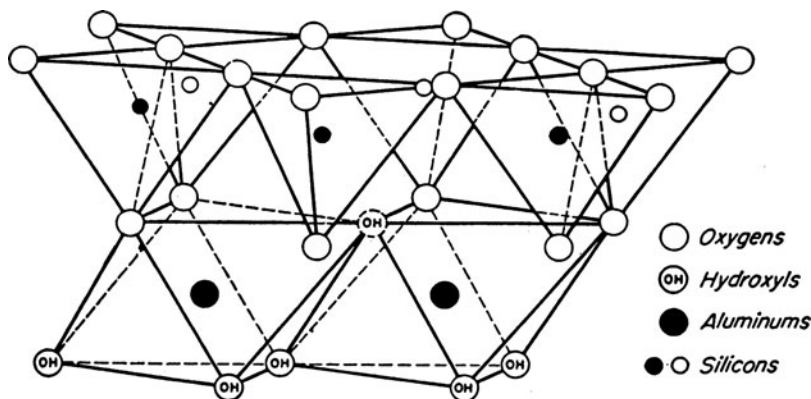


Fig. 2.3 Structure of kaolinite (after Gruner 1932)

Summarizing the structural properties of kaolinite, Dixon (1989) noted that the composed tetrahedral and octahedral sheets form a 0.7-nm layer in a triclinic unit cell. Two-thirds of the octahedral positions are occupied by Si and Al, which are located in two rows parallel to the x -axis. Every third row of the octahedral sheet is vacant. The surface plane of octahedral anions and a third layer of the inner plane are built up by hydroxyl (OH) groups. The surface hydroxyls bond through their hydrogens to the oxygen sheet of the bordering layer.

The kaolinite structure exhibits covalent sharing of H which leads to conceptualization of the presence of two inner surface hydroxyls perpendicular to the layer bonded to the O of an adjacent layer (Giese 1982). As a result of polarization of the Si–O and O–H groups, the surface oxygen and proton plane become negatively or positively charged. Electrostatic attraction and van der Waals forces determine the stacking of kaolinite unit layers. Kaolinite exhibits a very low cation exchange capacity, in general lower than $1 \text{ cmol}_c \text{ kg}^{-1}$ (Schofield and Samson 1953) at $\text{pH} = 7$ (Lim et al. 1980). The positive charge on kaolinite occurs on the edges of the plates which become positive by acceptance of H^+ in the acid pH range (Schofield and Samson 1953).

Morphological characteristics of kaolinite crystals from the clay fraction of some Brazilian soils as related by Melo et al. (2001) are reproduced in Fig. 2.4. As a function of type of soil, kaolinite crystals are hexagonal exhibiting either six euhedral faces or otherwise an anhedral form. The dominant forms of the soil clay fraction kaolinite are elongated and rounded with relatively lower proportion of hexagonal particles. These findings are in accordance with a previous observation of Sings and Gilkes (1990) showing that the hexagonal form is found commonly in kaolin deposits but rarely in weathered soils.

Kaolinite surface charge is heterogeneous because different reactions occur on a variety of distinct crystallographic sites. Brady et al. (1996) showed, for example, that the pH-dependent, multi-site surface charge on kaolinite is explained by proton donor–acceptor reactions occurring simultaneously on Si and Al sites exposed on basal planes and edges.

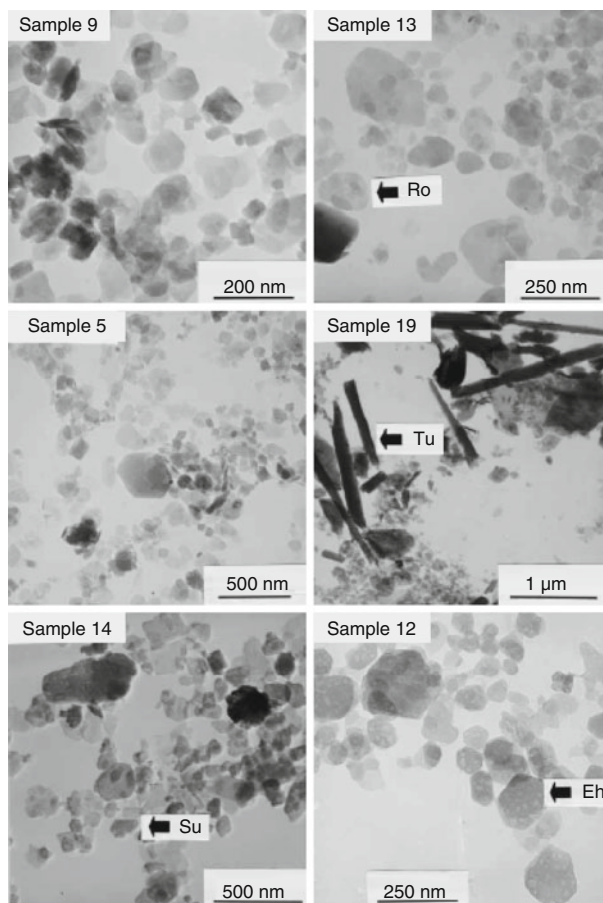
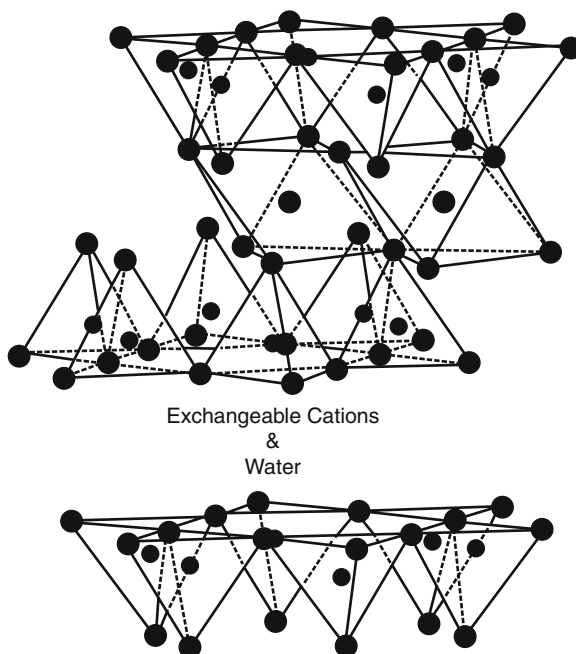


Fig. 2.4 Transmission electron microscope (TEM) micrographs of kaolinite from the clay fraction of some representative Brazilian soils showing a wide range of crystal morphologies and size. Various morphologies are indicated: *Ro* rounded, *Su* subeuhedral faces, *Eh* euhedral, and *Tu* tubular (after Melo et al. 2001). Copyright 2001, Soil Science Society of America. Reprinted with permission

Smectites are clay minerals with an expanding nature, a negative charge, and a large total surface area. These properties are of major importance in controlling the fate of chemical contaminants in the soil–subsurface system by affecting their retention, transport, and persistence. The idealized structure of a smectite clay mineral as depicted by Kaviratna et al. (1996) is presented in Fig. 2.5. The oxyanion layer consists of two inverted silicate tetrahedral sheets sharing their oxygens with an octahedral sheet. The 2:1 relation between the tetrahedral and octahedral sheets within a layer accounts for classification of these clays as 2:1 phyllosilicates. The layer charge originates from the substitution of octahedral Al^{3+} by Mg^{2+} . In a unit cell formed from 20 oxygens and four

Fig. 2.5 Idealized structure of a smectite clay mineral. *Large circles*, oxygen atoms; *small circles*, hydroxyl groups. Silicon and sometimes aluminum normally occupy tetrahedral positions in the oxygen frame work. Aluminum, magnesium, iron, or lithium may occupy octahedral sites. Exchange cations and water occupy the interlayer region (after Kaviratna et al. 1996). Reprinted from Kaviratna PD, Pinnavaia TJ, Schroeder PA, Dielectric properties of smectites clay. J Phys Chem Solids 57:1897–1906, Copyright (1996), with permission from Elsevier



hydroxyl groups, there are eight tetrahedral sites and six octahedral sites, along with four cavities surrounded by a six-membered oxygen ring on the surface.

