

Influence of Mineralogy and Particle Size on the Technological Properties of Ball Clays for Porcelainized Stoneware Tiles

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Abstract

The influence of the mineralogical and granulometric characteristics of ball clays on the technological properties of ceramic tiles was investigated with special reference to porcelainized stoneware production. The raw materials currently used by the tilemaking industry are fine-grained clays consisting mainly of kaolinite, quartz, illite and randomly interstratified illite/smectite, with occasional smectite. The particle size distribution affects in particular the plasticity and the size changes of tiles during processing, the finest fraction ($<0.2 \mu\text{m}$) being the most effective. The mineralogical composition has a relevant effect on the mechanical properties and pressing behaviour: smectite and interstratified I/S play a prevalent role, together with the structural order of kaolinite and illite. Sintering is to a large extent conditioned by the amount of fluxing components (i.e. feldspars, illite, iron oxyhydroxides, etc.) while the firing shrinkage is also related to the powder compressibility.

Keywords: mineralogy, particle size, ball clays, porcelainized stoneware tiles, technological properties, specific surface

1 Introduction

Porcelainized stoneware is a ceramic material coupling low porosity (<0.1 mass-% water absorption) with excellent mechanical, tribological, and functional performances, such as chemical and frost resistance [1–2]. Combining these technical properties with a successful aesthetic appearance, porcelainized stoneware has been rapidly increasing its output worldwide, gaining new market shares every year. Nowadays, porcelainized stoneware tiles are largely produced in Italy (about 308 Mm^2 in 2001) as well as in China, Spain, Brasil, Indonesia and Turkey [3–4].

The technical and aesthetic evolution of porcelainized stoneware is bringing about a progressive change of body formulation, with an ever-decreasing amount of the clay component that at present ranges from 30 to 40 mass-%, depending on the type of stoneware: glazed or unglazed (ordinary, white, translucent, etc.) [5]. This tendency has introduced a brand new problem to the traditional ceramics sector: how to shape, move and glaze bodies made up to a large extent of non-plastic powders? As a matter of fact, classical ceramic formulations are constituted almost exclusively of clay (e.g. stoneware, terracotta, majolica) or clay and non-plastic components in a ratio close to 1:1 (e.g. porcelain, earthenware). Therefore, the role of clay is changing: in the porcelainized stoneware body it acts primarily to ensure the proper compactness and mechanical resistance to unfired tiles [5–6].

In ceramic production, ball clays are traditionally used for tableware and sanitaryware, but in recent decades they began to be extensively used in tilemaking too. In particular, a ball clay can be defined as “a fine-grained highly plastic, mainly kaolinitic, sedimentary clay,

the higher grades of which fire to a white or near white colour in an oxidising atmosphere” [7]. A ball clay suitable for porcelainized stoneware must fulfil the following technological requirements:

- high plasticity
- easy dispersion of particles in water
- suitable rheological behaviour of the slip
- noteworthy fluidity during pressing
- not excessive refractoriness
- amount of chromophore elements as low as possible.

The ever-stricter application of these requirements by the tilemaking industry has induced a severe selection of clay raw materials for porcelainized stoneware. This empirical process, based essentially on chemical and technological criteria, has singled out a class of clays suitable for porcelainized stoneware, which is characterised by a rather narrow range of chemical composition [8] and by technological performances over a minimum limit conventionally accepted in industrial practice. Within this class, changes of the technological properties do not strictly depend on chemistry; thus, it is very difficult to reliably predict the clay behaviour in tilemaking just on the basis of the chemical composition [9–12].

This study is aimed at outlining the influence of clay mineralogy and particle size on the technological properties of both unfired and fired porcelainized stoneware tiles. The approach consisted in:

- selecting commercial clays from a dozen basins among the most important in Europe
- analysing these raw materials from the mineralogical and granulometric viewpoints
- thoroughly characterising their technological behaviour by simulating the tilemaking process in the laboratory.

2 Experimental

Twenty-three samples of commercial clays for porcelainized stoneware tiles – representative of the main European ball clay basins [13–14] – were taken into account. Together with the eight more productive districts, some minor deposits were considered, in order to include clays with peculiar composition and/or technological features, though not fully corresponding to the definition of ball clay. We are generally dealing with fine-grained sediments of fluvio-lacustrine environment, ranging in age from Jurassic to Pleistocene (Table 1).

Within every basin, the samples were selected – taking care to get clays actually used for porcelainized stoneware – according to the following chemical and technological criteria:

- declared Fe_2O_3 and TiO_2 concentrations below 1.5 mass-% each
- declared Al_2O_3 amount between 23 and 28 mass-%
- high claimed plasticity
- suitable behaviour during fast drying and firing cycles.

However, these parameters not always being intercorrelated, in some cases it happened – in order to fulfil a certain criterion (e.g. high plasticity) – that iron or aluminum contents outside the above-mentioned ranges had to be accepted.

The clay samples were characterised from both the chemico-physical and the technological viewpoints through:

- chemical analysis by XRF-WDS (Philips PW1480)
- content of organic matter by the Walkley-Peech method

- mineralogical composition (XRPD, CuK α) of both the bulk sample (Rigaku Miniflex) and the <2 μm fraction extracted by gravity sedimentation (Philips PW1730, natural and ethylene glycol-saturated oriented specimens)
- structural disorder of kaolinite (Hinckley index HI [36]) and illite (Kübler index IC [37]) by interpreting the XRPD patterns of the bulk, randomly oriented specimen (HI) and the <2 μm , oriented one (IC)
- thermal behaviour by simultaneous DTA-TGA (Setaram)
- particle size distribution by photosedimentation (ASTM C 958, Micromeritics SediGraph 5100) and wet sieving (ASTM C 325)
- specific surface by nitrogen adsorption and BET method (ASTM C 1069, Micromeritics FlowSorb II 2300)
- plasticity (Atterberg consistency limits, CNR UNI 10014)
- methylene blue index (ASTM C 837)
- sintering temperature (hot-stage microscope, Expert System Misura).

The tilemaking process was simulated in the laboratory by:

- dry grinding with a jaw crusher and a hammer mill (0.5 mm grid)
- manual humidification and pelletizing (1 mm sieve)
- uniaxial pressing (40 MPa) of 110 x 55 x 5 mm³ tiles (length x width x thickness)
- drying in an electric oven (105 °C overnight)
- firing in an electric roller kiln (maximum temperature 1200 °C, 60 min cold-to-cold).

Semifinished and fired tiles were characterised from the technological point of view by measuring:

- working moisture (ASTM C 324)
- pressing expansion: $100 \times (L_g - L_m)/L_m$, where L_g and L_m are the length of the green tile and the mould respectively
- powder compressibility (mould depth to green tile thickness ratio)
- drying and firing shrinkage (ASTM C 326)
- water absorption (ISO 10545-3)
- green, dry and fired bending strength (ISO 10545-4).

3 Results and Discussion

3.1 Clay Composition

The ball clays taken into account consist basically of kaolinite, quartz, illite and expandable clay minerals (randomly interstratified illite/smectite and sometimes smectite). Besides, low amounts of feldspars, iron oxyhydroxides and organic matter were found (Table 2).

Nevertheless, the clays from the various provenances exhibit a different mineralogical composition (Fig. 1):

- the raw materials from the Latium, Provins, Saxony and Teruel deposits are to a large extent kaolinitic, quite rich in quartz, with low amounts of illite and/or expandable clay minerals
- the ball clays from the Barracão, Devon, Sile and Westerwald basins contain kaolinite prevailing over illite and expandable phyllosilicates as well as moderate amounts of quartz
- the Ukrainian clays exhibit a high content of clay minerals and a low percent of quartz, with rather high amounts of interstratified illite/smectite
- the argillaceous materials from the Sarcidano area contain illite, kaolinite and quartz in analogous quantity, together with minor amounts of interstratified I/S

- the Tournon Saint-Martin and Nançay clays consist basically of kaolinite associated to quartz and expandable clay minerals: smectite in the former and interstratified I/S rich in the smectitic component in the latter.

