SECTION 1: CLAY MINERALOGY

1.1. *INTRODUCTION/ABSTRACT*

Clay minerals belong to the phyllosilicate family of minerals, which are characterized by their layered structures composed of polymeric sheets of silica tetrahedra attached with octahedral sheets. Research on clay minerals has received considerable attention because of their natural prevalence, reactivity, low cost, nonhazardous nature in handling, etc. Clay minerals have been widely investigated for their significance in various environmental, industrial, and geological settings. In this review, we will discuss the four major groups of clay minerals (kandite, illite, smectite, and vermiculite) as well as some other minerals in this family. This chapter summarizes the types, structural chemistry, and characteristics of various clay minerals; describes their emerging role in the immobilization of hazardous heavy metals and organic contaminants; highlights their significance in natural and engineered environments to reduce and manage mobilization of toxic metals; and partially elucidates the role of clay minerals for the sequestration of carbon dioxide at geological carbon sequestration sites.

1.2. FULL EXPLANATION

Clay minerals are a diverse group of hydrous layer aluminosilicates that constitute the greater part of the phyllosilicate family of minerals.They are commonly defined by geologists as hydrous layer aluminosilicates with a particle size <2 μm, while engineers and soil scientists define clay as any mineral particle <4 μm (*see* SOILS | Modern). However, clay minerals are commonly >2 μm, or even 4 μm in at least one dimension. Their small size and large ratio of surface area to volume gives clay minerals a set of unique properties, including high cation exchange capacities, catalytic properties, and plastic behaviour when moist.

According to britannica.com, in an article written by Hideomi Kodama, Clay mineral, any of a group of important hydrous aluminum silicates with a layer (sheetlike) structure and very small particle size. They may contain significant amounts of iron, alkali metals, or alkaline earths.

The term *clay* is generally applied to (1) a natural material with plastic properties, (2) particles of very fine size, customarily those defined as particles smaller than two micrometres (7.9×10^{-5} inch), and (3) very fine mineral fragments or particles composed mostly of hydrous-layer silicates of aluminum, though occasionally containing magnesium and iron. Although, in a broader sense, clay minerals can include virtually any mineral of the above-cited particle size, the definition adapted here is restricted to represent hydrous-layer silicates and some related short-range ordered aluminosilicates, both of which occur either exclusively or frequently in very fine-size grades.

The development of X-ray diffraction techniques in the 1920s and the subsequent improvement of microscopic and thermal procedures enabled investigators to establish that clays are composed of a few groups of crystalline minerals. The introduction of electron microscopic methods proved very useful in determining the characteristic shape and size of clay minerals. More recent analytical techniques such as infrared spectroscopy, neutron diffraction analysis, Mössbauer spectroscopy, and nuclear magnetic resonance spectroscopy have helped advance scientific knowledge of the crystal chemistry of these minerals.

Clay minerals are composed essentially of silica, alumina or magnesia or both, and water, but iron substitutes for aluminum and magnesium in varying degrees, and appreciable quantities of potassium, sodium, and calcium are frequently present as well. Some clay minerals may be expressed using ideal chemical formulas as the following: $2SiO_2 \cdot Al_2O_3 \cdot 2H_2O$ (kaolinite), $4SiO_2 \cdot Al_2O_3 \cdot H_2O$ (pyrophyllite), $4SiO_2 \cdot 3MgO \cdot H_2O$ (talc), and $3SiO_2 \cdot Al_2O_3 \cdot 5FeO \cdot 4H_2O$ (chamosite). The SiO_2 ratio in a formula is the key factor determining clay mineral types. These minerals can be classified on the basis of variations of chemical composition and atomic structure into nine groups: (1) kaolin-serpentine (kaolinite, halloysite, lizardite, chrysotile), (2) pyrophyllite-talc, (3) mica (illite, glauconite, celadonite), (4) vermiculite, (5) smectite (montmorillonite, nontronite, saponite), (6) chlorite (sudoite, clinochlore, chamosite), (7) sepiolite-palygorskite, (8) interstratified clay minerals (e.g., rectorite, corrensite, tosudite), and (9) allophane-imogolite. Information and structural diagrams for these groups are given below:

