

Chapter 2

Clay and Clay Mineral Definition

Abstract Any science, scientific field, or scientific domain requires a well-established and defined object of study as well as appropriate methodologies to develop knowledge about that object. However, over time the definition or concept of the object of study can undergo modifications and adaptations due to scientific advances, both in theoretical and experimental terms.

Clay science is multidisciplinary with the object of study both clay and clay minerals. It receives important contributions from other sciences or disciplines, such as mineralogy, crystallography, chemistry, geochemistry, sedimentology, geology, pedology, agronomy, soil mechanics, colloid chemistry, materials science, biology and biotechnology, medicine and public health, pharmacy, geoengineering, and environmental engineering. As in other sciences the object or objects of study referred to require a definition that would deserve general acceptance by all those interested in it, both theoretically and practically, despite the historical evolution of the concepts. Different from other sciences, the enormous diversity of the natural material denominated clay, in geological, compositional (physical, chemical, and physicochemical), and technological terms, as well as the enormous diversity of clay fields of interest and applications, may justify the lack of consensus on clay and clay mineral definition that is shown in this chapter.

2.1 Introduction

Through the ages clays have received definitions adapted to the state of knowledge at the time and the uses to which they were put. As universal materials they cannot be limited to only one definition. The vocabulary of every language is rich in characteristic and descriptive terms; all these minerals are common to all our activities. Near the word “clay,” a generic universal name is that of “earth,” associated with qualifying names such as potter’s clay, fire clay, or green clay. The term “clay” comes from the Greek word *argilla*, the root of which, *argos*, signifies “white,” the color of kaolin clay used in ceramics. The relation to purity was quickly established with this color even though most clays are not white.

Clay science is less than 100 years old, and during its evolution the definition of clay and clay minerals, the objects of study of this science, has shown significant changes that have been proposed, developed, and adopted by several authors and

clay groups or clay societies. Such changes were founded not only on basic but selective criteria heavily dependent upon the particular academic education and professional experience of the authors, for instance, soil scientists, mineralogists, geologists, or material scientists, and on scientific advances, particularly provided by the increasing capability of the analytical instrumentation and methodologies, informatics, and computing.

Clay occurs where we less expect (Moll 2001), not only in rocks of any type (sedimentary, igneous, metamorphic), but also dispersed in atmospheric aerosols (Sanfeliu 2002) and suspended in the water of oceans, seas, lakes, lagoons, and rivers (Gomes 1988). Naturally and industrially produced dusts can contain clay minerals, that could have deleterious effects on human health.

There are several types of clay based on geological, technological, and commercial arguments: primary or residual clay, secondary or sedimentary clay; swelling clay, plastic clay, absorbent clay, refractory clay, nanoclay, commercial special clay (ball clay, bentonite, kaolin, Fuller's Earth, fibrous clay, fire clay, flint clay), and commercial common clay (pottery clay, heavy clay). *Special clays* relative to *common clays* are characterized, as a rule, by the smaller number and size of the deposits, simpler composition (although requiring more complex and expensive processing), and higher commercial value of the manufactured products.

Clay is also a major constituent of the so-called *healing clays* and *edible clays*. Within the healing clays some are used solely for external applications with therapeutic and/or cosmetic purposes, either in the natural environment, or inside specialized spas, as are the cases of *natural peloids* and *peloids s.s. (stricto sensu)*. Other healing clays, the so-called edible clays, are used for internal or oral applications.

Each clay has its own *clay fraction* in which the clay particles and clay minerals—the essential constituents of clay—are more concentrated. Conventionally some disciplines set a maximum size for clay particles: pedology <2 μm ; geology, sedimentology, and geoenvironment <4 μm ; and colloid science <1 μm . However, the upper limiting size of an individual particle or crystal for clay minerals has not been established.

When the optical microscope was the only instrumental tool to analyze geological materials, that is, during the last decades of the nineteenth century and the first decades of the twentieth, clay was defined as an association of fine-grained minerals with particle diameters of less than 2 μm , that is, beyond the resolution of the optical microscope.

Earlier chemical analysis became a fundamental tool to determine the chemical composition of both clays and clay minerals, allowing the establishment of their typology. Soil science and colloidal chemistry and the development of analytical techniques, such as differential and gravimetric thermal analysis, transmission and scanning electron microscopy have contributed a great deal to the identification and quantification, as well as the explanation of clay and clay minerals' basic properties.

Starting with the third decade of the twentieth century X-ray diffraction became a powerful tool for investigating the structure of fine-grained materials, clay minerals

included, allowing the differentiation of clay mineral structures, an achievement fundamental to explaining their distinctive properties. Many other analytical methods that became available, such as scanning electron microscopy (SEM) associated with X-ray energy dispersive spectrometry (EDS), and synchrotron X-ray diffraction (SR-XRD), have played essential roles in modern clay research.

2.2 Definition, Classification, and Nomenclature of Clays and Clay Minerals

After the works of precursor researchers, both the AIPEA (Association Pour l'Étude des Argiles) and CMS (Clay Mineral Society) Nomenclature Committees have been involved for several years in the definition, classification, and terminology of clays, clay minerals, related materials, and specific properties. For instance, the AIPEA Nomenclature Committee has proposed several reports with recommendations: Brindley and Pedro (1970, 1972, 1976); Bailey (1980, 1982, 1989); Bailey et al. (1986); Guggenheim et al. (1997, 2002, 2006). Recommendations have also been proposed in joint reports of the AIPEA and CMS Nomenclature Committees: Guggenheim and Martin (1995, 1996), and by the CMS Nomenclature Committee: Brindley et al. (1968); Bailey et al. (1971a,b, 1979); Martin et al. (1991).

Despite the continued efforts of these nomenclature committees, the definitions of clay and clay minerals still are not unanimous. This can be understood because clay is most probably the mineral resource exhibiting the highest variability in geologic, textural, and mineralogical terms and the most diverse applications. Thus either the professionals or the disciplines interested in clay try to enhance the property or properties relevant for a particular application in its definition, situations well expressed by Gomes (1988, 2002):

1—Geologists consider clay as a geologic product of generalized occurrence and of fine granularity that occurs at the surface or near the surface of the Earth, and that is formed at the interfaces between the earth crust and the atmosphere, hydrosphere, and biosphere as the result of the mechanical and/or chemical alteration of rocks; also *geologists* classify clays on the basis of their origin and occurrence: residual or primary and sedimentary or secondary; marine, alluvial, glacial, eolian, etc.; *2—Mineralogists* consider clay as an aggregate or mixture of minerals of fine granularity, consisting principally of clay minerals, which are hydrous phyllosilicates based on Si, O, OH, H₂O, and that elements such as Al, Mg, Fe, K, Ca and Mg can participate on their composition; *3—Petrologists* consider clay as a rock, as a rule weakly consolidated, formed by very fine mineral particles non identifiable at naked eye or using a magnifying glass; *4—Sedimentologists* consider clay as a granulometric term that identifies the sediment fraction composed of particles with e.s.d. (equivalent spherical diameter less than 2 μm); *5—Civil and geotechnical engineers* consider clay as the less than 4 μm fraction of the soil and classify clays or clayey soils as swelling or non swelling, soft or hard, that is selecting the most relevant properties that should be taken into account when the foundation of housing and public construction works is based on them; *6—Ceramists* consider clay as a natural material that whenever mixed with water in adequate quantity becomes plastic allowing its workability and shaping, and that hardens and maintains the acquired shape after drying or firing; ceramists classify clays

on the basis of their plasticity, firing properties and uses: low plasticity, medium plasticity, high plasticity; white-burning, red-burning, high or low refractory; common clay (brick clay and pottery clay); special clay (china clay, fire clay, ball clay, fibrous clay); 7—*Pedologists* consider clay as the active fraction of the soil that comprises particles of colloidal size ($<0.1\ \mu\text{m}$) that results from the action of pedological processes upon rocks, and which are responsible for the reversible fixation of cations and anions, such as NH_4^+ , K^+ , PO_4^{3-} and NO_3^- , etc.; 8—*Agronomists* consider *clay* as being the colloidal fraction of the soil, important in terms of structure, texture and composition for vegetal fixation and growth; 9—even the *non educated people* consider clay as a type of earth that gets slippery when wet, and that could be moulded or shaped.

With regard to clay minerals' definition, classification, and nomenclature, over time there has been some controversy as well.

Clay minerals occur in rocks of all lithologies and ages. Also, clay minerals are common and important constituents of the fine fraction of clay as well as of the fine fraction of soils that are fundamental for life in general, and for human life in particular.

Clay minerals are fine-grained hydrous phyllosilicates, minerals of planar or nonplanar structures that could impart plasticity (if the right amount of water is added) and hardening (if dried or fired) to the clay in which they occur. Clay may contain other materials that impart plasticity and harden when dried or fired. Clay minerals are not defined a priori as fine-grained minerals because clays are fine-grained, but rather they may be of any crystallite size so that the term “clay mineral” is consistent with the definition of mineral, which is unrelated to crystallite size. The particle-size issue has been separated from the clay mineral definition.

As a rule, in addition to clay minerals, clay may contain the so-called *associated minerals* (silicates such as quartz and feldspar; carbonates such as calcite, oxides, and hydrated oxides of iron and aluminum such as hematite, goethite, and gibbsite), X-ray amorphous materials such as organic matter, and inorganic X-ray quasi-amorphous materials such as opal A and ferrihydrite.

