CHAPTER

2

CLASSIFICATION AND COMPOSITION OF CLAY CONSTITUENTS

Classification of clays by some rational basis into groups facilitates the convenient studies of its properties and application. Clays belonging to the same group have similarities in physical and chemical properties, and may be related to corresponding industrial and environmental applications. Chemical composition is one of the major criteria for classification of clays, along with internal structures, origin, natural occurrence etc.

2.1 INTRODUCTION

Most of the solid components of the Earth's crust, i.e. rocks, sediments, clays etc. are largely made up of various mineral species. A mineral species is defined as: *A naturally occurring, inorganic, homogeneous solid, having a definite (but not necessarily fixed) chemical composition and a fixed, ordered internal structure, i.e. crystalline*. This ordered internal structure is reflected in the external morphology when the mineral has a well *crystalline* form. When the crystalline form is not perceptible externally called cryptocrystalline, its crystalline nature can be detected by scientific analytical techniques like X-Ray Diffraction. Amorphous natural solids like coal, volcanic glasses etc. do not qualify as minerals. The abundance of any mineral in the Earth is decided by the availability of the constituent elements of the mineral in the earth's crust and also the stability of that mineral in the surface or near-surface environment.

Silicon and oxygen being the most abundant elements of Earth crust, *silicate, oxide* and *hydroxide* class of minerals are most commonly available

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there. Mineral classes are identified (anionic) by J.D. Dana as (i) Native elements, (ii) Sulphides, (iii) Oxides and hydroxides, (iv) Halides, (v) Carbonates, nitrates, borates, (vi) Sulphates, chromates, molybdates, (vii) Phosphates, arsanates, vanadates and (viii) Silicates.

The mineral groups are identified with similar chemical composition or internal structure e.g. when chemical composition is considered, both calcite ($CaCO_3$) and aragonite ($CaCO_3$) belong to the carbonate group. But, when crystal structures are considered, calcite belongs to Calcite group with many other carbonate minerals, like magnesite ($MgCO_3$), siderite ($FeCO_3$) etc. having similar hexagonal crystal structure. On the other hand, aragonite with orthorhombic crystal structure, belongs to aragonite group with cerrusite ($PbCO_3$) and strontianite ($SrCO_3$) etc.

Several groups with structural and chemical similarities are bunched together as mineral subclass. In silicate minerals the basic silica tetrahedral may form rings, sheets etc. forming different mineral subclasses like sorosilicates, sheet silicates etc. And the silicate subclass forms a mineral class. A particular mineral class have the same anion or anionic groups.

A prolonged weathering, erosion and disintegration of rock materials over the surface of Earth produce clays. The constituent minerals of clays are highly stable in the surface environment and resistant to chemical weathering. Clays may also contain a non-mineral part, e.g. amorphases and organic matter.

The clay constituents can be described as shown in Fig. 2.1.

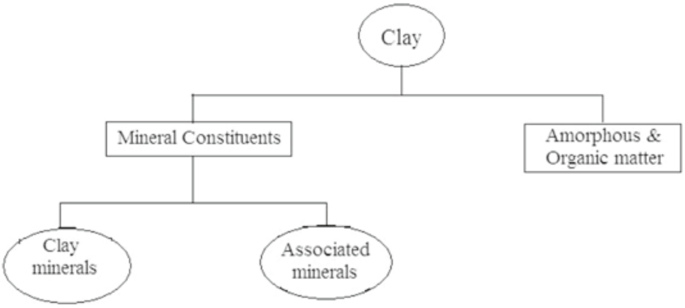

Fig. 2.1: Constituents of clay.

Table 2.1: Properties of clay and associated minerals

Minerals	*Properties*	*Drying/firing*	*Examples*
Clay minerals	Import plasticity	Hardens on drying/firing	Kaolinite, montmorillonite, illite, vermiculite, palygorskite etc.
Associated minerals	Do not import plasticity		Magnetite, hematite, maghemite, goethite, lepidocrocite gibbside, boehmite, diaspore.

2.2 CLASSIFICATION OF CLAY MINERALS

Clay minerals belong to the phyllosilicate subclass of silicate class. They have been abundantly studied by X-ray diffraction, which is the basic tool for their identification as it is difficult to observe without using electron microscope.

Let us know first about the silicate minerals and then the clay minerals in the silicate group. All silicate minerals have the anionic group $[SiO_4]^{-4}$ consisting of one Si^{+4} surrounded by four O^{-2}. The tetrahedron obtained by joining the centres of the four O^{-2} is known as $[SiO_4]^{-4}$ tetrahedron.

