



Research Paper

Comparative study of technological behavior of German ball clay and Italian kaolinitic clay in unconventional porcelain stoneware body

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ABSTRACT

This work focused on obtaining a porcelain stoneware body containing only Italian raw materials. The starting mixtures differed in the feldspathic fraction, one pumice-based and one lapillus-based. German ball clay was gradually replaced by Italian kaolinitic clay. The influence of Italian kaolinitic clay on the technical and aesthetic properties of the final product was analyzed by comparing it with the references. The work was carried out in collaboration with a ceramic company which allowed the tile production process to be simulated in the laboratory and fired in an industrial kiln using the production cycle (48 min, 1210 °C). Ceramic bodies were characterized in order to evaluate technological performance by measuring efflux time and density of slip, flexural strength on green, linear shrinkage and water absorption in vacuum on fired samples. Mineralogical, microstructural (ESEM) and colorimetric analyses were also performed on the fired samples. Efflux time and density are processing parameters; these were in line with the reference in the lapillus-based bodies with kaolinitic clay replacement rates of 100%; in the case of the pumice-based bodies, they were considered acceptable only for replacements of 25%. The lapillus-based body showed a microstructure similar to that of porcelain stoneware. Vacuum water absorption values were better in lapillus-based formulations than in pumice-based formulations but showed higher linear shrinkage values for 100% replacements. According to UNI EN 14411 ISO 13006, some of the products obtained can be classified as porcelain stoneware (group B1a).

1. Introduction

The ceramic industry in recent years has been stressed firstly by the arrival of the pandemic, which caused a mandatory stop in production, and then by the conflict between Ukraine and Russia, which caused an increase in the prices of key raw materials such as methane gas and a drastic reduction in the export of Ukrainian clays. In addition to this, it must also be considered that ceramic industries must contribute to the achievement of the goals of the 2030 Agenda for Sustainable Development (United Nations, 2024). In this regard, the Italian ceramic tiles industry, in recent years, has worked to reduce its emissions and be increasingly sustainable. Indeed this sector has achieved high energy savings, significant reductions in water consumption thanks to the wastewater recycling (56% of water needs) and the reuse of almost all production wastes (De Ceglia, 2022; Confindustria Ceramica, 2024; Boschi et al., 2020; Settembre Blundo et al., 2019).

Due to the aforementioned events, the ceramic industries are always looking for new raw materials that can replace those already in use,

because both are difficult to find and the need to become independent from raw material imports is growing.

A porcelain stoneware body consists of a mixture of raw materials:

- plastic component provided by clays, in Italy the clays used come mainly from Ukraine and Germany;
- flux component, given by feldspars that come mainly from Turkey;
- inert component, provided by quartz sands and chamotte.

Numerous papers related to the study of formulations for stoneware or ceramic tiles bodies can be found in the literature. Analyzing the scientific works it is possible to find papers in which the technological properties of ceramic tiles were studied, where the clay fraction consisted of iron-rich clays: Italian red clay (Fantini et al., 2024) and Thai red clay (Nawaukaratharnant et al., 2022.) for the production of porcelain stoneware, lower clays rich in CaO and Fe₂O₃ for obtaining industrial prototypes of excellent quality with reduced firing temperature (Jiang et al., 2017). Mixtures for the production of porcelain stoneware

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based on Spanish kaolinitic clays after reducing, through physical processes, the impurities of iron compounds and organic matter (Barrachina et al., 2017) and based on Colombian kaolinitic clays, introducing different fluxes to increase the degree of sintering (Ramírez Calderón et al., 2019) have been studied. The behavior of Tunisian plastic clays has been compared with that of plastic clays commonly used in Italy for the production of porcelain stoneware (Molinari et al., 2023) but the behavior of white-baked plastic clays from central and eastern European regions has also been studied (Galos, 2011). Still, the use of serpentinite waste sludge from dunite quarries as raw materials in the ceramic industry has been evaluated (Díaz and Torrecillas, 2007), the replacement of part of the clay fraction with bentonites has been studied (Andreola et al., 2009), and the effect of hematitic iron ore and limestone additives on the stiffness of bentonite clay materials in porcelain stoneware paste has been investigated (Ismail et al., 2017).

The aim of this study was to obtain a body consisting only of Italian raw materials, starting from a porcelain stoneware body obtained in a previous work, where technological properties had been studied and evaluated. The starting porcelain stoneware bodies consisted of German ball clay, Italian kaolinite and Italian kaolinitic clay (the latter in a very low percentage) for the plastic component, mining and processing scraps of volcanic-sedimentary rocks (pumice rock or lapillus rock), Italian feldspar scraps for the flux component, and feldspathic sand and chamotte (from the same production cycle) for the inert component (Altimari et al., 2023). Italian kaolinitic clay gradually replaced German ball clay at 25%–50%–100%. The obtained products were compared by analyzing the main technological parameters to assess the differences due to substitution and any strengths or weaknesses.

2. Materials and Methods

2.1. Raw materials and samples preparation

Raw materials used in this work were: commercial ball clay from central-western Germany (Westerwald region, loc. Meudt), the deposits are of a fluvio-lacustrine environment (dating from the Eocene-Oligocene period) and result from the alteration and erosion of Devonian groves, shales and quartzites; commercial kaolinitic clay from northern Italy (Piedmont region, loc. Novara), the deposits are of a fluvio-lacustrine environment (dating from the Pliocene-Pleistocene); commercial kaolinite from central Italy (Lazio region), originating from kaolinitic deposits formed by hydrothermal alteration phenomena at Quaternary volcanites; sedimentary-rock scraps (pumice rock and lapillus rock) from central Italy, located between Viterbo and Grosseto (Barbieri et al., 2023); feldspar scraps from northern Italy (Piedmont region); feldspathic sand from northern Italy (Emilia Romagna region) and chamotte (ground fired ceramic scraps).

