

## SOIL MINERALOGY

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### Summary

Minerals are natural inorganic compounds with definite physical, chemical, and crystalline properties. They can be classified into primary (chemically unaltered) or secondary (chemically altered) minerals, silicates and non-silicates, crystalline and non-crystalline minerals. Silicate minerals dominate in most soils. Other major soil mineral groups include: sulfides, oxides and hydroxides, halides, sulfates, carbonates and phosphates.

The most common methods used for soil mineral characterization include x-ray diffraction, thermal, elemental, and optical analyses. Through these techniques unique mineral features, which are essential in predicting their impact on the overall soil behavior, are identified and quantified. Most primary minerals undergo structural and chemical alterations (weathering) driven by physical, chemical, and biological gradients. These processes cause redistribution of primary and secondary soil minerals resulting in a soil profile which is consistent with the surrounding climatic and topographic setting.

Soil minerals play also a significant role in dictating the suitability and behavior of the soil for various land uses. They provide physical support for plants, contribute to soil structural formation, are sources of many plant nutrients, and can act as sorbents for several environmental pollutants. Therefore, having a good grasp of soil mineralogy is essential to understanding many facets of land use, including misuse, and is often a key to solving specific environmental problems.

## **1. Introduction**

Minerals are natural inorganic compounds with definite physical, chemical, and crystalline properties. They are classified as primary or secondary, silicates or non-silicates, and crystalline or non-crystalline minerals. Primary minerals have not been substantially altered chemically since deposition or crystallization from molten lava and are usually found in the sand and coarse silt fractions. Secondary minerals form as a result of the weathering of primary minerals and are found in the clay and fine silt fractions.

Most soil minerals contain silica as their major structural constituent (silicates), while non-silicates are composed mainly of oxides, carbonates, and sulfates. Crystalline minerals are composed of atoms arranged in a three dimensional periodic pattern, while non-crystalline minerals are lacking this structural periodicity. Most mineral structures are bonded with ionic and covalent bonds to form coordinated polyhedrons with a unique composition and inter-atomic distance characteristics, which affect their overall physicochemical behavior. Ionic substitutions occurring within the mineral crystal lattice and broken bonds exposed on structural edges result in net positive or negative surface charge that plays an important role in adsorption/desorption processes critical for plant nutrient availability and environmental contaminant remediation. The nature of counter ions neutralizing the surface charge also has important ramifications on dispersion/flocculation phenomena impacting soil erosion, land stability, and groundwater quality.

## **2. Classification and Distribution of Minerals**

Minerals are divided into eight classes depending upon their chemical composition, and specifically their dominant anion or anionic group. The classes include:

- native elements;
- sulfides;
- oxides and hydroxides;

- carbonates, nitrates, and borates;
- sulfates, chromates, and molybdates;
- phosphates, arsenates, and vanadates; and
- silicates.

These classes are subdivided further according to chemical and structural similarities. Some of them, such as the native elements, nitrates, borates, chromates, molybdates, arsenates and vanadates, are rarely found in soil environments. Silicate minerals dominate in most soils.

Soil minerals are also referred to as primary and secondary minerals. Primary minerals have not experienced significant chemical or structural alteration since their crystallization within igneous or metamorphic rocks or their deposition in sedimentary rocks. They are inherited from the parent material, and are usually found in the sand and silt fraction of soils. Common primary minerals in soil environments include: silicates, oxides of iron (Fe), zircon (Zr) and titanium (Ti), and phosphates (P).

Secondary minerals are re-crystallized or transformed products of the chemical breakdown and/or alteration of primary minerals under ambient conditions. Secondary minerals are mainly found in the clay and fine-silt fractions because the particle size of primary minerals usually decreases during weathering. Typical secondary minerals found in soils include aluminosilicates, oxides and hydroxides, carbonates, sulfates, and amorphous minerals.

The separation of soil minerals in primary and secondary classes is not necessarily mutually exclusive since some of the minerals can occur in both classes (quartz, mica, carbonates). Non-silicate minerals commonly found in soil environments are listed in Table 1, while silicate minerals are shown in Figure 1.