Moreover, significant differences in the structural order of clay minerals were found, both in terms of kaolinite and illite 'crystallinity' indices. A low crystallinity kaolinite ($HI < 0.8$) and a well-ordered illite ($IC < 0.25 \cdot 2\theta$) seem to be present in most samples. However, in the clays from Ukraine and Provins both kaolinite and illite are poorly ordered, while in the raw materials from Devon and Barracão both illite and kaolinite exhibit high crystallinity (Fig. 2). The chemical composition of these ball clays is quite uniform, the following being rather narrow ranges of variation respected with few exceptions (Table 3): SiO_2 60–68 mass-%, Al_2O_3 22–28 mass-%, Fe_2O_3 <1.8 mass-%, TiO_2 <1.5 mass-%, MgO and organic carbon <1 mass-%, CaO and Na_2O <0.5 mass-%, while K_2O exhibits the widest variability (0.1–3.4 mass-%).

Among the minor components with technological significance, strong differences from one sample to another are registered for sulphur (80 to 2890 $mg \cdot kg^{-1}$) and even chlorine (up to 200 $mg \cdot kg^{-1}$). In contrast, vanadium and chromium vary in a narrower range (20 to 200 $mg \cdot kg^{-1}$ approximately) usual for ball clays [38].

3.2 *Physical Properties*

The particle size distribution is significantly different in the samples from the various basins (Table 2 and Fig. 3a):

- the finest grained clays are those from Ukraine, Devon and Provins
- the clay materials from the Latium, Sarcidano, Sile and Teruel deposits are the richest in silty fraction
- the Westerwald and Barracão clays present the widest range of particle size distributions
- the argillaceous material from Saxony is rather coarse grained.

The particle size distribution correlates well with the specific surface, as it can be seen in Fig. 3b, where the <2 μm fraction contrasts the BET- N_2 values. Exception is made for samples N1 and N2, due to their relatively high amounts of smectite or smectite-rich interstratified I/S, which are probably in nanosized particles able to give a noteworthy contribution to the specific area value, by no means detectable considering only the size fraction <2 μm or even that <0.2 μm .

Taking into account the values of Atterberg limits and methylene blue index, the most plastic materials result those from Ukraine, Tournon Saint-Martin and Nançay, which correspond to the samples richest in smectite and interstratified I/S. In contrast, the lowest plastic indices are characteristic of the Latium, Sarcidano and Saxony materials, that are the coarsest grained samples (Table 4).

On the other hand, both the particle size distribution and the specific surface are strictly correlated with the Atterberg plastic index (Fig. 4a) and the methylene blue index (Fig. 4b). All these chemico-physical properties being dependent to a large extent on the surface activity of clay minerals, they appear to be particularly sensitive to the occurrence of expandable clay minerals (Fig. 4c) and the degree of structural order of kaolinite and illite.

3.3 *Technological Properties*

The clays here considered exhibit a rather wide range of technological behaviour, as it can be appreciated by taking into account the parameters of both unfired and fired tiles (Table 4).

In the pressing and drying conditions adopted in the tilemaking simulation, some samples developed thin cracks on the tile edge, that deteriorated the flexural resistance ('not determined' in Table 4).

The technological properties do not present any statistically significant correlation with single mineralogical, granulometric or chemico-physical parameters of clays. This suggests that there is a complex dependence of the technological behaviour on several variables, related to both processing and clay composition. In order to point out the characteristics with a relevant effect on the technological parameters, a multivariate statistical approach was followed by:

- selecting the most significant variables through a factor analysis with extraction of the principal components
- quantifying the influence of the single variables and setting up a simple predictional model by means of a stepwise multiple regression analysis.

The principal components analysis extracted six factors that on the whole explain about 87 % of the total variance (Fig. 5). Factor 1 highlights, on the one side a positive correlation among the following variables: firing shrinkage, fired bending strength, particle size fractions $<2 \mu\text{m}$ and $<0.2 \mu\text{m}$, plastic index, methylene blue index, specific surface, and amount of expandable phyllosilicates; on the other side, an opposite relation was found for the amounts of quartz, silty fraction and water absorption. Factor 2 explains the sintering temperature, that is inversely proportional to the sum of fluxing components ($\text{Fe}_2\text{O}_3 + \text{MgO} + \text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O}$), and the green bending strength, which is positively correlated with the kaolinite content and negatively related to the coarser particle fraction. Factors 3 and 4 explain to a large extent the variance due to illite and drying shrinkage respectively.

The multiple regression analysis was performed taking a technological parameter at a time as dependent variable and the main compositional and process features as independent variables. Then the stepwise procedure selected the variables contributing significantly to set up a simple predictional model: those selected and their relative weight as well as the multiple correlation coefficient and its significance are summarised in Tables 5–6.

The Atterberg plastic index is predictable with good confidence using specific surface data, with a significant contribution by the structural disorder of both kaolinite and illite (Fig. 6a).

The elastic response of the green tile once the pressure is released (i.e. the pressing expansion E_p) proved to depend essentially on particle size, specific surface and kaolinite content. Furthermore, an influence of some processing parameters is appreciable: the E_p increases with the powder compressibility and when the working moisture diminishes (Fig. 6b).

A reliable prediction of green bending strength MOR_g is difficult (Fig. 6c). However, the most significant variables are kaolinite and quartz, which tend to increase the MOR_g , and the silty fraction and illite disorder, that are inversely related with the green strength.

The drying shrinkage S_d is affected to a large extent by process variables. In fact, the S_d tends to augment with working moisture, while it decreases if powder compressibility and/or pressing expansion increase. Besides, the S_d is inversely proportional to the quartz content and coarse particle fraction ($>20 \mu\text{m}$); it is decreased even by illite, especially if well ordered (Fig. 7a).

The dry bending strength MOR_d appears to be primarily enhanced by the amounts of kaolinite and expandable clay minerals; in parallel, the higher the methylene blue index, the higher the MOR_d (Fig. 7b). Unlike expected, the dry strength is reduced by both the finest ($<0.2 \mu\text{m}$) and the intermediate ($2\text{--}20 \mu\text{m}$) grain fractions as well as the specific surface. This trend is presumably connected with the hindrances to densify fine particles by pressing.

During firing, the more fusible clays (i.e. those with a lower water absorption) are characterised by higher amounts of 'fluxing' elements (i.e. Na, K, Mg, Ca and Fe), illite and feldspars, and by a finer particle size distribution (fraction $<2\ \mu\text{m}$ and specific surface). All these variables promote the sintering kinetics, either accomplishing the particles contact and adhesion, or forming a liquid phase at high temperature (Fig. 8a).

The firing shrinkage S_f is basically affected by both granulometric and processing variables. Its prediction can be done on the basis of both the finer ($<2\ \mu\text{m}$) and the coarser ($>20\ \mu\text{m}$) particle sizes, as well as the powder compressibility, which somehow takes into account the green density and therefore the porosity of tiles before firing. Other relevant parameters are the pressing expansion, methylene blue index and illite disorder (Fig. 8b).

The water absorption depends on grain size with an opposite effect of the finer ($<2\ \mu\text{m}$) and the coarser ($>20\ \mu\text{m}$) fractions. Further, illite and feldspars act reducing the porosity during firing, while kaolinite tends to increase it (Fig. 8c).

The bending strength MOR_f is fundamentally a function of both the particle size and specific surface. The most significant mineralogical variables are kaolinite and its crystallinity. A minor influence is exerted by the powder compressibility and pressing expansion (Fig. 8d).

4 Conclusion

The ball clays used by the manufacturers of porcelainized stoneware tiles are very fine-grained materials (at least 80 % below $20\ \mu\text{m}$) consisting essentially of kaolinite, quartz, illite and randomly interstratified illite/smectite. Some peculiar clays contain smectite or interstratified with a high smectitic component; others are relatively coarse-grained.

Notwithstanding the compositional features being quite uniform, these ball clays exhibit a well-differentiated technological behaviour, which appears to depend on several mineralogical and particle size variables.

The plasticity of clays depends to a large extent on the specific surface, though a minor influence of the kaolinite and illite crystallinity is appreciable.

The pressing expansion is basically governed by the specific surface and particle size of ball clays, while the drying shrinkage is affected mainly by the amounts of quartz and illite. In both cases, a significant role is played by process variables, such as moisture content and powder compressibility.

The mechanical resistance of semifinished products depends on clay mineralogy and particle size. The higher the kaolinite and smectitic phase amounts, or the lower the silty grain fraction, the higher the bending strength.

Both the sintering temperature and water absorption are reduced by the fluxing components (i.e. illite, feldspars, etc.) and the finer particle fraction, but contrasted by kaolinite. The firing shrinkage values are affected by grain size and processing variables, such as pressing expansion and powder compressibility. The mechanical strength of fired tiles is essentially a function of the particle size distribution of ball clays.

