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## *Chapter 4*

### *Structure and Properties: General Treatment*

Clay minerals are hydrous aluminum silicates and are classified as phyllosilicates, or layer silicates. There is considerable variation in chemical and physical properties within this family of minerals, but most have in common platy morphology and perfect (001) cleavage, a consequence of their layered atomic structures. Historically, useful information was collected by using staining techniques and the petrographic microscope, but much of what we understand, to this point, about the structural and chemical details of these minerals has been *extrapolated from X-ray diffraction studies of their macroscopic counterparts* because clay minerals are usually  $< 2 \mu\text{m}$  and, therefore, too small for study by optical or single crystal X-ray methods. Surprising amounts of information and insight into the nature of clay minerals has been gained in the last two decades by an interplay between modeling of the XRD tracings of clay minerals and improved XRD equipment and accessories. Modeling requires that we know just what happens as X-rays interact with the atoms of the clay minerals that serve as scattering centers.

In this chapter, first let's consider the structural features common to the five most common clay minerals. Then we'll deal with some of the properties that are consequences of structural features such as layer charge, cation-exchange capacity, and interaction with water and other compounds, and finish with general nomenclature and classification for clay minerals.

#### GENERAL STRUCTURAL FEATURES

All layer silicates can be imagined as constructed from two modular units: A sheet of corner-linked tetrahedra and a sheet of edge-linked octahedra. (At the end of Chapter 5 you will find patterns for making paper octahedra and tetrahedra and directions to guide you in the construction of models of clay minerals.) Our discussion of structural features is quite dependent on figures. You probably will need to flip back and forth to relate one figure to another to follow our descriptions.

### ***Tetrahedral Sheets***

In the tetrahedral sheet (Fig. 4.1A), the dominant cation T is  $\text{Si}^{4+}$ , but  $\text{Al}^{3+}$  substitutes for it frequently and  $\text{Fe}^{3+}$  occasionally. The T/O (oxygen) ratio for layer silicates is  $\text{T}_2\text{O}_5$ . Picture this sheet as extending infinitely in two dimensions, each tetrahedron resting on a triangular face in this infinitely extending plane and sharing the oxygens at all three corners with three other tetrahedra. This plane is referred to by some as the siloxane surface. The fourth, or apical, oxygen points upward in the direction normal to the base. Assembled without distortions, this sheet is hexagonal (Fig. 4.1A) with the Si–O bond distance about 1.62 Å and the O–O distance about 2.64 Å. Al may replace up to half of the Si, and when it does the dimensions of the sheet increase because  $\text{Al}^{3+}$  is larger than  $\text{Si}^{4+}$ . The Al–O distance is about 1.77 Å.

### ***Octahedral Sheets***

The octahedral sheet can be thought of as two planes of closest-packed oxygen ions with cations occupying the resulting octahedral sites between the two planes. When we connect the centers of the six oxygen ions packed around an octahedral cation site, we have an octahedron. Sharing of neighboring oxygen ions forms a sheet of edge-linked octahedra, again extending infinitely in two dimensions (Fig. 4.1B). The cations are usually  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ , or  $\text{Fe}^{3+}$ , but all the other transition elements (except Sc, which hasn't been reported as far as we know) and Li have been identified in cation sites of the octahedral sheet. The structure of the macroscopic minerals gibbsite [ $\text{Al}(\text{OH})_3$ ] and brucite [ $\text{Mg}(\text{OH})_2$ ] would fit the description for an octahedral sheet except that they are composed of two planes of closest-

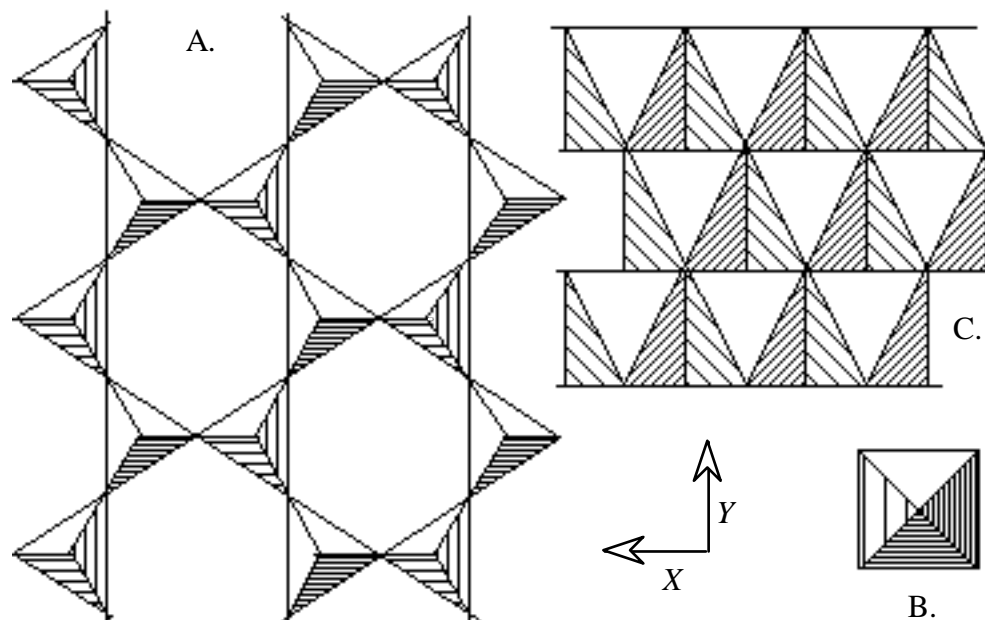


Fig. 4.1. A. Part of a sheet of corner linked tetrahedra. B. An isolated octahedron viewed down the 4-fold axis perpendicular to the page. C. Part of a sheet of edge-linked octahedra. These octahedra are sitting on a triangular face with a 3-fold axis perpendicular to the page.

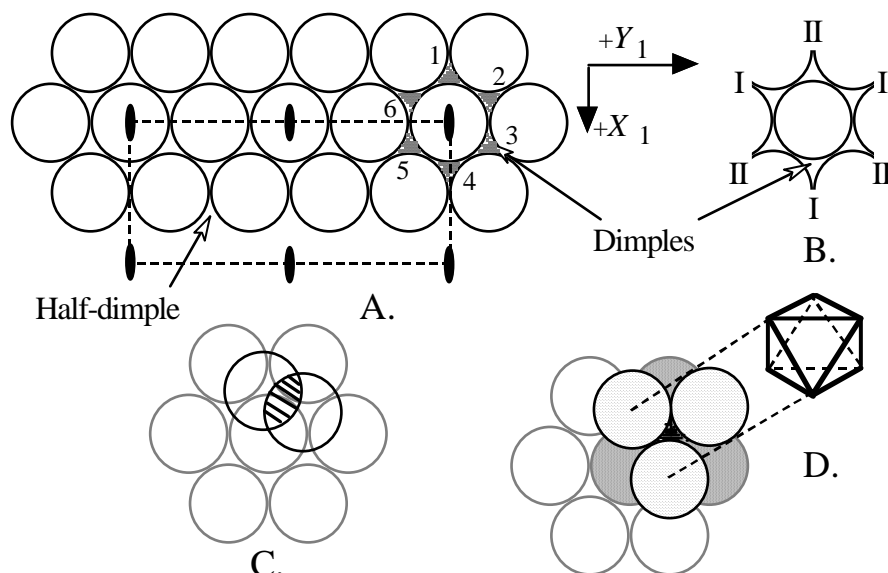


Fig. 4.2. Coordination in the octahedral sheet. A. Looking down on a plane of oxygen or hydroxyl ions (a plane in the  $X$ - $Y$  dimension) with a cell imposed on it. Note that each anion has six nearest neighbors in this closest-packing arrangement and each is surrounded by six dimples (shaded) numbered 1 to 6. B. The six dimples make two sets, I and II, one set of which will be octahedral sites, the other tetrahedral (the latter are almost never occupied). C. The lighter circles represent oxygen or hydroxyl ions in the lower plane of anions. We assume the upper anions come to rest in the dimples of the lower sheet, consistent with closest packing. See that only three of the six dimples can be occupied. If adjacent dimples were occupied, both anions would have to occupy the volume represented by the shading in C. D. Note that a cation in dimple 2 would be surrounded by six oxygens or hydroxyls, three above it (lightly shaded) and three below (more heavily shaded). This site is, therefore, an octahedral site because if the centers of the six anions are joined by straight lines, an octahedron resting on a triangular base (the dashed lines) is created around the cation in the octahedral site.

packed hydroxyls, instead of oxygen ions. But the diameter of the hydroxyl ion is so similar to that of oxygen that there is essentially no difference. Therefore the structures of these two minerals serve as analogs in two ways: (1) For the octahedral sheets in clay minerals, the cation-to-anion ratio determines whether the mineral is referred to as dioctahedral or trioctahedral (see the next section); and (2) for the dimensions of the hydroxyl sheet within the 2:1 or 1:1 layer (see the section *Joining the Sheets*). The terms *gibbsite-like* and *brucite-like* should be used when discussing these analogs in the structure of clay minerals.

### ***Dioctahedral and Trioctahedral***

In layer silicates, octahedral sheets are either gibbsite-like  $\text{Al}(\text{OH})_3$  or brucite-like  $\text{Mg}(\text{OH})_2$  without too much overlap; there is limited solid solution between the two end members. In the brucite-like sheet the cation-to-anion ratio is 1:2. If you picture a plane of closest-packed hydroxyls and remember that they are essentially the same size as oxygen ions, you will recall that each hydroxyl ion has six nearest neighbors making six “dimples” (Fig. 4.2A) around it. When the next plane of closest-packed hydroxyls is fitted into the dimples of this first plane of hydroxyls, the six dimples will become three octahedrally coordinated and three tetrahedrally coordinated cation sites. For an octahedral sheet, we will use only the octahedral sites. By counting the octahedral sites in Fig. 4.2, you see that there is the same number of them as there are hydroxyl ions in a single plane or half as many sites as there are in two planes of hydroxyl ions. So, for the brucite-like sheet with divalent cations, all three octahedral sites around each hydroxyl must be filled to have electrical neutrality. These three sites are equivalent, in the

crystallographic sense. Layer silicates with this arrangement are called *trioctahedral*. (You should find some sort of balls, Styrofoam, wooden, Ping Pong, or whatever, and try packing them so you can see the tetrahedral and octahedral sites.)

In layer silicates with gibbsite-like octahedral sheets, the cation-to-anion ratio in the sheet is 1:3. Here, to have electrical neutrality, only two  $\text{Al}^{3+}$  cations are needed instead of three  $\text{Mg}^{2+}$  ions. Therefore only two of every three octahedral sites around each hydroxyl need to be filled. Layer silicates with this arrangement are called *dioctahedral*. Trioctahedral and dioctahedral 2:1 clay minerals can usually be referred to the space groups  $C2/m$  or  $C2$ . The mirror, or pseudomirror in the case of  $C2$ , bisects one of the octahedral sites. This site is called M(1). The two sites on either side of the mirror are the M(2) sites. The M(2) sites are equivalent to one another, but not to the M(1) site. Until recently, it was assumed that the vacant site in the dioctahedral sheet of mica-like minerals was always the M(1) site. However, Tsipursky and Drits (1984) concluded that many smectites have an occupied M(1) site, and one occupied and one vacant M(2) site. Dioctahedral sheets with vacant sites located on a mirror are called *trans-vacant*, i.e., the mirror “*transverses*” the vacant site (how’s that for a mnemonic device?); those with an occupied site on the mirror are called *cis-vacant* (Fig. 4.3). We will come back to this point in Chapter 10 when we discuss *trans-vacant* and *cis-vacant* dioctahedral sheets in illite polytypes.

