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1 **The Effect of Kaolin properties on their Behaviour** 2 **in Ceramic Processing as Illustrated by a Range of** 3 **Kaolins from the Santa Cruz and Chubut** 4 **Provinces, Patagonia (Argentina)**

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18 **Abstract**

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

33
34 **Key-words:** ball clay, ceramic properties, drying behaviour, kaolin, methylene blue index, plasticity,
35 slip rheology.

38 **1. Introduction**

39
40 The use of kaolin and ball clay has been growing in recent years as a consequence of
41 the increasing ceramic output worldwide. Besides, the ceramic industry has undergone a
42 considerable technological innovation in recent decades, fostering the development of new
43 types of ceramic products and their further diversification, (Dondi, 2003; Fiederling-

44Kapteinat, 2005). Kaolins and ball clays are now utilised not only in classical whiteware
45production, but even more widely in ceramic tile manufacturing, especially for new product
46types, such as porcelain stoneware or white *monoporosa* tiles (Lombardo, 1996; Dondi et
47al., 2001a; Fiederling-Kapteinat, 2005).

48 These new applications are imposing technological requirements that are different with
49respect to the conventional use of kaolin and ball clay in slip cast, extruded or solid
50moulded products, such as tableware, sanitaryware and alumino-silicate refractories.
51Furthermore, the latest innovation in tilemaking (e.g. large-size tiles, double pressing,
52pressing without mould, cutting of green tiles) is particularly stressing properties like
53plasticity, powder flowability, ability to densify during dry pressing and to toughen green
54tiles (Dondi, 2003). Thus a new class of clay materials – able to couple high plasticity and
55suitable rheological behaviour with the usual requirements for ball clays – is now
56encountering a growing commercial success worldwide (Dondi et al., 2003a; Fiederling-
57Kapteinat, 2005).

58 However, the desired set of technological properties appears to present difficulties for
59mineral processing, even by selective clay exploitation and blending, because of its
60complex dependence on mineralogy, particle size distribution and surface activity of clays.
61Frequently, these characteristics are not adequately monitored by routine analyses with
62conventional ceramic procedures (Worrall, 1975; Powell, 1996). In fact, it is often a hard
63task to infer backwards the whole chain interconnecting ceramic behaviour, clay
64composition, mining processing and geological features. From this viewpoint, the
65Patagonian kaolins offer an exceptional opportunity for investigating the interdependence
66of these factors, as a wide set of : i) origin of deposits (primary and sedimentary clays), ii)
67mineral processing (i.e. washing and settling of primary kaolin), iii) mineralogical
68composition and particle size distribution, and iv) ceramic properties is available (Table 1
69and Dominguez et al., 2007). In addition, these raw materials are utilised by two distinct
70end-users: a) the whiteware industry (i.e. sanitaryware and tableware) and b) ceramic tile
71manufacturers. These sectors are well differentiated from each other for their production
72cycles and the processes which the clays undergo (e.g. wet dispersion, filterpressing, slip
73casting, slow drying and firing for whitewares; wet grinding, spray-drying, powder pressing,
74fast drying and firing for ceramic tiles). As a consequence, the technological requirements
75that kaolins and ball clays have to fulfil are also different in whiteware and tilemaking
76(Maxwell and Dinger, 1992; Wilson, 1998; Dondi, 2003; Capoğlu and Kutbay, 2002).

77 Therefore, this paper is aimed at assessing how mineralogy, particle size distribution
78and surface activity affect the technological behaviour of kaolins and sedimentary clays in
79sanitaryware and porcelain stoneware production.

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82. **Materials and Methods**

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84 Twenty-one samples were taken into consideration:

85– 7 primary deposits (6 kaolins and 1 bentonite),

86– 8 sedimentary deposits (so-called *ball clays*),

87– 6 beneficiated products (the primary kaolins after washing and settling).

88 For sampling criteria and procedures as well as methodologies followed in mineralogical,
89 geochemical and granulometric analyses, the reader is addressed to the first part of this
90 study (Dominguez et al., 2007).

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

94– *the tilemaking cycle*, involving a mixture of clay and soda-potash feldspar (50:50%wt),
95 wet grinding (planetary mill, 20 min), slip drying and powder deagglomeration,
96 humidification (7-8%wt) and pelletizing, uniaxial pressing of 110·55·5 mm³ tiles (40
97 MPa), drying in an oven (100°C) and firing in an electrical roller kiln (maximum
98 temperatures 1200 and 1250°C, 51 min cold-to-cold);

99– *the sanitaryware cycle*, involving clay dispersion and filterpressing, slip preparation
100 (100% clay plus a clay:quartz mixture 50:50%wt) and casting in gypsum moulds
101 (ambient pressure) of 13·26·220 mm³ tiles, drying in an oven (100°C) and firing in an
102 electrical chamber kiln (maximum temperature 1250°C, 3 h cold-to-cold).

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

109– *Atterberg consistency limits*, thus plastic limit W_P , liquid limit W_L and plastic index
110 $I_P = W_L - W_P$, with a relative standard deviation of data $C < 5\%$ (Atterberg, 1911; UNI
111 10014, 1964);

112– *Pfefferkorn index* PI with about 5% relative error (Pfefferkorn, 1924; Van der Velden,
113 1979);

114– *tensional strength and resistance to shear* (Linseis, 1951; Singer and Singer, 1963)
115 with a Netzsch 405 apparatus ($C \sim 5\%$).

116 The surface activity was evaluated by the *methylene blue index* (MBI, Hang and
117 Brindley, 1970; Avena et al., 2001) measured on both buffered (pH 4.5, ASTM C 837,
118 experimental uncertainty 0.25 meq/100g) and unbuffered suspensions (natural pH,
119 experimental uncertainty 0.5 meq/100g).

120 The main ceramic applications of kaolin and ball clay require their dispersion in water
121 and/or wet grinding, making a suitable rheological behaviour a critical requirement for clay
122 raw materials (Worrall, 1975; Maxwell and Dinger, 1992; Dondi, 2003). Rheological
123 properties were determined with both a Brookfield viscosimeter (Steffe, 1992) and a
124 cylinder for gravity flow (Singer and Singer, 1963). Brookfield *viscosity* was measured at
125 20 rpm with spindle #1 (<500 cps) or #3 (>500 cps) on the as-prepared slip (VB0) and
126 after 1, 5 and 10 min (VB1, VB5 and VB10 respectively) with an experimental relative error
127 around 5%. The slip density was set as close as possible to $\rho_s = 1.60 \text{ g} \cdot \text{cm}^{-3}$, but in 8
128 cases we had to lower the solid load, in order to shift the viscosity into the operative
129 window of our equipment. The time dependence (*thixotropy*) was expressed as $T_B =$
130 $(VB10 - VB0) \cdot VB0^{-1} \cdot 100$. The *resistance to shear* was estimated as time of flow of the as-
131 prepared slip (τ_0) and after 60 min (τ_{60}) with an experimental error of about 1 s.
132 Furthermore, the *electrolyte concentration* in the slip was determined by both electrical
133 conductivity (error $\sim 10 \mu\text{S}$) and soluble sulphate content (ASTM C 867, error $\sim 5 \text{ mg} \cdot \text{kg}^{-1}$).

134 Shaping behaviour was appraised by measuring:

135 – *slip density* by pycnometry (ρ_s , error 0.01 g·cm⁻³), *casting rate* as weight of the cast
136 cake after 15 min settling (M_c , error 1 g) and *suction time* as the time necessary to
137 make the slip surface in the mould dull (t_s , error 2 s) for slip casting;

138 – *green bulk density* (ρ_g , geometric method, error 0.002 g·cm⁻³), *post-pressing*
139 *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
140 mould respectively, $C < 5\%$) and *green modulus of rupture* (σ_g , ISO 10545-4, $C \sim 5\%$)
141 for pressing.

142 Drying behaviour was investigated by measuring:

143– the *Bigot curve* and *drying shrinkage* (S_d , ASTM C 326, experimental error 0.5 cm·m⁻¹)
144 on slip cast clays;

145– *drying shrinkage/expansion* (S_d^* , experimental error 0.01 cm·m⁻¹) on pressed bodies;

146– *dry modulus of rupture* (ASTM C 689, $C \sim 5\%$) of ceramic bodies on both slip cast (σ_d)
147 and pressed specimens (σ_d^*).

148 The Bigot curve was determined (Adamel barelattograph, ambient temperature and RH
149 40-60%) on two plastic moulded prisms (40·10·10 mm³) measuring working moisture
150 (W_B , $C < 2\%$), drying shrinkage (S_B , error 0.1 cm·m⁻¹) and weight loss with shrinkage and
151 without shrinkage (W_1 and W_2 respectively, $C \sim 2\%$). Two *drying sensitivity indices* were
152 calculated: $BI = W_1 \cdot (W_1 + W_2)^{-1}$ (Barna, 1967; Ginés et al., 1997) and $ISE = W_1 \cdot S_B \cdot 0.01$
153 (von Chiari, 1986; Dondi et al., 1998).

154 Firing behaviour was appraised by determining:

155– *fusibility* of clay materials by hot-stage microscopy (Expert System Misura, 10°C·min⁻¹
156 up to 1600°C) inferring the characteristic temperatures T_{sint} (beginning of densification)
157 and T_{soft} (softening) through morphological changes occurring to a cylindrical specimen
158 (3 mm height and 2 mm diameter) with an uncertainty of 5-10°C (Dondi et al., 2001b);

159– *firing shrinkage* (S_f , ASTM C 326, error 0.5 cm·m⁻¹) and *water absorption* (E , ASTM C
160 373, $C \sim 2\%$) on slip cast clays:

161– *firing shrinkage* (S_f^* , ASTM C 326, error 0.1 cm·m⁻¹), *water absorption* (E^* , ASTM C
162 373, error 0.1%wt), *bulk density* (ρ_f^* , ASTM C 373, error 0.002 g·cm⁻³) and *sintering*
163 *rate* (hot-stage microscopy, isothermal firing at 1200°C, error 0.01 mm·s⁻¹) on pressed
164 porcelain stoneware bodies.