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Table 1
 Provenance, geological features and appimate output
 (thousand tons per year) of ball clays

Country	Basin	Geological age	Genesis	t x 10 ³	References
France	Provins	Eocene	Lacustrine	400	[15]
	Tournon St-Martin	Eocene	Lacustrine	100	[14]
	Nançay	Eocene	Lacustrine	100	[14]
Germany	Saxony	Eocene	Fluvio-lacustrine	100	[16–17]
	Westerwald	Eo-Oligocene	Fluvio-lacustrine	2000	[18–20]
Italy	Santa Severa	Pleistocene	Exhalative	60	[21–22]
	Sarcidano	Jurassic	Fluvio-lacustrine	200	[23–24]
Portugal	Barracão-Pombal	Plio-Pleistocene	Fluvio-lacustrine	500	[25–26]
Spain	Teruel-Ariño	Cretaceous	Fluvio-deltaic	300	[27–28]
Turkey	Silé-Istanbul	Plio-Pleistocene	Fluvio-lacustrine	600	[29–30]
Ukraine	Donbas	Eocene	Fluvio-lacustrine	1500	[31–33]
Great Britain	Devon	Eocene	Fluvio-lacustrine	600	[34–35]

Table 2
Mineralogical composition [mass-%], particle size distribution [mass-%] and specific surface [m²·g⁻¹]
of ball clays; the degree of 'crystallinity' of kaolinite and illite are expressed by the Hinckley index (adim.)
and the Kübler index (°2θ) respectively

	B1	B2	D1	D2	G1	K1	K2	L1	N1	N2	P1	P2
Kaolinite	52	57	55	50	36	50	52	56	45	38	62	53
Illite-Mica	12	16	12	18	3	18	15	-	5	-	6	8
Interstratified I/S	-	7	10	14	-	8	9	-	-	18	-	-
Smectite	-	-	-	-	-	-	-	6	21	-	-	-
Quartz	33	17	21	16	41	21	21	37	28	42	29	38
Plagioclase	-	1	-	1	-	1	1	-	1	-	-	-
K-Feldspar	3	1	2	1	20	-	-	-	-	-	1	-
Accessories	-	1	1	1	1	2	2	1	-	2	2	1
Hinckley index	1.30	0.67	1.58	0.60	0.40	0.83	0.40	0.37	0.71	0.61	0.32	0.40
Kübler index	0.08	0.10	0.14	0.08	0.20	-	0.12	-	0.20	-	0.28	0.24
Fraction <20 µm	84.0	91.8	94.1	94.8	46.0	87.9	95.2	90.3	87.9	91.7	94.2	83.9
Fraction <2 µm	47.0	68.0	69.0	72.1	32.1	35.0	61.0	66.0	58.0	68.0	74.0	67.0
Fraction <0.2 µm	14.4	35.5	30.2	33.2	10.4	15.5	24.9	11.4	22.1	37.6	47.9	44.0
Specific surface	14.0	29.9	24.7	23.9	10.7	13.8	22.7	6.3	36.2	54.4	32.2	25.7
	S1	S2	T1	T2	U1	U2	W1	W2	W3	W4	W5	
Kaolinite	32	32	53	48	47	52	47	40	46	50	39	
Illite-Mica	22	30	6	8	16	17	12	10	10	17	10	
Interstratified I/S	14	5	2	3	22	18	2	5	13	7	14	
Smectite	-	-	-	-	-	-	-	-	-	-	-	
Quartz	26	30	36	38	12	10	35	42	27	22	34	
Plagioclase	3	2	-	-	-	-	3	2	1	1	1	
K-Feldspar	3	1	3	3	1	1	-	1	1	1	1	
Accessories	-	-	-	-	2	2	1	-	2	2	1	
Hinckley index	0.14	0.21	0.70	0.30	0.15	0.56	0.47	0.76	0.24	0.28	0.31	
Kübler index	-	0.12	0.12	0.16	0.28	0.14	0.14	0.16	0.20	0.16	0.10	
Fraction <20 µm	90.2	89.9	87.9	83.0	95.6	95.9	85.0	77.9	92.8	93.5	85.9	
Fraction <2 µm	38.0	47.0	53.1	45.0	77.1	82.0	47.1	37.1	75.1	71.1	63.1	
Fraction <0.2 µm	7.0	13.1	28.7	15.8	37.3	46.4	18.3	16.8	45.5	40.9	32.8	
Specific surface	8.9	10.7	17.4	13.2	31.0	32.1	21.5	12.2	27.2	23.3	23.9	

Table 3
Chemical composition of ball clays; concentration expressed in mass-%
(major components) and mg · kg⁻¹ (minor components)

	B1	B2	D1	D2	G1	K1	K2	L1	N1	N2	P1	P2
SiO ₂	60.87	56.79	62.3	60.64	66.99	56.4	60.64	66.24	61.75	67.46	61.02	67.07
TiO ₂	0.26	0.53	1.39	1.39	0.36	1.08	1.13	0.28	0.49	1.38	1.5	1.16
Al ₂ O ₃	27.47	28.18	25.38	26.58	21.35	27.24	26.16	23.31	24.13	18.11	24.68	21.26
Fe ₂ O ₃	1.11	1.76	0.94	0.94	0.55	2.37	2.25	1.44	1.47	2.52	1.75	1.19
MnO	0.03	0.04	0.04	0.04	0.04	0.04	0.04	0.03	0.04	0.04	0.04	0.04
MgO	0.50	0.99	0.65	0.64	0.57	0.81	0.85	0.31	1.14	0.88	0.50	0.69
CaO	0.12	0.19	0.19	0.23	0.20	0.13	0.22	0.16	0.55	0.47	0.36	0.33
Na ₂ O	<0.10	<0.10	0.21	0.25	0.13	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
K ₂ O	1.34	1.30	1.87	2.19	3.40	1.98	1.79	0.35	0.62	0.16	0.34	0.18
P ₂ O ₅	0.05	0.06	0.07	0.06	0.05	0.05	0.04	0.06	0.03	0.05	0.07	0.06
L.o.i.	8.25	10.18	6.96	7.04	6.39	9.90	6.88	7.81	9.79	8.93	9.74	8.03
C _{org}	0.09	0.12	0.63	0.20	0.11	0.40	0.09	0.05	0.26	0.65	0.33	0.56
V	117	89	173	153	131	149	132	52	72	20	69	81
Cr	75	66	210	182	180	109	104	33	50	15	50	61
S	424	234	656	83	229	1803	954	566	757	2887	78	92
Cl	<20	198	<20	<20	<20	221	<20	<20	<20	<20	<20	109
	S1	S2	T1	T2	U1	U2	W1	W2	W3	W4	W5	
SiO ₂	55.08	61.02	62.84	61.00	61.66	60.35	60.53	68.21	62.57	61.37	67.67	
TiO ₂	1.21	1.14	0.43	0.67	1.32	1.37	1.12	1.01	1.65	1.41	1.2	
Al ₂ O ₃	27.94	25.42	23.88	25.44	25.40	26.00	26.55	21.71	23.79	24.25	20.39	
Fe ₂ O ₃	1.94	1.50	1.02	1.01	0.89	0.99	1.34	0.87	1.78	1.65	1.10	
MnO	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	
MgO	1.22	1.01	0.57	0.68	0.86	1.03	0.57	0.51	0.69	0.51	0.92	
CaO	0.24	0.22	0.20	0.20	0.36	0.37	0.27	0.25	0.25	0.25	0.26	
Na ₂ O	0.12	0.10	<0.10	<0.10	0.32	0.34	<0.10	<0.10	0.18	0.10	0.10	
K ₂ O	3.20	2.86	1.07	1.45	1.91	2.02	1.57	1.61	1.78	2.20	1.65	
P ₂ O ₅	0.02	0.03	0.04	0.05	0.06	0.06	0.04	0.04	0.07	0.05	0.05	
L.o.i.	8.99	6.66	9.92	9.46	7.19	7.43	7.97	5.73	7.20	8.16	6.60	
C _{org}	0.91	0.37	0.65	0.27	0.09	0.06	0.70	0.06	0.06	0.04	0.13	
V	78	115	46	143	135	146	106	143	139	156	161	
Cr	63	92	15	92	79	156	146	108	99	149	157	
S	514	134	95	1387	191	505	363	333	130	155	97	
Cl	<20	<20	125	<20	<20	169	<20	173	<20	<20	<20	