The montmorillonite and beidellite minerals, which are the most common smectites in the earth, contain significant amounts of tetrahedral Al and octahedral Fe. A detailed description of smectite structure and properties is given by Borchard (1989). Montmorillonite ($\text{Si}_4\text{Al}_{3.5}\text{Mg}_{0.5}$) with a cation exchange capacity of $135 \text{ cmol}_c \text{ kg}^{-1}$ has an octahedral sheet that shares oxygen atoms between two tetrahedral sheets, with cationic substitution occurring in the tetrahedral and octahedral sheets. The layer charge originates from the substitution of octahedral Al^{3+} by Mg^{2+} . In a unit cell formed from 20 oxygens and four hydroxyl groups, there are eight tetrahedral sites and six octahedral sites along with four cavities surrounded by a six-membered oxygen ring on the surface.

The expanding characteristics of smectites are affected by the nature of adsorbed ions and molecules. The interlayer cations are replaced when the clay is wetted with an electrolyte solution, affecting the interlayer spacing. The hydration water of the interlayer exchangeable cation forms the first water layer followed by an additional water layer held with less energy (Barshad 1960). According to Barrer and Jones (1970), layer charge and the type of cations in galleries of clay determine the extent of water adsorption, thereby controlling the swelling of the gallery region. The dielectric properties of smectites are controlled by their water content and saturating cation. Kaviratna et al. (1996) report that, in general, the dielectric constant of a smectite changes slowly as the first monolayer of adsorbed water builds up in the clay galleries. Water loading beyond the first monolayer causes the dielectric constant to rise rapidly

to very high values. Environmental temperature may affect the mineral hydration status. Smectite loses pore water below 110°C, adsorbed water below 300°C, and OH water at a temperature above 300°C. Borchard (1989) reported on the effect of saturating cations on the basal spacing of smectites (a mixture of montmorillonite and beidellite from a Californian soil) using XRD measurements. All magnesium-saturated smectites give a peak corresponding to a d-spacing of 1.5 nm at 54% relative humidity, while potassium-saturated smectites give a peak corresponding to a d-spacing of 1.25 nm at the same moisture content. These differences are explained by variations in the hydration status of the saturating ions. When smectites are kept at 0% relative humidity after 110°C heating, they yield a peak corresponding to a d-spacing of 1.0 nm. Simultaneous morphological observation by HRTEM and chemical analysis by AEM (EDS) techniques provide a comprehensive, nanoscale level understanding of smectite interlayer configuration and composition.

TEM images (Yaron-Marcovich et al. 2005) show the morphology of a sodium montmorillonite along with the corresponding selected area electron diffraction (SAED) pattern (Fig. 2.6). At lower magnification, crystalline aggregates composed of relatively small, thin, flake-like, and pointed nanoscale silicate particles (about 10–50 nm wide and 50–400 nm long) with no obvious orientation are visible. The interlayer compositional variation of the same smectite clay sample, determined by X-ray energy dispersive spectroscopy (EDS), shows that the nanoparticles are of similar composition containing Na, K, Al, Mg, and O.

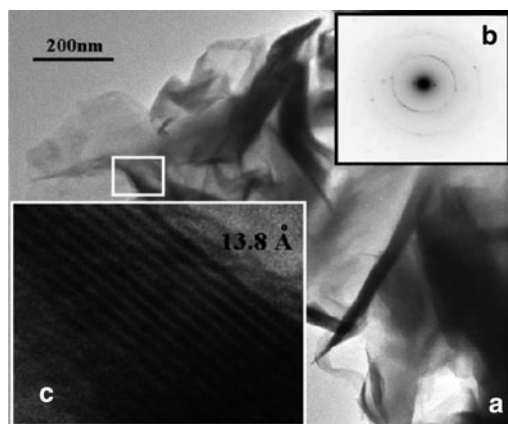


Fig. 2.6 TEM images of Na-montmorillonite particles: (a) low-magnification TEM image showing a typical crystalline aggregate; (b) the corresponding SAED pattern: note the 001 diffraction spots corresponding to the planes parallel to the e-beam; the calculated spacing is 13.83 Å; (c) high-resolution TEM image of a particle attached to the edge of the aggregate (white frame in (a)) exhibiting the layered structure; the measured lattice spacing (13.8 Å) is in agreement with calculations from the SAED in (b) (Yaron-Marcovich et al. 2005). Reprinted with permission from Yaron-Marcovich D, Chen Y, Nir S, Prost R (2005) High resolution electron microscopy structural studies of organo-clay nanocomposites. *Environ Sci Technol* 39:1231–1239. Copyright 2005 American Chemical Society

Infrared analysis of smectite provides additional information on its structural properties. Silicate minerals have strong Si–O bands near 600 and 1,000 cm^{-1} which can be affected by substitution of Si atoms by Al atoms. The OH banding vibrations produce the adsorption characteristics of the octahedral sheet. When Al is present, the absorption is near 920 cm^{-1} and when only Fe is present, the absorption is near 820 cm^{-1} . A mixture of Al, Fe, and Mg leads to intermediate values. Hydroxyl adsorption is in the 3,000–3,800 cm^{-1} region. Farmer and Russel (1967) showed that this band appears to broaden as a result of Al substitution by Si in tetrahedral sheets and reflects the type of saturating cation and the hydration status in the interlayer space. The surface oxygen atoms are weak electron donors and form weak hydrogen bonds. As a consequence and as a result of their association with exchangeable cations, water molecules on the smectite surface are more acidic than the interlayer water (Borchard 1989).

Of particular interest for chemical transport into a predominantly smectite medium is the shrink–swell property of the clay material. The swelling properties of smectites are explained by two different concepts. The first one, developed by Sposito (1973), shows that smectite swelling is caused by the hydration and mobility of the cations, which in turn balance the negative charge of the layer silicates. The second concept, presented by Low (1981), emphasizes the direct interaction of water molecules with the silicate surface. Both viewpoints fit the common observation that smectite swells in a high hydration environment and at low electrolyte concentrations, and shrinks when water is lost and salt is added to the bulk solution.

A mixture of intercalating clays may be found in the soil–subsurface medium. Interstratification of kaolinite and smectite has been reported in some cases (e.g., Herbillon et al. 1981; Yerima et al. 1985). This fact is reflected in a XRD spacing of about 0.8 nm (Dixon 1989) or in HRTEM micrographs (Fig. 2.7).

Environmentally induced processes occurring in the subsurface (e.g., leaching and acidification) may induce weathering processes and structural changes in natural clays. For example, in soils with low organic matter, moderate leaching and a pH of about 5 cause smectites to be transformed into pedogenetic chlorites (Barnhisel and Bertsch 1989). Laboratory studies proved a direct transformation of smectites into kaolinite during intense weathering. Under natural environmental conditions, the transformation of smectite to kaolinite, in the presence of iron oxide, may occur under enhancement of drainage conditions during landscape evolution. In the case of sedimentary environments (Morgan et al. 1979) and of well-drained red–black soils (Herbillon et al. 1981), the transformation may proceed through an intermediate step consisting of interstratified kaolinite–smectite.

2.1.1.4 Minerals Other Than Silicates

In addition to quartz and clay minerals, the subsurface contains a variety of minerals (e.g., oxides and carbonates) which may react with organic and inorganic contaminants. Gilkes (1990), summarizing the properties of the metal oxides

