

Contaminant Geochemistry

Brian Berkowitz • Ishai Dror • Bruno Yaron

Contaminant Geochemistry

Interactions and Transport
in the Subsurface Environment

 Springer

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*To our wives, Melanie, Tali and Angie;
and
To our children, Noa, Sari and Yotam;
Yaara, Maayan and Adar; Dana
... with love and respect.*

Preface

Contaminant Geochemistry: Interactions and Transport in the Subsurface Environment combines the earth science fields of subsurface hydrology and environmental geochemistry and aims to provide a comprehensive background for students and researchers interested in protection and sustainable management of the subsurface environment. This book focuses on the upper part of the earth's crust, covering the region between the land surface and the groundwater zone; anthropogenic contamination occurs primarily in this well-defined geosystem.

Water and land are limited natural resources, and it is incumbent on humankind to manage knowledge and technology in a way that avoids, or at least minimizes, deterioration of these resources. In this context, an understanding of the interactions between subsurface components (solid, liquid and gaseous phases) and chemical contaminants is required. Because the subsurface is an open system, contaminants may be transported, transformed, and redistributed in the subsurface under a variety of environmental influences. Contaminant interactions in the subsurface are subject to continuous changes, being affected by fluctuations in climatic conditions (particularly precipitation) and microbiological activity. Additionally, these interactions are controlled by the structure and properties of the earth materials, the molecular properties of the contaminants, and the hydrogeology of each specific location. As a consequence, a multidisciplinary approach is fundamental to understanding the governing processes.

Because our book was conceived for readers with different backgrounds, we devote Part I to revisiting aspects of classical geochemistry, focusing on the constituents of subsurface water and earth materials (Chapter 1) and selected processes related to potential interactions between subsurface liquid and solid phases with toxic chemicals (Chapter 2). Part II is an overview of potential subsurface contaminants of anthropogenic origin; properties of these chemicals are described together with their environmental hazards. Chapter 3 is devoted to inorganic chemicals, while the characteristics and hazards of organic toxic chemicals are presented in Chapter 4.

The retention of contaminants in the subsurface, controlled by properties of both chemicals and subsurface constituents as well as contaminant partitioning among the solid, aqueous, and gaseous phases, are the focus of Part III. Chapter 5 deals

with the sorption, retention, and release of contaminants, while Chapters 6 and 7 examine contaminant partitioning in the aqueous phase and partitioning of volatile compounds.

Contaminant redistribution in the subsurface, as a result of transport (in dissolved form, as an immiscible-with-water phase, or adsorbed on colloids) is discussed in Part IV. These phenomena do not occur in a static domain, and contaminants are redistributed, usually by flowing water, from the land surface, through the partially saturated subsurface down to the water table, and within the fully saturated aquifer zone. After a basic presentation of water movement in the subsurface environment (Chapter 9), we focus on transport of passive contaminants (Chapter 10) and reactive contaminants (Chapter 11).

Transformation and reactions of contaminants in the subsurface are addressed in Part V. From an environmental point of view, we do not restrict the contaminant transformation to molecular changes; we also consider the effects of such changes on contaminant behavior in the subsurface. Abiotic and biologically mediated reactions of contaminants in subsurface water are discussed in Chapter 13. Abiotic transformations of contaminants at the solid-liquid interface are described in Chapter 14, while biologically mediated changes in subsurface contaminants are the subject of Chapter 15.

We used our own results and selected research findings reported in the literature to provide numerous examples of contaminant retention, redistribution, and transformation in the subsurface (Chapters 8, 12, and 16). Because a limited number of published research findings had to be selected from the vast number of available publications, the choice was very difficult. Many other research results of equal value could have been used to illustrate processes governing the fate of contaminants in the subsurface environment.

Contaminant Geochemistry was written for the use of geochemists, soil scientists, water specialists, environmental chemists, and engineers involved with understanding, preventing, controlling, and remediating subsurface contamination by chemicals of anthropogenic origin. This book also provides beginning graduate students in environmental sciences an overview of contaminant behavior in the geosystem, as a basis for their future professional development. We hope that we have succeeded in presenting the reader with a comprehensive—but not exhaustive—review of current knowledge in the field of subsurface contaminant geochemistry.

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Rehovot, Israel
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Part I

Geochemistry Revisited: Selected Aspects

We conceived this book on contaminant geochemistry not only for researchers in hydrology, soil science, and geochemistry but also for advanced undergraduate and graduate students in environmental sciences and various specialists working on environmental pollution problems. As a consequence, we consider it useful and necessary to include introductory material that presents a short characterization of porous media together with selected geochemical processes. Part I characterizes subsurface components and the geochemical pathways and processes related to potential contamination. Keeping in mind that contaminant geochemistry covers a diverse range of natural and human-induced processes, we have selected only those that are most relevant to our field of interest.

The first chapter presents the porous medium solid, liquid, and gaseous phases in an environment controlled generally by fluctuations of rainy and dry periods, reflected by a variety of saturated and partially saturated conditions. A description of mineral and organic components in porous media is followed by a discussion of the electrically charged surface properties that affect the near solid phase water. The composition of the subsurface water solution as affected by the surrounding solid phase, by the natural biological environment, and possibly by human factors also is discussed. The gaseous composition of porous media, which affects the chemistry of the liquid phase, is another part of the subsurface environment. Consideration of the aquifer environment, characterized by a saturated regime, includes a brief discussion of groundwater geology and composition.

