# SOIL COMPONENTS

## Volume 2
## Inorganic Components

Edited by
**JOHN E. GIESEKING**

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# *Inorganic Components*

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*John E. Gieseking*

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# Preface

The major components of most soils are inorganic. These constituents are derived from the weathering of rocks and minerals or from subsequent reactions and interactions of the weathering products. During the weathering and interactions of weathering products, inorganic soil colloids are formed.

Large amounts of inorganic colloids are essential in soils if they are to support luxurious plant growth. The colloids adsorb water and nutrient elements that might be lost from the soil system and they release these as plants need them. They also adsorb and buffer the soil system against large excesses of soluble toxic substances that might otherwise exist as free moieties in soils.

Soil and plant root interactions occur across two interfaces. One is the interface between plant roots and the liquid phase and the other is the interface between the soil particles and the liquid phase.

Reactions across the interface between colloid crystals and the soil liquid phase may also suppress the availability of nutrient elements to plants. The effectiveness of these interfacial reactions in supporting optimum plant growth ultimately depends on the arrangements of ions in the surfaces and subsurfaces of the mineral crystals. For this reason much of this volume is devoted to the arrangement of ions in crystalline mineral particles commonly occuring in soils and the properties that these particles contribute to soil systems.

The authors of chapters in this volume are widely known for their extensive research on problems related to their chapters. Their contributions are scholarly evaluations of the results that have been obtained in the areas covered by their topics.

The editor wishes to express his appreciation for the many reference materials provided by the library of the University of Illinois. He also wishes to express his appreciation to his wife, Flossie Y. Gieseking, for her help with every operation during the production of this volume.

JOHN E. GIESEKING

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# Contents

Chapter 1

# The Classification of Soil Silicates and Oxides

*R. C. Mackenzie*

## Contents

## A. Introduction

Soils may be developed on either sedentary or transported materials, but irrespective of which of these is involved, all soils may be traced back to parent rocks. Hence all rock-forming minerals can occur in soils, in addition to minerals formed as a result of pedogenic processes.

Division of the minerals in soils into primary (i.e., inherited) and secondary minerals is by no means as easy as it might appear, since secondary minerals from a geological aspect may well be regarded as primary on a pedological basis—and sedimentary rocks introduce even greater complications. Fortunately, however, such a division is largely irrelevant for the present purpose, since the principles of classification should apply to all minerals irrespective of their origin.
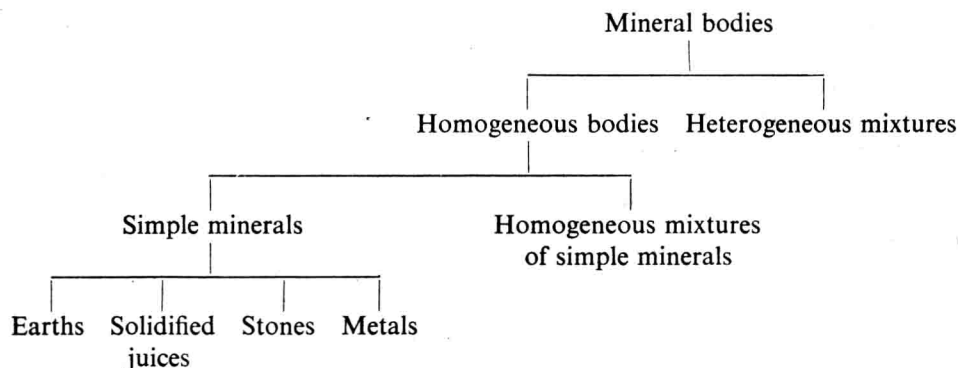
Despite the enormous range of minerals that may occur in soil, those predominating are, except under peculiar circumstances, silicates and oxides, and it is with these we are presently concerned.

## B. Historical Developments

From archaeological evidence, it is believed that not more than about 20 minerals were known in the palaeolithic age and that this number had incieased to about 40 by the end of the neolithic period. With such small numbers, classification was obviously of little relevance, but the number of known minerals appears to have increased almost logarithmically with time, and hence classification is now essential to an understanding of the minerals themselves. Nomenclature, however, has never been systematized, and very few mineral names give an indication of their chemical composition or refer to other attributes; most are derived from the locality of origin or commemorate famous people, particularly mineralogists.

