CLAYS FROM VILA NOVA DA RAINHA (PORTUGAL): APPRAISAL OF THEIR RELEVANT PROPERTIES IN ORDER TO BE USED IN CONSTRUCTION CERAMICS

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ABSTRACT

The clay deposit of Vila Nova da Rainha (VNR) is included in the lithostratigraphic formation named "Argilas de Tomar", and is located at the lower section of the Tertiary Tagus' river basin. Clay from one quarry is being extracted for the production of construction ceramics.

In this work the firing transformations undergone by VNR clays containing quartz, alkaline feldspar, iron oxy-hydroxides, and clay minerals have been studied. Carbonates have not been identified in these raw materials. The clay layers can be subdivided in three groups based upon composition and ceramic properties. The first group, VNR0, is represented by smectite-kaolinite sandy-silty clay, the second group (VNR1 and VNR2) corresponds to illite-kaolinite bearing clay and the third group (VNR3 and VNR4) is represented by illite-smectite silty clay.

The firing process involves the formation of hematite and mullite both influencing the technical properties of the fired products. With regards to the ceramic properties assessed at 1100 °C the first group showed the lowest total shrinkage value (7.35 %) the highest water absorption value (12.2 %) and the lowest mechanical bending strength value (12.0 MPa); the same properties assessed in the second group provided the highest firing shrinkage values (7.0-5.0 %), the lowest values of water absorption (0.1-0.2 %) and relatively high mechanical bending strength values (47.8-48.0 MPa); the third group showed firing shrinkage values within the range 3.5-4.2 %, water absorption values within the range 1.4-4.5 %, and the highest mechanical bending strength values (49.2-52.0 MPa). The results of the ceramic properties being appraised indicate that the raw materials being studied are suitable for the production of high-quality construction ceramics, such as brick, roof tile and rustic floor tile.

KEYWORDS: Vila Nova da Rainha, clays, ceramic raw materials, construction ceramics

1. INTRODUCTION

The outcrops of clayey sediments in Vila Nova da Rainha (VNR) correspond to the distal sediments of the so-called Tagus River basin. The characteristics of these clayey deposits are significantly distinctive from those of other lithostratigraphically correlated deposits. The global reserves of clay appear to be quite large based both on the extension of the outcropping areas and on lithostratigraphic arguments. Therefore, there will be sufficient reserves to allow the feeding of several plants with clay raw materials for the production, for instance, of construction ceramics shaped both by extrusion and by pressing adequate for distinctive functions (Coroado, 2000).

This study deals with the evaluation of the mineralogical and technological properties of representative clay samples collected in the quarry from Vila Nova da Rainha.

Composite or blended samples have been prepared in order to find out if these clays could be utilized in the manufacture of high added-value construction ceramics.

2. GEOLOGICAL SETTING

The clay deposit of Vila Nova da Rainha is located at 60 km, approximately, to the northeast of Lisbon, Portugal. It is positioned in the Lower Tertiary Basin of the Tagus River (LTBT), and belongs to the Miocene lithostratigraphic unit named "Argilas de Tomar" (AT) according to Barbosa (1995).

The limits of the LTBT basin, at north and northeast, are coincident with a structural accident that separates the metasediments (mainly quartzites and slates) of the Central Iberian Zone (CIZ) defined by Lotze (1945) from the complex of migmatite, schist



Fig. 1 Geologic map of Vila Nova da Rainha region where is located the quarry (modified from Barbosa, 1995).

and granitoids of the Ossa-Morena Zone (OMZ); the northwest limit, represented by a thurst fault, is the socalled "Maciço Calcário Estremenho" (MCE) consisting of Jurassic limestone overlaid by siliciclastic sediments dated from Cretaceous up to Miocene; at south and southeast the Tertiary deposits have discontinued limits with the Ossa-Morena Zone (OMZ).

The siliciclastic sediments transported from CIZ, mainly from the Hesperic Massif (HM), but also from the Cretaceous siliciclastic sediments that overlie MCE, provide the formation of the lower lithostratigraphic units of LTBT. The upper litostratigraphic units of LTBT contain carbonate sediments responsible for the less interest of the clayey raw materials from these units for ceramic applications.