The raw materials described were included in different percentages within the mixture depending on their function: 45 wt% the plastic component, about 35 wt% the flux component, and about 20 wt% the inert component. The formulations taken as reference, L0 and P0 in Table 1, were developed in a previous work (Altimari et al., 2023).

Table 1

Batch prepared with pumice-based or lapillus-based bodies by replacing German ball clay with Italian kaolinitic clay. All values are in percentages (%).

	L0	L25	L50	L100	P0	P25	P50	P100
German ball clay	35	26	17.5	–	35	26	17.5	–
Italian kaolinitic clay	2	11	19.5	37	2	11	19.5	37
Italian kaolin	8	8	8	8	8	8	8	8
Lapillus	15	15	15	15	–	–	–	–
Pumice	–	–	–	–	16	16	16	16
Italian feldspar	19	19	19	19	17	17	17	17
Italian sand	3	3	3	3	5	5	5	5
Chamotte	18	18	18	18	17	17	17	17

Starting from these formulations, German ball clay was gradually replaced by Italian kaolinitic clay at 25%, 50% and 100% in order to evaluate the influence on technological properties as the percentage of replacement increased. The batches differed from each other in the presence of lapillus rock or pumice rock, so for simplicity below we will refer to lapillus-based or pumice-based products. The two clays have been characterized chemically, mineralogically, and thermally. The chemical and mineralogical characterization of the different raw materials was carried out and provided by the manufacturers of those raw materials. The thermal behavior of the clays was evaluated in terms of reactivity and weight variation with increasing temperature using differential thermal and thermogravimetric analysis. TGA/DTA analyses were performed with a NETZSCH STA 429 CD simultaneous thermal analyzer. The analysis was performed at a heating rate of 10 °C/min on ground samples with average particle diameters <20 µm.

The formulations prepared can be seen in Table 1. The letters L and P designate the lapillus-based or pumice-based mixtures respectively, the following numbers indicate the percentage of substitution of German ball clay in favor of Italian kaolinitic clay (e.g. L25 indicates a mix containing volcanic lapillus scraps with 25 wt% of Italian kaolinitic clay and 75 wt% of German ball clay, the percentages calculated refer to the clay component only).

Before further testing, all raw materials were dried in an oven at 150 °C ± 5 °C for 4–5 h. The slip was obtained by mixing in a fast ball mill (7 min) the raw materials with water in a ratio of 1:0.45 with a commercial deflocculant to increase the workability of the mixture; then the slip was dried, ground and moistened to 6%. Using a hydraulic press, the powders were compacted (pressure of 70–75 MPa) to obtain samples with a diameter of 50 mm for firing (industrial cycle: 48 min at 1210 °C) and with dimensions of 50 mm × 100 mm for calculating the flexural strength. These pressures are much higher than those normally used for laboratory samples, but they make it possible to compensate for the effect of the refractory support used for firing in an industrial kiln (the firing mode used for the samples under study).

2.2. Slip and green samples characterization

The slip is characterized by evaluating efflux time, density, and residual fraction.

The efflux time was calculated as the time required to empty a Ford cup with a nozzle diameter of 4 mm.

Density was calculated in accordance with Eq. 1 by placing the obtained suspension inside a pycnometer with a capacity of 1000 cm³ and of known weight:

$$d \text{ (kg/cm}^3\text{)} = (w_{p+s} - w_p) / 1000 \quad (1)$$

where: d is density, w_{p+s} is the total weight represented by pycnometer plus sample (kg) and w_p is the pycnometer weight (kg).

The residual fraction was calculated using a sieve with a mesh diameter of 63 µm by running slip through it and weighing the remaining solid mass on the sieve after drying.

The flexural strength was calculated on a minimum of four unfired ceramic samples (green) measuring 50 mm × 100 mm, using a Gabrielli Technology mini-CRC 2 Chrometer. The flexural strength on green was calculated because the tile must be able to withstand static and dynamic loads during the movement inside the factory. According to the standard, the tile is placed, like a beam, on two rollers at a distance from each other and a central force is applied by a third roller, which allows the breaking load to be determined, i.e., the weight that the specimen can support before it breaks. The breaking modulus (σ) is calculated from Eq. 2b, once the breaking stress (S) is known, which is equal to the product of the force applied to the working surface (F) and the ratio of the roller spacing to the tile width (L/b) as reported in Eq. 2a (Palmonari and Timellini, 2016).

$$S(N) = F \cdot L/b \quad (2a)$$

$$\sigma = 3FL/2bh^2 \quad (2b)$$

2.3. Fired samples characterization

2.3.1. Physical properties

Using Eq. 3, the weight loss (WL) was calculated:

$$WL (\%) = (w_i - w_f)/w_i \cdot 100 \quad (3)$$

where w_i is the weight of the green sample and w_f is the weight of the fired sample.