Table 4
Technological behaviour of ball clays during the tilemaking process

Property	Unit	B1	B2	D1	D2	G1	K1	K2	L1	N1	N2	P1	P2
Methylene blue index	meq/100g	5.8	9.5	8.5	5.5	5.0	4.5	8.5	3.0	17.5	20.0	7.5	9.5
Plastic limit (WP)	mass-%	28.2	27.3	28.4	26.7	25.2	33.2	30.3	27.3	37.5	25.3	27.1	22.4
Liquid limit (WL)	mass-%	44.1	58.3	56.6	46.6	36.0	53.1	52.7	35.5	78.8	67.4	58.9	55.5
Plastic index (IP)	mass-%	15.9	31.0	28.2	19.9	10.8	19.9	22.4	8.2	41.3	42.1	31.8	33.1
Pressing moisture	mass-%	5.1	5.4	5.7	5.1	5.6	6.0	5.4	4.5	7.5	5.9	5.6	5.6
Powder compressibility	adim.	3.3	2.7	2.4	2.6	3.0	2.7	2.8	3.3	3.1	2.1	2.1	2.2
Pressing expansion	cm·m ⁻¹	0.7	0.6	0.6	0.8	0.8	0.8	0.8	0.6	0.8	0.5	0.5	0.5
Green MOR	MPa	1.1	1.1	1.2	1.0	0.8	1.2	1.1	0.4	1.1	1.9	1.0	1.1
Drying shrinkage	cm·m ⁻¹	-0.3	-0.1	0.0	-0.2	-0.1	-0.1	-0.1	-0.4	0.3	0.4	0.1	0.1
Dry MOR	MPa	1.9	1.6	2.2	1.7	2.0	1.7	1.5	1.2	2.4	n.d.	0.7	1.3
Firing shrinkage	cm·m ⁻¹	2.7	4.7	8.0	8.7	0.8	7.8	7.3	0.0	3.5	n.d.	n.d.	4.3
Water absorption	mass-%	13.5	9.7	2.3	2.3	11.4	4.9	5.4	19.3	15.7	7.8	8.2	9.9
Fired MOR	MPa	20.4	18.8	24.8	39.3	3.1	31.4	n.d.	0.9	n.d.	n.d.	n.d.	n.d.
Sintering temperature	10 ³ °C	1.50	1.43	1.40	1.40	1.35	1.40	1.40	1.55	1.43	1.43	1.40	1.48
Property	Unit	S1	S2	T1	T2	U1	U2	W1	W2	W3	W4	W5	
Methylene blue index	meq/100g	3.5	4.0	7.0	5.0	13.5	10.5	5.0	4.5	10.0	8.5	6.0	
Plastic limit (WP)	mass-%	25.0	22.4	22.9	21.7	30.0	34.6	27.4	21.6	25.5	23.3	21.2	
Liquid limit (WL)	mass-%	37.6	32.7	40.0	36.7	68.2	72.0	45.7	36.4	55.2	48.2	40.7	
Plastic index (IP)	mass-%	12.6	10.3	17.1	15.0	38.2	37.4	18.3	14.8	29.7	24.9	19.5	
Pressing moisture	mass-%	4.8	5.9	5.2	5.1	5.6	6.0	5.2	5.3	5.7	5.0	6.0	
Powder compressibility	adim.	2.7	3.2	2.5	2.9	2.5	2.5	2.4	2.6	2.6	3.2	2.4	
Pressing expansion	cm·m ⁻¹	0.7	0.6	0.5	0.6	0.7	0.7	0.7	0.7	0.7	0.7	0.6	
Green MOR	MPa	0.8	0.6	1.9	1.1	1.0	1.0	1.0	0.8	0.9	0.9	1.2	
Drying shrinkage	cm·m ⁻¹	0.1	0.1	0.1	-0.2	0.1	0.1	-0.1	-0.3	-0.1	-0.4	-0.1	
Dry MOR	MPa	2.5	1.9	5.0	2.6	2.1	2.3	1.6	1.1	1.3	1.5	1.7	
Firing shrinkage	cm·m ⁻¹	2.6	2.4	2.4	2.5	8.1	8.0	6.7	1.6	8.2	7.0	4.5	
Water absorption	mass-%	3.4	6.0	10.2	9.5	2.1	1.9	8.1	11.3	2.4	3.4	6.2	
Fired MOR	MPa	31.4	19.4	20.3	21.4	29.0	30.0	13.4	10.1	38.7	21.1	22.2	
Sintering temperature	10 ³ °C	1.33	1.40	1.48	1.48	1.38	1.33	1.48	1.48	1.38	1.35	1.40	

Table 5
Stepwise multiple regression analysis of a technological parameter at a time (dependent variable) and the main process and clay composition features as independent variables; multiple correlation coefficients and probability level are shown together with the variables selected and their correlation coefficient [B] and standardised correlation coefficient [β] with respective standard errors (std. err.)

Dependent variable	Multiple coeff.	Variables selected	β	std. err.	B	std. err.	p-level
Atterberg plastic index	R = .965	intercept			-7.6085	2.8016	0.0159
	R ² = .932	specific surface	0.8651	0.0730	1.0511	0.0887	0.0000
	p < .00000	illite crystallinity	0.2368	0.0796	37.2987	12.5420	0.0095
		Hinckley index	0.1379	0.0741	3.5715	1.9191	0.0825
Pressing expansion	R = .846	intercept			1.0343	0.2745	0.0023
	R ² = .716	powder compressibility	0.3826	0.1836	0.0965	0.0463	0.0575
	p < .00294	specific surface	1.8454	0.4025	0.0207	0.0045	0.0005
		grain size <0.2 μm	-1.2374	0.3164	-0.0088	0.0022	0.0018
		kaolinite	-0.5542	0.1986	-0.0058	0.0021	0.0153
	moisture content	-0.6341	0.2455	-0.0996	0.0386	0.0227	
Green modulus of rupture	R = .753	intercept			0.1454	0.3969	0.7205
	R ² = .568	kaolinite	0.6761	0.2255	0.0120	0.0040	0.0111
	a	grain size 2–20 μm	-0.4103	0.2137	-0.0066	0.0034	0.0790
		Hinckley index	0.1042	0.2318	0.0422	0.0939	0.6611
		pressing expansion	0.2990	0.2080	0.5078	0.3532	0.1761
		quartz	0.3799	0.2298	0.0090	0.0054	0.1242
	illite crystallinity	-0.3404	0.2532	-0.8390	0.6242	0.2037	
Drying shrinkage	R = .921	intercept			-0.1730	0.3270	0.6073
	R ² = .848	moisture content	0.7261	0.1483	0.2278	0.0465	0.0005
	p < .00094	powder compressibility	-0.2606	0.1658	-0.1313	0.0835	0.1444
		quartz	-0.6523	0.1927	-0.0182	0.0054	0.0061
		pressing expansion	-0.2742	0.1423	-0.5477	0.2842	0.0801
		grain size >20 μm	0.5311	0.2254	0.0081	0.0034	0.0381
		illite	-0.4900	0.2438	-0.0088	0.0044	0.0696
	illite crystallinity	0.1827	0.1362	0.5297	0.3948	0.2067	
Dry modulus of rupture	R = .838	intercept			2.3207	0.5756	0.0017
	R = .702	grain size <0.2 μm	-1.0753	0.3548	-0.0436	0.0144	0.0105
	p < .01085	expandable clay minerals	0.7203	0.2010	0.0576	0.0161	0.0038
		methylene blue index	0.5089	0.3099	0.0751	0.0458	0.1265
		grain size 2–20 μm	-0.9622	0.3211	-0.0520	0.0174	0.0111
		kaolinite	0.8280	0.2850	0.0492	0.0169	0.0132
	specific surface	-0.8449	0.4534	-0.0540	0.0290	0.0870	

Table 6
Stepwise multiple regression analysis of the technological parameters of fired clays (dependent variable) and the main process and clay composition features as independent variables; multiple correlation coefficients and probability level are shown together with the variables selected and their correlation coefficient [B] and standardised correlation coefficient [β] with respective standard errors (std. err.)