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166

1673. Results

168

1693.1. Plasticity

170 The plasticity of a clay material depends on its surface activity, particle size distribution
171 and mineralogical composition (Fitzjohn and Worrall, 1980; Ginés et al., 1997; Raimondo
172 et al., 2003). From this viewpoint, the MBI represents a useful “mean indicator” of all the
173 above-mentioned features, presenting a linear positive correlation with specific surface
174 area (Fig. 1a) and a non-linear, direct relationship with the finer particle fraction, implying a
175 slower increase of the MBI with the amount of particles $< 2\mu\text{m}$ for kaolins and a faster one
176 for sedimentary clays (Fig. 1b). These differing slopes are connected with the
177 mineralogical composition: the increased amount of kaolinite (and halloysite) consequent

178to beneficiation of kaolins justifies the slower trend (Fig. 1c) while the varying amount of
179expandable clay minerals explains the trend of sedimentary clays (Fig. 1d).

180 The various plasticity indices gave on the whole comparable results, though with a
181clearly different data dispersion, that highlight the increasingly plastic behaviour of the
182series: primary kaolins < beneficiated kaolins < sedimentary clays. In particular, the
183Atterberg plastic index appears to be strictly related to the MBI (Fig. 2a) while the
184correspondent relations become less and less statistically significant moving to the
185Pfefferkorn index (Fig. 2b) or the Linseis resistance to shear (Fig. 2c) and tensional
186strength (Fig. 2d). These results confirm to a large extent the observations of Fitzjohn and
187Worrall (1980), Amarante and Boutros (1981), Ginés et al. (1997), Baran et al. (2001),
188Raimondo et al. (2001) and Schmitz et al. (2004).

189 There was a good correspondence between the Pfefferkorn index and the Atterberg
190plastic limit (Fig. 3a) as expected, because both parameters account for the capacity of a
191clay material to retain water prior behaving plastically (Van der Velden, 1979; Baran et al.
1922001). These values seem to be chiefly linked to the amount of kaolinite, but two samples
193(BG and FP) that are outliers contain the most smectite (Fig. 3b).

194

1953.2. *Slip rheological properties*

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

197– low viscosity and low resistance to shear measured on most primary and beneficiated
198 kaolins, due essentially to their relatively coarse-grained particle distribution, low
199 concentration of electrolytes and lack of expandable clay minerals;

200– intermediate values of both viscosity and shear resistance, which are mutually
201 correlated in most sedimentary clays, justified by different amounts of soluble salts and
202 expandable clay minerals in fine-grained raw materials;

203– high viscosity linked to large amounts of smectite (samples BG and FP) or soluble salts
204 and/or halloysite (samples CA, RP and RF) that do not seem to increase the resistance
205 to shear;

206– low viscosity of samples PRL and SRL, which, however, exhibited a strong resistance
207 to shear that might be explained by the occurrence of noteworthy amounts of halloysite
208 fibers (Dominguez et al., 2007).

209 Overall, a time-dependence of both viscosity and resistance to shear can be seen for
210all the clay types. Brookfield measurements suggested there is a direct relationship
211between viscosity and thixotropy, though it is significant only for the sedimentary clays,
212being to a large extent dependent on the amount of colloidal fraction.

213 In most cases, the rheological properties described above are clearly affected by the
214concentration of electrolytes in the slip, measured as electrical conductivity, which are
215mainly constituted by soluble sulphates (Fig. 4a). The dependence of viscosity on the
216electrical conductivity, however, follows three parallel trends, one for each type of raw
217materials (Fig. 4b) that are even more appreciable in the case of thixotropy (Fig. 4c). This
218result implies a substantial influence of the clay surface activity that becomes conspicuous
219when the MBI is contrasted with viscosity and thixotropy, except for samples CA, RF and
220RP because of their high content of soluble salts.

221 A thoroughful assessment of slip viscosity and its time-dependence is in progress

222

2233.3. *Shaping behaviour*

224 The main technological parameters describing how clays and clay bodies (i.e. 50% clay
225 and 50% filler) behave during forming are summarised in Table 4. The clay behaviour
226 during slip casting seems to be mostly dependent on surface activity, as both the casting
227 rate, expressed as weight of the cast cake, and the slip suction time are well correlated
228 with the MBI (Fig. 5a and 5b). Two samples (RF and RP) cannot accomplish slip suction,
229 chiefly because of their high viscosity and large amount of soluble salts. As expected, the
230 casting rate shows an inverse relationship with the colloidal particle fraction ($<0.3\mu\text{m}$) and
231 the amount of expandable clay minerals, even if this trend seems to be limited to primary
232 kaolins. Interesting enough, once primary kaolins are omitted, a certain dependence of the
233 casting rate on kaolinite percent is revealed: the larger the amount of kaolinite+halloysite,
234 the faster the slip casting (Fig. 5c). This is probably connected with the tendency of
235 kaolinite platelets to arrange face-to-face, as is often observed in the sedimentary clay
236 deposits (Dominguez et al., 2007).

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

248

249 3.4. *Drying behaviour*

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

253 All these parameters appear to be intercorrelated: for instance, the Barna index BI in an
254 exponential way with the drying sensitivity ISE (Fig. 6a) or linearly with the drying
255 shrinkage (Fig. 6b). The sedimentary clays and the bentonitic sample BG present the
256 highest drying sensitivity, while the primary kaolins and even some beneficiated kaolins
257 exhibit no sensitivity to the drying process. Interestingly, for analogous values of BI (e.g.
258 0.4 in Fig. 6b) the beneficiated kaolins shrink less than the natural ones, in spite of the
259 consistent enrichment in kaolinite and depletion in quartz. Once more, this behaviour might
260 be explained by claiming a high-volume, face-to-face arrangement of kaolinite crystals,
261 which is accomplished less and less efficiently when the filler concentration is increased.

262 The drying sensitivity increases linearly with the MBI (Fig. 7a). However, this correlation
263 is just partially attributable to the finest grain fraction, as expected by the drying theory
264 (Scherer, 1990), being limited basically to sedimentary clays and primary, untreated
265 kaolins (Fig. 7b). In fact, it can be clearly seen that for the same drying sensitivity (e.g. BI
266 ~ 0.4) there are very different amounts of colloidal particles (i.e. $<0.3\mu\text{m}$) in beneficiated
267 kaolins.

268 Hence, in the overall picture, the occurrence of expandable clay minerals – markedly
269 increasing the drying sensitivity (Fig. 7c) – may be balanced by an opposite effect played
270 by kaolinite (and halloysite) which seem to reduce the Barna index (Fig. 7d); in any case,

271 this trend might be apparent, being simultaneously affected by both expandable clay
272 minerals and particle size distribution (Blanchart, 1996; Dondi et al., 1998).

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

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

286

287 3.5. Firing behaviour

288

289 The Patagonian clays behave rather refractorily: their softening temperature is often
290 over 1400°C and the densification begins in most cases over 1100°C (Table 6). This is
291 expected on the basis of their abundant content of kaolinite and quartz as well as their low
292 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,
293 both the sintering and the softening temperatures show an inverse, though quite indistinct,
294 relationship with the fluxing content.

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

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

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

312

313 4. Discussion

314

315 The study of the Patagonian kaolins and ball clays offers a unique chance to seek the
316 interdependence of geological origin, clay mineralogy, microstructure and particle size

317distribution, beneficiation process, and ceramic behaviour. These raw materials can be
318grouped in six main “classes”, according to their genesis and compositional features
319(Dominguez et al., 2007) and these each exhibit their own technological behaviour and
320ceramic properties (Table 1). These are:

321A) The sedimentary clays of the *Lower Member of the Baqueró Fm, related to the Bajo*
322*Grande basement* (i.e. FP, PU and CZ), are chiefly characterised by a kaolinite+smectite
323assemblage, very fine-grained particle distribution and microstructure, which account for
324their very high surface activity. These features bestow excellent properties on clays,
325especially in terms of plasticity and powder flowability, resulting in the best values of bulk
326density and mechanical strength of greenware. Furthermore, these clays show a notable
327fusibility essentially due their relatively high concentrations of fluxing components, so
328permitting a lowering of the firing temperature. The substantial fluxing components present
329nevertheless imply a darker color after firing that may constitute an important limitation in
330whiteware applications. On the other hand, strong constraints occur in wet processing,
331where these clays cause a consistent increase of slip viscosity and thixotropy as well as a
332reduction of casting rate and an increment of drying shrinkage and sensitivity.

333B) The sedimentary clays of the *Lower Member of the Baqueró Fm related to the Chon*
334*Aike or Marifil Fms* (i.e. TS, TZ, FA and CH) exhibit intermediate values of surface activity,
335a relatively coarse particle size distribution associated with a quite fine-grained texture and
336a predominantly kaolinitic composition. The occurrence of interstratified I/S ensures rather
337high values of plasticity, without compromising rheological properties and casting
338behaviour, but inducing a certain drying sensitivity, even if clearly lower than that of the
339previous class of clays. The main limits arise during pressing (i.e. difficult compaction: low
340bulk density and green/dry mechanical strength) and firing, due to the greatest refractory
341behaviour, as expected from their very low amount of fluxing components.

342C) The sedimentary clays of the *Upper Member of the Baqueró Fm* received a
343considerable pyroclastic supply, fostering the development of a fine-grained microstructure
344and granulometry of the sedimentary clays with a prevalently kaolinite (\pm halloysite)
345paragenesis with higher values for kaolinite structural order (sample CA). This unique
346mixture of characteristics allows improvement of the drying and firing kinetics, due to a low
347Barna index and refractoriness. In addition, the pressing behaviour and casting rate exhibit
348intermediate values, despite the low plasticity of this kind of clay, accounting for the low
349mechanical strength of unfired ware. Rheological properties represent the main problem:
350slip viscosity and thixotropy are very high, mostly connected with abundant soluble salts,
351supplied through the pyroclastic ash-fall.

352D) The *primary kaolins*, deriving from weathering of pyroclastic sequences of the Chon
353Aike and Marifil Fms (e.g. IL, MA, RF, RP, SR), are coarse-grained materials,
354characterised by a kaolinite+quartz \pm halloysite mineralogy and a very low surface activity,
355which makes them unsuitable for every ceramic application unless previously beneficiated
356by washing and settling.

