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The effect of kaolin properties on their behaviour in ceramic processing as illustrated by a range of kaolins from the Santa Cruz and Chubut Provinces, Patagonia (Argentina)

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Abstract

The Patagonian kaolins offer a wide set of origin of deposits, composition, mineral processing and ceramic properties, giving a rare opportunity for investigating the interdependence of mineralogy, chemical composition, particle size distribution, texture, and surface activity with their technological behaviour in sanitaryware and porcelain stoneware production. Plasticity is strictly dependent on surface activity, <2 μm fraction and expandable clay minerals; slip rheology is affected by soluble salts and expandable clay minerals, but also by high specific surface or tubular halloysite. Kaolinite/halloysite play an opposite role versus smectite/interstratified I/S in slip casting and tile pressing: the former allow faster casting rates, while the latter improve powder flowability and mechanical strength. Kaolinite and quartz are beneficial for drying behaviour while high surface activity or expandable clay minerals increase significantly drying sensitivity. Firing behaviour is mainly affected by minor components supplying “fluxing” (i.e. iron, alkali and alkaline-earth) oxides. A great deal of technological parameters seem to be reasonably predicted by the surface activity of clays and especially the Methylene Blue index, which is the most reliable, simple and economic method to predict and control the ceramic response of kaolins and ball clays.

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1. Introduction

The use of kaolin and ball clay has been growing in recent years as a consequence of the increasing ceramic output worldwide. Besides, the ceramic industry has undergone a considerable technological innovation in recent decades, fostering the development of new types of

ceramic products and their further diversification (Dondi, 2003; Fiederling-Kapteinat, 2005). Kaolins and ball clays are now utilised not only in classical whiteware production, but even more widely in ceramic tile manufacturing, especially for new product types, such as porcelain stoneware or white *monoporosa* tiles (Lombardo, 1996; Dondi et al., 2001a; Fiederling-Kapteinat, 2005).

These new applications are imposing technological requirements that are different with respect to the conventional use of kaolin and ball clay in slip cast,

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Table 1

Summary of geological and compositional features of Patagonian kaolins (after Dominguez et al., 2008)

| Sample | Type | Formation | Ka+Ha (wt.%) | Sm+I/S (wt.%) | Qz+Fd (wt.%) | Median size (μm) | <.3 mm fraction (wt.%) | SSA (m^2/g) |
|--------|------|-----------|--------------|---------------|--------------|-------------------------------|------------------------|-------------------------------|
| CZ | S | Ba-LM | 48 | 3 | 41 | 0.68 | 39.0 | 24.3 |
| PU | S | Ba-LM | 49 | 12 | 35 | 0.67 | 38.7 | 28.0 |
| FP | S | Ba-LM | 37 | 28 | 27 | 0.37 | 46.9 | 44.5 |
| BG | P | BG | 15 | 59 | 18 | <0.30 | 80.9 | 31.7 |
| CA | S | Ba-UM | 65 | tr. | 27 | 0.33 | 47.8 | 25.6 |
| FA | S | Ba-LM | 50 | 9 | 38 | 0.88 | 35.0 | 21.7 |
| TZ | S | Ba-LM | 43 | 8 | 46 | 1.47 | 34.2 | 21.2 |
| TS | S | Ba-LM | 52 | 9 | 36 | 0.88 | 35.6 | 22.7 |
| PR | P | CA | 29 | 2 | 68 | >63 | 2.5 | 3.1 |
| CH | S | Sa | 49 | 9 | 38 | 1.11 | 30.6 | 21.3 |
| IL | P | Ma | 28 | 15 | 54 | 4.29 | 26.6 | 13.3 |
| RF | P | Ma | 35 | tr. | 59 | 63.5 | 4.0 | 13.1 |
| RP | P | Ma | 31 | tr. | 65 | >63 | 7.9 | 7.4 |
| MA | P | Ma | 35 | 17 | 46 | 1.00 | 32.6 | 14.2 |
| SR | P | Ma | 32 | 5 | 58 | >63 | 9.5 | 8.8 |
| PRL | B | | 28 | 2 | 69 | 2.39 | 5.8 | 5.8 |
| ILL | B | | 63 | 3 | 32 | 0.45 | 41.7 | 22.4 |
| RFL | B | | 70 | 3 | 24 | 0.58 | 34.6 | 27.7 |
| RPL | B | | 68 | 15 | 15 | 1.26 | 22.6 | 25.6 |
| MAL | B | | 57 | 12 | 29 | 0.40 | 42.3 | 21.2 |
| SRL | B | | 63 | 17 | 18 | 1.09 | 25.0 | 18.7 |

Type: P=primary, S=sedimentary, B=beneficiated. Formation: Ba=Baqueró (LM=lower member, UM=upper member), BG=Bajo Grande, CA=Chon Aike, Ma=Marifil, Sa=Salamanca. Mineralogy: Ka=Kaolinite, Ha=Halloysite, Sm=Smectite, I/S=interstratified illite/smectite, Qz=Quartz, Fd=Feldspars. SSA=surface specific area.

Table 2

Plasticity of the Patagonian kaolins, clays and beneficiated products

| Clay sample | Methylene Blue Index (MBI) | | Pfefferkorn plasticity | Atterberg consistency limits | | | Linseis plasticimeter | | |
|-------------|----------------------------|-----------|------------------------|------------------------------|------------------------|-------------------------|-----------------------|---------------------|---------------------|
| | Natural pH | 3<pH<4 | index (PI) | Plastic limit (W_P) | Liquid limit (W_L) | Plastic index (I_P) | Water content | Resistance to shear | Tensional strength |
| | meq/100 g | meq/100 g | wt.% | wt.% | wt.% | wt.% | wt.% | kg cm ⁻² | kg cm ⁻² |
| CZ | 109.6 | 12.0 | 40.7 | 29.2 | 55.9 | 26.7 | 28.7 | 23.7 | 0.76 |
| PU | 113.5 | 12.5 | 41.3 | 28.7 | 57.0 | 28.3 | 29.0 | 23.0 | 0.67 |
| FP | 231.0 | 32.0 | 59.1 | 30.7 | 93.2 | 62.5 | 35.6 | 23.3 | 0.74 |
| BG | 579.4 | 67.5 | 76.7 | 49.9 | 248.0 | 198.1 | 42.7 | 21.5 | 0.89 |
| CA | 62.6 | 7.0 | 39.4 | 30.1 | 49.3 | 19.2 | 30.2 | 25.6 | 0.76 |
| FA | 68.5 | 9.5 | 40.3 | 29.4 | 56.1 | 26.7 | 29.2 | 25.9 | 1.47 |
| TZ | 66.6 | 7.5 | 33.0 | 23.6 | 45.3 | 21.7 | 25.7 | 25.0 | 0.86 |
| TS | 84.2 | 8.5 | 38.0 | 28.2 | 52.3 | 24.1 | 28.4 | 18.7 | 0.53 |
| PR | 4.7 | 2.0 | 32.2 | 29.7 | 33.3 | 3.6 | 25.3 | 16.6 | 0.27 |
| CH | 80.3 | 8.5 | 38.3 | 30.7 | 47.7 | 17.0 | 28.1 | 20.9 | 0.69 |
| IL | 43.1 | 5.0 | 33.4 | 26.6 | 40.6 | 14.0 | 26.6 | 19.7 | 0.56 |
| RF | 25.1 | 4.5 | 32.1 | 28.5 | 36.5 | 7.9 | 26.1 | 13.0 | 0.41 |
| RP | 11.0 | 2.5 | 24.0 | 21.2 | 25.3 | 4.1 | 21.6 | 42.7 | 0.47 |
| MA | 36.2 | 3.5 | 34.6 | 28.3 | 43.0 | 14.7 | 25.0 | 19.6 | 0.61 |
| SR | 41.1 | 3.0 | 31.1 | 27.5 | 34.0 | 6.4 | 25.6 | 22.1 | 0.45 |
| PRL | 14.9 | n.d. | 48.2 | 42.1 | 50.3 | 8.2 | 33.7 | 26.3 | 0.38 |
| ILL | 68.9 | n.d. | 43.6 | 33.4 | 56.1 | 22.7 | 30.7 | 23.6 | 0.65 |
| RFL | 72.8 | n.d. | 52.7 | 43.6 | 59.8 | 16.2 | 35.3 | 11.9 | 0.36 |
| RPL | 45.4 | n.d. | 43.3 | 37.3 | 47.9 | 10.6 | 30.1 | 11.8 | 0.48 |
| MAL | 56.8 | n.d. | 39.7 | 31.7 | 49.0 | 17.3 | 28.4 | 18.7 | 0.53 |
| SRL | 62.6 | n.d. | 47.9 | 40.2 | 58.2 | 17.9 | 34.0 | 19.2 | 0.46 |

n.d.=not determined.

extruded or solid moulded products, such as tableware, sanitaryware and alumino-silicate refractories. Furthermore, the latest innovation in tilemaking (e.g. large-size tiles, double pressing, pressing without mould, cutting of green tiles) is particularly stressing properties like plasticity, powder flowability, and ability to densify during dry pressing and to toughen green tiles (Dondi, 2003). Thus a new class of clay materials – able to couple high plasticity and suitable rheological behaviour with the usual requirements for ball clays – is now encountering a growing commercial success worldwide (Dondi et al., 2003a; Fiederling-Kapteinat, 2005).