Although it is clear from evidence left by the ancient Oriental and Egyptian cultures that the properties of many minerals were then known, the first documented classification appears to be that of THEOPHRASTUS [c. 300 B.C.], who recognized metals, stones, and earths. It is worthy of comment that even in his time the last-named were prized for their properties, and indeed exploited, and that distinctions could be made between those of different mineralogical constitution (ROBERTSON [1949, 1958, 1963]), despite the very primitive methods of investigation.

Early descriptions of minerals were also given by PLINY THE ELDER [79 A.D.] and others, but the next development in classification seems to have been made by AVICENNA [980–1037 A.D.], who employed this system: stones and earths, sulfur minerals, metals, and salts. The major advance, however, came with the scheme of AGRICOLA [1546].*

```
                              Mineral bodies
                                    |
                   ┌────────────────┴────────────────┐
            Homogeneous bodies              Heterogeneous mixtures
                    |
        ┌───────────┴───────────┐
  Simple minerals         Homogeneous mixtures
        |                   of simple minerals
  ┌─────┼──────┬──────┐
Earths Solidified Stones Metals
        juices
```

Indeed this may be regarded, despite archaic terminology, as the first distinction of rocks from minerals, and it marks the commencement of the development of present-day mineralogy. Subsequent to this, the pace of development was slow, and despite works by ENCELIUS [1557], CAESALPINUS [1596], CAESIUS [1636], and LACHMUND [1669], perhaps the first obvious sign of progress is the Regnum Minerale of KÖNIG [1687], where chemical aspects are considered, the book abounding in old chemical symbols.

The great naturalist and systematist C. LINNAEUS [1707–1778] applied to minerals the concept of "genus and species," which he developed so successfully for plants and animals, and although it was less successful here, largely because of the nonreproductive nature of minerals, this terminology persisted for many years (e.g., KIRWAN [1794]). As early as 1758, A. CRONSTEDT [1723–1765] classified minerals as chemical compounds, but the succeeding

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* Based on the notes of Hoover and Hoover in De Re Metallica (AGRICOLA [1556]) and Bandy and Bandy in De Natura Fossilium (AGRICOLA [1546]).

years were dominated by the school of A. G. WERNER [1750–1817], who gave "à ses nombreux auditeurs le goût de la minéralogie par la clarté de ses descriptions, la pureté de son language et la chaleur de ses improvisations" (DUFRÉNOY [1856]). Werner's system was based largely on external physical characteristics, with subsidiary chemistry, but was somewhat distorted by his pupils—particularly his successor at Freiberg, F. MOHS [1773–1839]—to a purely physical classification.

Thus, at the beginning of the nineteenth century, there were two distinct schools of thought: those who based classification on crystal form and other external characteristics, as represented by Mohs, and, to a lesser extent perhaps, by ROMÉ DE LISLE [1736–1790] and ABBÉ R. J. HAÜY [1743–1822]; and those who used only chemical composition, as represented by J. J. BERZELIUS [1779–1848]. Yet many less eminent mineralogists such as R. KIRWAN [1733–1812] were well aware that both physical and chemical attributes (see KIRWAN [1794]) were essential for the distinction of species and the development of classification. The importance of structure, as deduced by Haüy from crystal form and particularly cleavage, in classification was stressed by PHILLIPS [1823], but because of difficulties, he, in fact, uses a chemical classification as being the most easily understood.

The chemical classification of Berzelius is (apart from native elements) based on the nature of the anion, but because of difficulties due to the complexity of many minerals, this appears to have been replaced later by classification on the basis of the principal cation (e.g., PHILLIPS [1823]). A valuable discussion of the merits of several classification schemes of this period, i.e., those of Werner, Haüy, Mohs, Berzelius, Brongniart, Rose, d'Halloy, and Necker, is given by DUFRÉNOY [1856], and some others are considered by NICOL [1849]. By the middle of the nineteenth century, a combined physical and chemical basis appears to have been in general favor (*inter alia:* NICOL [1849]; NAUMANN [1850]; DUFRÉNOY [1856]), although BREITHAUPT [1836–1847] still tended to use physical characteristics. Great advances were made in determinative mineralogy in the latter part of this century through the use of optical microscopy (for an early account see DUFRÉNOY [1856]), and the end of the century saw the publication of the classical works of TSCHERMAK [1888], DANA [1894], and HINTZE [1897], which are still widely employed as reference books. In general, these use chemical distinctions with subsidiary physical characterization.