Kaolinite is derived from the commonly used name *kaolin*, which is a corruption of the Chinese Gaoling (Pinyin; Wade-Giles romanization Kao-ling), meaning “high ridge,” the name of a hill near Jingdezhen where the occurrence of the mineral is known as early as the 2nd century BCE. Montmorillonite and nontronite are named after the localities Montmorillon and Nontron, respectively, in France, where these minerals were first reported. Celadonite is from the French *céladon* (meaning grayish yellow-green) in allusion to its colour. Because sepiolite is a light and porous material, its name is based on the Greek word for cuttlefish, the bone of which is similar in nature. The name *saponite* is derived from the Latin *sapon* (meaning soap), because of its appearance and cleaning ability. Vermiculite is from the Latin *vermiculari* (“to breed worms”), because of its physical characteristic of exfoliation upon heating, which causes the mineral to exhibit a spectacular volume change from small grains to long wormlike threads. Baileychlore, brindleyite, corrensite, sudoite, and tosudite are examples of clay minerals that were named after distinguished clay mineralogists—Sturges W. Bailey, George W. Brindley, Carl W. Correns, and Toshio Sudō, respectively.

Given the requirement of water, clay minerals are relatively rare in the Solar System, though they occur extensively on Earth where water has interacted with other minerals and organic matter. Clay minerals have been detected at several locations on Mars, including Echus Chasma, Mawrth Vallis, the Memnonia quadrangle and the Elysium quadrangle. Spectrography has confirmed their presence on asteroids including the dwarf planet Ceres and Tempel 1, as well as Jupiter's moon Europa.

1.3. DISTINCTIVE PROPERTIES

1.3.1. Clay minerals as electron acceptors and/or donors in organic reactions

The electron-accepting and the electron-donating sites of clay can be explained by the fact the electron acceptor sites are aluminium at crystal edges and transition metals in the lower valency state. The catalysed polymerizations involve the conversion of the organic molecule to a reactive intermediate; hence, the clay mineral accepts an electron from the vinyl monomer and a radical cation is formed, where the organic compound gains an electron and forms a radical anion.

The inhibition of polymerization processes involves the conversion of reactive organic intermediate, such as free radicals, which has been formed by heat or radical initiators, to non-reactive entities. An example of a thermal polymerization is illustrated by the loss of an electron from the free radical which gives a carbonium ion.

In predicting the electron-accepting or electron-donating behaviour, colour reactions on clay minerals are useful for the reason that it similarly proceeds with mechanisms of polymerization reactions. For example, a blue reaction of benzidine: here there is one electron transfer from the organic molecule to the electron-accepting sites in the mineral (aluminium edges, transition metals in the higher valency state).

In order to understand the many abilities of electron exchange of clay minerals, masking the crystal edge with polyphosphate destroys the electron-accepting properties of the crystal edges. This method is used to assess the control of the reactivity of the mineral and distinguish the crystal edge from the transition metal sites as electron-acceptor sites in the clay minerals. (Solomon, 1968)

1.3.2 Ion exchange and cation exchange capacity

When erosion, transport, and deposition take place, clay minerals react to change in the environment. Ion exchange, reconstruction of degraded mineral, and formation of one type clay-based mineral from another or simpler substance appear as a result of those processes. Exchange reactions are dominated by physicochemical laws and depend upon the clay mineral, the nature, and ion population of the exchange sites and on the concentration and the composition of the solution in which the clay mineral is found. However, the increase in salinity when in a marine environment results in a decrease in the total exchange capacities of clay mineral when clay enters the sea. So the crystal chemistry of clay mineral is considered when exchange of cations takes place. Interlayer water cations and layer charge appear to be particularly important in the understanding of selective adsorption and fixation in the process of cation and ion exchange (Gillott, 2012).