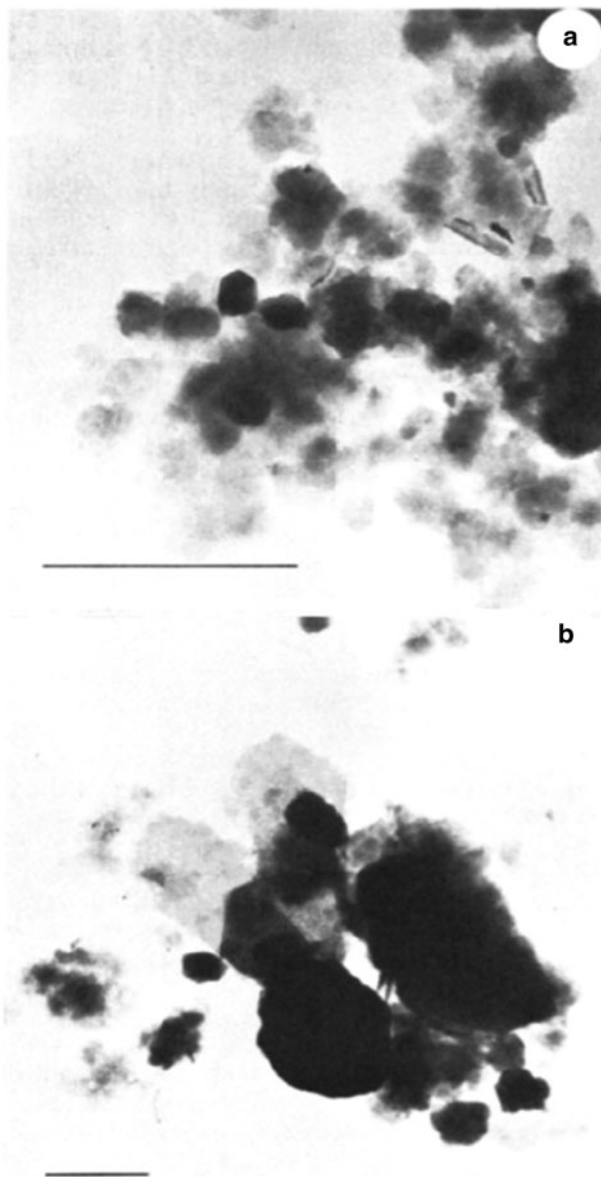


Fig. 2.7 Transmission electron micrographs of (a) fine (<0.2 μm) and (b) coarse (2–0.2 μm) clay from the Atiocoyo pedon (horizon 2A2) showing subrounded and hexagonal shapes characteristic of interstratified kaolinite–smectite. Each *bar* represents 0.5 μm (after Yerima et al. 1985). Copyright 1985, Soil Science Society of America. Reprinted with permission

in earth materials, states that iron oxides (e.g., hematite α -Fe₂O₃, maghemite β -Fe₂O₃, goethite α -FeOOH, and lepidocrocite β -FeOOH) are common constituents with crystals that vary greatly in size, shape, and surface morphology. The surface of

iron oxides in the subsurface environment is often hydroxylated either structurally or through hydration of iron atoms. Crystals of the aluminum oxides that commonly occur (e.g., gibbsite and boehmite) are small but often larger than the associated iron oxides. Other oxide minerals are less abundant than iron and aluminum oxides, but because of their very small crystal sizes and large surface areas, they may affect very significantly the geochemical properties of the subsurface and their interaction with chemicals. For example, the various manganese oxides that can be found in the subsurface can occur as very small (about 10 nm), structurally disordered crystals. Similarly, titanium oxides (rutile, anatase, TiO_2) and even corundum, a rare pyrogenic mineral, occur within the clay fraction as approximately 30-nm crystals. The ability of iron and certain other metal ions to undergo redox reactions further increases the role of metal oxides in the activity of the solid phase.

Other major components found in the subsurface include significant quantities of relatively high surface area, soluble calcium carbonate (CaCO_3), and calcium sulfate (CaSO_4). It is difficult to estimate the contribution of amorphous materials (e.g., allophane or imogolite) to the surface activity of earth materials. Amorphous materials often coat crystal minerals, which may further affect interaction of these minerals with contaminants.

2.1.2 The Organic Phase

The natural organic matter in the soil solid phase is “a heterogeneous mixture composed largely of products resulting from microbial and chemical transformations of organic debris” (Hayes and Swift 1978) disposed on land surface. Stevenson (1994) regards the soil organic matter in the solid phase as a mixture of vegetation litter, microbial biomass light fractions, and stabilized decomposed natural organic materials named *humus*. The transformation process of natural organic matter into humus is called humification. Humic substances include a series of relatively high molecular weight yellow- to black-colored substances formed in secondary synthesis reactions (Stevenson 1994). Major components of the soil organic matter and their definition are presented in Table 2.3.

Although humus – comprising the humic substances and other organic non-humic components – forms a minor part of the total solid phase, it is of major importance in defining the surface properties of the solid phase and has an enormous impact on the retention and persistence of anthropogenic chemicals reaching the land surface. In the soil–subsurface system, humus may be found as a free organic fraction or coating the mineral constituents of the solid phase. The main mass of natural organic materials is deposited in the soil layer and the soil offers optimum conditions for the humification process. However, organic matter may also be transported from the soil as suspended particles into the subsurface porous medium or even into the groundwater region.

Table 2.3 Definition and characterization of soil organic matter. Reprinted from Stevenson FJ (1994) *Humus Chemistry*, 2nd edn. Wiley, New York. Copyright 1994 with permission of John Wiley and Sons

Term	Definition
Litter	Macroorganic matter (e.g., plant residues) that lies on the soil surface
Light fraction	Undecayed plant and animal tissues and their partial decomposition products that occur within the soil proper and that can be recovered by flotation with a liquid of high density
Soil biomass	Organic matter present as live microbial tissue
Humus	Total of the organic compounds in soil exclusive of undecayed plant and animal tissues, their “partial decomposition” products, and the soil biomass
Soil organic matter	Same as humus
Humic substances	A series of relatively high molecular weight, yellow- to black-colored substances formed by secondary synthesis reactions. The term is used as a generic name to describe the colored material or its fractions obtained on the basis of solubility characteristics. These materials are distinctive to the soil (or sediment) environment in that they are dissimilar to the biopolymers of microorganisms and higher plants (including lignin)
Non-humic substances	Compounds belonging to known classes of biochemistry, such as amino acids, carbohydrates, fats, waxes, resins, and organic acids. Humus probably contains most, if not all, of the biochemical compounds synthesized by living organisms
Humins	The alkali-insoluble fraction of soil organic matter or humus
Humic acid	The dark-colored organic material that can be extracted from soil by dilute alkali and other reagents and that is insoluble in dilute acid
Hymatomelanic acid	Alcohol-soluble portion of humic acid
Fulvic acid	Fraction of soil organic matter that is soluble in both alkali and acid
Generic fulvic acid	Pigmented material in the fulvic acid fraction

2.1.2.1 Genesis and Structure

In general, the genesis of soil organic matter may be described by two major pathways of humus formation: (1) biologically induced degradation of dead plant tissue, involving the modification of lignine, suberine, and cutine (Hatcher and Spiker 1988; Clapp et al. 2005), and (2) abiotic synthesis process (Stevenson 1994; Essington 2004). However, Wershaw (2000) in his work on “Humic Substances – In Search of a Paradigm” stated that 100 years of research has not advanced knowledge on the structure of humic acids. Moreover, based on a large overview of humic substances, Burdon (2001) reached the conclusion that there is insufficient biological or chemical information to define their structure in the soil environment.

Numerous structures have been proposed for humic substances in the past, based mainly on speculative or “in vogue” research results over the years. A basic structure for the modeling of humic substances was the preliminary concept of a two-dimensional representation of humic acid (Schulten and Schnitzer 1993, 1997). Another model, which embraces the concept of molecular association based on ordered aggregates of amphiphiles – compounds with hydrophobic stretches and charged or

polar center – is based on the assumption of acidic functionality of the altered plant molecular functions (Wershaw 1986, 1993). The humic molecules are held together by hydrophobic bonding, charge transfer, and H-bonding interactions (Piccolo 2001). Models were also developed on the basis of analytical and spectroscopic data associated with computer calculations (e.g., Jansen et al. 1996; Bailey et al. 1971). Schulten (2001) improved this model (Schulten and Schnitzer 1993, 1997) by trapping biological substances such as sugars and peptides, thus developing different models for terrestrial humic acids, soil organic matter, and dissolved organic matter.

Because organic matter is such an important component of soil, development of models to describe subsurface behavior now incorporates chemical interaction studies, molecular mechanism calculations, structural modeling, and geometry optimization. A reevaluation of molecular structure of humic substances based on data obtained primarily from nuclear magnetic resonance spectroscopy, X-ray absorption near-edge structure spectroscopy, electrospray ionization-mass spectrometry, and pyrolysis studies was presented by Sutton and Sposito (2005). The authors consider that “humic substances are collections of diverse, relatively low molecular mass components forming dynamic associations stabilized by hydrophobic interactions and hydrogen bonds.” These associations are capable of organizing into micellar structures in suitable aqueous environments.

