

# Basic Guidelines for Prospecting and Technological Assessment of Clays for the Ceramic Industry, Part 1

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**Abstract:** Clays are irreplaceable raw materials for ceramic processing. The availability of clay deposits of suitable quality and quantity is an important competitive factor and a key issue for the economic sustainability of ceramic production. The identification of adequate sources of clay materials is an important issue that requires an appropriate methodological approach. In the form of simple guidelines, this article reports on how to conduct clay prospecting and evaluate the technological properties of raw materials. This first part describes the deposits of different types of ceramic clays, illustrating their origin, composition and geological criteria in the prospection. The second part will introduce the technological evaluation of clay materials, and describe in detail the four steps of clay prospecting.

**Keywords:** ball clay, clay deposit, clay prospection, kaolin, technological properties

## 1. Introduction: Why search for clays?

Developing countries have recently been approaching the ceramic market, especially in Africa, with domestic productions made in new local factories. This is due to the growing demand for commodities such as sanitary-ware, wall and floor tiles, and also because of the large costs of and duties on imported ceramic products. The high technological level and performance of ceramic plants by the best machinery suppliers allow excellent results, even where experience, industrial culture, and technical skills are not available.

In any case, ceramics require suitable raw materials. They must be constant in quantity

and quality over time for a reliable production. In Europe and in most industrialized countries, specialized mining companies supply ceramic raw materials with high standards of quality control. On the contrary, in many cases, developing countries cannot afford the import cost of high-quality raw materials, and industrialists are obliged to search for locally available mineral resources.

Over several years of activity in the field, the authors had the opportunity to study raw material deposits in many countries, including those where the ceramic industry was not yet developed. The authors would like to introduce the reader to the basics of pros-

pecting and technological assessment of clays for the ceramic industry. The goal is to summarize simple elements, as a sort of guideline, to support raw material research focusing on clays that are essential for any valuable ceramic production. For this purpose, these guidelines have been divided into two parts: the first part illustrates the various types of ceramic clays (their origin, composition and geological criteria in the prospection), while the second part, to be published in *Interceram 1, 2022*, concerns the technological assessment and prospection of ceramic clays.

## 2. Clays and clay minerals

Clays can be defined as naturally occurring, fine-grained materials, which develop plasticity when mixed with a limited amount of water and harden when dried and after firing [1][2][3]. The clay represents, due to its behaviour, the “plastic part” necessary for the correct shaping and cohesion of every ceramic formulation. From the grain size viewpoint, clay is considered a material with particle sizes smaller than 4 or 2 µm, depen-

### The key facts at a glance

- This article is part one of two papers on the identification of adequate sources of clay materials in form of guidelines on how to conduct clay prospecting and evaluate the technological properties of raw materials.
- Part one introduces the deposits of different types of ceramic clays divided into main categories based on their technological behaviour in ceramic production. Afterwards, the geological criteria in the prospection of each type of clay is illustrated.

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ding on the classification scheme [4]. In reality, ceramic clay materials have a wide particle size distribution, always including a silty fraction (4–63 μm) and often a sandy portion (> 63 μm). From the mineralogical point of view, clays are mainly constituted by *clay minerals* (mostly phyllosilicates), i.e. silicates with a crystal structure arranged in sheets composed of octahedral hydroxide layers (O) and tetrahedral silicate layers (T). The O layers can be occupied by trivalent ions (Al or Fe) or divalent ions (Mg, Fe, etc.) in dioctahedral and trioctahedral terms, respectively [3][5]. The presence of cations (and water molecules) in the lattice interlayer space deeply influences their physical behaviour (Figure 1).

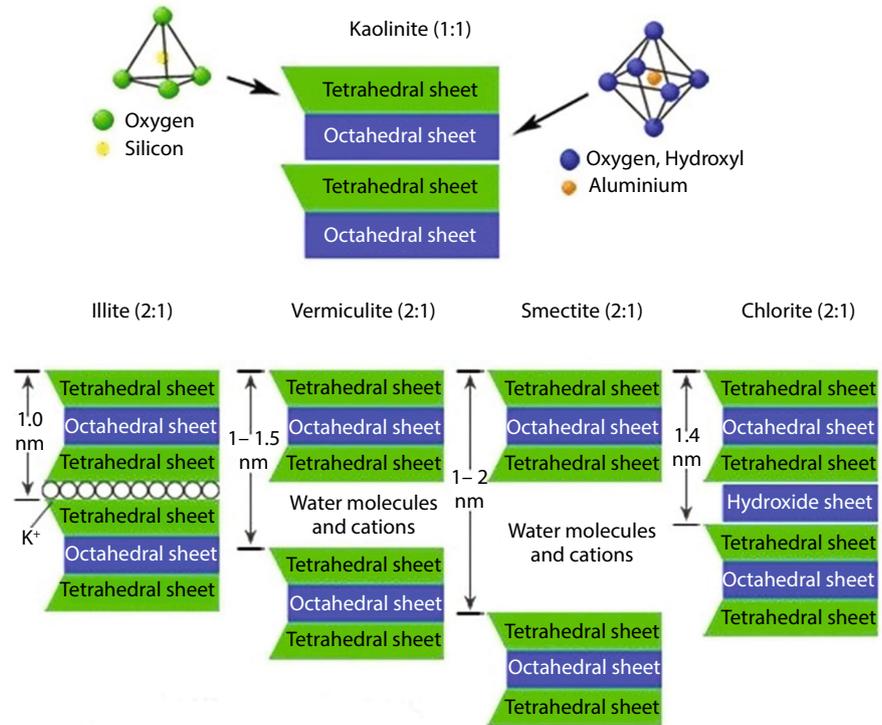


Figure 1 Scheme of the crystal structure of main groups of clay minerals (modified after [6]). © Bertolotti

The main groups – kaolinite, illite, smectite, chlorite, together with mixed-layer terms – encompass several clay minerals with different chemical composition, crystal structure and physical properties [5]. They are distinguished by the structure type (TO, TOT), the interlayer (charge and material), and the octahedral sheet (di- or trioctahedral), as summarized in Table 1.