The dimensional variations of the samples after firing, at five different points, were measured using an electronic caliper (accuracy: ± 0.01) to obtain the linear shrinkage (LS) value, according to Eq. 4.

$$LS (\%) = (d_i - d_f)/d_i \cdot 100 \quad (4)$$

where d_i is the diameter of unfired pieces (50 mm) and d_f is the diameter of the sample after firing.

The water absorption under vacuum with automatic cycles of porcelain tiles was measured by placing the samples after firing inside a laboratory instrument (ISOVACUUM 650, Gabbrielli Technology) according to ISO 10545 standards. Water absorption (WA) is a parameter that determines the classification of ceramic tiles based on their open porosity. Porcelain stoneware belongs to the B1a group with WA (%) 0.5% (B means the product was formed by pressing).

2.3.2. Mineralogical analysis

Mineralogical analysis was performed on the clays and the fired samples in order to assess whether or not new crystalline phases were formed as a function of the amount of Italian kaolinitic clay substituted compared to those found in the samples containing German ball clay taken as reference. The patterns have been recorded on the powdered samples ($< 38 \mu\text{m}$ in size) for the clays and entire for the fired samples (specimen length 10.00 mm) in the $5-70^\circ 2\theta$ range (step size 0.013° and 1 s counting time for each step), operating at 40 mA and 40 kV mA at room temperature. The measures were conducted using an X-ray diffractometer from PANALYTICAL model Empyrean, with Ni-filtered $\text{Cu K}\alpha$ radiation using brackets holder. The identification of the crystalline phases occurred using the software Highscore Plus software version 3.0.

2.3.3. Microstructural analysis

Microstructural investigation was performed in order to evaluate the effect of the replacement of German ball clay with Italian red one. The instrument used is an environmental scanning electron microscope (ESEM-Quanta 200), combined with an X-ray EDS microanalysis system (X-EDS Oxford INCA-350). The fired samples analyzed were reduced to appropriate size ($< 1 \text{ cm}$ per side) and were metallized with a gold layer of a few nanometers to make the sample conductive.

2.3.4. Colorimetry

The change in the aesthetic properties of the samples and was evaluated by colorimetric testing with a UV-vis spectrophotometer (SPECTROPHOTOMETER CM-2600d, KONIKA MINOLTA), which operates in the $CIE L^*a^*b^*$ color space, allowing the set of colors perceived by the human eye to be described.

The analysis was performed by taking measurements at four different points on the sample surface to calculate the average values of $L^*a^*b^*$. Once these values are known for each sample, the parameter ΔE^* can be calculated by comparing two samples with each other, Eqn 5.

$$\Delta E^* = \sqrt{(L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2} \quad (5)$$

Values of $\Delta E^* > 1$ indicate that there is visible difference between two samples.

3. Results and discussion

3.1. Characterization of clays

The clays were characterized chemically, mineralogically and thermally to assess the similarities and differences between them.

Chemical and mineralogical analysis can be seen in Table 2.

Chemical analysis, performed by X-ray fluorescence spectroscopy and provided by the raw material producers, allows to say that the two clays are comparable to each other in terms of SiO_2 and Al_2O_3 contents. The kaolinitic clay have a higher Fe_2O_3 content than the ball clay but a lower TiO_2 content therefore the sum of the chromophores seems to be comparable in the two cases. The presence of higher Fe_2O_3 content could changes the densification process as observed by other authors (Jiang et al., 2017; Nawaukkaratharnant et al., 2022; Ismail et al., 2017). The Italian kaolinitic clay contain a high Na_2O content, and a slightly higher K_2O content. The alkali oxides increase the fusibility of the system (Bayer Ozturk and Ay, 2012) and thus could prolong the liquid phase and risk obtaining a less sintered product. The sum of alkali-earth oxides, CaO and MgO , is 0.86% for German ball clay and 1.46% for Italian kaolinitic clay. On the other hand, ball clay shows a higher loss by combustion than the kaolinitic clay, probably this could be due to the presence of organic carbon and sulfur.

The quantitative mineralogical analysis showed that the two clays are equal in quartz and kaolinite content. Ball clay contains more illite while kaolinitic clay contains illite and feldspar. Higher illite content results in more plasticity so Italian kaolinitic clay will be less plastic. The potassium in the German ball clay most likely can be linked to the presence of illite while the sodium, calcium and potassium detected in the Italian kaolinitic clay could be linked to the presence of plagioclase and orthoclase.

The thermal analysis performed on German ball clay is shown in Fig. 1 while on Italian kaolinitic clay in Fig. 2. The red curve (TG) shows

Table 2

Chemical, elemental and quantitative mineralogical analyses of clays (Font: Ceramic suppliers).

Chemical analysis		
Oxide (wt%)	German ball clay	Italian red clay
SiO_2	65.5	67.1
Al_2O_3	21.2	19.8
Fe_2O_3	1.86	2.5
TiO_2	1.27	0.8
CaO	0.32	0.72
MgO	0.54	0.74
K_2O	2.22	2.5
Na_2O	0.22	1.8
L.O.I.	6.66	5
Elemental analysis		
(%)	German ball clay	Italian red clay
C	0.17	0.18
S	0.1	0.05
Mineralogical analysis		
(%)	German ball clay	Italian red clay
Quartz	39	40
Kaolinite	33	34
Illite/Mica	23	14
Plagioclase/Orthoclase	-	8
Other	5	-