Humic components display contrasting molecular motion behavior and may be spatially segregated on a scale of nanometers. Within this structural context, these components comprise any molecules closely associated with a humic substance. Sutton and Sposito (2005) consider that biomolecules which bind strongly within humic fractions are by definition humic components. Kleber et al. (2007), continuing the assumptions of Wershaw et al. (1996), Piccolo (2001), and Sutton and Sposito (2005), showed that soil organic matter consists of organic molecular fragments of varying degrees of amphiphilicity or surfactant-like properties. The organic fragments and mineral surfaces arrange themselves in structures that maximize entropy, a fact that suggests the formation of a layered mineral–organic association. Kleber et al. (2007) suggest that the soil organic matter sorbs to mineral surfaces in a discrete zonal sequence where a contact zone, a hydrophobic zone, and a kinetic zone (Fig. 2.8) are involved.

In the *contact zone*, amphiphilic fragments accumulate on charged surfaces through electrostatic interactions, directing hydrophobic portions outward toward the polar aqueous solution. The *zone of hydrophobic interactions* expresses the hydrophobic region. This region is the result of entropically driven shielding of the hydrophobic portions of adsorbed organic molecules from the polar aqueous phase by a second layer of amphiphilic molecules.

Progression from model structures to molecular structures of natural organic matter (NOM) components was discussed by Leenheer et al. (2003). Based on the hypothesis that humification processes occur as extensive condensation/oxidative coupling, reactions were developed in the previous NOM models as macromolecular random coil shapes. Ulterior molecular models were developed on the basis of analytical evidence showing that NOM is an aggregate of small molecules. The progression from NOM model structure to molecular structure, however, requires better analytical and instrumental techniques. Because the genesis of component molecules of humic substances is still not known, the best indication of their nature

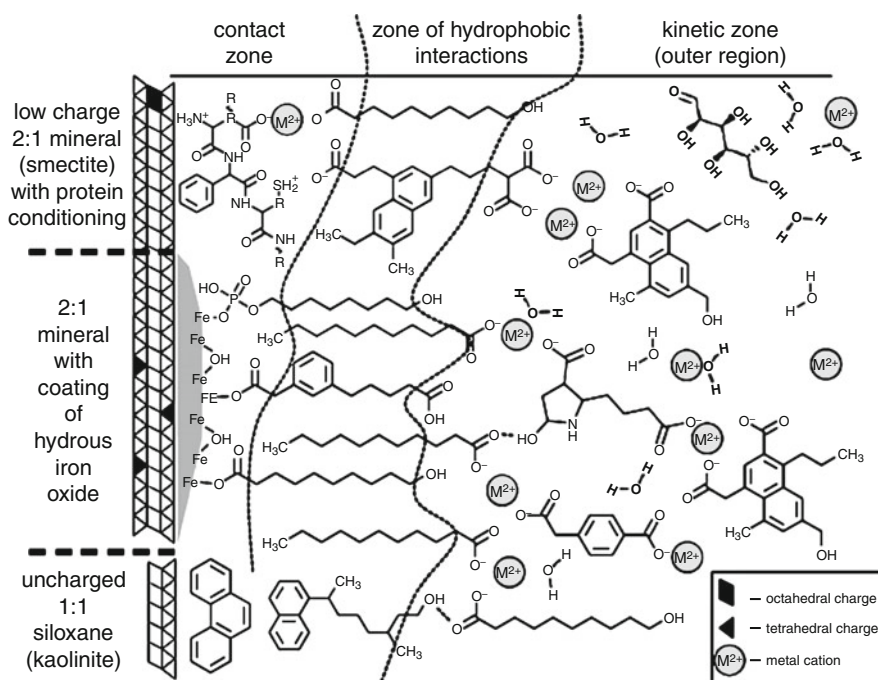


Fig. 2.8 The zonal model of organo-mineral interactions (after Kleber et al. 2007)

is the identification of the degradation products using various advanced techniques (e.g., NMR, FTIR, and Raman spectroscopy).

Humic components include humic acid (soluble in alkaline solution, insoluble in acid solution), fulvic acid (soluble in aqueous media at any pH), humatomelamic acid (alcohol-soluble part of humic acid), and humin (insoluble in alkaline solution at any pH value). Humin is a major component of the soil humic fraction, representing more than 50% of the organic carbon of soil (Kononova 1966). It should be noted, however, that this fractionation of soil organic matter does not lead to a pure compound; each named fraction consists of a very complicated heterogeneous mixture of organic substances. For example, biomolecules which are not part of humic substances may precipitate at pH 1 or 2 with the humic acid (Hayes and Malcom 2001), and more polar compounds with fulvic acids.

Dark-colored pigments extracted from earth materials are produced as a result of multiple reactions, the major pathway being through condensation reactions involving polyphenols and quinones. According to Stevenson (1994), polyphenols derived from lignin are synthesized by microorganisms and enzymatically converted to quinines, which subsequently undergo self-condensation or combine with amino compounds to form N-containing polymers. The number of molecules involved in this process, as well as the number of ways in which they combine, is almost unlimited, explaining the heterogeneity of humic materials.

The major atoms comprising humic materials are C (50–60%) and O (30–35%). Fulvic acid has lower carbon and higher oxygen contents. The percentage of hydrogen (H) and nitrogen (N) in fulvic acid varies between 2 and 6%, and that of sulfur (S) varies from 0 to 2%. The various fractions of humic substances obtained on the basis of solubility characteristics are part of a heterogeneous mixture of organic molecules, which originate from different earth materials and locations and might have molecular weights ranging from several hundred to several hundred thousand. Humic acids have an average molecular weight of the order 10,000–50,000, and a typical fulvic acid has a molecular weight in the range of 500–7,000.

The humic fraction in the soil represents a colloidal complex including long-chain molecules or two- or three-dimensional cross-linked molecules whose size and shape in solution are controlled by the pH and the presence of neutral salts. Under neutral or slightly alkaline conditions, these molecules are in an expanded state as a result of the repulsion of the charged acidic groups, whereas at a low pH and high salt concentration, molecular aggregation occurs due to charge reduction. These large organic molecules may exhibit hydrophobic properties, which govern their interaction with nonionic solutes.

Nonhumic components of humus include the organic components of the humus – originating from plants and microorganisms – which are insoluble in aqueous acidic or basic media. Clapp et al. (2005) show that this group may include the following organic compounds:

- *Polysaccharides*, with origins in plants and microorganisms, are important components of the soil organic matter with major environmental impact
- *Peptides and proteins*, which may comprise amino acids, amino groups, amino sugars, or nucleic acid derivatives and many other N-containing compounds
- *Tannins* are the fourth in order of abundance in terrestrial plants after cellulose, hemicelluloses, and lignins. In soils, organic matter occurs as hydrolyzable tannins. Because the ester linkages of the hydrolyzable tannins are readily cleaved by esterases, tannins are assumed to have a limited persistence in the soil environment
- *Lipids* including fats, waxes, and natural hydrocarbons are naturally occurring compounds that produce fatty acids when hydrolyzed. In the soil environment, they form strong associations with humic acids and humin components
- *Glomalin*, a glue contributing to soil aggregation, is produced by mycorrhizal fungi
- *Black carbon*, or char, is a term to describe forms of pyrogenic carbon produced by incomplete combustion of organic substances

2.1.2.2 Stabilization of Soil Organic Matter

Studies of stabilization and destabilization of soil organic matter may provide some understanding of the effects of anthropogenic chemicals on natural soil constituents. Soil organic matter can be (a) physically stabilized or protected from decomposition

through microaggregation, (b) associated with salt and clay particles, and (c) biochemically stabilized through the formation of recalcitrant compounds (Six et al. 2002). The largest proportion of carbon input into stable soil organic matter pools was found in microaggregates (Kong et al. 2005). The formation of organo-mineral microaggregates (20–250 μm) is hypothesized to result from interactions of polyvalent metals and organic ligands with mineral surfaces, the nature and binding strength being controlled by the surface area of the mineral (Guggenberger and Keiser 2003). Occlusion of organic debris by the clay minerals was suggested as an additional type of organo-mineral formation (e.g., Tisdall and Oades 1982; Jastrow 1996).