Mineral class	Mineral	Chemical formula
Halides	Halite	NaCl
Sulfates	Gypsum	CaSO <sub>4</sub> • 2H <sub>2</sub> O
	Jarosite	KFe <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
Sulfides	Pyrite	FeS <sub>2</sub>
Carbonates	Calcite	CaCO <sub>3</sub>
	Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>
	Trona	Na <sub>2</sub> CO <sub>3</sub> • NaHCO <sub>3</sub> • 2H <sub>2</sub> O
Phosphates	Apatite	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (OH, F, Cl)
Oxides and hydroxides		
Aluminum	Gibbsite	Al(OH) <sub>3</sub>
Iron	Hematite	Fe <sub>2</sub> O <sub>3</sub>
	Goethite	FeOOH
	Lepidocrocite	FeOOH

	Maghemite	$Fe_2O_3$
	Ferrihydrite	$Fe_5O_7(OH) \cdot 4H_2O$
	Magnetite	$Fe_3O_4$
Manganese	Birnessite	$(Na, Ca, Mn^{2+}) Mn_7O_4 \cdot 2.8H_2O$
	Lithiophorite	$LiAl_2Mn_2^{4+}Mn^{3+}O_6(OH)_6$
	Todorokite	$(Na, Ca, K)_{0.3-0.5}(Mn^{4+}, Mn^{3+})_6O_{12} \cdot 3.5H_2O$
Titanium	Rutile	$TiO_2$
	Anatase	$TiO_2$
	Ilmenite	$Fe^{2+}TiO_3$

Table 1. Common non-silicate soil minerals (Source: Dixon and Schultze, 2002).