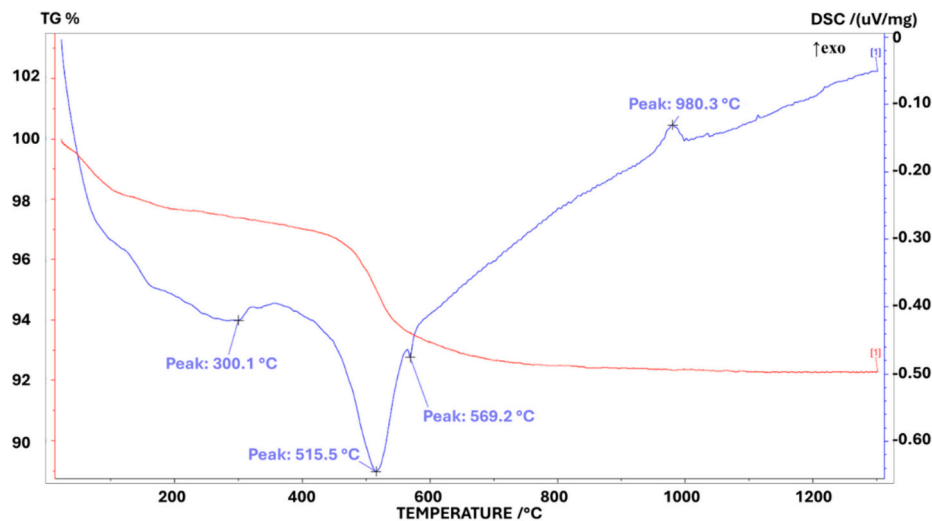


Fig. 1. Thermal analysis of German ball clay.

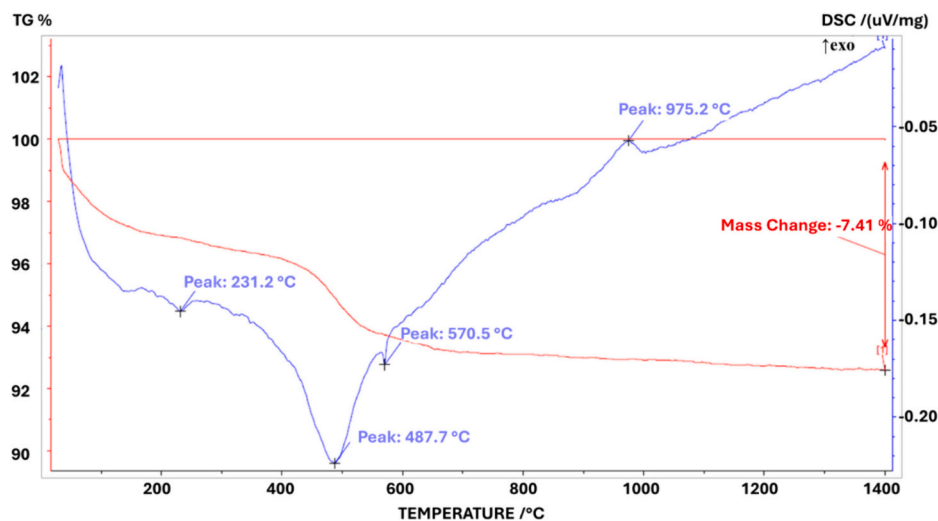


Fig. 2. Thermal analysis of Italian kaolinitic clay.

the weight loss while the blue curve (DTA) describes the *endo*-*exo* events:

- Total weight loss is slightly lower in the case of kaolinitic clay (~ 7.4% vs. ~ 8%) confirming the LOI results;
- The endo event loss of zeolitic water occurs up to higher temperatures for ball clay, but is quantified as a weight loss of about 3% in both cases;
- At temperatures between 487 °C and 570 °C, the endo events are associated to the dehydroxylation, most likely the second peak, which occurs at the same temperature in the two clays, is given by the transformation of kaolinite to metakaolinite with loss of the water of crystallization, resulting in a large weight loss;

- Around 980 °C for ball clay and around 975 °C for kaolinitic clay, there is an exothermic peak probably related to the formation of mullite without weight variation.

3.2. Slip and green samples characterization

Table 3 shows the variation of the analyzed parameters on the slip and unfired samples.

Considering the efflux time, it is possible to say that as the Italian kaolinitic clay content increases this parameter tends to increase. In the case of the lapillus-based mix it is possible to note that, except in the sample containing 100% Italian kaolinitic clay, the values obtained are still acceptable as an industrial parameter. Most likely, in the measurement of the efflux time of sample L100, a problem occurred, such as

Table 3
Analyzed parameters on slip and unfired samples.

	L0	L25	L50	L100	P0	P25	P50	P100
Efflux time (s)	16 ± 0.5	18 ± 0.5	22 ± 0.5	n.a.	21 ± 0.5	22 ± 0.5	37 ± 0.5	n.a.
Density (kg/m ³)	1.731 ± 0.050	1.727 ± 0.050	1.725 ± 0.050	1.773 ± 0.050	1.723 ± 0.050	1.714 ± 0.050	1.717 ± 0.050	1.732 ± 0.050
Residual fraction (g)	3.65 ± 0.01	3.91 ± 0.01	4.14 ± 0.01	4.88 ± 0.01	3.48 ± 0.01	3.59 ± 0.01	3.68 ± 0.01	4.14 ± 0.01
Green flexural strength (MPa)	40.28 ± 0.50	42.21 ± 0.50	39.64 ± 0.50	37.83 ± 0.50	41.3 ± 0.5	34.03 ± 0.50	28.07 ± 0.50	26.05 ± 0.50

a few grains clogging the outlet hole, and did not allow its proper evaluation. In the case of the pumice-based mixture, on the other hand, already with the substitution of 50% clay, the efflux time turns out to be high; therefore, as a result, the efflux time for sample P100 could not be evaluated. The limit value of efflux time, which can be considered acceptable at laboratory scale, is 50 s.