However, in nature it is very rare to find pure clay minerals, and clay deposits are usually made of an assemblage of different clay minerals together with quartz, feldspars, carbonates, organic matter and others (mica, sericite, Fe and/or Al oxyhydroxides, etc.).

Clay minerals originate by weathering (alteration by atmospheric agents) or hydrothermal (alteration by hot fluids) actions

Table 1 Clay minerals occurring in ceramic clays. © Dondi)

Group	Type	Interlayer (material and charge)	O	Main species
Kaolinite serpentine	TO	None, water ~0	di tri	<b>Kaolinite, halloysite</b> , dickite, nacrite, lizardite, chrysotile
Pyrophyllite talc	TOT	None ~0	di tri	<b>Pyrophyllite</b> talc
Smectite	TOT	Hydrated exchangeable cations ~0.2-0.6	di tri	<b>Montmorillonite, beidellite</b> , nontronite, saponite, stevensite
Mica	TOT	Non-hydrated monovalent cations ~0.6-1.0	di tri	<b>Illite, muscovite</b> , paragonite, biotite
Chlorite	TOTO	Hydroxide sheet Variable	di tri	Donbassite <b>clinochlore</b> , chamosite

mainly at the expense of feldspars and micas forming a range of parent rocks [7]. Clay deposits are the result of three important stages:

- ▶ Weathering (hydrothermal) alteration
- ▶ Erosion, transportation, and deposition
- ▶ Burial diagenesis and low-grade metamorphism

Based on their geological origin, clay deposits can be classified as primary or secondary. Primary clay deposits are the result of in-situ alteration of parent rocks, generally igneous and metamorphic acidic terms (e.g. granite, rhyolite). In some cases, in clays it is possible to identify, depending on the extent of alteration, residual structures and minerals inherited from parent rocks.

Secondary clay deposits consist of sediments transported and settled in a broad range of depositional environments, from continental to marine. It is essential to take into account that the clay bodies of economic interest have different dimensions and geometry, according to the depositional environments, as exemplified in Figure 2. This has an important impact on the prospecting and extraction techniques for clay materials [2]. In continental environments, for instance in fluvial and lacustrine deposits, single clay bodies typically have a modest

thickness and a particularly limited lateral continuity. In the case of fluvio-glacial sediments and deltaic (river-dominated) environments, the lateral extension is usually greater, although the thickness of the exploitable bodies generally remains limited. In the context of marine sedimentation, there are deposits of remarkable lateral continuity, referable to both the continental shelf and the abyssal plain. In other marine depositional environments, such as slope and submarine fans, clay bodies often have moderate extensions and complex geometries.

Ceramic clays can be in the original depositional conditions or have undergone burial, with the related effects of diagenesis (or, in some cases, metamorphism of very low degree). This can lead to the progressive consolidation of the sediment (from clay to claystone to shale) up to lithification (slate) with consequent modifications of the mineralogical composition (e.g. illite-smectite interstratified > illite > sericite) and physical properties (especially plasticity and grindability). Ceramic plants are able to process from unconsolidated sediments to moderately consolidated clay materials, but strongly lithified claystones usually need to be treated as “hard materials” (e.g. feldspathic rocks).

### 3. Clays for the ceramic industry

To simplify geological prospecting work, it is helpful to divide clay deposits into main categories based on their technological behaviour in ceramic production:

- ▶ Kaolins (china clays)
- ▶ White-firing plastic clays (ball clays)
- ▶ Medium-low plasticity white-firing clays
- ▶ Red-firing plastic clays
- ▶ Red-firing clays with carbonates

#### 3.1 Kaolins (china clays)

The word kaolin is derived from *Kauling*, which in Chinese means “high ridge”, a place in the Jiangxi Province where white clays were mined many years ago, particularly during the Ming Dynasty [10][11]. For this reason, kaolin is also called *china clay*.

Kaolin deposits are the result of the alteration of feldspar-rich rocks – such as granite, rhyolite or gneiss – by hydrothermal and weathering processes. In some cases, kaolinitic bodies are formed by erosion and sedimentation of primary deposits. Therefore, the mineralogical and chemical composition of kaolin depends on the nature of the parent rocks, as well as the conditions and extent of alteration (Table 2).

