hydroxyoxides is responsible for the irreversible hardening, upon drying, of *plinthite* (*laterite*) of tropical soils into stonelike materials. Chemically, the Fe hydroxyoxides behave similarly to gibbsite as described above. *Magnetite* (Fe_3O_4) is a magnetic Fe oxide inherited from the parent rock. It usually occurs as sand-sized grains of high specific gravity. Magnetite oxidizes to *maghemite* (Fe_2O_3), which is also magnetic.

The Ti oxides commonly found in soils and clay sediments are *rutile* and *anatase*, both TiO_2 and inherited from the parent rock. Because Ti oxides resist weathering so strongly, they are often used as indicators of the original amount of parent material from which a soil has formed.

Manganese oxides are a poorly understood and amorphous mixture of Mn(III) and Mn(IV). Pure *pyrolusite* (MnO_2) is rare, a more accurate formula would be approximately $MnO_{1.8}$. Many transition metal ions have the same size as the Mn ions so isomorphous substitution is common. Hence, Mn hydroxyoxides can retain these other cations. For a time some workers believed that Mn hydroxyoxides were an important part of the soil's retention of trace metals. Per unit weight, this may be so. Soils, however, contain about 0.1% Mn hydroxyoxides, little compared to the amounts of Al and Fe hydroxyoxides. The *manganese nodules* that receive attention as a Mn ore are Mn-rich iron oxide nodules that are found on some ocean floors. Manganese nodules have not been found in soils.

5.6 CHARGE DEVELOPMENT IN SOILS

The two properties that most account for the reactivity of soils are surface area and surface charge. Surface area is a direct result of particle size and shape. Most of the total surface area of a mineral soil is due to clay-sized particles and soil organic matter. Charge development in soils is due to these same two fractions, although the sand- and silt-size fractions may contribute some cation exchange capacity if coarse-grained vermiculite is present. Charge development in soils occurs as a result of isomorphic substitution and of ionization of functional groups on the surface of solids, again primarily in the colloidal fraction, resulting in the permanent and the pH-dependent charges of soils.

5.6.1 Permanent Charge

Isomorphic substitution is the substitution of one ion for another of similar size within a crystal lattice. The substituting ion may have a greater, equal, or lower charge than the ion for which it substitutes. In layer silicate structures, cations can substitute for coordinating cations in either the tetrahedral or the octahedral sheets. If a cation of lower valence substitutes for one of higher valence, such as Mg^{2+} for Al^{3+} or Al^{3+} for Si^{4+}, the negative charge of O^{2-} and OH^- ions in the structure is left unsatisfied, yielding a net negative charge. Isomorphic substitution can also result in positive charge, by Al^{3+} substituting for Mg^{2+} in the brucite layer of chlorite, but negative charge tends to predominate in soil minerals.

Isomorphic substitution occurs during crystallization of layer silicate minerals in magmas and in soils. If the primary cation is unavailable as the unit cell forms, another cation can sometimes squeeze in. The resulting permanent charge is essentially independent of the soil solution composition surrounding the particle. Isomorphic substitution is the principal source of negative charge for the 2:1 and 2:1:1 layer silicates, but is of minor importance for the 1:1 minerals.

5.6.2 pH-Dependent Charge

The total charge of soil particles varies with the pH at which the charge is measured. Figure 5.10 illustrates *pH-dependent charge*, where some portion of the soil changes from positive charge at low pH to negative charge at higher pH. The soil's total charge is the algebraic sum of its negative and positive charges. The relative contribution of permanent and pH-dependent charge depends on the composition of soil colloids. Relatively young and weakly weathered soils characteristic of Europe and North America have a net negative charge, because of the higher pH and layer silicate and organic matter content of these soils. Highly weathered and volcanic soils, on the other hand, are dominated by allophane and hydrous oxides, may have a low pH, and may have a net neutral to positive charge (Table 5.5). Subsoils are usually lower in organic matter so the relative amount of negative charge relative to positive charge decreases. The *zero point of charge* (ZPC) is an index of the positive and negative charge on soil colloids. The ZPC is the pH at which negative and positive charges of a colloid are equal. The ZPC for the soil of Fig. 5.10 would be pH < 3.