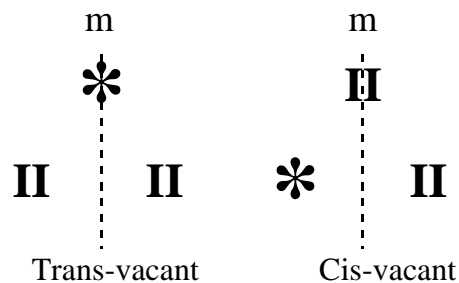


Fig. 4.3. Trans- and cis-vacant configurations for dioctahedral layer silicates. \* = vacant site, m = pseudomirror.

### Joining the Sheets

Now we must imagine these modular units, the tetrahedral and octahedral sheets, linked if we are to visualize the structure of clay minerals. (At the end of the chapter there is an exercise that gives some directions for making models of the layer silicates.) The oxygen-to-oxygen or hydroxyl-to-hydroxyl

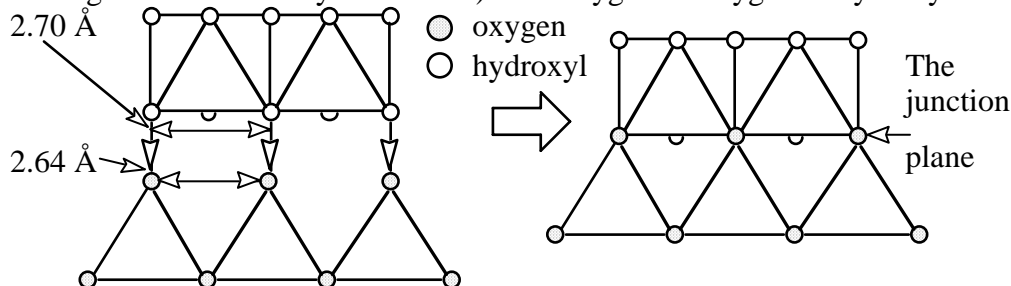


Fig. 4.4. Joining an octahedral sheet and a tetrahedral sheet into a 1:1 layer silicate at the junction plane. Dimensions from different sources differ, but these illustrate the general case. This makes a tetrahedral-octahedral-tetrahedral sandwich.

ionic dimensions of the octahedral the tetrahedral sheets are approximately the same (Fig. 4.4), so the apical oxygens of the tetrahedra can be seen as replacing two out of three of the hydroxyl ions in the lower plane of the octahedral sheet. This assemblage of one tetrahedral sheet and one octahedral sheet is called a *1:1 layer silicate structure*. Notice that one-third of the hydroxyl ions were not replaced but fit into, in the ideal hexagonal pattern of the tetrahedral sheets, the hole in the hexagonal ring made by the apical oxygens of the tetrahedral sheet (combined view of Figs. 4.1 and 4.4). A *2:1 layer silicate*, two tetrahedral sheets to one octahedral sheet, is formed by inverting a tetrahedral sheet, bringing it down on top of the 1:1 layer in Fig. 4.4, and again replacing two-thirds of the hydroxyls with apical oxygen ions. This assemblage makes a tetrahedral-octahedral-tetrahedral sandwich.

Not all, or even most, fits are as neat as that portrayed in Fig. 4.4. The lateral dimensions of the tetrahedral sheet are usually larger than those of the octahedral sheet because the larger  $\text{Al}^{3+}$ , or sometimes  $\text{Fe}^{3+}$ , has been substituted for the smaller  $\text{Si}^{4+}$ . Therefore, distortions or adjustments in one or both sheets are necessary if they are to combine at a common plane, called the *junction plane* by Bailey (1984). By referring the three sheets to  $X$  and  $Y$  coordinates in a plane parallel to their sheet dimensions, we can assign approximate values to unit cell dimensions in this plane (Fig. 4.2A, in which  $a$  is the unit distance along  $X$  and  $b$  along  $Y$ ). The size of the  $b$  dimension discriminates trioctahedral from dioctahedral layers, the latter being the smaller. The way in which we approximate the  $b$  dimensions for such sheets is to use the values of those we find in the free state, and they are, for gibbsite, 8.64 Å (8.67 Å for bayerite, a polymorph of gibbsite), and for brucite, 9.43 Å. For an ideal tetrahedral sheet with no  $\text{Al}^{3+}$  substituted for  $\text{Si}^{4+}$ ,  $b = 9.15$  Å. We can see that such a tetrahedral sheet has dimensions intermediate to dioctahedral and trioctahedral sheets: the dioctahedral sheet is about 6% smaller and the trioctahedral sheet is about 3% larger. As  $\text{Al}^{3+}$  is substituted into the tetrahedral sheet, its  $b$  dimension increases in response to the larger  $\text{Al}^{3+}$  ion. With half of the  $\text{Si}^{4+}$  replaced by  $\text{Al}^{3+}$ , the  $b$  dimension becomes about 9.55 Å, or about 2% larger than that of the trioctahedral sheet. Adjustments can be made in either the tetrahedral sheet or the octahedral sheet to accommodate a fit between them.

It might help to see this structure in three dimensions. Figure 4.5 shows the imaginary process of fitting two tetrahedral sheets to a dioctahedral sheet. We use the term *imaginary* so that you won't get the idea that this is how the crystals grow in nature! The triangular planes (shaded) on the top of the tetrahedral sheet are indicated as are the triangular planes (shaded) on the top of the gibbsite-like octahedral sheet. As this arrangement is put together, visualize that the apical oxygens indicated by arrows replace the hydroxyls of the octahedral sheet that are at the other ends of the arrows. But two hydroxyls stay put, so to speak, and they are indicated by the black balls at the center of the upper and lower oxygen-hydroxyl planes of the octahedral sheet. These occupy positions just below the centers of the ideally hexagonal holes in the outer oxygen planes of the tetrahedral sheets. You can see that these two black balls are displaced from each other with respect to an axis normal to the sheets. The direction of this displacement in the  $X$ - $Y$  plane is along the  $-X$  crystallographic axis, and the two tetrahedral sheets are similarly displaced. This displacement converts what could have been trigonal symmetry to monoclinic symmetry. Ideally, the amount of this displacement for the 2:1 clay minerals (and micas) is  $1/3$  of the  $a$  dimension.

The lateral dimensions of the tetrahedral sheet can be reduced in three ways: (1) by rotating adjacent tetrahedra in opposite directions on axes through their apices and perpendicular to the (001) plane (Fig. 4.6), (2) by thickening the sheet, and (3) by tilting the tetrahedra. Tetrahedra are never, to our knowledge, rotated as far as they are shown in Fig. 4.6, but they do frequently rotate enough to form fat triangles. Changing the sheet thickness can be thought of as changing the ideal angle for a tetrahedron. (The ideal angle, measured from the center of the apical oxygen ion to the center of the tetrahedral cation to the center of one of the basal oxygen ions, equals  $109^\circ 28'$ .) The sheet thickens when the angle increases, thereby reducing the lateral, or  $a$ - $b$ , dimensions of the sheet.

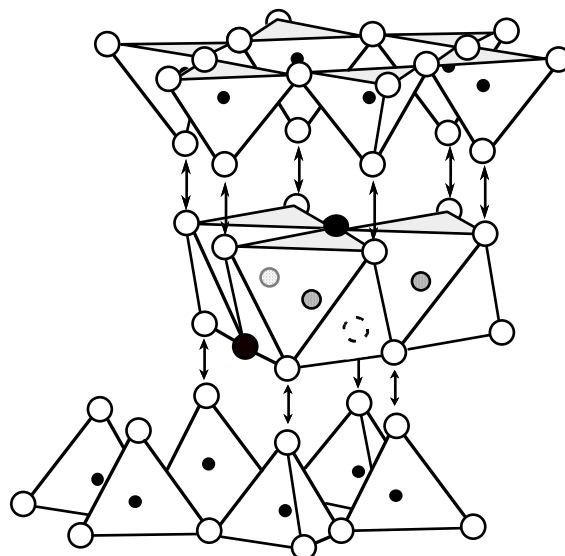


Fig. 4.5. Three-dimensional polyhedra showing how a 2:1 clay mineral can be imagined assembling. Large black balls are hydroxyls; small black balls are tetrahedrally coordinated cations; shaded balls are octahedrally coordinated cations; and unshaded balls are oxygens.

Tilting of pairs of tetrahedra toward one another along the hinge line  $r$  in Fig. 4.6A and away from another along  $s$  results in corrugations of the basal plane of the tetrahedral sheet. Dioctahedral micas frequently show this corrugation (Bailey, 1984).

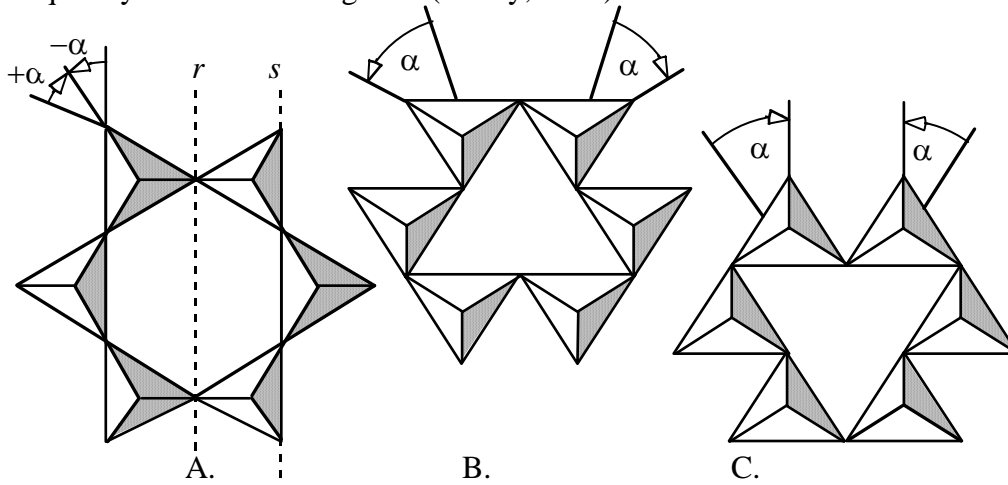


Fig. 4.6. All viewed in the X-Y plane. A. An ideal hexagonal ring. B. The result of rotating them away from one another. C. The result of rotating pairs of tetrahedra toward one another. (After Zoltai and Stout, 1984, p. 329.)

Tilting of successive rows of tetrahedra in the same direction results in the sheet forming a tube. We will see this type of distortion in the 1:1 layer silicates, which often have fiber-like or tube morphologies.

Adjustments in the octahedral sheets range from rather simple in the trioctahedral to more complex in the dioctahedral types. In trioctahedral sheets, distortion from the ideal is visualized by pulling each anion in three directions along three shared edges toward the cation plane with the resultant force inward (Fig. 4.7). The result is a thinner sheet with larger lateral dimensions.