However, the desired set of technological properties appears to present difficulties for mineral processing, even by selective clay exploitation and blending, because of its complex dependence on mineralogy, particle size distribution and surface activity of clays. Frequently, these characteristics are not adequately monitored by routine analyses with conventional ceramic procedures (Worrall, 1975; Powell, 1996). In fact, it is often a hard task to infer backwards the whole chain interconnecting ceramic behaviour, clay composition, mining processing and geological features. From this viewpoint, the Patagonian kaolins offer an excep-

tional opportunity for investigating the interdependence of these factors, as a wide set of: i) origin of deposits (primary and sedimentary clays), ii) mineral processing (i.e. washing and settling of primary kaolin), iii) mineralogical composition and particle size distribution, and iv) ceramic properties is available (Table 1 and Dominguez et al., 2008). In addition, these raw materials are utilised by two distinct end-users: a) the whiteware industry (i.e. sanitaryware and tableware) and b) ceramic tile manufacturers. These sectors are well differentiated from each other for their production cycles and the processes which the clays undergo (e.g. wet dispersion, filterpressing, slip casting, slow drying and firing for whitewares; wet grinding, spray-drying, powder pressing, fast drying and firing for ceramic tiles). As a consequence, the technological requirements that kaolins and ball clays have to fulfil are also different in whiteware and tilemaking (Maxwell and Dinger, 1992; Wilson, 1998; Dondi, 2003; Capoğlu and Kutbay, 2002).

Therefore, this paper is aimed at assessing how mineralogy, particle size distribution and surface activity affect the technological behaviour of kaolins and sedimentary clays in sanitaryware and porcelain stoneware production.

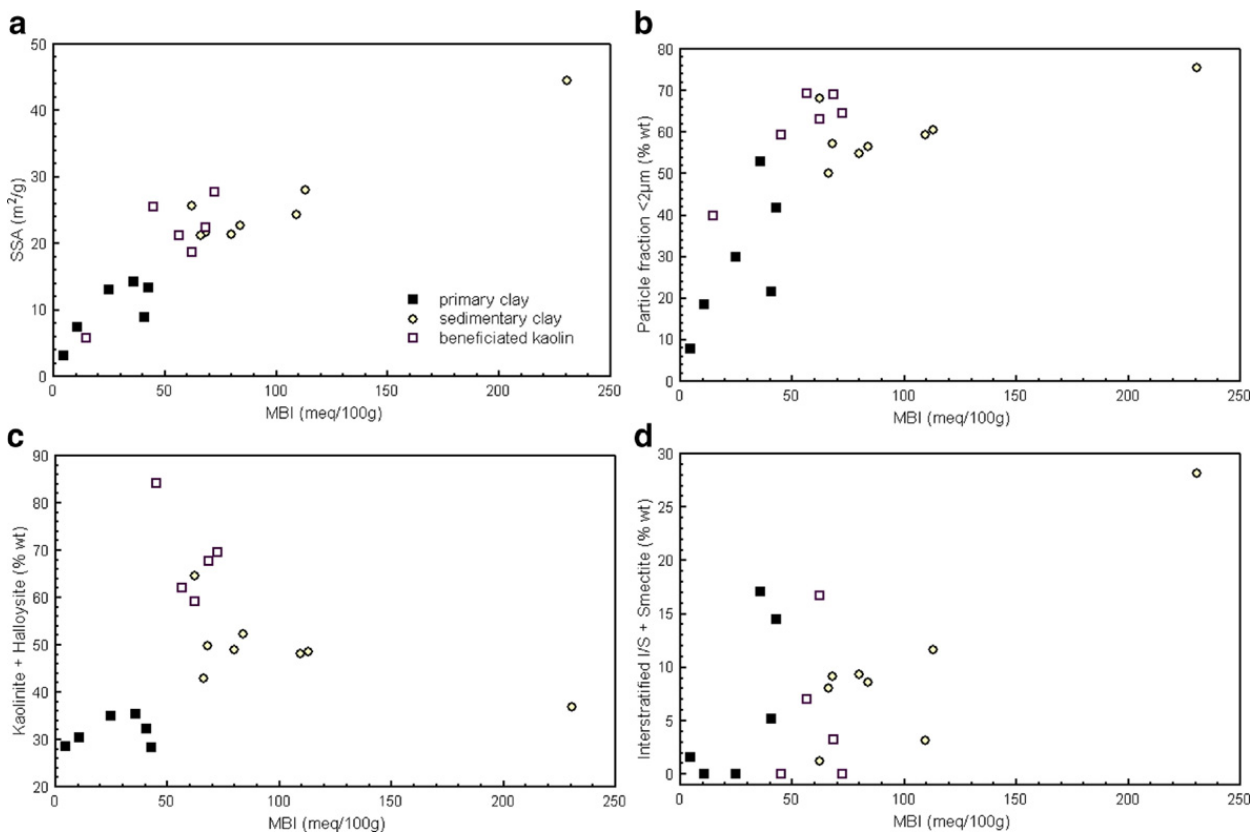


Fig. 1. Methylene Blue Index vs (a) specific surface area, (b) particle fraction <2 µm, (c) kaolinite group minerals and (d) expandable clay minerals as a proportion of kaolins and clays.

2. Materials and methods

Twenty-one samples were taken into consideration:

- 7 primary deposits (6 kaolins and 1 bentonite),
- 8 sedimentary deposits (so-called *ball clays*),
- 6 beneficiated products (the primary kaolins after washing and settling).

For sampling criteria and procedures as well as methodologies followed in mineralogical, geochemical and granulometric analyses, the reader is addressed to the first part of this study (Dominguez et al., 2008).

The technological characterisation dealt with plasticity, slip rheological properties, and behaviour in the shaping, drying and firing stages of ceramic processing. For this purpose, a laboratory simulation was performed of both:

- *the tilemaking cycle*, involving a mixture of clay and soda-potash feldspar (50:50 wt.%), wet grinding (planetary mill, 20 min), slip drying and powder deagglomeration, humidification (7–8 wt.%) and pelletizing, uniaxial pressing of $110 \cdot 55 \cdot 5$ mm³ tiles (40 MPa), drying in an oven (100 °C) and firing in an electrical roller kiln (maximum temperatures 1200 and 1250 °C, 51 min cold-to-cold);
- *the sanitaryware cycle*, involving clay dispersion and filterpressing, slip preparation (100% clay plus a clay:quartz

mixture 50:50 wt.%) and casting in gypsum moulds (ambient pressure) of $13 \cdot 26 \cdot 220$ mm³ tiles, drying in an oven (100 °C) and firing in an electrical chamber kiln (maximum temperature 1250 °C, 3 h cold-to-cold).

A suitably plastic behaviour, though still appraised mostly by an empirical viewpoint, is a very important requirement for a great deal of ceramic applications of kaolin and ball clay, especially porcelain stoneware and sanitaryware bodies that contain low amounts of clay raw materials (currently 35–45 wt.%). Thus four different methods were followed, including the methylene blue index (MBI), Atterberg and Pfefferkorn plastic indices, and Linseis tensional strength (Table 2):

- *Atterberg consistency limits*, thus plastic limit W_P , liquid limit W_L and plastic index $I_P = W_L - W_P$, with a relative standard deviation of data $C < 5\%$ (Atterberg, 1911; UNI 10014, 1964);
- *Pfefferkorn index* PI with about 5% relative error (Pfefferkorn, 1924; van der Velden, 1979);
- *tensional strength and resistance to shear* (Linseis, 1951; Singer and Singer, 1963) with a Netzsch 405 apparatus ($C \sim 5\%$).

The surface activity was evaluated by the *methylene blue index* (MBI, Hang and Brindley, 1970; Avena et al., 2001)

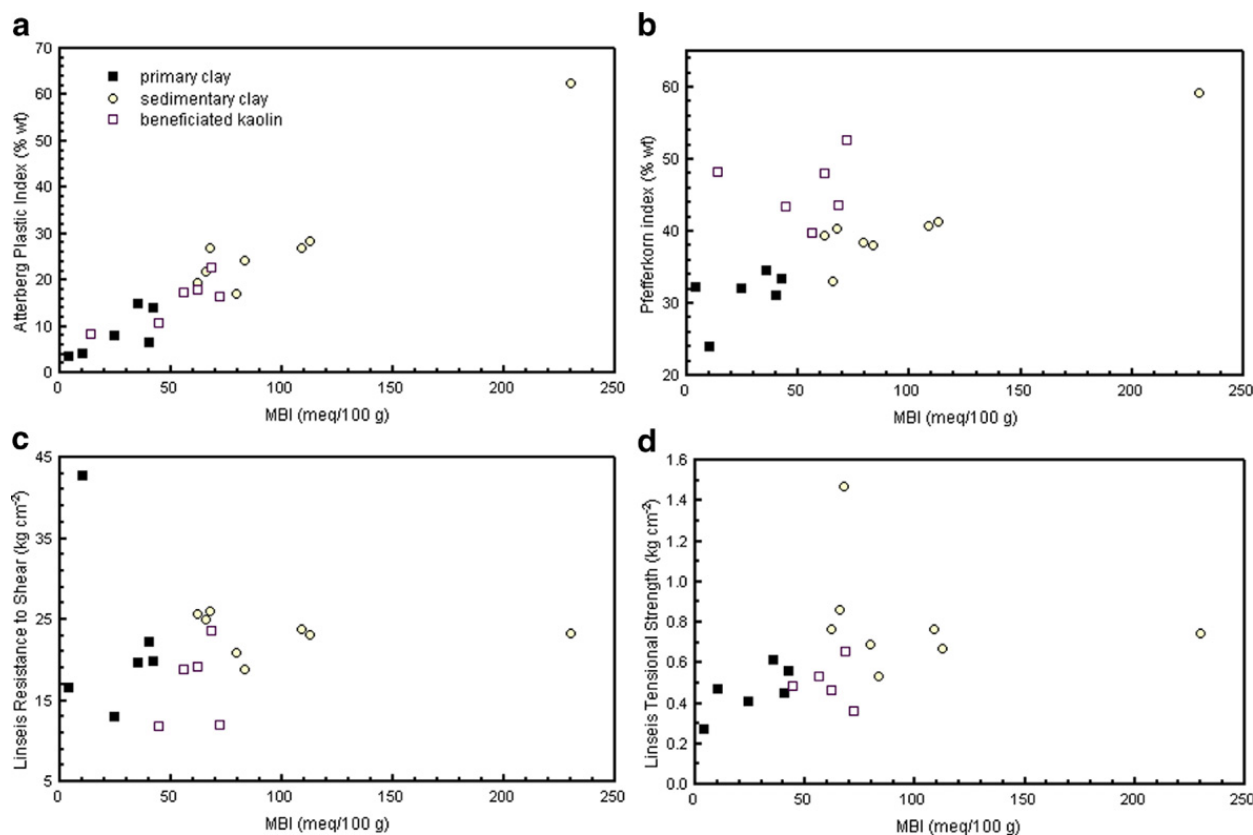


Fig. 2. Methylene Blue Index vs plasticity of kaolins and clays expressed as: a) Atterberg plastic index; b) Pfefferkorn index; c) Linseis resistance to shear and d) tensional strength.

measured on both buffered (pH 3.5, ASTM C 837, experimental uncertainty 0.25 meq/100 g) and unbuffered suspensions (natural pH, experimental uncertainty 0.5 meq/100 g).