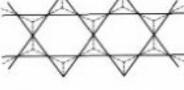
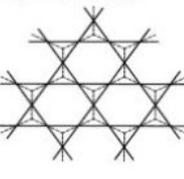
Silicate class, unit composition, arrangement of SiO <sub>4</sub> tetrahedra	Mineral	Ideal formula
<b>Nesosilicates (SiO<sub>4</sub>)<sup>4-</sup></b> 	Olivine Forsterite Fayalite Zircon Sphene Topaz Garnets  Andalusite Sillimanite Kyanite Staurolite Epidote	(Mg, Fe) <sub>2</sub> SiO <sub>4</sub> Mg <sub>2</sub> SiO <sub>4</sub> Fe <sub>2</sub> SiO <sub>4</sub> ZrSiO <sub>4</sub> CaTiOSiO <sub>4</sub> Al <sub>2</sub> SiO <sub>5</sub> (F, OH) <sub>2</sub> X <sub>2</sub> Y <sub>2</sub> (SiO <sub>4</sub> ) <sub>3</sub> , where X = Ca, Mg, Fe <sup>2+</sup> , Mn <sup>2+</sup> Y = Al, Fe <sup>3+</sup> , Cr <sup>3+</sup> Al <sub>2</sub> SiO <sub>5</sub> Al <sub>2</sub> SiO <sub>5</sub> Al <sub>2</sub> SiO <sub>5</sub> Fe <sub>2</sub> Al <sub>2</sub> O <sub>4</sub> (SiO <sub>4</sub> ) <sub>2</sub> (OH) <sub>2</sub> Ca <sub>2</sub> (Al, Fe)Al <sub>2</sub> O <sub>6</sub> (SiO <sub>4</sub> ) <sub>2</sub> (OH)
<b>Sorosilicates (Si<sub>2</sub>O<sub>7</sub>)<sup>4-</sup></b> 		
<b>Cyclosilicates (Si<sub>6</sub>O<sub>18</sub>)<sup>4-</sup></b> 	Beryl Tourmaline	Be <sub>3</sub> Al <sub>2</sub> (Si <sub>6</sub> O <sub>18</sub> ) <sub>3</sub> (Na, Ca)(Li, Mg, Al)(Al, Fe, Mn) <sub>3</sub> (BO <sub>3</sub> ) <sub>3</sub> (Si <sub>6</sub> O <sub>18</sub> ) <sub>3</sub> (OH) <sub>3</sub>
<b>Inosilicates (single chains) (SiO<sub>3</sub>)<sup>2-</sup></b> 	Pyroxenes Augite Enstatite Hypersthene Diopside Hedenbergite Pyroxenoids Wollastonite Rhodonite	(Ca, Na)(Mg, Fe, Al)Si <sub>2</sub> Al <sub>2</sub> O <sub>6</sub> MgSiO <sub>3</sub> (Mg, Fe)SiO <sub>3</sub> CaMgSi <sub>2</sub> O <sub>6</sub> CaFeSi <sub>2</sub> O <sub>6</sub> CaSiO <sub>3</sub> MnSiO <sub>3</sub>
<b>Inosilicates (double chains) (Si<sub>4</sub>O<sub>11</sub>)<sup>2-</sup></b> 	Amphiboles Hornblende  Tremolite Actinolite Cummingtonite Grunerite	(Ca, Na) <sub>4</sub> (Mg, Fe, Al) <sub>8</sub> Si <sub>8</sub> (Si, Al) <sub>8</sub> O <sub>22</sub> (OH) <sub>2</sub> (Ca, Mg, Si) <sub>4</sub> O <sub>11</sub> (OH) <sub>2</sub> Ca <sub>2</sub> (Mg, Fe) <sub>2</sub> Si <sub>4</sub> O <sub>11</sub> (OH) <sub>2</sub> (Mg, Fe) <sub>2</sub> Si <sub>4</sub> O <sub>11</sub> (OH) <sub>2</sub> Fe <sub>2</sub> Si <sub>4</sub> O <sub>11</sub> (OH) <sub>2</sub>
<b>Phyllosilicates (Si<sub>4</sub>O<sub>10</sub>)<sup>2-</sup></b> 	Micas Muscovite Biotite Phlogopite Chlorites  Clay minerals (selected) Talc Pyrophyllite Kaolinite Smectite Vermiculite Serpentines Antigorite Chrysotile	KAl <sub>3</sub> (AlSi <sub>3</sub> O <sub>10</sub> )(OH) <sub>2</sub> KMg <sub>3</sub> (Fe <sub>2</sub> AlSi <sub>3</sub> O <sub>10</sub> )(OH) <sub>2</sub> KMg <sub>3</sub> (AlSi <sub>3</sub> O <sub>10</sub> )(OH) <sub>2</sub> (Mg, Fe) <sub>3</sub> (Si, Al) <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> (Mg, Fe) <sub>2</sub> (OH) <sub>2</sub> Mg <sub>3</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> Al <sub>2</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> Al <sub>2</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> variable variable Mg <sub>3</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> Mg <sub>3</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>
<b>Tectosilicates (SiO<sub>2</sub>)<sup>0</sup></b> 	Feldspars Orthoclase Albite Anorthite SiO <sub>2</sub> Group Quartz Tridymite Cristobalite Zeolites Analcime Clinoptilolite Feldspathoids Nephelene	KAISi <sub>3</sub> O <sub>8</sub> NaAlSi <sub>3</sub> O <sub>8</sub> CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> SiO <sub>2</sub> SiO <sub>2</sub> SiO <sub>2</sub> NaAlSi <sub>3</sub> O <sub>8</sub> ·H <sub>2</sub> O (Na <sub>2</sub> K) <sub>2</sub> (Al <sub>2</sub> Si <sub>4</sub> O <sub>20</sub> )·24H <sub>2</sub> O Feldspathoids Nephelene (Na, K)AISiO <sub>4</sub>

Figure 1. Classification of silicate minerals (after Dixon and Weed, 1989).

Mineral occurrences in soil environments are the result of inheritance from parent materials, precipitation from soil solution (neof ormation), or alteration of existing minerals into new phases (diagenesis). Climatic changes have a paramount effect in these processes and in the overall distribution of minerals in soils of different regions, different soil horizons, and even different soil fractions. Therefore, the mineralogical composition of an individual soil is determined mostly by the make-up of the parent material(s), and the intensity and duration of the weathering regime.