The authors of this monograph, particularly as teachers and researchers, introduce here some information and comments with regard to the convergences and divergences one actually could face in the literature relative to the definitions of clay and clay minerals.

2.2.1 *Historical Retrospective Showing the Lack of Consensus on Clay and Clay Mineral Definitions*

A short historical retrospective follows, showing the lack of consensus with regard to clay and clay mineral definitions over the last 70 years.

Grim (1953), a pre-eminent founder of clay science, considers *clay* as:

... a rock term and also as a particle-size term; as a rock term, clay is a natural, earthy, fine-grained material which develops plasticity when mixed with a limited amount of water; as a particle-size term, the clay fraction is that fraction composed of the smallest particles,

which maximum size in geology in the Udden-Wentworth scale is 4 μm and in soil science is the soil separate comprising particles less than 2 μm , according to the Atterberg classification.

Mackenzie (1963) noted the inappropriateness of defining *clay mineral* as “any mineral which occurs in clay” inasmuch as, among several reasons, it would include many accessory minerals that are not characteristic of clay.

Bailey (1980) equated clay minerals with phyllosilicates. However, it is well known that some nonsilicate minerals can impart properties such as plasticity which are characteristic of clays.

Worrall (1982) considers clay as:

... an earth that forms a coherent sticky mass when mixed with water; when wet, this mass is readily mouldable but if dried it becomes hard and brittle and retains its shape; moreover, if heated to redness, it becomes still harder and is no longer susceptible to the action of water; clay is seldom pure, but the substance responsible for its characteristic properties is usually called the clay mineral or clay substance; in addition to the clay mineral, which as was said is the essential and preponderant substance, and so is responsible for the characteristic properties, a number of adventitious minerals, such as quartz, mica and iron oxides are present.

Wilson (1987), a soil scientist, considers that clays are “an important component of soils, where they exert a dominant influence on soil structure and plant nutrition”; also, he considers that one of the fundamental properties of clays is the electric charge on their unit particles, responsible for cations and/or anions sorption, on a reversible basis.

Gomes (1988), as said above, considers various clay concepts depending on the academic education as well as on the technical and professional preparation of those (geologists, pedologists, sedimentologists, mineralogists, petrologists, ceramists, chemists, geotechnists, etc.) interested in this important natural material and resource, either for its genesis, its properties, or for its diverse applications.

Weaver (1989) considers that the term “clay” should only be used in the textural sense to indicate “a natural geomaterial that is finer than 4 μm ”; he suggested the term “physils” for the whole family of phyllosilicates (including palygorskite and sepiolite) irrespective of grain size.

Millot (1964, 1970, 1989) considers clay as

... a very complex geomaterial; even in the case of being monomineralic clay is composed by a population of distinctive particles, in terms of composition and size, each particle being a population of microdomains; if changes take place in the environment where the particle occurs, each microdomain changes too and, consequently, that particle moves at a proper rate towards a new thermodynamic equilibrium; the dynamics of populations could be also applied to clays.

As mentioned above, in recent years the Nomenclature Committees of AIPEA (Association Internationale Pour l'Étude des Argiles) and of CMS (Clay Minerals Society) have made attempts to achieve the unification of the basic criteria that should be part of clay and clay mineral definitions.

For instance, those nomenclature committees through a joint report by Guggenheim and Martin (1995) introduced the following clay concept: “natural

geomaterial essentially composed of fine grained (e.s.d. $< 2 \mu\text{m}$) minerals, mainly hydrated phyllosilicates, the so-called clay minerals, that exhibits plastic behaviour in the wet state and that gets hard after drying and firing; associated to clay minerals other minerals can occur, the so-called non clay minerals, composing the coarser fractions, but they could be present in the fraction $< 2 \mu\text{m}$ too.”

One year later Guggenheim and Martin (1996) rationalized and reinforced the concept of clay:

... a naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden when dried or fired; although clay usually contains phyllosilicates, it may contain other materials, the so-called “associated phases” that can impart plasticity and harden when dried or fired or may include materials that do not impart plasticity and organic matter.

The term clay mineral refers to “phyllosilicate minerals which impart plasticity to clay and which harden upon drying and firing.”

It worthwhile noting that for the first time it is clearly said that plasticity is not a specificity of clay minerals.

According to Harben and Kuzvart (1996) clay means different things to different people, inferring that for the geologist the term “clay” may be used in three senses: (1) to designate particle size < 0.002 to 0.004 mm , (2) as a name for a group of minerals known as clay minerals, and (3) as a rock composed essentially of clay minerals.

Moore (1996) and Moore and Reynolds (1997) consider that particle size should be a key parameter in all definitions of clay, and consider that “in geology, sedimentology, and geo-engineering the size limit is commonly set at less than $4 \mu\text{m}$ e.s.d.”

Paquet and Clauer (1997) consider that clay and clay minerals are synonymous terms and distinguish two main types of clays and clay minerals on the basis of the layer charge of clay minerals: “(1) low activity clays or clays of the kaolin group containing phyllosilicates with neutral and slightly hydrated layers; (2) high activity clays or clays of the 2/1 group containing phyllosilicates with charged and more hydrated layers.” Other authors have the same understanding about the concepts of clay and clay mineral, that is, they consider both terms synonymous.

Velde and Druc (1999) consider clay as “a natural material composed of about 80% clay minerals and other fine-grained material of different mineral species; this material has a natural grain size of less than $2 \mu\text{m}$ in diameter.” Also, they consider clay minerals, “those particles smaller than $2 \mu\text{m}$ in diameter which have a specific structure, called a layer or sheet silicate; their grain size and particle structure gives them special physical properties; clay mineral particles form plastic phase in most materials used to make ceramics.”

Gomes (2002) distinguishes three concepts: *clay*, *clay mineral*, and *clayey material* or *clay-bearing material*. He considers clay as being “a natural material, mostly composed by fine-grained minerals, mainly hydrated phyllosilicates the so-called clay minerals; clay, in general, exhibits plastic behaviour and hardens after drying or firing; associated to clay minerals other minerals and non-minerals (inorganic and organic cryptocrystalline or amorphous compounds) can occur in clay.” Also

he considers clay minerals as being “phyllosilicates, essentially hydrous aluminosilicates, fundamental constituents of clay and accessory constituents of clayey rocks and clayey soils, responsible for clay plasticity and hardening after drying and firing.” Finally he considers clayey material or clay-bearing material as being “those geologic materials, such as shale, slate, phyllite, marl, marly limestone, lapilli tuff, hyaloclastic tuff, and soils that could bear clay minerals in significant quantity. Despite of some of these materials do not exhibit plasticity in the natural state they could be used, for instance, as ceramic raw materials after being finely ground or blended with other adequate minerals.”

Since 2002 *Clay Minerals*, the journal of the European Clay Groups, has changed its name to *Clay Minerals: Journal of Fine Particle Science*. With this title the journal extends the object of clay science to fine-grained minerals and nonminerals that can occur in nature associated with clays other than clay minerals.

Bergaya and Lagaly (2006) consider that the terms “clay” and “clay mineral” are difficult to define, and consider that there is, as yet, no uniform nomenclature for clay and clay mineral.

As a first approximation they consider “clay mineral” as “a class of hydrated phyllosilicates that participate in the fine-grained fraction of rocks, sediments, and soils.”

Nonetheless, a consensus about the definition of the clay science objects, clay and clay minerals, is being pursued by the Joint Nomenclature Committees of the AIPEA and CMS.

Distinctive parameters for clay and clay minerals should be taken into account in their concepts, well summarized by Bergaya and Lagaly (in *Handbook of Clay Science*, Elsevier, 2006). For clay: “natural; fine-grained ($<2\ \mu\text{m}$ or $<4\ \mu\text{m}$); phyllosilicates as main constituents; plastic; hardens on drying or firing.” For clay mineral: “natural and synthetic; any size; may include non-phyllosilicates; plastic; hardens on drying or firing.”

Size is not a distinctive property of a mineral species, which is characterized by a specific structure constructed on the basis of certain chemical elements (in some circumstances these basic chemical elements can be isomorphously replaced).

The same mineral species, for instance, quartz, an associated mineral frequently found in clays, can exhibit metric or submicron crystal sizes. It is well established that crystal size in the same clay mineral species is variable. Therefore, size is a parameter or criterion that should not be considered in clay mineral and clay definitions. Considering clay as a fine-grained geological material would be sufficient.

Much of our understanding of clay mineral structures is derived from XRD analysis of macrocrystalline forms of phyllosilicates, such as muscovite, chlorite, and vermiculite. These mineral species regardless of their crystal size are included in clay mineral systematics. However, could a $10\ \text{cm} \times 5\ \text{cm} \times 1\ \text{cm}$ crystal of phlogopite or vermiculite that does not occur in any clay deposit be considered a clay mineral?

Meunier (2006) considers that “clay minerals being the most abundant silicates formed at the Earth surface, whatever their origin are always of small grain size.” He puts forward the question of why the growth of clay minerals is limited to a few

micrometers or nanometers. Based on his experience and on information from published papers he considers that this specificity is related to particular structural aspects (order–disorder and crystal defects).

Any clay has its own *clay fraction* in which the clay particles and clay minerals—the essential constituents of clay—are more concentrated. Conventionally some disciplines set a maximum size for clay particles: pedology <2 μm ; geology, sedimentology, and geoengineering <4 μm ; colloid science <1 μm .