The main ceramic applications of kaolin and ball clay require their dispersion in water and/or wet grinding, making a suitable rheological behaviour a critical requirement for clay raw materials (Worrall, 1975; Maxwell and Dinger, 1992; Dondi, 2003). Rheological properties were determined with both a Brookfield viscosimeter (Steffe, 1992) and a cylinder for gravity flow (Singer and Singer, 1963). Brookfield viscosity was measured at 20 rpm with spindle #1 (<500 cps) or #3 (>500 cps) on the as-prepared slip (VB0) and after 1, 5 and 10 min (VB1, VB5 and VB10 respectively) with an experimental relative error around 5%. The slip density was set as close as possible to $\rho_s = 1.60 \text{ g cm}^{-3}$, but in 8 cases we had to lower the solid load, in order to shift the viscosity into the operative window of our equipment. The time dependence (thixotropy) was expressed as $T_B = (VB_{10} - VB_0) \cdot VB_0^{-1} \cdot 100$. The resistance to shear was estimated as time of flow of the as-prepared slip (τ_0) and after 60 min (τ_{60}) with an experimental error of about 1 s. Furthermore, the electrolyte concentration in the slip was determined by both electrical conductivity (error $\sim 10 \mu\text{S}$) and soluble sulphate content (ASTM C 867, error $\sim 5 \text{ mg kg}^{-1}$).

Shaping behaviour was appraised by measuring:

- slip density by pycnometry (ρ_s , error 0.01 g cm^{-3}), casting rate as weight of the cast cake after 15 min settling (M_c , error 1 g) and suction time as the time necessary to make the slip surface in the mould dull (t_s , error 2 s) for slip casting;
- green bulk density (ρ_g , geometric method, error 0.002 g cm^{-3}), post-pressing expansion ($E_p = (L_p - L_m) \cdot L_m^{-1} \cdot 100$, where L_p and L_m are the length of pressed tile and mould respectively, $C < 5\%$) and green modulus of rupture (σ_g , ISO 10545-4, $C \sim 5\%$) for pressing.

Drying behaviour was investigated by measuring:

- the Bigot curve and drying shrinkage (S_d , ASTM C 326, experimental error 0.5 cm m^{-1}) on slip cast clays;
- drying shrinkage/expansion (S_d^* , experimental error 0.01 cm m^{-1}) on pressed bodies;
- dry modulus of rupture (ASTM C 689, $C \sim 5\%$) of ceramic bodies on both slip cast (σ_d) and pressed specimens (σ_d^*).

The Bigot curve was determined (Adamel barelattograph, ambient temperature and RH 40–60%) on two plastic moulded prisms ($40 \cdot 10 \cdot 10 \text{ mm}^3$) measuring working moisture (W_B , $C < 2\%$), drying shrinkage (S_B , error 0.1 cm m^{-1}) and weight loss with shrinkage and without shrinkage (W_1 and W_2 respectively, $C \sim 2\%$). Two drying sensitivity indices were calculated: $BI = W_1 (W_{1+} W_2)^{-1}$ (Barna, 1967; Ginés et al., 1997) and $ISE = W_1 \cdot S_B \cdot 0.01$ (von Chiari, 1986; Dondi et al., 1998).

Firing behaviour was appraised by determining:

- fusibility of clay materials by hot-stage microscopy (Expert System Misura, $10 \text{ }^\circ\text{C min}^{-1}$ up to $1600 \text{ }^\circ\text{C}$) inferring the characteristic temperatures T_{soft} (beginning of

densification) and T_{soft} (softening) through morphological changes occurring to a cylindrical specimen (3 mm height and 2 mm diameter) with an uncertainty of $5\text{--}10 \text{ }^\circ\text{C}$ (Dondi et al., 2001b);

– firing shrinkage (S_f , ASTM C 326, error 0.5 cm m^{-1}) and water absorption (E , ASTM C 373, $C \sim 2\%$) on slip cast clays:

– firing shrinkage (S_f^* , ASTM C 326, error 0.1 cm m^{-1}), water absorption (E^* , ASTM C 373, error $0.1 \text{ wt.}\%$), bulk density (ρ_f^* , ASTM C 373, error 0.002 g cm^{-3}) and sintering rate (hot-stage microscopy, isothermal firing at $1200 \text{ }^\circ\text{C}$, error 0.01 mm s^{-1}) on pressed porcelain stoneware bodies.

3. Results

3.1. Plasticity

The plasticity of a clay material depends on its surface activity, particle size distribution and mineralogical composition (Fitzjohn and Worrall, 1980; Ginés et al., 1997; Raimondo et al., 2003). From this viewpoint, the MBI represents a useful “mean indicator” of all the above-mentioned features, presenting a linear positive correlation

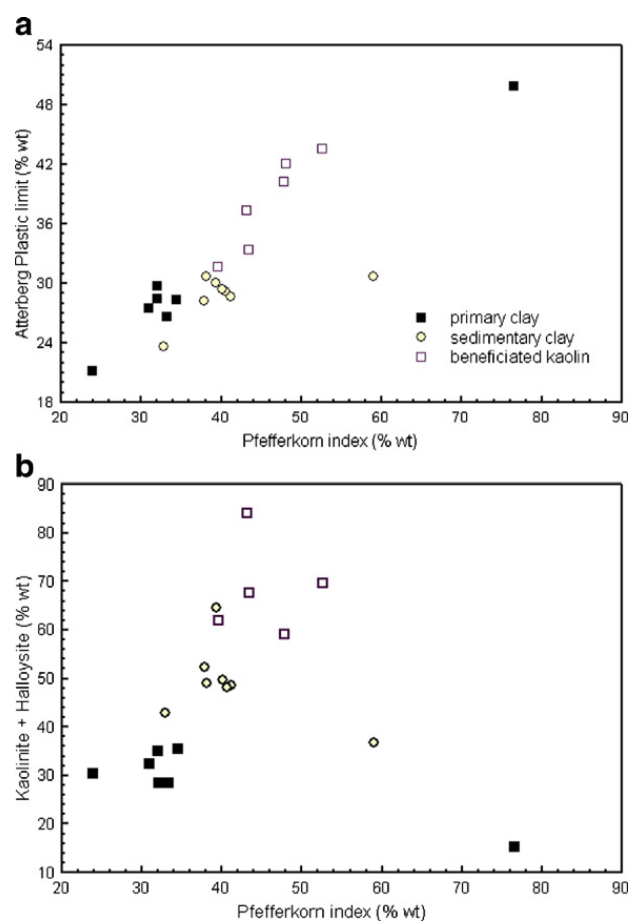


Fig. 3. Pfefferkorn index vs (a) Atterberg plastic limit and (b) amount of kaolinite group minerals.

with specific surface area (Fig. 1a) and a non-linear, direct relationship with the finer particle fraction, implying a slower increase of the MBI with the amount of particles $<2\ \mu\text{m}$ for kaolins and a faster one for sedimentary clays (Fig. 1b). These differing slopes are connected with the mineralogical composition: the increased amount of kaolinite (and halloysite) consequent to beneficiation of kaolins justifies the slower trend (Fig. 1c) while the varying amount of expandable clay minerals explains the trend of sedimentary clays (Fig. 1d).

The various plasticity indices gave on the whole comparable results, though with a clearly different data dispersion, that highlight the increasingly plastic behaviour of the series: primary kaolins < beneficiated kaolins < sedimentary clays. In particular, the Atterberg plastic index appears to be strictly related to the MBI (Fig. 2a) while the correspondent relations become less and less statistically significant moving to the Pfefferkorn index (Fig. 2b) or the Linseis resistance to shear (Fig. 2c) and tensional strength (Fig. 2d). These results confirm to a large extent the observations of Fitzjohn and Worrall (1980), Amarante and Boutros (1981), Ginés et al. (1997), Baran et al. (2001), Raimondo et al. (2003) and Schmitz et al. (2004).

There was a good correspondence between the Pfefferkorn index and the Atterberg plastic limit (Fig. 3a) as expected, because both parameters account for the capacity of a clay material to retain water prior to behaving plastically (Van der Velden, 1979; Baran et al. 2001). These values seem to be chiefly linked to the amount of kaolinite, but two samples (BG and FP) that are outliers contain the most smectite (Fig. 3b).