Sand and silt fractions tend to be composed mainly of inherited primary minerals, while clay fractions are dominated by secondary minerals, either formed *in-situ* or transported from other environments. However, it is not unusual for carbonates, sulfates, secondary silica minerals, as well as Fe- and Al-hydroxides to be meaningful components of the coarse soil fraction, and for quartz, feldspars, and mica minerals to be present in clay fractions. Yet, the diversity of global weathering environments generates some distinct soil mineral distribution trends.

## 2.6. Sulfides

Pyrite ( $\text{FeS}_2$ ) is the most common mineral of this group, although it is found only in a few soils. It forms under prolonged anaerobic conditions typical in current-day or ancient wetlands, which explains its common association with coal deposits. Pyrite is unstable and weathers readily into other sulfate minerals and sulfuric acid under oxidizing conditions. The released acidity constitutes a serious environmental problem in reclaimed coal-mined areas and in drained pyritic soils.

## 2.7. Oxides and Hydroxides

The most common soil occurrences of this group are Fe and Al minerals, often referred to as sesquioxides (Schwertmann and Fitzpatrick, 1992). Typical representatives include: goethite, hematite, and gibbsite, which are abundant in intensely weathered tropical soils. They exhibit amphoteric surface charge properties depending on pH conditions. They also act as chemical binding agents playing an important role in soil aggregation and structural formation. The presence and abundance of Fe-minerals exert a significant influence on the color of the soil due to their pigmentation properties. Under oxidizing conditions, they exhibit brownish-yellow to bright-red hues, while under reducing conditions they turn gray due to  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  transitions. These color changes are used as soil development and wetness indicators in pedogenic (degree of weathering) and land use interpretations (soil drainage classes, septic systems, wetland delineations).

Manganese oxides and hydroxides are also commonly found in soils in the form of concentric brown/black nodules (Photo 1A) or black coatings of soil structural units, reflecting current or past periodic water saturation conditions. Birnessite and lithiophorite are the most prevalent Mn soil minerals. They are often associated with Fe-oxide minerals.

Another group of minerals found in small quantities in soils includes titanium oxides, such as rutile, anatase, and ilmenite. They are usually found in sand and silt fractions as

common accessory minerals of igneous and metamorphic rocks. Because of their increased weathering stability they are frequently used as pedogenic indicators of soil maturity and uniformity.

### 2.8. Halides, Sulfates and Carbonates

These mineral groups contain some of the most soluble soil minerals and are easily broken down by physical and chemical weathering. Therefore, they occur mainly in arid/semiarid regions or in immature soils where weathering is minimal. Halite (a mineral within the halide group), gypsum (Photo 1B), calcite, and dolomite constitute the most common soil occurrences. Their solubility decreases in the anionic sequence  $Cl > SO_4 > CO_3$ . Halite is found only in salt affected soils. Gypsum is also common in saline soils either under arid or hydromorphic conditions, but it could also form in weathering interfaces where sulfide and carbonate minerals dissolve.

Calcite and dolomite, while prevalent in arid and semiarid climatic zones can also be found in more diverse soil environments where the dissolution of calcareous parent materials provides opportunities for secondary carbonate formation in lower soil depths. These minerals are also introduced in soil environments through land management practices including liming.

### 2.9. Phosphates

Phosphate minerals are found in only a few soils, with the orthophosphate ion ( $PO_4^{2-}$ ) forming a tetrahedron as the basic structural unit. Apatite is the most frequently reported phosphate mineral of igneous or sedimentary origin. Along with their weathering products, usually Al- and Fe-phosphates, apatites are considered a natural source of P for plants.

### 2.10. Silicates

Silicates constitute the largest and most important group of soil minerals, comprising nearly 40% of the common minerals in the world. They occur as primary minerals resulting from the breakdown of parent materials or secondary minerals formed from weathering of primary minerals (Table 2). The fundamental structural building unit of silicates is the Si-tetrahedron, in which one  $Si^{4+}$  is coordinated with four apical  $O^{2-}$ . Different arrangements of individual Si-tetrahedra linked by shared  $O^{2-}$  form more complex structures, consisting of single tetrahedral (neso-silicates), double tetrahedral (soro-silicates), rings (cyclo-silicates), single or double chains (ino-silicates), sheets (phyllo-silicates), or three-dimensional frameworks (tecto-silicates) (Fig. 1).