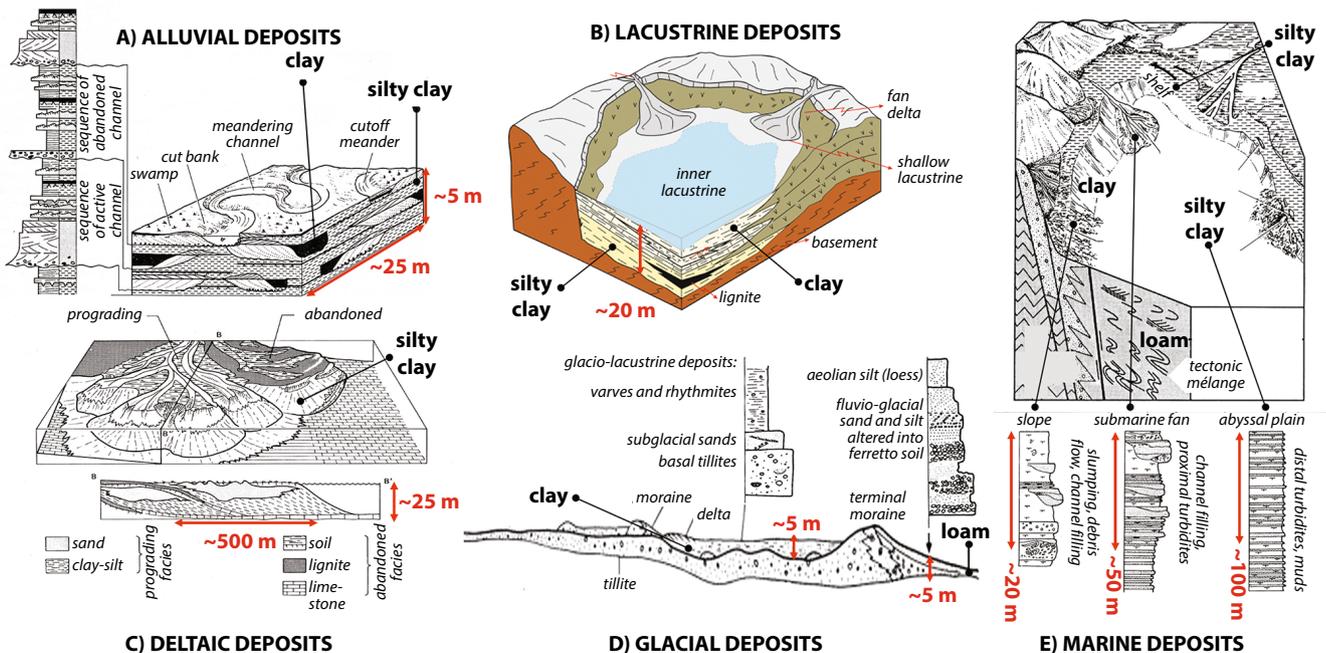


Figure 2 Depositional environments relevant for ceramic clay deposits (modified after [8]), scheme B (modified after [9]). © Dondi

Industrial kaolins are refined materials, obtained by the beneficiation of kaolinized rocks, mainly composed of kaolinite (with an ordered or disordered crystal structure). In

association, there are frequently other clay minerals (halloysite, dickite, illite, illite-smectite mixed layers, Al-oxyhydroxides). Residual minerals, such as feldspars,

micas and quartz, can be abundant in kaolinized rocks, and the beneficiation treatments are essentially addressed to separate them selectively from the clay fraction.

**Table 2** Descriptive models of ceramic clay mineral deposits (modified after [12]). (© Dondi)

Deposit	Product [byproduct]	Genetic synopsis	Host rocks	Clay minerals	Other minerals
<b>Kaolin</b> (residual)	Kaolin (muscovite, sericite)	Saprolite formed from chemical weathering of feldspathic rocks	Felsic rocks from Precambrian to Tertiary (e.g. granitoid, gneiss, nepheline syenite, volcanites, anorthosite)	Kaolinite (parent rock with a high mica content) or halloysite (parent rock with a low mica amount), gibbsite or other Al-oxyhydroxides	Quartz, muscovite anatase, ilmenite and further heavy minerals
<b>Kaolin</b> (hydrothermal)	Kaolin, halloysite (kaolinized felsic rock)	From alteration of feldspar-rich rocks by reaction with acidic hydrothermal fluids	Granitic and rhyolitic rocks, altered tuffaceous beds	Kaolinite (ordered) and/or halloysite, sometimes dickite, sericite, illite, smectite, pyrophyllite	Quartz, opal, cristobalite, alunite, traces of sulfides, fluorite, and tourmaline
<b>Kaolin</b> (sedimentary)	Kaolin (silica sand, kaolinitic loam)	Erosion of kaolinized rocks and deposition in tidal, estuarine, or lacustrine environments	Fluvial to coastal sedimentary sequences (sand, silt, clay, lignite, pisolitic clay)	Kaolinite, minor 2:1 clay minerals, sometimes gibbsite or other Al-oxyhydroxides	Quartz, ilmenite, muscovite
<b>Ball clay</b> (plastic clay)	Plastic, white-firing clay (lignite, sand)	Fluvial, lacustrine, and swamp sediments (from felsic parent rocks)	Continental terrigenous sedimentary sequences (sand, silt, lignite shale)	Kaolinite (disordered), illite and illite-smectite or kaolinite-smectite mixed-layers; sometimes smectite, chlorite	Quartz, carbonaceous matter, feldspars, carbonates, anatase, marcasite, zircon
<b>Fireclay</b> (high alumina kaolin, flint clay, underclay)	Refractory clay (low plasticity or non-plastic clay) with flintlike features and conchoidal fracture	Severe leaching of alkali and silica from fine-grained sediments in acid swamps	Shale, sandstone, claystone, coal, conglomerate	Kaolinite (ordered), minor diasporite and/or boehmite	Quartz, sericite, siderite, pyrite, anatase, carbonaceous matter
Deposit	Ore controls	Typical ore dimensions	Limitations (composition)	Limitations (process)	Typical deposits
<b>Kaolin</b> (residual)	Zones of groundwater movement protected from subsequent erosion	Deposits are irregularly shaped	Content of titanium minerals and Al-oxyhydroxides	Recovery of kaolin from saprolite requires beneficiation	Cornwall (UK), North Carolina (USA), Chubut (Argentina), Galicia (Spain)
<b>Kaolin</b> (hydrothermal)	Faulting and fractures, composition and reactivity of host rocks, proximity to sources of hydrothermal fluids	Variable, for example a large body was 1800 m long, 230 m wide, and 8 m deep	Abundant quartz, opal and/or cristobalite	Presence of abundant quartz, opal and/or cristobalite requires beneficiation	Matauri Bay (New Zealand), Itaya (Japan), Cornwall (UK), Brittany (France)
<b>Kaolin</b> (sedimentary)	Diagenesis and burial can cause recrystallization of kaolinite and leaching of silica to produce bauxite	Lenticular deposits, for example: 1-20 km long, 300-1500 m wide, 10-20 m thick	Iron and titanium minerals, and silt or sand fractions (mostly quartz)	Abundant quartz or muscovite may lead to excessive processing cost	Hirschau (Germany), Jarí (Brazil), Georgia (USA)
<b>Ball clay</b> (plastic clay)	Deeper and/or longer burial lithifies plastic clay into non-plastic fireclay	Lengths range from 100 to 800 m, width from 50 to 300 m, and thickness from 1 to 5 m	Iron minerals and carbonates may make the material unusable	Levels enriched in organic matter and sulfides must be discarded	Devon (UK), Donbass (Ukraine), Tennessee (USA), Westerwald (Germany)
<b>Fireclay</b> (high alumina kaolin, flint clay, underclay)	Diagenesis and burial can cause recrystallization of kaolinite	Deposits tend to be lenticular, e.g., up to 250 m long, up to 150 m wide, and less than 8 m thick			Pennsylvania and Missouri (USA), Asturias (Spain), Wingen (Australia)