Crystal bonding ends at the particle–soil solution interface. At the particle edge, the charge of the structural cations and O^{2-} ions is not compensated by surrounding structural ions. Electrical neutrality is necessary and is maintained by interacting with H^+, OH^-, and water, and by adsorbing cations or anions from the soil solution. The primary source of pH-dependent charge is considered to be the loss of adsorbed H^+ and OH^- on inorganic solids and H^+ from organic acids, phenols, and other functional groups in soil organic matter.
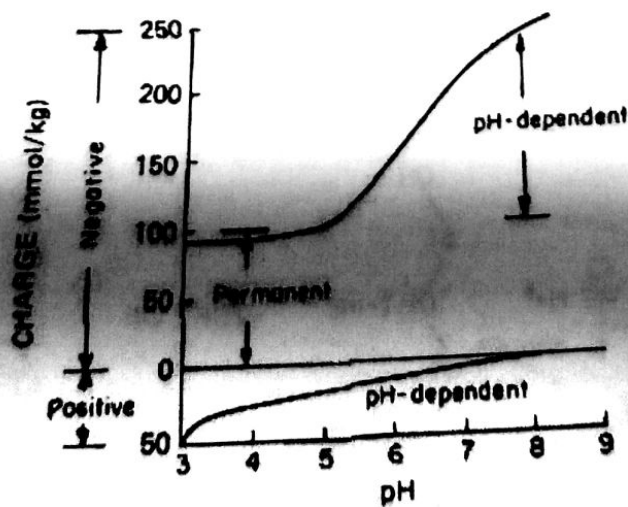

FIGURE 5.10. Representative change of positive and negative charges on soils with pH. (From W. D. Guenzi, ed. 1974. *Pesticides in Soil and Water.* American Society of Agronomy, Madison, WI.)

The soil solids that contain functional groups capable of developing positive pH-dependent charge include layer silicates, allophane, hydroxyoxides, and organic matter. In organic matter, the functional groups that create pH-dependent positive charge include hydroxyl (—OH), carboxyl (—COOH), phenolic (—C_6H_4OH), and amine (—NH_2). Equation 5.1 shows how an inorganic hydroxyoxide, an Al hydroxyoxide in this case, can change from negative to positive charge by adsorbing H^+:

$$(Al)-OH^{1/2+} + H^+ = (Al)-OH_2^{1/2+} \tag{5.1}$$
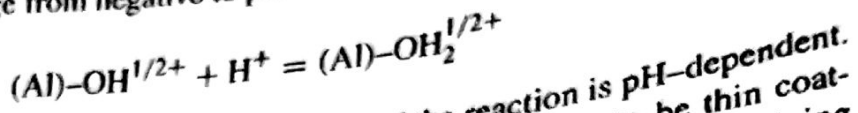
The other hydroxyoxides are similar. The extent of the reaction is pH-dependent. This effect is accentuated by the tendency of these hydroxyoxides to be thin coatings on soil particles, which increases their activity per unit mass. Soils containing large amounts of Al and Fe oxides have a strongly pH-dependent charge and highly variable CEC.

Figure 5.11 shows how pH-dependent charge develops at the crystal edges of kaolinite. Depending on the pH of the soil solution, the charge can be either positive or negative. Jackson suggested that the dissociation of H^+ occurred at $pK_a = 5.0$ for the Al–OH_2 group, 7.0 for (Al,Si)–OH, and 9.5 for Si–OH. The high pK_a for Si–OH groups indicates that the deprotonation (H^+ loss) occurs only at high pH. The pH-dependent charge of layer silicates is more likely due to reversible protonation and deprotonation of Al–OH rather than Si–OH groups.