The value of density is related to the efflux time one, normally as efflux time increases, density also increases. As can be seen in both cases, the formulations containing 100% substitution, and which exhibited unmeasurable efflux time values showed higher density values. In general, density tends to maintain similar values up to 50% replacement rates in both the lapillus-based and pumice-based mixtures. To decrease density values and obtain measurable viscosity values, it will be necessary to add more water during grinding.

The residual fraction represents an important process parameter, and by looking at the values given in the table it is possible to say that this increases as the content of Italian kaolinitic clay inserted increases. In all cases the grinding time of the mixtures was 7 min. Most likely as the content of Italian kaolinitic clay within the mix increases, it will be necessary to extend the grinding time by a few minutes (at laboratory scale).

During the production process, the tiles must resist the stresses to which they may be subjected during transport within the plant to move from one production stage to another; for this reason, the flexural strength on the unfired product was calculated. In the case of the lapillus-based mix, the flexural strength tends to decrease as the percentage of clay replacement increases but still remains at fairly high values. In the case of the pumice-based mixture, however, the only acceptable value is the one obtained with 25% clay replacement since in the other two cases the values are very low (minimum acceptable value 35 MPa). The green bending strength is positively correlated with the kaolinite content and negatively related to the coarser particle fraction as reported by [Dondi et al. \(2023\)](#). It must be considered that these are still process parameters that can be improved by modifying the recipe and perhaps substituting some raw materials.

3.3. Characterization of fired samples

3.3.1. Physical properties

The physical properties analyzed were loss of ignition, water absorption and linear shrinkage whose values are reported in [Table 4](#).

Weight loss (WL) values are comparable with each other. The mixture containing a higher percentage of Italian kaolinitic clay has lower losses to the fire, this may be due to a lower presence of organic substances in Italian kaolinitic clay than the German ball clay.

The Italian kaolinitic clay has a coarser grain size than the German ball clay and, this can be inferred from the residual fraction values ([section 3.2](#)). The presence of harder minerals such as quartz and kaolinite led to a larger grain size, which may have changed the firing behavior of the samples. Italian kaolinitic clay is less plastic, and the increase in porosity could be due to this, as porosity may have been created on the green during pressing. Clays with higher illite content are more plastic and tend to fill the pores better during pressing. A less plastic clay with a larger grain size might have led to a different result than would be expected: usually, as the average grain size increases, water absorption increases and linear shrinkage decreases ([Jiang et al., 2017](#); [Fantini et al., 2024](#); [Nawaukkaratharnant et al., 2022](#)). However, these unconventional porcelain stoneware bodies, as shown in previous

work by the authors, tend to have the opposite behavior: if shrinkage increases, absorption increases in turn ([Altimari et al., 2023](#)). A higher presence of quartz and kaolinite (2%) in Italian kaolinitic clay compared to German ball clays made the mixture more refractory. The presence of feldspars in kaolinitic clay contributes to sintering and thus to increase linear shrinkage during firing. Again, iron increases the liquid phase around temperatures of 1130 °C ([Jiang et al., 2017](#)) helping the densification phase and increasing linear shrinkage. However, the presence of iron also goes to affect water absorption values because, during firing, as it reduces, it contributes to gas formation by creating porosity and increasing absorption.

It should be kept in mind that compositionally there are not great differences between the two clays, however, in this case, the variables to be considered increase because of the starting mix, which is not a conventional porcelain stoneware mix since it contains rocks such as pumice or lapillus that affect the behavior of the starting material.

In general, it is possible to say that the water absorption values are very different between pumice-based and lapillus-based mixtures. In each case, as the Italian kaolinitic clay content increases, this value tends to increase, but all values are <0.5% (B1a group).

The linear shrinkage values are higher in samples L100 and P100 than in L0 and P0. It is possible to hypothesize that the higher presence of fluxing components (Fe₂O₃, MgO, CaO, Na₂O, K₂O) in the Italian clay (8,26%) respect to German clay contribute to the sintering and densification process.

3.3.2. Mineralogical analysis

Mineralogical analysis was performed on all fired samples ([Figs. 3–4](#)). In [Figs. 3 and 4](#), the lower curves represent the spectrum of sample L0 and P0 respectively, that is, those with German ball clay, while the upper curves are for samples L100 and P100 respectively, thus containing only Italian kaolinitic clay. In both figures, a raised curve can be seen on the right side between the 5°–33° 2 Theta positions of the spectra, indicating the presence of a glassy phase, normally present in this type of body.

Porcelain stoneware is undergoing to complex transformations during firing with regard to the mineral components of the mixture. The resulting products contain a vitreous phase that can normally be associated with quartz, mullite, and feldspars. Quartz (SiO₂) and mullite (3Al₂O₃•2SiO₂) were detected in both batches of products. Clay minerals around 1000 °C form mullite due to the reaction between Al₂O₃ and SiO₂, contained in the raw materials, especially kaolinitic ones ([Nawaukkaratharnant et al., 2022](#)). The formation of mullite is very important for the mechanical properties of porcelain stoneware.