In dioctahedral sheets, every third cation site is vacant so there are distortions in addition to those necessary for articulation with a tetrahedral sheet. Some of the distortions of dioctahedral sheets are shown in Fig. 4.8. Notice that the six anions around the vacant site all move away from one another and towards occupied cation sites. As a result of this movement, the edge length of the octahedra around the vacant sites increases from an ideal dimension of about 2.7 Å to about 3.2 to 3.4 Å. The anions in upper and lower planes moving toward one another shorten shared edges with the same effect as in the trioctahedral sheet: the sheet thickness decreases. Movement of anions around vacant sites has two results: reduction of sheet thickness, and combined but opposite movements for the upper and lower triangular faces of an octahedron. The upper face rotates counterclockwise and is pulled

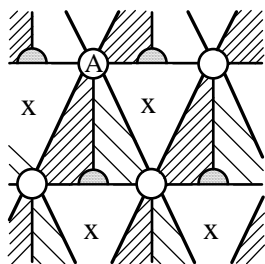


Fig. 4.7. Thinning of trioctahedral sheet. Open circles = upper plane of anions; X = central plane of cations; shaded half circles = lower plane of anions. Anion A is pulled along shared edges toward three closest anions in lower plane. This causes thinning of sheet.

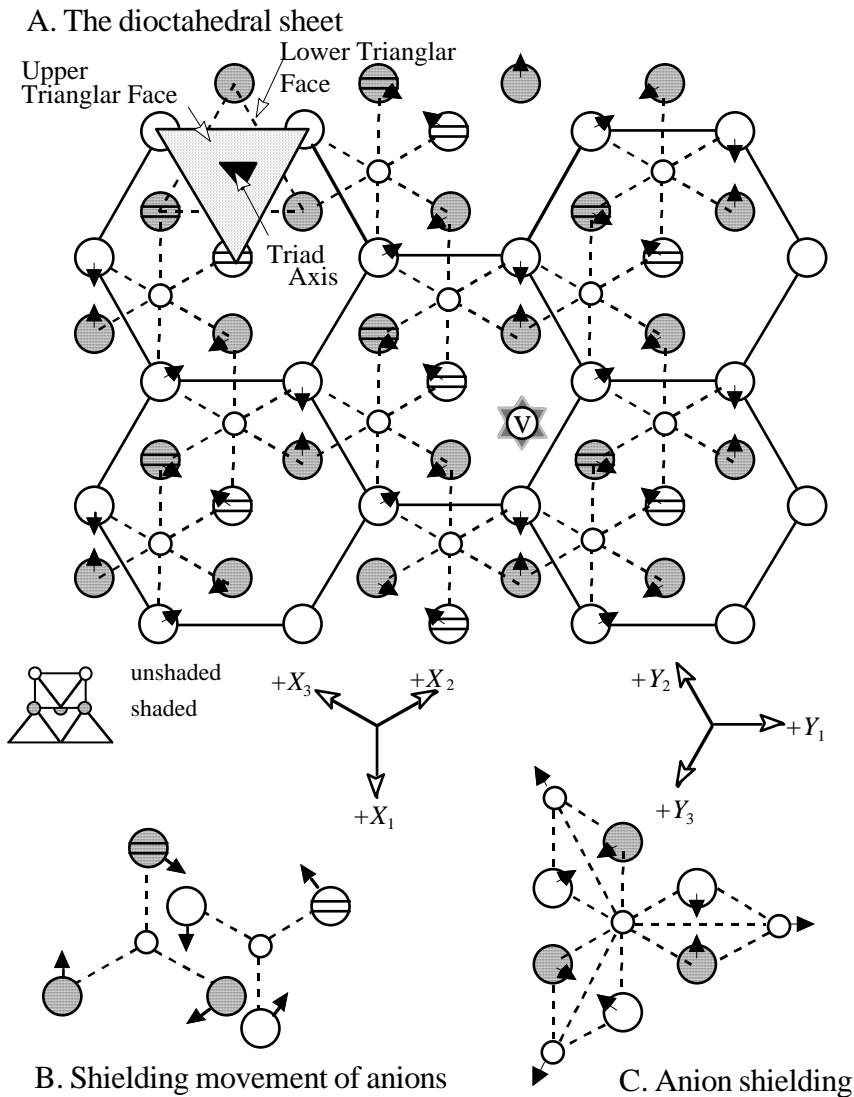


Fig. 4.8. Dioctahedral sheet configuration. The larger spheres are oxygens or hydroxyls; the ones with the horizontal bars are the hydroxyls. The unshaded ones are in the upper plane and the shaded ones are in the lower plane. The smaller spheres are aluminums. How has the upper plane shifted with respect to the lower plane along  $-X_3$ ? The oxygens of the upper plane are arranged in a hexagonal net as shown by the solid lines drawn from oxygen to oxygen. There is a hydroxyl in the center of each hexagonal cell. This pattern is repeated in the lower plane except the oxygens are not joined by lines. The oxygens of both the upper and lower planes may also be thought of as apical oxygens attached to tetrahedral sheets. A. General view. Only one vacant octahedral site is marked with a v. How many others can you pick out? B. Shielding movement of anions results in rotation in opposite directions around the triad axis of upper and lower faces of the octahedra (upper and lower anions offset for clarity). C. Anions tend to shield and therefore shorten shared octahedral edges: O–O and O–OH  $\sim 2.3$ – $2.5$  Å, whereas unshared edges  $\sim 2.7$ – $2.9$  Å (modified from Bailey, 1967, with permission).

downward, while the lower face rotates clockwise and is pulled upward. Because a pair of upper and lower anions move closer together and are between two octahedrally coordinated cations, this movement is sometimes referred to as shielding one cation from another (see Fig. 4.8B and C). The combination of these distortions changes the sheet thickness from that for an ideal sheet, about  $2.6$  Å, to  $2.04$  to  $2.14$  Å.

We have emphasized that clay minerals are small,  $< 2 \mu\text{m}$  or  $< 4 \mu\text{m}$ . Perhaps the misfit of the tetrahedral and octahedral sheets at the junction plane (Fig. 4.4) contributes to the smallness of their grain size.

### Stacking the Layers

Disorder is caused by unsystematic rotations and/or translations of one layer with respect to the one under it in a stacking sequence along  $Z$ , but polytypes are generated if these displacements are systematic, that is, if they are distributed according to some pattern, and if their magnitudes are *special* (Brindley, 1980) with respect to the symmetry of the silicate layers.

Turbostratic disorder is the most extreme kind of stacking disorder. It is found in halloysite and in most smectites. For the smectites, the low layer charge permits only a low concentration of hydrated cations in the interlayer space, and the weak mutual attraction between them and the adjacent 2:1 layers leads to relatively large distances across the interlayer. Thus there is no “keying” effect between layers, and their relative positions and orientations are haphazard. A given layer can be displaced by any amount in the  $X$ - $Y$  plane, and it can be rotated by any amount. These have been termed *arbitrary*

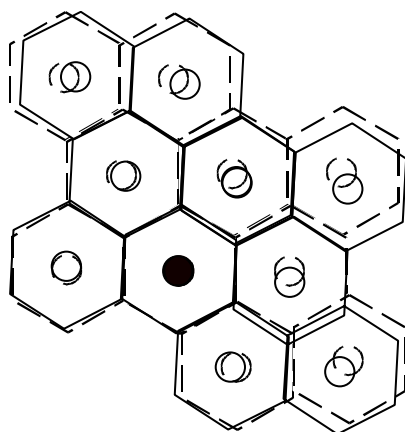


Fig. 4.9. Misalignment of 2:1 interlayer K coordination centers caused by a layer rotation of  $3^\circ$ .

displacements/rotations by Brindley. There is no layer regularity along  $Z$ , and the mineral is an assemblage of two-dimensional crystallites, although the basal diffraction pattern is sharp because the layers are perfectly parallel to one another. An example of such an arbitrary rotation is given in Fig. 4.9, which shows a lower hexagonal net (dashed lines) and an upper net that has been rotated  $3^\circ$  to the right. K atoms are drawn in the centers of the hexagonal holes. The center of rotation lies through the K atom shaded black, and you can see that the farther you go from that center, the poorer the alignment of the K sites will be with respect to the nets. Now a typical illite crystallite surface has dimensions of perhaps 40 by 40 hexagonal cells, so no matter where you pick the center of rotation, the distal hexagons are going to be poorly aligned indeed. The alignment required for three-dimensional diffraction is so demanding, that a  $3^\circ$ , or even  $1^\circ$ , rotation is enough for the X-ray machine to see the result as fully

turbostratic. The nature and origin of the so-called two-dimensional diffraction patterns produced by such structures is discussed in Chapter 10.

We now turn our attention to the mica polytypes. The attractive force between 2:1 layers and the interlayer cation exceeds the dehydration energy of the interlayer cation because of the high layer charge. The layers collapse about the interlayer cations (usually K) that are located in the hexagonal or trigonal holes in the surface planes of the tetrahedral sheets. Because of the regular spatial distribution of these holes, the adjacent 2:1 layers are keyed into positions that make any layer displacements and arbitrary rotations impossible in the  $X$ - $Y$  plane. The only stacking irregularity allowed is the special rotational kind, and if all the K sites are going to line up between adjacent layers, such interlayer rotations must be integral multiples of  $60^\circ$ . By far the most common special rotations are integral multiples of  $120^\circ$  because of the trigonal (3-fold) symmetry of the surface oxygen planes, though rarely, rotations of  $n60^\circ$  ( $n$  is odd) do occur (see Chapter 10).

A layer rotation in the micas causes a shift in the  $X$ - $Y$  plane of the unit cell center (Fig. 4.10A). Two 2:1 layers are shown in the  $1M$  configuration, i.e., they have identical orientations. For each of them, the upper and lower K sites are displaced in the  $-X$  direction by the amount  $a/3$ , caused by the slant in the

octahedral sheet. Any rotation, which must be an integral multiple of  $60^\circ$ , takes place about an axis normal to (001) and passing through the interlayer K ion. Study Fig. 4.10A and satisfy yourself that such a rotation must result in a shift of the center of the unit cell and the upper K in the X-Y plane. Because rotations shift the position of the layers with respect to the idealized *IM* geometry, the diffraction pattern will not be identical to that of the *IM* structure. Table 7.7 lists the diffraction data for the polytypes generated by the various layer rotation schemes, and Chapter 10 discusses the diffraction theory and the results that apply to micas in which the sites of the special rotations are distributed randomly, leading to disordered structures. But here, we discuss the various regular patterns of rotations and the polytypes that are produced.