The contribution of edge OH groups to pH-dependent charge is related to the acidity of the edge groups and to the area of edge surface. For 2:1 minerals such as montmorillonite, the functional groups are apparently weakly acidic and dissociate only at high pH. In addition, the amount of edge surface for 2:1 minerals is small relative to the basal (planar) surface. Kaolinite, on the other hand, tends to stack without swelling in the c dimension, increasing the edge area compared to the basal plane area. For both reasons, pH-dependent charge is more important for kaolinite than for smectites or vermiculites. As a rule of thumb, only 5 to 10% of the negative charge on 2:1 layer silicates is pH dependent, whereas 50% or more of the charge developed on 1:1 minerals can be pH dependent.

Figure 5.12 shows the pH-dependent charge in kaolinite. The Cl^- anion is retained by kaolinite in acid solutions, indicating the presence of positive sites, prob-
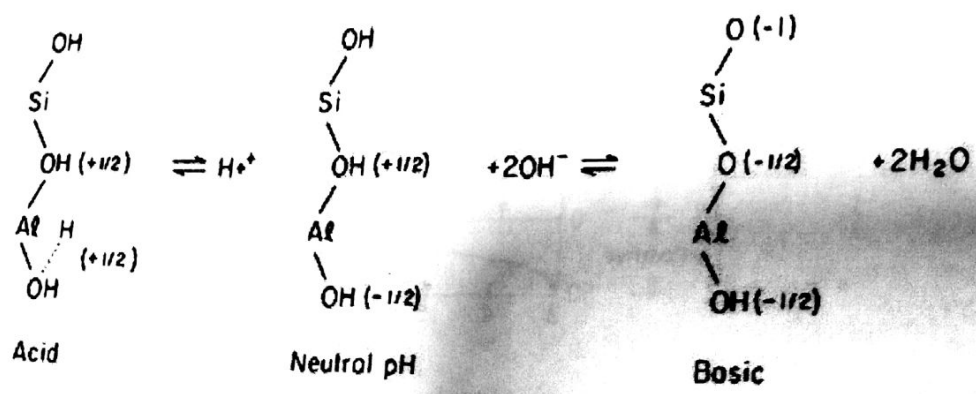

FIGURE 5.11. Representation of pH-dependent charge at kaolinite edges. (By permission from R. K. Schofield and H. R. Samson. 1953. *Clay Miner. Bull.* 2:45.)
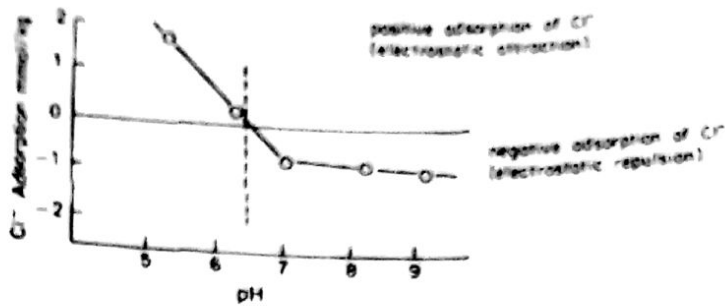
FIGURE 5.12. Chloride adsorption by kaolinite at various pH values. (By permission from R. K. Schofield and H. R. Samson. 1953. *Clay Miner Bull.* 2:45.)

ably $Al-OH_2^+$. In basic solutions, the functional group changes to the negatively charged $Al-OH^-$, which repels anions. The pH at which positive and negative charges are balanced, ZPC, for this kaolinite is indicated by the vertical dashed line at about pH 6.5.