In this period too, W. C. RÖNTGEN [1845–1923] discovered X-rays, but the impact this discovery was to have on mineralogy was not appreciated until the second decade of the twentieth century, when M. Laue and co-workers (FRIEDRICH, KNIPPING, and LAUE [1912]; LAUE [1912]) discovered that crystals could diffract the X-ray beam and the classical researches of W. H. and W. L. Bragg led to elucidation of the structures of a whole host of minerals (see BRAGG and CLARINGBULL [1965]). These studies enabled a logical crystallochemical classification—envisaged by PHILLIPS [1823] and foreshadowed by Rose in his classification of 1852 (DUFRÉNOY [1856])—to be worked out, and it is this system that is generally in use today (HURLBUT [1952]; STRUNZ [1957]; DEER *et al.* [1962–1963]; LAZARENKO [1963]; POVARENNYKH [1972]). It is interesting to note that such schemes hark back to Berzelius, in that major divisions are based essentially on the electronegative part of the compound and that subdivisions are on crystallographic considerations.

But there has, in recent years, been considerable doubt as to whether a strict crystallo-chemical scheme is the best from the practical viewpoint—for example, the natural association of minerals having the same electropositive ion may not be evident—and considerable ingenuity is being devoted to finding some compromise scheme (see several papers in the book edited by BATTEY and TOMKEIEFF [1964]). Evolution of classification systems is, therefore, still in progress, and it will undoubtedly be some time before one equally acceptable to mineralogists, crystallographers, and chemists is evolved.
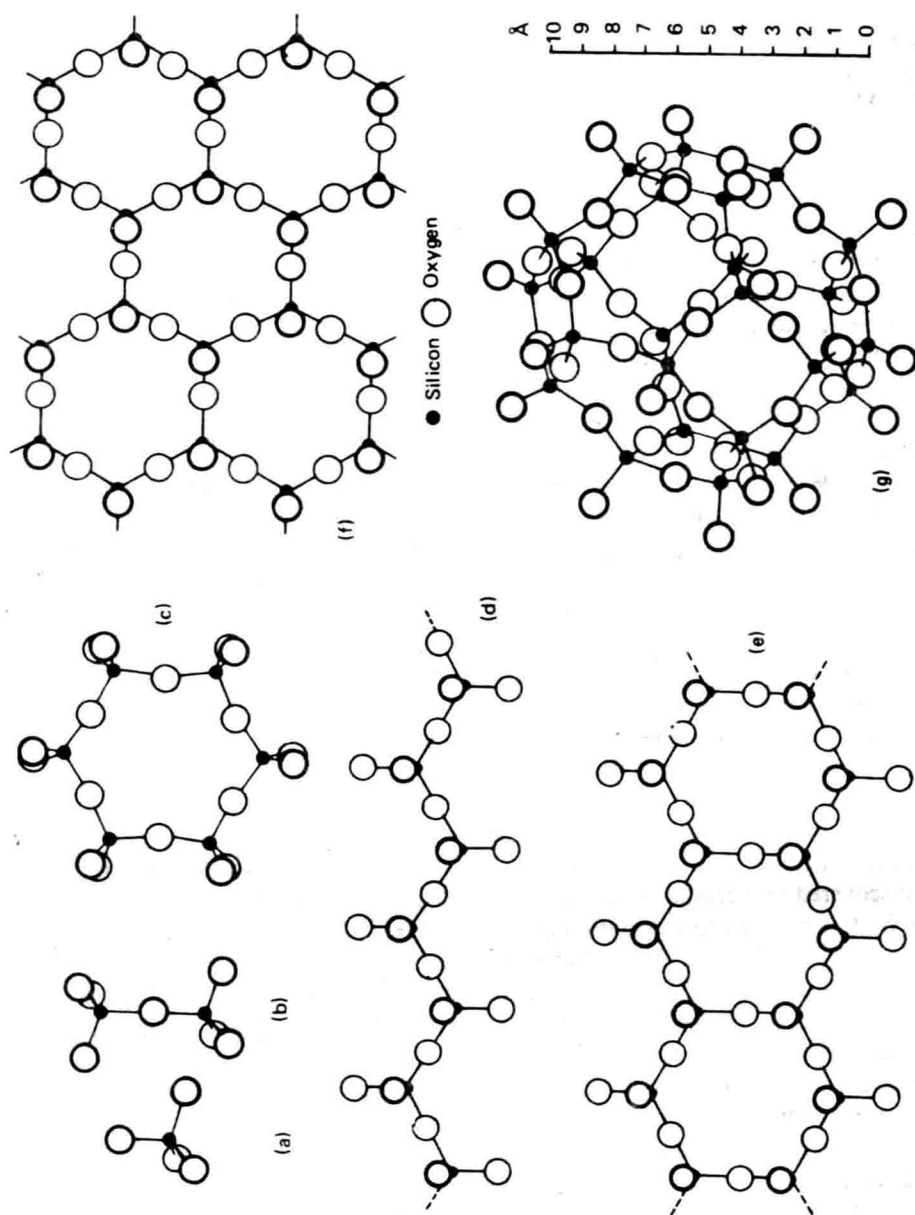
**Figure 1.** Illustration of the linkage of SiO$_4$ tetrahedra in different classes of silicates. (a) Nesosilicates (separate tetrahedra); (b) sorosilicates (linked tetrahedra); (c) cyclosilicates (closed rings); (d) and (e) inosilicates (single and double chains); (f) phyllosilicates (sheets); (g) tectosilicates (framework).