The general feature of the AT lithostratigraphic unit is the red to orange colours of the clayey sediments. Also its suitability as ceramic raw materials is widely recognized by the existent regional ceramic plants. The outcrops of this unit present several discontinuities along an extensive area (Figure 1). The overburden, when it occurs, consists mainly of gravel which thickness increases northward, and is exploited for the production of aggregates used in road works and concrete.

3. MATERIALS AND METHODS

Clay sampling was carried out at the exploitation front of Vila Nova da Rainha quarry. Five distinctive layers could be defined on the basis of colour and



Fig. 2 Lithostratigraphic log of the exploited Vila Nova da Rainha quarry.



Fig. 3 Particle size distribution of sands and clays (total sample) from Vila Nova da Rainha quarry.

texture and to which the references VNR0, VNR1, VNR2, VNR3 and VNR4 were attributed. Clay layers thickness range from 3 to 5 m. Two sandy layers VNRA1 and VNRA2 with mean thickness around 3 m, intercalate the VNR0-VNR1 and VNR3-VNR4 clay layers, respectively (Figure 2).

Granulometric analysis of total sample was carried out using dry sieving for grain sizes above 63 μ m according to the standard ASTM C371 and for fraction less than 63 μ m was performed with a X-ray grain size analyser Sedigraph 5100, according to the standard procedure BS 3406-2.

Mineralogical analysis was determined by X-ray diffraction (XRD) using a Philips PW 1710 controller with PW 1050/81 goniometer, and CuK α radiation. The operating settings were 45 kV and 40 mA. The bulk mineralogical composition of all samples was determined on random powder samples in the 4-60 ° 2 θ range, and for semi-quantitative analysis the methodologies proposed by Schultz (1964) and Thorez (1976) were adopted.

Chemical analysis was determined by X-ray fluorescence spectrometry (XRF) using a Philips PW 1840 spectrometer, and CrK α radiation. A sample prepared with 1:9 clay/flux (Spectromelt A12) ratio was fused to a glass bead. The Na₂O and K₂O contents were determined by flame photometry using a Corning 400 spectrometer. Loss on ignition was determined by heating the samples at 1000 °C for 3 hours. Fluorine content was determined using Metrohm equipment and the method of ion selective electrodes (ISE).

Atterberg plasticity index (Atterberg, 1911) was obtained following the determination of the consistency limits according to NP 143 standard.

Finally abrasiveness was determined following the procedure described by Neubold et al. (1982) and the operational conditions are reported to 174000 revolutions.

Ceramic properties, such as moisture content (NP 84), dry shrinkage (ASTM C326) and dry bending strength (ASTM C689) were determined on test specimens obtained by extrusion under vacuum. Firing shrinkage (ASTM C689), firing bending strength (ASTM C674), and water absorption (ASTM C373) were assessed on test specimens that were submitted to firing at 875 °C, 950 °C, 1025 °C and 1100 °C, being the firing rate 5 °C/min and the soaking time 1 hour.

4. RESULTS AND DISCUSSION

The bulk VNR clays show distinctive properties depending upon their granulometric and mineralogical compositions, properties which condition the technological properties before and after firing.

The granulometric parameters (Figure 3 and Table 1) allowed the classification of the studied clays into three groups: group 1 represented by the VNR0 clay is classified as a sandy-silt clay on which the clay fraction was estimated at 25 % and the D50 parameter was estimated at 15.6 μ m; group 2 represented by VNR1 and VNR2 clays is characterized by the highest contents of the less than 2 μ m fraction, and the D50 parameter being estimated at 0.5 and 0.7 μ m, respectively; and group 3 represented by VNR3 and VNR4 clays is characterized by the highest contents of silt fraction, and the D50 parameter being estimated at 2.3 μ m.

The inter-layered sand raw materials VNRA1 and VNRA2 show D50 values estimated at 494 μ m

Clays	< 2 µm (%)	2 - 20 µm (%)	> 20 µm (%)	2 - 63 µm (%)	>63 µm (%)	D50 (µm)
VNR0	25.0	28.2	46.8	36.2	38.8	15.6
VNRA1	-	-	-	$< 63 \ \mu m = 6.9$	93.1	493.7
VNR1	67.4	27.1	5.5	29.7	2.9	0.5
VNR2	67.3	29.0	3.7	31.2	1.5	0.7
VNR3	48.2	47.3	4.5	51.6	0.3	2.3
VNRA2	3.2	3.1	93.7	7.2	89.5	191.5
VNR4	47.5	46.1	6.4	51.1	1.4	2.3

 Table 1
 Grain size parameters of sands and clays from Vila Nova da Rainha quarry.



