Zeolite-feldspar epiclastic rocks as flux in ceramic tile manufacturing

Roberto de Gennaro[a], Michele Dondi[b], Piergiulio Cappelletti[c], Guido Cerri[d], Maurizio de' Gennaro[c], Guia Guarini[b], Alessio Langella[e], Luigi Parlato[c], and Chiara Zanelli[b]

[a]Centro Interdipartimentale Interdip.le di Servizio C.I.S.A.G. Università Federico II, via Mezzocannone 8, 80134 Napoli, Italy Email: robdegen@unina.it

[b]Istituto di Scienza e Tecnologia dei Materiali Ceramici (CNR-ISTEC), via Granarolo 64, 48018 Faenza, Italy

[c]Dipartimento di Scienze della Terra Università Federico II, via Mezzocannone 8, 80134 Napoli, Italy.

[d] Istituto di Scienze Geologico-Mineralogiche, Corso Angioy 10, 07100 Università di Sassari, Italy

[e] Dipartimento Dip.to di Studi Geologici e Ambientali, Via Port'Arsa 11, 82100 Università del Sannio, Benevento, Italy

Abstract

Low-cost, naturally-occurring mixtures of feldspar and zeolite occurring in volcanoclastic rocks are promising substitutes for conventional quartz-feldspathic fluxes in ceramic bodies, since their fusibility and low hardness are expected to improve both grinding and sintering. Three volcanoclastic rocks, affected by epiclastic processes (hereafter "epiclastic rocks") and with a different zeolite-to-feldspar ratio, were characterised (XRPD, fusibility) and tested in porcelain stoneware bodies; their behaviour during processing was appraised and compared with that of a reference. The addition of an epiclastic rock (20% wt.), replacing rhyolite and aplite fluxes, brought about some significant advantages, mainly represented by better grindability, lower firing temperature with improved mechanical strength and lower porosity. Disadvantages concern increased slip viscosity, worse powder compressibility, resulting in larger firing shrinkage, and a darker colour of the tiles due to relatively high amounts of iron oxide.

Keywords: Epiclastic rock; Porcelain stoneware; Tiles; Traditional ceramics; Zeolites.

1. Introduction

The ceramic tile industry is being progressively moving its worldwide production toward new materials with improved aesthetic and technical properties, e.g. porcelain stoneware tiles, that are able to successfully compete with ornamental stones and other building products [1-2]. Porcelain stoneware tiles are manufactured using large amounts of fluxes, i.e. from 50% to 60% in weight, such as sodic and potassic feldspars [3], nepheline syenite [4], talc [5], glasses [6-7] and glass-ceramics [8-9].

The availability of these raw materials in the huge amounts required by the tile industry is a problem in many areas, while in other contexts it is the high price of fluxes to make the tile manufacture disadvantaged in competition with other producers of building materials, whose manufacturing costs are lower. Thus, the ceramic industry is continuously searching for cheap raw materials able to replace the traditional fluxes without altering the process and product characteristics.

Zeolite-rich rocks could actually represent suitable low-cost materials, as large deposits of natural zeolites occur in several countries (e.g. Italy [10]). Previous works proved that some technological features of zeolites (e.g. low melting temperatures and low hardness) can improve the grinding and firing behaviour of ceramic bodies in the tilemaking cycle, though their high cation exchange capacity and specific surface area cause drawbacks during the wet grinding (i.e. increased slip viscosity). Moreover, the relatively high iron oxide contents of many zeolitic rocks affect considerably the colour of ceramic wares [11-13].

However, some naturally-occurring epiclastic rocks, consisting in zeolite-feldspar mixtures, were found to be promising substitutes for conventional quartz-feldspathic fluxes due to their suitable fusibility and grindability as well as their low iron content [13]. Epiclastic rocks, consisting mainly of clinoptilolite+sanidine and minor smectite, outcrop extensively in western Sardinia, Italy [14-16].

This study is aimed at assessing both the technological behaviour and technical performance of porcelain stoneware tiles produced with three different materials collected within a wide epiclastic formation ("Badu e Giaga Epiclastics" [16]) in order to ensure a variable zeolite-to-feldspar ratio. The experimental approach consists in a laboratory simulation of the tilemaking process carried out by replacing conventional fluxes (rhyolite and aplite) with epiclastic rocks in a typical porcelain stoneware body. Properties of both unfired and fired products were appraised comparing epiclastic rock-bearing formulations with a reference epiclastic rock-free body.