Figure 4.10B shows, schematically, the *IM* stacking. All the layers are identically oriented. In this example, and the ones that follow, an arrow depicts the orientation of the vector corresponding to the intralayer shifts of  $a/3$  along  $-X$ . Figure 4.10C shows the  $\pm 120^\circ$  rotations that define the  $2M_1$  polytype. Figure 4.10D depicts the spiral axis produced by successive  $120^\circ$  rotations that generate the  $3T$  polytype. The  $a/3$  shifts cancel for a complete cycle, so the final structure is not monoclinic, but hexagonal, or more accurately, trigonal. Not shown on Fig. 4.10 are two other rare mica polytypes. One is the  $2O_r$ , or 2-layer orthorhombic structure that is formed by alternate rotations of plus and minus  $180^\circ$ , and the last is the  $2M_2$ , which has alternate layers rotated by plus and minus  $60^\circ$  with respect to each other. The

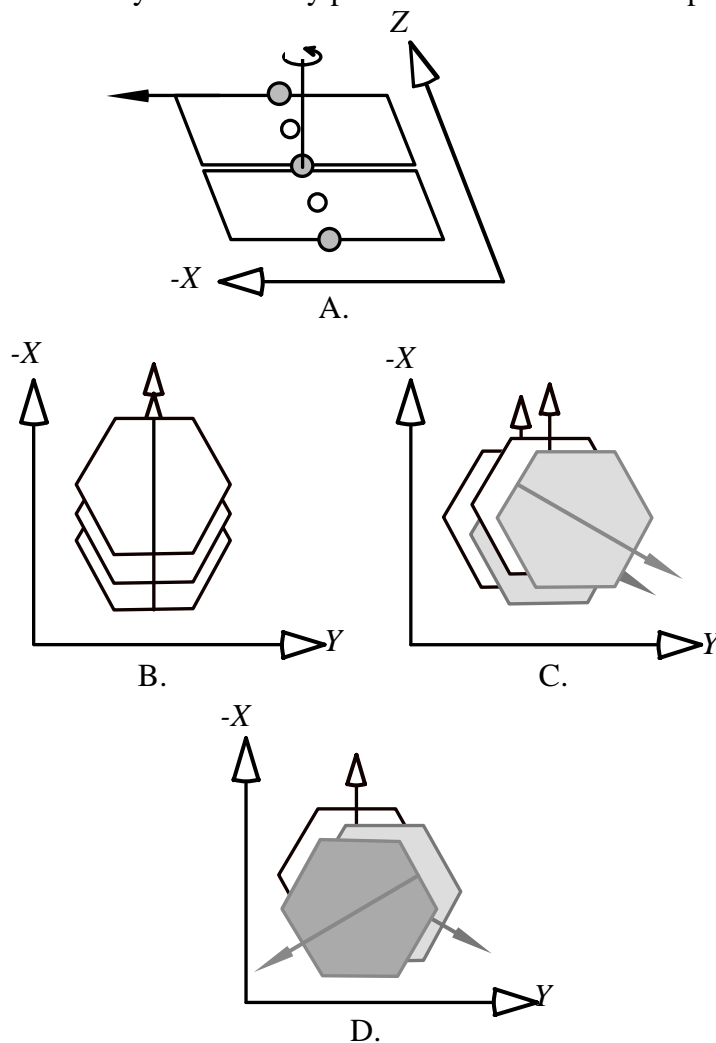


Fig. 4.10. A. Demonstration that a layer rotation in the micas causes a translation of the unit cell in the X-Y plane. Viewed normal to the (001) plane are B. the *IM* stacking, C. plus and minus  $120^\circ$  rotations forming the  $2M_1$  polytype and D. successive  $120^\circ$  rotations producing the  $3T$  polytype. Translation magnitudes are not to scale.

latter two polytypes have rotations that are odd-integral multiples of  $60^\circ$ , and as we discuss in Chapter 10, these are energetically unfavorable for the oxygen coordination about K and are rare probably for that reason (Bailey, 1975). There are many other possible polytypic stacking schemes, but they have, so far, not been found in nature.

Layer stacking constraints are different for kaolinite and chlorite because these minerals have no naked cation “keys” in the interlayer spaces, and bonding of the silicate layers is between a hexagonal oxygen surface on one side and a close-packed hexagonal hydroxyl surface on the other. The alignment of two adjacent silicate layers in the  $X$ - $Y$  plane must be consistent with the spatial requirements of hydrogen bonding between these two surfaces (Bailey, 1980b).

Figure 4.11 is a cartoon of the stacking schemes for the kaolin minerals kaolinite, dickite, and nacrite viewed normal to (001). The shifts are not to scale, but have been exaggerated for clarity of presentation. The three octahedral sites are shown (A, B, and C) only two of which are occupied (circles). The unoccupied site (square) is almost always the B position in the kaolin minerals (Bailey, 1993).

The interlayer shift along  $-X$  is close to  $a/3$  for the same reason that applies to the micas, namely, that the shift is due to the slant of the octahedral sheet, the upper atomic plane of which is displaced from the lower plane by  $a/3$ . For kaolinite this produces a simple  $1M$  stacking pattern. In dickite, alternating B and C site occupancy leads to a  $2M$  structure. The structure of nacrite is more complicated. Here, alternating 1:1 layers are rotated by  $180^\circ$  with respect to the zero degree datum, and the unit cells are displaced along  $b$  by the distance  $b/3$ . If you think about this arrangement, perhaps you can see that the structure will repeat on the sixth layer (three times  $b/3$  times two because of the alternate 0-180 rotations).

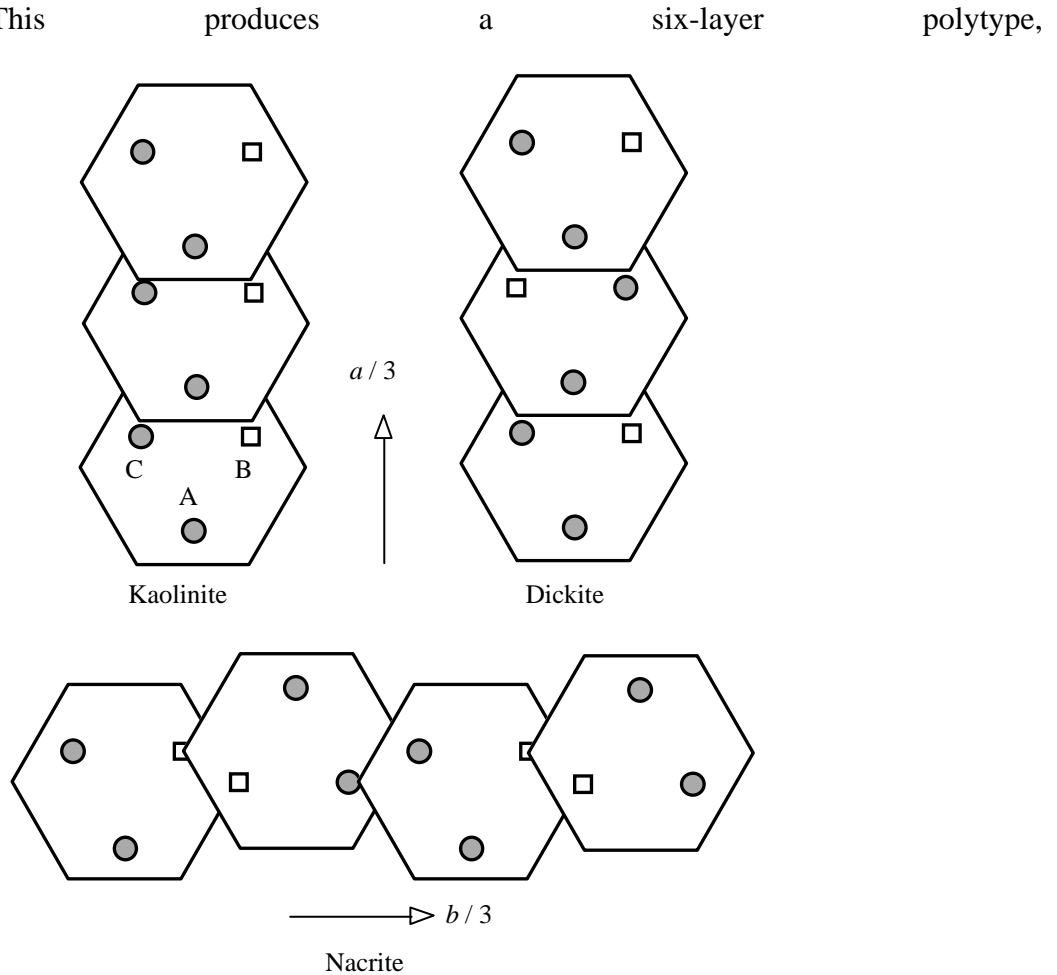


Fig. 4.11 Stacking sequences in kaolinite, dickite, and nacrite viewed normal to the (001) plane. Filled circles represent occupied octahedral sites. Squares depict the vacant site. Translation magnitudes have been exaggerated for clarity.

but as Bailey (1993) has demonstrated, the axes can be redefined so that  $X$  becomes  $Y$ ,  $Y$  becomes  $X$ , and then  $Z$  lies in the plane that is normal to the page and includes the new  $X$  axis (the old  $Y$ ). If this is done, then the pattern repeats every two layers. Nacrite is a 2-layer polytype, but one that is very different from the dickite  $2M$  structure.

Stacking disorder in kaolinite is caused by an apparent random distribution of octahedral cation vacancies among A, B, and C positions (Fig. 4.11, but disorder not shown), although there is still discussion concerning the nature of the crystallographic operations necessary to produce this disorder. The work of Plançon and his co-workers on disordered kaolinite is summarized and discussed by Giese (1988), who concludes that such minerals are physical mixtures of moderate-defect and low-defect phases. Diffraction data for the kaolin polytypes are given in Table 7.6.

Different chlorite polytypes are produced by different translations of 2:1 layers with respect to the hydroxide sheets and by the direction of slant of the hydroxide octahedral sheet compared to the slant of the octahedral sheet in the silicate layers. If the octahedral sheets slant in the same direction, the polytype is called type I, and if they slant in opposite directions (caused by a  $180^\circ$  rotation of the hydroxide sheet), type II is the proper designation (see Fig. 4.12). Any translations of 2:1 layers in the  $X$ - $Y$  plane must be consistent with the geometric constraints of hydrogen bonding between O and OH surfaces, and the two possibilities,  $a$  and  $b$  are shown by Fig. 4.13. Position  $a$  locates the hydroxide sheet cations directly over the tetrahedral Si positions in the underlying 2:1 layer (the  $Iaa$  polytype in Fig. 4.13). Position  $b$  superimposes the hydroxide cations over the octahedral 2:1 sheet cations (Fig. 4.13  $Ibb$ ).

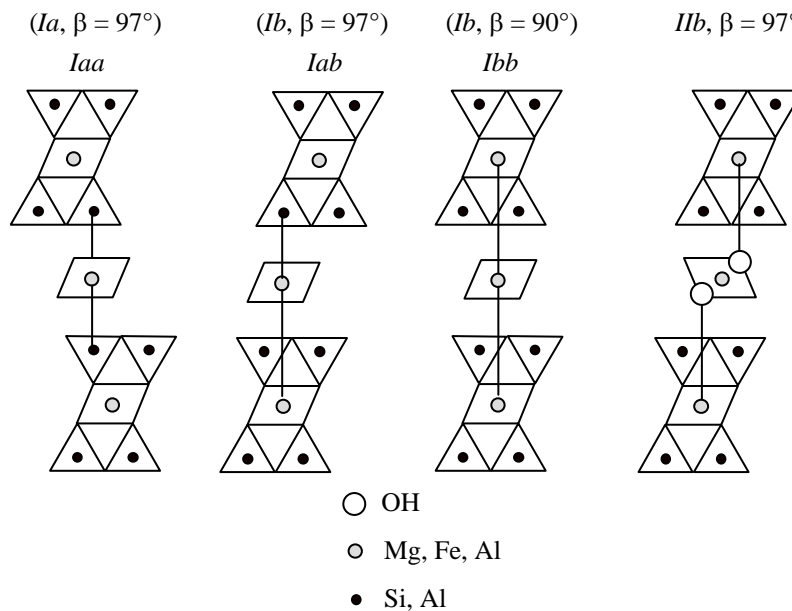


Fig. 4.12 Projection onto the (010) plane of the structures of four common chlorite polytypes. Modified from Shirozu and Bailey (1965).

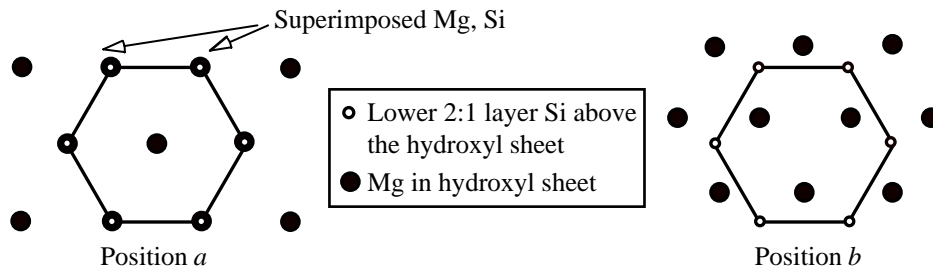


Fig. 4.13. Projection onto the (001) plane of the positions of the octahedral cations of the hydroxide sheet (Mg) and the Si positions in the tetrahedral sheet of the lower 2:1 layer.