Dependent variable	Multiple coeff.	Variables selected	β	std. err.	B	std. err.	p-level
Sintering temperature	R = .963	intercept			1524.74	46.671	0.0000
	R ² = .926	fluxing components	-0.216	0.123	-12.619	7.166	0.1037
	p < .00000	grain size <2 μm	-0.484	0.171	-1.702	0.602	0.0152
		kaolinite	0.497	0.124	2.994	0.746	0.0017
		specific surface	-0.374	0.150	-2.424	0.970	0.0279
		illite	-0.341	0.142	-1.775	0.738	0.0331
		feldspars	-0.163	0.114	-3.482	2.440	0.1791
Firing shrinkage	R = .962	intercept			-7.115	3.682	0.0795
	R ² = .926	grain size <2 μm	0.772	0.161	0.142	0.030	0.0006
	p < .00001	pressing expansion	0.490	0.098	15.460	3.100	0.0004
		methylene blue index	-0.521	0.143	-0.396	0.109	0.0039
		powder compressibility	-0.195	0.101	-1.586	0.820	0.0793
		grain size >20 μm	-0.328	0.139	-0.075	0.032	0.0383
		illite crystallinity	0.215	0.115	10.472	5.621	0.0894
Water absorption	R = .969	intercept			5.059	4.472	0.2800
	R ² = .939	feldspars	-0.472	0.102	-0.836	0.181	0.0006
	p < .00000	grain size >20 μm	0.520	0.134	0.191	0.049	0.0021
		methylene blue index	0.401	0.092	0.498	0.114	0.0009
		kaolinite	0.294	0.115	0.147	0.058	0.0250
		grain size <2 μm	-0.451	0.146	-0.132	0.043	0.0093
		illite	-0.154	0.107	-0.067	0.046	0.1739
Fired modulus of rupture	R = .952	intercept			-15.253	16.802	0.3905
	R ² = .907	grain size <2 μm	2.141	0.336	1.303	0.205	0.0002
	p < .00097	specific surface	-1.799	0.410	-2.307	0.526	0.0023
		powder compressibility	-0.409	0.157	-12.434	4.774	0.0314
		kaolinite	0.399	0.144	0.432	0.156	0.0245
		pressing expansion	0.258	0.127	38.945	19.190	0.0769
		Hinckley index	-0.231	0.129	-5.476	3.042	0.1096