In highly weathered soils, Fe and Al oxides are abundant and can develop considerable pH dependent charge, as can Ti, Cr, and Mn oxides. For example, Fe^{3+} in hematite is in sixfold coordination with O^{2-}. Each valence bond of an oxygen supplies -0.5 charge to the Fe ion. The remaining -1.5 charge of each O is satisfied by Fe cations in adjacent octahedra. At the soil solution interface (the edge of the crystal), however, the ion charges in the crystal have to be satisfied by H^+ and OH^- ions in the soil solution. In effect, the ions in the crystal complete their coordination spheres by interacting with the soil solution. The result is that the crystal is coated with a layer of H or OH ions (Fig. 5.13). This charge development is similar to that developed by silicates. The sesquioxides have no permanent charge so their charge depends solely on, and varies greatly with, the pH of the soil solution. Allophane, an amorphous hydrous oxide with high surface area, also develops pH-dependent charge. Because its surface area is greater than crystalline materials, its charge is even more pH dependent.

Soil organic matter also has a strongly pH-dependent charge. The charge develops mostly by H^+ dissociation from carboxylic and phenolic groups. Table 5.5 summarizes the colloidal properties of the major components of the soil's clay fraction.
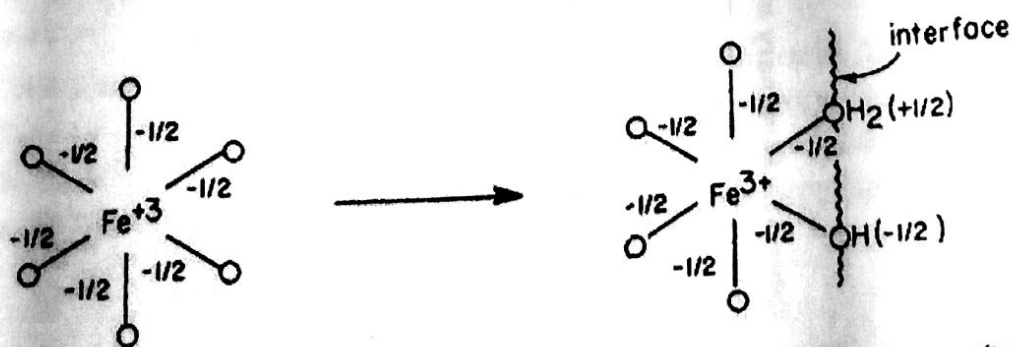

FIGURE 5.13. Fe^{3+} and ligands in the interior and at the surface of hematite.

Table 5.5. Summary of selected properties of inorganic solid-phase components

Component	Mineral Type	Chemical Formula	Layer Charge	Cation Exchange Capacity (mmol(+) kg^{-1})	Surface Area× 10^3 m^2 kg^{-1}	c Spacing (nm)	Expansible	pH Dependency of Charge	Colloidal Activity
Kaolinite	1:1	$Al_2Si_2O_5(OH)_4$	~0	10–100	10–20	0.72	No	Extensive	Low
Montmorillonite	2:1	$Na_x[(Al_{2-x}M_x)Si_4O_{10}(OH)_2]$	0.25–0.6	800–1200	600:800	Variable	Yes	Minor	Extremely high
Vermiculite	2:1	$Na[Mg_3(Si_{4-x}Al_x)O_{10}(OH)_2]$	0.6–0.9	1200–1500	600–800	1.0–1.5	No	Minor	High
Mica	2:1	$K_x[Al_2(Si_{4-x}Al_x)O_{10}(OH)_2]$	1.0	200–400	70–120	1.0	No	Medium	Medium
Chlorite	2:1:1	$[AlMg_2(OH)_6]_x[Mg_3(Si_{4-x}Al_x)O_{10}(OH)_2]$	~1	200–400	70–150	1.4	No	Extensive	Medium
Allophane	—	$Si_xAl_y(OH)_{4x+3y}$	—	100–1500	70–300	—	—	Extensive	Medium

APPENDIX 5.1   SURFACE AREA MEASUREMENTS

An impressive property of colloids, including layer silicate minerals, is their large area of reactive surface. Various physical and chemical properties, including water retention and cation exchange capacity, are highly correlated with the surface area of soils. Several techniques estimate the amounts of reactive surface area of soils and are briefly described below.