1.3.3 Swelling behaviour

Clay mineral swelling is dependent on clay mineral type, the electrolyte concentration, and the nature of the cations in the solution. The swelling mechanism can be divided into mechanical and physicochemical processes. Through burial diagenesis, expandable layers are removed in the clay mineral structure such that inter and intralayer swelling of expandable clay mineral types can be expected to be at a minimum in older rocks than in younger rocks. Mechanical swelling occurs in response to elastic and time-dependent stress unloading, which can be brought by man in digging excavations or by nature in tectonic uplift and erosion because the clay is free to expand in the vertical direction but not in the horizontal direction. On the other side, physicochemical swelling is governed by intrinsic effective stress which commands the size disparity between larger, inter-aggregate voids and smaller intra-aggregate voids within clay mineral domains and between clay minerals themselves, all those forces which exist in a clay–electrolyte system subject to unloading after water had entered the system in response to mechanical cause (Taylor & Smith, 1986).

1.3.4 Adsorptive and low permeability properties

As absorptive material, there are three ways clay minerals and clay-based minerals can exert non-covalent adsorptive power on various molecules from liquid to gaseous states. Firstly, physical adsorption: there is non-ionic adsorption onto the surfaces of finely divided material (large surface areas of clay minerals are comprised in small volumes), secondly ion exchange adsorption through electrostatic interaction and exchange, and finally, the inclusion of small molecules in pore or cavities, and partial or complete exclusion of larger molecules by those cavities through the zeolitic adsorption action. (Giese & van Oss, 2002). Permeability properties of clay minerals can be explained by the type and distribution of the clay minerals within the pore system**.** Generally, in rocks which are predominantly argillaceous, permeability is low. The mineralogy of different types of rocks semi-permeable in nature gives a noticeably different set of chemical parameters, whereas low to medium permeability can be assimilated to a closed system where rocks and fluid are effectively part of the same physicochemical unit.

SECTION 2: GEOLOGY OF NIGERIA

2.1. INTRODUCTION/ABSTRACT

The geology of Nigeria formed beginning in the Archean and Proterozoic eons of the Precambrian. The country forms the Nigerian Province and more than half of its surface is igneous and metamorphic crystalline basement rock from the Precambrian. Between 2.9 billion and 500 million years ago, Nigeria was affected by three major orogeny mountain-building events and related igneous intrusions. Following the Pan-African orogeny, in the Cambrian at the time that multi-cellular life proliferated, Nigeria began to experience regional sedimentation and witnessed new igneous intrusions. By the Cretaceous period of the late Mesozoic, massive sedimentation was underway in different basins, due to a large marine transgression. By the Eocene, in the Cenozoic, the region returned to terrestrial conditions.

Nigeria has tremendous oil and natural gas resources housed in its thick sedimentary basins, as well as reserves of gold, lead, zinc, tantalite, columbite, coal and tin.

2.2.Stratigraphy, Tectonics & Geologic History

The oldest Precambrian rocks in Nigeria likely formed during the Archean or the Paleoproterozoic, forming the Beninian gneiss, in the Benin-Nigeria Orogen, formed during the Proterozoic Pan-African orogeny. The crystalline basement rock of the country is grouped as the Nigerian Province, a southern continuation of the central Hoggar reactivated basement.

The ancient rocks of the Nigerian Province are split up by thrust and shear zones. The Migmatite-Gneiss Complex covers half of Nigeria's surface area and encompasses Archean gray gneisses, with tonalite and granodiorite consistencies. Within this complex are occurrences of schist, migmatite, garnet, sillimanite, kyanite and staurolite, which together indicate high-grade metamorphism up to the level of amphibolite on the sequence of metamorphic facies. Granites are associated with charnockite bodies and granulite facies metamorphism.

The Migmatite-Gneiss Complex differs in the Ibadan area, in the southwest. Banded gneiss, schist and quartzite formed from the metamorphism of greywacke, shale and interbedded sandstones. Some amphibolite layers record the metamorphosed remains of a tholeiitic magma series. The early folding and metamorphism in the Ibadan area was followed by the emplacement of aplite schist and microgranodiorite dikes during the Liberian orogeny 2.75 billion years ago. More intense deformation followed 2.2 billion years ago during the Eburnean orogeny.