Shirozo and Bailey (1965) concluded that the *a* position is energetically unfavorable because of cation-cation (Mg-Si) repulsion over the relatively short distance involved, and indeed, such polytypes are rare compared to the *b* types. Powder diffraction data for the chlorite polytypes are given in Table 7.5.

## PROPERTIES

The properties of minerals are directly or indirectly related to their primary property, their structure. Clay minerals are no exception. In what follows, however, we will be concerned with properties that result from the interaction of clay minerals with other substances, mainly water. These properties depend on the nature of water, the ions that exist in the water, and the size, character, and distribution of charges on the surfaces of the minerals. Important aspects of the ions are their size, valence, electronegativity, and hydration energy. As Newman (1987b, p. 237) recalled, Cairns-Smith, in his discussion about the origin of life, described clay as “the story of sloppy, sticky, lumpy, and tough,” indicating the stages clay goes through as it dries. This description indirectly acknowledges the overwhelming importance and presence of water. Many of the properties of clay minerals and other clay-sized materials are related to water attached to edges and to (001) surfaces. This includes such characteristic properties as plasticity, nutrient-holding and nutrient-exchange capacities, as well as bonding, compaction, and suspension capabilities. Understanding the different “states” suggested by Cairns-Smith, and reversing the process so that samples can be prepared for study, requires an understanding of the properties of clay mineral particles, or more generally, colloidal properties. The ones we will take up here are layer and surface charge, the electrical double layer, exchangeable ions, the nature of water when it is adsorbed on edges or in the interlayer space, and interaction with organic compounds. We will finish this chapter with a section on classification of the clay minerals. In the discussion of some of these properties, we include the group of clay-sized metal oxides and hydroxides called *soil oxides*.

Soil oxides are important because they offer insights into the pedogenic conditions prevailing during their formation and because of their contribution to the retention and release of nutrients. They frequently are intimately overgrown on the surfaces of other minerals. If we are to be able to read paleosols for the information they contain, we must understand both the soil oxides and the minerals with which they are associated. Taylor (1987) and Schwertmann and Taylor (1989), to whom we defer for a more extensive discussion, have offered thorough reviews of this important group. We offer only the briefest of introductions to these properties, and suggest references where you may pursue them. The classical works on the colloidal state of clay minerals are Marshall (1977) and van Olphen (1977).

### *Total Charge, Layer or Permanent Charge, and Variable Charge*

Clay minerals and clay-sized minerals have charges on their surfaces. These determine ion-exchange capacities (see the section below on ion exchange); the dispersion/flocculation behaviors (next section); the transport and fate of solutes; and govern the rates of chemical weathering and the erodibility of the land surface. There are two kinds of charges at the surfaces of clay-sized minerals. One arises from substitution of a cation with one less valence charge than the one it replaces in the structure of the mineral. When the tetrahedral and octahedral sheets are assembled into layers, they may be electrically neutral or they may be negatively charged. Electrical neutrality exists if an octahedral sheet contains  $R^{3+}$  cations in two out of three octahedral sites, or  $R^{2+}$  cations in all octahedral sites, combined with the tetrahedral sheets containing  $Si^{4+}$  in all tetrahedral sites. Such minerals, other than kaolinite, are not particularly common, at least not in the clay-sized fractions of soils and sedimentary rocks. More often, there is some deviation from the ideal number of sites occupied exclusively by a single kind of cation resulting in a *layer charge*. Most commonly,  $Al^{3+}$  is substituted for  $Si^{4+}$  in the tetrahedral sheet, which, unless compensated for in the octahedral sheet, gives the layer a net negative charge. Two other ways of getting a negative layer charge are  $Mg^{2+}$  substitution for  $Al^{3+}$  in a dioctahedral sheet or substitution of vacancies in octahedral positions. There are many variations on this theme. The maximum layer charge for most 2:1 clay minerals is about -1.00 based on  $T_4O_{10}$ , or 4 tetrahedral cations and 10 oxygens. This is a formula unit or half of the unit cell of a layer silicate.

Neutrality is restored by having either single ions or ionic groups in the space between the layers, called, not too surprisingly, the *interlayer space*. Potassium (as in muscovite and biotite), sodium, and calcium are the most common interlayer cations. Complete and incomplete sheets of octahedrally coordinated cations occupy the interlayer space in chlorite and vermiculite. These sheets seem to be a consequence of hydrated cations, usually  $Fe^{2+}$ ,  $Mg$ ,  $Al$ , or  $Fe^{3+}$ , that organize  $OH$  ions or water molecules around them in the same configuration as in the brucite- or gibbsite-like sheets. Ammonium ions  $NH_4^+$  and organic molecules may enter this space also, and if the bonds are electrostatic, they neutralize the negative charge on the silicate part of the clay mineral.

An understanding of layer charge is important for at least two reasons: (1) it is used as one of the criteria for classification, as you will see in a section that follows shortly, and (2) it controls how the (001) surface of a 2:1 clay mineral interacts with the rest of the world. It seems possible that the tetrahedral sheet that faces the outside world may have a different charge than interior tetrahedral sheets. Some things for you to think about: (1) Do you suppose that the distribution of charges seen by a cation in the interlayer space is the same from a layer in which the charge arises from tetrahedral substitution as that from a layer with octahedral substitution? (2) What might be the consequences for the distribution of charges, and therefore the distribution of cations in the interlayer space, if the tetrahedra have had to rotate or tilt to fit with an octahedral sheet? Current thinking is undergoing some reconsideration. Güven (1992) has given a summary of the old and the new views, crediting Bleam (1990a and 1990b) for stimulating renewed discussion on the topic of layer charge. Complexes formed with different materials in the interlayer space are summarized and discussed by MacEwan and Wilson (1980).

The other charge is at edges of mineral particles, the boundaries where structural patterns end as broken bonds. Here, the chemical composition and structure cannot be maintained without additional ions, usually  $H^+$  or  $OH^-$ , to satisfy the unsatisfied bonds. Some refer to the charge that results from the interaction of broken bonds and  $H^+$  or  $OH^-$  as the *variable charge* and distinguish it from the layer charge that is referred to as the *permanent charge*. *Total charge* on a particle is then the sum of variable and permanent charges. For minerals with permanent charge, variable charge is a small fraction of the total, usually <1%, but becomes more important as layer charge gets smaller. Variable charge is important for the oxides, the hydroxides, and aluminosilicates imogolite, allophane, and perhaps kaolinite. It's called variable because it is a function of the pH of the medium in which the clay-sized particles are immersed. For minerals without permanent charge, ions that neutralize the variable charge

are the potential-determining or net-charge-determining ions. Changes in pH, and therefore in net charge, control dispersion and flocculation behavior (see section on the double layer). These changes are measured and described in terms of *isoelectric points* or *points of zero charge* (McBride, 1989). Some authors consider these two slightly different properties. Some also use the term zero point of charge ZPC instead of point of zero charge (Taylor, 1987). When there is a surplus of  $H^+$  in the surrounding environment, mineral particles have a positive net surface charge because  $H^+$  ions have attached themselves to the surface, and, surprise, they have the opposite surface charge in the presence of excess  $OH^-$  ions. The pH at which negative variable charge equals positive variable charge ranges widely for different minerals. Manganese oxides reach this point, the isoelectric or point of zero charge, at a pH of about 1.5, goethite ( $\alpha\text{-FeOOH}$ ) and boehmite ( $\gamma\text{-AlOOH}$ ) reach the point of neutrality in the vicinity of  $pH = 10$ , and kaolinite at  $pH = 4.7$ .

### Electric Double Layer

The number of theories to explain the interaction between surfaces of colloidal particles and ions of the fluid in which they are immersed clearly points out that the finer points of this subject are not fully agreed upon or understood. The basic features of the double layer are, however, pretty straightforward, and are shown in Fig. 4.14. Given that the plane of atoms facing the outside world of a clay mineral is made up of anions ( $O^{2-}$  or  $OH^-$ ),

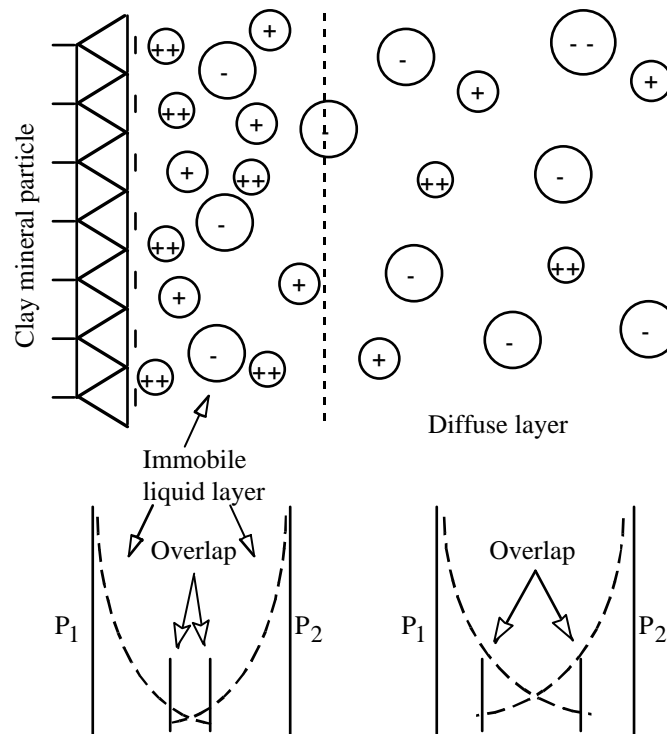


Fig. 4.14. The electrical double layer. The negative surface of the clay mineral attracts oppositely charged ions from the liquid in which the particle is immersed. This band of relatively tightly held positive ions attracts a less tightly distinguishable band of anions, which, in turn, attracts an even less distinguishable band of cations. These progressively less distinguishable bands around the particle form the diffuse layer part of the double layer. The effect of the charge or potential of the particle drops off along a line perpendicular to its surface.  $P_1$  is the potential of one particle and  $P_2$  that of a second particle. The two diagrams showing the dropping off of potential indicate that for thinner immobile layers, particles can approach one another more closely than when the immobile layer is thicker. The greater overlap of the  $P_1$ - $P_2$  pair on the right would result in greater repulsion than for the pair on the left.

it is easy to imagine that such surfaces would attract swarms of cations. First, however, such surfaces attract a layer of water that is relatively rigidly held (the water molecules still have thermal motions that can be detected by infrared spectroscopy). Within this layer, cations (in this context often called counterions) concentrate in a volume near the surface of the clay mineral. This, in turn, attracts anions, but less rigidly held. And these anions attract cations and so on until no segregation is apparent and electrical neutrality is achieved. Neutrality can be reached only in suspensions dilute enough in clay mineral particles. The importance of the concept of the double layer is to help explain dispersion and flocculation of clay minerals. When particles can approach one another closely enough, van der Waals forces come into play and bind the particles together into composites or clumps larger than colloid size, i.e., they *flocculate*. This causes them to settle because they become particles large enough that the random motions of Brownian movement can no longer keep them in suspension. When the cations in the surrounding fluid are divalent or trivalent, not as many are required to neutralize the clay mineral surface and the “immobile” layer is thinner, and therefore, particles can get closer to one another. In this case, they are more easily joined by van der Waals forces. On the other hand, univalent cations form a thicker immobile layer, keeping particles apart by a respectable distance, making it more difficult for the van der Waals forces to be effective (Fig. 4.14). In this case, clay mineral particles remain discrete entities, and their small size allows them to stay in suspension, i.e., to be *dispersed*. The thicknesses of the immobile layer and the diffuse layer also are affected by the concentration of ions in the fluid in which the clay mineral is immersed. As ions crowd together, the thicknesses of these layers decrease allowing closer approach of one particle to another, and therefore, more possibility for flocculation.