## C. Crystalline Silicates

The fact that silicates are the most common minerals in the earth's crust has led to much study of these over the years. All are based on the $SiO_4^{4-}$ tetrahedron, and their variety is due in large measure to the various ways in which these tetrahedra can link both to themselves and to other units—reminiscent, indeed, of the role of the carbon atom in organic chemistry.

Six types of silicates are recognized from the manner in which the $SiO_4$ tetrahedra occur in the structure, and two systems of nomenclature have been employed—one descriptive, and one employing Greek prefixes (STRUNZ [1957]). The two may be correlated as follows (STRUNZ [1957]; BRAGG and CLARINGBULL [1965]):

| Class | Arrangement of $SiO_4$ tetrahedra |
|---|---|
| Nesosilicates | Separate tetrahedra ($SiO_4$) |
| Sorosilicates | Two or more linked tetrahedra ($Si_2O_7$, $Si_5O_{16}$, ...) |
| Cyclosilicates | Closed rings or double rings of tetrahedra ($SiO_3$, $Si_2O_5$) |
| Inosilicates | Single or double chains of tetrahedra ($SiO_3$, $Si_4O_{11}$) |
| Phyllosilicates | Sheets of tetrahedra ($Si_2O_5$) |
| Tectosilicates | Framework of tetrahedra ($SiO_2$) |

Nesosilicates and sorosilicates are sometimes grouped together under the name "island silicates" (KOSTOV [1954]). The way in which individual tetrahedra may link to give these formulas is illustrated in Figure 1. It should be mentioned at this point that $Al^{3+}$ may frequently substitute for $Si^{4+}$ in tetrahedra, so that instead of, e.g., $SiO_3$, one may have $AlSi_3O_{12}$. The nomenclature of STRUNZ [1957] is employed in the following discussion.

Each of the six classes contains many groups of minerals that are closely related structurally and chemically: those that contain minerals commonly occurring in soils (see PAK FENOVA and YARILOVA [1962]) are listed in Table 1, and some notes are appended regarding individual minerals or end members of these groups. All other silicates could conceivably occur in soils, and under special circumstances, some might even predominate; for these, reference should be made to standard textbooks (SOBOLEV [1949]; BETEKHTIN [1950]; STRUNZ [1957]; DEER et al. [1962–1963]; LAZARENKO [1963]; BRAGG and CLARINGBULL [1965]), and when they are published, to the volumes on silicates of *Dana's System of Mineralogy* (PALACHE et al. [1944–1951]; FRONDEL) and *Mineraly* (Chukhrov [1961–1972]).