Fig. 4 XRD patterns of clays (total sample) from Vila Nova da Rainha quarry. Q – quartz, F – alkaline feldspars, I/M – illite/moscovite, K – kaolinite, S – smectite, G – goethite

and 192 $\mu m,$ respectively, and the contents of their fine fractions (less than 63 $\mu m)$ were estimated at ≈ 7 %.

The VNR clays (Figure 4) are characteristic by high contents of quartz and phyllosilicates, minor contents of alkaline feldspar, and vestigial contents of goethite. The studied samples have the following mineral compositions (Table 2): VNR0 clay contains quartz, smectites, kaolinite, and alkaline feldspars; the VNR1 and VNR2 contain quartz, illite, kaolinite and alkaline feldspar; finally, the VNR3 and VNR4 contain quartz, illite-smectite, and alkaline feldspar. These groups established on the basis of mineral composition are consistent with the groups which have been established on the basis of particle size distribution. Smectite is enriched in the less clay-rich layers, whereas illite is enriched in the high clay-rich lavers. These trends cannot be related to hydrodynamic conditions, because in general terms, the more proximal zones of the basin, having smaller clay contents, are richer in kaolinite, whereas the more distal ones, having higher clay contents, become enriched in illite and smectite (Chamley, 1989). Smectite-rich layers may have a detrital contribution resulting from soil erosion under hydrolyzing conditions, and such contribution would be favoured by a gradual evolution towards a better defined prevalence of alternating wet and dry climatic periods (Chamley, 1989). Therefore, a greater flux of detritus could be carried to the basin due to degradation of pre-existing cover of source areas, followed by sediment mobilization and redeposition by the rivers (Thiry and Jacquin, 1993; Rocha and Gomes, 1995; Gibson et al., 2000). Illite is a clay mineral even more

Total sample							< 2 µm frac	tion	
Clays	Q (%)	F (%)	G (%)	K (%)	I/M (%)	S (%)	K (%)	I/M (%)	S (%)
VNR0	46	23	1	10	9	11	34	28	38
VNR1	30	16	2	20	27	5	39	51	10
VNR2	31	16	2	17	24	10	34	47	19
VNR3	36	19	1	13	16	15	30	37	33
VNR4	33	21	3	12	20	11	28	45	27

 Table 2
 Mineralogical compositions, by XRD, of clays from Vila Nova da Rainha quarry.

Q-quartz, F-alkaline feldspars, G-goethite, K-kaolinite, I/M-illite/muscovite, S-smectite



Fig. 5 XRD patterns of VNR4 sample after fired at different temperatures. Q – quartz, F – alkaline feldspars, I/M – illite/muscovite, K – kaolinite, S – smectite, H – hematite, M – mullite

abundant than kaolinite in the less smectite-rich layers, suggesting that hydrolysis was not extreme and that deposition fundamentally has occurred in distal fluvial environments (Weaver, 1989; Rocha and Gomes, 1995).

After firing, as expected, the crystalline phases being identified immediately after 1025 °C are as follows: quartz, mullite, and minor amounts of hematite. The contents of these phases increase as temperature increases up to 1175 °C. Also, a glassy phase responsible for the broad diffusion band shown in the section 16-32° 2 θ of the X-ray diffraction patterns has been identified (Figure 5).

Chemical analysis data, in Table 3, shows afterwards a slightly correspondence in terms of SiO₂, Al₂O₃ and Fe₂O₃ contents with the three clay groups: VNR0 (68 %, 15 %, 5 %); VNR1 and VNR2 (57 %,

20 %, 7 %); and VNR3 and VNR4 (\approx 60 %, 18 %, \approx 6.5 %).

 Al_2O_3 contents are not very high and the concentrations of MgO, TiO₂, CaO and MnO are rather uniform, while among the alkalis there is clearly more K₂O (3.5±0.4 %) than Na₂O (0.2±0.1 %), except for VNR0 (0.8 %), condition that is mainly related with the alkaline feldspar content.