Figure 3 Example of raw kaolin mining, Rwanda. (© Bertolotti)

Table 3 Chemical and mineralogical composition of refined kaolins. (© Dondi)

Oxide (mass-%)	Typical range	Mineralogical composition
SiO <sub>2</sub>	47–50	Kaolinite group minerals (kaolinite, halloysite, dickite) predominant over quartz and minor amounts of feldspars, illite-muscovite, titanium and iron minerals
TiO <sub>2</sub>	< 0.5	
Al <sub>2</sub> O <sub>3</sub>	35–38	
Fe <sub>2</sub> O <sub>3</sub>	< 0.6	
MgO	< 0.5	
CaO	< 0.5	
Na <sub>2</sub> O	< 0.5	
K <sub>2</sub> O	0.5–1.5	
Loss on Ignition	12–13	

In any case, the term *kaolin* is not linked to mineral purity, as often used in ceramic production, and the same term can refer to any raw clay that is refractory and looks white or light grey after firing (Figure 3). In this case, the alumina content is generally between 15 and 30 %, while the silica amount is in the range of 55–70 % (kaolinite contains nominally ~ 39 % Al<sub>2</sub>O<sub>3</sub> and ~ 46 % SiO<sub>2</sub>) due to the occurrence of quartz, feldspars and mica.

Kaolin increases the total amount of alumina in the ceramic body. In particular, it provides kaolinite, which at around 1000 °C transforms into mullite (and amorphous silica). Mullite is an important constituent of

ceramic bodies, responsible for mechanical strength, toughness and control over pyroplasticity. Therefore, kaolin is widely used in sanitaryware and tableware production (and is a minor ingredient recommended in porcelain stoneware tiles) for its lower content of colouring oxides compared to other clay raw materials.

Kaolin is generally less plastic than other clays but, in any case, it provides enough strength and particle cohesion in the shaping of ceramic products (which is more effective in slip casting than pressing). In addition, it reduces the amount of pyroplastic deformation in the process of firing. However, to be used in sanitaryware and tableware produc-

tion, kaolin must be refined through an industrial treatment of the primary kaolinized rock (Table 3). A suitable beneficiation plant requires a considerable investment, and it usually implies expensive treatments that need a water source to wash the parent rock, then separate and concentrate the fine fraction, rich in kaolinite particles. At the rule of thumb, refined kaolin represents only 15–20 % of raw kaolinized rock.

### Geological criteria in the search for kaolin deposits

The field research for kaolin deposits, originated by hydrothermal or residual alteration, must be oriented towards geological areas where feldspar-rich rocks outcrop: primarily granitoids, rhyolite-rhyodacite-dacite volcanics, orthogneisses (but also anorthosite, gabbro or arkose can host economic deposits). In many cases, only a part of the parent rock is kaolinized, and in prospecting special care must be devoted to the key factors of the composition and geometry of the orebody.

Residual kaolin deposits typically have a blanket-like geometry, and kaolinization decreases steadily downwards to fade into the parent rocks. Any zonation is primarily affected by the paleosurface and groundwater flow rate at the time of weathering. Key minerals are anatase and aluminium oxyhydroxides (gibbsite, boehmite, diaspore).

Hydrothermal deposits are usually linked to major structural lineaments that supplied the hot fluids necessary for kaolinization. Thus, they are less extended and typically exhibit a geometry connected with the fault system. A clear compositional zonation and a certain vertical development of alteration are clues of hydrothermal action, especially if key minerals occur (dickite, sericite, pyrophyllite, fluorite). In the case of kaolin deposits in silica-rich volcanic rocks (such as rhyolite, dacite or analogous pyroclastic rocks) attention must be paid to verify the possible occurrence of sulphur-bearing minerals, such as alunite (or jarosite), that can create serious problems in ceramics manufacturing, especially in fast firing cycles.

Sedimentary kaolin deposits require specific formation conditions: prevailing erosion of kaolinized rocks, transport over short distances and settling in restricted basins in

order to allow kaolinite concentration and to avoid contamination from other sources. Such conditions are classically found in continental environments, like fluvio-lacustrine and deltaic systems, especially endorheic basins. Compositional clues are the occurrence of minerals unrelated to hydrothermal and laterization processes (such as carbonates) or fossils, fragments of sedimentary rocks, etc.

Generally speaking, to make the extraction and processing economically viable, a deposit must contain reserves for at least five million tons of raw kaolin.

### 3.2 White-firing plastic clays

The white-firing plastic clays used in ceramics are typically fine-grained sediments with kaolinite being predominant, but also a significant presence of illite and, in some cases, mixed-layer clay minerals [13][14][15]. These clays are grey/dark grey because of organic impurities, but after firing they look white or light coloured (Figure 4). They are commonly known as ball clays due to the old-fashioned method of exploitation, which consisted of the extraction of rough clay cubes by hand tools. The following handling and storage operations smoothed the cube corners and they became rounded, hence “ball” shaped.