357E) The *beneficiation of altered, to a large extent crystalline pyroclastics*, both coarse-
358grained (ILL) or fine-grained (MAL), resulted in a kaolinite+illite (\pm halloysite) paragenesis,
359fine texture and particle size distribution, and intermediate values of surface activity. These
360kaolins present the best rheological properties (the lowest slip viscosity and thixotropy) as
361well as the best slip casting and drying behaviour (the lowest suction time, drying
362shrinkage and sensitivity) together with a good fusibility and fast firing kinetics. The

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

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

374 The technological properties of the Patagonian kaolins and sedimentary clays are to a
375 large extent analogous to those of European ball clays, especially those utilised in
376 porcelain stoneware production (Dondi et al., 2003a). In essence, by contrasting plasticity
377 versus surface activity (Fig. 10) it can be appreciated that:

378– sedimentary clays (e.g. classes B and C) correspond to widely used ball clays, such as
379 those from Westerwald (Germany);

380– clays related to the Bajo Grande basement (i.e. class A) have a rather wide range of
381 plastic properties, which are analogous to those of highly plastic ball clays and blends
382 (e.g. Ukrainian);

383– primary kaolins (class D) fall outside the field of suitable plastic behaviour;

384– beneficiated kaolins (classes E and F, not present in Fig. 10) have performances
385 equivalent to intermediate to low plasticity ball clays.

386 A multivariate statistical analysis, involving the extraction of principal components
387 (Cooley and Lohnes, 1971), confirms to a large extent the relationships between kaolin
388 composition and ceramic behaviour, as outlined in the previous chapter (Fig. 11). In
389 particular, Methylene Blue index exhibits a strict correlation with rheological properties
390 (e.g. Atterberg plastic index, slip viscosity and thixotropy) and processing variables (e.g.
391 positive with Barna index, drying shrinkage, green and dry strength; negative with pressing
392 expansion, water absorption, sintering temperature). At the same time, MBI is directly
393 related with specific surface area, finer particle fraction, smectite and interstratified I/S, and
394 indirectly with kaolinite structural order (HI). Notwithstanding that kaolinite+halloysite and
395 quartz are the most abundant components of kaolins, their correlations with processing
396 parameters are not highly significant (apart from firing shrinkage and Linseis resistance-to-
397 shear).

398

399 5. Conclusions

400

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

405 The clay behaviour during body preparation, shaping, drying and firing is mainly
406 affected by the occurrence of expandable clay minerals, amount of kaolinite/halloysite,
407 particle size distribution and surface activity. The rheological properties of clay slips are
408 influenced by soluble salts and tubular halloysite, while sintering kinetics is accelerated by

409 fluxing components (e.g. iron oxy-hydroxides, feldspars, illite). A great deal of
410 technological parameters seem to be reasonably predictable by taking into consideration
411 the surface activity of clay materials and especially the MBI, which appears to be the most
412 reliable, simple and economic method to predict and control the ceramic response of
413 kaolins and ball clays.

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

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

423– Highly plastic ball clays, recovered from low energy sedimentary basins (particularly
424 close to a smectite-bearing basement), are increasingly utilised to improve the
425 properties of unfired tiles.

426– Intermediate to low plasticity ball clays, settled in higher energy sedimentary basins
427 supplied essentially by kaolinized source areas, are suitable for both whitewares and
428 tilemaking.

429– Primary kaolinization of porous and highly crystalline pyroclastics led to kaolinite+illite
430 paragenesis well suited for slip casting and especially to enhance rheological
431 performances.

432– Weathering of mainly vitreous pyroclastic rocks produced predominantly halloysitic
433 kaolins, which are utilisable in slip cast products, such as sanitaryware.

434

435

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437

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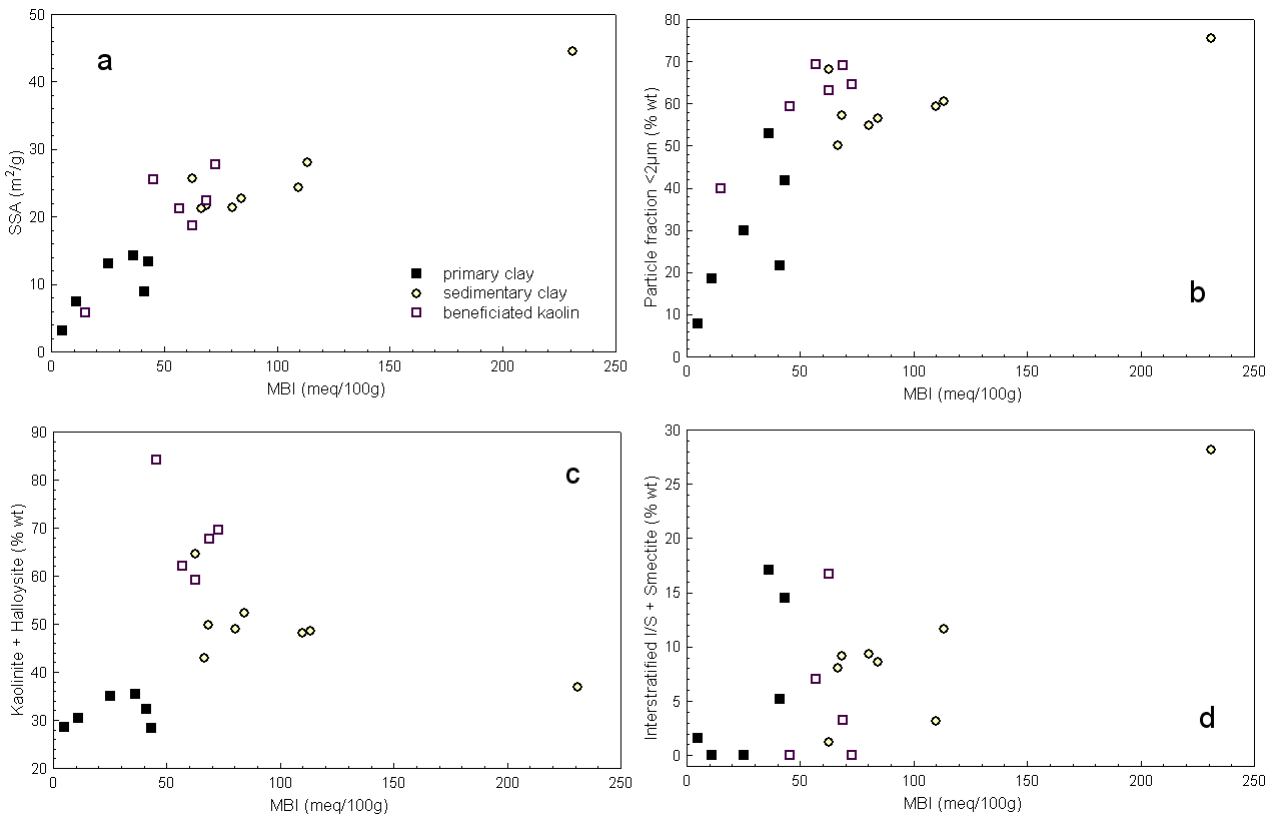
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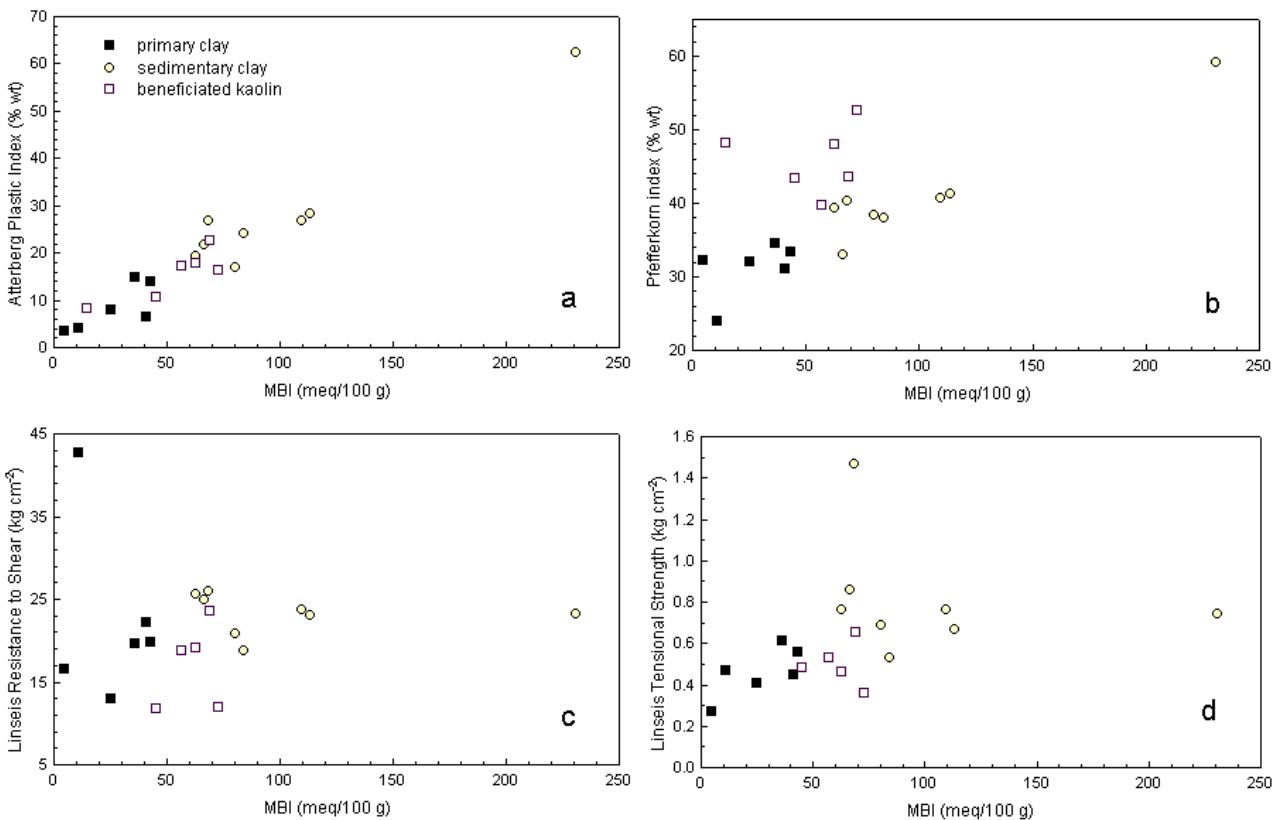
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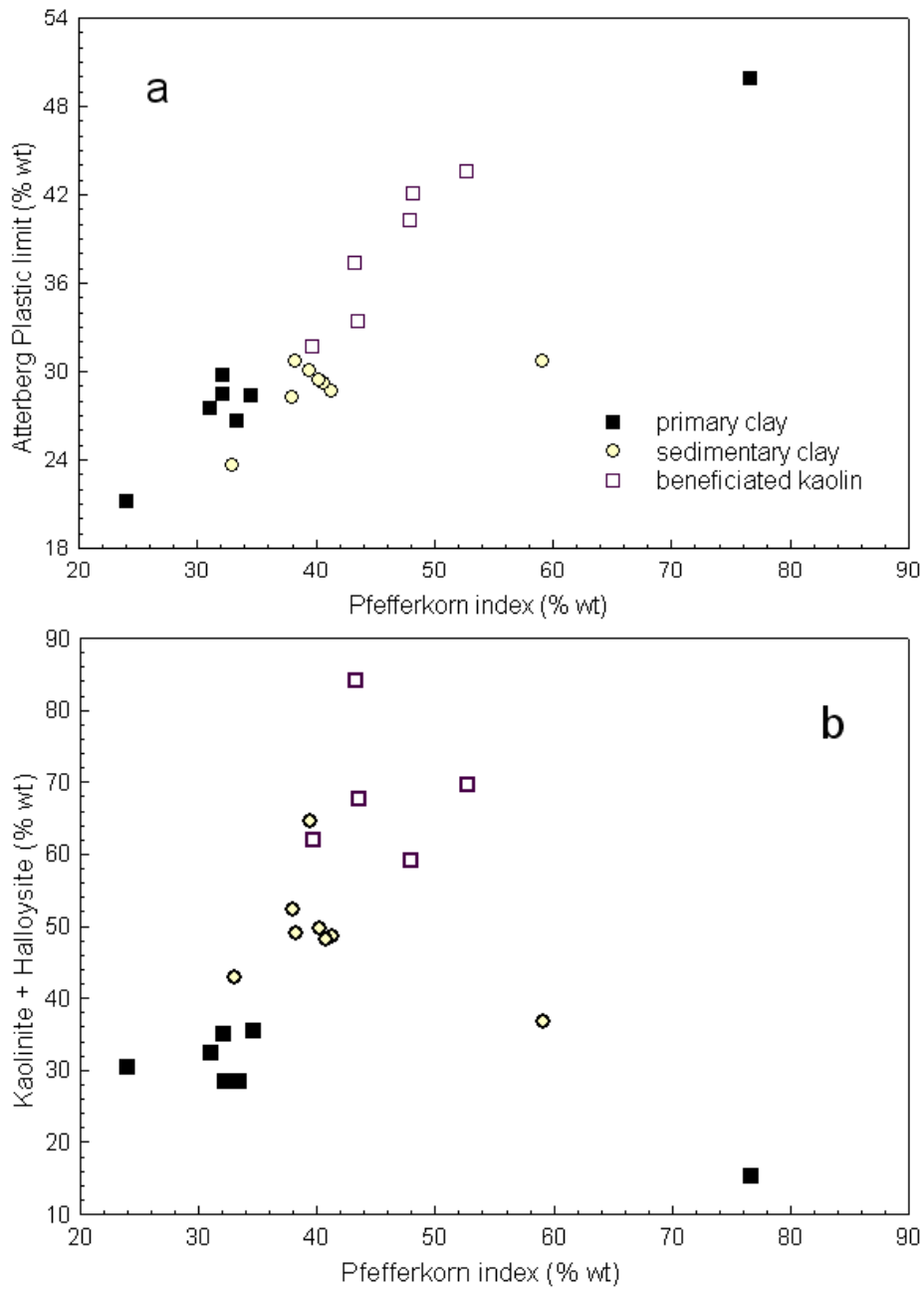
[Fig. 1. Methylene Blue Index vs specific surface area \(a\), particle fraction <2 µm \(b\), kaolinite group minerals \(c\) and expandable clay minerals \(d\) of kaolins and clays.](#)