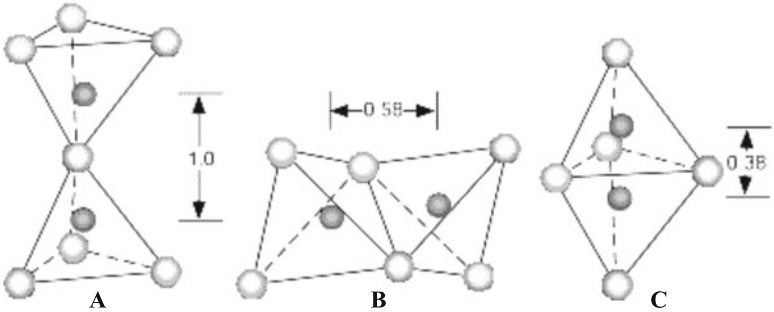

Fig. 2.2: Sharing of apical oxygen between SiO_4^{-4} tetrahedra. **A** (corner sharing) is stable. **B** (side sharing) and **C** (edge sharing) are not stable.

Each $[SiO_4]^{-4}$ tetrahedron has an unbalanced charge of – 4, which can be neutralized in the following two ways:

- **Bonding with cations:** An SiO_4^{-4} tetrahedral group can be bonded to cations. Generally bivalent cations like Mg^{+2}, Fe^{+2}, Ca^{+2} etc. are bonded to the tetrahedral group in common silicate minerals. The monovalent cations like Na^{+}, K^{+} and the trivalent cations like Fe^{+3} , Al^{+3} etc. are also common.
- **Linking of tetrahedra:** Two or more tetrahedra can be linked together by their apical oxygens. The O^{-2} that links two adjacent tetrahedra is known as *bridging oxygen*, and its charge is shared by two Si^{+4}. Different arrangements of linking of apical oxygens give rise to the different silicate subclasses, as discussed in Table 2.2.

Table 2.2: Description of some elements

Elements	*Description*
Apical oxygen	The unpaired oxygen in a tetrahedral sheet. These oxygens lie in a plane.
Basal oxygen	Any of the three shared oxygens in the tetrahedral sheet.
Sheet	The planes of atoms associated with either the Si/Al tetrahedra or the octahedra. Oxygens lying in the plane between the plane of Si and the plane of Al atoms are bonded to both sets of cations and are considered to be members of both sheets.

Subclass Nesosilicate: In this subclass, no apical oxygen of one SiO_4^{-4} tetrahedron is shared with other SiO_4^{-4} tetrahedra, i.e. no bridging oxygen in the tetrahedron. In this group the oxygens are shared with octahedral groups that contain other cations like Mg^{+2}, Fe^{+2} or Ca^{+3}. Common examples are olivines, garnets, Al_2SiO_5 minerals (andalusite, kyanite and sillimanite), staurolite, and sphene.

Subclass Sorosilicate: In this case, one of the apical oxygens of one tetrahedron is shared with another tetrahedron, i.e. one bridging oxygen in each tetrahedron. The basic structural unit is $Si_2O_7^{-6}$. Example: hemimorphite – $Zn_4Si_2O_7(OH) \cdot H_2O$.

Subclass Cyclosilicate (Ring Silicates): In cyclosilicates, two of the apical oxygens of each tetrahedron are shared with two adjacent tetrahedra, and the linked tetrahedra are arranged in a ring. The ring may be formed by linking of 3, 4, 5 or 6 tetrahedra, forming the structural units $Si_3O_9^{-6}$, $Si_4O_{12}^{-8}$, $Si_5O_{15}^{-10}$ and $Si_6O_{18}^{-12}$ respectively. In each case Si:O ratio is 1:3. Example: beryl – $Be_3Al_2Si_6O_{18}$.

Subclass Inosilicate – Single Chain: In this structure two apical oxygens of each SiO_4 tetrahedron are shared in a way to form a long single chain of linked tetrahedra. The basic structural unit of single chain inosilicates is $Si_2O_6^{-4}$ or SiO_3^{-2} with an Si:O ratio of 1:3. In some cases Al^{+3} can replace Si^{+4} in the tetrahedral site.