Selected geochemical processes that relate to the behavior of contaminants in the subsurface are described in the second chapter. We focus on thermodynamic considerations and equilibrium processes in the subsurface, accounting for interactions among solid, liquid, and gaseous phases. Kinetic considerations in defining the solubility of organics and minerals, as well as knowledge of chemical potentials, ion activities and reaction rate laws, also are included. The weathering of subsurface solid phases, which occurs as a result of interactions with the liquid phase, is a natural geological process that may be accelerated by anthropogenic influences. Dissolution-precipitation and redox mechanisms are other important processes affecting subsurface weathering that are included. The solid phase is a potential contaminant adsorbent, and we therefore consider adsorption as a main geochemical pathway, relevant in defining the retention, release, and persistence of pollutants in the subsurface.

Chapter 1

Characterization of the Subsurface Environment

The zone between land surface and the water table, which forms the upper boundary of the groundwater region, is known as the *vadose zone*. This zone is mostly unsaturated—or more precisely, partially saturated—but it may contain a saturated fraction in the vicinity of the water table due to fluctuations in water levels or capillary rise above the water table. The near-surface layer of this zone—the soil—is generally partially saturated, although it can exhibit periods of full saturation. Soil acts as a buffer that controls the flow of water among atmosphere, land, and sea and functions as a sink for anthropogenic contaminants.

Soil forms from the disintegration or decomposition of parent rock material, due to weathering processes and decomposition of organic materials. The mineral fraction of soil is formed by physical weathering of rock, resulting from thermal expansion of minerals along crystallographic axes or expansion of water in rock fissures. Stable weathering products from mineral decomposition may consist of ionic or neutral organic and inorganic components, solid organic residues, and newly formed silicates, oxides, hydroxides, carbonates, sulfides, and other solids (Greenland and Hayes 1978). The organic fraction of soil is a heterogeneous mixture of products resulting from microbial and chemical transformation of nonliving organic residues, plant roots, and living microorganisms.

Natural subsurface zones of the earth are characterized by heterogeneous assemblies of materials, forming a porous medium where solid, liquid, and gaseous phases are present. The open boundaries between the solid, liquid, and gaseous phases, as well as the activity of microorganisms, create conditions suitable for developing processes of chemical and biological origin, which dynamically affect the properties of subsurface environments. The porosity of the near surface (soil layer) is controlled mainly by the association of mineral and organic parts, with solid particles tending to be molded into aggregates, or peds, by biologically induced exudates, plant roots, fungi, soil microorganisms, and animals. The porosity of this region may be changed either by a shrink-swell phenomenon under wetting and drying-freezing conditions or by a redistribution of the colloidal fraction under water transport from the land surface to the water table. Over time, activity between the solid and liquid phases also can affect the stability of the porous medium itself and subsequently change the physicochemical properties of the solid phase.

1.1 Subsurface Solid Phase

The solid phase of the subsurface is a porous medium composed of a mixture of inorganic and organic natural materials in various stages of development. The surface area and the surface (chemical) properties of the solid phase are major factors that control the behavior of chemicals.

Based on their origin, minerals are grouped into two broad classes: primary minerals and secondary minerals. Primary minerals have not been altered chemically since the time of their crystallization from molten lava and their subsequent deposition. This group includes quartz (SiO_2), feldspars (e.g., $(\text{Na,K})\text{AlSi}_3\text{O}_8$; i.e., aluminosilicates containing varying amounts of calcium, potassium, or sodium), micas (e.g., muscovite: $\text{KAl}_2(\text{Al Si}_3\text{O}_{10})(\text{OH})_2$ and/or chlorites: $(\text{Mg,Fe})_3(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2-(\text{Mg,Fe})_3(\text{OH})_6$, which belong to the phyllosilicate mineral group), amphibole (e.g., hornblende: $(\text{Ca,Na})_{2,3}(\text{Mg,Fe,Al})_5\text{Si}_6(\text{Si,Al})_2\text{O}_{22}(\text{OH})_2$, i.e., magnesium-iron silicates, often with traces of calcium, aluminum, sodium, titanium, and other elements), pyroxenes (e.g., augite: $(\text{Ca,Na})(\text{Mg,Fe,Al})(\text{Si,Al})_2\text{O}_6$, i.e., silicate minerals rich in calcium, iron, and magnesium and commonly found in basalt), olivine (magnesium-iron silicate $(\text{Mg,Fe})_2\text{SiO}_4$) and rutile (TiO_2). Secondary minerals originate from the decomposition of primary minerals and subsequent reprecipitation into new, chemically distinct minerals. This group contains many minerals, including kaolinite, smectite, vermiculite, chlorite, imogolite, gibbsite, goethite, hematite, birnessite, calcite, and gypsum. Layer aluminosilicates are the dominant minerals formed in most temperate region soils. These layer silicates are composed of various arrangements of silicon/oxygen sheets in tetrahedral coordination and aluminum/oxygen sheets in octahedral coordination.

Primary minerals with low surface area (e.g., silica minerals) and low reactivity mainly affect the physical transport of water, dissolved chemicals, colloids, immiscible (in water) liquids, and vapors. Secondary minerals generally have high surface area (e.g., clay minerals) and high reactivity that affect the transport of chemicals, their retention and release onto and from the solid phase, and their surface-induced transformations. The solid phase also can indirectly induce the degradation of chemical compounds, through its effects on the water-air ratio in the system and, thus, on microbiological activity.

1.1.1 Silica Minerals

Silica minerals are a primary mineral classified as tectosilicates, characterized by repeating SiO_4 units in a framelike structure. Quartz, one of the most abundant minerals on earth, often comprises up to 95% of all sand and silt fractions. It therefore is representative of the structure and properties of silica minerals.

