tions tend to dictate the kinds of clay minerals found in soils.

8.6 SOURCES OF CHARGES ON SOIL COLLOIDS

There are two major sources of charges on soil colloids: (1) hydroxyls and other functional groups on the surfaces of the colloidal particles that by releasing or accepting H^+ ions can provide either negative or positive charges, and (2) the charge imbalance brought about by the isomorphous substitution in some clay crystal structures of one cation by another of similar size but differing in charge.

All colloids, organic or inorganic, exhibit the surface charges associated with OH groups, charges that are largely **pH dependent**. Most of the charges associated with humus, 1:1-type clays, the oxides of iron and aluminum, and allophane are of this type. In the case of the 2:1-type clays, however, these surface charges are complemented by a much larger number of charges emanating from the isomorphous substitution of one cation for another in the octahedral and/or tetrahedral sheets. Since these charges are not dependent on the pH, they are termed **permanent** or **constant charges**. We will consider these constant charges first.

Constant Charges on Silicate Clays

We noted in Section 8.2 that isomorphous substitution could be the source of both negative and positive charges. Examples of specific substitutions will now be considered.

NEGATIVE CHARGES. A net negative charge is found in minerals where there has been an isomorphous substitution of a lower-charged ion (e.g., Mg^{2+}) for a higher-charged ion (e.g., Al^{3+}). Such substitution commonly occurs in some aluminum-dominated dioctahedral sheets. As shown in Figure 8.5 (right), this leaves an unsatisfied negative charge. The substitution of Mg^{2+} for Al^{3+} is an important source of the negative charge on the smectite, vermiculite, and chlorite clay micelles.

A second example is the substitution of an Al^{3+} for an Si^{4+} in the tetrahedral sheet, which also leaves one unsatisfied negative charge from the tetrahedral oxygen atoms. Such a substitution is common in several of the important soil silicate clay minerals, such as the fine-grained micas, vermiculites, and even some smectites.

POSITIVE CHARGES. Isomorphous substitution can also be a source of positive charges if the substituting cation has a higher charge than the ion for which it substitutes. In a trioctahedral sheet, there are three magnesium ions surrounded by oxygen and hydroxy groups, and the sheet has no charge (review Figure 8.5). However, if an Al^{3+} ion substitutes for one of the Mg^{2+} ions, a positive charge results.

Such positive charges are characteristic of the trioctahedral hydroxide sheet in the interlayer of clay minerals such as chlorites, a charge that is overbalanced by negative charges in the tetrahedral sheet. Indeed, in several 2:1-type silicate clays, including chlorites and smectites, substitutions in both the tetrahedral and octahedral sheets can occur. The net charge in these clays is the balance between the negative and positive charges. In all 2:1-type silicate clays, however, the **net charge is negative** since those substitutions leading to negative charges far outweigh those producing positive charges.

Chemical Composition and Charge

Because of the numerous ionic substitutions just discussed, simple chemical formulas cannot be used to identify specifically the clay in a given soil. However, type formulas for the major silicate clays shown in Table 8.4 can be used to illustrate the sources of both positive and negative charges in the tetrahedral and octahedral sheets. These formulas are commonly referred to as ***structural formulae*** or ***unit layer formulae***.

on the micelles of each of the minerals

pH-Dependent Charges

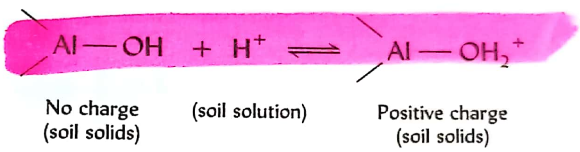
The second source of charges noted on some layer silicate clays (e.g., kaolinite) and on humus, allophane, and Fe, Al oxides, is dependent on the soil pH and consequently is termed **variable** or **pH-dependent**. Both negative and positive charges come from this source.

NEGATIVE CHARGES. The pH-dependent charges are associated primarily with hydroxyl (OH) groups on the surfaces of the inorganic and organic colloids. Broken edges of mineral colloids also generate pH-dependent charges (see Figure 8.15). The OH groups or oxygen atoms are attached to iron and/or aluminum in the inorganic colloids (e.g., $>$Al—OH) and to the carbon in humus (e.g., —C—OH). Under moderately acid conditions, there is little or no charge on these particles, but as the pH increases, the hydrogen dissociates from the colloid OH group, and negative charges result.

$$>\mathrm{Al{-}OH} + \mathrm{OH}^- \rightleftharpoons\ >\mathrm{Al{-}O}^- + \mathrm{H_2O} \qquad (8.2)$$

$$\underset{\substack{\text{No charge}\\\text{(soil solids)}}}{\mathrm{{-}C{-}OH}} + \underset{\text{(soil solution)}}{\mathrm{OH}^-} \rightleftharpoons \underset{\substack{\text{Negative charge}\\\text{(soil solids)}}}{\mathrm{{-}C{-}O}^-} + \underset{\text{(soil solution)}}{\mathrm{H_2O}} \qquad (8.3)$$

POSITIVE CHARGES. Under moderate to extreme acid soil conditions, some silicate clays and Fe, Al oxides may exhibit net positive charges. Once again, exposed OH groups are involved. In this case, however, as the soils become more acid, **protonation**—the attachment of H$^+$ ions to the surface OH groups—takes place. The reaction for silicate clays may be shown simply as:



$$\text{Al—OH} + H^+ \rightleftharpoons \text{Al—}OH_2^+ \tag{8.5}$$

Thus, in some cases, the same site on the inorganic soil colloid may be responsible for negative charge (high pH), no charge (intermediate pH), or positive charge (very low pH) (Figure 8.15).

Since a mixture of humus and several inorganic colloids is usually found in soil, it is not surprising that positive and negative charges may be exhibited at the same time. In most soils of temperate regions, the negative charges far exceed the positive ones (Table 8.5). However, in some acid soils high in Fe, Al oxides or allophane, the overall net charge may be positive. The effect of soil pH on positive and negative charges on such soils is illustrated in Figure 8.16.

The charge characteristics of selected soil colloids are shown in Table 8.5. Note the