### I. Nesosilicates

The end members of the olivine group, the structure of which consists of individual $SiO_4$ tetrahedra linked by divalent ions in sixfold coordination, are forsterite ($Mg_2SiO_4$) and fayalite ($Fe_2SiO_4$). Those commonly found in soils are usually intermediate in composition and partially altered because of the ease with which olivine weathers. The structure is orthohombic.

The garnet group is more complex, with the general formula $R_3^{2+}R_2^{3+}Si_3O_{12}$, and there are several end members. Thus, when $R^{3+}$ is $Al^{3+}$, $R^{2+}$ may be $Fe^{2+}$, $Mg^{2+}$, or $Mn^{2+}$ and when $R^{2+}$ is $Ca^{2+}$, $R^{3+}$ may be $Al^{3+}$, $Fe^{3+}$, or $Cr^{3+}$. These minerals have cubic symmetry.

The only mineral of the zircon group commonly found in soils is zircon, $ZrSiO_4$, itself. Some hafnium is invariably present, and uranium and thorium may also substitute for zirconium. Other ions may occur in the frequent inclusions. The symmetry is tetragonal.

Andalusite and kyanite are found in soils derived from metamorphic rocks; sillimanite is perhaps rarer. These minerals have chains of aluminum-oxygen octahedra linked by $SiO_4$

**Table 1.** Groups of Minerals, Members of Which Commonly Occur in Soils

| Class | Group |
|---|---|
| Nesosilicates | Olivine<br>Garnet<br>Zircon<br>Sillimanite–andalusite–kyanite<br>Topaz<br>Chloritoid<br>Sphene |
| Sorosilicates | Epidote |
| Cyclosilicates | Beryl<br>Tourmaline |
| Inosilicates | Pyroxene<br>Amphibole<br>Wollastonite |
| Phyllosilicates | See Table 2 |
| Tectosilicates | Nepheline<br>Analcime–leucite<br>Felspar<br>Sodalite<br>Zeolite |

tetrahedra and 5-, 6-, or 4-coordinated aluminum-oxygen groups, respectively. All have the formula $Al_2SiO_5$. Sillimanite and andalusite are orthohombic, and kyanite is triclinic.

Topaz has the formula $Al_2SiO_4(OH,F)_2$, the amounts of OH varying from low values to about 30% of the (OH,F) group. The structure consists of $SiO_4$ tetrahedra, together with linked octahedral groups around aluminum. It belongs to the orthorhombic system.

Although chloritoid has a sheet structure, the fact that it has independent $SiO_4$ groups brings it into the nesosilicate class. It has the formula $(Fe,Mg) Al_2(OH)_2SiO_5$ and crystallizes with monoclinic symmetry.

Sphene, $CaTiSiO_5$, itself is the most commonly encountered member of the sphene group. Calcium may be partially replaced by sodium, rare earths, etc., and titanium by niobium, iron, manganese, etc. In addition, OH and F may partially substitute for some oxygen. The symmetry is monoclinic.

## II. Sorosilicates

The structure of the minerals of the epidote group contains both individual and linked $SiO_4$ tetrahedra, the latter giving the grouping $Si_2O_7$. Zoisite, $Ca_2Al_3Si_3O_{12}OH$; clinozoisite, $Ca_2Al_3Si_3O_{12}OH$; and epidote, $Ca_2(Al,Fe)_3Si_3O_{12}OH$, are the most common members. In zoisite there may be very minor replacement of silicon by aluminum and aluminum by iron; clinozoisite and epidote, on the other hand, may have up to one aluminum atom replaced by iron. Zoisite is orthorhombic, and clinozoisite and epidote are monoclinic.

## III. Cyclosilicates

Both beryl, $Be_3Al_2Si_6O_{18}$, and cordierite $(Mg,Fe)_2Al_4Si_5O_{18}$, contain in their structure six-membered hexagonal rings of tetrahedra; in beryl these tetrahedra are of $SiO_4$, but in

cordierite one silicon atom out of six is replaced by aluminum to give the ring formula $(Si_5Al)O_{18}$. Most cordierites are magnesium rich. Beryl has hexagonal symmetry, whereas cordierite is orthorhombic.