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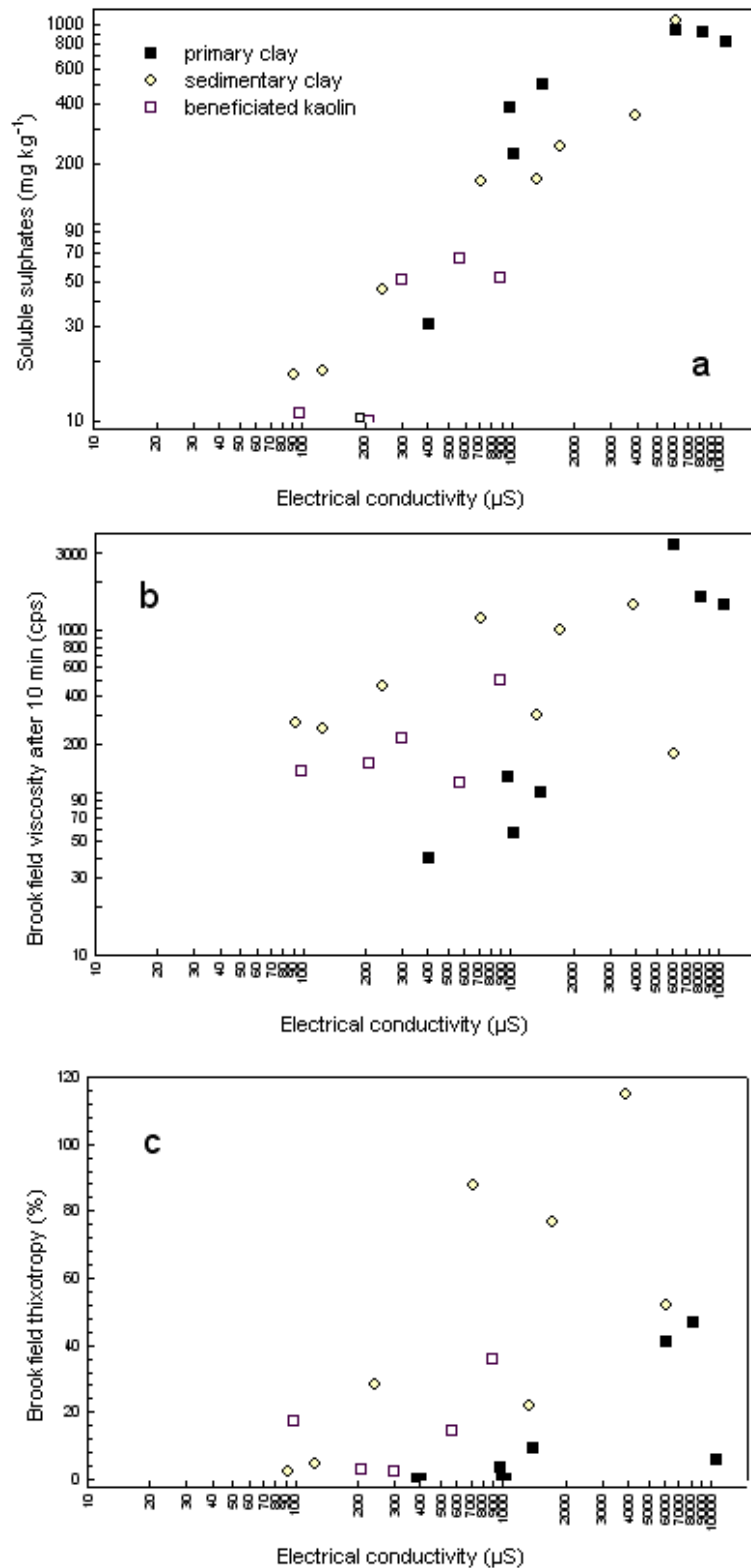
[Fig. 2. Methylene Blue Index vs plasticity of kaolins and clays: a\) Atterberg plastic index; b\) pfefferkorn index; Linseis resistance to shear \(c\) and tensional strength \(d\).](#)

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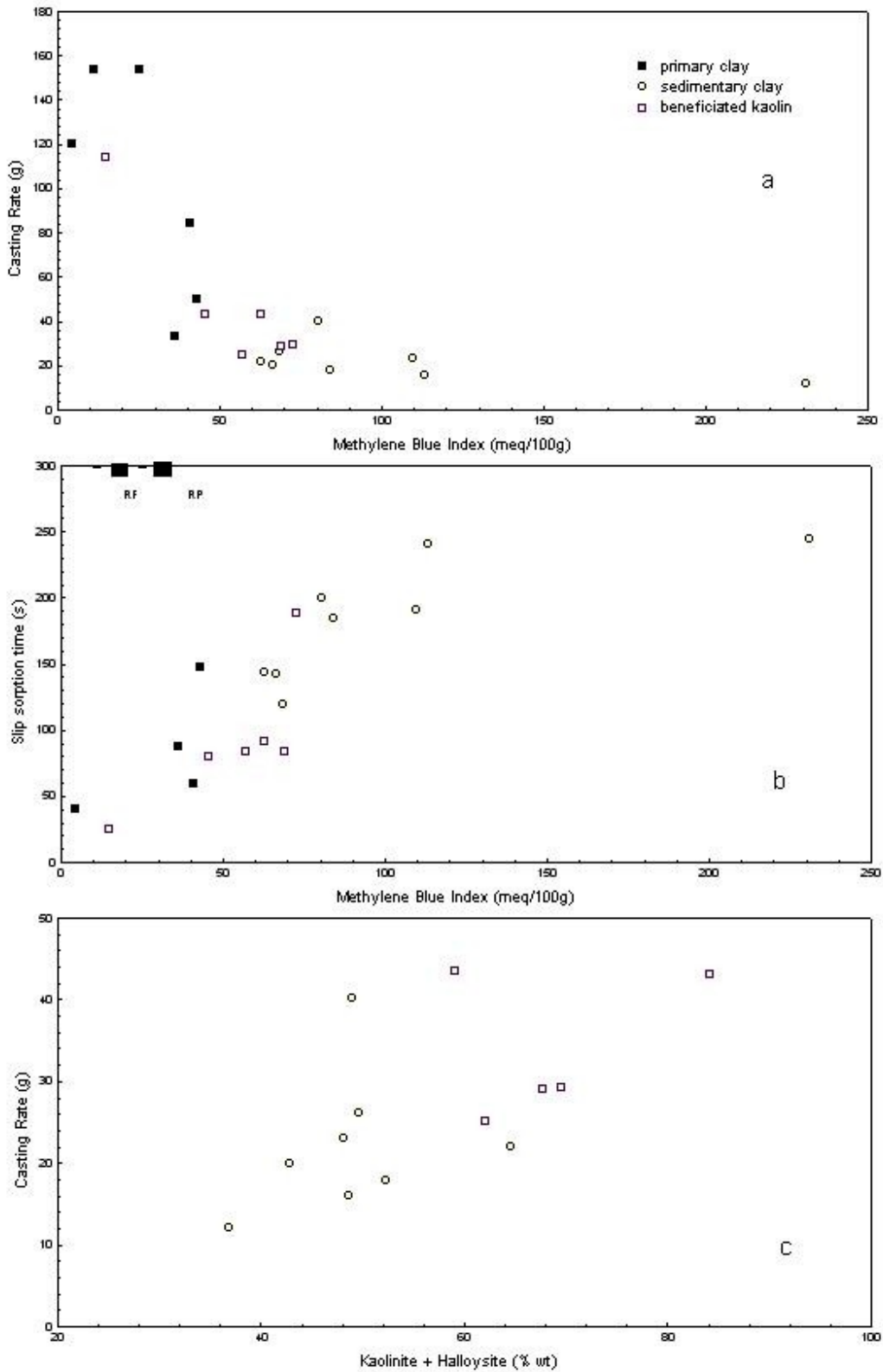
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Fig. 3. Pfefferkorn index vs Atterberg plastic limit (a) and amount of kaolinite group minerals (b).