2. Experimental

The samples examined in this work were picked in Logudoro Region, north-western Sardinia (Fig.1). They belong to a volcano-sedimentary succession linked to a calcalkaline eruptive activity, Oligo-Aquitanian in age [14-16], which generally rests on the Palaeozoic basement. In the Logudoro region the circulation of hydrothermal fluids through fault systems often caused the transformation of the rhyolitic glassy fraction of epiclastic and unwelded pyroclastic deposits into clinoptilolite, smectite and opal-CT.

In this area the volcanoclastic succession consists of the following units, from the bottom to the top: "Lower Ignimbrite", "Badu e Giaga Epiclastics" and "Upper Ignimbrite". The "Badu e Giaga Epiclastics" is a pomiceous-ashy epiclastite that mainly deposited in a lacustrine environment. The thickness of this unit ranges between a few to 30 m, and shows the most abundant and uniform zeolitization with respect to the two ignimbrite units [14-16].

Three samples, from the localities Sas Coas (marked E1), Sa Suarzola (E2) and Pianu Edras (E3) [17] were taken into consideration in order to get zeolite-to-feldspar ratios ranging from 2.8 to 0.

In the laboratory trials, a typical porcelain stoneware body was reproduced with raw materials currently used by the tilemaking industry (Table 1): ball clays from Westerwald, Germany (B) and Donbass, Ukraine (DBY3); quartz-feldspathic fluxes, such as sodic feldspar from Southwestern Anatolia, Turkey (ST/C), potassic aplite from Tuscany, Italy (AP), rhyolite from Piedmont, Italy (S1) and arkosic sand from Northern Apennines, Italy (COL).

The mineralogy of the epiclastic rocks was investigated by X-ray powder diffraction (XRPD, Philips, PW 1730/3710, CuK_α radiation) performing the quantitative interpretation of XRD patterns by both the Reference Intensity Ratio [18] and the Rietveld techniques [19]. Chemical analyses of raw materials were carried out by XRF (PW1400 Philips equipped with a W tube) at C.I.S.A.G. (Centro Interdipartimentale di Servizio per Analisi Geomineralogiche), Federico II University. Data were corrected for drift and background effects. Data reduction was performed using the methods proposed for major elements by Franzini and coworkers [20].

The fusibility and firing behaviour of epiclastites were determined by hot-stage microscopy [21] with a thermal rate of 10°C min^{-1}.

The technological behaviour of ceramic bodies was assessed by simulating, at a laboratory scale, the tilemaking process (1 replication per body) and by characterizing both unfired and fired products. The porcelain stoneware bodies were designed by replacing two feldspathic fluxes (i.e. rhyolite and aplite) with a 20% of epiclastic rock. The raw materials were mixed and wet ground in a planetary mill, using porcelain jar with dense alumina grinding media, then the slip was dried in oven (105±5 °C). Powders were deagglomerated by hammer milling and pelletized after adding water (7.5% wt). After adequate storage, 110x55x5 mm tiles were uniaxially pressed (40 MPa), dried in oven (105±5 °C) and fast fired in electric roller kiln at three maximum temperatures in the 1200-1240 °C range for 54 minutes cold-to-cold.

The particle size distribution of the slips was analysed by photosedimentation [22] while water content and weight/volume by gravimetric methods. Working moisture [23] was determined on green tiles. Dry tiles were characterized by measuring drying shrinkage [24], bulk density (weight/volume) and modulus of rupture [25]. Firing shrinkage [24], modulus of rupture [25], water absorption, open porosity (OP) and bulk density [26] were measured on fired tiles. Total porosity (TP) was determined by the ratio between bulk density and specific weight of the ceramic material [27]; close porosity (CP) was calculated as CP = TP – OP. Colour was measured by a HunterLab Miniscan XE Plus spectrophotometer in the 400– 700 nm range, using a white glazed tile (x=0.315, y=0.333) as reference, with standard illuminant D_{65} and observer 10°. CIELab coordinates were calculated from the spectra, expressing brightness L* (0=black, 100=white) and chroma (+a*=red, –a*=green, +b*=yellow, –b*=blue).