Tourmaline is very variable in composition, the main varieties being magnesian tourmalines or dravites, $NaMg_3Al_6B_3Si_6O_{27}(OH,F)_4$; iron tourmalines or schorl, $Na(Fe,Mn)_3Al_6B_3Si_6O_{27}(OH,F)_4$; and alkali tourmalines or elbaites, $Na(Li,Al)_3Al_6B_3Si_6O_{27}$ $(OH,F)_4$. The $SiO_4$ tetrahedra are in the form of six-membered rings with the formula $Si_6O_{18}$; the boron may also be regarded as being in tetrahedral coordination, each tetrahedron sharing one corner with a $SiO_4$ tetrahedron. The symmetry is trigonal.

## IV. Inosilicates

The pyroxenes comprise one of the main groups of rock-forming minerals, with a structure based on single chains of $SiO_4$ tetrahedra, each sharing two oxygen atoms with its neighbors to give the overall formula $SiO_3$. Most pyroxenes crystallize with monoclinic symmetry (clinopyroxenes), and some are orthohombic (orthopyroxenes). The orthopyroxenes range in composition from enstatite, $MgSiO_3$, to ferrosilite, $FeSiO_3$, with several intermediates such as hypersthene $(Mg,Fe)SiO_3$. The clinopyroxenes are more complex, and a classification scheme proposed by POLDERVAART and HESS [1951] is shown in Figure 2. Those commonly occurring in soils may be related to diopside, $CaMgSi_2O_6$; hedenbergite, $CaFeSi_2O_6$; and augite, $(Ca,Mg,Fe,Ti,Al)(Si,Al)O_3$.

The amphiboles are another widespread group of rock-forming minerals common in soils. Their structure is based on double chains of $SiO_4$ tetrahedra, having the formula $Si_4O_{11}$.
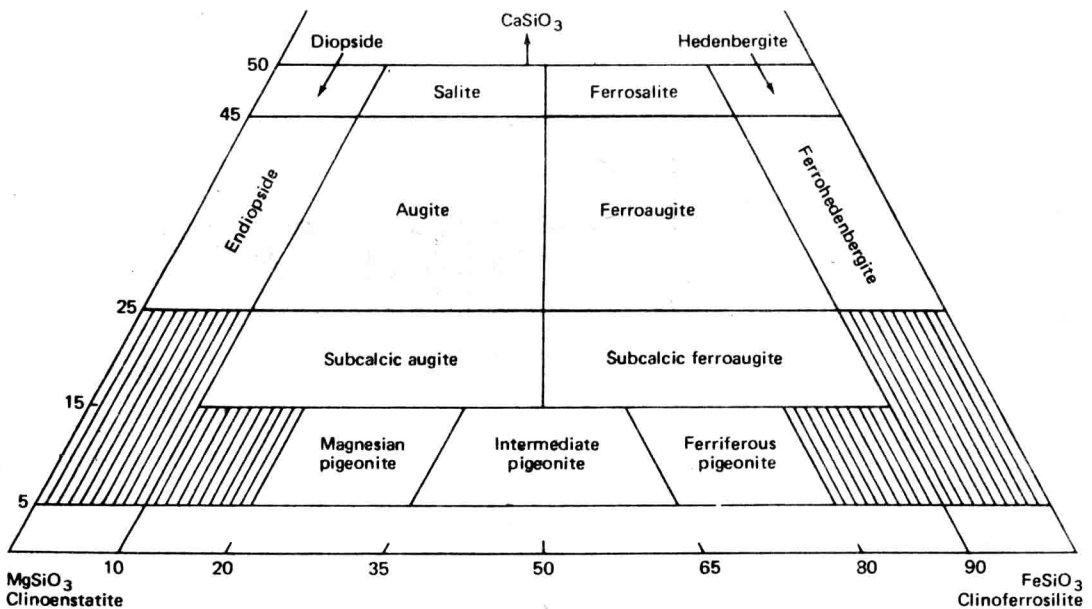


**Figure 2.** Nomenclature of clinopyroxenes in the system $CaMgSi_2O_6$–$CaFeSi_2O_6$–$Mg_2Si_2O_6$–$Fe_2Si_2O_6$. (After POLDERVAART and HESS [1951].)