Ball clay deposits originate by erosion of kaolinized rocks and transportation by the action of water and wind in sedimentary basins within continental environments (alluvial, lacustrine, deltaic, tidal). Typical ball clays have a rather simple mineralogical composition, consisting essentially of kaolinite (disordered), illite (interstratified illite-smectite or kaolinite-smectite terms) and quartz. In addition, there are accessory minerals (feldspars, carbonates, iron oxyhydroxides, etc.) and some carbonaceous material [13][14][16]. The organic matter present in ball clay is important to ensure the proper rheological behaviour in casting operations. On the contrary, the carbon content must be very low in wall and floor tile production to prevent defects in fast firing cycles, especially for porcelain stoneware tiles. The diagenesis of ball clays must be limited to avoid any mineral transformations that can deteriorate key properties, like plasticity. In fact, increasing burial brings about illitization of smectite-rich interstratified terms, modifica-



Figure 4 Example of white-firing plastic clay mining, South Africa. (© Bertolotti)

tion of kaolinite (disordered → ordered → dickite → pyrophyllite), illite conversion into sericite and so on.

There are ball clays of average plasticity (type I) that are used mainly in whiteware production. They contain kaolinite (ordered to disordered) prevailing over illite and quartz, with minor feldspars, I/S mixed-layers and organic matter (Table 4). The particle size distribution of ball clays is generally rather fine, since it is expected that this improves plasticity in shaping and the mechanical strength of semi-finished ceramic products.

Highly plastic clays, frequently utilized for tile production, pertain to the white-firing materials of type II. They are similar to the previous ball clays but have a lower content of kaolinite, usually disordered (Table 4). The considerable amount of illite (and often interstratified illite-smectite terms) promotes plasticity and also enhances fusibility, but it worsens the rheological characteristics. In fact, this kind of clay is not suitable for slip casting (e.g. sanitaryware). The colour after firing of the best quality is white/light grey for low iron content (< 1.5 % Fe<sub>2</sub>O<sub>3</sub>).

Table 4 Chemical and mineralogical composition of ball clays. (© Dondi)

Oxide (mass-%)	Type I (typical range)	Type II (typical range)
SiO <sub>2</sub>	52–68	54–68
TiO <sub>2</sub>	0.3–1.2	0.5–1.5
Al <sub>2</sub> O <sub>3</sub>	19–28	20–30
Fe <sub>2</sub> O <sub>3</sub>	0.5–2.0	0.8–2.4
MgO	0.2–1.2	0.5–1.5
CaO	0.1–0.3	0.2–0.6
Na <sub>2</sub> O	< 0.2	< 0.4
K <sub>2</sub> O	0.4–3.5	0.2–2.5
Loss on ignition	6–10	5–12
Mineralogical composition	45–65 % kaolinite, 10–30 % illite, 15–35 % quartz (minor feldspars, I/S mixed-layers, organic matter)	20–40 % illite and mixed-layers, 35–45 % kaolinite, and 10–30 % quartz (minor smectite, feldspars, chlorite, organic matter)

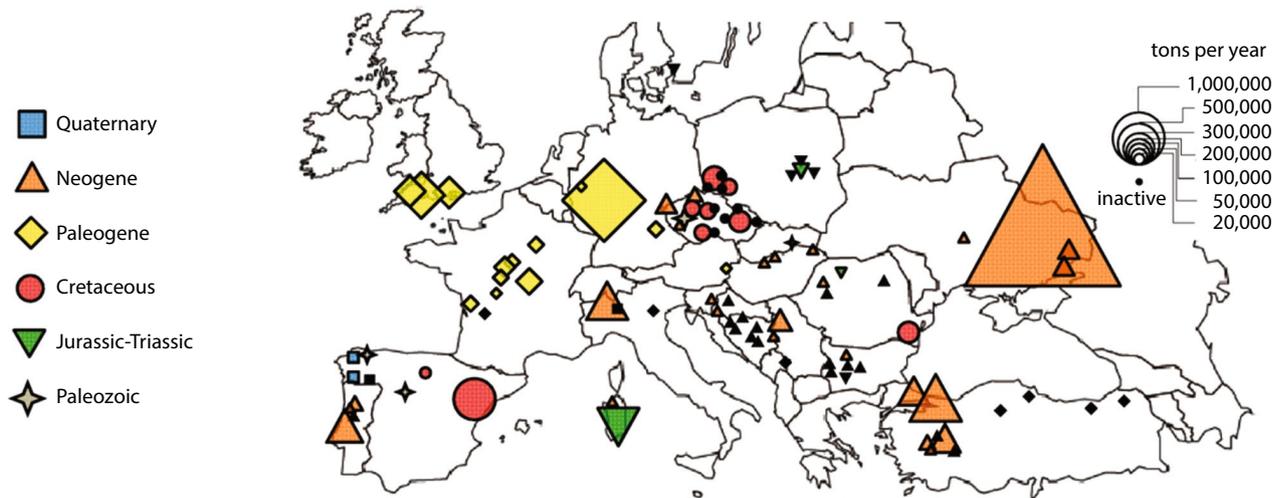


Figure 5 Distribution and age of the major deposits of white-firing clays in Europe [17]. (© Dondi)

Geological criteria in the search for white-firing plastic clay deposits

In general, geological clues for these clay deposits are:

- ▶ Proximity to crystalline massifs (with abundant granitoids and felsic metamorphic) or volcanic complexes (with acidic rocks)
- ▶ Occurrence of periods with humid-warm climate, which promoted some chemical alteration of parent rocks (kaolinization)
- ▶ Contemporaneous erosion of kaolinized rocks, transportation over short distances and clay sedimentation in restricted continental basins, such as lakes, swamps, and meandering rivers
- ▶ Mainly tertiary sediments, even though Mesozoic deposits are known; the cases of Paleozoic or Precambrian age are rare (Figure 5)

The exploitation of these clays is organized in open air areas, starting from evident outcrops present on rolling hills with low slope. The thickness ratio overburden/clay is a key issue for the economic exploitation. It must be as low as possible, even though a ratio until 5/1 is affordable in the case of high alumina and low iron/titanium clays.