The fluorine content is within the range 0.058-0.074 % values which are consistent with those reported the literature for clays with similar bulk mineralogical and granulometric composition (Galán et al., 2002; Strazzera et al., 1997). The fluorine emission values could be minimised or inhibited by the adoption of abatement factors in the several stages of the ceramic process or by the incorporation in the ceramic pastes of additives like micronized calcium

Clays	SiO ₂	Al_2O_3	Fe_2O_3	MgO	TiO ₂		MnO	Na_2O	$\mathbf{K}_{2}\mathbf{O}$	L.o.I.	F
v	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
VNR0	68.3	15.0	4.9	1.2	1.0	0.2	0.02	0.8	3.9	4.3	0.034
VNR1	57.9	19.8	7.3	1.3	0.9	0.2	0.02	0.2	3.2	7.8	0.074
VNR2	57.3	19.6	7.0	1.7	0.9	0.3	0.04	0.1	3.3	8.1	0.080
VNR3	59.3	18.0	6.7	2.1	0.9	0.4	0.04	0.2	3.3	7.3	0.058
VNR4	60.1	18.2	6.6	1.7	1.0	0.3	0.03	0.1	3.5	7.3	0.064

 Table 3
 Chemical compositions, by XRF, of clays (total sample) from Vila Nova da Rainha quarry.

L.o.I. - Loss on ignition at 1000 °C

 Table 4 Consistency limits, Atterberg plasticity index and abrasiveness of clays from Vila Nova da Rainha quarry.

Clays	Liquid Limit (%)	Plastic Limit (%)	Atterberg plasticity index (%)	Abrasiveness @ 174000 rev. (mg)
VNR0	32	19	13	360
VNR1	47	24	23	233
VNR2	59	23	36	310
VNR3	52	27	25	350
VNR4	45	23	22	367



Fig. 6 Plastic properties of VNR clays (Bain, 1970; Bain and Highley, 1966).

carbonate (González et al., 1998; Dehne, 1987; González et al., 2002) since the VNR clays do not show carbonates in their composition.

Plasticity analysis values (Table 4 and Figure 6) indicate that VNR1, VNR3 and VNR4 clays are appropriate for plastic shaping, whereas VNR0 clay is the one that shows the lowest plasticity. VNR2 shows the highest plasticity reason why it needs to be blended in case of plastic shaping.

Abrasiveness analysis values (Table 4) are within the range 233-367 mg, the lowest values 233 and 310 mg corresponding to clay raw materials VNR1 and VNR2, respectively, these values being justified by their higher clay fraction contents. These values are correlated with D50 values ($R^2 = 0.752$), the D50 value for VNR0 being recalculated for the less than 63 µm fraction. In this context the correlation between abrasiveness values and quartz

Clays	Extrusion moisture (wet base - %)	Dry shrinkage (%)	Dry bending strength (MPa)
VNR0	19.3 ± 0.2	5.8 ± 0.3	7.2 ± 0.1
VNR1	18.0 ± 0.2	5.3 ± 0.2	10.8 ± 1.0
VNR2	19.6 ± 0.2	6.9 ± 0.2	15.8 ± 1.2
VNR3	16.0 ± 0.4	7.7 ± 0.2	21.6 ± 1.8
VNR4	21.0 ± 0.3	6.5 ± 0.1	13.9 ± 1.1

Table 5 Ceramic properties of clays from Vila Nova da Rainha quarry after extrusion and drying at 110 °C.

 Table 6
 Ceramic properties of clays from Vila Nova da Rainha quarry after firing at different temperatures.