Like the pyroxenes, some are orthorhombic and some are monoclinic. They exhibit an extremely wide range of chemical composition, and for a proper understanding of their relationships, reference should be made to standard mineralogical texts. Probably the most common in soils are tremolite, $Ca_2Mg_5Si_8O_{22}(OH)_2$; actinolite, $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$; and hornblende, $(Ca,Na,K)_{2-3}(Mg,Fe,Al)_5(Si,Al)_8O_{22}(OH)_2$.

Wollastonite, $CaSiO_3$, is common in metamorphosed limestones and similar rocks, and may be inherited in the soil. Its structure is based on single chains of $SiO_4$ tetrahedra, but these are arranged differently from those in the pyroxene chains. Calcium may sometimes be partially replaced by iron, manganese, and magnesium. The structure is triclinic.

## V. Phyllosilicates

So far as the phyllosilicates are concerned, the majority are based on sheets with six-membered rings of $SiO_4$ tetrahedra, but some are based on those with four-membered rings. The former are the most important in soil mineralogy, since the so-called clay minerals, which
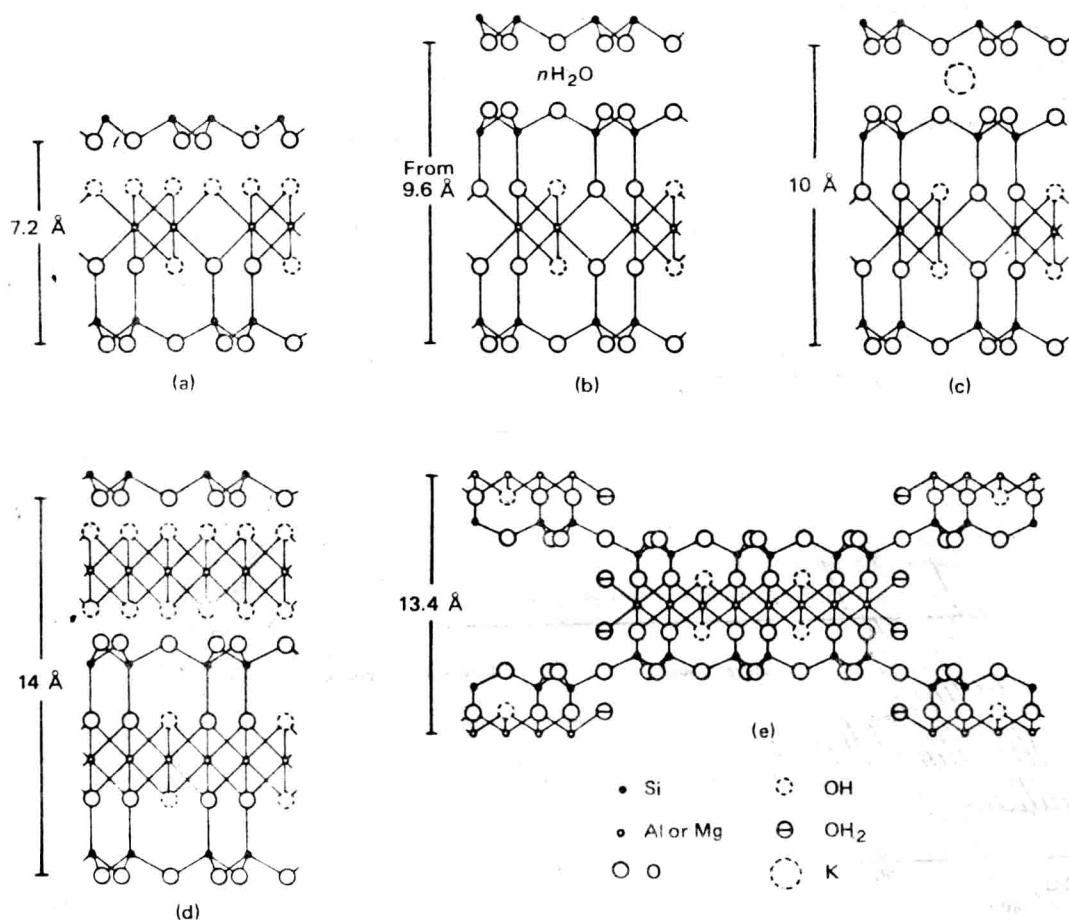


**Figure 3.** Diagrammatic projections of the structures of clay minerals. (a) Kaolinite; (b) montmorillonite; (ç) mica; (d) chlorite; (e) sepiolite. (After MACKENZIE and MITCHELL [1966].)

in some instances form the major part of the soil, belong to this class. They, therefore, deserve more detailed consideration than the other classes, which are adequately characterized in classical mineralogy.