Wilding et al. (1977) showed that the silica tetrahedron in quartz is almost symmetrical and has a Si-O distance of 0.16 nm. They noted that the structure of quartz can be visualized as a spiral network of silica tetrahedra around the z -axis. From

Fig. 1.1 it is seen that each tetrahedron is repeated in the network by a rotation of 120° and a translation of $c/3$.

Quartz yields a characteristic X-ray pattern with well-defined peaks exhibiting a d-spacing ranging between 0.426 and 1.182 nm (Dress et al. 1989). Quartz is distinguished from other silica polymorphs by a distinctive infrared (IR) absorption band at 692 cm^{-1} , with two strong doublets at 798 cm^{-1} and 780 cm^{-1} and at 395 cm^{-1} and 370 cm^{-1} (Chester and Green 1968).

Quartz in the subsurface usually is altered by in situ chemical and physical weathering. Quartz appears as an anhydrous grain losing its prismatic form and containing trace elements other than silicon and oxygen. Aluminum is the major potential contaminant of the quartz mineral, but other trace elements such as Ti, Fe, Na, Li, K, Mg, Ca, and H (OH) also are present (Dennen 1966). Quartz grains are in general rounded or have an angular morphology due to physical attrition. A cleavage mechanism leads to the formation of flat grains when the quartz particles are $<100\mu\text{m}$ (Krinsley and Smalley 1973). Scanning electron micrographs of quartz grains are presented in Fig. 1.2.

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). Quartz in the subsurface includes chemically-precipitated forms commonly associated with carbonates or carbonate-cemented sandstones (Dapples 1979). In soil, quartz generally is found in sand and silt fractions, the amount of silica mineral being determined by the parent material and the degree of weathering.

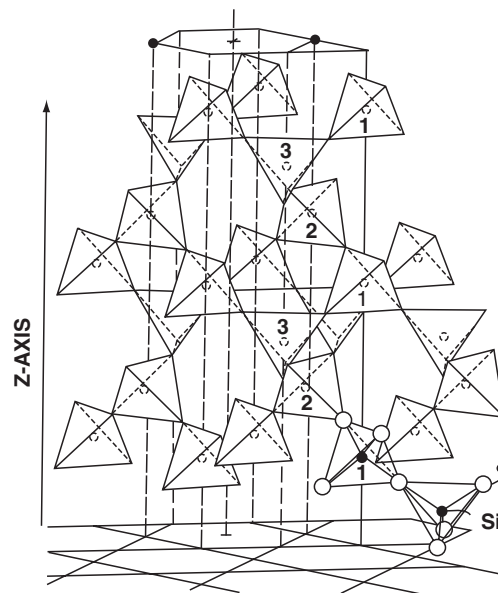


Fig. 1.1 The structure of quartz (Dress et al., 1989)

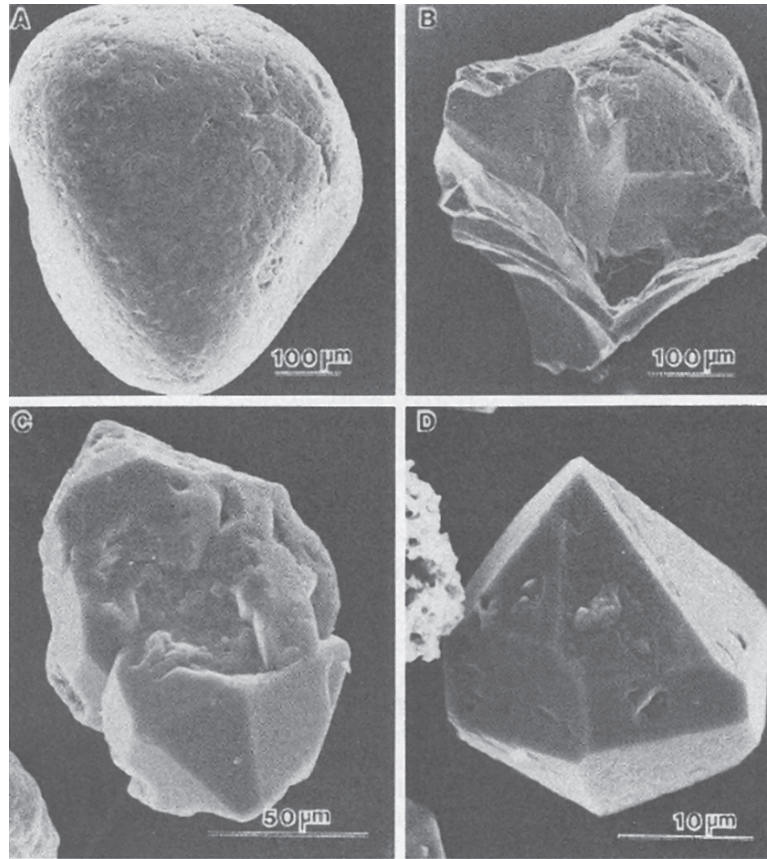


Fig. 1.2 Electron Scanning Microscope picture of various quartz grains (Dress et al., 1989)

1.1.2 Clay Minerals

Clay minerals are natural nanomaterials that constitute the smallest particles in the subsurface. They are defined as the fraction of particles smaller than a nominal diameter of $2\ \mu\text{m}$. Many clay minerals have layer structures in which the atoms within a layer are strongly bound to each other, with the binding between layers being weaker. As a consequence, each layer can behave as an independent structural unit. Several layer arrangements exist, but they do not differ greatly in their free energy. The most common inorganic structural units in clay minerals present in the subsurface are the silica tetrahedron SiO_4 and octahedral complex $\text{MX}_{6\text{m-6b}}$ composed of a metal unit ($\text{M}^{\text{m}+}$) and six anions ($\text{X}^{\text{b}-}$). Figure 1.3 shows sheet structures formed by polymerization of these two structural units.