2.3 Definition of Kaolin and Kaolinite: Inconsistencies Shown in the Literature

2.3.1 Introduction

Concepts can be expressed differently by people from different educational backgrounds and experience. Concepts can also evolve over time.

The concept or definition of kaolin is a good example of such evolution and is of paramount importance for scientific, industrial, commercial, and legal purposes.

Kaolin, one highly valued industrial clay due to its specific functions, for instance, in paper and white ceramics (porcelain, sanitary ware, and porcelain stoneware tiles), could be one such weathering product. If the quantity of kaolin is scarce, for example, not over than 5–8% it would be more appropriate to talk of argillized rock or kaolinized rock instead of kaolin. However, if that quantity, for example, is over 50%, the ultimate product would behave as real clay.

The term “kaolin” is often defined and used differently in science than in industry and commerce. These differences may have legal implications.

In defining kaolin, some questions can be raised. Is kaolin a rock? Is kaolin a mineral? Is kaolin a clay? Is the term kaolin synonymous with the term kaolinite? Is the term kaolin synonymous with the term china clay? What properties must the clay exhibit in order to be called kaolin? Is kaolin only a geological product? Is kaolin a processed or an engineered product too? Is kaolin also a commercial good? Are all kaolins equal? Is the white color of both bulk and processed kaolin a fundamental property? Could other clays rich in kaolin minerals, such as the so-called flint clay, ball clay, and fire clay be considered kaolin as well? What definition of kaolin would meet the joint approval of academia, industry, and the governmental agencies competent to authorize both the exploration and exploitation of kaolin?

Attempts to answer these questions are presented in the following, as far as the aim of this paper is getting fulfilled.

Science privileges the fundamentals of kaolin as a geological product such as genesis, mineralogy, and chemistry.

Industry, on the other hand, privileges the properties of this important industrial mineral and product, such as color, mean grain size and grain size distribution, particle shape, chemical inertia, plasticity, viscosity, brightness, whiteness, opacity,

gloss, abrasiveness, and refractoriness. These properties can condition kaolin's manifold uses, markets, and prices.

Kaolin is an industrial product and thus, naturally, a commercial product as well. It is used in the form of certain functional grades, for instance, in ceramics, paper, paint, rubber, fiberglass, medicine, cosmetics, food additives, and agriculture. Commercial grades of kaolin are supplied and transported as dry powder, semi-dry noodle, or as liquid slurry. Recently kaolin has been incorporated into formulations, which as a spray, are applied to fruits and certain vegetables to repel or deter insect damage or to prevent sun scald.

An extensive review of the historical evolution of kaolin definition, from the launching of clay science up to the present time, is presented. This includes the fundamental geological, mineralogical, and technological properties of kaolin as defined by various authors, although not in a well-integrated way.

2.3.2 Background

In regard to kaolin geology, kaolin genesis is diverse and, consequently, the typology of kaolin occurrences/deposits is diverse too. Also, the typology, the volume, and the quality of a kaolin deposit determine the choice of both extractive and industrial processes as well as kaolin economics.

The expressions *kaolin deposit* and *kaolin occurrence* should have different meanings, kaolin deposit being applied only to a kaolin occurrence justified by volume and quality, at both industrial and economic scales, kaolin exploitation, processing, and commercialization.

Kaolin mineralogy and chemistry are fundamentals of kaolin quality, being decisive in terms of kaolin industrial applications and functions. Also their specific properties determine kaolin bulk color.

The white or near-white color in bulk and after drying and firing could be a decisive factor for many important industrial applications of kaolin. However, other types of clay can exhibit a white color (e.g., some deposits of bentonite from Kimolos Island, in the Cyclades, Greece). Even bulk kaolin can exhibit colors other than white or nearly white without being impeditive of certain industrial applications. In mineralogy it is well established that color is not a discriminating property of mineral species. Hence other basic arguments contemplating, for instance, kaolin genesis, mineralogy, and chemistry, common to all types and varieties of kaolin, should be considered.

The emphasis on one or more than one particular property greatly depends on the academic education or professional experience and interest of the individuals seeking a definition of kaolin able to deserve general acceptance.

As a result of all this, a consensual kaolin definition appears to be difficult to achieve.

The volume and quality of a kaolin deposit could be appropriate for its exploitation, but environmental, legal, and administrative factors could hamper such usage.

In Portugal, for example, the concession for exploration and exploitation of kaolin, a highly valuable special clay due to its multiple and specific properties as well as manifold industrial applications, is presently regularized by the so-called Mines' Law issued in 1990. This law is applied to rare mineral resources of high unit value such as gold, cassiterite, massive sulphides, and feldspar/quartz of pegmatite, which are considered to belong to the public domain. The competent authority that approves any proposal submitted for exploration and exploitation of these resources, kaolin included, is the Central Administration through the Department of Energy and Geology with headquarters in Lisbon. Such authority classifies kaolin as industrial rock and as special clay. This same situation has been in force since 1920.

Because in Portugal the adopted kaolin definition considers that raw kaolin is the white or nearly white alteration product of feldspar-rich rocks, this simple fact could be a decisive factor impeding kaolin exploration and exploitation.

On the other hand, the so-called Mineral Masses' law, currently called Quarries' law, governs or regularizes the exploration and exploitation of common mineral resources of low unit value, such as limestone, marble, granite, sand, and common clay, which are considered to belong to the private domain. The exploration and exploitation of these resources, ball clay included, are regularized by the Quarries' law and the competent authority that emits the required license is the local administration, through the county's municipality.

In several countries all mineral resources occurring in, on, or underneath the Earth's surface belong to the state. In China, for instance, a very important country where mineral resources are concerned, both exploration and exploitation of mineral resources depend upon government authorization.

Due to legal regulations not all mineral deposits, including kaolin deposits, despite their interesting reserves and quality, can be exploited, such as mineral resources located inside the so-called protected areas (e.g., agricultural, ecological, or cultural heritage areas), classified on the basis of their unique natural values, such as fauna, flora, agricultural potential, and cultural heritage. When kaolin deposits are not located inside protected areas, and even when the competent exploration and exploitation licenses have been issued, either the potential hazardous environmental impacts raised by nongovernmental environmental groups, or the protest of nearby living populations, could impede any exploration and mining works. And, when justice is involved any decision could be issued so late that the interest in kaolin exploration and exploitation works would disappear.

Kaolin is commonly referred to as "china clay" inasmuch as it was first discovered in China, the term kaolin being derived from *Gaoling* or *Kao-Ling*, meaning "High Hill," a site located near the town of Jingdezhen, in Jiangxi province. Use of the terms *china clay* and *kaolin* is not well defined, but in our opinion similarly to what happened in Kao-Ling, the term "china clay" should be restricted to primary kaolin, the in situ alteration product of the action of hydrothermal and/or weathering processes over feldspar-rich rocks.

All kaolin deposits and the corresponding industrial and commercial products are different. In fact, individual kaolin deposits and natural kaolins vary particularly

in many physical properties, which in turn influence kaolin end uses. For many years kaolin's white or nearly white color, both in the raw or bulk state and after firing, was a decisive parameter for kaolin selection in certain industrial applications, particularly in fine ceramics and paper. However, new applications have been found for kaolin, and new advances have been achieved in kaolin processing involving new refining and beneficiation methods, which made possible the use of raw kaolin that exhibits colors other than white. Effectively, kaolin exhibiting yellow, grey, and even other pale colors can be used in many other industrial applications, such as certain types of ceramics (earthenware, stoneware, sanitary ware, as well as wall and floor tiles of earthenware and stoneware), plastics (as filler), cement, paint (as extender), rubber, silico-aluminous refractories, and certain types of pharmaceuticals and cosmetics. Therefore, should the color be a limiting factor in kaolin definition? We do not think so. Properties other than color, such as genesis and composition (mineralogical and chemical), plasticity, and firing behavior should be decisive factors in kaolin definition.

The term kaolin has been applied not only to designate the rock-bearing kaolin minerals, kaolinite and halloysite being the most common kaolin minerals, but also to designate the industrially processed products in which kaolin minerals become concentrated and beneficiated through refining and beneficiation processes, as well as to designate the respective commercial products. However, other names are currently attributed to the rock-bearing kaolin minerals, including kaolinized granite, kaolinized gneiss, kaolinized anorthosite, kaolinized arkose, and kaolinite-bearing sand or clay.

The fundamental properties that make kaolin an industrially important mineral resource, also called industrial mineral, are as follows: chemical inertia within a wide range of pH (3–9), white or near-white color, low electrical and thermal conductivity, easy dispersion in water, low hardness and abrasiveness, high coating capacity when used as pigment, good binder capacity or adhesiveness, and high refractoriness.

Kaolin minerals (kaolinite, halloysite, dickite, and nacrite) are clay minerals; these are fine-grained hydrous phyllosilicates, characterized by planar or nonplanar structures, which are the essential minerals of any clay.

There are no two kaolin exhibiting equal properties. Experience shows that kaolin properties are influenced by the environmental formation and deposition conditions.

A clay-bearing significant amount of kaolin minerals should be called kaolin. Other kaolin minerals-bearing clays, such as ball clay, fire clay, and flint clay, could show similarities to kaolin, in terms of composition (mineralogical and chemical) and color (in the natural state or after firing), although in regard to other properties, for instance, plasticity, viscosity, green-strength, and refractoriness, they could show distinctive behavior. Some types and grades of these sedimentary clays could be called sedimentary kaolin, because the parent or source rocks could be the same as those in the original residual kaolin.