The terms "clay" and "clay mineral" are particularly difficult to define (MACKENZIE and MITCHELL, [1966]), but for the present purpose, it is sufficient to state that the majority at least belong to the phyllosilicate class, since they contain sheets of six-membered rings of $SiO_4$ tetrahedra having the formula $Si_2O_5$. Sepiolite and palygorskite might be regarded as inosilicates, but the ribbons of sheets of $SiO_4$ tetrahedra are so much broader than those normally found in inosilicates and their structure is, in general, so closely related to that of the phyllosilicates that they are better considered here.

Many classification schemes have been proposed for these minerals (GRIM [1953]; BRINDLEY [1955a]; BROWN [1955]; CAILLÈRE and HÉNIN [1957a]; HOSKING [1957]; STRUNZ [1957]; FRANK-KAMENETSKII [1958, 1960]; MACKENZIE [1959, 1965]; LAZARENKO [1958]; CHUKHROV et al. [1961]; WARSHAW and ROY [1961]; PEDRO [1965]), and much international discussion has taken place (BRINDLEY et al. [1951]; MACKENZIE [1959, 1965]; CAILLÈRE [1960]), but only recently has it been possible to get a reasonable measure of international agreement on a scheme consistent with the classification of the phyllosilicates as a whole.

Because of their small particle size, the minerals in clays have, from earliest times, posed problems for the mineralogist. Yet even the ancients (e.g., THEOPHRASTUS [ca. 300 B.C.]) were able to distinguish different "earths" because of their properties, and these distinctions usually coincide with what we know to be differences in mineralogy. The history of the development of clay mineralogy (MACKENZIE [1963]; MACKENZIE and MITCHELL [1966]) is a fascinating subject, but out of place here. Suffice it to say that the scientific basis of clay mineralogy was laid in the late 1920s and early 1930s, when X-ray diffraction techniques were applied to clays (ROSS [1927]; HENDRICKS and FRY [1930]; ROSS and KERR [1931]) and the basic structures of the main groups of minerals elucidated (PAULING [1930a, b]; HOFMANN et al. [1933]). In order to understand the classification and nomenclature systems—and problems—associated with clay minerals, it is necessary to elaborate briefly their basic structures (Figure 3).

These structures may be regarded essentially as formed by the condensation of sheets of $SiO_4$ tetrahedra with sheets of alumina or magnesia octahedra (as in gibbsite and brucite), and the major types are designated 1:1 (or *diphormic*), 2:1 (*triphormic*), and 2:2 or 2:1:1 (*tetraphormic*), depending on the ratio of tetrahedral to octahedral sheets in one repetitive layer. Thus, kaolinite [Figure 3(a)] belongs to the 1:1 type, montmorillonite [Figure 3(b)] and mica [Figure 3(c)] to the 2:1 type, and chlorites [Figure 3(d)] to the 2:1:1 type; palygorskite and sepiolite [Figure 3(e)] also have a basic 2:1 layer, although this is sharply limited in one direction with inversion of the sheet around an oxygen atom, resulting in a chainlike structure with channels along the fiber length.

Much isomorphous substitution occurs in some of these minerals, frequently leading (e.g., when $Al^{3+}$ is replaced by $Mg^{2+}$) to a charge on the sheet surface satisfied by cations external to the layer, which may or may not be readily exchangeable with others from solution. The charge density on the sheet surface has important repercussions, since variation in its magnitude leads to minerals with different properties—e.g., as regards swelling in water or other polar liquids—and must be considered as a principle in defining groups. The electron charge per layer-unit-cell* in the 2:1 type varies from 0 to 4. At a charge of 0, there are no substitutions, no extraneous ions, and no swelling in polar liquids; at a charge of about 0.5 to 1, the cation-exchange capacity (c.e.c.) is about 100 meq/100 g, and swelling in water is such that

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* In some minerals the unit cell comprises several layers, but it is convenient here to consider only one layer—hence the term layer-unit-cell. If charge per formula unit is employed, these values would be halved.