The architecture of a silicate layer results from SiO_2 coordination in which each SiO_2 unit shares oxygen atoms with three neighboring SiO_4 groups, thus forming

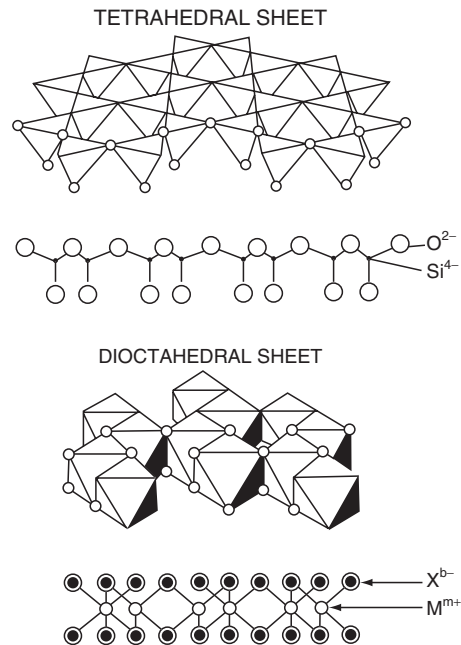


Fig. 1.3 Typical three-layered phyllosilicate structures (Sposito, 1984)

rings containing six Si and six O atoms. Each ring joins the neighboring ring through shared oxygen atoms. An additional structural element in layered silicate is an octahedral sheet that contains cations in MO_6 coordination between the two planes of oxygen atoms.

As a function of their structural properties, clays interact differently with organic and inorganic contaminants. Two major groups of clay minerals are selected for discussion here: (a) kaolinite, with a 1:1 layered structured aluminosilicate and a surface area ranging from 6 to $39\text{m}^2\text{g}^{-1}$ (Schofield and Samson 1954); and (b) smectites with a 2:1 silicate layer and a total surface area of about $800\text{m}^2\text{g}^{-1}$ (Borchardt 1989).

Kaolinite

Kaolinite crystals in the subsurface are submicron sized and exhibit a platelike morphology. They usually are found mixed with other layered structured minerals. In a comprehensive review, Dixon (1989) summarizes the structural properties of kaolinite. This mineral is composed of tetrahedral and octahedral sheets constituting a 0.7 nm layer in a triclinic unit cell. Two thirds of the octahedral positions are occupied by Al; the tetrahedral positions are occupied by Si and Al, which are

located in two rows parallel to the x -axis. Every third row of octahedral sites is vacant. The surface plane of octahedral anions and a third layer of the inner plane containing anions in each 0.7 nm layer is built up by hydroxyl (OH^-) groups. The surface hydroxyls bond through their hydrogens to the oxygen sheet of the bordering layer. The idealized structural diagram of a kaolinite layer, as suggested by Brindley and MacEwan (1953) and modified by Dixon (1989), is shown in Fig. 1.4.

Giese (1982) showed that the kaolinite structure exhibits covalent sharing of H, which leads to conceptualization of a kaolinite structure with two inner surface hydroxyls perpendicular to the layer, bonded to the O of an adjacent layer. 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, in addition to van der Waals forces, contributes to the stacking of kaolinite unit layers. The negative charge of kaolinite was proven by demonstrating that the surface retains Na^+ under acidic conditions (Schofield and Samson, 1953). The exchangeable cations are bound only to the tetrahedral basal plane of kaolinite (Weiss and Russow 1963). Kaolinite exhibits a very low cation exchange capacity, in general lower than $1 \text{ cmol}_c \text{ kg}^{-1}$ (centimoles per kg) at $\text{pH}=7$ (Lim et al. 1980). Schofield and Samson (1953) also show that the positive charge on kaolinite occurs on the edges of the plates, which become positive by acceptance of H^+ in the acid pH range.

Smectites

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 chemicals in the subsurface, by affecting their retention, transport, and persistence.

Of the naturally existing smectites, montmorillonite is a clay of major interest in the subsurface environment. Figure 1.5 shows the crystal structure of montmorillonite,

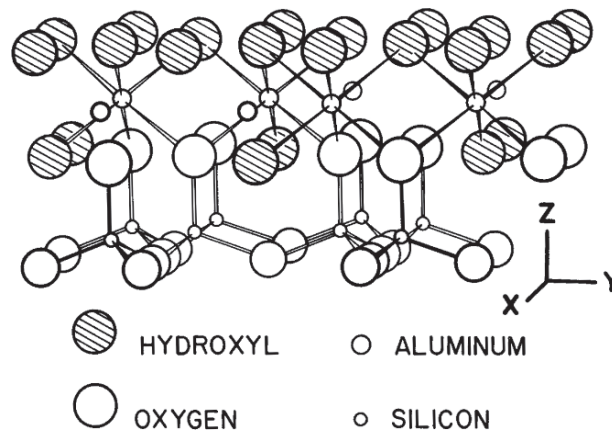


Fig. 1.4 Idealized structural diagram of kaolinite layer viewed along one axis (from Dixon, 1989)