Generally, no beneficiation is performed on plastic clays but special care is necessary for the extraction of individual bodies and levels. Alluvial and lacustrine environments imply

that sedimentary deposits usually exhibit short-range changes in mineralogy and granulometry. Thus, to ensure and keep under control constancy, it is strongly suggested to set up a selective and monitored excavation. For this purpose, it is necessary to study all the possible clay qualities carefully, due to the different bodies and sedimentary gradients identified in each deposit. This will help an efficient exploitation and storage to blend different clay grades in proper proportions.

Any economically viable clay deposit must have reserves of not lower than one million tons to ensure a constant supply of pro-

duction for many years. The distance between the clay deposit and the future factory site must be as short as possible, but in some cases, it can be up to 1000 km or more for clay specialties.

### 3.3 Medium-low plasticity white-firing clays

Among the white-firing clays, those with a moderate to scarce plasticity are more common in nature than the highly plastic clays (Figure 6). Clays with a medium-low plasticity usually have as dominant minerals: quartz 35–55 %, kaolinite 10–30 %, illite up



Figure 6 Example of: medium-low plasticity white-firing clay mining (Italy). (© Bertolotti)

**Table 5** Chemical and mineralogical composition of medium-low plasticity white-firing clays.  
(© Bertolotti)

Oxide (mass- %)	Medium plasticity (typical range)	Low plasticity (typical range)
SiO <sub>2</sub>	65–67	68–72
TiO <sub>2</sub>	0.5–2.0	1–2
Al <sub>2</sub> O <sub>3</sub>	20–22	16–18
Fe <sub>2</sub> O <sub>3</sub>	1–2	1–2
MgO	0.2–0.5	0.2–0.5
CaO	0.1–0.2	0.2–0.4
Na <sub>2</sub> O	0.1–0.5	0.1–0.5
K <sub>2</sub> O	1.5–3.0	1–4
Loss on ignition	6–8	4–6
Mineralogical composition	Kaolinite, quartz, illite, feldspars	Kaolinite, quartz, illite, illite-smectite mixed layers, feldspars

to 30 % and minor amounts of K-feldspar, mica, iron oxyhydroxides (Table 5). Sometimes, chlorite, pyrophyllite and carbonates can occur, while smectite and illite-smectite mixed layers are generally absent or present in very low amounts [13]. They are white/light grey in colour after firing, when the Fe<sub>2</sub>O<sub>3</sub> content is approximately between 1 and 2 % [18].

Since no beneficiation is normally affordable for these clay materials, selective mining is highly recommended, at least to discard any level or body of the sedimentary sequence that may contain undesired components (e.g. pyrite, marcasite, carbonaceous matter, high amounts of Fe<sub>2</sub>O<sub>3</sub>) or may have unsuitable technological properties (due to a high amount of sandy-silty fractions, excessive percentage of Al<sub>2</sub>O<sub>3</sub>, etc.).

#### Geological criteria in the search for medium-low plasticity white-firing clays

Most of the clues described above for highly plastic clays are valid for medium-low plasticity types as well. At variance, these latter raw materials originated after a moderate weathering of parent rocks and in continental environments with a higher energy of transportation and deposition than highly plastic clays. Overall, these circumstances lead to the predominance of illite over kaolinite, smectite and mixed-layers, and to a

greater amount of residual minerals (quartz, feldspars, mica).

These clay materials essentially have a local market, and mining operations are frequently directly in the charge of the ceramic manufacturers. In any case, the distance from the mine to the ceramic factory must be as short as possible to lower transportation costs.

### 3.4 Red-firing plastic clays (without carbonates)

Red-firing plastic clays can be found in a wide range of depositional environments, from continental to deep sea. The most important deposits, currently exploited by the ceramic tile industry, pertain essentially to fluvio-lacustrine up to tidal plain sequences, as it occurs in Brazil [19], Poland [20] and Spain [21][22]. At variance, marine sequences – including shelf, slope, and abyssal plains – have been extracted in Italy [23]. Economic deposits are known also from glacio-lacustrine and fluvio-glacial sediments.

Even so, it must be considered that individual levels with relatively high amounts of Fe<sub>2</sub>O<sub>3</sub> frequently occur in the fluvio-lacustrine sequences of white-firing clays described above. In this case, red-firing clays are not too different from the white-firing ones, except for the amount of iron and manganese oxides. The best qualities do not contain carbonates and must have a very low sulphur and chlorine content. Their raw appearance shows different colours from grey, green to brown, but after firing they turn to brown or reddish shades (Figure 7). These



**Figure 7** Example of red-firing plastic clays mining (Jeddah, Saudi Arabia). (© Bertolotti)

**Table 6** Chemical composition of red-firing clays (non-carbonatic). (© Dondi)

Oxide (mass-%)	Fluvio-lacustrine				Marine
	Buntsandstein	Corumbatai	Weald	Paleogene	Paleogene
SiO <sub>2</sub>	56–62	56–73	47–67	53–66	56–59
TiO <sub>2</sub>	< 1	< 1	< 1	1.0–1.5	< 1
Al <sub>2</sub> O <sub>3</sub>	17–22	12–20	16–28	20–30	18–21
Fe <sub>2</sub> O <sub>3</sub>	6–8	3–7	5–9	3–9	7–8
MgO	0.5–2.5	1–4	0.5–2	0.5–2	2.5–3
CaO	0.5–2.5	< 3	0.5–2	< 1	< 2
Na <sub>2</sub> O	< 0.5	1–4	< 1	< 1	< 1.5
K <sub>2</sub> O	3–7	2–5	3–6	1–4	3–4
Loss on ignition	4–8	2–10	4–8	5–10	5–8

raw materials, which come from the same sequences of white-firing clays, can reach temperatures of up to 1200 °C without any intolerable deformation. However, red-firing clays from other occurrences are frequently more fusible, so their use may be restricted to lower temperatures (1100–1170 °C).