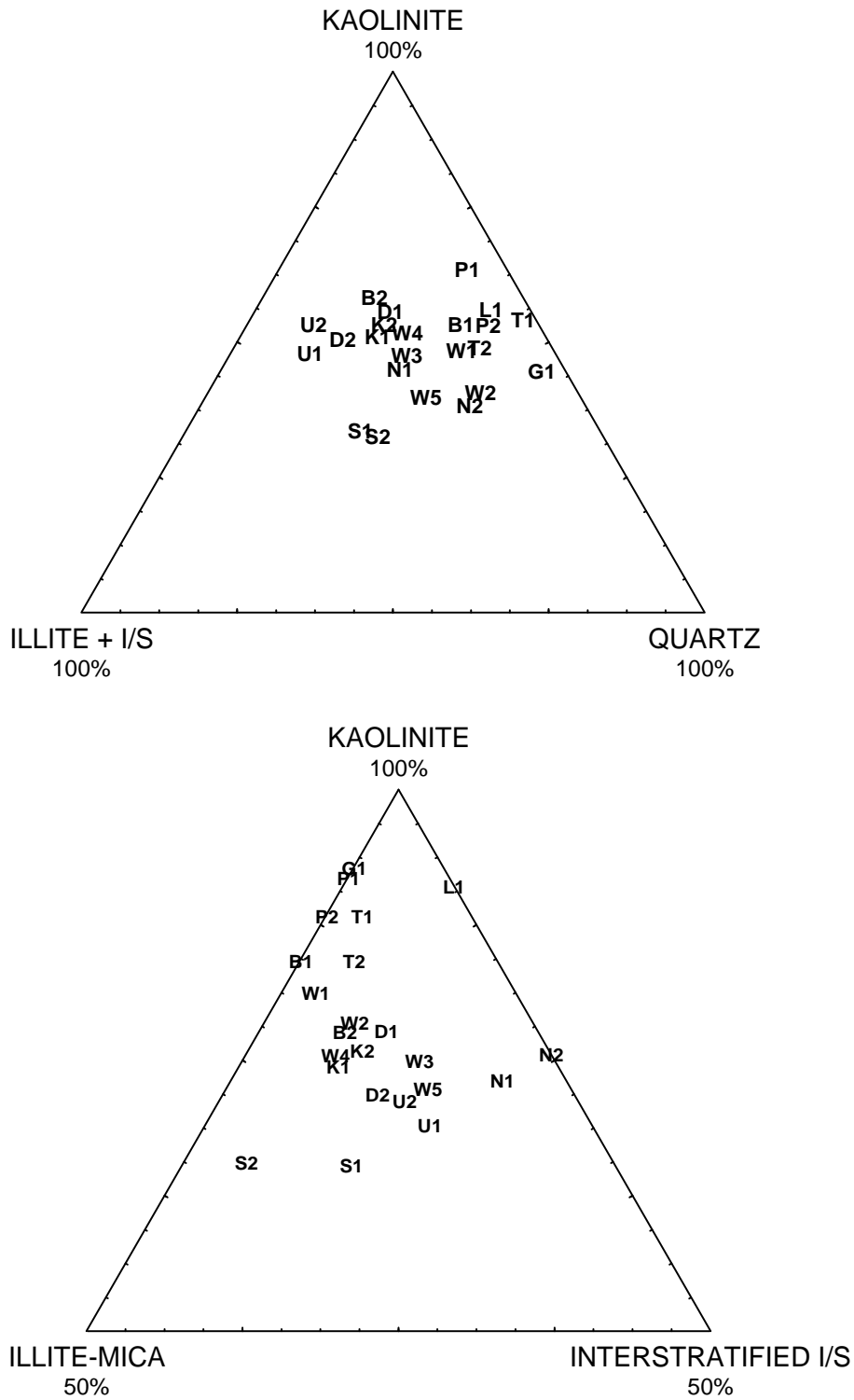


Fig. 1 Mineralogical composition of ball clays; symbols as in Table 1

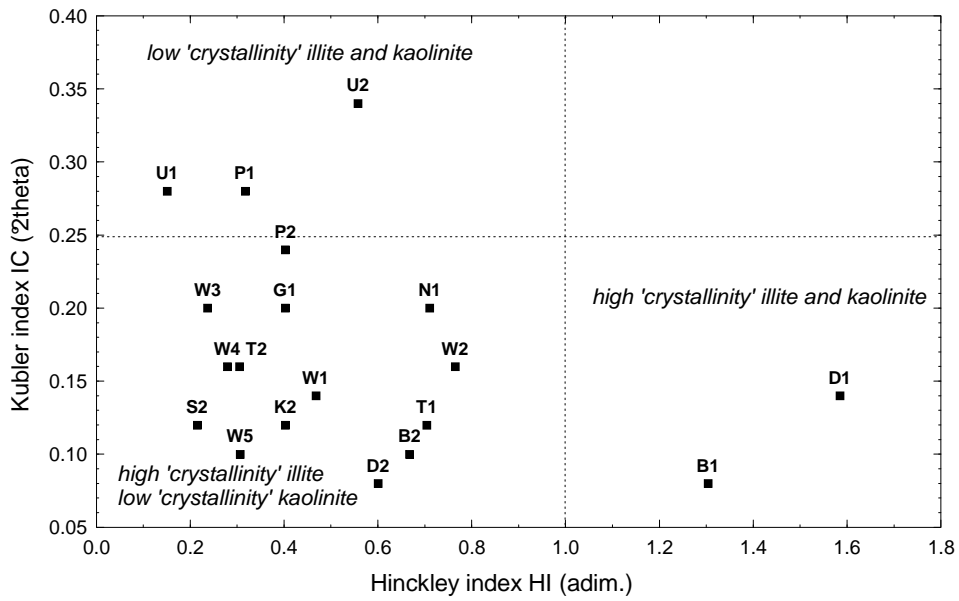
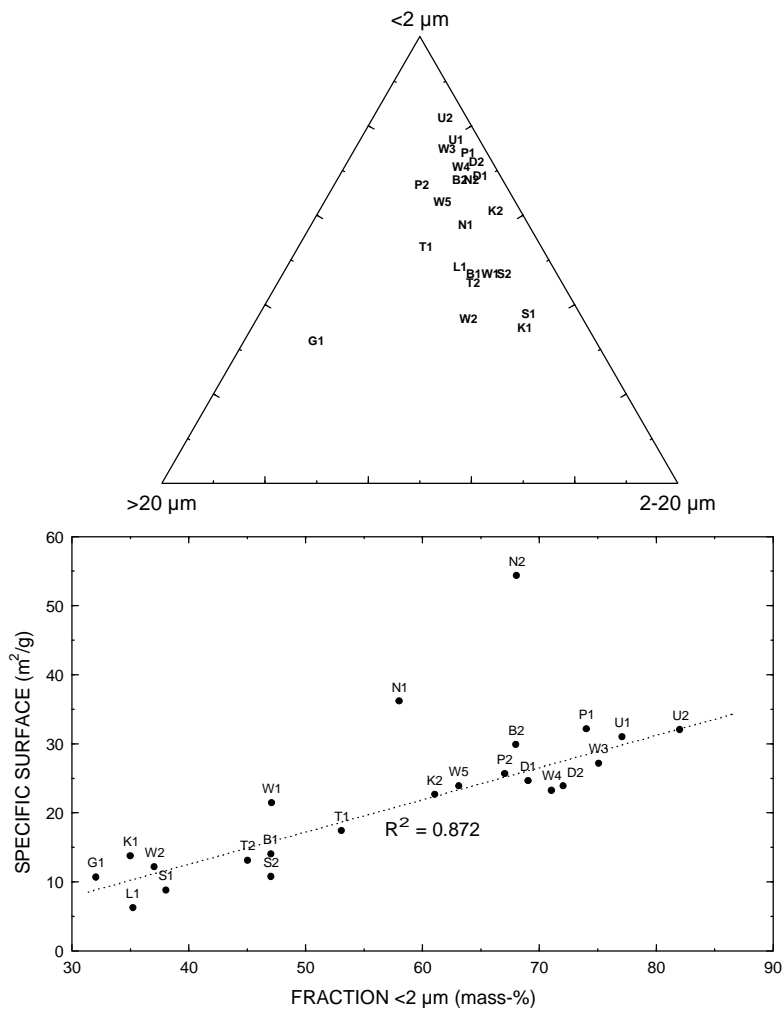
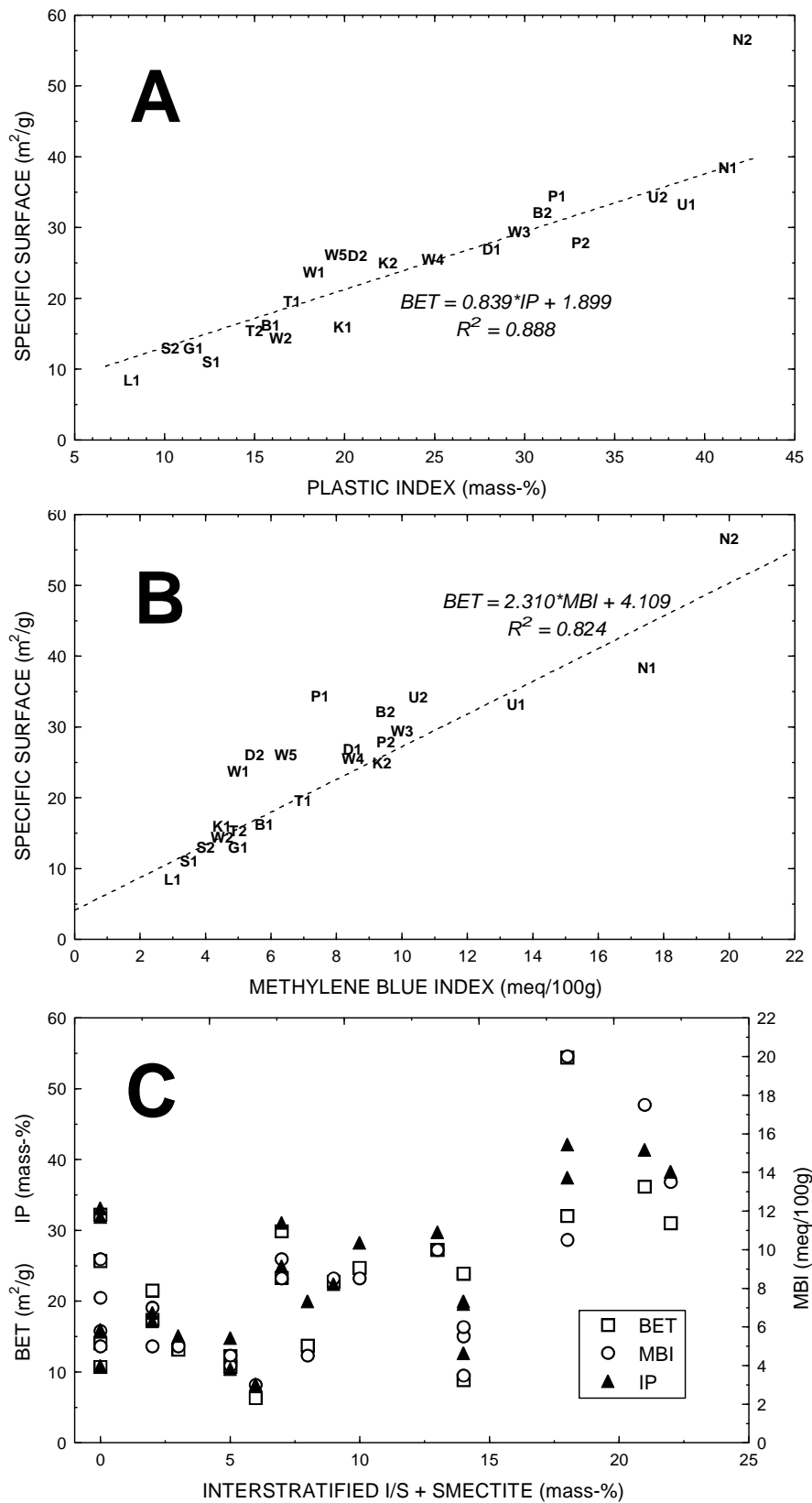


Fig. 2 Degree of structural disorder in kaolinite and illite; symbols as in Table 1



Figs. 3 a–b a) Particle size distribution of ball clays; b) correlation between particle fraction <2 μm and specific surfaceB.; symbols as in Table 1



Figs. 4 a–c Correlation between specific surface and a) Atterberg plastic index or b) methylene blue index; Cc) relationships among the former variables with the amount of expandable clay minerals; symbols as in Table 1