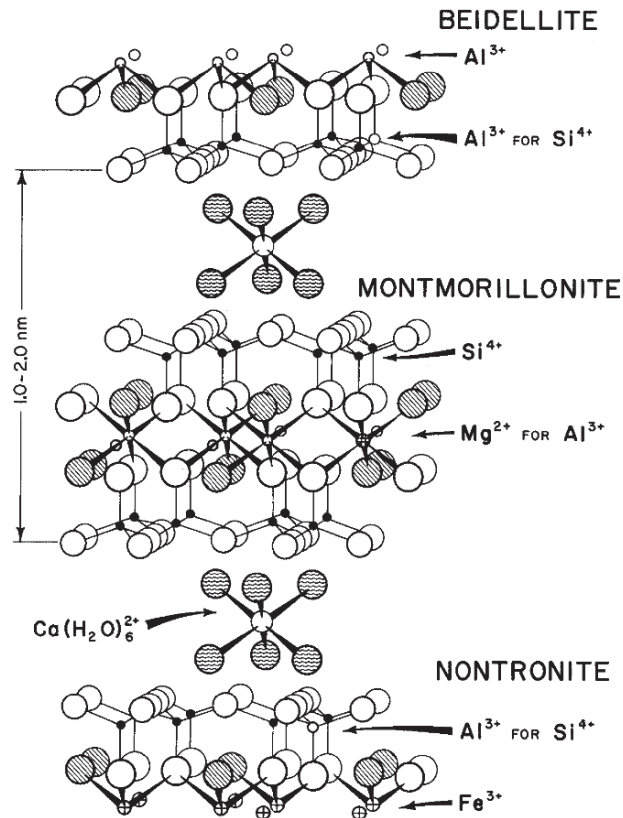


Fig. 1.5 The crystal structure of smectite, illustrating beidellite, montmorillonite and nontronite (Borchard 1989 after Brindley and MacEwan 1953)

compared to those of beidellite and nontronite, and their possible substitutions. Montmorillonite has an octahedral sheet that shares oxygen atoms between two tetrahedral sheets. Cationic substitution may occur in the octahedral or tetrahedral sheets.

Smectites are classified according to differences in properties and chemical composition. For example, a typical formula for montmorillonite is $\text{Si}_4\text{Al}_{1.5}\text{Mg}_{0.5}$ with a cation exchange capacity of $135.5 \text{ cmol}_c \text{ kg}^{-1}$, while beidellite is $\text{Si}_{3.5}\text{Al}_{0.5}\text{Al}_2$ with a cation exchange capacity of $135.2 \text{ cmol}_c \text{ kg}^{-1}$. Note that montmorillonites contain significant amounts of tetrahedral Al and octahedral Fe. Layer separation in smectite depends both on the interlayer cation and the amount of water associated with the cation. The interlayer cations are replaced when the clay is wetted with an electrolyte solution, and this affects the interlayer spacing. The hydration water of the exchangeable cation forms the first layer, and an additional water layer is held with less energy (Barshad 1960). Changes in the hydration status of smectites, as a result of an increase in ambient temperature, are determined by differential thermal analysis (DTA). Smectites lose water that originates from three different sources:

pore water lost below 110°C, adsorbed water lost below 300°C, and OH water at a temperature above 300°C.

Structural patterns of smectites may be obtained by X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), and Fourier transform infrared spectroscopy (FTIR). Borchardt (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. 1.6). At lower magnification, the presence of crystalline aggregates composed of relatively small, thin, flakelike, and pointed nanoscale silicate particles (about 10–50 nm wide and 50–400 nm long) with no obvious orientation are visible. Closer inspection of the microstructure clearly discloses a layered structure with layers occurring as well-defined stacks separated by a regular van der Waals gap along the *c*-axis. The interlayer spacing measured from HRTEM images was 0.138 nm; this result (compared to 0.149 nm obtained by XRD) may be explained by the influence of interlayer hydration on the d-spacing of montmorillonite. The interlayer compositional variation of the same clay sample determined by X-ray energy dispersive spectroscopy (EDS) is shown in Fig. 1.7. It may be observed that the nanoparticles are of similar composition, containing Na, K, Al, Mg, and O. The presence of copper, iron, and carbon signals can be ignored, as they arise from the analytical technique.

Infrared analysis of smectites provides considerable information on their structural properties. Silicate minerals have strong Si-O bands near 600 and 1000 cm⁻¹, which can be affected by substitution of silicon atoms by Al atoms. The OH bending vibrations produce the absorption characteristics of the octahedral sheet. When Al is present, the absorption is near 920 cm⁻¹, and when only Fe is present, absorption is near 820 cm⁻¹. A mixture of Al, Fe, and Mg leads to intermediate values. Hydroxyl stretching vibrations absorb in the 3000–3800 cm⁻¹ region. Farmer and Russell (1967) show that this band appears to broaden as a result of Al substitution for Si in the tetrahedral sheet and, at the same time, reflect 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 (Borchardt, 1989). Hydrogen migration from exchangeable positions into the tetrahedral sheet may occur. Heating of