The double-layer interactions between particles can vary from particle pair to particle pair. Because the van der Waals attraction can be different for attractions that are face to edge (FE), face to face (FF), or edge to edge (EE), and because pH can influence particularly edge charges, all three geometries can cause flocculation. The FE association is the arrangement that has led to the term *cardhouse structure*, and is the arrangement that has been the general perception of the way flocs form. However, scanning electron micrographs have recently called into question this arrangement. At least for smectites, clumps seem to form by faces attracted to faces (FF) (Güven, 1992). Newman (1987a) includes a full chapter on dispersion and flocculation (van Olphen, 1987). For additional information and a sense of different views on theoretical aspects of the double layer, see Greathouse et al. (1994), Low (1992), and Sposito (1992). In addition, J. W. Stucki, of the Department of Agronomy, University of Illinois, has written and made available a tutorial program entitled *An Introduction to Double Layer Theory*.

### ***Exchangeable Ions or Cation-Exchange Capacity***

Perhaps the earliest work on this reversible, low-energy transfer of ions between clay-sized material and surrounding liquid was by Way (1852) in his report on the power of soil to retain the nutrients of manure. Interest in exchange of ions is currently stimulated by four major needs: (1) to remediate radioactive wastes and other environmental contaminants either at disposal or accident sites; (2) to understand diagenetic processes; (3) to understand the properties of soils and the releasing and trapping of nutrients; and (4) to use the differences in cation-exchange capacity (CEC) qualities necessary for industrial techniques. In the everyday life of the clay mineralogist, exchangeable cations are important for at least three reasons, all of which are important in studying and preparing samples, they: (1) neutralize the layer charge; (2) have a physical influence (e.g., engineering properties and X-ray data for clay minerals vary with the nature and number of the exchangeable cations); and, (3) have a chemical influence. The distribution in interlayer space of exchangeable cations is probably controlled by the distribution of charges on the adjacent silicate layers that they neutralize. When there is  $\text{Al}^{3+}$  substituted for  $\text{Si}^{4+}$  in some of the tetrahedra, and the  $\text{Al}^{3+}$  may be regularly or irregularly distributed, those

pseudo-hexagonal holes with more  $\text{Al}^{3+}$ -substituted tetrahedra around them are preferred spots for the location of cations (see Fig. 4.1). Do you see why? (See discussion on this topic in Güven, 1992, and his reference to Bleam, 1990a and b.) The mystery of why the ocean is  $\text{Na}^+$ -rich and not  $\text{K}^+$ -rich is probably best explained by an understanding of CEC and the average clay mineral's selectivity for these two ions.

The consequences of the colloidal size, and therefore the extremely large ratio of surface area to volume, cannot be overestimated. We, as large bulky objects, have surface charge, but it is quite inconsequential compared to our volume. It in no way influences our behavior. On the other hand, one important consequence of so much surface area on the clay minerals is the charge on their surfaces, the great majority of which is on the (001) surfaces, with the remaining charges on the much smaller surface of broken, unsatisfied bonds on edges (see sections on layer and surface charge). Ions and molecules, water most commonly, are attracted to and held by the charges on clay mineral particles. In most cases, with some important exceptions, cations are attracted to the (001) surfaces, anions to the edges. We are interested primarily in the cations. Especially in those clay minerals that expand, cations may be exchanged when the clay minerals holding them come in contact with a solution rich in other cations. Cation exchange needs to be viewed as a dynamic process governed by the law of mass action, at least in a first approximation, especially in the laboratory where the clay minerals can be exposed to strong concentrations of single-cation solutions. However, in the case of clay minerals exposed to solutions of low concentrations of a mix of cations, predictions are quite difficult to make. Cations in the fluid and those on the (001) surface interchange at some rate reflecting temperature, concentration, pH, the size and charge of the cation, the energy of hydration of the cation, and the amount and distribution of the layer charge of the clay mineral. The relative ease with which one cation will replace or exchange another is seldom predictable. For a series of montmorillonites, Eberl (1980) collected data from the literature that suggested for this mineral, under the same conditions, the following series:



i.e., generally  $\text{K}^+$  is more stable, or more firmly fixed, in the interlayer space than is  $\text{Na}^+$ , for this mineral and for the conditions used in the experiments as reported. This series will vary with conditions or type of clay mineral, e.g., in acidic conditions  $\text{H}^+$  is included in the series. The relatively common  $\text{NH}_4^+$  wasn't among the ions tested but, for similar conditions, seems to usually be about in the middle of this series. Measuring the amount of cations freed and replaced by others, when carefully done, is a measure of both the negative charge on a layer and the cation-exchange capacity (CEC).

Beyond these simple generalizations, there is much to learn. CEC values are not only partly a consequence of the method of measurement, there are three or four actively used units for this value. Layer charge values, the charges these cations are supposed to be neutralizing, are most often determined from structural formulas (see end of chapter), whereas CEC values are based on the oven-dried weight of samples. Nevertheless, for pure, fully expandable samples, it is generally agreed that CEC values and total charge values match closely (Laird, 1994). Some of the points of contention about theoretical and empirical points of view can be read in McBride (1989) and Laudelout (1987), who observed, "Regularities in behavior [of exchangeable cations] seem fairly easy to observe and *ad hoc* theoretical interpretations not too difficult to find. At present, the predictive value of the latter seems limited."

### ***Interaction of Water with Clay Mineral Surfaces***

You might think that the subject of water interacting with clay mineral surfaces, water in the interlayer space, would be pretty straightforward. Ha! In spite of having thrown almost all the technology of modern instrumentation at the problem, there remains confusion and disagreement about a number of

the details, e.g., the density of water in the interlayer space or the presence or absence of the hydronium ion  $\text{H}_3\text{O}^+$ . There are a few things that seem to be generally accepted, and these are: (1) some clay minerals swell with water, others do not; (2) the influence of the layer charge of a clay mineral extends only a few water layers away from the surface (and there is little agreement on what is meant by a few); (3) water forms a coordination “sphere” or shell around most cations and this sphere is more tightly held by some cations than others; (4) water in the interlayer space is dynamic, i.e., as measured by infrared and NMR spectroscopy, it is rotating, vibrating, and stretching; that water held at or very near the surface of a clay mineral doesn’t freeze at temperatures as low as  $-30^\circ\text{C}$ ; and (5) it is in a state somewhere between that of bulk liquid water and that of ice.

Swelling clay minerals seem to take in water as single, double, or triple layers of water. Swelling or expansion is exclusively along the [001] or  $Z^*$  direction; there is no variation in the  $a$  and  $b$  dimensions of the crystals. Crystallographic integrity is maintained in the process of expansion. Compared to the rest of the mineral world, this is a remarkable and unique feat. Water in the interlayer space of expandable clay minerals is controlled by three factors: (1) the polar nature of the water molecule; (2) size and charge of cations in the interlayer space; and (3) the value and localization of the charge on the adjacent silicate layers, as discussed in the section on total charge. Expanded clay minerals carry water into their depositional sites. During the process of diagenesis, this water is released, carrying with it cations and anions in solution. This may be one of the primary driving factors in diagenetic changes such as the neoformation of clay minerals and the formation of other cementing minerals. Bruce (1984) suggested that it is a factor in the accumulation of petroleum. Bird (1984), commenting on engineering properties of shales, noted that adsorption of water in smectite can increase volume 80 percent and decrease friction by a factor of three. And Bethke et al. (1988) implicated it as a source of overpressuring in oil reservoirs. Hall (1993) offered a wider review of overpressuring that included the expulsion of interlayer water during diagenesis.

In the interlayer space of expandable clay minerals, water apparently takes the form of two-dimensional structures, or sheets. Extrapolating from work done on Na-smectite (Moore and Hower, 1986), these sheets are always present in integral numbers, 0, 1, 2, or 3, as a function of relative humidity, i.e., the activity of water. Each hydration state has a discrete  $d(001)$ : 9.6,  $\sim 12.4$ ,  $\sim 15.2$ , and  $\sim 18.0$  Å, respectively. In response to the amount of water available,  $d(001)$  varies continuously but not linearly. It does not vary in a step function because intermediate values of apparent  $d(001)$  result from an ordered interstratification of two appropriate hydrates. For example, at the low end of the relative humidity scale, the dehydrated clay mineral is interstratified with the form that contains one sheet of water so that the apparent  $d(001)$  is between 9.6 and 12.4 Å.

As an example of an unsettled question about water, Loucks (1991) argued that the hydronium ion  $\text{H}_3\text{O}^+$  is a far more common occupant of the interlayer space than generally recognized. Jiang et al. (1994) however, countered this argument by suggesting that the environments in which clay minerals were formed would have to have quite low pH’s to form this ion, and that, perhaps, the analytical data used by Loucks were from mixed phases rather than single minerals.

As another example, agreement concerning the details of the structure of water in the interlayer space isn’t too good (Table 4.1). Some argue for an increase in its density relative to free water; some argue for a density decrease relative to free water. Data of Carman (1974) and Colton (1986) show experimentally (approximating  $\sim 13$  and  $\sim 1.2$  km deep in the earth’s crust, respectively) that  $d(001)$  of expandable 2:1 layer silicates remains about the same with increasing pressure. Under burial pressures, Le Châtelier’s Principle (or, quantitatively, the Clapeyron equation) indicates that water would come out of the interlayer space if it were less dense than pore water, or pore water would move into the interlayer space if it would be more dense in the interlayer space. Therefore, we think water must have about the same density in the interlayer space as outside in pore spaces. Based on Monte Carlo simulations to

determine time-averaged thermodynamic quantities, Skipper et al. (1993) concluded that the density of water in the interlayer space of Mg- and Na-smectites ranged in density from 0.85 at a pressure of zero to 1.91 at approximately 300 km depth. Throughout the increase in pressure, with enough water for two layers of water, they pictured the Mg ions arranged close to the plane midway between the two silicate layer surfaces, whereas the Na ions had a tendency to bind to the layer surface.

Vermiculite exists in macroscopic crystals, and its interaction with water in the interlayer space has, therefore, received more attention with more precise results than that for smectites. Walker (1958) offered a detailed analysis for the hydration and dehydration of vermiculite that has been little modified by subsequent work. He showed dramatic photographs of hydration in progress, and identified five phases with  $d(001)$  values of 9.02, 11.59, 13.82, 14.36, and 14.81 Å. (For more on hydrogen bonding and the structure of ice and water, start with Cotton and Wilkinson, 1972, pp. 157ff.)

Since most sedimentary rocks, buried sediments becoming rocks, and soils are really aqueous systems, one would think that the problems surrounding the interaction of water and minerals, in our case clay minerals, would have been solved. That they are not is a signal to upcoming generations that there is no shortage of problems for them.