Ball clay deposits, in particular, are less abundant worldwide than kaolin deposits, but ball clay could be as important as standard kaolin in industrial applications.

In general, ball clay shows finer grain size and is of much higher plasticity than standard kaolin; also, its color can range from off-white to black, but after drying and firing, becomes white or near white.

The clays that have determined the origin of the term “ball clay” occur in deposits dating from the Lower Tertiary that fill sedimentary basins in Dorset and Devon, in southwest England. The weathering products from the surrounding deeply weathered uplands of Paleozoic granite and schist were washed and deposited in deltas and lagoons. The layered deposits consist of sand, sandy clay, and clay. Also, clay seams, more or less rich in carbonaceous matter, look brown or black. Kaolinite and illite are the essential clay minerals, but small amounts of interstratified illite–smectite, smectite, and chlorite can also be identified in some clay seams. The distinctive clay mineral assemblages indicate a wide range of ball clay properties, depending on the distinctive contribution of the sedimentation process of the weathering products of both granitic and schistose rocks, the kaolinite structural order being higher or lower, respectively. Therefore, should ball clay deserve to be redefined too? The Al_2O_3 content of some ball clay seams is within the range 30–34%, values typical of high-quality kaolin. Also the K_2O content of ball clay is around 2%, whereas the K_2O content of kaolin is around 1%.

Also, in the Lower Tertiary, sedimentary kaolin of distinctive typology was deposited in tectonic basins of northwestern Portugal, consisting of beds of sand bearing kaolin-rich matrix and ball clay-like beds do occur. In some ball clay seams pseudo-morphs of sillimanite and andalusite have been identified indicating the major contribution of weathered Silurian schistose rocks as source rocks. Also, the kaolinite found in these clay seams is classified as the D (disordered) type.

Ball clay and kaolin are essential components of formulations used in the manufacture of the same products, for instance, tableware, sanitary ware, and wall and floor tiles. Ball clay due to its relatively higher plasticity helps to shape the ceramic bodies, adding green-strength to the body before firing, whereas kaolin provides extra whiteness.

Kaolin could be named special clay, a term attributed to a particular type of clay only produced in a few countries from deposits of small to medium/large size, and characterized as having specific markets and commercially high unit price. The same happens with other kaolin minerals-bearing clays such as ball clay, fire clay, and flint or hard clay, as well as with bentonite, fibrous clays (sepiolite and palygorskite), and Fuller’s Earth.

Some treated and modified clays, such as acid-activated and organophillic bentonite, acid-activated kaolin, and synthetic clays could also be classified as special clays. But the so-called calcined kaolin, the product of heating natural kaolin at high temperatures in a kiln, could not be called kaolin. In fact, calcination alters the size and shape of natural kaolin, increases whiteness and hardness, and improves electrical properties. Calcination at 700–750°C produces metakaolin that can be used either to improve the dielectric properties of PVC cable insulation or used as a pozzolanic concrete additive. The product of kaolin calcination at around 1000°C can be used, especially when coated with silane, to improve both the mechanical properties and the chemical resistance of rubber.

Also, for instance, could ball clay, fire clay (also called *underclay* due to the geological position under coal seams), and flint or hard clay be considered kaolin for scientific, industrial, and legal purposes? In our opinion some particular qualities or grades of these clays, which are rich in kaolin minerals (consequently rich in Al_2O_3 , as a rule showing values higher than 30%), and poor in fine-grained staining impurities (iron oxides/hydroxides, titanium oxides, organic matter), should be considered as so. The associated minerals found in these clays are the same as commonly found in kaolin: illite/mica, chlorite, quartz, feldspar, iron oxides/hydroxides (hematite, goethite), titanium oxides (anatase and/or rutile), and organic matter. Therefore, an actual kaolin definition able to integrate the properties common to the above-mentioned geological products and raw materials, the object of many fundamental and applied studies and applications by academic and industrial professionals, would be rather convenient and interesting.

2.3.3 *Retrospective of Kaolin and Kaolinite Definition*

Concepts or definitions are never final. For instance, the definitions of mineral and mineral species have frequently changed during the long history of mineralogy (Povarennykh 1972; Nickel 1995, 1996). Therefore, changes of the kaolin definition have to be considered too, in spite of the relatively short history of clay science, in order to make the kaolin definition compatible with the advances achieved in both fundamental and applied clay science.

According to Ross and Kerr (1931) the name kaolin is a corruption of the Chinese term *kauling* meaning *high ridge*, the name of a hill near Jauchou Fu in China where the material was obtained for the manufacture of whiteware centuries ago. Also, according to the same authors, Johnson and Blake (1867) appear to have first clearly intended the name kaolinite for the “mineral of kaolin”.

The first appearance of the term “kauling earth” in a Chinese document was in 1604 AD (i.e., in the middle of the Ming dynasty), and the use of kaolin clay extracted in the Kauling mines located near the town of Chingtehchien, Kiangsi province, for whiteware (mainly porcelain) manufacture, has been documented since the seventeenth century (Chen et al. 1997). These authors consider that the name kaolin would be very likely derived from the name of the actual village Gaoling (Kauling). Also, the authors mention that the term kaolin was introduced in Europe by Père d'Entrecolles, a Jesuit missionary who, in 1712, sent kaolin samples to French authorities (Kuzvart 1977). Kauling mines were abandoned long ago, and presently kaolin is mined in the Dazhou residual deposits about 50 km to the northwest of Gaoling.

Ross and Kerr (1931) defined kaolin as “a rock mass which is composed essentially of a clay material that is low in iron and usually white or nearly white in colour; the kaolin-forming clays are hydrous aluminium silicates of approximately the composition $2\text{H}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ and it is believed that other bases if present

represent impurities or adsorbed materials; kaolinite is the mineral that characterises most kaolin.”

Grim (1968) defined kaolin as a “fine-grained rock having kaolinite as the main constituent mineral, which containing low iron content shows white or near white colour.”

Millot (1964) defined kaolin as “the clay rich in kaolinite, and that the true kaolin deposits are hydrothermal, and that the term kaolin was extended to deposits of sedimentary kaolin and kaolin resulting from atmospheric weathering.”

Patterson and Murray (1975) defined kaolin as a “clay consisting of substantially pure kaolinite or related minerals, that is naturally or can be beneficiated to be white or nearly white, will fire white or nearly white and is amenable to beneficiation by known methods to make it suitable for use in white ware, paper, rubber, plastics, paint, ink, and similar uses.”

Souza Santos (1975) defined kaolin as the “product of weathering or hydrothermal alteration of feldspar-bearing rocks.” The author stated that kaolin could be either formed in situ, the so-called primary or residual kaolin, or transported and redeposited, the so-called secondary or sedimentary kaolin. Also the author stated that in Brazil raw kaolin shows color variations: white, cream, yellow, or rose.

Kuzvart (1977) defined kaolin as a “rock characterized by a useful content of kaolin minerals.”

The AIPEA Nomenclature Committee (*in* Bailey 1980), in the classification of phyllosilicates with 1:1 and 2:1 layer types, recommended division into groups on the basis of electrical charge per formula unit, for instance, the group kaolinite-serpentine for 1:1 phyllosilicates. The subdivision of the group into two subgroups: subgroup kaolinite and subgroup serpentine, on the basis of dioctahedral and trioctahedral characteristics, has also been recommended.

Worrall (1982) defined kaolin “as one of two main groups of clay mineral or clays: kaolins and montmorillonites.” For the author the chemical composition of these clays was coincident with the chemical composition of their main representative clay minerals, kaolinite and montmorillonite. Also, the author classified clays into two types—residual and sedimentary—and considered other clays, ball clay and fire clay, close to kaolin (china clay) in chemical composition, but differing a great deal in other properties and application fields.

Wilson (1987) defined kaolin as “the clay which consists principally of the clay mineral kaolinite.”

López-Colmenar (1992) defined kaolin as “all massive rock containing a variable percentage of clay minerals of composition equal or approximate to the composition of kaolinite – $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ – easy to concentrate through the separation of the associated minerals”; in the case of its being a clayey rock, making the concentration of the hydrous aluminosilicates difficult and expensive, it is called *kaoliniferous* or *refractory clay* in Spain.

Manning (1995) considered kaolin (or china clay), ball clay, and bentonite as the “dominant industrial clays, due to their diverse and very important industrial applications.” The author defined kaolin as “chemically inert material that can be

prepared as a white powder specified (in part) according to its whiteness and brightness; in terms of genesis the author distinguished primary and secondary kaolinite deposits, including kaolin (china clay) in the primary deposits, and ball clay in the secondary deposits".

Guggenheim and Martin (1995) made a clear distinction between clay and clay mineral. These authors defined "clay as a natural geologic material mainly composed of fine-grained (less than 2 μm) minerals essentially hydrous phyllosilicates, the so-called clay minerals which, in general, show plastic behaviour and that harden after drying or firing; associated to clay minerals other minerals can occur, the so-called non clay minerals, more concentrated in coarse fractions, but that could be still present in the less than 2 μm fraction." Also, the same authors defined "clay minerals as phyllosilicates, essentially hydrous aluminosilicates, which are essential components of clays and accessory components of many other rocks, being responsible for clay plasticity and for its hardening after drying or firing."

The AIPEA Nomenclature Committee (Guggenheim and Martin 1996) recommended that the term "kaolin-serpentine" should be used instead of the term "kaolinite-serpentine."