3.2. Slip rheological properties

The Patagonian clays exhibit different rheological behaviours (Table 3):

- low viscosity and low resistance to shear measured on most primary and beneficiated kaolins, due essentially to their relatively coarse-grained particle distribution, low concentration of electrolytes and lack of expandable clay minerals;
- intermediate values of both viscosity and shear resistance, which are mutually correlated in most sedimentary clays, justified by different amounts of soluble salts and expandable clay minerals in fine-grained raw materials;

Table 3
Slip rheology of the Patagonian kaolins, clays and beneficiated products

| Sample | Brookfield viscosimeter | | | | | | | | Gravity flow | | Soluble salts | |
|--------|-------------------------|-----|------|-----------|-----------|-----------|-------------|-------|--------------|-------------|---------------------|-------|
| | ρ_s | NC | NS | VB0=0 min | VB1=1 min | VB5=5 min | VB10=10 min | T_B | τ_0 | τ_{60} | SO ₄ | EC |
| | g cm ⁻³ | g | mL | cps | cps | cps | cps | % | S | s | mg kg ⁻¹ | MS |
| CZ | 1.58 | 2.0 | 8.1 | 565 | 665 | 905 | 1000 | 77 | 35 | 42 | 242 | 1717 |
| PU | 1.54 | 1.0 | 6.5 | 250 | 265 | 285 | 305 | 22 | 15 | 30 | 166 | 1330 |
| FP | 1.25 | 1.0 | 0.5 | 635 | 740 | 960 | 1200 | 88 | 20 | 23 | 164 | 716 |
| BG | 1.05 | 2.0 | 11.0 | 2410 | 2485 | 3250 | 3400 | 41 | 21 | 25 | 948 | 6140 |
| CA | 1.60 | 2.0 | 4.4 | 665 | 1045 | 1210 | 1430 | 115 | 21 | n.d. | 351 | 3910 |
| FA | 1.60 | 2.0 | 4.8 | 354 | 360 | 380 | 454 | 28 | 26 | 30 | 46 | 243 |
| TZ | 1.62 | 2.0 | 4.5 | 241 | 241 | 245 | 252 | 5 | 18 | 20 | 18 | 126 |
| TS | 1.60 | 2.0 | 4.7 | 266 | 266 | 268 | 272 | 2 | 18 | 18 | 17 | 92 |
| PR | 1.60 | 1.0 | 2.5 | 43 | 42 | 40 | 40 | 0 | 21 | n.d. | 31 | 404 |
| CH | 1.55 | 1.0 | 4.6 | 116 | 134 | 155 | 176 | 52 | 13 | 25 | 1047 | 6110 |
| IL | 1.60 | 1.6 | 3.7 | 121 | 121 | 123 | 125 | 3 | 18 | 21 | 384 | 978 |
| RF | 1.40 | 1.6 | 4.6 | 1100 | 1350 | 1550 | 1615 | 47 | 15 | 25 | 924 | 8290 |
| RP | 1.43 | 1.6 | 4.7 | 1350 | 1390 | 1400 | 1430 | 6 | 12 | 13 | 812 | 10620 |
| MA | 1.60 | 1.6 | 4.5 | 58 | 57 | 57 | 57 | 0 | 12 | 14 | 225 | 1031 |
| SR | 1.60 | 1.4 | 3.4 | 93 | 93 | 97 | 102 | 9 | 19 | 24 | 500 | 1408 |
| PRL | 1.55 | 1.8 | 1.9 | 37 | 37 | 38 | 39 | 5 | 58 | n.d. | 5 | 122 |
| ILL | 1.60 | 1.6 | 3.6 | 148 | 148 | 150 | 152 | 3 | 17 | 18 | 10 | 207 |
| RFL | 1.60 | 1.6 | 4.7 | 365 | 416 | 450 | 496 | 36 | 23 | 39 | 53 | 890 |
| RPL | 1.60 | 1.6 | 2.6 | 101 | 106 | 112 | 116 | 14 | 19 | 20 | 66 | 572 |
| MAL | 1.60 | 1.6 | 2.1 | 115 | 120 | 129 | 135 | 17 | 15 | 17 | 11 | 98 |
| SRL | 1.60 | 1.6 | 3.1 | 210 | 210 | 211 | 215 | 2 | 45 | 47 | 52 | 301 |

ρ_s : slip density; deflocculant addition: sodium carbonate (NC) and sodium silicate (NS). Brookfield rheological testing: viscosity measured after 0, 1, 5 and 10 min; T_B : thixotropy. Time of gravity flow measured after 0 min (τ_0) and 60 min (τ_{60}). Soluble salts: concentration of sulphate ion (SO₄) and electrical conductivity (EC).

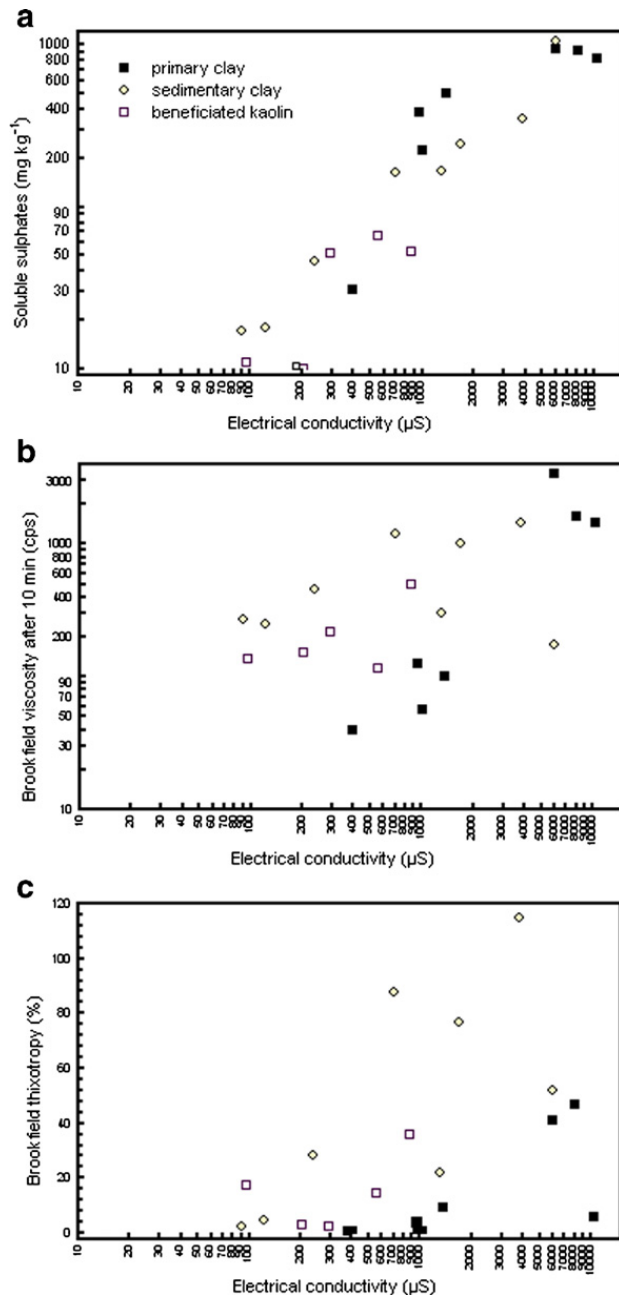


Fig. 4. Soluble salts in the clay slips: electrical conductivity vs (a) amount of sulphates, (b) Brookfield viscosity and (c) thixotropy.

- high viscosity linked to large amounts of smectite (samples BG and FP) or soluble salts and/or halloysite (samples CA, RP and RF) that do not seem to increase the resistance to shear;
- low viscosity of samples PRL and SRL, which, however, exhibited a strong resistance to shear that might be explained by the occurrence of noteworthy amounts of halloysite fibers (Dominguez et al., 2008).

Overall, a time-dependence of both viscosity and resistance to shear can be seen for all the clay types. Brookfield measurements suggested there is a direct relationship

between viscosity and thixotropy, though it is significant only for the sedimentary clays, being to a large extent dependent on the amount of colloidal fraction.

In most cases, the rheological properties described above are clearly affected by the concentration of electrolytes in the slip, measured as electrical conductivity, which are mainly constituted by soluble sulphates (Fig. 4a). The dependence of viscosity on the electrical conductivity, however, follows three parallel trends, one for each type of raw materials (Fig. 4b) that are even more appreciable in the case of thixotropy (Fig. 4c). This result implies a substantial influence of the clay surface activity that becomes conspicuous when the MBI is contrasted with viscosity and thixotropy, except for samples CA, RF and RP because of their high content of soluble salts.

A thorough assessment of slip viscosity and its time-dependence is in progress.

3.3. Shaping behaviour

The main technological parameters describing how clays and clay bodies (i.e. 50% clay and 50% filler) behave during forming are summarised in Table 4. The

Table 4
Shaping behaviour of the Patagonian kaolins, clays and beneficiated products

| | Slip casting | | Uniaxial pressing | | |
|-----|--------------|-------|--------------------|--------------------|------------|
| | M_c | t_s | ρ_g | E_p | σ_g |
| | g | s | g cm ⁻³ | cm m ⁻¹ | MPa |
| CZ | 23 | 191 | 1.989 | 0.45 | 1.01 |
| PU | 16 | 241 | 1.999 | 0.42 | 1.17 |
| FP | 12 | 245 | 2.018 | 0.40 | 1.51 |
| BG | 29 | 307 | n.d. | n.d. | n.d. |
| CA | 22 | 144 | 1.933 | 0.44 | 1.26 |
| FA | 26 | 119 | 1.870 | 0.55 | 0.62 |
| TZ | 20 | 142 | 1.749 | 0.60 | 0.36 |
| TS | 18 | 184 | 1.858 | 0.53 | 0.60 |
| PR | 120 | 40 | n.d. | n.d. | n.d. |
| CH | 40 | 200 | 1.963 | 0.48 | 0.88 |
| IL | 50 | 147 | n.d. | n.d. | n.d. |
| RF | 154 | >300 | n.d. | n.d. | n.d. |
| RP | 154 | >300 | n.d. | n.d. | n.d. |
| MA | 33 | 87 | n.d. | n.d. | n.d. |
| SR | 84 | 60 | n.d. | n.d. | n.d. |
| PRL | 114 | 25 | 1.737 | 1.00 | 0.22 |
| ILL | 29 | 84 | 1.812 | 0.60 | 0.51 |
| RFL | 29 | 188 | 1.822 | 0.60 | 0.87 |
| RPL | 43 | 80 | 1.833 | 0.69 | 0.58 |
| MAL | 25 | 84 | 1.860 | 0.53 | 0.63 |
| SRL | 44 | 91 | 1.795 | 0.74 | 0.46 |

M_c : casting rate measured as weight of the slip cast cake; t_s : slip suction time. Pressing of clay:feldspar (1:1) mix: green bulk density (ρ_g); post-pressing expansion (E_p); green modulus of rupture (σ_g). n.d. = not determined.

clay behaviour during slip casting seems to be mostly dependent on surface activity, as both the casting rate, expressed as weight of the cast cake, and the slip suction time are well correlated with the MBI (Fig. 5a and b). Two samples (RF and RP) cannot accomplish slip suction, chiefly because of their high viscosity and large amount of soluble salts. As expected, the casting rate shows an inverse relationship with the colloidal particle fraction ($<0.3 \mu\text{m}$) and the amount of expandable clay

minerals, even if this trend seems to be limited to primary kaolins. Interesting enough, once primary kaolins are omitted, a certain dependence of the casting rate on kaolinite percent is revealed: the larger the amount of kaolinite+halloysite, the faster the slip casting (Fig. 5c). This is probably connected with the tendency of kaolinite platelets to arrange face-to-face, as is often observed in the sedimentary clay deposits (Dominguez et al., 2008).