The quantitative phase composition of fired tiles was determined by XRPD (Rigaku, Geigerflex, CuK_α radiation) with the RIR-Rietveld method using α -Al_2O_3 as internal standard.

3.   Results and discussion

3.1. Properties of epiclastic raw materials

The mineralogical composition of the zeolitized materials E1 and E2 is characterized by the presence of clinoptilolite (Table 2). In particular, E1 shows the highest zeolite-to-feldspar ratio (51/18), while E2 is characterized by comparable amounts of the two phases considered (46/34). Both display present similar contents of opal (10-12%), smectite values lower than 20% and total absence of glass. The non-zeolitized sample E3 is characterized by a higher amount of feldspar (55%) and smectite (33%) and by a noteworthy content of glass fraction (12%).

From the chemical viewpoint, E1 is characterized by the highest SiO_2/Al_2O_3 ratio, along with low amounts of K_2O, CaO and Fe_2O_3; E3 show the lowest SiO_2/Al_2O_3 ratio and higher iron, alkaline and alkaline-earth oxides values. E2 generally shows an intermediate composition between E1 and E2 (Tab. 2).

These epiclastic rocks have softening temperatures around 1250 °C, while melting (half-sphere temperature) occurs in the 1335-1390 °C range (Table 2). Therefore, they develop the fusibility process within a temperature range lower than that of most feldspathic fluxes: e.g. sodic feldspars exhibit softening and melting temperatures in the 1270-1330 °C and 1400-1500 °C ranges, respectively [12, 19].

3.2. Behaviour of unfired products

The addition of epiclastic rocks in the porcelain stoneware body promoted an enhanced grindability, inferred by the finer particle size of bodies F1, F2 and F3 with respect to F0. At the same time, however, it caused an increase of slip viscosity, appreciable by the increased water content necessary to unload the jar, especially in the case of the body F3. This rheological behaviour is due to a large extent to the smectite content, that is, the larger the smectite content, the higher the water content of slips, or the lower their weight/volume (Table 3).

The finer particle size distribution of bodies containing epiclastic rocks brought about a lower powder compressibility during pressing, as this operation was carried out with the same working moisture. In fact, the lower the median particle size, the lower the bulk density of dry tiles (Table 3).

Zeolite-bearing bodies are characterised by improved mechanical strength of unfired tiles [13]. This aspect was confirmed by the body F2 which showed a modulus of rupture higher than reference F0. The tiles F1 and F3 have the same dry strength of F0, but a noteworthy lower bulk density (1903-1942 *vs.* 1997 kg/m^3) that would imply a proportionally lower modulus of rupture.

3.3. Firing behaviour

The firing behaviour is similar for the four porcelain stoneware bodies (Table 4). Shrinkage increased up to 1220 °C, remaining steady at 1240 °C, as the maximum densification is achieved. De-sintering phenomena began to reduce bulk density at the highest temperature, where water absorption values $\leq 0.5\%$ are reached, so complying the standard limit for porcelain stoneware. Open porosity gradually decreased for increasing temperature, but closed porosity persisted as high as 5-6% and even grew at 1240 °C, so that the total amount of pores diminished up to 1220 °C, then slightly increased at 1240 °C (Table 4). Exception is the body F2, whose bulk density and total porosity are practically unchanged at the highest temperature.

The addition of epiclastic rocks brought about an increase of firing shrinkage and sintering kinetics with respect to the reference body. The lower bulk density of unfired epiclastic rock-bearing bodies explains the increased contraction, implying a higher starting porosity of dry tiles that is filled by the liquid phase during sintering, so resulting in a larger firing shrinkage. On the other hand, the finer particle size of epiclastic rock-containing bodies is able to faster the sintering kinetics, as at the same firing temperatures the values of bulk density are higher and those of water absorption are lower (Table 4).