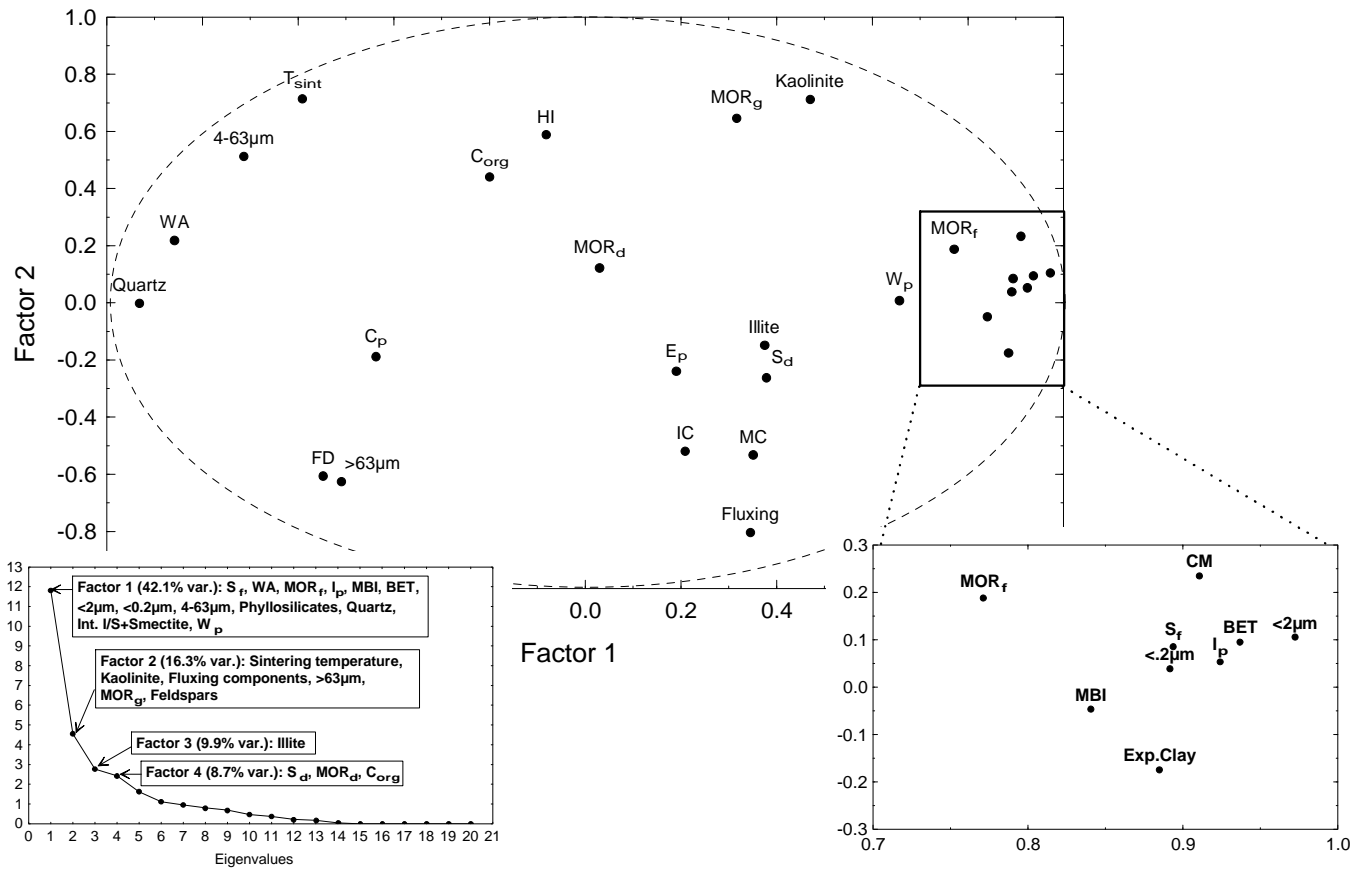
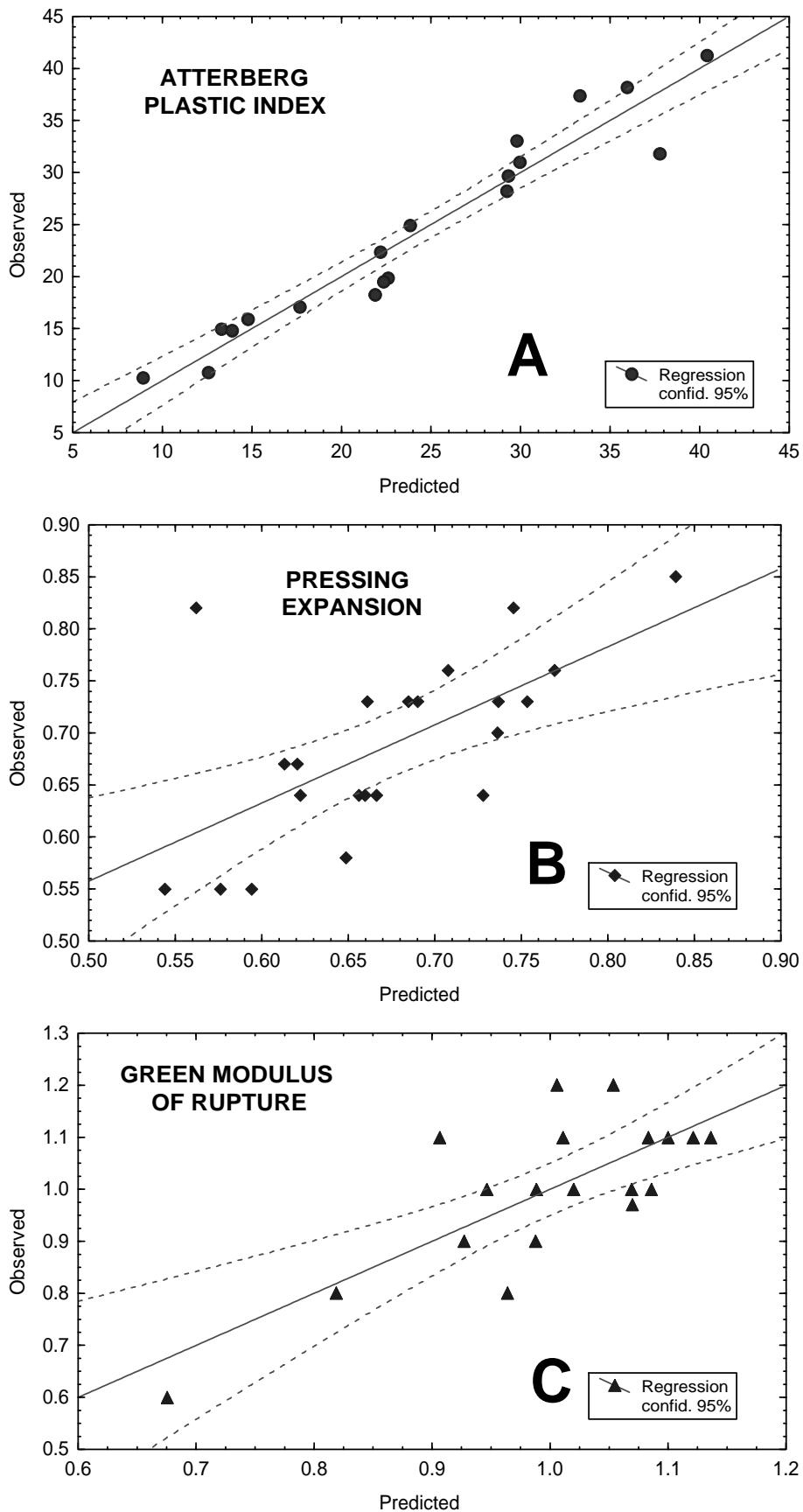
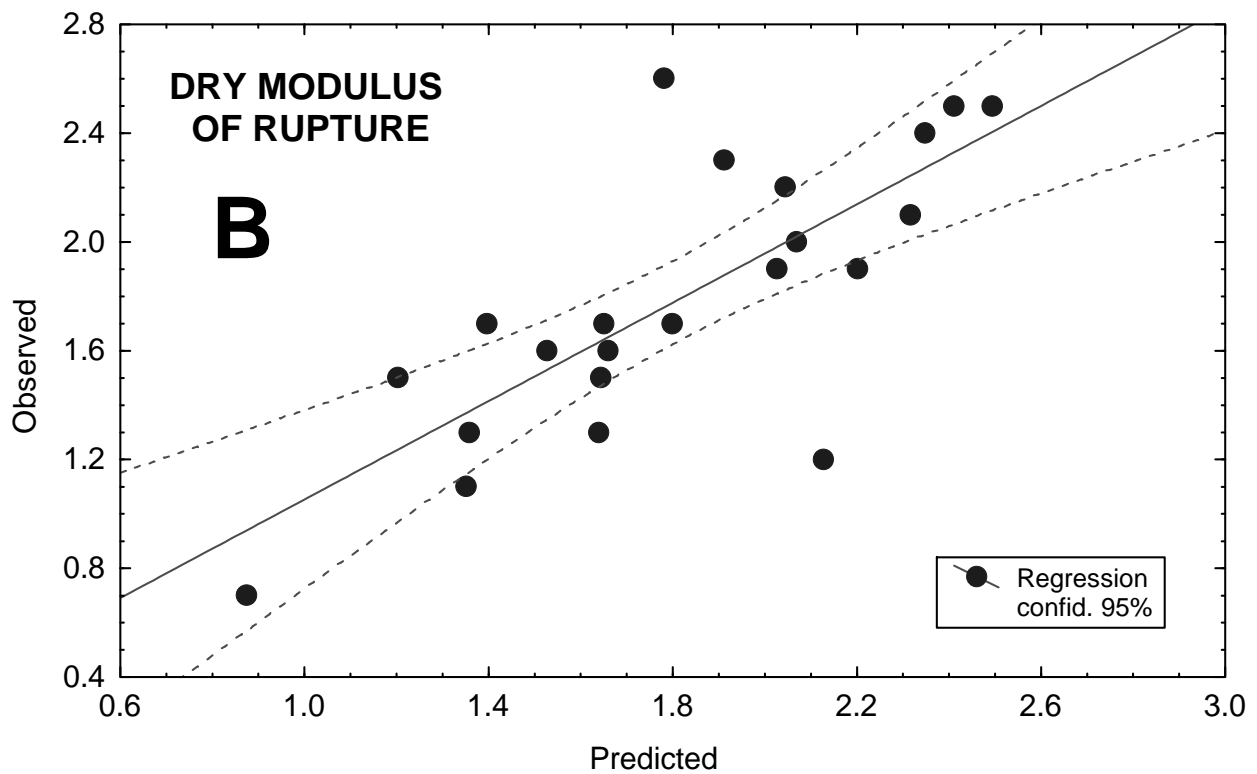
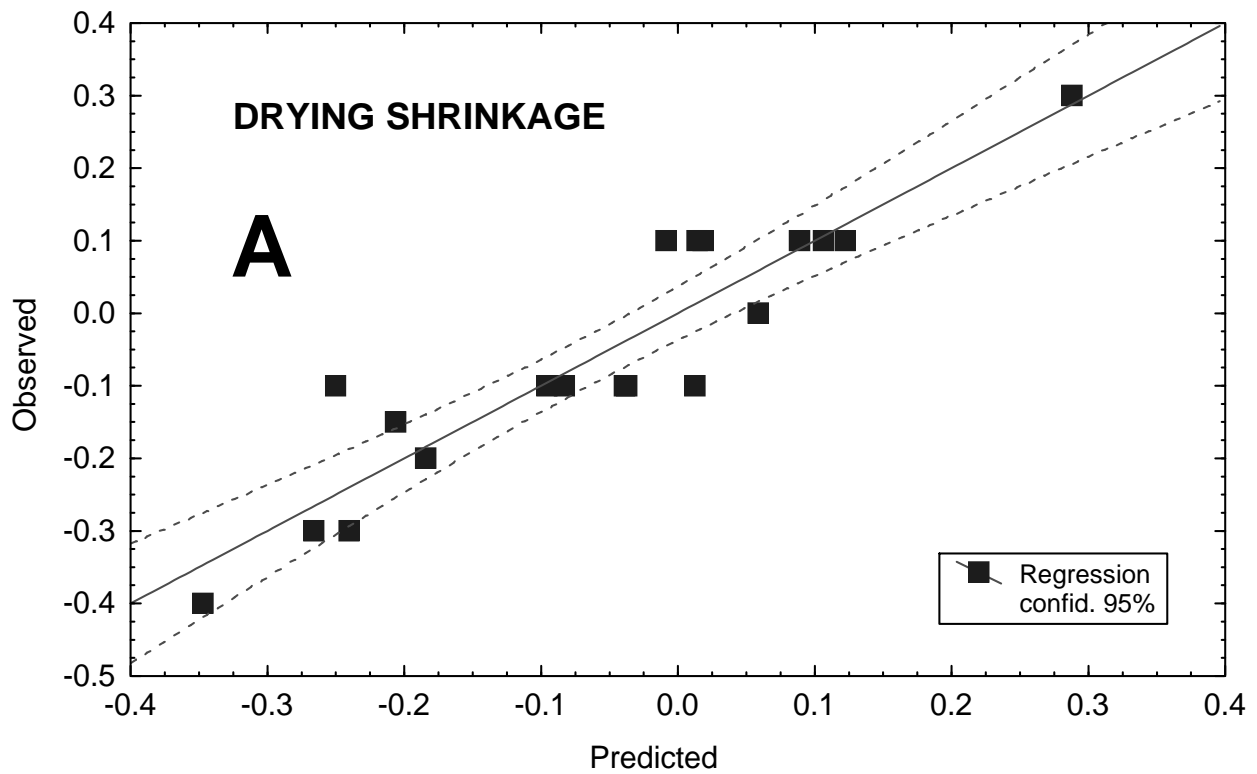