Subclass Inosilicate – Double Chain: In the double chain inosilicates, two parallel chains are linked together by their alternate tetrahedra. The basic structural group is $Si_4O_{11}^{-6}$. The amphibole group of minerals are double chain silicates, for example the tremolite-ferroactinolite series – $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_3$.

Subclass Phyllosilicates (sheet silicates): In this structure each SiO_4 tetrahedron is linked to three adjacent tetrahedra to form an infinite sheet of tetrahedra. Each tetrahedron in the sheet thus shares three (out of four) apical oxygens, having the basic structural unit $Si_2O_5^{-3}$. Some Si^{+4} of the tetrahedral site may be replaced by Al^{+3}, and the charge is balanced by inclusion of additional cations. The micas, clay minerals, chlorite, talc and serpentine minerals are examples of phyllosilicates.

Subclass Tectosilicates (framework silicates): The tectosilicates or framework silicates have a structure where all of the four oxygens of an SiO_4^{-4} tetrahedron are shared with four adjacent tetrahedra. The ratios of Si to O is thus 1:3. The basic structural group then becomes SiO_3. The minerals – quartz, cristobalite, tridymite etc. – are based on this structure. If some of the Si^{+4} ions are replaced by Al^{+3}, a charge imbalance is produced which is neutralized by incorporation of other cations in different coordination sites within the framework structure. Thus, the feldspar and feldspathoid minerals are also based on the tectosilicate framework.

The phyllosilicate subclass, like the other silicate subclasses, is divided into a number of groups, based on chemical and structural affinities. The mineral species belonging to six phyllosilicate groups show the properties specified in the definition of clay minerals. They are: kaolinite group, smectite group, illite group, vermiculite group, palygorskite-sepiolite group and mixed layer group.

2.3 ASSOCIATED MINERALS AND PHASES

Some minerals of silicate class and oxide and hydroxide class are stable in the environment prevailing at or near the Earth's surface, and they are resistant to chemical weathering. These minerals, when pulverised to very fine grain size by natural processes, classified as in Table 2.3, can be present as associated minerals in the clays. These minerals are not plastic when wet or harden by drying or firing; neither do they impart these properties to the clay. On the contrary, the plasticity of clay decreases as the proportion of associated minerals increases in them. Some associated minerals, especially the oxides and hydroxides of iron, imparts to clay some red or reddish-brown colour, which even persists after firing of those clays. Thus the increase of associated minerals decreases the economic value of clay. Some common associated minerals are listed below.

Table 2.3: Clay mineral groups

Mineral class	Silicate: SiO_4^{-4} tetrahedron is the basic structural unit of all silicate minerals in which each Si^{+4} is surrounded by four O^{-2} ions in tetrahedral coordination.
Silicate subclass	Phyllosilicate: In the structure of phyllosilicate, each SiO_4 tetrahedron is linked to three adjacent tetrahedra to form an infinite sheet of tetrahedra. Each tetrahedron in the sheet thus shares three (out of four) apical oxygens, having the basic structural unit $Si_2O_5^{-2}$. The micas, clay minerals, chlorite, talc and serpentine minerals are examples of phyllosilicates.

Clay Group

Kaolinite	*Smectite*	*Illite*	*Vermiculite*	*Palygorskite-sepiolite*	*Mixed layer*
Kaolinite, Dickite, Nacrite, Halloysite, Lizardite	Montmorillonite, Beidellite, Nontronite, Hectorite, Sauconite	Illite, Glauconite, Brammallite, Wonesite	Trioctahedral vermiculite, Dioctahedral vermiculite	Sepiolite, Loughlinite, Falcondoite, Palygorskite	Aliettite, Kulkeite, Rectorite

Like iron oxides, Mn-oxides in the form of various mineral species are typical constituents of many clays and are formed by oxidation of Mn^{2+}, contained in low temperature solutions in the hypergene minerals.

Zeolites are microporous, crystalline solids with well-defined structures. Generally they contain silicon, aluminium and oxygen in their framework and cations. Many occur naturally as minerals, and are extensively mined in many parts of the world. Others are synthetic zeolites which have a porous structure that can accommodate a wide variety of cations, such as Na^+, K^+, Ca^{2+}, Mg^{2+} and others. These positive ions are rather loosely held and can readily be exchanged for others in a contact solution. Some of the more common mineral zeolites are analcime, chabazite, clinoptilolite, heulandite, natrolite, phillipsite and stilbite. An example of mineral formula is: $Na_2Al_2Si_3O_{10} \cdot 2H_2O$, the formula for natrolite. Natural zeolites form where volcanic rocks and ash layers react with alkaline groundwater. Zeolites are widely used in industry for water purification, as catalysts, for the preparation of advanced materials and in nuclear reprocessing. Their biggest use is in the production of laundry detergents. They are also used in medicine and in agriculture.