Another important consideration can be done about data reported in Table 4, which somehow contrast with those obtained in a previous investigation on the use of zeolite-bearing rocks into porcelain stoneware bodies [13]. This is particularly evident if total porosity, bulk density and modulus of rupture of stoneware tiles are considered. A small improvement of all these parameters is here observed. In particular, the addition of epiclastic rocks determined a decrease of the total porosity and an increase of bulk density. These differences are evident when compared with samples fulfilling the standard water absorption requirement (i.e. ≤ 0.5%). Moreover, the modulus of rupture is consistently increased when compared to reference tiles, regardless the different epiclastic rock. Good results were also obtained when a zeolite-rich epiclastic rock was used. These data are in contrast with those reported in de Gennaro et al. [13]. A reliable hypothesis to explain these different behaviours accounts for a different body preparation, that in de Gennaro et al. [13] was partly by wet milling and partly by dry grinding (of zeolitic tuffs). The procedure followed in the present study, entirely by wet milling, was allowed by the favourable properties of the epiclastic rocks instead of zeolitic tuffs.

The main drawback of the use of epiclastic rocks is their relatively high iron content that caused some color darkening of stoneware bodies, witnessed by the lower values of the L* parameter (brightness) and the total chromatic change ΔE^* with respect to the reference body (Table 5). Account must be taken that tolerable ΔE^* values are usually below 5. The colour, as expressed by the chroma parameters a* and b*, did not change significantly in the F1 and F2 bodies in respect of the reference one, while F3 appears to be slightly redder (higher a*) and less yellow (lower b*).

3.4. Phase composition

The epiclastic rocks play a relevant effect on the phase composition, as it can be appreciated in Figure 2, determining the persistence of a significant amount of feldspar even after firing at 1240 °C, especially in the body F2 (Fig. 2C). This phenomenon is presumably connected with the chemical evolution of the liquid phase, that undergoes a "saturation" in alkalis and alkaline-earth oxides when epiclastic rocks replace quartz-feldspathic fluxes. Analogous behaviours were observed when soda-lime or Ba-Sr-rich glasses are added to porcelain stoneware bodies [7, 28-29].

On the other hand, the occurrence of epiclastites provokes a strong reduction of the quartz amount, that in epiclastic rock-bearing bodies is 5-6% lower than in the reference one (Fig 2A). However, these values are in good correspondence with the difference of the initial quartz percentages of the rhyolite and aplite on one side and the epiclastic rocks on the other side.

An increase of mullite is observed at 1200 °C, but it turns within the experimental error for the higher temperatures (Fig. 2B). This phase, which composition is close to $3Al_2O_3 \cdot 2SiO_2$, is formed after metakaolinite during firing at temperatures around 950 °C (primary mullite) but undergoes the chemical attack of liquid phase, that is formed at temperatures over 1100 °C. Therefore, the conspicuous drop of mullite in the epiclastite-bearing bodies is connected with larger amounts of alkaline-earth oxides in the liquid phase.

Due to the fast dissolution rate of the epiclastite components, bodies F1 and F3 develop more vitreous phase than the reference body (Fig. 2D). In contrast, F2 exhibits a slower increase of liquid phase versus temperature, connected with its larger amount of plagioclase that persisted undissolved even at the higher temperature.

4. Conclusion

Zeolitized epiclastic deposits can be exploited as raw material for ceramic tiles, being able to suitably replace conventional quartz-feldspathic fluxes. The use of epiclastic rocks – consisting of mixtures of zeolite (clinoptilolite) and/or potassic feldspar and/or smectite – has been successfully experimented in the production of porcelain stoneware tiles at a laboratory scale, resulting in pros and cons.

The advantages are mainly represented by a better grindability and a lower firing temperature, with improved mechanical strength and lower porosity. Disadvantages are the higher slip viscosity and the worse powder compressibility, implying a larger firing shrinkage, and the darker colour due to relatively high iron oxide amounts.

References

[1] P. Burzacchini, Ceram. World Rev. 10 (37) (2000) 96.

[2] L. Esposito, A. Tucci, D. Naldi, J. Eur. Ceram. Soc. 25 (9) (2005) 1487.

[3] M. Dondi, Tile & Brick Int. 10 (2) (1994) 77.

[4] S. Balkwill, A.K. Bougher, Ceram. Eng. Sci. Proc. 22 (2) (2001) 77.