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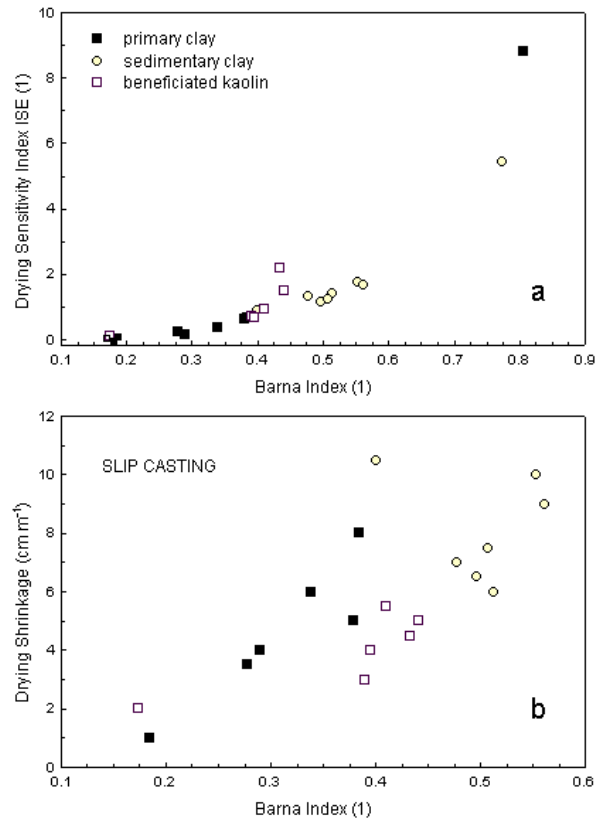
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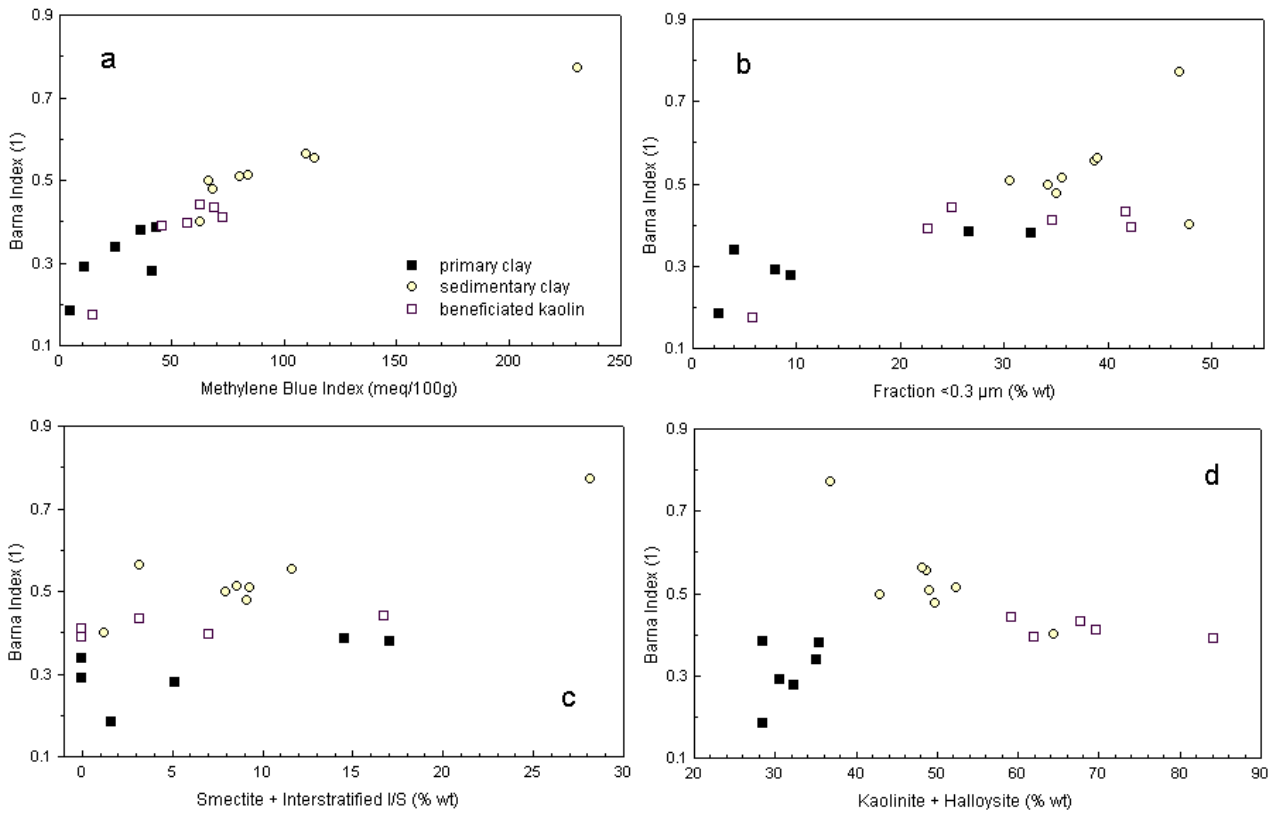
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536 [Fig. 5. Casting behaviour of clay slips: Methylene Blue Index vs casting rate \(a\) and slip](#)
 537 [suction time \(b\); amount of kaolinite group minerals vs casting rate \(c\).](#)

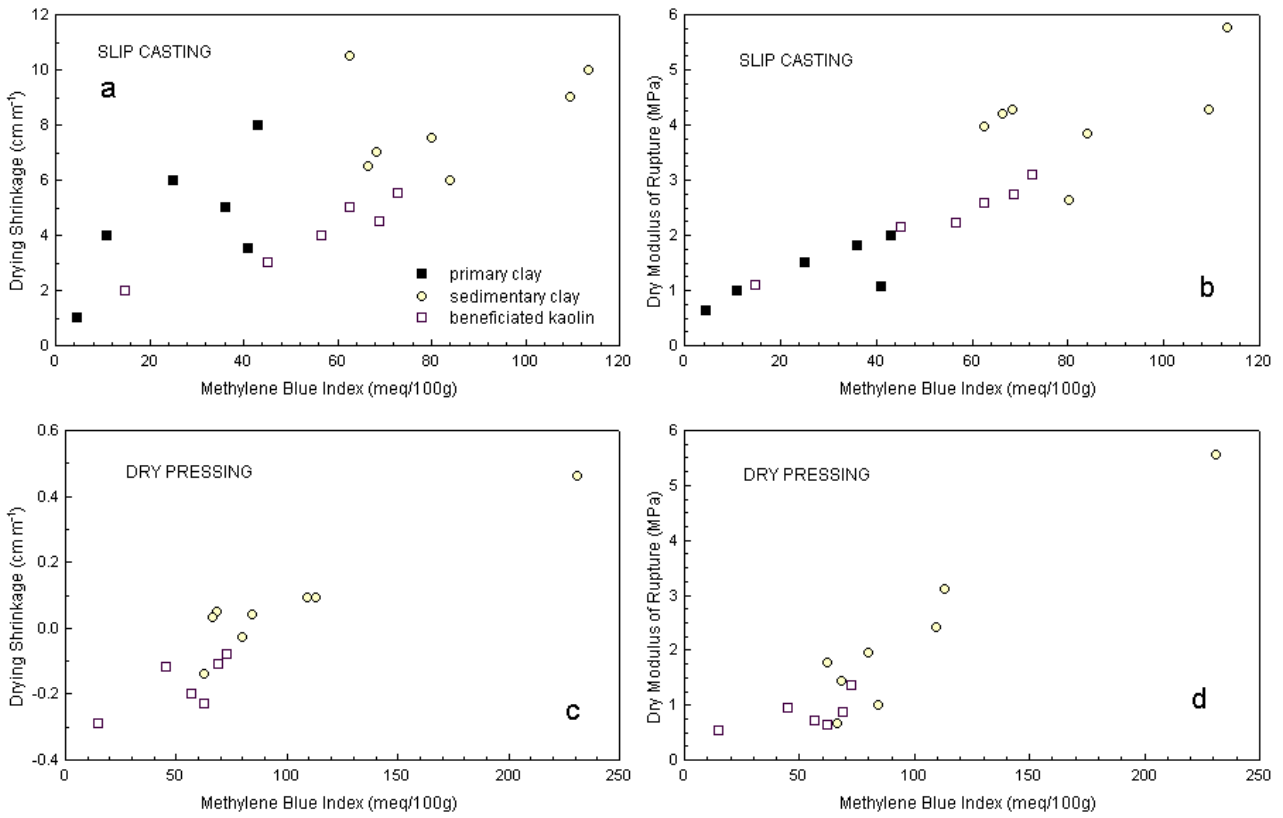


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539 [Fig. 6. Drying behaviour kaolins and clays: Barna Index vs drying sensitivity \(a\) and drying](#)
540 [shrinkage \(b\).](#)