Metazquartzites in the Ibadan area, likely from the Proterozoic, are overlain by pelite schist, intruded by mafic sills rich in magnesium. They are overlain by Neoproterozoic pelites, including phyllite and both muscovite and biotite schists, as well as quartzites that form strike ridges in several parts of Nigeria.

Younger metasediments are found in the southwest and northwest in synclinorial schist belts. Compared to the surrounding migmatite-gneiss complexes, these low-grade metamorphic rocks have isoclinal folding and steeply dipping foliation. They have faulted and sheared boundaries with the surrounding rock.

Geologists have interpreted these schist belts the remains of paleo-rift systems. The Pan-African orogeny in the late Proterozoic affected all of the Archean and Paleoproterozoic rocks in the region. Continent-continent collision and eastward subduction affected the southern Trans-Saharan mobile belt and emplaced granitoids throughout the Nigerian Province. In Nigeria, Pan-African orogeny related granite, syenite and diorite intrusions formed between 700 and 500 million years ago and are known as the Older Granites.

Paleozoic (541-251 million years ago)

In the Cambrian, at the beginning of the Paleozoic, volcanic debris filled molasse grabens, forming dacite and shoshonite, as the Older Granites continued to emplace. In some cases, granite intrusions formed large batholiths and charnockite. The end of the Pan-African orogeny was also accompanied by the intrusion of basalt and dolerite dikes.

Mesozoic (251-66 million years ago)

In the Mesozoic, during the Jurassic, ring complexes known as the Younger Granites intruded Neoproterozoic and Paleozoic basement rocks in the Jos Plateau, as well as in the Air region in Niger. The Younger Granites are primarily alkali-feldspar granites, although the ring complexes also include rhyolite, gabbro and syenite. The ring dikes tend to be highly mineralized and enriched in niobium and tin.

Large sedimentary basins formed in southern Nigeria, divided by the Okitipupa Ridge. The basins did not begin to fill with sediment until the Albian age of the Cretaceous. In the southeast, poorly bedded sandy shale alternates with layers of sandstone and sandy limestone, containing ammonite, radiolarian, echinoid and gastropod fossils. Subsequently, some of these sedimentary rock layers experienced lead and zinc mineralization.

The arkose sandstone, limestone and shale of the 600 meter thick Odukpani Formation formed during the Cenomanian until the early

Turonian, in the vicinity of modern-day Calabar. Fish teeth, ammonites and echinoids date the Eze-Aku Formation to the Turonian, while the blue-gray shales and marl limestone of the Awgu Formation dates to the Coniacian. During the Santonian age of the Cretaceous, sea levels dropped. However, by the Campanian and the Maastrichtian, the Nkporo Formation records shale, mudstone, limestone and sandstones formed in an offshore environment. In other parts of Nigeria, the Owelli Sandstone, Enugu Shale and Asata Shale formed around the same time in shallow water environments. Other formations of similar age include the ammonite-bearing coals of Mamu Formation and the Nsukka Formation, both from the Maastrichtian.

The Maastrichtian age brought a large marine transgression to southwest Nigeria, depositing the Abeokuta Formation. The Iullemeden Basin, also known as the Sokoto Basin spans Mali, western Niger, northwest Nigeria and northern Benin and began accumulating sediments in the Jurassic, followed by the Maastrichtian Rima Group, which records a brackish environment. Approximately one-tenth of the Chad Basin is situated in Nigeria. Albian Bima sandstone lie unconformably atop Precambrian basement rock, followed by the Turonian limestone and shale sequences of the Gongila Formation. Marine shales of the Fika Formation formed during the Senonian. The Maastrichtian brought a shift to an estuary environment, leading to the deposition of the Gombe Sandstones, which are intercalated with ironstone, siltstone and shales.