[5] M. Dondi, V. Biasini, G. Guarini, M. Raimondo, A. Argnani, S. Di Primio, Key Eng. Mat. 206-213 (2002) 1795.

[6] A. Moreno, J. Garcia-Ten, V. Sanz, A. Gozalbo, J. Cabedo, R. Berge, J. Colom, S. Carmena, in: Proc. 4th World Congress on Ceramic Tile Quality - QUALICER, (2000) 237.

[7] F. Matteucci, M. Dondi , G. Guarini, Cer. Int. 28 (2002) 873.

[8] G. Baldi, E. Generali, L. Rovatti, D. Settembre Blundo, Ceram. World Rev. 11 (42) (2001) 72.

[9] V. Biasini, M. Dondi, S. Guicciardi, C. Melandri, M. Raimondo, E. Generali, D. Settembre Blundo, Key Eng. Mat. 206-213 (2002) 1799.

[10] M. de' Gennaro, A. Langella, Mineral. Deposita 31 (1996) 452.

[11] F. Andreola, T. Manfredini, E. Passaglia, G.C. Pellacani, P. Pozzi, M. Romagnoli, Materials Engineering, 1994, 5, 299-312.

[12] P. Di Bartolomeo, M. Dondi, M. Marsigli, Tile & Brick Int. 12 (4) (1996) 311.

[13] R. de Gennaro, P. Cappelletti, G. Cerri, M. de' Gennaro, M. Dondi, G. Guarini, A. Langella, D. Naimo, J. Eur. Ceram. Soc. 23 (2003) 2237.

[14] A. Langella, P. Cappelletti, G. Cerri, D.L. Bish, M. de' Gennaro, in: Natural Microporous Materials in Environmental Technology, Kluwer Academic Pub., Dordrecht, The Netherlands, 1999, p. 516

[15] G. Cerri, P. Cappelletti, A. Langella, M. de' Gennaro, Contrib. Mineral. Petrol. 140 (2001) 404.

[16] G. Cerri, G. Oggiano, Boll. Soc. Geol. It. 121 (2002) 3.

[17] Topographic map of Italy, Sheet 480, Section II – Foresta di Burgos

[18] D.L. Bish, S.J. Chipera, Adv. X-ray Anal. 31 (1988) 295.

[19] D.L. Bish, J.E. Post, Am. Mineral. 78 (1993) 932.

[20] M. Dondi, G. Guarini, I. Venturi, Industrial Ceramics 21 (2001) 67.

[21] M. Franzini, L. Leoni, M. Saitta, X-Ray spectr. 1 (1972) 151.

[22] ASTM C 958. Standard Test Method for Particle Size Distribution of Alumina or Quartz by X-Ray Monitoring of Gravity Sedimentation (1992)

[23] ASTM C 324. Standard Test Method for Free Moisture in Ceramic Whiteware Clays (1988)

[24] ASTM C 326. Standard Test Method for Drying and Firing Shrinkages of Ceramic Whiteware Clays (1988)

[25] UNI EN ISO 10545-4. Ceramic tiles - Determination of modulus of rupture and breaking strength (2000)

[26] ASTM C 373. Standard Test Method for Water Adsorption, Bulk Density, Apparent Porosity, and Apparent Specific Gravity of Fired Whiteware Products (1988)

[27] ASTM C 329. Standard Test Method for Specific Gravity of Fired Ceramic Whiteware Materials (1988)

[28] M. Dondi, J.B. Labrincha, F. Matteucci, M. Raimondo, C. Zanelli, Ceram. Int., in press, on-line since 02-28-2006

[29] C. Zanelli, M. Dondi, G. Baldi, G. Ercolani, G. Guarini, M. Raimondo, Ceram. Int., in press, on-line since 12-22-2006

Table 1
Formulation of porcelain stoneware bodies

Raw material	F0	F1	F2	F3
Clay DBY3 (% wt.)	20	20	20	20
Clay B (% wt.)	20	20	20	20
Sodium feldspar ST/C (% wt.)	25	25	25	25
Quartz-feldspathic sand COL (% wt.)	15	15	15	15
Aplite AP (% wt.)	10	-	-	-
Riolite S1 (% wt.)	10	-	-	-
Epiclastic rock E1 (% wt.)	-	20	-	-
Epiclastic rock E2 (% wt.)	-	-	20	-
Epiclastic rock E3 (% wt.)	-	-	-	20

Table 2
Mineralogical and chemical composition and fusibility of epiclastic rocks.