The lapillus-based batch also showed the presence of feldspars, orthoclase (K Al Si₃ O₈) and albite (Na (Al Si₃ O₈)). As the content of Italian kaolinitic clay increases, the content of SiO₂ and K increase in the mixture, and the intensity of quartz peaks tends to increase as well as that of orthoclase.

In the pumice-based batch, unlike the lapillus-based batches, both mullite and quartz peaks tend to decrease this despite the fact that the amount of iron in the mixture is lower ([Nawaukkaratharnant et al., 2022](#)); this could be due to a higher presence of potassium contributed not only by Italian kaolinitic clay but also by pumice ([Barbieri et al., 2023](#)).

3.3.3. Microstructural analysis

ESEM images of the lapillus-based samples can be observed in [Fig. 5](#)

Table 4
Weight loss (WL %), water absorption (WA %) and linear shrinkage (LS %) of fired samples.

	L	L25	L50	L100	P	P25	P50	P100
WL (%)	3.29 ± 0.10	3.35 ± 0.10	3.24 ± 0.10	2.94 ± 0.10	3.70 ± 0.10	3.50 ± 0.10	3.11 ± 0.10	3.31 ± 0.10
WA (%)	0.05 ± 0.01	0.10 ± 0.01	0.06 ± 0.01	0.19 ± 0.01	0.12 ± 0.01	0.22 ± 0.01	0.35 ± 0.01	0.47 ± 0.01
LS (%)	4.46 ± 0.05	4.46 ± 0.05	4.94 ± 0.05	6.12 ± 0.05	4.94 ± 0.05	5.36 ± 0.05	5.56 ± 0.05	5.66 ± 0.05

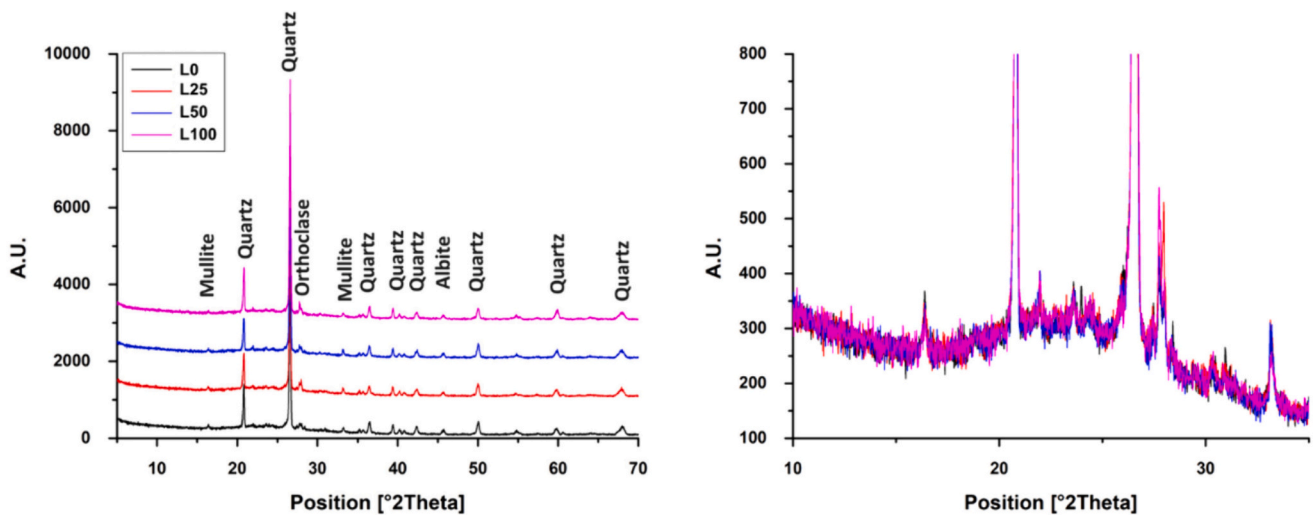


Fig. 3. Mineralogical analysis on lapillus-based materials. On the left are spectra of the formulations, with the percentage of Italian kaolinitic clay increasing from bottom (L0) to top (L100). On the right, magnification between 10 and 30 2 theta to highlight the presence amorphous phase.

