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# The use of illitic clays in the production of stoneware tile ceramics

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**Abstract**

Illite is one of the main clay phases used for the preparation of mixtures for traditional ceramics. The raw materials used for production of white porcelain stoneware tiles mainly consist of feldspars, quartz, and clay minerals (kaolinite, smectite and illite). In this study, eight clayey raw materials with a different content of illite up to 70 wt.%, have been considered. The crystalline phases present in different amounts are illite, smectite, kaolinite, illite–smectite mixed-layers, K-feldspar, plagioclases, quartz, and accessory phases (anatase, goethite). The clays have been chemically and physically characterized as raw and fired materials with X-ray diffraction, X-ray fluorescence, and SEM. Moreover they were added in the percentage of 35 wt.% to a mixture composed of albite, feldspar sand and quartz sand, to reproduce that commonly used for the production of porcelain stoneware tiles. We focused on the quantitative mineralogical aspects of the unfired and fired bodies and their relationship with the technological properties due to the presence of illite. Increasing illite content yields higher percentage of glass phase and lower water absorption because of the lowering of the melting point. Because of the pyroplastic deformation, linear shrinkage decreases with illite content. The presence of illite inhibits the formation of mullite and cristobalite, since silica and alumina tend to form alkaline glass. Although in clays from Hungary, transition elements are present in very low percentage, the colour of the fired bodies is darker. These clays contain goethite, which may be rapidly oxidized with temperature, and show a very low percentage of newly formed mullite which could eventually host Fe in its structure.


*Keywords:* Illitic clays; Traditional ceramics; Firing; Glass; Ceramic tiles; Porcelain stoneware

## 1. Introduction

Knowledge of the mineralogical phase composition and especially clay fraction of the raw materials used for the preparation of ceramic mixtures is of paramount importance for understanding of the technological properties of ceramic products and optimization of firing cycles in production.

The term "illite" was first introduced by Grim et al. (1937) describing a colloidal mica-like mineral, commonly found in clayey sediments. Nowadays, the term "illite" refers to an aluminum–potassium mica-like, non-expanding, dioctahedral mineral, present in the clay fraction. Together with kaolinite, chlorite and smectite, illite is in fact one of the four major phases of clayey sedimentary rocks.

In accordance with the recent IMA (International Mineralogical Association) protocol on micas nomenclature (Rieder et al., 1998), dioctahedral K-micas with an interlayer cation content ranging between 0.85 and 1 per half-cell are defined muscovites, while illite forms a series with an interlayer cation content from 0.6 to 0.85. Since little is still known about the nature and stability of illite, it is not appropriate to give an ultimate

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definition of this phase upon a chemical basis. A more suitable term would be K-deficient mica, at least until the relationship between muscovite and illite is definitely resolved.

An approximate formula for illite, deduced by studies on natural materials (Inoue et al., 1987), can be written as (Rosenberg, 2002): $K_{0.88}Al_2(Si_{3.12}Al_{0.88})O_{10}(OH)_2 \times nH_2O$. An example of chemical analysis of a pure illite sample from Kaube (Japan), was given by Środoń and Eberl (1984): $SiO_2$ 47.4%, $TiO_2$ 0.23%, $Al_2O_3$ 35.60%, $Fe_2O_3$ 1.50%, MgO 0.30%, CaO 0.02%, $Na_2O$ 0.53%, $K_2O$ 9.12%.

Illite can be formed under several minerogenetic conditions (Środoń and Eberl, 1984). The most abundant ores were originated in weathering, diagenetic, metamorphic or hydrothermal environment, where formation mechanism is termed *illitization*. This process mainly involves the transformation of smectite into illite. Sedimentary environments may also contain illite although, because of their limited spatial distribution, they have minor importance.

There are many fields where illitic clays play an important role: illite is one of the major component of clays used in traditional ceramics for the production of cooking pots, plates, tiles and bricks. Of great importance is the application for the production of stoneware tiles, the top product in the market of traditional ceramics. Stoneware tiles present a white body whose surface may or may not be glazed, having very low water absorption and outstanding technological properties. The manufacture process basically consists of a wet milling, spray-drying, pressing, drying at 150–250 °C and firing in roller kilns (Biffi, 1997) with a $T_{max}$ = 1190–1230 °C. Stoneware tiles are generally characterized by high mechanical strength, resistance to abrasion, frost and common chemical agents (acids, cleaning products, etc.). The latest trends in porcelain stoneware tile design require reformulating compositions to produce intense white color and close to zero porosity.

A recent study (Aras, 2004) reports the changes of the technological properties of mixtures with different clay composition (kaolinite-and illite-rich clay-based ceramic bodies) and shows that cristobalite formation is inhibited in illite/sericite-rich bodies. On the other hand, formation of mullite and cristobalite is observed in fired kaolinitic clays. In illite/sericite-rich mixtures, high K content produces in temperature a large amount of melt that inhibits mullite formation.

Here, we systematically studied eight clays containing different proportions of kaolinite and illite and focused the attention on the technological characteristics of the unfired and fired bodies. The first attempt is the interpretation of variations of phase composition and properties of the fired clays with respect to different content of illite in the raw material. Secondly, behavior of stoneware mixtures prepared using the eight clays has been thoroughly investigated. To this aim, we focused on the quantitative mineralogical aspects of the raw and fired bodies and relationship with the technological properties.

## 2. Materials and methods

### *2.1. Sample selection and preparation*

Six clays characterized by different contents of illite and two kaolins were selected for the study. The raw materials were labeled C1 C2 C3 C4 C5 C6 C7 and C8:

- C1 kaolin from the Podborany basin (Czech Republic);
- C2 kaolin from the Troup basin (U.S.A.);
- C3 illitic clay from the Allier basin (France);
- C4 illitic clay from the Donetsk sedimentary basin (Ukraine);
- C5 and C6 illitic clays from Turkey;
- C7 and C8 illitic clays from Füzérradvány (Hungary).

Prior to the preparation of the mixtures, the eight clays were fully characterized. For each raw material a chemical, physical and mineralogical characterization was accomplished. The clays were heated up to 1200 °C, using a standard ceramic firing cycle (43′) to monitor the variation of linear shrinkage and water absorption with temperature.

An ideal formulation similar to those used in the Sassuolo (Italy) district has been chosen for the preparation of the white stoneware tile mixtures. Each mixture contains 35 wt.% of one clay phase (C1 C2 C3 C4 C5 C6 C7 and C8), 40 wt.% of sodium feldspar (albite from Menderes Turkey), 15 wt.% of feldspar rich sand (from Valsugana, Italy), and 10 wt.% of quartz sand (from Florinas Sardinia, Italy). These are high quality raw material commonly used for the manufacture of stoneware tiles. The mixtures were labeled A (with C1), B (with C2), C (with C3), D (with C4), E (with C5), F (with C6), G (with C7), and H (with C8).

### *2.2. Sample characterization*

Both the raw materials and the mixtures were ground using a lab wet mill (M.M.S. 1 l porcelain jar). The ground agglomerates were dried, powdered and humidified to 6 wt.%. The humid powders were pressed at 350 kg/$cm^2$ to obtain 5 cm diameter and 1 cm thick discs. Once dried, the discs were fired using a Gabbrielli (1.5 m) laboratory electric roller kiln and a 43 min long cycle