Component/property	E1	E2	E3
Clinoptilolite (% wt.)	51 ± 3	46 ± 2	-
K-Feldspar (% wt.)	18 ± 2	34 ± 4	55 ± 7
Smectite (% wt.)	19 ± 1	10 ± 1	33 ± 2
Biotite (% wt.)	traces	traces	traces
Quartz (% wt.)	-	traces	-
Opal (% wt.)	12 ± 1	10 ± 1	-
Glass (% wt.)	-	-	12 ± 8
SiO_2 (% wt.)	65.73	60.82	57.46
TiO_2 (% wt.)	0.28	0.43	0.67
Al_2O_3 (% wt.)	11.28	14.87	15.46
Fe_2O_3 (% wt.)	3.82	5.25	7.03
MnO (% wt.)	0.14	0.19	0.19
MgO (% wt.)	1.48	1.41	1.52
CaO (% wt.)	2.67	5.56	5.17
Na_2O (% wt.)	2.13	2.54	3.09
K_2O (% wt.)	1.79	1.02	1.96
P_2O_5 (% wt.)	0.04	0.12	0.18
L.o.I. (% wt.)	10.63	7.79	7.28
Softening temperature (°C)	1255	1260	1250
Melting temperature (half-sphere) (°C)	1390	1335	1345

Table 3
Technological properties of semi-finished products

Property	F0	F1	F2	F3
Slip water content (% wt.)	35.2 ± 0.2	37.1 ± 0.2	36.3 ± 0.2	43.7 ± 0.3
Slip weight/volume (kg·m^{-3})	1620 ± 5	1585 ± 5	1600 ± 5	1495 ± 5
Median particle size (μ m)	4.8 ± 0.1	3.4 ± 0.1	3.8 ± 0.1	3.6 ± 0.1
Working moisture of powders (% wt.)	7.7 ± 0.1	7.6 ± 0.1	7.6 ± 0.1	7.4 ± 0.1
Bulk density of dry tiles (kg·m^{-3})	1997 ± 7	1903 ± 15	1967 ± 5	1942 ± 10
Drying shrinkage (cm·m^{-1})	0.01 ± 0.01	0.01 ± 0.01	0.02 ± 0.01	0.02 ± 0.01
Modulus of rupture of dry tiles (MPa)	3.3 ± 0.3	3.3 ± 0.7	4.3 ± 0.3	3.4 ± 0.4

Table 4
Technological properties of porcelain stoneware tiles

Body	Firing Temp. (°C)	Firing shrinkage (cm·m^{-1})		Water absorption (% wt.)		Open porosity (% vol.)		Closed Porosity (% vol.)		Total porosity (% vol.)		Bulk density (kg·m^{-3})	Modulus of rupture (MPa)	
F0	120	4.5	±	2.6	±	5.9	±	6.3	±	12.2	±	2247	35.6	±
	122	4.8	±	1.4	±	3.2	±	5.5	±	8.7	±	2293	36.5	±
	124	4.8	±	0.5	±	1.2	±	8.1	±	9.3	±	2290	37.4	±
F1	120	5.9	±	2.4	±	5.3	±	5.9	±	11.2	±	2241	٣٧.٩	±
	١٢٢	6.5	±	0.7	±	1.6	±	6.2	±	7.8	±	2307	38.0	±
	124	6.2	±	0.1	±	0.3	±	7.7	±	8.0	±	2295	42.5	±
F2	120	5.0	±	2.4	±	5.4	±	6.5	±	11.9	±	2255	37.2	±
	122	5.6	±	0.9	±	2.1	±	6.3	±	8.4	±	2317	36.9	±
	124	5.6	±	0.2	±	0.4	±	7.6	±	8.0	±	2318	42.3	±
F3	120	5.7	±	2.1	±	4.9	±	5.1	±	10.0	±	2271	39.3	±
	122	6.1	±	0.5	±	1.1	±	5.9	±	7.0	±	2333	42.2	±
	124	6.1	±	0.1	±	0.3	±	7.5	±	7.8	±	2326	48.3	±