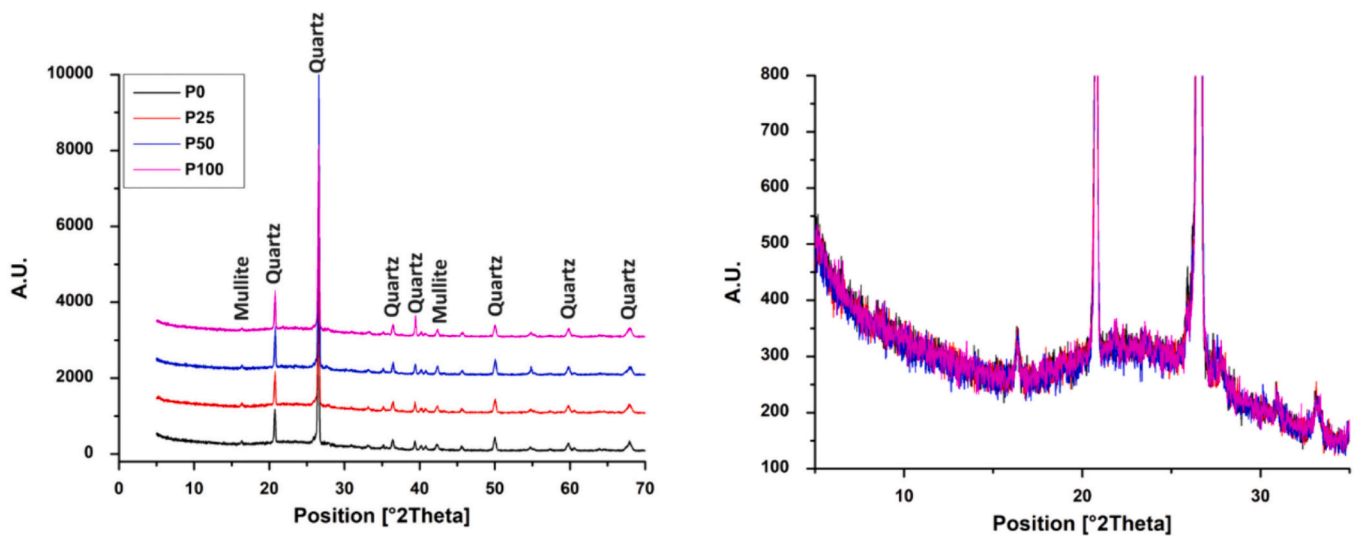


Fig. 4. Mineralogical analysis on pumice-based materials. On the left are spectra of the formulations, with the percentage of Italian kaolinitic clay increasing from bottom (P0) to top (P100). On the right, magnification between 10 and 30 2theta to highlight the presence amorphous phase.

(a-d). The images were acquired in secondary electron mode. Images (a) referring to sample L0 show diffuse porosity, with pores of various sizes. There are many small pores ($<10\ \mu\text{m}$) and some larger ones that reach sizes on the order of $45\text{--}50\ \mu\text{m}$. Looking at the L25 (b), L50 (c) and L100 (d) samples, it is possible to see that as the Italian kaolinitic clay content increases, the porosities continue to be widespread but the small pores decrease and the larger ones increase. It would also appear that the shape of the porosities is more regular in the sample containing only German ball clay and that as the percentage of clay replacement increases pores show increasingly irregular shapes. The presence of the diffuse porosity and the increase in pore size also confirm the results obtained from the water absorption; this adsorption increases, making the material less resistant to stress due to the voids that are formed.

A further observation that can be made is related to the presence of the amorphous phase, which seems to increase as the amount of German ball clay decreases, and these results appear to agree with the diffractometric analysis performed on the samples, where the presence of glassy phase was revealed.

Sample L0 compared to the other samples appears to be more sintered while L100 is the one that would appear to be less densified.

ESEM images of the pumice-based samples can be observed in Fig. 5 (a-d). The P0 sample, identified by (e), shows a spherical porosity with a size of $10\ \mu\text{m}$ and an intergranular porosity with a size of $30\ \mu\text{m}$; the pores are larger in size than in the lapillus-based sample containing only German ball clay. Also in the pumice-based samples, as happened in the lapillus-based samples, as the Italian kaolinitic clay content increases, the porosity increases in both size and quantity. Samples P25 (f), P50 (g) and P100 (h) have much larger pores than their lapillus-based analogs, and this could strongly affect the flexural strength values on the fired pieces.

The pumice-based samples appear less sintered than their P0 reference, but they also appear less sintered than the lapillus-containing samples. The amorphous phase present could also be attributable to a lower degree of sintering or to an overfiring of the samples at the industrial temperatures due to the high amount of amorphous fraction.

3.3.4. Colorimetry

The $CIE\ L^*a^*b^*$ system, which is widely used in the ceramic industry, has made it possible to obtain colorimetric data. The parameters determined and processed by the visible spectra were the lightness (L^*),