	Total shrinkage (%)	Fired bending strength (MPa)	Water absorption (%)
VNR0			
875 °C	5.24 ± 0.10	7.07 ± 0.30	15.90 ± 0.10
950 °C	5.03 ± 0.16	7.36 ± 0.20	15.91 ± 0.22
1025 °C	5.71 ± 0.16	8.45 ± 0.20	15.32 ± 0.13
1100 °C	7.29 ± 0.33	12.00 ± 0.31	12.23 ± 0.31
VNR1			
875 °C	5.45 ± 0.13	20.09 ± 1.65	12.56 ± 0.16
950 °C	7.13 ± 0.14	33.05 ± 3.18	9.53 ± 0.21
1025 °C	10.49 ± 0.08	41.45 ± 3.77	3.47 ± 0.13
1100 °C	12.29 ± 0.16	48.04 ± 4.81	0.15 ± 0.04
VNR2			
875 °C	6.31 ± 0.15	18.80 ± 1.99	12.07 ± 0.10
950 °C	8.49 ± 0.17	36.21 ± 1.49	7.70 ± 0.28
1025 °C	11.22 ± 0.11	44.47 ± 3.62	2.91 ± 0.29
1100 °C	11.91 ± 0.36	47.80 ± 4.71	0.13 ± 0.03
VNR3			
875 °C	7.39 ± 0.16	31.96.± 2.79	10.18 ± 0.07
950 °C	7.90 ± 0.18	33.61 ± 1.77	9.41 ± 0.28
1025 °C	9.03 ± 0.22	33.73 ± 1.32	6.57 ± 0.42
1100 °C	11.20 ± 0.23	49.20 ± 4.62	4.48 ± 0.76
VNR4			
875 °C	5.82 ± 0.10	17.36 ± 1.01	11.48 ± 0.05
950 °C	6.94 ± 0.26	31.96 ± 1.52	10.26 ± 0.13
1025 °C	8.22 ± 0.17	34.90 ± 1.26	7.06 ± 0.48
1100 °C	11.77 ± 0.24	52.02 ± 4.03	1.41 ± 0.29



Fig. 7 Ceramic properties after firing of VNR0 sample.

and alkaline feldspar contents ($R^2 = 0.759$), is also significant, if VNR0 sample is excluded. In the industrial processing, particularly in the case of roofing tile, the abrasiveness of raw materials play an important role to prevent and control the abrasion of the layout equipment and specially the plaster moulds used in the shaping of roof tiles, reducing the necessary periodical maintenance, and premature replacement.

In agreement with the plasticity limits, the values of the moisture content after extrusion calculated on a wet base, method current in the ceramic industry, show linear correlation ($R^2 = 0.849$) with grain size. This is true for all samples, except for VNR0 sample that is characterized by relatively coarse grain size. The behaviour of VNR3 clay, which has the lowest extrusion moisture content and the highest plasticity, is explained by its smectite content and silt characteristics. Therefore, the behaviour of VNR3 and VNR4 clays to extrusion shaping is related with their intrinsic characteristics.

Ceramic properties assessed after drying (Table 5) show shrinkage values within the range 5-8 % and mechanical bending strength values within the range 11-22 MPa, except for VNR0 clay that shows a mechanical bending strength value estimated at 7 MPa. The values of mechanical bending strength (11 MPa) are good to support the mechanical movements involved in the layout of the ceramic products, when compared with the current values found in construction ceramic materials (Grade and Moura, 1985).

The drying shrinkage depends on various factors, the main ones being the clay mineral content and the grain size distribution. The role of smectite content introduces differential behaviours in mechanical properties related with the moisture content, particularly during extrusion shaping, as is the case of the expected mechanical bending strength values. In that sense, the energy required for the extrusion of VNR3 clay is necessarily higher than the energies required for the other clays which have lower water contents. This fact can be justified by the highest value of dry bending strength. Therefore, the dry shrinkage values are directly correlated with dry bending strength values (R^2 =0.919), both for clay and silt-clay samples.

After firing (Table 6) the values of linear total shrinkage determined at 875 °C are within the range 5.2-7.4 %, and within the range 7.3-12.3 % at 1100 °C. Beyond the temperature of 1025 °C most of the clays show shrinkage values higher than 10 % which are considered excessive.

Mechanical bending strength values determined at 875 °C are within the range 7-32 MPa, and within the range 12-52 MPa at 1100 °C. At both temperatures, water absorption values are within the range 10-16 % at 875 °C, and within the range 0.1-12 % at 1100 °C. The test specimens do not show any kind of efflorescence (Dondi et al., 1997).