Table 5
Colour of porcelain stoneware tiles (CIE Lab parameters)

Body	Firing Temperature (°C)	L*	a*	b*	Δ E*
F0	1200	71.5 ± 0.2	3.9 ± 0.1	13.2 ± 0.2	ref.
	1220	68.8 ± 0.2	2.7 ± 0.1	12.0 ± 0.2	ref.
	1240	67.6 ± 0.2	2.1 ± 0.1	11.2 ± 0.2	ref.
F1	1200	60.1 ± 0.2	3.9 ± 0.1	11.6 ± 0.2	11.5
	1220	58.1 ± 0.2	2.7 ± 0.1	12.8 ± 0.3	10.7
	1240	58.2 ± 0.2	2.3 ± 0.1	11.8 ± 0.2	9.4
F2	1200	60.0 ± 0.2	3.0 ± 0.1	14.1 ± 0.2	11.6
	1220	57.7 ± 0.2	2.0 ± 0.1	12.0 ± 0.2	11.1
	1240	58.3 ± 0.3	1.5 ± 0.1	11.0 ± 0.2	9.3
F3	1200	54.0 ± 0.3	4.9 ± 0.2	12.1 ± 0.2	17.6
	1220	52.7 ± 0.2	3.5 ± 0.1	10.1 ± 0.2	16.2
	1240	52.9 ± 0.2	3.0 ± 0.1	9.8 ± 0.2	14.8

