

The mineral fraction reaches up to 50% in volume of most soils. It is organized in particles, whose surfaces retain and exchange chemical elements and nutrients (cations and anions) by means of complex physical and chemical mechanisms.

Soil particles present various sizes ranging from boulders and stones to sand grains and clay minerals. Arbitrary conventions divide soils in 2 fractions: Skeleton:  $\emptyset > 2$  mm Fine earth (terra fina):  $\emptyset > 2$  mm

### Attemberg scale for particle diameters.



We divide 1 cube (side, 1 dm) in four (side 0.5 dm) and then in sixteen (side 0.25 dm). Then, the ratio surface/volume and the surface of contact with a liquid phase will increase progressively:





Surface =  $6^{*}(1)^{2} = 6 \text{ dm}^{2}$ Volume =  $(1)^{3} = 1 \text{ dm}^{2}$ Ratio S / V = 6 Surface =  $6^*(0.5)^2 = 1.5 \text{ dm}^2$ Volume =  $(0.5)^3 = 0.125 \text{ dm}^2$ Ratio S / V = 12



Surface =  $6^*(0.25)^2 = 0.375 \text{ dm}^2$ Volume = $(0.25)^3 = 0.0156 \text{ dm}^3$ Ratio S / V = 24

Specific surface is measured in m<sup>2</sup>/g and it is related to the size of the particle.

Please, bear in your mind this basic concept. It is of extreme importance when we observe the surface properties of soil particles, especially soil minerals.

### Specific surface for mineral type or mineral size

Mineral / size class	Specific surface (m² g⁻¹)	Method of measure
Coarse sand	0.01	Adsorption of N <sub>2</sub> at low temperature (BET*)
Fine sand	0.1	
Silt	1.0	
Caolinites	5-100	
Illites	100-200	BET
Vermiculites & mixed minerals	300-500	Adsorption of ethyleneglycol
Montmorillonite (Na saturated)	750	Adsorption of ethyleneglycol
Ozides & hydroxydes of Fe e Al	100-300	BET
Allofanes	1000	Includes internal and external surfaces

BET: Branauer, Emmet and Teller

#### Surface charge. Electric charge on soil particles derive from:

- Isomorphic substitution (*permanent charge*)
- Surface functional groups reactions with ions in soil solution (*variable charge*)

The charge is expressed in centimoles of charge per kilogram ( $\text{cmol}_{c} \text{ kg}^{-1}$  o  $\text{cmol}_{(+)} \text{ kg}^{-1}$ ). The *total net charge of the particle* is the result of at least 4 surface charge types and assumes positive, neutral or negative value as a function of the soil chemical conditions. The permanent charge is expressed as density of surface charge, i.e. the ratio between the layer charge and the surface area of the mineralogical cell unit. The charge of cation and anion adsorbed on the surface of soil particles determine the Cationic Exchange Capacity (CEC) and the Anionic Exchange Capacity (AEC), respectively.

Phyllosilicate	CEC cmol <sub>(+)</sub> kg <sup>-1</sup>	Surface density (T), (cmol <sub>(-)</sub> m <sup>-2</sup> )
Caolinites	3-20	2-6 x 10 <sup>-4</sup>
Illites	10-40	1-2 x 10 <sup>-4</sup>
Smectites	80-120	1-1.5 x 10 <sup>-4</sup>
Vermiculites	100-150	3 x 10 <sup>-4</sup>

### Non silicate minerals of soils

Class	Mineral	Chemical formula
Halides	Halite	NaCl
Sulphates	Gypsum	$CaSO_4 \cdot 2H_2O$
	Jarosite	KFe <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
Sulfides	Dolomite	FeS <sub>2</sub>
Carbonates	Nahcolite	CaCO <sub>3</sub>
	Trona	CaMg(CO <sub>3</sub> ) <sub>2</sub>
		NaHCO <sub>3</sub>
		$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$
	Soda	$Na_2CO_3 \cdot 10H_2O$

Class	Mineral	Chemical formula
Oxides & hydroxides		
Alluminum	Gibbsite	AI(OH) <sub>3</sub>
	Nordstrandite	AI(OH) <sub>3</sub>
	Boehmite	AIOOH
	Diasporo	AIOOH
	Corindon	$Al_2O_3$
Iron	Ematite	Fe <sub>2</sub> O <sub>3</sub>
	Goethite	FeOOH
	Lepidocrite	FeOOH
	Maghemite	Fe <sub>2</sub> O <sub>3</sub>
	Ferridrite	$Fe_5O_7(OH) \cdot 4H_2O$
	Magnetite	Fe <sub>3</sub> O <sub>4</sub>
Manganese	Lithiophorite	(AI,Li)MnO <sub>2</sub> (OH) <sub>2</sub>
	Birnessite	variable
	Hollandite	Ba <sub>2</sub> Mn <sub>8</sub> O <sub>16</sub>
	Pyrolusite	MnO <sub>2</sub>
	Todorokite	variable
	Manganite	MnOOH
Titanium	Rutile	TiO <sub>2</sub>
	Anatase	TiO <sub>2</sub>
	Ilmenite	FeTiO <sub>3</sub>

# Silicate minerals of soils and earth crust

Silicates are Silicon (Si) oxides whose structural units are *tetrahedrons* Si<sup>4+</sup>O<sub>4</sub><sup>8-</sup>  $\rightarrow$  (SiO<sub>4</sub>)<sup>4-</sup>.



Tetrahedrons are isolated or linked together by 1, 2, 3 or 4 apices to form structures more and more complex, ordered in classes.



sorosilicates



cyclosilicates



phyllosilicates

# Soil aggregate



Interparticle forces of attraction involved in aggregate formation

#### **Electrostatic forces**

(clay-clay, clay-oxide, clay-organic interactions):

- Positively charged edge of a clay negatively charged face of an adjacent mineral
- Positively charged sesquioxide film "sandwiched" between two negative clay mineral surfaces
- Positively charged groups (e.g. amino groups) of an organic molecule attracted to a negative clay mineral surface.
- Clay-polyvalent cation-organic anion linkages or "cation bridges". Very large anion (polyanion) may interact with several clay particles through cation bridges, positively charged edge faces or isolated sesquioxide film.

Interparticle forces of attraction involved in aggregate formation

van der Waals forces

(clay-organic interactions):

- Specific dipole-dipole attraction between constituent groups of an uncharged organic molecule and a clay mineral surface
- Non-specific forces between large molecules when in very close proximity, which are proportional to the number of atoms in each molecule (polysaccharides and polyuronide gums and mucilages on soil particles, *coat of paint*)

Cumulative frequency distributions of soil particle sizes in a typical clay, sandy silt loam and sandy soil





The mineral fraction reaches in average up to 50% in volume of most soils.

Soil minerals can be classified in *primary* and *secondary* minerals.

They usually present a crystalline structure but some also show a short-range order (amorfous state).

# Cell unit or mineralogical cell



In general, earth crust and soils are composed of only few elements. Oxigen (O) and Silicon (Si) represent most of the weight whereas Oxigen is almost 90% of the volume. Oxigen anions are closely packed together by much smaller cations occurring in the intersticial spaces.

Minerals are defined as natural homogeneous solids with definite chemical composition (usually not fixed) and ordered atomic packing.

#### Chemical bonds, ionic charge and ionic radius in soil minerals



Chemical bonds in mineral structures present a mixed behaviour in between ionic and covalent bond. Si-O bond is equally distributed (50 % each); Al-O bond results ~ 40% covalent and ~ 60% ionic.

Ionic radius of Oxigen is considered constant and equals 0.140 nm. Cation radius changes slightly according the mineral species to which belongs.