A more recent study on spatial distribution of organic carbon in free stable microaggregates (Lehman and Solomon 2007) shows no discernible gradient between the interior and exterior of aggregates. Carbon distribution maps in three soils, obtained by near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, are presented in Fig. 2.9a, b. These results suggest – at least for the soils studied – that microaggregate formation is initiated mainly by accumulation of organics on clay particle surfaces and not by occlusion of organic debris by clay minerals.

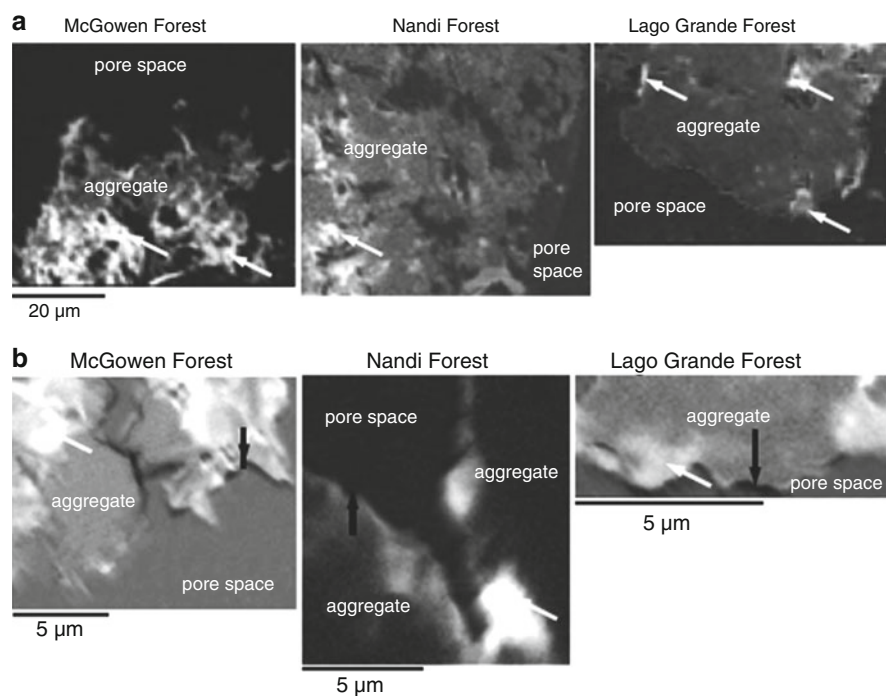


Fig. 2.9 Carbon distribution in three different soils using C (1 s) NEXAFS (0.5- μm resolution) (a) in free stable microaggregates; white arrows point at regions of high C content shown as white areas (b) near microaggregate surfaces; white arrows point at regions of high C content shown as white areas; black arrows point at dark areas of high absorbance consisting of clay coatings (after Lehman and Solomon 2007)

2.2 Soil and Subsurface Liquid Phase

Within the soil–subsurface system, two liquid phases can be defined. One region, containing *near solid phase water*, has a composition controlled mainly by the properties of the surrounding surfaces. The second region, containing *free water*, has a composition affected by lithogenic and biogenic processes, the amount and quality of incoming water, and climatic changes reflected in drying/rewetting or freezing/thawing of subsurface water. The subsurface liquid phase is generally an open system and its composition is a result of dynamic transformations of dissolved constituents over a range of reaction time scales. At any particular time, the liquid phase is an electrolyte solution, potentially containing a broad spectrum of inorganic and organic ions and non-ionized molecules.

The composition of the subsurface liquid phase varies over time mainly due to recharge with rainwater, recharge with irrigation water, or the fluctuation of the water table (groundwater) level. In addition, anthropogenic chemicals discarded on the land surface as beneficial ingredients or hazard materials may change the natural quality of both near-surface and free soil and subsurface water.

2.2.1 Structure of the Water Molecule

The H₂O molecule has a dipolar character with a high negative charge density near the oxygen atom and a high positive charge density near the protons. Horne (1969) showed that the electron cloud of the angular water molecule results from the hybridization of electrons in two bonding orbitals between the O and the two H atoms. This specific character strongly influences the interaction of water with the solid and air phases in the soil–subsurface system.

The local structure of water has been compared to ordinary hexagonal ice structures and calculated spectra. Synchrotron X-ray measurements have led to contrasting opinions regarding the H-bond coordination environment in liquid water. Wernet et al. (2004) used this technique, together with X-ray Raman scattering, to probe the molecular arrangement in the first coordination shell of liquid water. Most molecules in liquid water are in two hydrogen-bonded configurations, with one strong donor and one strong acceptor hydrogen bond, in contrast to the four hydrogen-bonded tetrahedral structures specific to ice. Heating water to 90°C causes about 10% of the molecules to change from tetrahedral environments to a two hydrogen-bonded configuration.

Water is a dynamic liquid where H-bonds are continuously broken and reformed. Wernet et al. (2004) showed that water, probed on the sub-femtosecond time scale, consists mainly of structures with two strong H-bonds, implying that most molecules are arranged in strongly H-bonded chains, or in rings embedded in a disordered cluster network connected mainly by weak H-bonds. These results are consistent with neutron and X-ray diffraction data, and confirm the theoretical

model of Weinhold (1998); this model considers an asymmetric H-bonding pattern in agreement with general quantum mechanical principles underlying H-bonding.

2.2.2 *Near Solid Phase Water*

Water molecules that are oriented preferentially with the polar axis perpendicular to the solid surface, in the vicinity of a solid surface, are considered “*near solid phase water*.” When the net surface charge of the polar phase is negative, the hydration occurs through one hydrogen of water, forming a hydrogen bond with specific atoms at the boundary of the polar surface in such a way that the second hydrogen can still form a hydrogen bond with another water molecule outside the primary hydration level. In contact with a nonpolar solid, water molecules are oriented such that the positive hydrogen points into the bulk solution (Yariv and Cross 1979).

A water molecule exhibits a series of spatial arrangements with great irregularity as it moves through a bulk liquid phase. Unlike a solid, which has a well-defined structure, the liquid phase has instantaneous structures comprised of molecules in highly irregular arrangements. Stillinger (1980) conceives of liquid water as consisting of macroscopically connected random networks of hydrogen bonds with frequent, strained and broken bonds that continually undergo topological reformation. The water properties arise from competition among relatively bulky means of connecting molecules into local patterns, characterized by strong bonds and nearly tetrahedral angles, and more compact arrangements characterized by more strain and bond linkage.

The presence of an electrolyte introduces a localized perturbation of the “tetrahedral configuration.” This perturbation derives from several sequences. Near the ion, water molecules are dominated by a dense electromagnetic field, resulting in the formation of the primary solvation shell. In the next zone, called the secondary solvation shell, water molecules interact weakly with the ion. An example of such behavior of an electrolyte solution near a clay surface was discussed by Sposito (1984). It was shown that the primary solvation shell of a monovalent cation contains between three and six water molecules that exchange relatively rapidly with the surrounding bulk liquid. A secondary solvation shell, if it exists, is very weakly developed. The primary solvation shell of a bivalent cation contains between six and eight water molecules that exchange rapidly with the surrounding bulk liquid. A secondary solvation shell containing about 15 water molecules develops as the cation concentration decreases, and it also moves with the cation as a unit.

The presently accepted description of the energy characteristics of the liquid phase is based on the concept of matrix and osmotic potentials. Matrix potential is due to the attraction of water to the solid matrix, while the osmotic potential is due to the presence of solute in the subsurface water. Water may bond to the soil and subsurface matrix by a combination of adhesive forces described by Koorevar et al. (1983): (1) adhesive forces – binding between the solid phase and water molecules, (2) cohesive forces – binding between water molecules, and (3) osmotic forces – binding due to gradients in

chemical potentials in electric double layer. Water binding properties of the solid phase matrix can be described by its thermodynamic properties (Slayter 1967). Water bound to the matrix is less able to work than free water, hence it has lost energy.

The configuration of near solid phase water can be altered in close proximity to the phyllosilicate. The siloxane surface influences the character of the water due to the nature of the charge distribution and of the complexes formed between the cation and the surface functional groups. Both the type of charge and the degree of charge localization, as well as the valence and size of the complexed cations, control the characteristics of the water molecules near the surface. Clay minerals with their own surface properties affect the near-surface water in different ways. The adsorbed water in the case of kaolinite consists only of water molecules (“pure” water), whereas water adsorbed on a smectite-type mineral is an aqueous solution due to the presence of exchangeable cations on the 2:1 layer silicate.