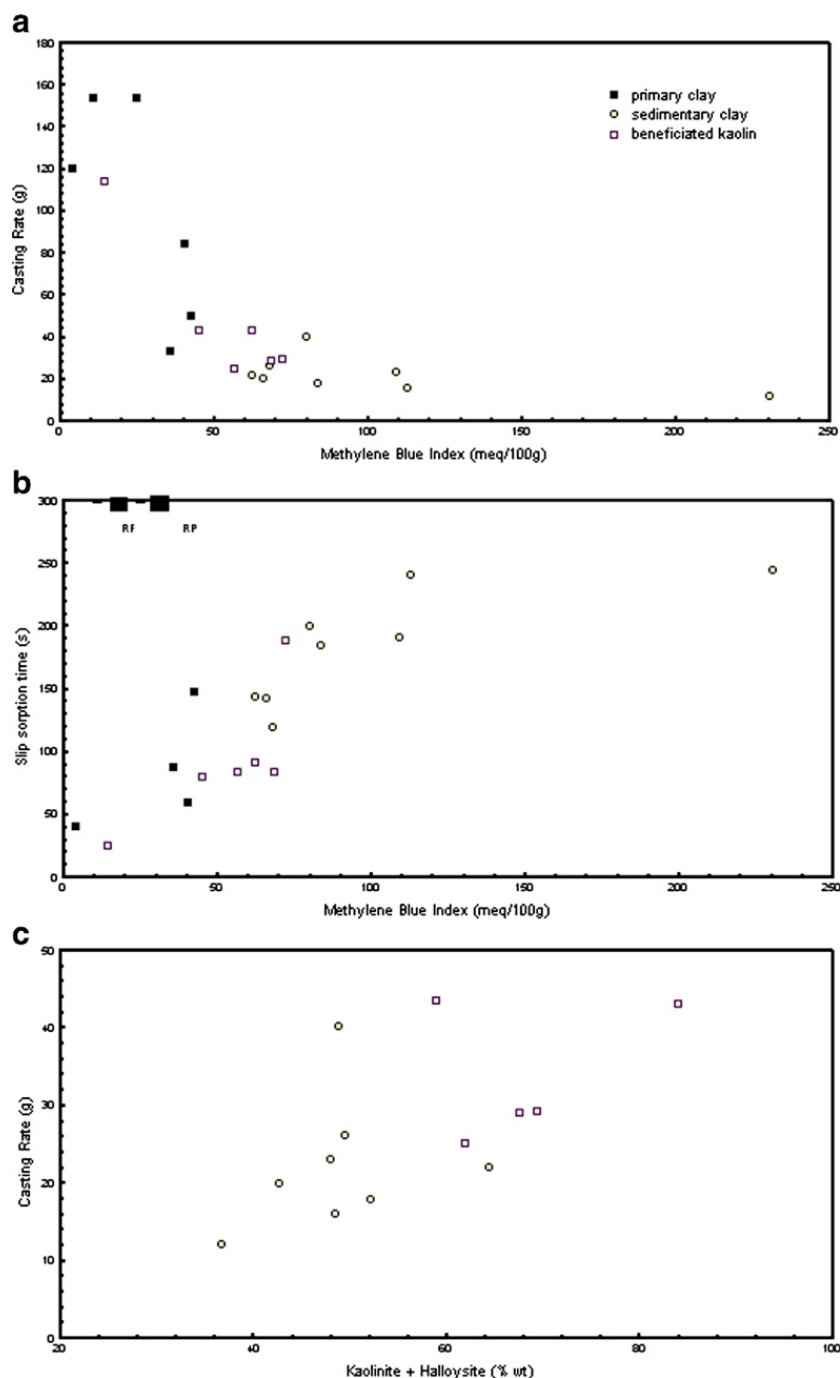


Fig. 5. Casting behaviour of clay slips: Methylene Blue Index vs (a) casting rate, (b) slip suction time, and (c) concentration of kaolinite group minerals vs casting rate.

Table 5
Drying behaviour of the Patagonian kaolins, clays and beneficiated products

| Sample | Bigot curve | | | | | | Slip casting | | Pressing | |
|--------|-------------|--------------------|-------|-------|------|------|--------------------|------------|--------------------|--------------|
| | W_B | S_B | W_1 | W_2 | BI | ISE | S_d | σ_d | S_d^* | σ_d^* |
| | wt.% | cm m ⁻¹ | wt.% | wt.% | 1 | 1 | cm m ⁻¹ | MPa | cm m ⁻¹ | MPa |
| CZ | 34.7 | 8.5 | 56.2 | 43.8 | 0.56 | 1.66 | 9.0 | 4.26 | 0.09 | 2.40 |
| PU | 37.2 | 8.4 | 55.4 | 44.6 | 0.55 | 1.74 | 10.0 | 5.75 | 0.09 | 3.11 |
| FP | 51.5 | 13.7 | 77.3 | 22.7 | 0.77 | 5.45 | n.d. | n.d. | 0.46 | 5.55 |
| BG | 67.1 | 16.3 | 80.5 | 19.5 | 0.81 | 8.80 | n.d. | n.d. | n.d. | n.d. |
| CA | 36.7 | 6.0 | 40.0 | 60.0 | 0.40 | 0.88 | 10.5 | 3.97 | -0.14 | 1.76 |
| FA | 35.8 | 7.6 | 47.7 | 52.3 | 0.48 | 1.30 | 7.0 | 4.28 | 0.05 | 1.43 |
| TZ | 31.0 | 7.5 | 49.7 | 50.3 | 0.50 | 1.15 | 6.5 | 4.19 | 0.03 | 0.67 |
| TS | 35.4 | 7.8 | 51.3 | 48.7 | 0.51 | 1.41 | 6.0 | 3.82 | 0.04 | 1.00 |
| PR | 28.8 | 0.6 | 18.5 | 81.5 | 0.19 | 0.03 | 1.0 | 0.62 | n.d. | n.d. |
| CH | 33.6 | 7.4 | 50.8 | 49.2 | 0.51 | 1.26 | 7.5 | 2.62 | -0.03 | 1.94 |
| IL | 31.0 | 5.7 | 38.5 | 61.5 | 0.39 | 0.68 | 8.0 | 2.00 | n.d. | n.d. |
| RF | 30.8 | 3.7 | 33.8 | 66.2 | 0.34 | 0.38 | 6.0 | 1.50 | n.d. | n.d. |
| RP | 22.4 | 2.5 | 29.0 | 71.0 | 0.29 | 0.16 | 4.0 | 0.99 | n.d. | n.d. |
| MA | 31.8 | 5.3 | 37.9 | 62.1 | 0.38 | 0.63 | 5.0 | 1.81 | n.d. | n.d. |
| SR | 28.5 | 3.0 | 27.8 | 72.2 | 0.28 | 0.24 | 3.5 | 1.06 | n.d. | n.d. |
| PRL | 43.8 | 1.2 | 17.4 | 82.6 | 0.17 | 0.09 | 2.0 | 1.10 | -0.29 | 0.53 |
| ILL | 37.7 | 13.3 | 43.3 | 56.7 | 0.43 | 2.17 | 4.5 | 2.74 | -0.11 | 0.86 |
| RFL | 47.2 | 4.9 | 41.0 | 59.0 | 0.41 | 0.95 | 5.5 | 3.10 | -0.08 | 1.35 |
| RPL | 39.7 | 4.7 | 39.0 | 61.0 | 0.39 | 0.73 | 3.0 | 2.14 | -0.12 | 0.94 |
| MAL | 35.8 | 4.9 | 39.5 | 60.5 | 0.40 | 0.69 | 4.0 | 2.22 | -0.20 | 0.72 |
| SRL | 46.8 | 7.2 | 44.1 | 55.9 | 0.44 | 1.49 | 5.0 | 2.57 | -0.23 | 0.64 |

Bigot curve of clay materials: working moisture (W_B), drying shrinkage (S_B), weight loss with shrinkage (W_1) and without shrinkage (W_2), Barna index (BI) and drying sensitivity index (ISE). Drying behaviour of ceramic bodies: drying shrinkage: S_d (slip casting) and S_d^* (pressing); dry modulus of rupture: σ_d (slip casting) and σ_d^* (pressing).

The behaviour of porcelain stoneware bodies is also related to the MBI, which appears to give a useful compromise of those mineralogical and particle size features able to improve the powder flowability during pressing, despite it being measured on the clay and being related here to the properties of a body where this clay is just 50 wt.%. In particular, the higher the MBI, the denser the green tiles and the lower the elastic response, i.e. the post-pressing expansion (Table 3). Furthermore, for a better compactness of green tiles, it corresponds to a higher modulus of rupture. In all events, sedimentary clays and beneficiated kaolins behave in a clearly distinct way: the former, being much more plastic, are able to give suitably dense and resistant green tiles; the latter indicate possible restrictions in the use of kaolinite-rich clays in tilemaking, as they seem to be rather difficult to press.