According to Moore (1996) the term "clay" has been used as a mineral term, as well as a size term and a rock term. Hence the term "kaolin" could be applied to clay and to clay mineral.

Paquet and Clauer (1997) classified clays into three groups: *low activity clays*, *high activity clays*, and *intermediate activity clays*. This classification was based on the electrical charge (z) of the structural unit cell, and they defined kaolin, represented principally by kaolinite, "as low-activity clay, having a low layer charge, nearly zero."

Harben (1999) defined kaolin "as white, soft and plastic clay predominantly composed of fine-grained platy kaolinite." As regards the color, the author states that kaolin can show white color, sometimes with red, brown, yellow, and blue tints. Also, the same author classified kaolin as a clay belonging to the group of kaolinite-bearing clays, a group that in addition to kaolin itself includes other special clays also predominantly composed of kaolinite, such as ball clay (a fine-grained, highly plastic kaolinite admixed with quartz, mica, illite, smectite, chlorite, and colloidal carbonaceous matter); flint clay (a smooth, microcrystalline, hard-slacking rock with a pronounced conchoidal fracture, composed mainly of kaolinite, which becomes plastic when ground in water); and fire clay (a silico-aluminous clay composed of a disordered variety of kaolinite capable of withstanding high temperatures without deforming).

The halloysite-bearing clay, called *halloysite clay*, is also classified as kaolin, being predominantly composed of halloysite, a clay mineral similar to kaolinite in terms of chemical composition and structure, but whereas halloysite particles can exhibit platy, rolled, or spheroidal shapes, kaolinite particles exhibit a platy shape.

Harvey (2000), based on studies carried out on industrial clays from various worldwide deposits, classified such clays into four categories (three for special clays, one for common clays), depending upon the sophistication and economics of

the products manufactured with them, and the sophistication of the technologies required for their development. In this classification kaolin could be included in the three categories of special clays.

The first category includes high-quality kaolin, whose large-scale production and processing require advanced and expensive technologies, and consequently high investment; this type of kaolin has a large circulation in both national and international markets, being represented, for instance, by kaolin from Cornwall, United Kingdom, by kaolin from Georgia, United States, and by kaolin from Amazonia, in Brazil.

The second category also includes high-quality kaolin whose production and processing, although on a small scale, requires high technologies; this type of kaolin is addressed to small markets, both national and international, and represented, for example, by kaolin mostly consisting of halloysite from Maugaparerua, Matauri Bay and Mahimali, in New Zealand. The third category includes medium-quality kaolin, whose production and processing requires medium technologies and investment, represented, for example, by central and western European kaolin, from Germany, Czech Republic, Ukraine, France, Spain, and Portugal.

Galán (2003) distinguished *commercial clays* from *noncommercial clays*, the former being those with possible industrial application. The author defined “commercial kaolin as a rock that contains a certain proportion of minerals of kaolin group (kaolinite, dickite, nacrite and halloysite), and that could be economically extracted and concentrated.” The author includes in commercial kaolin,

the kaolinite-bearing clays (ball clay, fire-clay and flint clay) predominantly composed of kaolin minerals; raw kaolin, in general, is not a clay, but a rock (kaoliniferous sand or arkose, and kaolinized granite, gneiss, rhyolite or anorthosite), reason why it needs to be processed in order to concentrate kaolin minerals; on the contrary, kaolinite-bearing clays, which in the natural state are, in general, richer in kaolin minerals than kaolin are not processed, requiring only milling, sieving, atomization, etc.

With regard to the distinction between *clay* and *clay mineral*, in 2006 the actual position of the JNCs (Joint Nomenclature Committees) of both the AIPEA and the CMS on using *clay as a rock term* was still indeterminate. Nevertheless, the literature often uses the term “clay” for clay mineral, for example, kaolin instead of kaolinite, because the former name is shorter and less cumbersome.

Bergaya and Lagaly (2006) established the distinction between *clay* and *clay mineral* based on the following parameters: genesis, granularity, mineralogy, plasticity, and behavior on drying or firing. Clay is natural, fine-grained (<2 or <4 μm), mainly constituted of phyllosilicates, plastic (except flint clays), and hardens on drying or firing. On the other hand, clay mineral is natural or synthetic, without size criterion, might include nonphyllosilicates, plastic, and hardens on drying or firing.

Such concepts could be extended to the clay kaolin and to the clay mineral kaolinite.

2.3.4 Discussion

From the information above and from the evolution of kaolin definition over the relatively short history of clay science the unconformity between the arguments found relevant for academic and industrial scientists in what concerns kaolin definition becomes clear.

Primary or residual kaolin and secondary or sedimentary kaolin are distinctive in terms of genesis, occurrence, and properties, and consequently in terms of industrial processing methodologies, uses, and functions.

Frequently, ball clay, flint clay, and fire clay, while in the bulk state, contain higher contents of kaolinite and/or halloysite than bulk kaolin, although after being refined, certain size fractions of kaolin, compared to equivalent size fractions of ball clay and fire clay, contain higher concentrations of kaolinite and/or halloysite.

Fire clays have very distinctive properties relative to ball clays. Fire clays occur underneath coal seams from the Carboniferous, the reason why they are also called *underclays*. Certain fire clays from Yorkshire, in England, contain dickite as an important constituent associated with kaolinite (Gomes 1979), and the Al_2O_3 content can reach values slightly above 30%.

In terms of industrial applications ball clay is more important than fire clay, despite the participation of this clay both in silico-aluminous refractories and in stoneware. As a matter of fact, ball clay is an essential constituent of ceramic pastes used for the production of certain types of porcelain, sanitary ware, earthenware, and stoneware (household ware and floor tiles of “porcellanic stoneware” or “porcelanato”).

Considered as secondary kaolin, ball clay is geologically associated with primary or residual kaolin. In southwest England Lower Tertiary ball clay deposits occur in small or medium sedimentary basins located near the kaolin deposits derived from the alteration of Hercynian granite outcroppings in the counties of Devon and Cornwall.

English ball clay is classified into groups according to their main properties: chemical and mineralogical composition, content of carbonaceous matter, grain size distribution, $<2\ \mu\text{m}$ content, unfired brightness, fired brightness, and viscosity concentration.

High grades of ball clay contain: 65–75% kaolinite (60–70%); 15–20% mica/illite (15–20%); 30–34% Al_2O_3 (28–32%); 1–2% Fe_2O_3 (1–1.5%); 2–3% C (0.1%); and $<2\ \mu\text{m}$ 75–90% (65–70%). Inside the parentheses are the corresponding contents of medium-grade ceramic kaolin.

Mitchell and Vincent (1997) considered four types of ball clay. Three of these types are distinguished by their multilayered structure, thickness of ball clay layers, and commercial value. Type 1 of ball clay is represented, for instance, by deposits in the Bovey and Petrockstow basins in England, dated Lower Tertiary. Types 2 and 3 of ball clay are represented by the deposits in Westerwald in Germany, by the deposits in Skalma in the Czech Republic, by the deposits in Tennessee and Jackson/Purchase in the United States of America, and the deposits in Dorset in England,

respectively, all dated Lower Tertiary as well. Type 4 ball clay corresponds to deposits of small to medium dimension and relatively small thickness, formed in lacustrine and lagoonal environments, and dated Pliocene–Pleistocene.

Kaolin definition is as difficult as clay definition. Indeed, clay definition differs a great deal among people having diverse educational and professional experience (Gomes 2002).

Similarly kaolin definition could show differences according to the educational or professional background of people interested in this special clay. The only disagreement we have with regard to the aforementioned definitions of clay and clay mineral by Bergaya and Lagaly (2006) is the attribution of clay mineral to either natural or synthetic products.

The designation *clay mineral* should be reserved only for natural, inorganic, crystalline, hydrous phyllosilicates. Synthetic or artificial inorganic, crystalline, hydrous phyllosilicates that could be produced in the laboratory, despite being analogues of clay minerals, should not be considered as such.

The AIPEA Nomenclature Committee (Guggenheim et al. 1997) endorses the use of both commercial names and synthetic names for the nomenclature established by the Commission on New Minerals and Mineral Names (CNMMN; Nickel 1996). Therefore, synthetic minerals should be referenced by enclosing the name in quotation marks, unless the synthetic mineral has been recorded as a trademark, in which case the name starts with a capital letter.

Trying to integrate all that was said before we consider kaolin as:

a geologic material that is the outcome product of the alteration of rocks bearing significant contents of feldspars (essentially aluminosilicates of potassium or sodium and calcium) and micas (essentially aluminosilicates of potassium), alteration due to either weathering or deuteric (essentially hydrothermal) processes, or due to both processes too. Those rocks could belong to distinct genetic types: igneous rocks, such as, rhyolite, granite, granodiorite and anorthosite; metamorphic rocks, such as, gneiss, migmatite and micaschist; or sedimentary rocks, such as, feldspar-bearing sandstone (named arkose) and quartz sand containing some feldspar, mica and a clayey matrix that could exhibit white, grey, and yellow colours. The term kaolin would be attributed to the kaolinite-bearing rock as well as to the products that would result from its refining and beneficiation in order to be commercialized for specific industrial applications.

In clay mineralogy, taking into account the recent recommendations of the AIPEA Nomenclature Committee (Guggenheim et al. 2006), the expression *kaolin minerals* is applied to the subgroup *kaolin minerals* which with the subgroup *serpentine minerals* constitutes the group *kaolin-serpentine minerals*.