Overall, red-firing plastic clays exhibit a complex mineralogical composition, including clay minerals in highly variable proportions (illite, chlorite, kaolinite, smectite, mixed-layers) along with quartz, feldspars, Fe-oxyhydroxides and sometimes low amounts of carbonates (Table 6). Smectite and other expandable clay minerals (vermiculite, illite/smectite and chlorite/smectite mixed layers) are beneficial, but they must be in low percentages for ceramic purposes. Their function is that of conferring plasticity to red-body formulations without inducing too much shrinkage after firing. For instance, fluvio-glacial sediments – once altered in Ferretto soil – present a peculiar assemblage of smectite with rock fragments (providing quartz, feldspars, micas, amphiboles, serpentine, chlorite, quartz and so on), which leads to plastic raw materials despite their prevailing silty and sandy fractions.

Geological criteria in the search for red-firing clays for tile production

Although plastic clays can be found in a wide range of geological contexts, the general criterion is that of looking for depositional

environments of low energy, possibly without contributes from high-energy episodes, which provide coarse-grained and non-plastic sediments. These conditions occur in both continental (lake, swamp and meander cut-off) and marine environments (shelf, slope, abyssal plain). Marine depositional sequences have the advantage of a much greater lateral continuity and often smooth compositional gradients (especially horizontal ones). However, they suffer from unavoidable coarse-grained intercalations such as channel fillings (slope) or distal turbidites (plain) along with intrabasinal contributions (typically carbonatic microfossils). Fluvio-lacustrine sediments usually exhibit a limited extension of individual clay bodies but are easier to exploit because sands and gravels are better constrained in coarsening-upward

or cut-bank sequences. Swamp and lagoonal deposits frequently include organic matter, up to lignite levels.

The ages of the major continental deposits exploited by the ceramic industry include Permo-Triassic (e.g. Buntsandstein and Corumbatai facies), Cretaceous (e.g. Weald facies) and Paleogene sequences (mostly fluvio-lacustrine). The most important marine deposits are Cretaceous to Oligocene in age. However, there are also examples of lower Paleozoic to Precambrian argillaceous sediments, as well as Neogene and Quaternary clay materials, all extracted for ceramic purposes.

In any case, key points are: The *degree of diagenesis*, which in principle should be as low as possible. A certain extent of lithification is tolerable, as long as the grinding process allows a good degree of plasticity to be recovered. The *occurrence of non-clay lithotypes*, such as limestone, sandstone, pyroclastic strata; the occurrence of these “hard rocks” must be managed through selective mining or effective separation on the quarry site prior to primary crushing. A *tout-venant* excavation is the option only in special cases, where selective extraction is not widely practicable, for example with landslide deposits or tectonic mélanges (where clay occurs intimately admixed with other lithotypes).

Another important issue is the number of *undesired components* – like pyrite, organic matter, gypsum or halite – which can cause defects (black core, glaze pinholes and coloured stains, etc.) or release harmful gases

**Table 7** Chemical composition of carbonatic red-firing clays. (© Dondi)

Oxide (mass-%)	Lacustrine	Tidal plain	Marine shelf	Distal turbidites
SiO <sub>2</sub>	33–53	28–30	45–53	55–59
TiO <sub>2</sub>	< 1	< 0.5	< 1	< 1
Al <sub>2</sub> O <sub>3</sub>	11–20	10–12	12–15	16–17
Fe <sub>2</sub> O <sub>3</sub>	3–6	4–6	4–6	6–7
MgO	1–2	1–2	3–4	3–6
CaO	8–23	23–26	9–13	2–4
Na <sub>2</sub> O	< 0.7	< 1	1–1.5	1–2
K <sub>2</sub> O	2–5	2–5	2–3	3–4
Loss on ignition	14–22	23–25	12–15	6–8



**Figure 8** Example of red-firing clays with carbonates (Algeria). (© Bertolotti)

during firing ( $\text{SO}_x$ , HCl). Also, the amount of fluorine must be kept under control, especially when illite is abundant. All these components are common in clays deposited in lacustrine, lagoonal or evaporitic environments, and their quantitative analysis is fundamental. It is best if the amounts are below 0.2 mass-% for sulphur and organic carbon and < 0.05 % for Cl and F. In the case of values exceeding these thresholds, it is recommended that the levels or bodies richer in contaminants be recognized and removed by selective extraction.

Geomorphology can be helpful to identify plastic clays, since they form rounded hills with gentle slopes. Despite their intrinsic value, these clays have a low price, and any production cost must be minimized. For this reason, deposits must be not far from the ceramics factory, and the overburden/clay thickness ratio must be very low, not exceeding 2/1. As the market is exclusively local, in many cases, mines are licensed directly to the tile manufacturers or managed by consortia at the ceramic district level. The reserves available for each deposit must be not lower than 500,000 to 1,000,000 t.

### 3.5 Red-firing clays with carbonates for wall tile production

Marly sediments, that are clay materials with a significant amount of carbonates, can be

found in a wide range of depositional environments, going from marine to frankly continental, as for non-carbonatic plastic clays. All known deposits provide red-firing raw materials, which are not suitable for low-porosity bodies (such as floor tiles). They can be utilized essentially for wall tile bodies, like monoporosa (single-fired) or birapida (double-fired). Their maximum firing temperature cannot be higher than 1050–1100 °C, with fast cycles.

The major deposits exploited by the ceramic tile industry include fluvio-lacustrine and tidal plain sequences [24], even though marine shelf formations are very common [23]. Fine-grained and detritic facies, like distal turbidites, can be low in CaO (Table 7).

These deposits typically appear in grey colour with bluish, greenish or reddish shades (Figure 8).

The mineralogical composition of these clay materials is similar to the previous category, apart from the significant presence of carbonates (calcite and/or dolomite), which can be either detritic or biogenic, or both. There is no recommended amount of carbonates, as the percentage of marly clay in the batch depends on the calcite and dolomite content. As a rule of thumb, typically 10–12 % of carbonates must be provided in a monoporosa batch (up to 20 % in a birapida formulation).