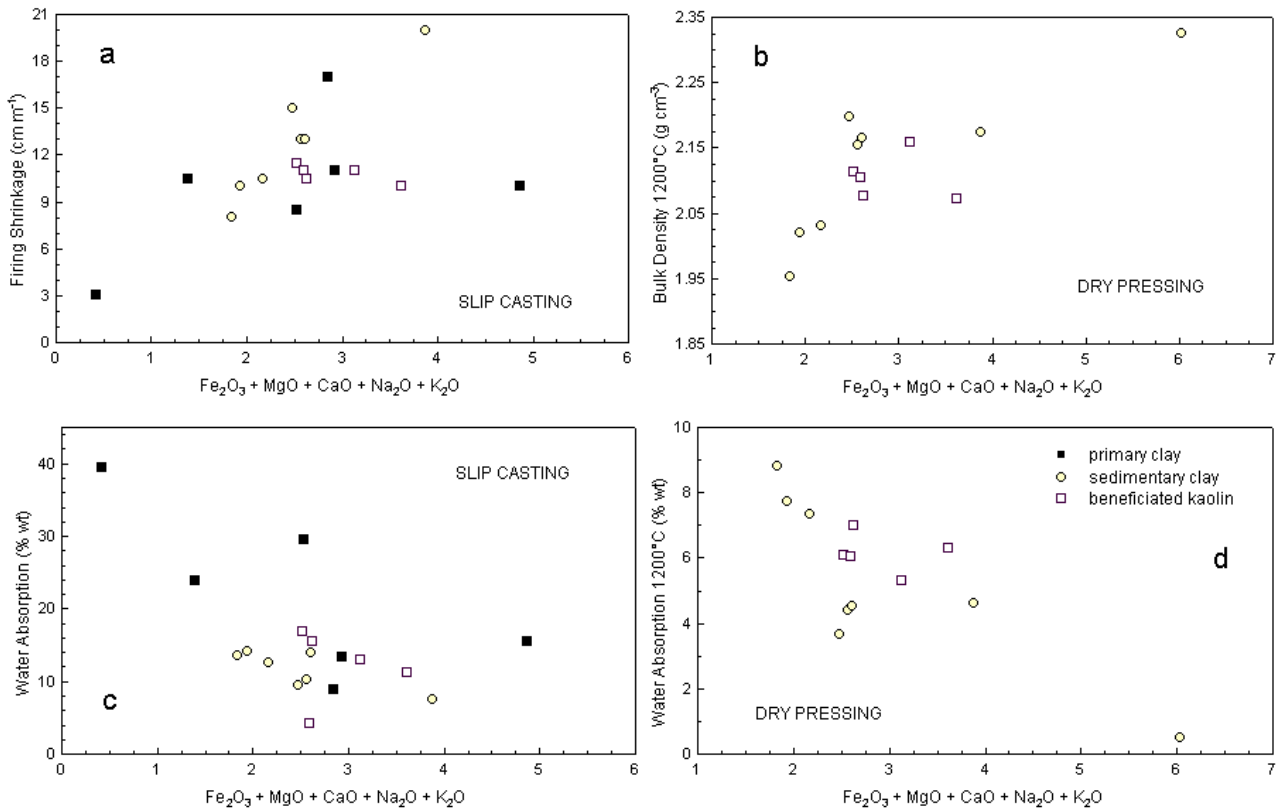
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543 [Fig. 7. Barna Index vs Methylene Blue Index \(a\), <0.3μm fraction \(b\), expandable clay](#)
544 [minerals \(c\) and kaolinite group minerals \(d\).](#)



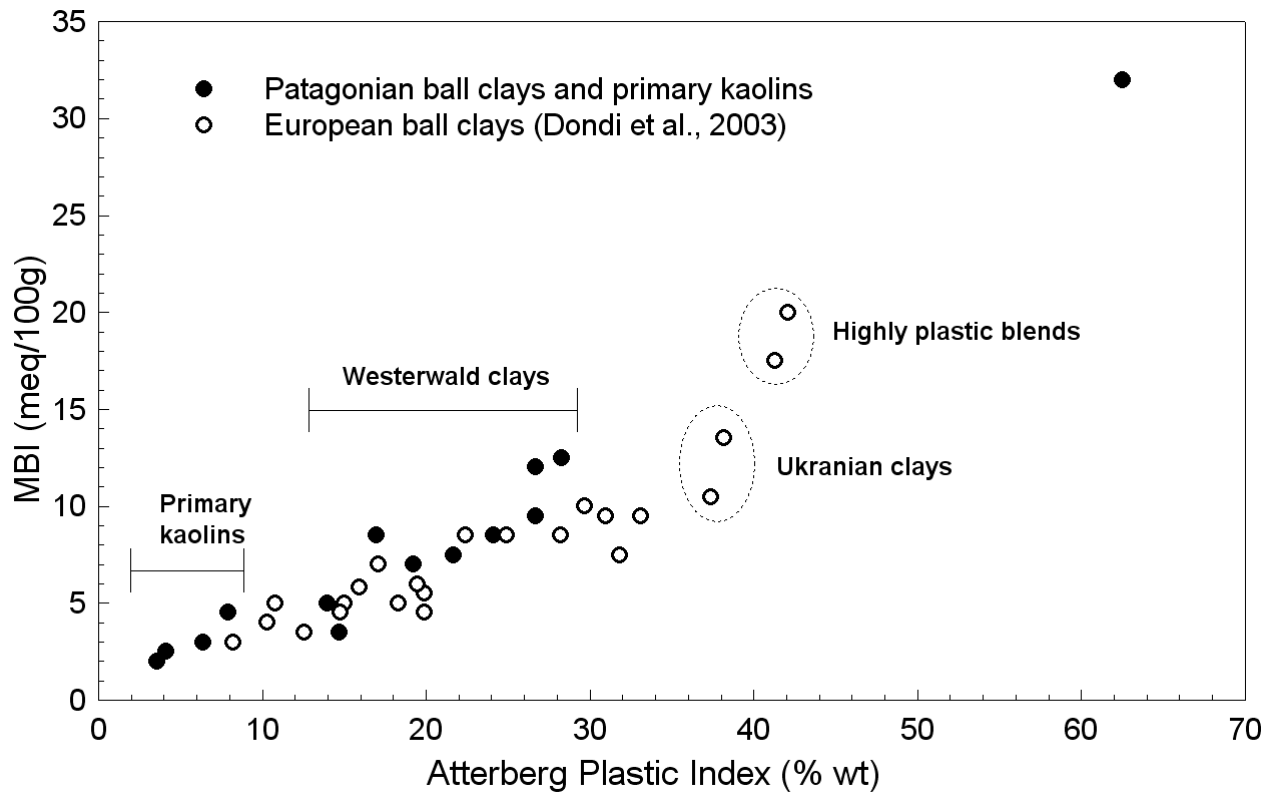
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 546 [Fig. 8. Methylene Blue Index vs drying shrinkage \(a\), dry modulus of rupture \(b\) of slip cast](#)
 547 [bodies; drying shrinkage \(c\), dry modulus of rupture \(d\) of pressed bodies.](#)
 548



549

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

553



554

555

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

| <u>Sample</u> | <u>Type</u> | <u>Formation</u> | <u>Ka + Ha</u> <u>(%wt.)</u> | <u>Sm + I/S</u> <u>(%wt.)</u> | <u>Qz + Fd</u> <u>(%wt.)</u> | <u>Media</u> <u>(μ</u> |
|---------------|-------------|------------------|---------------------------------|----------------------------------|---------------------------------|---------------------------|
| <u>CZ</u> | <u>S</u> | <u>Ba-LM</u> | <u>48</u> | <u>3</u> | <u>41</u> | <u>0.</u> |
| <u>PU</u> | <u>S</u> | <u>Ba-LM</u> | <u>49</u> | <u>12</u> | <u>35</u> | <u>0.</u> |
| <u>FP</u> | <u>S</u> | <u>Ba-LM</u> | <u>37</u> | <u>28</u> | <u>27</u> | <u>0.</u> |
| <u>BG</u> | <u>P</u> | <u>BG</u> | <u>15</u> | <u>59</u> | <u>18</u> | <u><0</u> |
| <u>CA</u> | <u>S</u> | <u>Ba-UM</u> | <u>65</u> | <u>tr.</u> | <u>27</u> | <u>0.</u> |
| <u>FA</u> | <u>S</u> | <u>Ba-LM</u> | <u>50</u> | <u>9</u> | <u>38</u> | <u>0.</u> |
| <u>TZ</u> | <u>S</u> | <u>Ba-LM</u> | <u>43</u> | <u>8</u> | <u>46</u> | <u>1.</u> |
| <u>TS</u> | <u>S</u> | <u>Ba-LM</u> | <u>52</u> | <u>9</u> | <u>36</u> | <u>0.</u> |
| <u>PR</u> | <u>P</u> | <u>CA</u> | <u>29</u> | <u>2</u> | <u>68</u> | <u>></u> |
| <u>CH</u> | <u>S</u> | <u>Sa</u> | <u>49</u> | <u>9</u> | <u>38</u> | <u>1.</u> |
| <u>IL</u> | <u>P</u> | <u>Ma</u> | <u>28</u> | <u>15</u> | <u>54</u> | <u>4.</u> |
| <u>RF</u> | <u>P</u> | <u>Ma</u> | <u>35</u> | <u>tr.</u> | <u>59</u> | <u>63</u> |
| <u>RP</u> | <u>P</u> | <u>Ma</u> | <u>31</u> | <u>tr.</u> | <u>65</u> | <u>></u> |
| <u>MA</u> | <u>P</u> | <u>Ma</u> | <u>35</u> | <u>17</u> | <u>46</u> | <u>1.</u> |
| <u>SR</u> | <u>P</u> | <u>Ma</u> | <u>32</u> | <u>5</u> | <u>58</u> | <u>></u> |
| <u>PRL</u> | <u>B</u> | | <u>28</u> | <u>2</u> | <u>69</u> | <u>2.</u> |
| <u>ILL</u> | <u>B</u> | | <u>63</u> | <u>3</u> | <u>32</u> | <u>0.</u> |
| <u>RFL</u> | <u>B</u> | | <u>70</u> | <u>3</u> | <u>24</u> | <u>0.</u> |
| <u>RPL</u> | <u>B</u> | | <u>68</u> | <u>15</u> | <u>15</u> | <u>1.</u> |
| <u>MAL</u> | <u>B</u> | | <u>57</u> | <u>12</u> | <u>29</u> | <u>0.</u> |
| <u>SRL</u> | <u>B</u> | | <u>63</u> | <u>17</u> | <u>18</u> | <u>1.</u> |