Table 4.1. Density of water in the interlayer space and free water

P, bars	Skipper et al. (1993)		Hawkins&Egelstaff <sup>a</sup>	Kennedy et al. (1958)
	With interlayer cation <sup>b</sup>		Free Water <sup>c</sup>	
	Mg	Na	Na	
0	1.38	1.15		
1			1.05	0.9957
10	1.38	1.14		0.9962
8500	1.38	1.08		1.2066 <sup>d</sup>
100000	1.91	1.84		

<sup>a</sup>(1980); <sup>b</sup>26.84°C <sup>c</sup>at 30°C <sup>d</sup>This value from Burham et al. (1969)

### ***Interaction with Organic Compounds***

A look at journals dedicated to clay mineralogy indicates that an understanding of organic compounds will be helpful. In this section, we will try to provide a toe-hold, a finger-grip, a starting place. We can, because of our own limitations and those of time and space, offer only an introduction to the simplest of compounds, a combined nomenclature-glossary, and their broad categories. We didn't find complete consistency in the vocabulary used by different disciplines, so you may expect some variation on the meanings of the terms we use here. We hope to offer enough to give you a starting point for such work as that of Mortland (1970), MacEwan and Wilson (1980), Rausell-Colom and Serratos (1987), and Oades (1989).

In general, when geologists think of organics in nature, they think of fossil fuels. Waples (1985) has offered a clear, concise discussion of organic compounds associated with petroleum. Krauskopf (1979) has given a particularly clear introduction to the chemistry of organic compounds. From the standpoint of those interested in clay minerals, a much broader view of organic chemistry is necessary. Incentives for the study of interactions of organics with clay minerals stem from such applications as: (1) their importance to the formation of, exploration for, and recovery of petroleum; (2) the use and misuse of organic herbicides and pesticides; (3) the property of the clay minerals to act as oxidants (Surdam et al., 1989), catalysts, and templates for synthesizing by the polymerization of organic molecules; (4) clay minerals as barriers to and adsorbers of organics in landfills; (5) the possibility of using clay mineral-organic derivatives for improving the physical properties of plastics; and, as mentioned in the first chapter, (6) their role in prebiotic syntheses and storage of molecules of biological interest.

Organic chemistry is the chemistry of carbon in the same way that much of mineralogy is the mineralogy of silicon; organic chemistry is the chemistry of compounds associated with living organisms as opposed to inorganic chemistry associated with the nonliving world. The structural mineralogy or crystal chemistry of the geologists is essentially the same as the *stereochemistry* of the organic chemist; the polymorphs of mineralogy are the *isomers* of organic chemistry. Si and C are both group IV elements on the periodic table. Therefore, they have the same outer electron configuration. The most common bonds from C to other elements are the tetrahedrally distributed  $2sp^3$  hybrid orbitals, just as are the  $3sp^3$  orbitals for Si. And, again, just as for Si, these rigid directional bonds account for many of the important features of organic compounds. For Si, the element at the other end of these bonds is most often O, for C it is most often another C or H, thus the common name *hydrocarbons*. If all the atoms at the ends of the  $sp^3$  orbitals were other carbons, the structure would be that of diamond.

Hydrocarbons, in the strictest sense, are compounds of C and H only. N, S, and O are the next three most common elements that occur in organic compounds. Therefore, an organic compound containing elements in addition to C and H is called a *heterocompound*, or an *NSO* compound. The hydrocarbons are classified in the same manner as the silicates, i.e., by structure. The broadest categories are as chains and rings. The chains are called *aliphatics* or *paraffins*. Rings come in two varieties; those with the prefix *cyclo-* and the *aromatics*. If all C-to-C bonds are single bonds in an aliphatic compound, it can then hold a maximum number of hydrogens. It is called, therefore, a *saturated hydrocarbon*. Chains can be straight, branched, or in rings. The prefix *n-* indicates that the chain is straight, *iso-* that it is branched, and *cyclo-* if it forms a ring. Aliphatic compounds can have C atoms linked by single, double, or triple bonds. When they do, they are no longer saturated, but are *unsaturated hydrocarbons*. The aromatic hydrocarbons have unique, flat, 6-membered rings of carbons, the bonds of which cannot be represented as either single or double but are best represented as a single bond between each pair of C atoms in the ring plus three nonlocalized bonds shared equally by all six carbons. The simplest of the aromatics is the benzene ring, with which you're probably familiar.

The structural details of organic compounds will be important when you think about organic compounds in the interlayer space of clay minerals. The structure of many organic compounds can be illustrated by a consideration of the simplest organic compound, methane,  $\text{CH}_4$ . It is represented by a tetrahedron as surely as is silica except that it doesn't polymerize in the same manner. In order for the C to polymerize, one of the four hydrogens must be dropped and the  $sp^3$  orbital it shared is then shared by another C atom. In so-called "straight chains" of tetrahedrally coordinated carbons, the tetrahedral bonding angle tends to be preserved. A zigzag chain would be a more accurate name. This also holds for the cyclo-aliphatics, in which the ring is not flat but puckered. This differentiates it from the flat ring of benzene, which has bonding more like that of graphite than like that of diamond.

Aliphatic complexes introduced into the interlayer space of clay minerals have been divided into  $\alpha$ - and  $\beta$ -complexes; the chains of  $\alpha$ -complexes are parallel to (001), whereas those of  $\beta$ -complexes are perpendicular or at steep angles to (001). Furthermore, it is often possible to determine if the plane of the zigzag is parallel or perpendicular to the (001), e.g., ethylene glycol (which we routinely introduce into our samples to diagnose the degree to which expandable clay minerals are present) orients the plane of its zigzag chain perpendicular to the (001) surface (Reynolds, 1965).

The aliphatic compounds are classified based on the number of carbon atoms in the chain and on whether they have single, double, or triple bonds (*alkanes*, *alkenes*, or *alkynes*, respectively). The bonding character is designated by the suffix *-anes*, *-enes*, and *-ynes*; the number of carbon atoms by the Greek prefix for the number, except for the first four compounds (see Table 4.2). These first four in the table make up most natural gases; a mixture from hexane to decane is gasoline; and those from  $\text{C}_{12}\text{H}_{26}$  to  $\text{C}_{22}\text{H}_{46}$  are the constituents of lubricants. The roots of the names for these groups provide the basis for much of the vocabulary of organic chemistry. We will not deal further with the alkenes or alkynes.

With the simple vocabulary developed so far and the compounds listed in Table 4.2, you can picture groups added to the chains, groups that replace the hydrogens. We can change any of the compounds listed in Table 4.2 to groups called *radicals* by taking away a H and changing the name by substituting *-yl* for *-ane*. There are four rules for giving names: (1) select the longest possible continuous chain of carbons and consider this as the base from which the compound in question has been derived; (2) number in succession the carbons in the chain so that the substitutions for hydrogens will be attached to the lowest numbered C possible; (3) use the prefixes *di-*, *tri-*, *tetra-*, *penta-*, etc. are used to indicate the presence of two, three, four, etc. groups on the parent C chain; and (4) when several groups are present, list them in either increasing complexity or alphabetically. For example, picture hexane, a straight aliphatic alkane chain with six carbons. One of the simplest things we can substitute for a H is the methyl group,  $\text{CH}_3^+$ . This would be methylhexane. To indicate which C the methyl radical was attached to, the carbon atoms are numbered. If the methyl radical were attached to the second C, we would have 2-methylhexane; if there were 2 methyl radicals attached to this carbon, it would be 2,2-dimethylhexane. You could probably diagram the structure of this molecule, right?

In addition to radicals, other groups called *functional groups*, also can be added to chains. A functional group is a specific group of elements that can be attached to the molecules such as those in Table 4.2. The presence of one of these groups confers on its host a chemical reactivity characteristic of that functional group, regardless of the form of the structural framework of C atoms of the host molecule. For example, for all alcohols the hydroxyl group,  $-\text{OH}$ , is bonded to a hydrocarbon framework, and the names have the suffix *-ol*, e.g., hexanol. All the alcohols have similar properties. There are only about six or seven functional groups that occur frequently. An organic acid has an  $-\text{OH}$  and an O bonded to a terminal C; the O is double bonded to the C; an *amino acid* is an  $-\text{NH}_2$  group attached to an organic acid. This latter is a simple example of a *polyfunctional compound*, i.e., has more than one

Table 4.2. Naming the alkanes

Name	Formula	Name	Formula
Methane	$\text{CH}_4$	Heptane	$\text{C}_7\text{H}_{16}$
Ethane	$\text{C}_2\text{H}_6$	Octane	$\text{C}_8\text{H}_{18}$
Propane	$\text{C}_3\text{H}_8$	Nonane	$\text{C}_9\text{H}_{20}$
Butane	$\text{C}_4\text{H}_{10}$	Decane	$\text{C}_{10}\text{H}_{22}$
Pentane	$\text{C}_5\text{H}_{12}$	Pentadecane	$\text{C}_{15}\text{H}_{32}$
Hexane	$\text{C}_6\text{H}_{14}$	In general	$\text{C}_n\text{H}_{2n+2}$

functional group. The greatly simplifying feature of these groups of atoms is that the majority of chemical reactions involve changes of the functional group only. Any organic chemistry textbook will show you the common functional groups and how they are structurally attached to the carbon frameworks.

Some of the more complex straight-chain hydrocarbons that are important in sediments are *isoprenoids*, *steranes*, and *triterpanes*. Regular isoprenoids consist of a straight chain of carbons with a methyl branch on every fourth carbon; steranes contain three six-carbon rings and one five-carbon ring; and triterpanes contain five, or sometimes six rings, one of which is a five-carbon, the others six-carbon rings.

Turning to the aromatic compounds, all have at least one benzene ring ( $\text{C}_6\text{H}_6$ ), some are a series of benzene rings linked together. There is a systematic nomenclature for this family of compounds, but it is difficult to find anyone who uses it. If one is to work with these, one just has to learn the formula and

structure of benzene, toluene, anthracene, naphthalene, etc. Radical and functional groups are attached to aromatics just as they are to aliphatics. The points of attachment are numbered clockwise with carbon number 1 at 12 o'clock. For example, a benzene ring with two bromine atoms substituted for two hydrogens could be 1,2-dibromobenzene, 1,3-dibromobenzene, or 1,4-dibromobenzene. Can you picture these? The terms *ortho*, *meta*, and *para* are also used to describe points of attachment. Orthodibromobenzene would indicate that the bromines are attached to carbons next to one another; meta-, that they were separated by one carbon; and para-, separated by two carbons. Benzene, with an OH replacing one of the hydrogens, is the most common of the group called *phenols*. For aromatic compounds, if elements other than C are present in the rings, they are referred to as *heterocyclic* compounds. Multiple aromatic rings bound together, called *polycyclic aromatic hydrocarbons PAH*, are important geologically.

The study of the interactions of organic compounds with clay minerals began in the 1930s. Giesecking (1939) demonstrated that inorganic cations in the interlayer space could be replaced by organic cations; MacEwan (1944) and Bradley (1945) showed that uncharged polar molecules, glycerol and glycol, could enter the interlayer space without displacing cations. From an enormous number of studies made in the intervening time, a few generalizations can be made.

The geometric relations between organic compounds and clay minerals can help understand properties and behaviors of both. There are several ways to explain the bonding of organic compounds to clay minerals. As with inorganic, exchangeable cations, organic cations are attracted to the layer charge of the siloxane surfaces exposed in the interlayer space of 2:1 clay minerals. Neutral organic molecules can be adsorbed by forming coordination complexes with transition metal cations that have previously been introduced. Hydrogen bonding of organic molecules to clay minerals can be important, especially for molecules containing OH, NH<sub>2</sub>, and NH<sub>3</sub> functional groups. Hydrogen bonding also apparently forms between the organic molecules, stabilizing whatever configuration they have assumed in the interlayer space.