Kaolin minerals are classified as hydrous phyllosilicates having planar structures (platy crystal shapes) based on a layer type 1:1 of dioctahedral character, and comprising the following minerals: kaolinite, dickite, nacrite, and halloysite (in the case where it has planar structure), the first three minerals having the same chemical composition but distinctive structures called polytypes.

Halloysite, in addition to the planar structure, can also exhibit nonplanar structures (rolled or spheroidal shapes), and differs from kaolinite because it also has the same amount of structural water as it has constitution water.

There are kaolin deposits in which kaolinite is the predominating kaolin mineral, represented, for instance, by Seilitz deposits of residual type, in Germany, by St. Austell deposits of mixed hydrothermal/residual type, in Cornwall, England, by Georgia deposits of sedimentary type in the United States, and by Rio Jari (tributary of the Amazon river) and Rio Capim deposits of sedimentary type in Brazil.

Other kaolin deposits exist in which halloysite is the predominating kaolin mineral represented, for instance, by Maungaparerua, Matauri Bay, and Mahimali deposits of hydrothermal/residual type in New Zealand. Also, there are kaolin deposits, represented by Suzhou and Dazhou kaolin deposits of hydrothermal/residual type in China, in which kaolinite and halloysite occur in similar contents.

Finally, there are kaolin deposits of hydrothermal origin, well represented, for example, in Guanajuato, São Luis Potosi, and Nayarit deposits in Mexico, in which dickite and nacrite are the predominating kaolin minerals. In Tragos (Mangualde, Portugal) there is a small but interesting kaolin occurrence of hydrothermal type related to uranium mineralization, in which dickite was the only kaolin mineral identified as occurring in relatively long and perfect pseudo-hexagonal crystals coating tiny bipyramidal quartz observable only through a microscope (Gomes 1979).

Kaolin and ball clay are mainly used in ceramics, rubber, plastics, and agrochemicals.

Kaolin can occur in distinctive geological environments, either as residual deposits, or as redeposited or sedimentary deposits, as with any other special clay or common clay. Kaolin from one deposit has specific characteristics or properties (color, chemistry, mineralogy, clay fraction content, grain size and grain size distribution, plasticity, and rheology) that differ from the corresponding properties of kaolin from any other deposit. Even in the same deposit the heterogeneity in terms of kaolin characteristics is a common occurrence, and within kaolin properties color variations from white to grey, yellow, brown, and red could be easily observable in the field. Therefore, the results of studies carried out in the kaolin from a certain deposit cannot be extrapolated to any other kaolin deposit.

The paper by Murray and Keller (1993) entitled “Kaolins, Kaolins, Kaolins” is a clear indication that all kaolins are not equal, being distinctive in terms of genesis, composition, and properties. Individual kaolins vary particularly in many physical characteristics (e.g., particle size, particle size distribution, particle shape, particle aspect ratio, viscosity, brightness, whiteness, abrasiveness, opacity, and gloss), which in turn influence their end uses.

Is kaolin a mineral that is a natural (formed as a result of geological processes), homogeneous inorganic solid, normally crystalline? The answer is negative although, presently, some researchers consider the term kaolin equivalent to the term kaolinite, a clay mineral commonly found in kaolin that is a real mineral species represented by the chemical formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. Experience shows that kaolin is an association of clay minerals (essentially belonging to the kaolin subgroup of minerals that comprises the mineral species, kaolinite, halloysite, dickite, and nacrite), nonclay minerals (quartz, feldspar, mica, and iron oxides/hydroxides),

and sometimes noncrystalline phases (organic matter, and noncrystalline iron or manganese hydroxides).

Could we call kaolin a rock that by definition is a natural consolidated or unconsolidated aggregate or association of minerals and, within these, the so-called kaolin minerals? Yes, it could be in particular cases when kaolin subgroup minerals are predominating, even when the structure of the parental rock (e.g., granite or arkose) is visible. In this situation, for instance, the expressions kaolinized granite or kaolinized arkose are also currently used, and such expressions with good reason would be applied if kaolin minerals do not predominate.

However, could the term kaolin be used if the kaolin minerals content of the geological material is low? Yes, it could, because we know that kaolin mineral content around 8–10%, constituting the white or nearly white matrix of sand and low consolidated sandstone deposits, could be sufficient for the economic extraction and concentration of both the fine fraction and the coarse fraction to be feasible, particularly if the coarse fraction (sand and pebble) could also be commercialized for ceramics or civil construction works after being submitted to appropriate washing and classification.

The designation “kaolin” attributed to the fine fraction (<0.074 mm or even finer) is quite acceptable in mineralogical, industrial, and commercial terms.

On the other hand, could the term “kaolin” be attributed to the fine white powder mainly consisting of kaolinite or halloysite identified by X-ray diffraction, and that partially replaces the individual feldspar or mica crystals which constitute a certain rock, such as granite, granodiorite, anorthosite, arkosic sandstone, and gneiss? No, if the alteration product could not be industrially and economically concentrated in order to be commercialized. Or could kaolin be the name of the very scarce white powder present in the interior of feldspar crystals in apparently unaltered or little altered granite, powder that is just observable through an optical microscope or after granite fragmentation and washing, and identified by XRD as being mainly composed of kaolinite? The answer is negative as well.

On the other hand, the reddish kaolinite-bearing clay size component of a ferrallitic soil that could be relatively abundant in some soils of this typology should not be called kaolin. This type of soil, also called lateritic soil, is used as construction material in civil works, for instance, bricks for housing and road pavement, should not be called kaolin.

In this specific case the clay size component, in spite of its reddish color, could be turned into white or nearly white color on a laboratory scale by dissolution of the iron-staining pigment.

The three mineral products referred to, despite the existence in them of the minerals characteristic of kaolin, should not be classified as kaolin; it is not only the scale (micro, meso, or mega) of the occurrences that matters, but also the feasibility and economics of the industrial processing as well as the existence of markets for the end products.

As the outcome of the preceding discussion the kaolin designation should contemplate and satisfy not only certain mineralogical requisites, but also industrial and commercial requisites that depend on specific kaolin properties, such as color,

brightness, mean particle size, particle size distribution, particle shape, viscosity, plasticity, abrasiveness, and refractoriness; a particular kaolin has its proper identity expressed by specific properties.

Up to the 1960s of the last century the main industrial use of kaolin was in ceramics to produce diverse types of whiteware ceramics, such as porcelain, earthenware, sanitary ware, stoneware, and bone china, the last belonging to the phosphatic type of whiteware, whereas the others belong to the feldspathic type of whiteware. At that time kaolin was defined as white or nearly white clay that after being dried and fired gets increasingly hard maintaining the white color.

The referred products require kaolin of distinct brightness; for instance, porcelain and bone china require kaolin of higher brightness grades than the other products. Many of these products (household porcelain, art porcelain, vitreous porcelain, electrical porcelain, and cookware porcelain) are glazed using adequate porcelain glazes, some more opaque than others, glazes that could hide the color base of the ceramic body. Therefore, distinctive kaolin brightness grades for distinct functions have been established, corresponding to their distinctive unit prices. Thereafter, for about 30 years kaolin became a fundamental raw material for the production of certain types of white paper, incorporated as a white pigment applied either as coating or as filler. Kaolin grades characterized by higher brightness, better perfection of particle shape, and lower abrasiveness are required more for coating grades rather than filler grades.

Kaolin is characterized in general by its current white color, fine granularity, low plasticity, and low viscosity compared to other special clays. Similar to any other clay, kaolin is essentially formed and occurs in surface environments of the Earth.

Raw kaolin usually shows white color, its fundamental property when fabricating products that require raw materials with high brightness, such as porcelain and high-quality printing paper. However, in its natural state kaolin frequently can show colors with tints of yellow, red, and grey, that in the first two cases is attributed to cryptocrystalline, weakly crystalline, or crystalline iron oxides/hydroxides, and in the third case is attributed to the presence of finely divided organic matter.

None of these color tints hinders kaolin use in equally important applications such as earthenware, sanitary ware, stoneware, rubber, thermoplastics, and certain types of cement, mortar, pozzolana, and refractories. During the thermal processing required for the manufacture of these products, the yellow and grey tints in particular change, depending upon the kiln atmosphere (reducing or oxidizing), into white or near white tints.

On the other hand, there are beneficiation processes of current applications for kaolin bleaching, for instance, chemical dissolution, selective flocculation, ultraflotation, froth flotation, delamination, and high-intensity magnetic separation, processes whose application intends significantly to reduce or eliminate certain contaminants or penalizers, such as iron oxides/hydroxides, titanium oxides, biotite, and tourmaline.

Exceptionally kaolin does not require refining and beneficiation, such as the kaolin from Mevaiela, Angola, that is the product of anorthosite alteration (Gomes et al. 1994). The chemical composition of raw kaolin and of its <0.038 and <0.002 mm fractions is almost invariable.

Kaolin in a particular geological deposit can exhibit chromatic variations, either laterally or vertically, and the kaolin showing these color variations could be selectively exploited and processed in order for the output of specific commercial grades for certain industrial applications and functions to be feasible. As a matter of fact, color is not a distinctive property of kaolin. Other special clays rich in kaolinite, such as flint clay, ball clay, and fire clay, can show in the natural state, or after firing, white or nearly white color.

Even special clays in the natural state not bearing kaolinite, such as fibrous clays (sepiolite and palygorskite), and bentonite and ball clay can show white or near-white color. These chromatic variations are related to the above-mentioned contaminants and, as a rule, they are more common in secondary than in primary kaolin deposits.