3.4. Drying behaviour

The behaviour during the drying stage was evaluated by the Bigot curve (plus corresponding drying sensitivity indices) and by measuring drying shrinkage and dry modulus of rupture of slip cast and pressed specimens (Table 5).

All these parameters appear to be intercorrelated: for instance, the Barna index BI in an exponential way with the drying sensitivity ISE (Fig. 6a) or linearly with the drying shrinkage (Fig. 6b). The sedimentary clays and the bentonitic sample BG present the highest drying sensitivity, while the primary kaolins and even some beneficiated kaolins exhibit no sensitivity to the drying process. Interestingly, for analogous values of BI (e.g. 0.4 in Fig. 6b) the beneficiated kaolins shrink less than the natural ones, in spite of the consistent enrichment in kaolinite and depletion in quartz. Once more, this behaviour might be explained by claiming a high-volume, face-to-face arrangement of kaolinite crystals, which is accomplished less and less efficiently when the filler concentration is increased.

The drying sensitivity increases linearly with the MBI (Fig. 7a). However, this correlation is just partially attributable to the finest grain fraction, as expected by the drying theory (Scherer, 1990), being limited basically to sedimentary clays and primary, untreated kaolins (Fig. 7b). In fact, it can be clearly seen that for the same drying sensitivity (e.g. BI ~ 0.4) there are very different amounts of colloidal particles (i.e. <0.3 μ m) in beneficiated kaolins.

Hence, in the overall picture, the occurrence of expandable clay minerals – markedly increasing the drying sensitivity (Fig. 7c) – may be balanced by an opposite

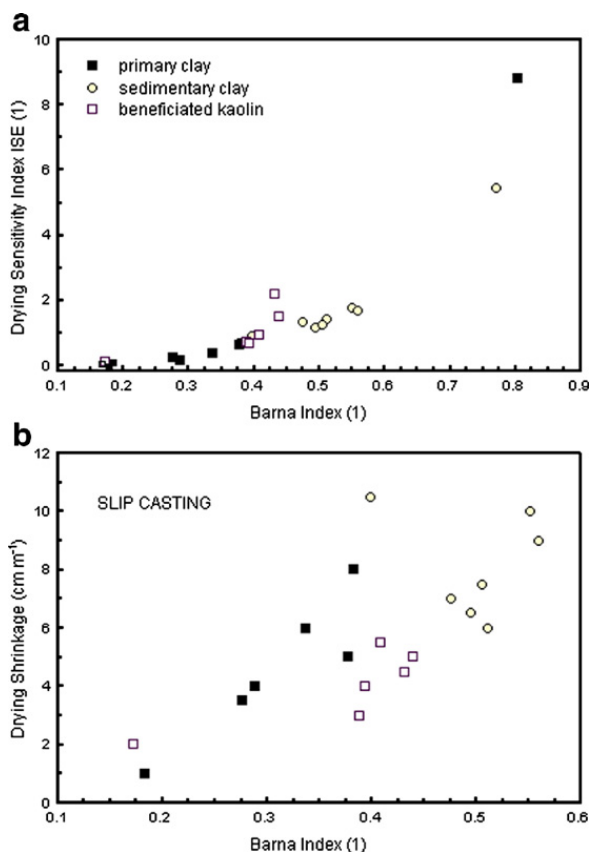


Fig. 6. Drying behaviour of kaolins and clays: Barna Index vs (a) drying sensitivity and (b) drying shrinkage.

effect played by kaolinite (and halloysite) which seem to reduce the Barna index (Fig. 7d); in any case, this trend might be apparent, being simultaneously affected by both expandable clay minerals and particle size distribution (Blanchart, 1996; Dondi et al., 1998).

Slip cast products behave with a complex dependence on mineralogy and granulometry: the kaolin beneficiation process, for instance, did not induce any increment of drying shrinkage in respect of primary rocks, even if it involved a significant kaolinite enrichment and an increased surface activity. To account for the large shrinkage values found with sedimentary clays, the presence of expandable clay minerals is more likely to be responsible than the particle size distribution, as sedimentary clays and beneficiated kaolins show similar fineness.

Again, the MBI is able to summarise in a single value the effects of several compositional parameters, so allowing a reasonable prediction of both drying shrinkage and dry modulus of rupture, given that the drying mechanisms are quite different in slip cast versus pressed bodies (Fig. 8). A clear trend of increasing drying shrinkage and dry flexural strength can be appreciated in progressing from primary kaolins through beneficiated kaolins to sedimentary clays.

3.5. Firing behaviour

The Patagonian clays behave rather refractorily: their softening temperature is often over 1400 °C and the densification begins in most cases over 1100 °C (Table 6). This is expected on the basis of their abundant content of kaolinite and quartz as well as their low amounts of the so-called “fluxing oxides” (i.e. $\text{Fe}_2\text{O}_3 + \text{MgO} + \text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O}$). In effect, both the sintering and the softening temperatures show an inverse, though quite indistinct, relationship with the fluxing content.

The viscous flow – characterising the whiteware sintering mechanism – depends on physical properties of the liquid phase formed at high temperature and on kinetic factors connected with particle size and surface activity (Zanelli et al., 2004). As far as the liquid phase is concerned, both its viscosity and surface tension are influenced by the occurrence of “sintering promoters”, which are mainly represented by those components summarised in the “fluxing” parameter (Matteucci et al., 2002; de’ Gennaro et al., 2003; Dondi et al., 2003b). Thus it is logical that these fluxing components show a direct correlation with firing shrinkage (Fig. 9a) and bulk density (Fig. 9b) or an inverse relation with water absorption (Figs. 9c and d), for both porcelain stoneware bodies and slip cast clays.

The effect of surface activity and particle size of clays on firing behaviour, exemplified by the MBI, is strongly affected by chemical factors, despite an influence which might be seen, for instance, in the MBI versus water absorption of both slip cast and pressed samples.

Interestingly, the sintering rate of porcelain stoneware bodies is faster with the most fusible clay FP as well as with some beneficiated kaolins (Table 6). Nevertheless, the sintering kinetics is surprisingly slower with fine-grained clays such as PU or FA.

4. Discussion

The study of the Patagonian kaolins and ball clays offers a unique chance to seek the interdependence of geological origin, clay mineralogy, microstructure and particle size distribution, beneficiation process, and ceramic behaviour. These raw materials can be grouped in six main “classes”, according to their genesis and compositional features (Dominguez et al., 2008) and these each exhibit their own technological behaviour and ceramic properties (Table 1). These are:

- A) The sedimentary clays of the *Lower Member of the Baqueró Fm*, related to the *Bajo Grande* basement (i.e. FP, PU and CZ), are chiefly characterised by a

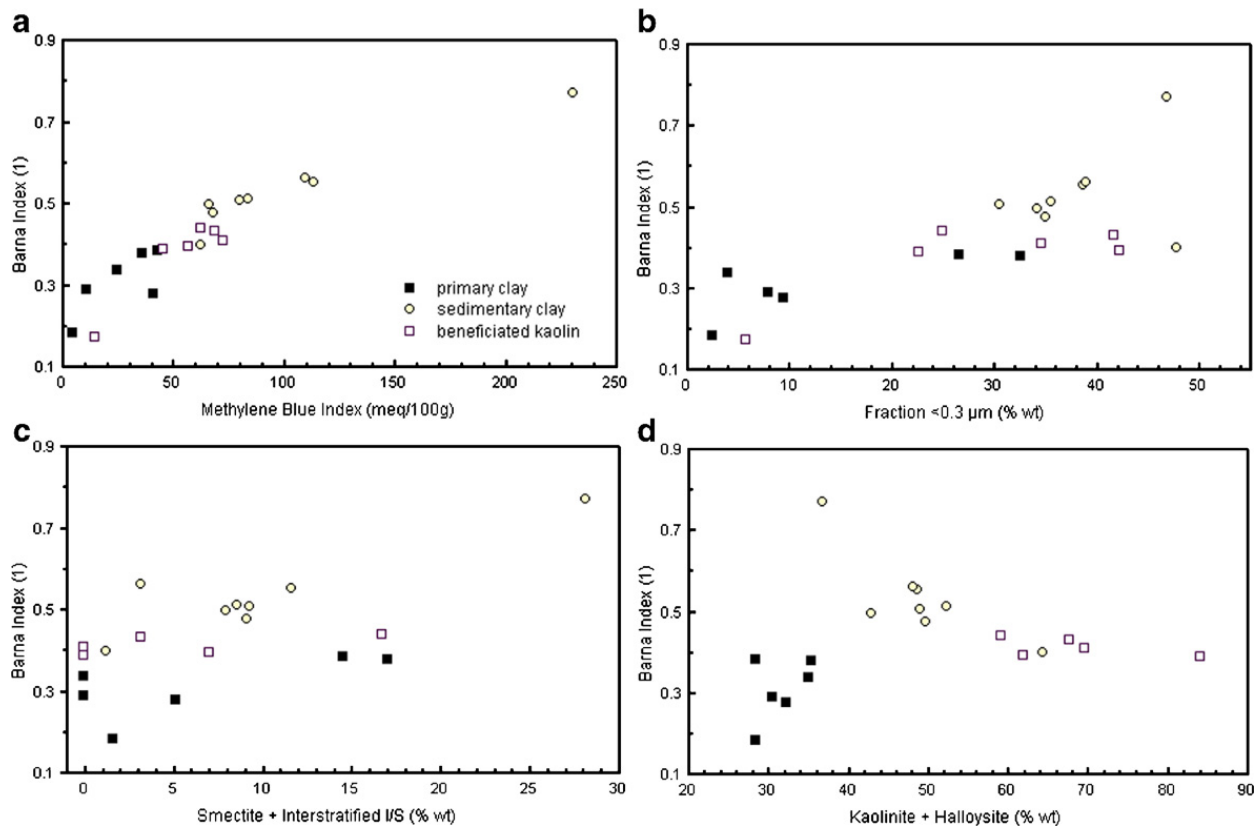


Fig. 7. Barna Index vs (a) Methylene Blue Index, (b) proportion of $<0.3 \mu\text{m}$ fraction, (c) proportion of expandable clay minerals and (d) proportion of kaolinite group minerals.

kaolinite+smectite assemblage, and a very fine-grained particle distribution and microstructure, which account for their very high surface activity. These features bestow excellent properties on clays, especially in terms of plasticity and powder flowability, resulting in the best values of bulk density and mechanical strength of greenware. Furthermore, these clays show a notable fusibility essentially due their relatively high concentrations of fluxing components, so permitting a lowering of the firing temperature. The substantial fluxing components present nevertheless imply a darker color after firing that may constitute an important limitation in whiteware applications. On the other hand, strong constraints occur in wet processing, where these clays cause a consistent increase of slip viscosity and thixotropy as well as a reduction of casting rate and an increment of drying shrinkage and sensitivity.