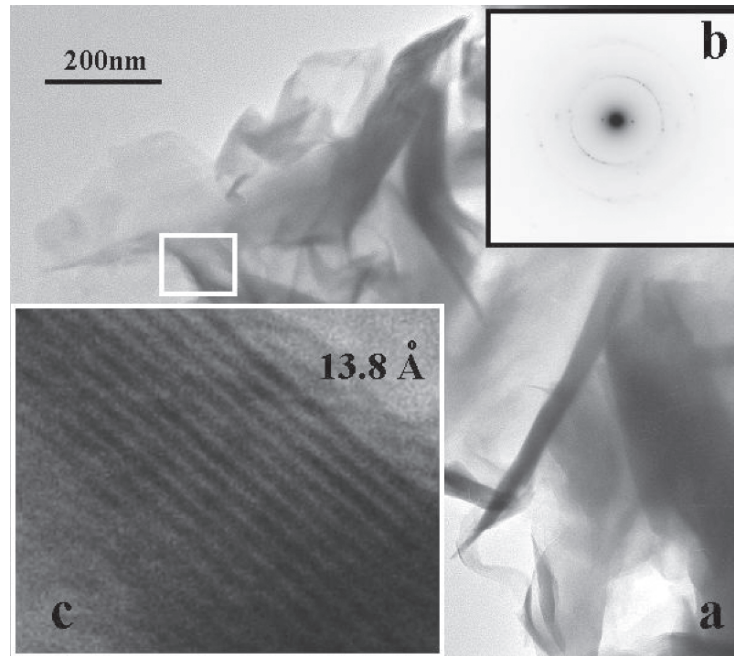


Fig. 1.6 TEM images of Na-montmorillonite particles: (a) low-magnification TEM image showing a typical crystalline aggregate; (b) the corresponding SAED pattern: note the 001 diffraction spots corresponding to the planes parallel to the e-beam; the calculated spacing is 13.83 Å; (c) high resolution TEM 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). Reprinted with permission from Yaron-Marcovich D, Chen Y, Nir S, Prost R (2005) High resolution electron microscopy (HRTEM) structural studies of organo-clay nanocomposites. *Environ Sci Technol* 39:1231–1239. Copyright 2005 American Chemical Society

Al- and H-saturated montmorillonite results in fading out of the 1700cm^{-1} band as a result of proton migration (Yariv and Heller-Kallai 1973).

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 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 is generally found in the subsurface. Interstratification of kaolinite and smectite has been reported in some cases (e.g., Schultz et al. 1971; Lee et al. 1975a, 1975b; Yerima et al. 1985). This fact is reflected in an XRD

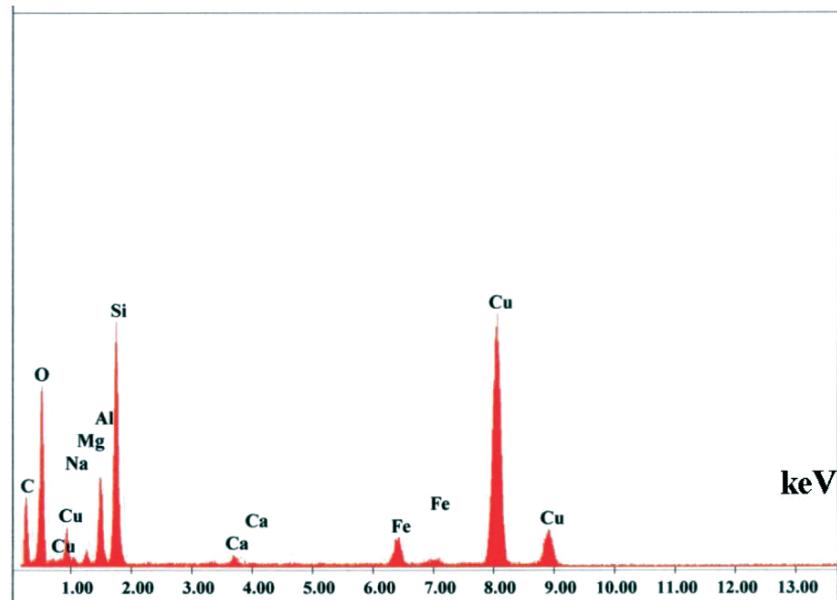


Fig. 1.7 Representative EDS spectra of Na-montmorillonite. Cu peaks arise from the TEM grid. Reprinted with permission from Yaron-Marcovich D, Chen Y, Nir S, Prost R (2005) High resolution electron microscopy (HRTEM) structural studies of organo-clay nanocomposites. *Environ Sci Technol* 39:1231–1239. Copyright 2005 American Chemical Society

spacing of about 0.8 nm (Dixon 1989) or in HRTEM micrographs (Fig. 1.8), which show the inclusion of mica (1:2 layer) and other layer silicates in kaolinite (Lee et al. 1975a, 1975b).

Environmentally induced processes occurring in the subsurface (e.g., leaching, 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 causes smectites to be transformed into pedogenetic chlorites (Barnhisel and Bertsch 1989). Laboratory studies proved a direct transformation of smectites into kaolinite during intense weathering. In 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 well-drained red-black soils (Herbillon et al. 1981), the transformation may proceed through an intermediate step consisting of interstratified kaolinite-smectite.

1.1.3 Minerals Other Than Silica and Clay

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

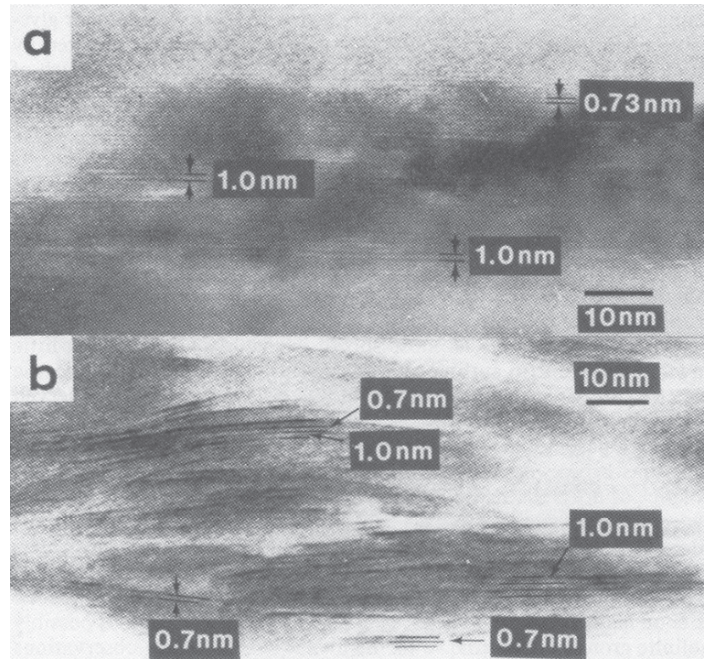


Fig. 1.8 High resolution electron micrographs of thin sections showing electron optical fringes (a) indicative of inclusion of mica in kaolinite and (b) interstratification of kaolinite and other layer silicates. Fringes shown indicate the spacings of basal plans viewed from the edge (Dixon, 1989)