582 [Table 2](#)583 [Plasticity of the Patagonian kaolins, clays and beneficiated products](#)

584

| Clay sample | Methylene Blue index (MBI) | | Pfefferkorn plasticity index (PI) % wt. | Atterberg consistency limits | | | Wa |
|-----------------------------|--|------------------------------|---|---|--|---|--------------------|
| | Natural pH | 3<pH<4 | | Plastic limit (W_P) | Liquid limit (W_L) | Plastic index (I_P) | |
| | meq/100g | meq/100g | | % wt. | % wt. | % wt. | |
| CZ | 109.6 | 12.0 | 40.7 | 29.2 | 55.9 | 26.7 | |
| PU | 113.5 | 12.5 | 41.3 | 28.7 | 57.0 | 28.3 | |
| FP | 231.0 | 32.0 | 59.1 | 30.7 | 93.2 | 62.5 | |
| BG | 579.4 | 67.5 | 76.7 | 49.9 | 248.0 | 198.1 | |
| CA | 62.6 | 7.0 | 39.4 | 30.1 | 49.3 | 19.2 | |
| FA | 68.5 | 9.5 | 40.3 | 29.4 | 56.1 | 26.7 | |
| TZ | 66.6 | 7.5 | 33.0 | 23.6 | 45.3 | 21.7 | |
| TS | 84.2 | 8.5 | 38.0 | 28.2 | 52.3 | 24.1 | |
| PR | 4.7 | 2.0 | 32.2 | 29.7 | 33.3 | 3.6 | |
| CH | 80.3 | 8.5 | 38.3 | 30.7 | 47.7 | 17.0 | |
| IL | 43.1 | 5.0 | 33.4 | 26.6 | 40.6 | 14.0 | |
| RF | 25.1 | 4.5 | 32.1 | 28.5 | 36.5 | 7.9 | |
| RP | 11.0 | 2.5 | 24.0 | 21.2 | 25.3 | 4.1 | |
| MA | 36.2 | 3.5 | 34.6 | 28.3 | 43.0 | 14.7 | |
| SR | 41.1 | 3.0 | 31.1 | 27.5 | 34.0 | 6.4 | |
| PRL | 14.9 | n.d. | 48.2 | 42.1 | 50.3 | 8.2 | |
| ILL | 68.9 | n.d. | 43.6 | 33.4 | 56.1 | 22.7 | |
| RFL | 72.8 | n.d. | 52.7 | 43.6 | 59.8 | 16.2 | |
| RPL | 45.4 | n.d. | 43.3 | 37.3 | 47.9 | 10.6 | |
| MAL | 56.8 | n.d. | 39.7 | 31.7 | 49.0 | 17.3 | |
| SRL | 62.6 | n.d. | 47.9 | 40.2 | 58.2 | 17.9 | |

585 [n.d. = not determined](#)

586 **Table 3**

587 Slip rheology of the Patagonian kaolins, clays and beneficiated products. ρ_s :
 588 slip density; deflocculant addition: sodium carbonate (NC) and sodium silicate
 589 (NS). Brookfield rheological testing: viscosity measured after 0, 1, 5 and 10 min;
 590 T_B : thixotropy. Time of gravity flow measured after 0 min (τ_0) and 60 min (τ_{60}).
 591 Soluble salts: concentration of sulphate ion (SO_4) and electrical conductivity
 592 (EC).

593

| Sample | Brookfield viscosimeter | | | | | | | T_B % |
|--------|--------------------------------|---------|----------|-----------------|-----------------|-----------------|-------------------|------------|
| | ρ_s g·cm ⁻³ | NC g | NS mL | VB0=0min cps | VB1=1min cps | VB5=5min cps | VB10=10min cps | |
| CZ | 1.58 | 2.0 | 8.1 | 565 | 665 | 905 | 1000 | 77 |
| PU | 1.54 | 1.0 | 6.5 | 250 | 265 | 285 | 305 | 22 |
| FP | 1.25 | 1.0 | 0.5 | 635 | 740 | 960 | 1200 | 88 |
| BG | 1.05 | 2.0 | 11.0 | 2410 | 2485 | 3250 | 3400 | 41 |
| CA | 1.60 | 2.0 | 4.4 | 665 | 1045 | 1210 | 1430 | 115 |
| FA | 1.60 | 2.0 | 4.8 | 354 | 360 | 380 | 454 | 28 |
| TZ | 1.62 | 2.0 | 4.5 | 241 | 241 | 245 | 252 | 5 |
| TS | 1.60 | 2.0 | 4.7 | 266 | 266 | 268 | 272 | 2 |
| PR | 1.60 | 1.0 | 2.5 | 43 | 42 | 40 | 40 | 0 |
| CH | 1.55 | 1.0 | 4.6 | 116 | 134 | 155 | 176 | 52 |
| IL | 1.60 | 1.6 | 3.7 | 121 | 121 | 123 | 125 | 3 |
| RF | 1.40 | 1.6 | 4.6 | 1100 | 1350 | 1550 | 1615 | 47 |
| RP | 1.43 | 1.6 | 4.7 | 1350 | 1390 | 1400 | 1430 | 6 |
| MA | 1.60 | 1.6 | 4.5 | 58 | 57 | 57 | 57 | 0 |
| SR | 1.60 | 1.4 | 3.4 | 93 | 93 | 97 | 102 | 9 |
| PRL | 1.55 | 1.8 | 1.9 | 37 | 37 | 38 | 39 | 5 |
| ILL | 1.60 | 1.6 | 3.6 | 148 | 148 | 150 | 152 | 3 |
| RFL | 1.60 | 1.6 | 4.7 | 365 | 416 | 450 | 496 | 36 |
| RPL | 1.60 | 1.6 | 2.6 | 101 | 106 | 112 | 116 | 14 |
| MAL | 1.60 | 1.6 | 2.1 | 115 | 120 | 129 | 135 | 17 |
| SRL | 1.60 | 1.6 | 3.1 | 210 | 210 | 211 | 215 | 2 |

594

595 Table 4596 Shaping behaviour of the Patagonian kaolins, clays and beneficiated products.597 M_c : casting rate measured as weight of the slip cast cake;598 t_s : slip suction time. Pressing of clay:feldspar (1:1) mix: green bulk density (ρ_g);599 post-pressing expansion (E_p); green modulus of rupture (σ_g). n.d.=not600 determined.

601

| | <u>Slip casting</u> | | <u>Uniaxial pressing</u> | | <u>M</u> |
|------------|-------------------------------------|-------------------------------------|--|---|----------|
| | <u>M_c</u> <u>g</u> | <u>t_s</u> <u>s</u> | <u>ρ_g</u> <u>g·cm⁻³</u> | <u>E_p</u> <u>cm·m⁻¹</u> | |
| <u>CZ</u> | <u>23</u> | <u>191</u> | <u>1.989</u> | <u>0.45</u> | <u>1</u> |
| <u>PU</u> | <u>16</u> | <u>241</u> | <u>1.999</u> | <u>0.42</u> | <u>1</u> |
| <u>FP</u> | <u>12</u> | <u>245</u> | <u>2.018</u> | <u>0.40</u> | <u>1</u> |
| <u>BG</u> | <u>29</u> | <u>307</u> | <u>n.d.</u> | <u>n.d.</u> | <u>1</u> |
| <u>CA</u> | <u>22</u> | <u>144</u> | <u>1.933</u> | <u>0.44</u> | <u>1</u> |
| <u>FA</u> | <u>26</u> | <u>119</u> | <u>1.870</u> | <u>0.55</u> | <u>0</u> |
| <u>TZ</u> | <u>20</u> | <u>142</u> | <u>1.749</u> | <u>0.60</u> | <u>0</u> |
| <u>TS</u> | <u>18</u> | <u>184</u> | <u>1.858</u> | <u>0.53</u> | <u>0</u> |
| <u>PR</u> | <u>120</u> | <u>40</u> | <u>n.d.</u> | <u>n.d.</u> | <u>1</u> |
| <u>CH</u> | <u>40</u> | <u>200</u> | <u>1.963</u> | <u>0.48</u> | <u>0</u> |
| <u>IL</u> | <u>50</u> | <u>147</u> | <u>n.d.</u> | <u>n.d.</u> | <u>1</u> |
| <u>RF</u> | <u>154</u> | <u>>300</u> | <u>n.d.</u> | <u>n.d.</u> | <u>1</u> |
| <u>RP</u> | <u>154</u> | <u>>300</u> | <u>n.d.</u> | <u>n.d.</u> | <u>1</u> |
| <u>MA</u> | <u>33</u> | <u>87</u> | <u>n.d.</u> | <u>n.d.</u> | <u>1</u> |
| <u>SR</u> | <u>84</u> | <u>60</u> | <u>n.d.</u> | <u>n.d.</u> | <u>1</u> |
| <u>PRL</u> | <u>114</u> | <u>25</u> | <u>1.737</u> | <u>1.00</u> | <u>0</u> |
| <u>ILL</u> | <u>29</u> | <u>84</u> | <u>1.812</u> | <u>0.60</u> | <u>0</u> |
| <u>RFL</u> | <u>29</u> | <u>188</u> | <u>1.822</u> | <u>0.60</u> | <u>0</u> |
| <u>RPL</u> | <u>43</u> | <u>80</u> | <u>1.833</u> | <u>0.69</u> | <u>0</u> |
| <u>MAL</u> | <u>25</u> | <u>84</u> | <u>1.860</u> | <u>0.53</u> | <u>0</u> |
| <u>SRL</u> | <u>44</u> | <u>91</u> | <u>1.795</u> | <u>0.74</u> | <u>0</u> |

602 Table 5603 Drying behaviour of the Patagonian kaolins, clays and beneficiated products.604 Bigot curve of clay materials: working moisture (W_B), drying shrinkage (S_B).605 weight loss with shrinkage (W_1) and without shrinkage (W_2), Barna index (BI)606 and drying sensitivity index (ISE).607 Drying behaviour of ceramic bodies: drying shrinkage: S_d (slip casting) and S_d^* 608 (pressing); dry modulus of rupture: σ_d (slip casting) and σ_d^* (pressing).