Name	Chemical formula
	<i>Primary Minerals</i>
Quartz	$SiO_2$
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$
Biotite	$K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$

Feldspars	
Orthoclase	$\text{KAlSi}_3\text{O}_8$
Microcline	$\text{KAlSi}_3\text{O}_8$
Albite	$\text{NaAlSi}_3\text{O}_8$
Amphiboles	
Tremolite	$\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$
Pyroxenes	
Enstatite	$\text{MgSiO}_3$
Diopside	$\text{CaMg}(\text{Si}_2\text{O}_6)$
Rhodonite	$\text{MnSiO}_3$
Olivine	$(\text{Mg, Fe})_2\text{SiO}_4$
Epidote	$\text{Ca}_2(\text{Al, Fe})_3\text{Si}_3\text{O}_{12}(\text{OH})$
Tourmaline	$(\text{Na, Ca})(\text{Al, Fe}^{3+}, \text{Li, Mg})_3\text{Al}_6(\text{BO}_3)_3(\text{Si}_6\text{O}_{18})(\text{OH})_4$
Zircon	$\text{ZrSiO}_4$
Rutile	$\text{TiO}_2$
	<i>Secondary Minerals</i>
Clay minerals	
Kaolinite	$\text{Si}_4\text{Al}_4\text{O}_{10}(\text{OH})_8$
Montmorillonite	$M_x(\text{Al, Fe}^{2+}, \text{Mg})_4\text{Si}_8\text{O}_{20}(\text{OH})_4$ ( <i>M</i> = interlayer metal cation)
Vermiculite	$(\text{Al, Mg, Fe}^{3+})_4(\text{Si, Al})_8\text{O}_{20}(\text{OH})_4$
Chlorite	$[M\text{Al}(\text{OH})_6](\text{Al, Mg})_4(\text{Si, Al})_8\text{O}_{20}(\text{OH, F})_4$
Allophane	$\text{Si}_3\text{Al}_4\text{O}_{12} \cdot n\text{H}_2\text{O}$
Imogolite	$\text{Si}_2\text{Al}_4\text{O}_{10} \cdot 5\text{H}_2\text{O}$
Goethite	$\alpha\text{-FeOOH}$
Hematite	$\alpha\text{-Fe}_2\text{O}_3$
Maghemite	$\gamma\text{-Fe}_2\text{O}_3$
Ferrihydrite	$\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$
Bohemite	$\gamma\text{-AlOOH}$
Gibbsite	$\gamma\text{-Al}(\text{OH})_3$
Pyrolusite	$\beta\text{-MnO}_2$
Birnessite	$\delta\text{-MnO}_2$
Dolomite	$\text{Ca Mg}(\text{CO}_3)_2$
Calcite	$\text{CaCO}_3$
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Jarosite	$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$

Table 2. Common primary and secondary soil minerals (Source: Sparks, 2003).

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### **Biographical Sketch**

**A.D. Karathanasis** is an Endowed Professor of Soil Science at the Department of Plant and Soil Sciences of the University of Kentucky. He holds a PhD in Soil Science from Auburn University (1982) and a MS in Agronomy from the University of Nebraska (1978).

He has been involved for more than 22 years in teaching and research focusing on thermodynamic modeling of mineral weathering and pedogenic processes, mediation of contaminant transport by colloid particles, and wetland technology applications for water quality improvement. He is the author of more than 110 scientific journal publications and book chapters. He is a fellow of the American Society of Agronomy, a fellow of the Soil Science Society of America, a Fulbright Senior Scholar, and the recipient of the Soil and Water Conservation Society of America National Honor Award. He has served on numerous national and international scientific committees addressing soil mineralogy and pedology issues and has been an invited speaker in more than 30 national and international scientific conferences.