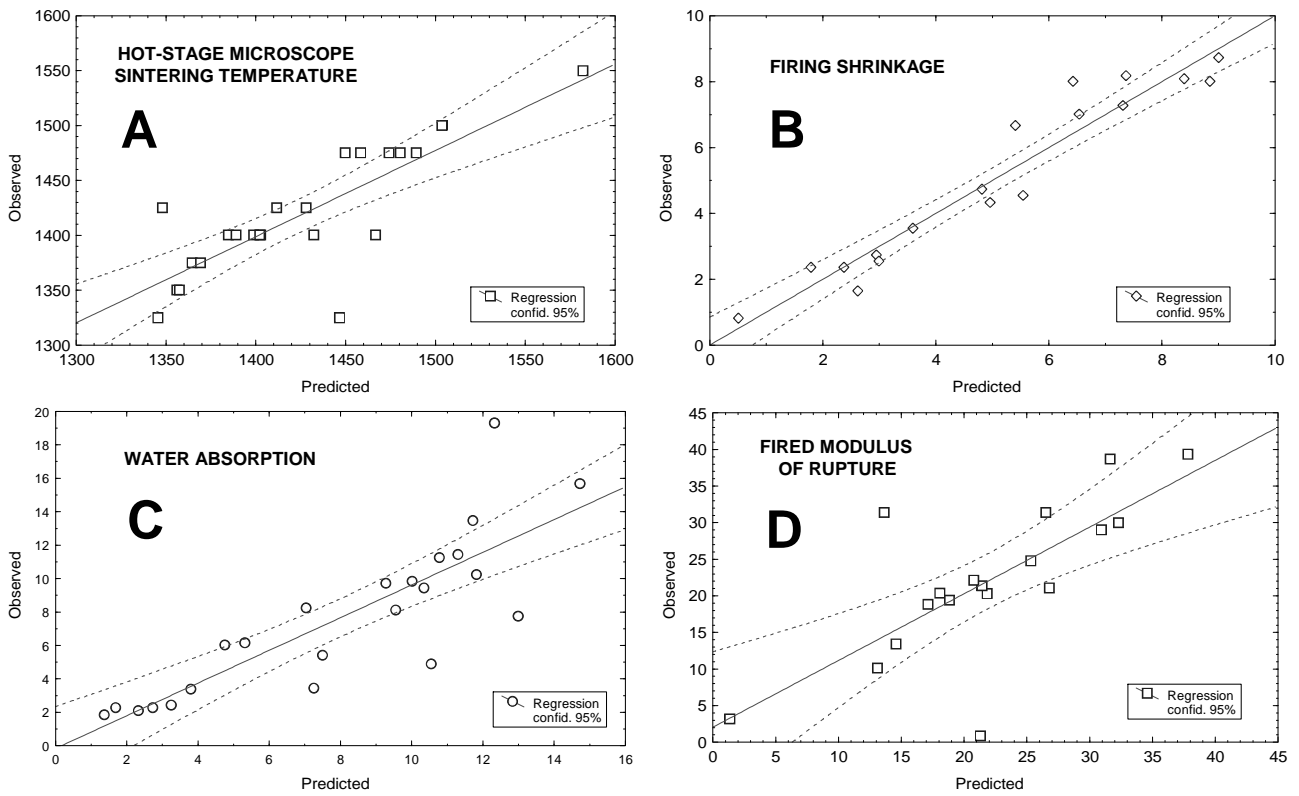
Fig. 5 Results of the principal components analysis: expandable clay minerals (Exp.Clay), crystallinity indices of illite (IC) and kaolinite (HI), feldspars (FD); specific surface (BET), Atterberg plastic limit (W_p) plastic index (I_p), methylene blue index (MBI); moisture content (MC), powder compressibility (C_p), pressing expansion (E_p), drying shrinkage (S_d); firing shrinkage (S_f), water absorption (WA), sintering temperature (T_{sint}); green (MOR_g), dry (MOR_d) and fired modulus of rupture (MOR_f)



Figs. 6 a–c Results of the multiple regression analysis, contrasting observed and predicted values of: a) Atterberg plastic index; b) pressing expansion; c) green bending strength



Figs. 7 a–b Results of the multiple regression analysis, contrasting observed and predicted values of: a) drying shrinkage; b) dry bending strength



Figs. 8 a–d Results of the multiple regression analysis, contrasting observed and predicted values of: a) sintering temperature; b) firing shrinkage; c) water absorption; d) fired bending strength