Based on the obtained results, the VNR0 clay (Figure 7) exhibits a slow sintering kinetics, compared with the clays from the other two clay groups (VNR1-VNR2 and VNR3-VNR4) which show a reduction of mechanical bending strength, a reduction of water absorption, and the lowest shrinkage, related with their lower clay fraction contents and smectitekaolinite content. The VNR1-VNR2 clay group (Figure 8 and Figure 9) shows similar sintering kinetics behaviour to the VNR3-VNR4 clay group (Figure 10 and Figure 11). Therefore, VNR1 and VNR2 clays exhibit higher densification, expressed by the water absorption values of 0.15 and 0.13 %, respectively, determined at 1100 °C. On the other hand, the mechanical bending strength values of VNR3 and VNR4 clays, determined at 1100 °C, show the highest values, 49.2 and 52.0 MPa, respectively. The illite-kaolinite composition of VNR1 and VNR2 clays is responsible for the higher refractoriness comparable to the illite-smectite composition of VNR3 and VNR4 clays. Even though, the grain size fineness of VNR1 and VNR1 clays promotes the



Fig. 8 Ceramic properties after firing of VNR1 sample.



Fig. 9 Ceramic properties after firing of VNR2 sample.



Fig. 10 Ceramic properties after firing of VNR3 sample.



Fig. 11 Ceramic properties after firing of VNR4 sample.

 Table 7 Required construction ceramic properties and the corresponding properties of Vila Nova da Rainha clays (EN 14411; Sousa at al., 2003).

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Properties	Bricks Rustic floor tiles (AIIb)		Roofing tile	VNR clays
Extrusion moisture (wet base - %)	15 – 22	15 – 22	15 – 22	18 - 22
Dry shrinkage (%)	3 - 12	3 - 8	3 - 8	5 - 8
Dry bending strengh (MPa)	> 3	> 3	> 3	7 – 22
Firing shrinkage (%) ≅1000 °C	4 - 14	_	3 - 9	5 - 12
Water absorption (%) ≅1000 °C	9-17	6 – 10	4 - 12	16 – 0.1
Firing bending strength (MPa) ≅1000 °C	$6 - 14^{a} > 14^{b}$	10.4 - 15.5	12 – 22	7 – 52

a - perforated bricks b - hollow floor blocks

densification at a lower temperature than for VNR3 and VNR4 clays.

The ceramic properties shown by all the studied clays are comparable with the corresponding ceramic properties required for high quality hollow brick and roof tile.

Table 7 shows that the values obtained for Vila Nova da Rainha clays are, in general terms, suitable for the production of ceramic products with the typologies referred to Grade and Moura (1985) and established in the EN 14411 standard. In fact, they have suitable plasticity and wet-to-dry shrinkage characteristics which are appropriate for shaping using the extrusion process. Also, the properties of the fired specimens are comparable to those considered appropriate for high to very high quality construction ceramics exhibiting high to very high mechanical bending strength and low to very low water absorption.

5. CONCLUSIONS

The achieved results indicate that the clays from Vila Nova da Rainha are appropriate raw materials to be utilized on the production of construction ceramics of unit values higher than the ones which are proper of traditional hollow bricks. For instance, they could be used to produce facing bricks, roof tiles and extruded floor tiles, or even for floor clinker tiles in the particular case of VNR1, VNR2 and VNR4 clays, if fired at temperatures around 1100 °C, in order to obtain low water absorption ceramic products.

Both composition and ceramic properties of the studied clays are similar to those shown by other clays (Coroado et al., 2005; Strazzera et al., 1997; Fiore et al., 1989; Gonzalez-Garcia et al., 1990; Cuenca et al., 1993), showing suitable adequacy for extrusion shaping, since their mechanical bending strength values determined in the dry state are relatively high. The Italian clays (Strazzera et al., 1997; Fiore et al.,

1989) and the Spanish clays (Gonzalez-Garcia et al., 1990; Cuenca et al., 1993), which contain, in general, calcium carbonate, show lower mechanical bending strength values and higher water absorption values.

During firing, neither fissures nor other pyroplastic defects have been observed. Mechanical bending strength values increase and the water absorption values diminish as far as the firing temperature increases.

Clays from Vila Nova da Rainha were found to be suitable for the manufacture of a wide range of construction ceramics characterized for exhibiting high mechanic bending strength values and low water absorption values, properties suitable for the production of extruded floor and wall tiles. They could be suitable for pressed products too, but further technological tests are needed. Also, their low abrasiveness point out to their eventual use in production of technical roofing tile.

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