Cenozoic (66 million years ago-present)

High sea levels continued into the early Cenozoic. In the west, the Akinbo Formation and Ewekoro Formation both deposited in the Paleocene, while the Ino Formation took shape atop the Nsukka in the east, with layers of thick, clay shale. The Sokoto Group in the Iullemeden Basin contains marine sediments. However, by the Eocene, sea levels retreated and afterward Nigeria mainly experienced terrestrial sedimentation.

Around the end of the Cretaceous and the start of the Cenozoic, the sedimentary rocks in the Chad Basin were folded into anticlines and synclines. Erosion created an unconformity with younger rocks. Terrestrial sediments built up in the Paleocene Kerri Kerri Formation, followed by Pliocene lake sediments of the Chad Formation.

2.3.Hydrogeology

Unconsolidated sediments 15 to 30 meters thick line the Niger and Benue rivers and are recharged from rainwater, along with the near surface, shallow aquifers of the Niger Delta Basin and the partially consolidated Benin Formation. In central and eastern Nigeria, regional occurrences of volcanic rock contain groundwater in fractures, less than five meters deep.

Most of Nigeria's large sedimentary basins have intergranular flow, rainwater recharge and few water quality issues. Within the Chad Basin, the Chad Formation is unconfined in some locations, with artesian flow from some deeper layers and a water table depth of 10 to 15 meters. The Gombe Sandstone is comparatively low permeability and the deeper Kerri-Kerri Formation remains poorly studied. The water table in the Sokoto Group varies widely between 20 and 100 meters deep, unconfined near the surface and confined in lower layers of the Gwandu Formation. Within the Sokoto Group, the Wurno Formation has moderate yields and limited recharge, while the Gundumi Formation conglomerates are good aquifers, with artesian conditions, bounded by deeper clay layers. Other sedimentary aquifers include the Nupe Basin, Upper Benue Basin and Lower Benue Basin.

Precambrian crystalline basement rock supports regional aquifers in weathered zones, 10 to 25 meters thick, as well as in fractures. In particular, metasedimentary rocks often weather to be clay rich, forming aquitards

Natural resource geology

Nigeria has extensive natural resources and is the largest crude oil producer in Africa and 20 billion barrels of reserves. As such, petroleum is central to economy of Nigeria, producing 80 percent of government revenues and 95 percent of export earnings. Additionally, Nigeria has 2.6 trillion cubic meters of natural gas and a high overall gas to oil ratio. Seventy percent of both oil and gas resources are onshore.

The country also has extensive mineral deposits, although most are under-exploited. According to the Geological Survey of Nigeria Agency, Nigeria has some 34 known major mineral deposits across the country. Exploration of solid minerals like tin, niobium, lead, zinc and gold, goes back for more than 90 years, but there has been a world-wide scale production of tin and niobium only.[6]

Gold mines were active before World War II, extracting from crystalline basement rock in the northwest, but a combination of low gold prices and legal turmoil ended the industry, recently the demand for gold has gone up due its high prices and Gold can be found in commercial quantity in states like Osun, Zamfara and Cross River states in

Nigeria. The Younger Granites of the Jos Plateau contain significant tin deposits, mined since before European colonization. However, in recent years, tin mining has been significantly curtailed by flooding in the mines and low tin prices, as well as water pollution from the mines. Tantalite and columbite are both associated with the tin ore in the plateau.

The states of Anambra, Benue, Plateau and Taraba have small-scale lead and zinc mining, from deposits that also have large quantities of cadmium, arsenic and antimony. Barite veins commonly contain lead and zinc in Plateau State and other parts of eastern Nigeria. Kwara State has iron ore in Agbaja Plateau and Itakpe Hills.

Nigeria also has other resources useful for energy and construction, including a poorly understood lignite belt in the south, kaolin, gypsum and feldspar. Coal mining provided much of the country's energy between 1915 and 1960, although the industry has been in a long-running decline, now providing energy only for small-scale kilns and smelters.

NOTE:This article is gotten from Wikipedia, the free encyclopedia.

Compiled by: Mas’ud Ayeola