Sposito (1989) noted the generally accepted description that the spatial extent of adsorbed water on a phyllosilicate surface is about 1.0 nm (2–3 layers of water molecules) from the basal plane of the clay mineral. The interlayer water of clay minerals is structurally different from bulk liquid water or water in aqueous solution (Sposito and Prost 1982), and chemical reactions in this region are affected by a perturbed water structure. Another ability of the interlayer water is to diffuse widely over surface oxygens (e.g., smectites); a strong hydrogen bonding to the layer is not essential. The same patterns also follow when the cation is large and univalent. Under these conditions, a much less polar liquid can completely replace the interlayer water (Farmer 1978). Water is retained on oxides and hydroxides of aluminum and iron through the hydroxyl groups; it can also involve oxide bridges and water coordinated with structural cations. Retention of water on organic surfaces occurs also at a molecular level. Farmer (1978) stated that the principal polar sites where water adsorption occurs are likely to include carboxyl groups, e.g., phenolic and alcoholic groups, oxides, amines, aldehydes, and esters. Ionized carboxylic groups and their associated cations are likely to have the greatest affinity for aqueous solutes. It should be recalled that in addition to polar sites, organic surfaces exhibit important hydrophobic regions which are involved largely in the retention of toxic organic chemicals.

2.2.3 Soil and Subsurface Solution

The soil and subsurface solution refers here to free water in the soil and subsurface porous medium, having a composition affected by the interaction between the incoming water and the resident solid and gaseous phases. The solution composition is determined under a dynamic partitioning between rain or irrigation water transported from the land surface and natural biological and vegetative processes. The chemical composition of the soil and subsurface solution at a given time is the end product of all the reactions to which the liquid water has been exposed. Because of the diversity in physicochemical properties of the solid phase, as well as changes

in the amount of water in the subsurface as result of natural and human influences, it is difficult to provide generalizations regarding the chemical composition of the soil and subsurface solution.

The thermodynamic properties of soil and subsurface solutions are expressed in terms of a single-species solution activity coefficient for each molecular constituent. The composition should, however, be considered on the basis of molecular speciation in the aqueous solution, which in turn is related to biological uptake exchange reactions and transport through the subsurface.

Soil and subsurface solutions may be delineated in terms of the following main characteristics:

Acidity–alkalinity of the solution, measured as pH, is affected by the quality of the incoming water (generally acidic for rain, and neutral or alkaline for irrigation and effluents) and buffered by the environmental system. *Salinity*, or total salt concentration, is usually expressed in terms of total dissolved solids (TDS) or as electrical conductivity (EC) of the solution. The major fractions of anions are comprised of Cl^- , SO_4^{2-} , and NO_3^- , while the common cations are Ca^{2+} , Mg^{2+} , Na^+ , and K^+ . The composition of the subsurface solution varies between the composition of water entering the system and that of the solution in equilibrium with the solid phase.

Trace elements of natural or anthropogenic origin, such as alkali and cationic materials, transition metals, nonmetals, and heavy metals, are inorganic elements that may also be found in subsurface solutions. The presence and concentrations of typical trace elements can differ significantly from one region to another. However as an indication, Table 2.4 shows representative trace element concentrations as reported by Sauvé et al. (2000). The properties of the soil–subsurface environment play an important role in metal solubility in soil and subsurface solutions. Adsorption is the most significant mechanism for distributing trace elements between the solid and liquid phases in the subsurface.

Organic ligands originate from humic substances, root exudates, or microbial enzymatic products. In soil and subsurface solutions, they may cause complexation of inorganic trace elements, which influences the equilibrium status between solid and

Table 2.4 Range of trace elements observed for certain soil solution concentrations as estimated from the data compiled by Sauvé et al. (2000). Reprinted with permission from Sauvé S, Hendershot W, Allen HE (2000) Solid-solution partitioning of metals in contaminated soils: Dependence on pH, total metal burden, and organic matter. Environ Sci Technol 34:1125–1131. Copyright 2000 American Chemical Society

Element	Soil solution ($\mu\text{g L}^{-1}$)
As	0.5–60,000
Cd	0.01–5,000
Cr	2–500
Cu	5–10,000
Ni	0.5–5,000
Pb	0.5–500
Se	1–100,000
Zn	1–100,000

aqueous phases and affects their concentration in the subsurface solution. For example, humic acids in the soil and subsurface solution (1) are less aromatic and more highly oxidized than those that are components of solid humic substances, (2) have very few sugars and amino acids, and (3) are sterically protected from enzymatic attack in their humic association (Clapp et al. 2005). The organic trace compounds of natural or anthropogenic origin in soil and subsurface solutions are controlled by the nature and properties of subsurface colloids, the chemical and physicochemical characteristics of the organic molecules, and the nature of the environmental system.

Seasonal changes in soil and subsurface composition occur as result of climatic fluctuations and anthropogenic impacts. Soil drying and rewetting or freezing and thawing may affect soil and subsurface composition. The volume of solution in the subsurface, under partially saturated conditions, varies with the physical properties of the medium. In the soil layer, the composition of the soil solution fluctuates as a result of evapotranspiration or addition of water by rain or irrigation to the system. Changes in the solution concentration and composition, as well as the rate of change, are controlled by the buffer properties of the solid phase. Walworth (1992) note significant variability in the concentration of various parameters of soil solution composition, including EC, pH, NH_4 , Ca, K, Mg, Na Cl, F, NO_3 , and SO_4 . Seasonal changes in the soil moisture content affect the ionic concentration, speciation, and activity of the soil solution (Wolt 1994).

Dyer et al. (2008) showed that the characteristics of soils control the effect of soil moisture on soil solution concentration; soil solution was extracted from a variable-charge soil (oxisols) and from several permanent-charge soils (vertisols) at moisture content potential ranging from -5 to -230 kPa. For the vertisols, a decrease in moisture content resulted in a proportionate increase in the soil solution ionic strength at a rate similar to that expected from a solution without any solid phase interaction. In contrast, the ionic strength of the soil solutions in oxisols remained constant as the soil moisture content decreased, and was associated with a decrease in the total amount of cations in the soil solution at lower moisture content.

2.2.4 Aquifers and Groundwater

An aquifer is defined as a saturated geological unit that can transmit significant quantities of water under ordinary hydraulic gradients. Aquifers form the region below the vadose zone where the solid phase is in contact with a flowing groundwater phase and where a local chemical equilibrium between the solid and aqueous phases has a tendency to be reached. Within the context of aquifers, an aquitard is defined as a less permeable geological unit that has the potential to store water in significant quantities. In addition to geological controls of an aquifer, groundwater composition is affected by properties of recharge water, which originates from the initial incoming water constituents.

The lithology, stratigraphy, and structure of a geological system control the nature and distribution of aquifers. Lithology includes the mineral composition,

grain size, and grain aggregation of the sediments or rocks; stratigraphy defines the relation among the lenses, beds, and formations of geological sediments; and structural features describe the geometry of the geological system resulting from deformation.

According to their origins, aquifer materials may be classified as deposits of various origins, and as sedimentary or metamorphic rocks. Aquifers of fluvial origin are characterized by alluvial deposits composed of particles of gravel, silt, and clay of various sizes that are not bound or hardened by mineral cement, pressure, or temperature. The topography controls the deposition of sediments and their spatial redistribution as a function of their textural properties. Aeolian deposits consisting of sand or silt are more homogeneous in comparison to fluvial deposits. Glacial deposits including glacial till and glaciofluvial and glaciolacustrine sediment forms are also components of aquifers. The type and origin of sediments affect their permeability, which in turn controls the water transmission potential of aquifers.

Sedimentary rocks, consisting mostly of sandstones and carbonates, are bodies of major hydrological significance. Sandstone comprises about 25% of the sedimentary rocks, originating from environmental depositions (e.g., floodplain, deltaic and marine shoreline), which are characterized by cementing materials like quartz, calcite, and clays in various stages of alteration (Freeze and Cherry 1979). Porosity of sandstone in extreme cases can be as low as 1%, compared to that of sands that reach only as low as 30%. The relationship between porosity and permeability for various grain sizes shows that an increase in porosity of a few percent generally corresponds to a large increase in permeability (Chilingar 1963).