materials, states that iron oxides (e.g., hematite $\alpha\text{-Fe}_2\text{O}_3$, magnetite $\beta\text{-Fe}_2\text{O}_3$, goethite $\alpha\text{-FeOOH}$ and lepidocrocite $\beta\text{-FeOOH}$) are common constituents with crystals that vary greatly in size, shape, and surface morphology. The surface of iron oxides in the subsurface environment often is hydroxylated either structurally or through hydration of the Fe atoms. Crystals of the aluminum oxides that commonly occur (e.g., gibbsite, boehmite) are small but often larger than the associated iron oxides. Other oxide minerals are less abundant than Fe and Al 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 Mn 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 Fe 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., allophone 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.

1.1.4 Organic Matter

Soil organic matter is a general term for the nonliving portion of the organic fraction in the soil layer. It is a mixture of products resulting from microbial transformation of organic residues and includes organic compounds originating from undecayed plant and animal tissues, their partial decomposition products, and the near surface biomass. Major components of the soil organic matter and their definition are presented in Table 1.1.

Soil organic matter is found wherever organic matter is decomposed, mainly in the near surface. However soil organic matter may also be transported as suspended particles into deeper layers of the vadose zone or via surface- and groundwater-forming sediments. Although these components form a minor part of the total solid phase, they are of major importance in defining the surface properties of the solid phase and have a great impact on the chemical behavior.

Table 1.1 Definition and characterization of soil organic matter (Stevenson 1994)

| 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 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) |
| Nonhumic 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 |

(continued)

Table 1.1 (continued)

| Term | Definition |
|----------------------|---|
| Humin | 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 is insoluble in dilute acid |
| Hymatomelanic acid | Alcohol-soluble portion of humic acid |
| Fulvic acid fraction | Fraction of soil organic matter that is soluble in both alkali and acid |
| Generic fulvic acid | Pigmented material in the fulvic acid fraction |

Organic matter extracted from earth materials usually is fractionated on the basis of solubility characteristics. The fractions commonly obtained include humic acid (soluble in alkaline solution, insoluble in acidic solution), fulvic acid (soluble in aqueous media at any pH), hymatomelanic acid (alcohol-soluble part of humic acid), and humin (insoluble in alkaline solutions). This operational fractionation is based in part on the classical definition by Aiken et al. (1985). It should be noticed, 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. Hayes and Malcom (2001) emphasize that biomolecules, which are not part of humic substances, also may precipitate at a pH of 1 or 2 with the humic acids. Furthermore, the more polar compounds may precipitate with fulvic acids.

Dark-colored pigments extracted from earth materials result from 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 composing 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) 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 range in molecular weight from several hundred to several hundred thousand. The average molecular weight range for humic acids is on the order 10,000–50,000, and a typical fulvic acid has a molecular weight in the range of 500–7000. The humic fraction in the near surface 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.

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 modeling humic substances was the preliminary concept of a two-dimensional representation of humic acid (Schulten and Schnitzer 1993, 1997). Recent models were developed on the basis of analytical and spectroscopic data associated with computer calculations (e.g., Jansen et al. 1996; Bailey et al. 2001). Schulten (2001) improved the initial model 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.

An example of a structural model of organic matter is presented in Fig. 1.9, reproducing Schulten’s (2001) model for a terrestrial humic acid tetramer in open form (Fig. 1.9a) and of a tetramer formed by a trimer trapping an additional monomer (Fig. 1.9b). In these models, molecular mechanics calculations were used for geometry optimization and determination of total potential energy, bond, angle, dihedral, van der Waals, stretch bend and electrostatic energy derivatives, and tentatively association energy. Atomic and molecular properties were calculated at the nanometer level. Schulten (2001) compared the covalently bound tetramer humic acid, which is geometrically optimized in a widely open molecular structure (Fig. 1.9a), to the tetramer design formed by trapping a monomer in a trimer humic acid structure (Fig. 1.9b). Both molecules have the same number of atoms, molecular weight, and elemental composition. Surface areas, volumes, and density are quite similar in the wide-open and trapped tetramer forms. The only substantial difference is that the accessible surface area is much larger in the open (tetramer) system.

These types of models, while incomplete, are steps toward the formulation of composite models, which depend on future availability of compositional data. Moreover, these structural models are an important aid in understanding the interactions between anthropogenic chemicals and terrestrial organic matter. However, due to the heterogeneity of humic substances in the environment, provision of an exact, general structure does not seem feasible.