Colloid chemists commonly measure surface area by the adsorption of N_2 gas. The adsorption is conducted in vacuum and at temperatures near the boiling point of liquid nitrogen ($-196°$ C). The approach is based on the Brunauer–Emmett–Teller (BET) adsorption equation, and has been adapted to a commercially available instrument. Unfortunately, the technique does not give reliable values for expansible soil colloids such as vermiculite or montmorillonite. Nonpolar N_2 molecules penetrate little of the interlayer regions between adjacent mineral platelets of expansible layer silicates where 80 to 90% of the total surface area is located. Several workers have used a similar approach with polar H_2O vapor and have reported complete saturation of both internal (interlayer) and external surfaces. The approach, however, has not been popular as an experimental technique.

Soil chemists more commonly measure the retention of polar liquids such as ethylene glycol or glycerol by soils. The basic procedure involves applying excess and then removing all but a monolayer from the mineral surfaces. The excess is removed under vacuum in the presence of a desiccant, to eliminate competition with H_2O for retention sites. Some workers advocate a glycol–$CaCl_2$ mixture to maintain a relatively constant vapor pressure of glycol in the evacuated system, and hence to provide a more reproducible endpoint.

Glycol and glycerol retention are influenced by the species of exchangeable cation, since both the colloid surfaces and the surface cations are at least partially solvated during surface area determinations. Glycerol is preferred over glycol by some workers, because it distinguishes between vermiculitic (partially expanding) and montmorillonitic (freely expanding) surfaces under carefully controlled conditions. A single molecular layer of glycerol remains in vermiculitic interlayers, but two such layers remain in montmorillonitic interlayers.

Ethylene glycol monoethyl ether (EGME) is another polar molecule used increasingly for surface area measurements. Its results are essentially identical to the glycol method but are achieved more rapidly. It was graciously contributed to soil chemistry by a careless shipping clerk and an unknowing technician. The latter obtained unusual, but promising, results before he realized that the wrong reagent had been provided by a chemical supply firm.

Surface areas have also been measured by anion repulsion or by adsorption of certain organic solutes from aqueous solution. A particularly promising solute is cetyl pyridinium bromide, which orients differently on external and internal (interlayer) surfaces and can thus aid in distinguishing between the two types of surface.

APPENDIX 5.2   MINERAL IDENTIFICATION IN SOILS

X-ray diffraction has probably contributed more to the mineralogical characterization of soil layer silicates than any other single technique. Other techniques being increasingly used are infrared, electron spin resonance, fluorescence spectroscopy, differential thermal analysis, and x-ray absorption spectroscopy. The simplest and most common is x-ray diffraction, which exposes material to a filtered and monochromatic beam of x-rays from an appropriate metal target. When the beam enters the sample, part of the beam is reflected by successive repeating planes of atoms. The reflected beams are reinforced (intensified) at each locus of points where the reflected beam has moved an integral number of wavelengths before being reflected by the next plane of atoms (Figure 5.14). In quantitative terms, reinforcement occurs wherever

$$n\lambda = 2d \sin\theta \qquad (5.2)$$

where n is an integer, λ is the wavelength of the x-radiation, d is the "repeat" distance between successive layers of the crystal, and θ is the angle at which the radiation strikes the crystal. The loci of points can be detected either with a cylindrical photographic film placed around the irradiated sample or with a rotating detector. Radiation that has not traveled an integral number of wavelengths within the crystal emerges and strikes the film or detector out of phase with other radiation, so only minimal film darkening or detector counts are recorded. Radiation that has traveled an integral number of wavelengths within the crystal reinforces previously reflected radiation and produces strong film darkening or a peak of counts in the detector. Differences in crystal repeat distances as small as 0.01 to 0.001 nm can be detected by x-ray diffraction. The technique is particularly valuable for identifying soil colloid types, their degree of interleafing or interstratification, and variations in their interplatelet spacings resulting from pretreatments or additives.