Carbonate rocks consist mostly of calcite and dolomite with minor amounts of clay. The porosity of carbonate rocks ranges from 20 to 50%, but in contrast to sandstones, it tends to decrease with depth. Often carbonate rocks are fractured, providing a permeability that is much greater than the primary one. In some cases, initial small-scale fractures in calcite and dolomite are enlarged by dissolution during groundwater flow, leading to an increase in rock permeability with time. Igneous and metamorphic rocks, which exhibit a low porosity generally smaller than 2%, are characterized by a minute permeability. As result of changes in stress conditions occurring during geological periods, wide fractures are formed which lead to a substantial increase in the permeability of igneous and crystalline metamorphic rocks. Dissolution of siliceous rocks increases the widths of fractures and consequently increases their permeability. However, the permeability of crystalline rocks usually decreases with depth.

Groundwater composition is controlled by chemical and biochemical interactions with the geological materials through which water flows, as well as by the chemistry of incoming water. Because inorganic components dissolved in groundwater are mainly in an ionic form, groundwater may be considered an electrolyte solution with a conductance ranging from tens of microsiemens (a value close to that of rain water) to hundreds of thousands of microsiemens (for brines in sedimentary basins). Dissolved inorganic constituents are grouped in three classes: major constituents, with concentrations greater than 5 mg L^{-1} ; minor constituents with a concentration

Table 2.5 Dissolved inorganic substances in groundwater (modified from Freeze and Cherry 1979). Reprinted with permission

Category	Components
Major constituents (greater than 5 mg L ⁻¹)	Bicarbonate, calcium, carbonic acid, chloride, magnesium, silicon, sodium, sulfate
Minor constituents (0.1–10.0 mg L ⁻¹)	Boron, carbonate, fluoride, iron, nitrate, potassium, strontium
Selected trace constituents (less than 0.1 mg L ⁻¹)	Aluminum, arsenic, barium, bromide, cadmium, chromium, cobalt, copper, gold, iodide, lead, lithium, manganese, molybdenum, nickel, phosphate, radium, selenium, silver, tin, titanium, uranium, vanadium, zinc, zirconium

between 0.01 and 5.0 mg L⁻¹; and trace constituents having a concentration of less than 0.01 mg L⁻¹. Table 2.5 gives examples of constituents included in these groups.

Organic contaminants may be found in groundwater in dissolved forms, associated with ligands or adsorbed on colloidal materials. Natural products such as humic and fulvic acids have a low aqueous solubility but may serve as ligands for inorganic trace components. The majority of organic pollutants – including petroleum hydrocarbons, solvents and toxic organic chemicals of industrial origin known as nonaqueous phase liquids (NAPLs) – exhibit a limited solubility in aqueous solutions, with usually very low concentrations. However, it should be recognized that even low solubility limits (and the corresponding concentration) are usually several orders of magnitude higher than the maximal allowable concentrations for potable water. As a consequence, NAPLs as a mixture or as individual components can be found in groundwater in concentrations exceeding concentrations stipulated by environmental protection agencies. In addition, inorganic polymers, various natural ligands (e.g., bio-exudates), or surfactants may also serve as mediators that shuttle organic pollutants toward groundwater via the vadose zone.

Groundwater may contain dissolved gases as a result of exposure to the surface environment prior to water infiltration, contact with the subsurface gaseous phase, and gas produced biologically below the water table. The most important dissolved gas in groundwater is CO₂.

References

- Allen BL, Fanning DS (1983) Composition and soil genesis. In: Wilding EP (ed) *Pedogenesis and soil taxonomy: I concepts and interactions*. Elsevier, New York
- Bailey SW, Brindley GW, Johns WD, Martin RT, Ross M (1971) Clay mineral society report on nomenclature committee 1969–1970. *Clay Clay Miner* 19:132–133
- Barnhisel RL, Bertsch PM (1989) Chloride and hydroxy-interlayered vermiculite and smectite. In: Dixon JB, Weeds SB (eds) *Minerals in soils*. SSSA, Madison, WI, pp 730–789
- Barrer RM, Jones DL (1970) Chemistry of soil minerals 8. Synthesis and properties of fluorhectorites. *J Chem Soc A*: 1531–1537

- Barshad I (1960) Thermodynamics of water adsorption and desorption on montmorillonite. *Clays Clay Miner* 8:84–101
- Borchard G (1989) In: Dixon JB, Weeds SB (eds) *Minerals in soils*. SSSA, Madison, WI, pp 675–728
- Brady PV, Cygan RT, Nagy KL (1996) Molecular controls of kaolinite surface charge. *J Colloid Interf Sci* 183:356–364
- Brindley GW, MacEvan DMC (1953) Structural aspects of the mineralogy of clays and related silicates. In: Green AT, Stewart GH (eds) *A Symposium*. The British Ceramic Society, Stoke on Trent, UK, pp 15–59
- Burdon J (2001) Are the traditional concepts of the structure of humic substances realistic? *Soil Sci* 199:752–769
- Chester R, Green RN (1968) The infrared determination of quartz in sediments and sedimentary rocks. *Chem Geol* 3:199–212
- Chilingar GV (1963) Relationship between porosity, permeability and grain size distribution of sands and sandstones. *Proc inter Sedimentol Congr*, Amsterdam
- Clapp CE, Hayes MHB, Simpson AJ, Kingery WL (2005) Chemistry of soil organic matter. In: Tabatabai MA, Sparks DL (eds) *Chemical processes in soils*. SSSA Book Series, Madison WI, pp 1–150
- Dennen WH (1966) Stoichiometric substitution in natural quartz. *Geochim Cosmochim Acta* 30:1235–1241
- Dixon JB (1989) Kaoline and serpentine group minerals. In: Dixon JB, Weeds SB (eds) *Minerals in soils*. SSSA, Madison, WI, pp 468–527
- Drees LR, Wilding LP, Smeck NE, Senkayi AL (1989) Silica in soils, quartz and disordered silica polymorphs. In: Dixon JB, Weeds SB (eds) *Minerals in soil environments*. 2nded, SSSA Book Series 1, Madison, WI, pp 913–974
- Dyer CL, Kopitke PM, Sheldon AR, Memzies NW (2008) Influence of soil moisture content on soil solution composition. *Soil Sci Soc Am J* 72:355–361
- Essington ME (2004) *Soil and water chemistry: an integrative approach*. CRC, Boca Raton, FL
- Farmer VC (1978) Water on partial surfaces. In: Greenland DJ, Hayes NHB (eds) *The chemistry of soil constituents*. Wiley, NY, pp 405–449
- Farmer VC, Russel HD (1967) Infrared absorption spectrometry in clay studies. *Clay Clay Miner* 15:121–142
- Freeze RA, Cherry JA (1979) *Groundwater*. Prentice Hall, Engelwood Cliffs, NJ
- Fron del C (1962) Dana's system of mineralogy. III Silica minerals. Wiley, New York
- Giese RF Jr (1982) Theoretical studies of the kaolin minerals: electrostatic calculation. *Bull Mineral* 105:417–424
- Gilkes RY (1990) Mineralogical insights into soil productivity: An anatomical perspective. In: *Proc 14th Congress of Soil Sci*, Kyoto, Japan Trans Plenary Papers. pp 63:73
- Grim RE (1962) Clay mineralogy. *Science* 135:890–898
- Gruner JW (1932) Crystal structure of kaolinite. *Z Kristallogr* 83:75–88
- Guggenberger G, Keiser K (2003) Dissolved organic matter in soil: challenging the paradigm of sorptive preservation. *Geoderma* 113:293–310
- Hatcher PG, Spiker EC (1988) Selective degradation of plant biomolecules. In: Frimel FH, Christman RF (eds) *Humic substances and their role in the environment*. Wiley, Chichester, UK, pp 59–74
- Hayes MHB, Malcom RL (2001) Consideration of composition and aspects of the structure of humic substances. In: Clapp CE, Hayes MHB, Senesi N, Bloom PR, Jardine PM (eds) *Humic substances and chemical contaminants*. SSSA, Madison, WI, pp 1–39
- Hayes MHB, Swift RR (1978) The chemistry of soil organic colloids. In: Greenland DJ, Hayes MHB (eds) *The chemistry of soil constituents*. Wiley, Chichester, UK, pp 170–320
- Herbillon AJ, Frankart R, Vielvoye L (1981) An occurrence of interstratified kaolinite-smectite minerals in a red-black soil toposequence. *Clay Miner* 16:195–201
- Horne RE (1969) *Marine chemistry*. Wiley, NY
- Hurlbut CS, Klein C (1977) *Manual of mineralogy*. Wiley, New York