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| Sample | Bigot curve | | | | | | S_d cm·m |
|------------|----------------|-----------------------------|----------------|----------------|-------------|-------------|---------------|
| | W_B % wt. | S_B cm·m ⁻¹ | W_1 % wt. | W_2 % wt. | BI 1 | ISE 1 | |
| <u>CZ</u> | <u>34.7</u> | <u>8.5</u> | <u>56.2</u> | <u>43.8</u> | <u>0.56</u> | <u>1.66</u> | <u>9.0</u> |
| <u>PU</u> | <u>37.2</u> | <u>8.4</u> | <u>55.4</u> | <u>44.6</u> | <u>0.55</u> | <u>1.74</u> | <u>10.0</u> |
| <u>FP</u> | <u>51.5</u> | <u>13.7</u> | <u>77.3</u> | <u>22.7</u> | <u>0.77</u> | <u>5.45</u> | <u>n.d.</u> |
| <u>BG</u> | <u>67.1</u> | <u>16.3</u> | <u>80.5</u> | <u>19.5</u> | <u>0.81</u> | <u>8.80</u> | <u>n.d.</u> |
| <u>CA</u> | <u>36.7</u> | <u>6.0</u> | <u>40.0</u> | <u>60.0</u> | <u>0.40</u> | <u>0.88</u> | <u>10.5</u> |
| <u>FA</u> | <u>35.8</u> | <u>7.6</u> | <u>47.7</u> | <u>52.3</u> | <u>0.48</u> | <u>1.30</u> | <u>7.0</u> |
| <u>TZ</u> | <u>31.0</u> | <u>7.5</u> | <u>49.7</u> | <u>50.3</u> | <u>0.50</u> | <u>1.15</u> | <u>6.5</u> |
| <u>TS</u> | <u>35.4</u> | <u>7.8</u> | <u>51.3</u> | <u>48.7</u> | <u>0.51</u> | <u>1.41</u> | <u>6.0</u> |
| <u>PR</u> | <u>28.8</u> | <u>0.6</u> | <u>18.5</u> | <u>81.5</u> | <u>0.19</u> | <u>0.03</u> | <u>1.0</u> |
| <u>CH</u> | <u>33.6</u> | <u>7.4</u> | <u>50.8</u> | <u>49.2</u> | <u>0.51</u> | <u>1.26</u> | <u>7.5</u> |
| <u>IL</u> | <u>31.0</u> | <u>5.7</u> | <u>38.5</u> | <u>61.5</u> | <u>0.39</u> | <u>0.68</u> | <u>8.0</u> |
| <u>RF</u> | <u>30.8</u> | <u>3.7</u> | <u>33.8</u> | <u>66.2</u> | <u>0.34</u> | <u>0.38</u> | <u>6.0</u> |
| <u>RP</u> | <u>22.4</u> | <u>2.5</u> | <u>29.0</u> | <u>71.0</u> | <u>0.29</u> | <u>0.16</u> | <u>4.0</u> |
| <u>MA</u> | <u>31.8</u> | <u>5.3</u> | <u>37.9</u> | <u>62.1</u> | <u>0.38</u> | <u>0.63</u> | <u>5.0</u> |
| <u>SR</u> | <u>28.5</u> | <u>3.0</u> | <u>27.8</u> | <u>72.2</u> | <u>0.28</u> | <u>0.24</u> | <u>3.5</u> |
| <u>PRL</u> | <u>43.8</u> | <u>1.2</u> | <u>17.4</u> | <u>82.6</u> | <u>0.17</u> | <u>0.09</u> | <u>2.0</u> |
| <u>ILL</u> | <u>37.7</u> | <u>13.3</u> | <u>43.3</u> | <u>56.7</u> | <u>0.43</u> | <u>2.17</u> | <u>4.5</u> |
| <u>RFL</u> | <u>47.2</u> | <u>4.9</u> | <u>41.0</u> | <u>59.0</u> | <u>0.41</u> | <u>0.95</u> | <u>5.5</u> |
| <u>RPL</u> | <u>39.7</u> | <u>4.7</u> | <u>39.0</u> | <u>61.0</u> | <u>0.39</u> | <u>0.73</u> | <u>3.0</u> |
| <u>MAL</u> | <u>35.8</u> | <u>4.9</u> | <u>39.5</u> | <u>60.5</u> | <u>0.40</u> | <u>0.69</u> | <u>4.0</u> |
| <u>SRL</u> | <u>46.8</u> | <u>7.2</u> | <u>44.1</u> | <u>55.9</u> | <u>0.44</u> | <u>1.49</u> | <u>5.0</u> |

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611 Table 6

612 Firing behaviour of the Patagonian kaolins, clays and beneficiated products:
 613 firing shrinkage (S_f), water absorption (E), fired modulus of rupture (σ_f), fired
 614 bulk density (ρ_f). Hot-stage microscopy: isothermal sintering rate at 1200°C of
 615 porcelain stoneware bodies (SR); sintering temperature (T_{sint}) and softening
 616 temperature (T_{soft}) of clay materials. n.d.=not determined.

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| <u>Sample</u> | <u>Slip cast clay 1250°C</u> | | | <u>Pressed, fired 1200°C</u> | | | <u>Pressed, fired 1250°C</u> | |
|---------------|---|--------------------------|--|---|---------------------------|--|---|---------------------------|
| | <u>S_f</u> <u>cm·m⁻¹</u> | <u>E</u> <u>% wt.</u> | <u>σ_f</u> <u>MPa</u> | <u>S_f^*</u> <u>cm·m⁻¹</u> | <u>E*</u> <u>% wt.</u> | <u>ρ_f^*</u> <u>g·cm⁻³</u> | <u>S_f^*</u> <u>cm·m⁻¹</u> | <u>E*</u> <u>% wt.</u> |
| <u>CZ</u> | <u>4.0</u> | <u>10.2</u> | <u>4.3</u> | <u>4.1</u> | <u>4.4</u> | <u>2.155</u> | <u>5.4</u> | <u>0.2</u> |
| <u>PU</u> | <u>5.0</u> | <u>9.5</u> | <u>5.8</u> | <u>4.4</u> | <u>3.7</u> | <u>2.198</u> | <u>5.5</u> | <u>0.2</u> |
| <u>FP</u> | <u>n.d.</u> | <u>n.d.</u> | <u>n.d.</u> | <u>5.5</u> | <u>0.5</u> | <u>2.326</u> | <u>n.d.</u> | <u>n.d.</u> |
| <u>BG</u> | <u>n.d.</u> | <u>n.d.</u> | <u>n.d.</u> | <u>n.d.</u> | <u>n.d.</u> | <u>n.d.</u> | <u>n.d.</u> | <u>n.d.</u> |
| <u>CA</u> | <u>9.5</u> | <u>7.5</u> | <u>4.0</u> | <u>5.2</u> | <u>4.6</u> | <u>2.174</u> | <u>6.9</u> | <u>1.0</u> |
| <u>FA</u> | <u>3.5</u> | <u>12.5</u> | <u>4.3</u> | <u>3.8</u> | <u>7.3</u> | <u>2.030</u> | <u>6.7</u> | <u>0.9</u> |
| <u>TZ</u> | <u>1.5</u> | <u>13.6</u> | <u>4.2</u> | <u>4.1</u> | <u>8.8</u> | <u>1.952</u> | <u>8.9</u> | <u>0.4</u> |
| <u>TS</u> | <u>4.0</u> | <u>14.1</u> | <u>3.8</u> | <u>3.8</u> | <u>7.7</u> | <u>2.020</u> | <u>7.3</u> | <u>1.0</u> |
| <u>PR</u> | <u>2.0</u> | <u>39.5</u> | <u>0.6</u> | <u>n.d.</u> | <u>n.d.</u> | <u>n.d.</u> | <u>n.d.</u> | <u>n.d.</u> |
| <u>CH</u> | <u>5.5</u> | <u>14.0</u> | <u>2.6</u> | <u>4.4</u> | <u>4.5</u> | <u>2.165</u> | <u>6.0</u> | <u>0.2</u> |
| <u>IL</u> | <u>9.0</u> | <u>9.0</u> | <u>2.0</u> | <u>n.d.</u> | <u>n.d.</u> | <u>n.d.</u> | <u>n.d.</u> | <u>n.d.</u> |
| <u>RF</u> | <u>2.5</u> | <u>29.5</u> | <u>1.5</u> | <u>n.d.</u> | <u>n.d.</u> | <u>n.d.</u> | <u>n.d.</u> | <u>n.d.</u> |
| <u>RP</u> | <u>6.0</u> | <u>15.4</u> | <u>1.0</u> | <u>n.d.</u> | <u>n.d.</u> | <u>n.d.</u> | <u>n.d.</u> | <u>n.d.</u> |
| <u>MA</u> | <u>6.0</u> | <u>13.4</u> | <u>1.8</u> | <u>n.d.</u> | <u>n.d.</u> | <u>n.d.</u> | <u>n.d.</u> | <u>n.d.</u> |
| <u>SR</u> | <u>7.0</u> | <u>23.8</u> | <u>1.1</u> | <u>n.d.</u> | <u>n.d.</u> | <u>n.d.</u> | <u>n.d.</u> | <u>n.d.</u> |
| <u>PRL</u> | <u>3.0</u> | <u>40.4</u> | <u>1.1</u> | <u>4.1</u> | <u>12.2</u> | <u>1.890</u> | <u>9.2</u> | <u>2.2</u> |
| <u>ILL</u> | <u>5.5</u> | <u>11.2</u> | <u>2.7</u> | <u>4.8</u> | <u>6.3</u> | <u>2.071</u> | <u>8.1</u> | <u>0.2</u> |
| <u>RFL</u> | <u>6.0</u> | <u>16.8</u> | <u>3.1</u> | <u>6.1</u> | <u>6.1</u> | <u>2.114</u> | <u>9.0</u> | <u>0.3</u> |
| <u>RPL</u> | <u>8.0</u> | <u>13.1</u> | <u>2.1</u> | <u>6.5</u> | <u>5.3</u> | <u>2.158</u> | <u>9.3</u> | <u>0.1</u> |
| <u>MAL</u> | <u>7.0</u> | <u>4.2</u> | <u>2.2</u> | <u>5.0</u> | <u>6.1</u> | <u>2.105</u> | <u>8.3</u> | <u>0.2</u> |
| <u>SRL</u> | <u>5.5</u> | <u>15.4</u> | <u>2.6</u> | <u>5.5</u> | <u>7.0</u> | <u>2.077</u> | <u>8.7</u> | <u>0.5</u> |

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