In actuality, the most distinctive properties of kaolin relative to other special clays (ball clay, flint clay, and fire clay) are their mineral and chemical composition and the grain size distribution.

Kaolin fine fractions (<0.063 , <0.053 , <0.045 , and <0.010 mm), potentially interesting for specific industrial applications, are mainly composed of the clay minerals kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, and/or halloysite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$. Illite, chlorite, and smectite can occur as associated accessory clay minerals. Quartz, mica, feldspar, and oxides/hydroxides of Fe, Al, and Mn are other associated minerals that can occur. Also, as associated phases, organic matter and other noncrystalline compounds can occur as well.

Kaolin being special clay occurs in deposits that, not being frequent worldwide in the geologic environment, should be of medium to high dimension and volume in order to allow its economic exploitation. Kaolin mining and technological processing need extractive, refining, and beneficiation methods that require high financial investment and sophisticated technological processes.

The final product of kaolin processing will have a higher or lower unit value, depending upon either kaolin-specific natural characteristics, or the equally specific properties of the final refined and beneficiated product. Essentially, through the application of processes of hydraulic or aero-flotation treatment to the so-called kaolin parent rock, refining promotes the concentration of finest particles, and consequently the concentration of the clay minerals characteristic of kaolin. Therefore, kaolin, having specific granulometric characteristics (grain size less than 0.045 mm or less than 0.010 mm) and other specific properties, can be produced and commercialized.

Refining modifies the granulometric or textural composition of kaolin, and also modifies properties such as mineralogical and chemical composition. On the other hand, beneficiation promotes the modification of properties such as color, brightness, gloss, and rheology.

To be feasible, in economic terms, the exploitation of a kaolin deposit, the minimum content of the industrially processed and commercialized kaolin fraction, that is, the size fraction showing white or other colors showing grey, yellow, and other tints, should be within the range 8–10%.

Kaolin is, comparatively, one of the most important mineral resources in economic terms, due to its diversity of application fields and functions, such as coating and filler in paper, as an essential component of ceramic pastes to produce certain ceramics (diverse types of porcelain, earthenware, sanitary ware, and stoneware), as filler in rubber and plastics, and as important raw material to produce certain types of paint, glass fiber, cement, mortar, mortar, pozzolana, refractories, pharmaceuticals, cosmetics, and the like.

As said before, in terms of genesis and geologic occurrence, kaolin is classified into four types: residual, hydrothermal, residual-hydrothermal, and sedimentary, the first three included in the group of primary kaolin and the fourth in the group of secondary kaolin.

2.3.5 *Conclusions*

From the aforementioned information, and the questions and proposed answers, some conclusions may be drawn:

1. Kaolin in kaolin deposits, as a rule, is heterogeneous in terms of many relevant properties required for industrial applications, such as: (a) color of the kaolin-bearing materials shows changes, either laterally and vertically; (b) textural features of kaolin-bearing materials show changes, either laterally or vertically; (c) mineralogy and chemistry of both bulk kaolin and their size-fractions show changes, either laterally or vertically; (d) kaolin mineral quality and quantity, fundamental parameters in terms of deposit economics, show changes, either laterally or vertically.
2. In the same kaolin deposit kaolin-bearing materials having distinctive origin or genesis could occur in association; for instance, in a certain kaolin deposit, residual type kaolin could be overlaid by sedimentary type kaolin, and this last type of kaolin could show layers of diverse textural facies, kaolinitic clay, or fine sand and coarse sand both bearing kaoliniferous matrix.
3. Color of natural kaolin, despite being an important property for some industrial applications and functions, is not an impeditive factor of kaolin use for other important applications; raw kaolin colors other than white, such as beige, pink, yellow, and grey can be attenuated, submitting the natural refined kaolin either to adequate beneficiation treatment, or to adequate thermal treatment carried out during the transforming process of common application, for instance, in ceramics, refractories, cements, pozzolana, and metakaolin.
4. Color is not a necessary requisite to be included in a kaolin definition, as well as other properties, such as plasticity and hardening after drying or firing, because they are not exclusive to kaolin, and in addition, they are not common to all kaolins. For instance, flint or hard clay, in the natural state, is already very consolidated and hard, and is nonplastic unless after being finely ground.

5. Certain types of ball clay, an industrial clay having important applications in common with kaolin, in the case of showing high kaolinite content, high alumina content, low iron content, and near-white color after firing, should be considered sedimentary kaolin for scientific, industrial, and legal purposes.
6. The presence of kaolinite (or its polytypes, dickite and nacrite) and/or halloysite, either in the clay-bearing or argillized rock, or in its processed and commercial products, is a fundamental requisite for kaolin classification.

A proposal for a new kaolin definition, characterized by its more comprehensive character able to integrate its geology (origin and occurrence), mineralogy, technological properties, as well as the always decisive economic and legal criteria, is put forward:

Kaolin is a fine-grained natural or engineered product predominantly composed of clay minerals classified into the kaolin subgroup minerals; to fulfill the diverse and important industrial functions kaolin is extracted from geologic deposits of previously assessed quality, economics, and legality; to be commercialized kaolin could undergo appropriate refining and beneficiation in order to achieve its required ultimate white or near-white color and other relevant properties.

In conformity with this definition the term “kaolin” could be applied not only to the special kaolin-bearing clay currently called kaolin, but also to other special kaolin-bearing clays, particularly high-quality ball clay and flint or hard clay. Therefore, for scientific, industrial, commercial, and legal purposes, ball clay and flint clay deposits whose high quality and volume would have been recognized by the competent administrative entity, based upon adequate field and laboratory investigation, and conformity to national legislation, should deserve the same classification and treatment as kaolin deposits.

2.4 Evolution of the Definition of Illite

The concept of illite has also changed with time. Grim et al. (1937) proposed the term *illite* as “a general term, not as a specific clay mineral name, for the mica-like clay minerals.” The term *illite* includes both di- and trioctahedral structures, and has been used worldwide for a long time as a name for clay minerals with $d_{(001)} = 10 \text{ \AA}$ spacing that shows substantially no expanding-lattice characteristics, that is, no swelling clay components.

Bailey et al. (1984) in the report of the Clay Minerals Society Nomenclature Committee (in *Clay Minerals*, 32:239) have proposed a new definition for illite: “a non-expandable dioctahedral clay mineral; ionic substitutions in both octahedral and tetrahedral sites of the mica structure; contains a phengite component; the interlayer substitutions can include not only K^+ but also H_3O^+ ions; and an interlayer charge ranging between 0.8 and 0.6.”

Meunier and Velde (2004) following the investigation of illite from distinctive natural systems (soil and other geological systems) and processes (diagenesis,

supergene, and hydrothermal alteration) redefined illite as: “a low-potassium mica (i.e., with a 10 Å basal spacing); able to undergo crystal growth (what is proper of a mineral species); with a K content per unit cell near 0.9 and Mg and Fe contents depending upon the chemical system in which illite is formed; and that could occur as 1M and 2 M polytypes.”

Martin et al. (1991) in the report of the Clay Minerals Society Nomenclature Committee classify the hydrous phyllosilicates structure into two types: planar and nonplanar, illite being characterized by its planar structure.

Recently Guggenheim et al. (2006) in the report of the Nomenclature Committee for 2006 of AIPEA maintain the classification of hydrous phyllosilicates into two types: planar and nonplanar or modulated, and defined illite as “planar hydrous phyllosilicate that belongs to the interlayer-deficient mica group, and has a dioctahedral character. In the classification of planar hydrous phyllosilicates illite is considered as being an interlayer-deficient mica having non-hydrated mono-or divalent cations (~0.60–0.85).”

References

- Bailey SW (1980) Summary of recommendations of AIPEA nomenclature committee. *Clay Clay Miner* 28:73–78; *Clay Miner* 15:85–93
- Bailey SW (1982) Nomenclature for regular interstratifications, report of the clay minerals society nomenclature committee for 1980–1981. *Clay Clay Miner* 30:76–78; Report of the AIPEA Nomenclature Committee, AIPEA Newsletter No 18, Supplement of February, 1982
- Bailey SW (1989) Report of the AIPEA nomenclature committee. *AIPEA Newslett* 26:17–18
- Bailey SW, Brindley GW, Johns WD, Martin RT, Ross M (1971a) Summary of national and international recommendations on clay mineral nomenclature, 1969–70, CMS nomenclature committee. *Clay Clay Miner* 19:129–132
- Bailey SW, Brindley GW, Johns WD, Martin RT, Ross M (1971b) Clay mineral society report of nomenclature committee, 1969–70. *Clay Clay Miner* 19:132–133
- Bailey SW, Brindley GW, Kodama H, Martin RT (1979) Report of the clay minerals society nomenclature committee for 1977 and 1978. *Clay Clay Miner* 27:238–239
- Bailey SW, Brindley GW, Fanning DS, Kodama H, Martin RT (1984) Report of the clay minerals society nomenclature committee for 1982 and 1983. *Clay Clay Miner* 32:239
- Bailey SW, Alietti A, Formoso MLL, Konta J, Koster HM, Mackenzie R, Morgan DJ, Mumpton FA, Nagasawa K, Paquet H, Raussell-Colom JA, Zvyagin BB (1986) Report of the AIPEA nomenclature committee (Illite-Glaucanite-Volkonskoite). *AIPEA Newsletter No 22*, Supplement of February
- Bergaya F, Lagaly G (2006) General introduction: clays, clay minerals, and clay science. In: Bergaya F, Theng BKG, Lagaly G (eds) *Handbook of clay science, Developments in clay science*. Elsevier, New York, 1224 pp
- Brindley GW, Pedro G (1976) Meeting of the nomenclature committee of AIPEA, Mexico City, July 21, 1975. *AIPEA Newslett* 12:5–6
- Brindley GW, Pedro G (1970) Report of the AIPEA nomenclature committee. *AIPEA Newslett* 4:3–4
- Brindley GW, Pedro G (1972) Report of the AIPEA nomenclature committee. *AIPEA Newslett* 7:8–13
- Brindley GW, Bailey SW, Faust GT, Sa F, Rich CI (1968) Report of the nomenclature committee (1966–67) of the clay minerals society. *Clay Clay Miner* 16:322–324