- Jackson ML (1964) Chemical composition of soils. In: Bear FE (ed) *Chemistry of the soil*, 2nd edn. Van Nostrand-Reinhold, New York, pp 71–141
- Jansen S, Malaty AM, Nabara S, Johnson E, Ghabbour E, Davies G, Vanum JM (1996) Structural modeling in humic acids. *Mater Sci Eng C* 4:175–179
- Jastrow JD (1996) Soil aggregate formation and accrual of particulate and mineral associated organic matter. *Soil Biol Biochem* 28:665–676
- Katz MYA, Katz MM, Rasskazov AA (1970) Mineral studies in the gravitation gradient field 2. Changes of quartz and density due to natural and experimental “maturation”. *Sedimentology* 15:161–177
- Kaviratna PD, Pinnavaia TJ, Schroeder PA (1996) Dielectric properties of smectite clays. *J Phys Chem Solids* 57:1897–1906
- Kleber M, Sollins P, Sutton RA (2007) A conceptual model of organo mineral interactions in soils: self assembly of organic molecular fragments in multilayered structure on mineral surfaces. *Biogeochemistry* 85:9–24
- Kong AYY, Six J, Bryant DC, Denison RF, Kessel C (2005) The relationship between carbon input, aggregation and soil organic carbon stabilization in sustainable cropping systems. *Soil Sci Soc Am J* 69:1078–1085
- Kononova MM (1966) *Soil organic matter: its nature, its role in soil formation and fertility*, 2nd edn. Pergamon, Oxford, UK
- Koorevar P, Menelik G, Dirksen C (1983) *Elements of soil physics, developments in soil science* #13. Elsevier, Amsterdam
- Leenheer JA, Nanny MA, McIntyre C (2003) Terpenoids as major precursors of dissolved organic matter in landfill leachates, surface water, and groundwater. *Environ Sci Technol* 37: 2323–2331
- Lehman KJ, Solomon D (2007) Organic matter stabilization in soil microaggregates: implications from spatial heterogeneity of organic carbon contents and carbon forms. *Biogeochemistry* 85:45–57
- Lim CH, Jackson ML, Koons RD, Helmke PA (1980) Kaolons: sources of differences in cation-exchange capacities and cesium retention. *Clays Clay Miner* 28:223–229
- Low PF (1981) The swelling of clay: III dissociation of exchangeable cations. *Soil Sci Soc Am J* 45:1074–1078
- Margolis SV, Krinsley DH (1974) Processes of formation and environmental occurrence of microfeatures on detrital quartz grains. *Am J Sci* 274:449–464
- Melo VF, Singh B, Schaefer CEGR, Novais RF, Fontes MPF (2001) Chemical and mineralogical properties of kaolinite-rich Brazilian Soils. *Soil Sci Soc Am J* 65:1324–1333
- Morgan DJ, Highley DE, Bland DJ (1979) A montmorillonite, kaolinite association in the Lower Cretaceous of south-west England. In: Mortland M, Farmer VC (eds) *Proc Int Clay Conf*. Pergamon, Oxford, pp 301–310
- Piccolo A (2001) The supramolecular structure of humic substances. *Soil Sci* 166:810–832
- Sauvé S, Hendershot W, Allen HE (2000) Solid-solution partitioning of metals in contaminated soils: dependence on pH, total metal burden, and organic matter. *Environ Sci Technol* 34:1125–1131
- Schofield RK, Samson HR (1953) The deflocculation of kaolinite suspension and the accompanying change-over from positive to negative chloride adsorption. *Clay Miner Bull* 2:45–51
- Schofield RK, Samson HR (1954) Flocculation of kaolinite due to the attraction of oppositely charged crystal faces. *Discuss Faraday Soc* 18:135–145
- Schulten HR (2001) models of humic structure :association of humic acids and organic matter in soils and water. In: Clapp CE, Hayes MHB, Senesi N, Bloom PR, Jardine PM (eds) *Humic substances and chemical contaminants*. SSSA, Madison, WI, pp 73–88
- Schulten HR, Schnitzer M (1993) A state of the art: structural concept for humic substances. *Naturwissenschaften* 80:29–30
- Schulten HR, Schnitzer M (1997) Chemical model structures for soil organic matter and solid. *Soil Sci* 162:115–130

- Schulze DG (1989) An introduction to soil mineralogy. In: Dixon JB, Weed SB (eds) *Minerals in soil environments*. SSSA Book Series 1, Madison, WI
- Six J, Connant RT, Paul EA, Paustian K (2002) Stabilization mechanism of soil organic matter: implication for C-saturation of soils. *Plant Soil* 241:155–176
- Slayter RO (1967) *Plant-water relationships*. Academic, London, p 366
- Sposito G (1973) Volume changes in swelling soils. *Soil Sci* 115:315–320
- Sposito G (1984) *The surface chemistry of soils*. Oxford University Press, New York
- Sposito G (1989) *The chemistry of soils*. Oxford University Press, New York
- Sposito G, Prost R (1982) Structure of water on smectites. *Chem Rev* 82:553–573
- Stevenson FJ (1994) *Humus chemistry*, 2nd edn. Wiley, New York
- Stillinger FH (1980) Water revisited. *Science* 209:451–453
- Stober W (1967) Formation of silicic acid in aqueous suspension of different silica modification. In: Goulded RF (ed) *Equilibrium concepts in natural water systems*. *Adv Chem Ser* 67:161–172
- Sutton R, Sposito G (2005) Molecular structure in soil humic substances: the new view. *Environ Sci Technol* 39:9009–9011
- Tisdall JM, Oades JM (1982) Organic matter and water stable aggregates in soil. *J Soil Sci* 33:141–163
- Walworth JL (1992) Soil drying and rewetting or freezing and thawing affects soil solution composition. *Soil Sci Soc Am J* 56:433–437
- Weinhold F (1998) Quantum cluster equilibrium theory of liquids: illustrative application to water. *J Chem Phys* 109:373–384
- Wernet P, Nordlund D, Bergman U, Cavalleri M, Odelius M, Ogasawara H, Naslund LA, Hirsh TK, Ojamae L, Glazel P, Petterson LGM, Nilsson A (2004) The structure of the first coordination shell in liquid water. *Science* 304:995–999
- Wershaw RL (1986) A new model for humic materials and the interaction with hydrophobic chemicals in soil-water or sediment-water. *J Contam Hydrol* 1:29–45
- Wershaw RL (1993) Model for humus in soils and sediments. *Environ Sci Tech* 27:814–816
- Wershaw RL (2000) The study of humic substances – In search of a paradigm. In: Ghabbour EA, Devies G (eds) *Humic substances, versatile components of plants, soil and water*. Royal Soc Chem Cambridge, Cambridge, UK, pp 1–7
- Wershaw RL, Llaguno EC, Leenheer JA (1996) Mechanism of formation of humus coatings on mineral surfaces 3. Composition of adsorbed organic acids from compost leachate on alumina by solid-state (13) CNMR. *Coll Surf A-Physicochem Eng Aspects* 108:213–223
- Wilding LP, Smeck NE, Drees LR (1989) Silica in soils. In: Dixon JB, Weeds SB (eds) *Minerals in soils*. SSSA, Madison WI, pp 471–553
- Wolt JD (1994) *Soil solution chemistry; application to environmental science and agriculture*. Wiley, New York
- Yariv S, Cross H (1979) *Geochemistry of colloid systems*. Springer, Heidelberg
- Yaron-Marcovich D, Chen Y, Nir S, Prost R (2005) High resolution electron microscopy structural studied of organo-clay nanocomposites. *Environ Sci Technol* 39:1231–1239
- Yerima BPK, Calhoun FG, Senkayi AL, Dixon JB (1985) Occurrence of interstratified kaolinite-smectite in El Salvador vertisols. *Soil Sci Soc Am J* 49:462–466

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