Laterites, the source of Al-ore exists largly in clay minerals. Gibbsite, bohemite, and diaspore are the Al-hydroxides which provide a major source of Al and Fe ores.

Table 2.4: Name and composition of oxides and hydroxides minerals

Name	*Composition*
Hematite	Fe_2O_3
Maghemite	Fe_2O_3
Goethite	FeOOH
Lepidocrocite	FeOOH
Corundum	Al_2O_3
Gibbsite	AlOOH
Boehmite	AlOOH
Diaspore	AlOOH

Table 2.5: Name and composition of phyllosilicates minerals

Name	*Composition*
Talc	$Mg_3Si_4O_{10}(OH)_2$
Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$
Muscovite	$KAl_2(Si_3Al)O_{10}(OH,F)_2$
Chlorite group minerals	

Table 2.6: Name and composition of tectosilicates minerals

Name	Composition
Quartz	SiO_2
Feldspar group minerals	

Table 2.7: Description of sheet silicate (some of which occurs in clay)

Group mineral	*Mineral*	*Formula*	*Crystallography*	*Transparency*
Serpentine	Antigorite	$Mg_6Si_4O_{10}(OH)_{10}$	Monoclinic	Translucent
	Chrysolite	$Mg_6Si_4O_{10}(OH)_{10}$	Monoclinic	Translucent
	Lizardite	$Mg_6Si_4O_{10}(OH)_{10}$	Monoclinic	Translucent
Clay	Montmorillonite	$(Ca,Na)0.2\text{-}0.4\ (Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2.nH_2O$	Monoclinic	Translucent
	Kaolinite	$Mg_3Si_4O_{10}(OH)_2$	Triclinic	Translucent
	Pyrophyllite	$Al_2Si_2O_5(OH)_4$	Triclinic	Translucent
	Talc	$Al_2Si_4O_{10}(OH)_2$	Triclinic	Translucent
	Illite	Mica like clay mineral	Triclinic	Translucent
Mica	Phlogopite	$KMg_3(AlSi_3O_{10})(OH)_2$	Monoclinic	Transparent; In thin sheets
	Annite	$KFe_3(AlSi_3O_{10})(OH)_2$	Monoclinic	Translucent
	Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	Monoclinic	Transparent In thin sheets
	Lepidonite	$K(Li,Al)_{2\text{-}3}(AlSi_3O_{10})(OH)_2$	Monoclinic	Translucent
	Margarite	$CaAl_2(Al_2Si_2O_{10})(OH)_2$	Monoclinic	Translucent
Chlorite	Clinochlore	$(Mg_5Al)(AlSi_3)O_{10}(OH)_8$	Triclinic	Transparent
	Chamosite	$(Fe_5Al)(AlSi_3)O_{10}(OH)_8$	Monoclinic	Translucent
	Nimite	$(Ni_5Al)(AlSi_3)O_{10}(OH)_8$	Monoclinic	Translucent
	Pennantite	$(Mn,Al)_6(AlSi)_4O_{10}(OH)_8$	Triclinic	Transparent

Table 2.8: Description of clay mineral group

	Montmorillonite	*Kaolinite*
Origin of name	From its original discovery at Montmorillon, near Limoges, France	The name of hill Chinese Kao-ling was the first source of kaolinite.
Structure and composition	The structure is based on groups of three layers: Single sheet of (Al, Mg) (O, OH)$_6$ octahedra are sandwiched between two sheets of SiO_4 tetrahedra. Montmorillonite is a member of the smectite group and forms solid solution with beidellite.	It is a layer silicate. It has a two-layers structure: Layers of $Al(O,OH)_6$ octahedra alternate with sheets of SiO_4 tetrahedra. Several minor substitutions are possible: Alkalis or alkaline earth may be present, as well as excess H_2O.
Habit	Earthy masses are typical	It is usually massive or a fine grained aggregate: rare platy, pseudohexagonal crystals have been found.
Crystallography	Monoclinic, $a = 5.17$, $b = 8.94$, $c = 15.20$, $\beta = 90°$, $Z = 2$	Triclinic, $a = 5.15$, $b = 8.92$. $c = 7.38$, $\alpha = 90.8°$, $\beta = 104.8°$, $\gamma = 90°$, $Z = 2$