The relatively few and relatively simple organic compounds initially introduced into geologic environments become many and generally more complex through diagenetic processes. The temperature and pressure increases that accompany burial of sediments transforms, through the loss of O, N, and S, the mixture of organic compounds into a complex substance called *kerogen*, the insoluble portion of organic matter in sedimentary rocks. The soluble part is called *bitumen*. Some geochemists recognize three types of kerogen and some four (see Waples, pp. 31ff). One relation not yet settled is the importance of clay minerals as catalysts in the formation of petroleum. Ungerer (1990) argued that clay minerals are relatively unimportant, whereas Johns and McKallip (1989) argued for the effectiveness of diagenetic illite in the natural pyrolysis of kerogen that yields petroleum.

## CLASSIFICATION

Now that we have covered the properties and the rudiments of the structural features that help us identify clay minerals, we turn to their classification. We follow Bailey (1980b) and use layer type 1:1 or 2:1, as the main criterion for establishing divisions (Table 4.3). Within each division we use layer charge or charge per formula unit as the criterion for classification. Within these subdivisions, we make subgroups based on whether they are trioctahedral or dioctahedral. The other criteria seem real and distinct, whereas distinction on the basis of layer charge is approximate and somewhat arbitrary. It seems the least in accord with natural features of the minerals. This set of criteria will work moderately well except for mixed-layered clay minerals and for the transitional boundaries between micas and illites, illites and vermiculites, vermiculites and chlorites, and vermiculites and smectites. Table 4.3

shows this classification scheme. Mixed-layered clay minerals are not included in Table 4.3 because we assume that the components forming them are represented in this table.

Bowen (1928, Chapter XVIII, pp. 321-22) stated that a classification scheme will be of use and will endure to the extent that it coincides with real qualities of the nature of the things being classified. In addition, communication within a group of people with shared interests is effective in direct proportion to the extent that the group understands and agrees on the definitions covered by the classification scheme. This is somewhat abstract, so we'll give a concrete example or two. Perhaps the most useful classification scheme (and the oldest) is the binomial nomenclature for plants and animals. Still, when the boundaries between species are critically examined, some are blurred and are the basis for controversy. The problem is worse with minerals (and worse yet with rocks). The limitations of our understanding become apparent as we try to pin down definitions of minerals. It is certainly convenient to think of them as individual minerals. But in so many ways, most of them behave like members of a series, their properties grading from one to another. Some of them are more subtle in this regard than others. For example, consider illite and smectite. We are sure that muscovite is a discrete mineral. We are relatively sure illite- $2M_1$  is a distinct, discrete mineral. We are not so sure that illite- $1M$  ever occurs without some minimum amount of interlayered smectite, if there is such a mineral as smectite. Or perhaps what has been called smectite is really two minerals. We make do with perfect end-member species that probably don't exist but do seem to pin down both ends

Table 4.3. Classification of phyllosilicates, emphasis on clay minerals

Layer type	Group	Subgroup	Species
1:1	(z~0)	Serpentine-kaolin Serpentes (Tr)	Chrysotile, antigorite, lizardite, berthierine, odinite
		Kaolins (Di) nacrite, halloysite	Kaolinite, dickite,
.....			
	(z~0)	Talc-pyrophyllite Talc (Tr)	
		Pyrophyllite (Di)	
Smectite	(z~0.2-0.6)	Tr smectites	Saponite, hectorite
		Di smectites	Montmorillonite, beidellite, nontronite
Vermiculite	(z~0.6-0.9)	Tr vermiculites	
		Di vermiculites	
Illite	(0.6 > z < 0.9)	Tr illite?	
		Di illite	Illite, glauconite
Mica	(z~1.0)	Tr micas	Biotite, phlogopite, lepidolite
		Di micas	Muscovite, paragonite
Brittle mica	(z~2.0)	Di brittle micas	Margarite
Chlorite	(z variable)	Tr, Tr chlorites <sup>a</sup>	Common name based on Fe <sup>2+</sup> , Mg <sup>2+</sup> , Mn <sup>2+</sup> , Ni <sup>2+</sup>
		Di, Di chlorites	Donbassite
		Di, Tr chlorites	Sudoite, cookeite (Li)
		Tr, Di chlorites	No known examples
.....			

Based on Bailey (1980a, b), Brindley (1981), Hower and Mowatt (1966), and Š rodoń (1984) .

<sup>a</sup>2:1 layer first in name of chlorite; Tr = trioctahedral and Di = dioctahedral;  $z$  = charge per formula unit.

of this series. In general, most agree with the definitions of the two ends, but many disagree on the details.

In the end, we use a classification system that is based partly on logic and partly on intuition. The only “real” classification that comes to mind is the periodic law or periodic table. An element is either sodium or magnesium because a species between would require a fraction of a proton, and that apparently is impossible. In addition, there are no green or pink sodium atoms. All atoms of sodium in the universe are indistinguishable from each other except for isotopic variations, which, again, are distinct species. Do you understand that we are not satisfied that we understand everything about minerals? If that is clear, let us proceed to the next chapter in which individual clay minerals are considered. (If these last two paragraphs have left you cold, perhaps you should consider some more exact discipline.)

#### Box 4.1. Nomenclature

This is an aside to emphasize some recommended terms that apply to clay minerals. The first two paragraphs of what follows are from reports of the Nomenclature Committee of the Association Internationale pour l’Etude des Argiles (AIPEA) chaired by S. W. Bailey (Bailey, 1980a, 1982).

In the classification of clay minerals (Table 4.3), *smectite* is the accepted group name for clay minerals with layer charge between 0.2 and 0.6 per formula unit and that swell in the presence of water. Chlorite is a 2:1 layer type rather than a 2:2 or 2:1:1, and the interlayer hydroxyl sheet is to be treated like other interlayer material.

When discussing structures it is important to note that *lattice* and *structure* are not synonymous. Lattice is the abstract, invented pattern, whereas structure is the concrete, real mineral material. Keep this analogy in mind: Lattice is to the mind as crystal structure is to the brain. For using the terms *plane*, *sheet*, *layer*, and *unit structure*, a single *plane* of atoms, a tetrahedral or octahedral *sheet*, and 1:1 or 2:1 *layer* are the recommended designations. Plane, sheet, and layer refer to increasingly thicker arrangements. The assembly of one or more layers plus interlayer material is referred to as a *unit structure*. Brucite and gibbsite sheets are not acceptable terms. Either *hydroxide* or *interlayer sheet* for interlayer material or *brucite-like* or *gibbsite-like* should be used for indicating the trioctahedral or dioctahedral nature, respectively, of the interlayer material.

In referring to the composite peaks of mixed-layered clay minerals, we put the peak of the mineral with the smaller  $d(001)$  first, e.g., the illite/smectite 002/003 peak. To designate specific proportions, we use the familiar scheme for other silicate minerals like  $Ab_{37}$  but use the format that follows: chlorite(0.85)/smectite. A distinction is also made between the terms *clay* and *clay mineral*. *Clay* is a general term for material  $< 2 \mu\text{m}$  (sometimes  $< 4 \mu\text{m}$ ) in size; it is used to indicate rock, whereas *clay mineral* refers to a specific mineral (most of which, conveniently, occur in the clay-sized fraction).

We also include here the minimum necessary terms for discussing *diagenesis*, which we take to be the sum of all chemical and physical changes in minerals during and after their initial accumulation, a process limited on the high-temperature, high-pressure side by the lowest grade of metamorphism. Diagenesis involves addition and removal of material, transformation by dissolution and recrystallization or replacement, or both, and by phase changes. We include *pedogenesis*, the changes and formation of minerals in the soil environment, within diagenesis. Retallack (1983, p. 829) discussed the problems soil scientists have with the term and argued for including soil-forming processes within the concept of diagenesis. *Authigenic* refers to minerals formed in place. It is also applied to minerals

that are clearly the result of new crystal growth on older crystals of the same kind, e.g., K-feldspar overgrowths are referred to as authigenic overgrowths. We use authigenesis as a subprocess of diagenesis, and in most cases diagenesis is the better term. Of the two definitions offered in Bates and Jackson (1980), our use of the term diagenesis is closer to the second definition, diagenesis [sed], even though the first definition is framed in terms of clay minerals. We think that a convenient boundary between diagenesis and metamorphism is Weaver and Brockstra's (1984) boundary: that point at which all illite-*IM* has been converted to  $2M_1$ . Neither this definition nor the one for diagenesis adequately covers the changes in hydrothermal, geothermal, or simple thermal situations.

The terms *neof ormation* and *transformation* are widely used. Neof ormation is new formation from solution, and transformation is remodeling of an existing structure in which parts of the parent mineral are retained. Both are diagenetic changes. Examined on finer and finer scales, these distinctions begin to blur, as seen in an example from Smith et al. (1987). They showed that olivine may weather to a mixture of saponite (Mg-rich, trioctahedral smectite) and goethite, both showing an orientation related to the structure of the parent olivine as seen in transmission electron micrographs (Fig. 5.20, p. 188). Two terms we will find useful in discussing secondary and host minerals are *topotaxy* and *epitaxy*. They are defined in the report of the Joint Committee on Nomenclature of the International Mineralogical Association—International Union of Crystallography (Bailey et al., 1977): *Topotaxy* is the phenomenon of mutual orientation of two crystals of different species resulting from a solid-state transformation. *Epitaxy* is the phenomenon of mutual orientation of two crystals of different species, with two-dimensional lattice coincident (net or mesh in common), usually, though not necessarily, resulting in an overgrowth. So topotaxy is a more general term. The Committee recommended that the adjectival forms use the endings *-taxic* or *-tactic*, but not *-axial*. *Ostwald ripening* is another term related to crystal growth. It's a recrystallization process in which, within a solution containing the material of the crystals with which it is in contact, the smallest crystals are dissolved and their material is added to the larger crystals of the same phase (Ostwald, 1900; Baronnet, 1982; Eberl et al., 1990; and especially see Fig. 5.11 from Jahren, 1991). The driving mechanism is a shift to lower surface free energy. And then there are terms that have come into use recently enough so that they are used differently by different groups of workers. Until the Nomenclature Committee can act on the following terms, you will have to take their meanings from the context in which they appear: *fundamental particle*, *interparticle diffraction*, and *MacEwan crystallite*.

A few crystallographic terms seem appropriate. In X-ray crystallography, it has become a convention to use the unbracketed symbol to denote a family of structural planes and to bracket the index to denote the actual crystal face. Thus, 001 "reflections" arise from structural planes parallel to the face (001). 001 also is the first basal plane. For a *IM* polytype, the structural plane or actual face symbol is (001), and for a *2M* polytype, it is (002).  $d(001)$  is the repeat distance along a line perpendicular to the 001 face, or along  $Z^*$ . (We have chosen to continue to use Ångstroms rather than nanometers, although we see the change coming.) Square brackets, [321], enclose the coordinates of a zone axis, i.e., denote a line perpendicular to family planes 321 (after Phillips, 1971, p. 42, and Juster et al., 1987). Bailey's Committee (1977) recommended that  $X$ ,  $Y$ ,  $Z$  or [100], [010], [001] be used for directions of crystallographic axes,  $u$ ,  $v$ ,  $w$  or  $x$ ,  $y$ ,  $z$  are used for fractional coordinates of atom positions within the unit cell, and  $a$ ,  $b$ ,  $c$  for the repeat distances along these axes. Comparable directions and dimensions in reciprocal space are indicated with an asterisk \* following any of these same symbols.

Mackenzie (1963) reviewed nomenclature from the depths of history if you are interested in the twists and turns terms associated with our discipline have taken.

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