### Geological criteria in the search for red-firing clays with carbonates for tile production

The general criteria to follow in the search for marly clays are in common with the other red-firing clays. This is particularly true for the key points (diagenesis, contaminants, undesired lithologies). Although the depositional environments can be analogous to carbonate-free clays, marly clays are frequently found in marine basins. The carbonate content depends on several factors, including the source of sediments, any intrabasinal biogenic supply and the depth of original deposition (that must be below the carbonate compensation depth).

These deposits must be near the production factory and usually belong to the tile company.

## 4. Conclusions

As a first step in the prospection for clay deposits, the various types of clay materials of interest in ceramic manufacturing have been described. The origin and composition of such deposits, as well as the geological criteria in the prospection of ceramic clays, are illustrated. ◀

## References

- [1] Worrall, W.E., 1975. *Clays and Ceramic Raw Materials*. Applied Science Publishers, London.
- [2] Harvey, C. C., & Murray, H. H. (1997). Industrial clays in the 21<sup>st</sup> century: A perspective of exploration, technology and utilization. *Applied clay science*, 11(5-6), 285-310.
- [3] Bergaya, F. B. K. G., & Lagaly, G. (2013). General introduction: clays, clay minerals, and clay science. In *Developments in clay science* (Vol. 5, pp. 1-19). Elsevier.
- [4] Merriman, R. J., Highley, D. E., & Cameron, D. G. (2003). Definition and characteristics of very-fine grained sedimentary rocks: clay, mudstone, shale and slate. *British Geological Survey, Commissioned Report CR/03/281N*, 20 p.
- [5] Brigatti, M. F., Galan, E., & Theng, B. K. G. (2013). Structure and mineralogy of clay minerals. In *Developments in clay science* (Vol. 5, pp. 21-81). Elsevier.
- [6] Lory, J. (2015). *Clay Mineralogy*. <http://soilnews.feedsinews.com/clay-mineralogy/>
- [7] Galán, E., & Ferrell, R. E. (2013). Genesis of clay minerals. In *Developments in clay science* (Vol. 5, pp. 83-126). Elsevier.
- [8] Hallam, A. (1981). *Facies interpretation and the stratigraphic record*. Oxford Press, 291 p.
- [9] Şentürk, M., Tagliasacchi, E., & Yağmurlu, F. (2019). Depositional features and coal potential of the Gölbaşı-Bahçeköy Neogene Basin, Ankara (Central Turkey). *Arabian Journal of Geosciences*, 12(16), 1-14.

[10] Prasad, M. S., Reid, K. J., & Murray, H. H. (1991). Kaolin: processing, properties and applications. *Applied clay science*, 6(2), 87-119.

[11] Pei-Yuan Chen, Meh-Ling Lin, Zhi Zheng (1997). On the origin of the name kaolin and the kaolin deposits of the Kauling and Dazhou areas, Kiangsi, China. *Applied Clay Science*, 12, 1-25

[12] Orris, G.J. and Hosterman, J.W. (1998). Additional descriptive models of industrial mineral deposits. U.S. Geological Survey, Tucson, Arizona, Open-File Report 98-505.

[13] McCuiston, J., Wilson, I.R., 2006. Ball clays. *Industrial Minerals and Rocks*, 7<sup>th</sup> edition, pp. 343-356.

[14] Petrick, K., Diedel, R., Peuker, M., Dieterle, M., Kuch, P., Kaden, R., Krolla-Sidenstein, P., Schuhmann, R., Emmerich, K., 2011. Character and amount of I-S mixed-layer minerals and physical-chemical parameters of two ceramic clays from Westerwald, Germany: implications for processing properties. *Clays Clay Minerals* 59, 58-74.

[15] Dondi, M., Guarini, G., Raimondo, M., & Salucci, F. (2003). Influence of mineralogy and particle size on the technological properties of ball clays for porcelainized stoneware tiles. *Tile and Brick International*, 19(2), 76-85.

[16] Wilson, I. R. (1998). The constitution, evaluation and ceramic properties of ball clays. *Cerâmica*, 44, 88-117.

[17] Dondi M., *Raw Materials for Ceramic Tiles: Overview of the European Deposits*, European Innovation Partnership – Raw Materials Commitment CRAM, 2016, Paper no. 16-03, pp. 1-55.

[18] Dondi, M., Raimondo, M., & Zanelli, C. (2014). Clays and bodies for ceramic tiles: Reappraisal and technological classification. *Applied Clay Science*, 96, 91-109.

[19] Christofoletti, S., Moreno, M., & Motta, J. (2009). La Formación Corumbataí y su importancia en la industria cerámica del estado de São Paulo-Brasil. *Matéria* (Rio de Janeiro), 14, 705-715.

[20] Wyszomirski, P., & Galos, K. (2009). Polish clayey raw materials for the production of ceramic tiles. *Clay Minerals*, 44(4), 497-509.

[21] Martín, J. D. M. M., Sanfeliu Montolio, T., Gómez-Gras, D., & Jordán, M. M. (2006). Caracterización litológica y mineralógica de los materiales permotriásicos de Castellón utilizados como materia prima cerámica: la arcilla de Moró. *Boletín de la Sociedad Española de Cerámica y Vidrio*, 45(4), 239-244.

[22] Meseguer, S., Jordán, M. M., Pardo, F., & Sanfeliu, T. (2011). Geology and application of clays used in Castellon ceramic cluster (NE, Spain). *Journal of Geography and Geology*, 3(1), 132-140.

[23] Dondi, M. (1999). Clay materials for ceramic tiles from the Sassuolo District (Northern Apennines, Italy). *Geology, composition and technological properties*. *Applied Clay Science*, 15(3-4), 337-366.

[24] Bastida, J., & Beltran, V. (1986). Arcillas cerámicas de la provincia de Valencia. *Bol. Soc. Esp. Ceram*, 25, 231-235.

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