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 motional behavior and may be spatially segregated on a scale of nanometers. Within this new structural context, these components comprise any molecules

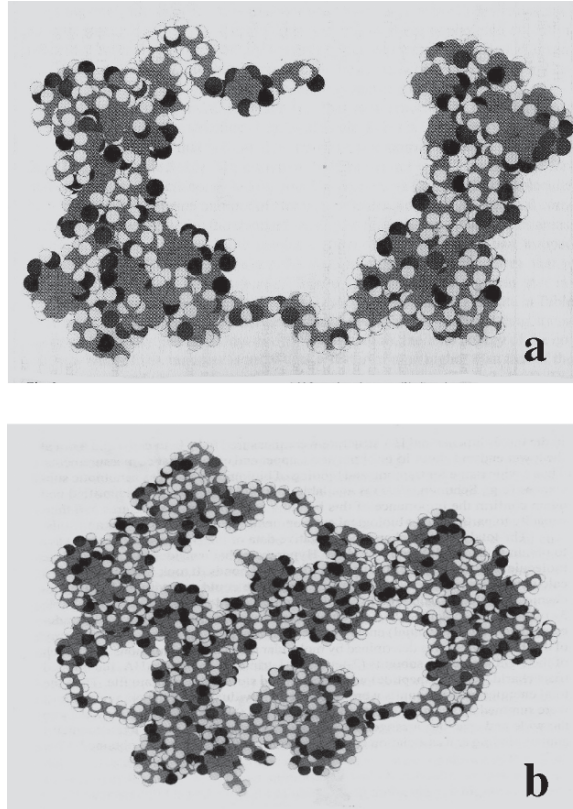


Fig. 1.9 Terrestrial humic acid model (a) tetramer open form and (b) trimer trapping an additional monomer (Schulten, 2001)

intimately associated with a humic substance.” Sutton and Sposito (2005) conclude by stating that biomolecules bound strongly within humic fractions are, by definition, humic components.

1.1.5 Electrically Charged Surfaces

The electrically charged surface of the solid phase is characterized by a net (positive or negative) charge on the solid surface 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 solutes onto a solid phase surface is subject to both chemical binding forces and an electric field at the interface, and it is controlled by an electrochemical system. Considerable differences exist between the surface properties of original minerals

constituting the bulk solid phase and surface properties of organic and inorganic colloids.

Some of the functional groups (e.g., OH) on the clay surface exhibit electrical charges. The magnitude of the electrical charge, as well as its character, are controlled by the properties of the surfaces to which the functional groups are bound and by the composition of the surrounding liquid. Sposito (1984) classified the surface charge density of soils as follows:

- *Intrinsic surface charge density*, defined by the number of Coulombs per square meter bound by surface functional groups, either because of isomorphous substitutions, or because of dissociation/protonation reactions.
- *Structural surface charge density*, defined as the number of Coulombs per square meter, as a result of isomorphous substitutions in soil minerals.
- *Proton surface charge density*, defined as the difference between the number of moles of complexed proton charges and of complexed hydroxyl charges per unit mass of colloids.

1.2 Subsurface Liquid Phase

Within the subsurface zone, two liquid phase regions can be defined. One region, containing water near the solid surfaces, is considered the most important surface reaction zone. This “near solid phase water,” which is affected by the solid phase properties, controls the diffusion of the mobile fraction of the solute adsorbed on the solid phase. The second region constitutes the “free” water zone, which governs liquid and chemical flow in the porous medium.

The composition and reactivity of the liquid phase (known as the *soil solution*) is defined by the quality of the incoming water and affected by fluxes of matter and energy originating from the vicinity of the solid phase, microbiological activity, and the gas phase. To understand the properties of the subsurface liquid phase, it is first necessary to consider the 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. Figure 1.10 depicts the electron cloud of the angular water molecule resulting from the hybridization of electrons, to yield 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 subsurface.

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 structure specific to ice. Heating water to 90°C causes about

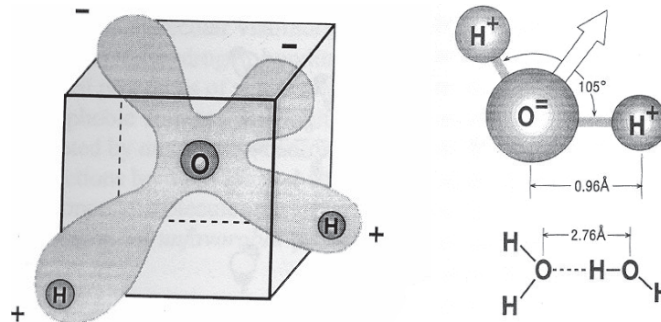


Fig. 1.10 Water as a solvent: electron cloud depiction for a water molecule and the structure of the angular water molecule and hydrogen bond (Horne, 1969)

10% of the molecules to change from tetrahedral environments to two hydrogen-bonded configuration.

Water is a dynamic liquid, where H-bonds are continuously broken and reformed. Wernet et al. (2004) show that water, probed on the subfemtosecond 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 (1996); this model considers an asymmetric H-bonding pattern in agreement with general quantum mechanical principles underlying H-bonding.

The subsurface liquid phase generally is an open system and its composition is a result of dynamic transformation of dissolved constituents in various chemical species 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 nonionized molecules. The presently accepted description of the energy characteristics of the liquid phase is based on the concept of matrix and osmotic potentials. The 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.

The composition of the subsurface liquid phase varies over time, mainly due to recharge with rainwater, irrigation water, or the fluctuation of the water table (groundwater) level. In addition, disposal and discharge of wastes and effluents and the application of agrochemicals are key sources of pollution into the subsurface, contributing significant changes to the composition of the liquid phase.

1.2.1 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 hydra-

tion 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 still can 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 (I type) comprising molecules in highly irregular arrangements. Sposito (1984) showed that, with lengthening of the time scale, two additional type structures are defined: vibrationally averaged (V type) and diffusionally averaged (D type). These structures highlight the fact that the concept of molecular structure in liquid water is a dynamic one.

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, which 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 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 their charge distribution and the complexes formed between the cation and the surface functional groups. Both the type of charge and degree of charge localization, as well 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 (two to three layers of water molecules) from the basal plane of the clay mineral.