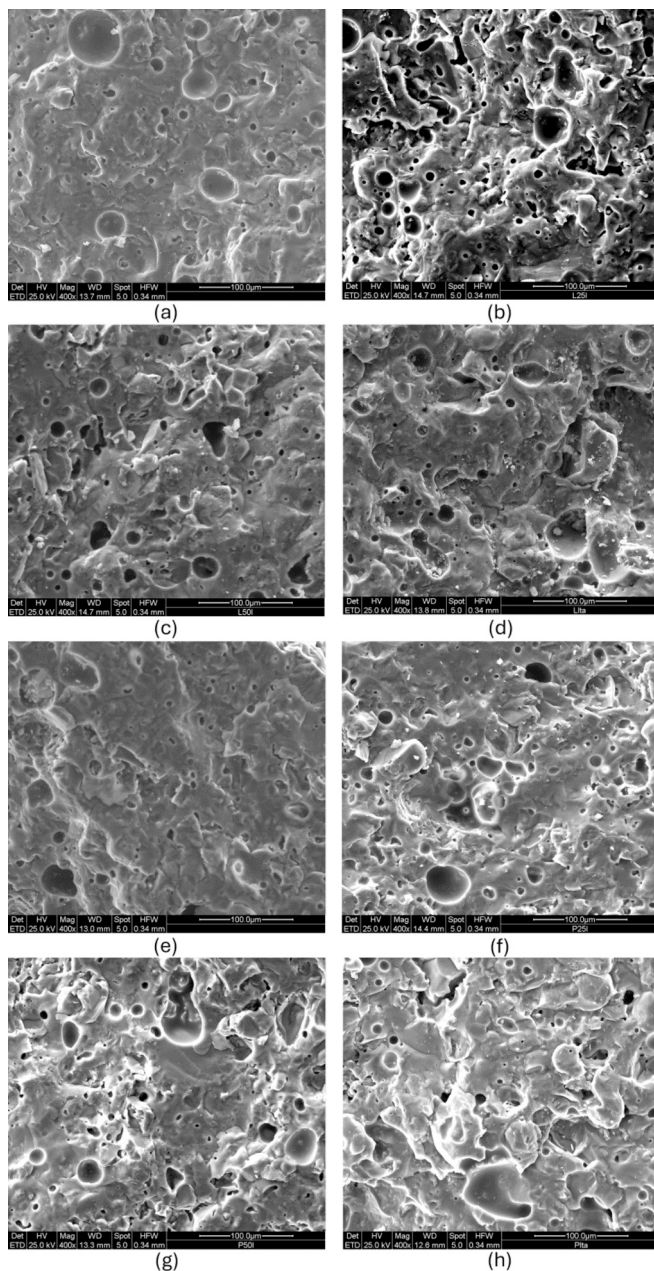


Fig. 5. ESEM images of lapillus-based and pumice-based samples. (a) L0, (b) L25, (c) L50, (d) L100, (e) P0, (f) P25, (g) P50, (h) P100.

which can vary between 0, corresponding to absolute black, and 100, corresponding to absolute white, a^* , which describes the variation of the reds and greens, and b^* , which describes the variation of the yellows to blue. The values obtained are shown Table 5.

The reported values of ΔE^* were obtained from the comparison with the L0 and P0 samples depending on the mixtures considered.

Looking at the values obtained for both the lapillus and the pumice samples, it can be seen that the brightness decreases with the increase of Italian kaolinitic clay in the mixture, while a^* and b^* , on the contrary, increase. Only in the case of P100, ΔE^* is lower than in the case of P50. In the case of the pumice-based mixtures, the initial value of L^* is higher due to a minor amount of iron in the composition. Regarding the ΔE^* value is also strongly influenced by the fact that the brightness tends to decrease with greater variation from one sample to another. The variation in the values shown in the table can be related to a major presence of Fe in the Italian kaolinitic clay. The colorimetric difference

Table 5

CIELab* values obtained for the best samples compared to the reference.

	L^*	a^*	b^*	ΔE^*
L0	46.54 ± 0.60	1.76 ± 0.03	5.45 ± 0.07	–
L25	43.90 ± 0.20	1.83 ± 0.07	5.51 ± 0.10	2.65 ± 0.40
L50	43.27 ± 0.20	2.10 ± 0.03	5.53 ± 0.04	3.29 ± 0.40
L100	38.87 ± 0.35	3.33 ± 0.03	5.50 ± 0.07	7.83 ± 0.25
P0	51.07 ± 0.40	3.55 ± 0.05	9.74 ± 0.15	–
P25	49.58 ± 0.36	4.26 ± 0.05	9.53 ± 0.09	1.66 ± 0.04
P50	46.22 ± 0.80	5.83 ± 0.10	10.20 ± 0.14	5.38 ± 0.34
P100	42.51 ± 0.33	6.10 ± 0.15	8.99 ± 0.25	8.96 ± 0.09

obtained highlights the achievement of a darker support than the previous one. This difference is positive in this case as the support tends to take on a color very close to some brown glazes currently produced in the ceramic company.

4. Conclusions

Ceramic supports were formulated containing German ball clay, which was progressively replaced by Italian kaolinitic clay, all with the aim of obtaining a body consisting in Italian raw materials. The reference mixes, one based on L0 volcanic lapillus scraps, and one based on P0 pumice, were naturally colored porcelain stoneware slurries, therefore Italian kaolinitic clay was replaced German ball clay to evaluate the technological and aesthetic properties.

The lapillus-based mixtures studied showed low absorption, rather high linear shrinkage, particularly sample L100, and an internal microstructure similar to that of porcelain stoneware. In this case, the German ball clay could theoretically be totally replaced, resulting in a porcelain stoneware mix containing only Italian raw materials.

Pumice-based mixtures have shown, with replacement percentages of Italian kaolinitic clay exceeding 50%, a water absorption at the limit of what is required by the standard for a product to be classified as porcelain stoneware. In this case, it is possible to partially substitute the German ball clay, up to 25%, to obtain technological properties similar to commercial porcelain stoneware.

In both batches, the internal microstructure of the samples changed. Although the obtained samples, by water absorption values, could be considered as belonging to the BIa group, ESEM analysis showed that there was an increase in closed porosity and that some particles had not fully reacted. The densification process took place, as evidenced by an increase in the linear shrinkage value. However, the water absorption value did not drop to zero. Italian kaolinitic clay is less plastic and the increase in porosity could be due to this; therefore, although a total substitution in the lapillus mix is possible, it would be better not to completely replace the German ball clay in order to control the formation of pores and improve the technological properties of the finished products.

CRediT authorship contribution statement

Fabiana Altamari: Writing – review & editing, Writing – original draft, Investigation, Data curation. **Fernanda Andreola:** Writing – review & editing, Formal analysis, Data curation. **Isabella Lancellotti:** Writing – review & editing, Validation, Conceptualization. **Luisa Barbieri:** Writing – review & editing, Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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