L*=brightness (+ white, - black). Chromatic parameters: a* (+ red, - green) and b* (+ yellow, - blue). $\Delta E^* = \sqrt{(L^*_{ref}-L^*)^2 + (a^*_{ref}-a^*)^2 + (b^*_{ref}-b^*)^2}$
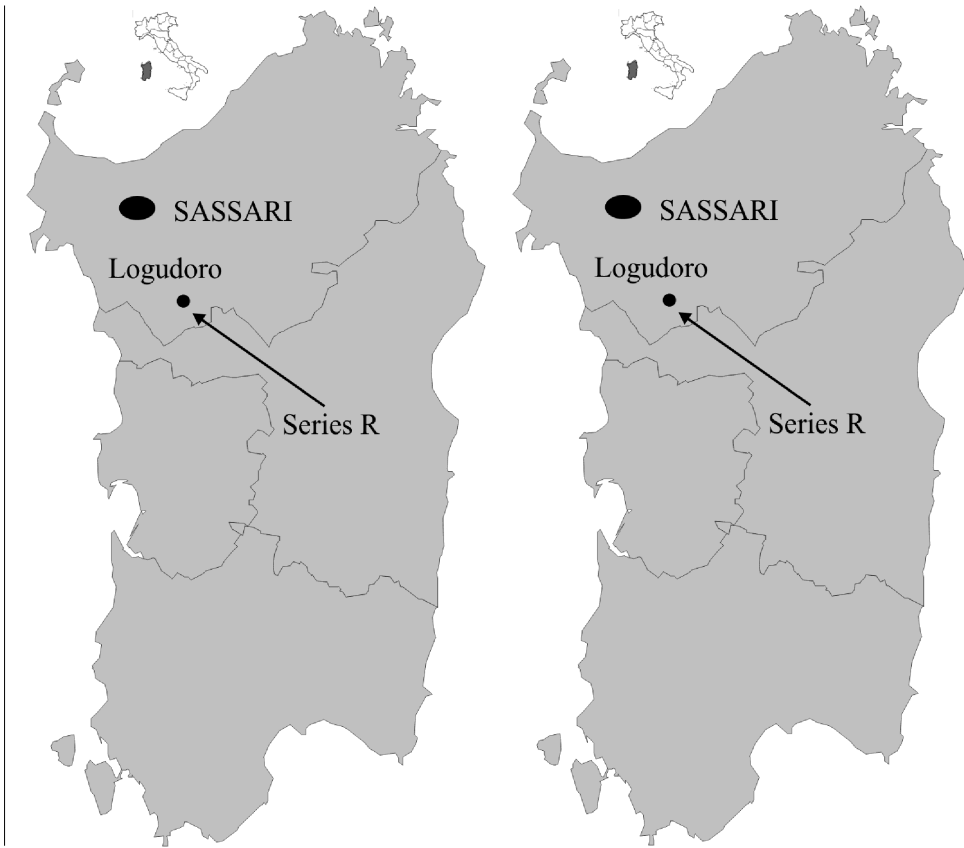
Fig. 1: Sampling site of the three epiclastic rocks (series R) in northwestern Sardinia, Italy.
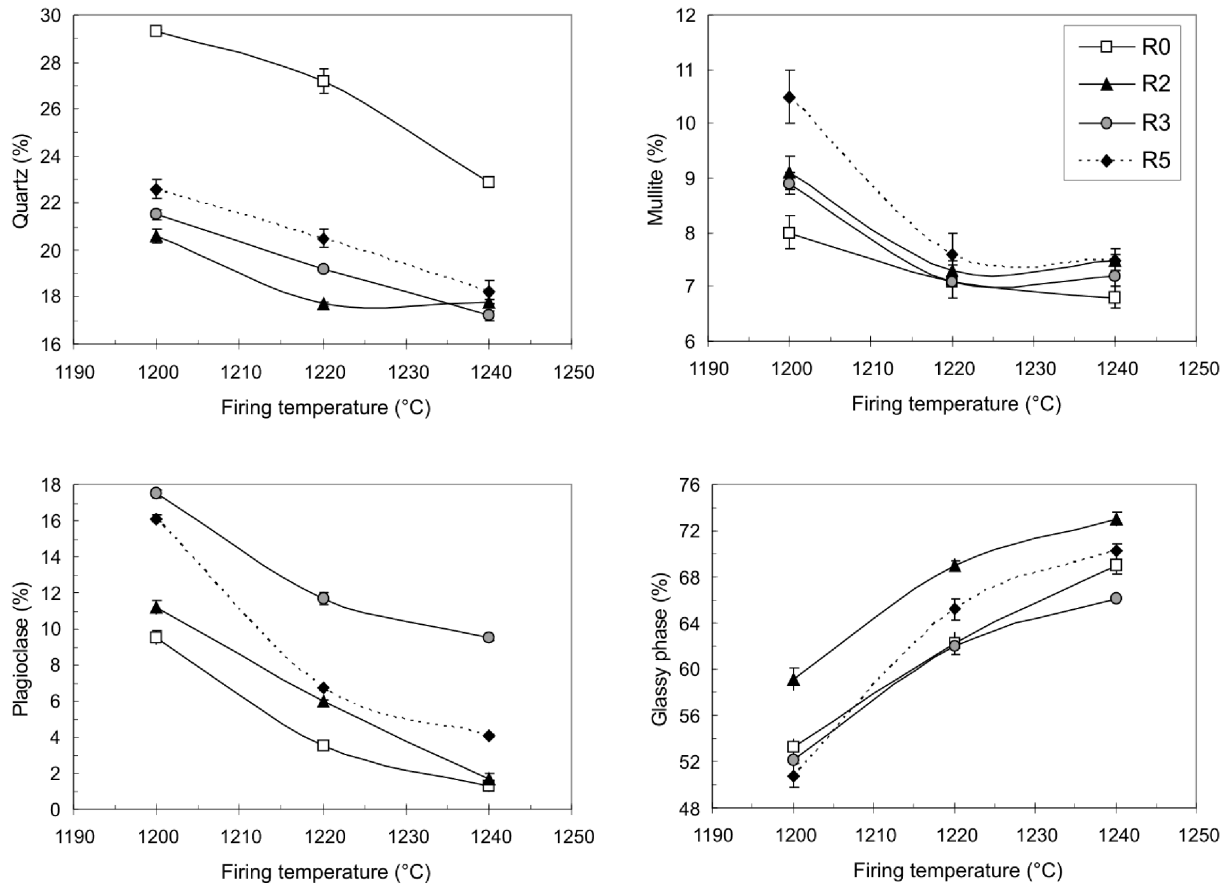
Fig. 2. Phase composition of porcelain stoneware tiles in function of firing temperature