(*Contd.*)

Table 2.8 (*Contd.*)

	Montmorillonite	*Kaolinite*
Hand Specimen Identification	When massive, they are earthy if wet, and appear as soft, very fine grained aggregates if dry.	Clay-like properties, including softness, habit, feel and earthy smell, help identify kaolinite.
Physical properties		
Colour	White, gray	White
Transparency	Translucent	Translucent
Lustre	Dull	Dull
Cleavage	Perfect {001} rarely visible	Perfect (001)
Fracture	Irregular	Rarely seen
Hardness	1-1$^{1/2}$	2-2$^{1/2}$
Specific gravity	2.0-2.7	2.6
Optical properties	Optical properties are highly variable due to variable chemistry and crystallinity.	Optical identification of kaolinite is very difficult. Biaxial (-), $\alpha = 1.556$, $\beta = 1.563$, $\gamma = 1.565$, $\delta = 0.007$, $2V = 40°$
Occurrence and associations	Clays are secondary minerals, often residual, formed by alternation of Al-rich silicates.	It is common rock-forming secondary mineral, forming after aluminous silicates, component of soils and replaces feldspar in rocks undergoing weathering. Associated mineral is quartz.

Table 2.9: Description of clay mineral group

	Pyrophyllite	*Talc*
Origin of name	From the Greek pyro and phyllon, meaning "fire" and "leaf", in reference to this mineral's behaviour when heated.	From the Arabic talq, meaning "pure".
Structure and composition	The three layered structure consists of individual sheets of $Al(O,OH)_6$ octahedra sandwiched between sheets of SiO_4 tetrahedra. Fe may replace some of Al: minor Mg, Ca and Na may be present.	Talc is isostructural with pyrophyllite, being composed of layers of SiO_4 tetrahedra. It may contain some Ti, Ni and Fe.
Habit	Individual crystals are unknown. It is usually massive and foliated, sometimes forming platy or radiating masses.	Rare tabular pseudohexagonal crystals have been found, but talc is usually very fine grained and massive.
Crystallography	Triclinic, $a = 5.16$, $b = 8.96$, $c = 9.35$, $\beta = 100.37°$, $\alpha = 90.03°$, $\gamma = 89.75°$, $Z = 2$	Monoclinic, $a = 5.29$, $b = 9.10$, $c = 18.81$, $\beta = 100.00°$, $Z = 4$

(*Contd.*)

Table 2.9 (*Contd.*)

Hand specimen identification	Greasy feel and cleavage help identify pyrophyllite, but it can't be told from other clays without X-ray data.	Greasy feel, massive habit, cleavage and association help identify talc.
Physical properties		
Colour	White	Grey, white
Streak	White	White
Transparency	Translucent	Translucent
Lustre	Pearly	Silky
Cleavage	Perfect basal (001)	Perfect basal (001)
Fracture	Not seen	Flexible
Hardness	1-2	1
Specific gravity	2.8	2-8
Optical properties	High birefringence, perfect cleavage, bird's-eye maple appearance and lack of colour identify pyrophyllite. Biaxial (-), $\beta = 1.588^\circ$, $\alpha = 1.553^\circ$, $\gamma = 1.600$, $\delta = 0.047$, $2V = 52^\circ\text{-}62^\circ$	Talc is similar to muscovite, chlorite and pyrophyllite, but has a smaller $2V$ and often appears smeared or poorly defined when viewed under crossed polars. Biaxial (-), $\beta = 1.58^\circ$, $\alpha = 1.54^\circ$, $\gamma = 1.58$, $\delta = 0.05$, $2V = 6^\circ\text{-}30^\circ$
Occurrence and associations	Pyrophyllite is found in low- and medium-grade metamorphosed shales. Associated minerals include kyanite, feldspar and quartz.	Talc is a primary mineral in some low-grade metamorphic rocks, including marbles and ultramafic rocks, and less commonly a secondary mineral in mafic igneous rocks.

Concluding Remarks

Industrial and environmental applications of a particular type of clay depend on its physical and chemical properties, which in turn are determined by its chemical composition and internal structure. This chapter prepares a background for such studies.

QUESTIONS

1. How will you distinguish the following minerals?
   (a) Kaolinite and montmorillonite
   (b) Talc and pyrophyllite

2. Differentiate between clay and clay mineral and explain elaborating the constituents and phases of clay.

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