All the techniques to identify soil minerals have difficulty coping with the heterogeneity of soils and with coatings of organic and weathered materials on soil particles, and have trouble detecting small amounts of a component in a very large
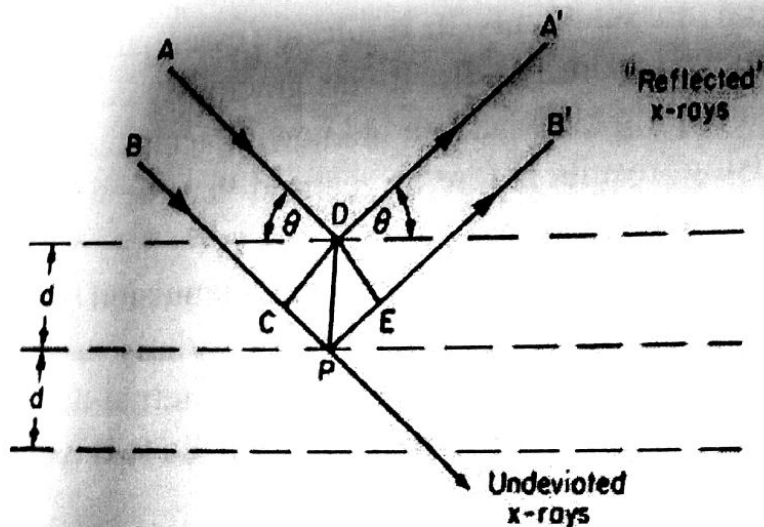

FIGURE 5.14. X-ray reflection from repeating mineral planes. For reinforcement, $CP + PE = 2d \sin\theta = n\lambda$, so that emerging radiation is in phase.

mixture of silicates and Fe and Al hydroxyoxides. If one constituent of the component has a much higher atomic weight, it can usually be more easily detected. Even Pb with atomic weight ~207 however had to be ~8% by mass before distinct Pb minerals could be identified in soil. A soil with that Pb content is a rich Pb ore. At normal Pb concentrations in soils, Pb and other trace elements more likely exist as isomorphous substitutes in the soil's major minerals. By going to great extremes to clean the mineral surface of coatings to reveal the minerals beneath, we may destroy the soil.

BIBLIOGRAPHY

Feldman, S. B., and L. W. Zelazny. 1998. In *Chemistry of Soil Minerals* (P. M. Huang, ed.). Soil Science Society of America Spec. Publ. 55, Madison, WI.

Putnis, A. 1992. *Introduction to Mineral Sciences*. Cambridge University Press, New York.

QUESTIONS AND PROBLEMS

1. Distinguish between primary and secondary minerals, and give examples of each. Which minerals are more important in determining soil properties?

2. Which minerals are commonly found in the sand and silt fractions of soil? Which are commonly found in the clay-sized fraction? Why?

3. Distinguish between ionic, covalent, hydrogen, and van der Waals bonding. Which type of bonding predominates in silicate structures?

4. What ion dominates silicate structures?

5. Calculate the theoretical range in hole size between oxygen ions in tetrahedral and octahedral coordination. Which cations "fit" in each configuration?

6. What is the dominant characteristic that determines whether ions may isomorphically substitute for one another?

7. What is a unit cell? How many unit cells are there in 1 mole of a particular mineral?

8. Why is the phrase "clay mineral" misleading, and what term is best used to describe phyllosilicate minerals of $>2\ \mu$m effective diameter?

9. Distinguish between 1:1, 2:1, and 2:1:1 layer silicates by drawing diagram of their structures.

10. Explain how layer charge influences the following layer silicate properties:
    (a) Interlayer bonds
    (b) Crystal size
    (c) Swelling