B) The sedimentary clays of the *Lower Member of the Baqueró Fm* related to the *Chon Aike* or *Marifil Fms* (i.e. TS, TZ, FA and CH) exhibit intermediate values of surface activity, a relatively coarse particle size distribution associated with a

quite fine-grained texture and a predominantly kaolinitic composition. The occurrence of interstratified I/S ensures rather high values of plasticity, without compromising rheological properties and casting behaviour, but inducing a certain drying sensitivity, even if clearly lower than that of the previous class of clays. The main limits arise during pressing (i.e. difficult compaction: low bulk density and green/dry mechanical strength) and firing, due to the greatest refractory behaviour, as expected from their very low amount of fluxing components.

C) The sedimentary clays of the *Upper Member of the Baqueró Fm* received a considerable pyroclastic supply, fostering the development of a fine-grained microstructure and granulometry of the sedimentary clays with a prevalently kaolinite (\pm halloysite) paragenesis with higher values for kaolinite structural order (sample CA). This unique mixture of characteristics allows improvement of the drying and firing kinetics, due to a low Barna index and refractoriness. In addition, the pressing behaviour and casting rate exhibit intermediate values, despite the low plasticity of this kind of clay, accounting for

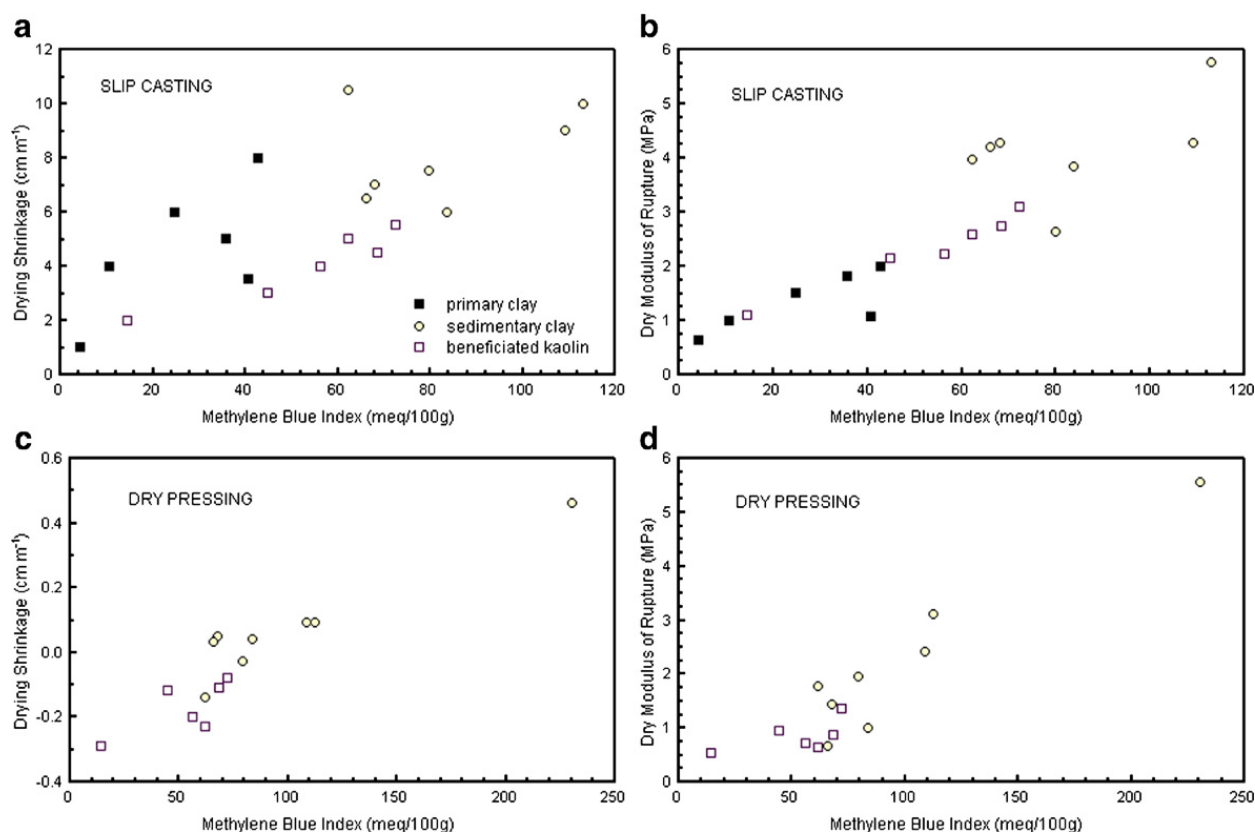


Fig. 8. Methylene Blue Index vs (a) drying shrinkage, (b) dry modulus of rupture of slip cast bodies, (c) drying shrinkage and (d) dry modulus of rupture of pressed bodies.

the low mechanical strength of unfired ware. Rheological properties represent the main problem: slip viscosity and thixotropy are very high, mostly connected with abundant soluble salts, supplied through the pyroclastic ash-fall.

- D) The *primary kaolins*, deriving from weathering of pyroclastic sequences of the Chon Aike and Marifil Fms (e.g. IL, MA, RF, RP, SR), are coarse-grained materials, characterised by a kaolinite+quartz±halloysite mineralogy and a very low surface activity, which makes them unsuitable for every ceramic application unless previously beneficiated by washing and settling.
- E) The *beneficiation of altered, to a large extent crystalline pyroclastics*, both coarse-grained (ILL) or fine-grained (MAL), resulted in a kaolinite+illite (±halloysite) paragenesis, fine texture and particle size distribution, and intermediate values of surface activity. These kaolins present the best rheological properties (the lowest slip viscosity and thixotropy) as well as the best slip casting and drying behaviour (the lowest suction time, drying shrinkage and sensitivity) together with a good fusibility and fast firing

kinetics. The principal limitation concerns the pressing stage, because of a small contribution towards the densification and strengthening of the greenware.

- F) The *treatment of kaolinized, mainly vitreous pyroclastics* produced a dominant halloysite (+kaolinite) association and a rather fine-grained texture and particle size distribution together with intermediate values of surface activity; in addition, soluble salts can attain significant concentrations. These features ensure a good drying and casting behaviour, but bring about some strict limits in terms of rheology and refractoriness. Slip viscosity and thixotropy are in some cases too high, due to both soluble salts and fibrous halloysite; this latter also interferes with the pressing process, causing low bulk density and mechanical strength of greenware (McLarin and Perera, 1986). The low amount of fluxing oxides justifies the high softening temperatures and water absorption values of these kaolins.

The technological properties of the Patagonian kaolins and sedimentary clays are to a large extent analogous

Table 6

Firing behaviour of the Patagonian kaolins, clays and beneficiated products: firing shrinkage (S_f), water absorption (E), fired modulus of rupture (σ_f), fired bulk density (ρ_f)