- Chen P-Y, Lin M-L, Zheng Z (1997) On the origin of the name kaolin and the kaolin deposits of the Kauling and Dazhou areas, Kiangsi, China. *Appl Clay Sci* 12:1–25
- Galán E (2003) Arcillas especiales I: caolines y arcillas caoliníferas. In: Galán E (ed) *Mineralogía aplicada*. Editorial Síntesis, Madrid, pp 105–135
- Gomes CSF (1979) Characterization of structural defects in kaolinite minerals, PhD thesis, Department of Ceramics, University of Leeds, United Kingdom, 240 pp
- Gomes CSF (1988) Argilas: O que são e para que servem, Fundação Calouste Gulbenkian (ed), 457 pp
- Gomes CSF (2002) Argilas: Aplicações na Indústria. In: Gomes C (ed), Universidade de Aveiro, 338 pp
- Gomes CSF, Worrall WE (1979) A dickite showing unusual crystal habit and structural disorder. In: *Mineralogy of ceramics. Proceedings of the British Ceramic Society*, vol 28, pp 21–105
- Gomes CSF, Velho J, Guimarães F (1994) Kaolin deposit of Mevaela (Angola), alteration product of anorthosite: assessment of kaolin potentialities for applications in paper. *Appl Clay Sci* 9:97–106
- Grim RE (1953) *Clay mineralogy*. McGraw-Hill, New York, 384 pp
- Grim RE (1968) *Clay mineralogy, geological science series*. McGraw-Hill, New York, p 29, 569 pp
- Grim RE, Bray RM, Bradley WF (1937) The mica in argillaceous sediments. *Am Mineral* 22:813–829
- Guggenheim S, Martin RT (1995) Definition of clay and clay mineral: Joint report of the AIPEA nomenclature and CMS nomenclature committees. *Clay Clay Miner* 1995(43):255–256; *Clay Miner* 30:257–259
- Guggenheim S, Martin RT (1996) Reply to the comment by more DM on “definition of clay and clay mineral”, Joint report of the AIPEA and CMS nomenclature committees. *Clay Clay Miner* 44:713–715
- Guggenheim S, Alietti A, Drits VA, Formoso MLL, Galán E, Köster HM, Paquet H, Watanabe T, Bain DC, Hudnall WH (1997) Report of the association internationale pour l’Étude des argiles (AIPEA) nomenclature committee for 1996. *Clay Clay Miner* 45:298–300; *Clay Miner* 32:493–496
- Guggenheim S, Bain D, Bergaya F, Brigatti MF, Drits V, Eberl DD, Formoso M, Galán E, Merriman RJ, Peacor DR, Stanjek H, Watanabe T (2002) Report of the AIPEA nomenclature committee for 2001: order, disorder, and crystallinity in phyllosilicates and the use of the “crystallinity index”. *Clay Clay Miner* 50:406–409; *Clay Miner* 37:389–393
- Guggenheim S, Adams JM, Bain DC, Bergaya F, Brigatti MF, Drits VA, Formoso MLL, Galán E, Kogure T, Stanjek H (2006) Summary of recommendations of nomenclature committees relevant to clay mineralogy: report of the association internationale pour l’Étude des argiles (AIPEA) nomenclature committee for 2006. *Clay Clay Miner* 54:761–772
- Harben PW (1999) *The industrial minerals handbook*, 3rd edn. IML, Tonbridge, 296 pp
- Harben PW, Kuzvart M (1996) *Industrial minerals: a global geology*. Industrial minerals information. Metal Bulletin PLC, London
- Harvey CC (2000) Categorization and economic assessment of industrial clays, the clay minerals society workshop on “industrial clay mineralogy”. Loyola University, Chicago
- Johnson SW, Blake JM (1867) On kaolinite and pholerite. *Am J Sci* 43:351–361
- Kuzvart M (1977) Aspects of kaolin genesis. In: Galán E (ed) *Proceeding of the 8th kaolin symposium and meeting on alunite*. Ministerio de Industria y Energia, Madrid-Rome, Madrid, p K-12
- López-Colmenar JMM (1992) Caolín y arcillas caoliníferas, recursos minerales de España. In: Guinea JG, Frias JM (ed) *Textos Universitarios, Consejo Superior de Investigaciones Científicas*, pp 27–44
- Mackenzie R (1963) De natura lutorum, clays and clay minerals. *Proceedings of the eleventh national conference on clays and clay minerals*, vol XI, Pergamon Press, Oxford, pp 11–28
- Manning DAC (1995) *Introduction to industrial minerals*. Chapman & Hill, London, 276 pp

- Martin RT, Bailey SW, Eberl DD, Fanning DS, Guggenheim S, Kodama H, Pevear DG, Srodon J, Wicks FJ (1991) Report of the clay minerals society nomenclature committee: revised classification of clay minerals. *Clay Clay Miner* 39:333–335
- Meunier A (2006) Why are clay minerals small? *Clay Miner* 41(2):551–566
- Meunier A, Velde B (2004) *Illite*. Springer, Berlin, 286 pp
- Millot G (1964) *Géologie des argiles*. Masson, Paris, 499 pp
- Millot G (1970) *Geology of clays*. Springer, Berlin, 429 pp
- Millot G (1989) Proceedings of the IX international conference, Strasbourg
- Mitchell D, Vincent A (1997) Exploration and appraisal of plastic sedimentary clays for the fine ceramics industry. *Appl Clay Sci* 11:311–327
- Moll B (2001) Industrial clay mineralogy. CMS Workshop. Loyola University, Chicago
- Moore DM (1996) Comment on: definition of clay and clay mineral, joint report of the AIPEA nomenclature and CMS nomenclature committees. *Clay Clay Miner* 44:710–712
- Moore D, Reynolds R (1997) X-ray diffraction and the identification and analysis of clay minerals, 2nd edn. Oxford University Press, Oxford
- Murray HH, Keller WD (1993) Kaolins, kaolins, kaolins. In: Kaolin genesis and utilization, Special publication No 1. The Clay Minerals Society, Boulder, Colorado, pp 1–24
- Nickel EH (1995) The definition of a mineral. *Can Mineral* 33(3):689–690
- Nickel EH (1996) Mineral names applied to synthetic substances. *Eur J Mineral* 8:461–462
- Paquet H, Clauer N (1997) Soils and sediments: mineralogy and geochemistry. In: Paquet H, Clauer N (eds) Springer, Berlin, 369 pp
- Patterson SH, Murray HH (1975) Clays. In: Lefond SJ (ed) *Industrial minerals and rocks*, 4th edn. American Institute of Mining, Metallurgical and Petroleum Engineers, New York, pp 519–585
- Povarennykh AS (1972) *Cristallochemical classification of minerals*. Plenum Press, New York
- Ross CS, Kerr PF (1931) The clay minerals and their identity. *J Sediment Petrol* 1:55–65
- Sanfeliu TA (2002) Evaluation of the particulate atmospheric aerosol in the urban area of Castellon, Spain, Proceedings of the 5th international symposium on the protection and conservation of monuments in the Mediterranean basin, Sevilla, Spain. In: Galán E, Zezza AA (eds) *Protection and conservation of the cultural heritage of the Mediterranean cities*. Balkema, Lisse, pp 621–665
- Souza Santos P (1975) Tecnologia de Argilas, v 1-Fundamentos, In: Blücher E (ed) Universidade de São Paulo, Brasil, 340 pp
- Velde B, Druc IC (1999) *Archeological ceramic materials: origin and utilization*. Springer, Berlin, 299 pp
- Weaver CE (1989) *Clays, muds, and shales*. Elsevier, Amsterdam, 819 pp
- Wilson MJ (1987) *Handbook of determinative methods in clay mineralogy*. Blackie, Glasgow, 308 pp
- Worrall WE (1982) *Ceramic raw materials*, second ed., Institute of ceramics textbook series. Pergamon Press, Oxford, 111 pp

Further Readings

- Gomes C, Silva J (2006) Minerals and human health: benefits and risks/Os minerais e a saúde humana: benefícios e riscos, bilingual edition of the authors. Multiponto, Porto, 142 pp
- Velho J, Gomes C, Romariz C (1998) Minerais industriais: geologia, propriedades, tratamentos, aplicações, especificações, produções em mercados. In: Velho J, Gomes C, Romariz C (eds) 591 pp

Clays and Health

Properties and Therapeutic Uses

Rautureau, M.; Figueiredo Gomes, C. de S.; Liewig, N.;

Katouzian-Safadi, M.

2017, XXIV, 217 p. 35 illus., 4 illus. in color., Hardcover

ISBN: 978-3-319-42883-3