| Sample | Slip cast clay 1250 °C | | | Pressed, fired 1200 °C | | | Pressed, fired 1250 °C | | | Hot-stage microscopy | | |
|--------|------------------------|-------|------------|------------------------|-------|--------------------|------------------------|-------|--------------------|----------------------|-------------------|-------------------|
| | S_f | E | σ_f | S_f^* | E^* | ρ_f^* | S_f^* | E^* | ρ_f^* | SR | T_{sint} | T_{soft} |
| | cm m ⁻¹ | wt. % | MPa | cm m ⁻¹ | wt. % | g cm ⁻³ | cm m ⁻¹ | wt. % | g cm ⁻³ | mm s ⁻¹ | °C | °C |
| CZ | 4.0 | 10.2 | 4.3 | 4.1 | 4.4 | 2.155 | 5.4 | 0.2 | 2.301 | 0.18 | 1140 | 1490 |
| PU | 5.0 | 9.5 | 5.8 | 4.4 | 3.7 | 2.198 | 5.5 | 0.2 | 2.301 | 0.10 | 1090 | 1480 |
| FP | n.d. | n.d. | n.d. | 5.5 | 0.5 | 2.326 | n.d. | n.d. | n.d. | 0.42 | 925 | 1290 |
| BG | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 890 | 1220 |
| CA | 9.5 | 7.5 | 4.0 | 5.2 | 4.6 | 2.174 | 6.9 | 1.0 | 2.323 | 0.22 | 1115 | 1315 |
| FA | 3.5 | 12.5 | 4.3 | 3.8 | 7.3 | 2.030 | 6.7 | 0.9 | 2.267 | 0.13 | 1100 | 1535 |
| TZ | 1.5 | 13.6 | 4.2 | 4.1 | 8.8 | 1.952 | 8.9 | 0.4 | 2.318 | 0.24 | 1170 | 1540 |
| TS | 4.0 | 14.1 | 3.8 | 3.8 | 7.7 | 2.020 | 7.3 | 1.0 | 2.302 | 0.19 | 1115 | 1545 |
| PR | 2.0 | 39.5 | 0.6 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 1310 | 1400 |
| CH | 5.5 | 14.0 | 2.6 | 4.4 | 4.5 | 2.165 | 6.0 | 0.2 | 2.304 | 0.16 | 1110 | 1390 |
| IL | 9.0 | 9.0 | 2.0 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 1325 | 1550 |
| RF | 2.5 | 29.5 | 1.5 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 1275 | 1335 |
| RP | 6.0 | 15.4 | 1.0 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 1195 | 1265 |
| MA | 6.0 | 13.4 | 1.8 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 1140 | 1530 |
| SR | 7.0 | 23.8 | 1.1 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 1185 | 1435 |
| PRL | 3.0 | 40.4 | 1.1 | 4.1 | 12.2 | 1.890 | 9.2 | 2.2 | 2.291 | 0.37 | 1225 | 1600 |
| ILL | 5.5 | 11.2 | 2.7 | 4.8 | 6.3 | 2.071 | 8.1 | 0.2 | 2.350 | 0.27 | 1140 | 1440 |
| RFL | 6.0 | 16.8 | 3.1 | 6.1 | 6.1 | 2.114 | 9.0 | 0.3 | 2.357 | 0.34 | 1170 | 1550 |
| RPL | 8.0 | 13.1 | 2.1 | 6.5 | 5.3 | 2.158 | 9.3 | 0.1 | 2.389 | 0.21 | 1150 | 1520 |
| MAL | 7.0 | 4.2 | 2.2 | 5.0 | 6.1 | 2.105 | 8.3 | 0.2 | 2.361 | 0.23 | 1080 | 1500 |
| SRL | 5.5 | 15.4 | 2.6 | 5.5 | 7.0 | 2.077 | 8.7 | 0.5 | 2.344 | 0.33 | 1125 | 1525 |

Hot-stage microscopy: isothermal sintering rate at 1200 °C of porcelain stoneware bodies (SR); sintering temperature (T_{sint}) and softening temperature (T_{soft}) of clay materials. n.d. = not determined.

to those of European ball clays, especially those utilised in porcelain stoneware production (Dondi et al., 2003a). In essence, by contrasting plasticity versus surface activity (Fig. 10) it can be appreciated that:

- sedimentary clays (e.g. classes B and C) correspond to widely used ball clays, such as those from Westerwald (Germany);
- clays related to the Bajo Grande basement (i.e. class A) have a rather wide range of plastic properties, which are analogous to those of highly plastic ball clays and blends (e.g. Ukrainian);
- primary kaolins (class D) fall outside the field of suitable plastic behaviour;
- beneficiated kaolins (classes E and F, not present in Fig. 10) have performances equivalent to intermediate to low plasticity ball clays.

A multivariate statistical analysis, involving the extraction of principal components (Cooley and Lohnes, 1971), confirms to a large extent the relationships between kaolin composition and ceramic behaviour, as outlined in the previous section (Fig. 11). In particular, Methylene Blue index exhibits a strict correlation with

rhological properties (e.g. Atterberg plastic index, slip viscosity and thixotropy) and processing variables (e.g. positive with Barna index, drying shrinkage, green and dry strength; negative with pressing expansion, water absorption, sintering temperature). At the same time, MBI is directly related with specific surface area, finer particle fraction, smectite and interstratified I/S, and indirectly with kaolinite structural order (HI). Notwithstanding that kaolinite+halloysite and quartz are the most abundant components of kaolins, their correlations with processing parameters are not highly significant (apart from firing shrinkage and Linseis resistance-to-shear).

5. Conclusions

The Patagonian clay deposits exhibit a complicated picture of geological, compositional and technological characteristics, which are clearly interdependent, so affecting the entire industrial processing from clay prospecting to selective mining and beneficiation, up to ceramic applications.

The clay behaviour during body preparation, shaping, drying and firing is mainly affected by the

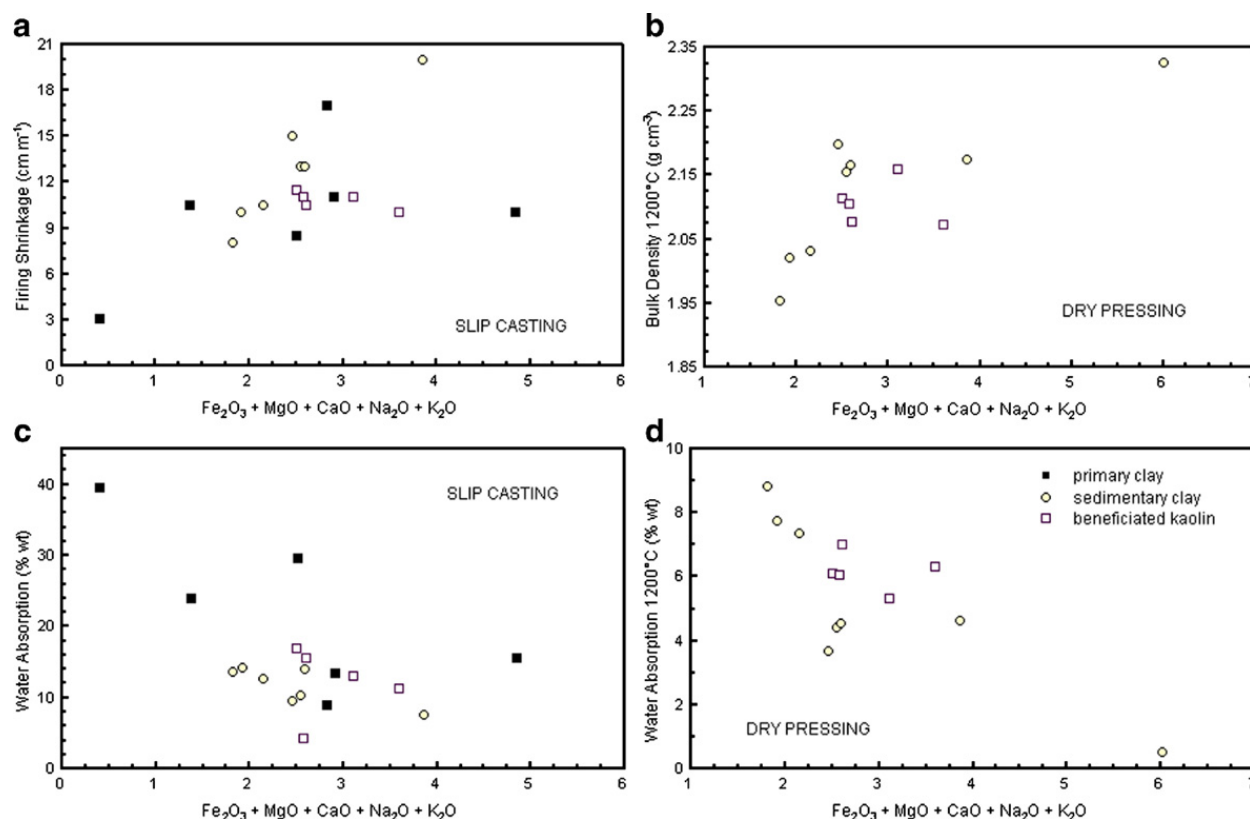


Fig. 9. Firing behaviour of kaolins and clays (slip casting) or porcelain stoneware bodies (dry pressing): fluxing oxides vs (a) firing shrinkage, (b) bulk density and (c and d) water absorption.

occurrence of expandable clay minerals, amount of kaolinite/halloysite, particle size distribution and surface activity. The rheological properties of clay slips are influenced by soluble salts and tubular halloysite, while sintering kinetics is accelerated by fluxing components (e.g. iron oxy-hydroxides, feldspars, illite). A great deal of technological parameters seem to be reasonably predictable by taking into consideration the surface activity of clay materials and especially the MBI, which appears to be the most reliable, simple and economic

method to predict and control the ceramic response of kaolins and ball clays.

The properties of ball clays are clearly influenced by the provenance of sediments and proximity to source areas, which govern kaolinite-to-quartz ratio, particle size distribution, and occurrence of expandable clay minerals or halloysite. In contrast, the characteristics of primary kaolins are mainly affected by the different texture and composition of parent rocks, which control kaolinite-to-halloysite ratio, structural order of kandite minerals, and illite or interstratified I/S formation.

All these features define some broad classes of raw materials, with technological performances comparable to kaolins and ball clays currently used in high-quality ceramic applications:

- Highly plastic ball clays, recovered from low energy sedimentary basins (particularly close to a smectite-bearing basement), are increasingly utilised to improve the properties of unfired tiles.
- Intermediate to low plasticity ball clays, settled in higher energy sedimentary basins supplied essentially by kaolinized source areas, are suitable for both whitewares and tilemaking.

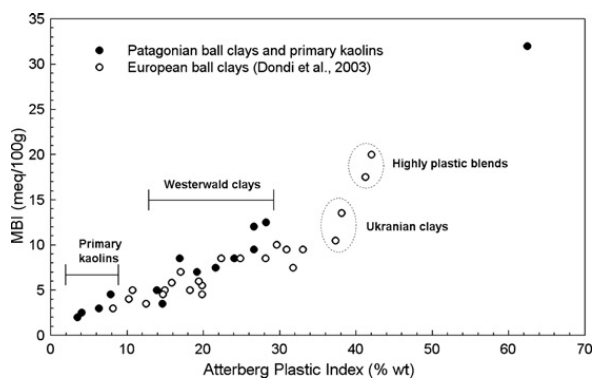


Fig. 10. Plasticity vs surface activity of the Patagonian clays and kaolins; comparison with European ball clays (Dondi et al., 2003a).

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