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ORIGINAL PAPER

Typological classification of clayey raw materials for ceramics manufacture, in the Tábua region (central Portugal)

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Abstract Mapping of clay resources in the Cenozoic deposits of the Tábua region (central Portugal) has been carried out, together with the chemical, mineralogical and technological characterization of seventeen clay samples. The study was undertaken to relate the lithostratigraphic units and the typology of raw materials with regard to the manufacture of ceramics. The sedimentary succession comprises two units with different suitability for the manufacture of ceramics: an upper unit, with clays that present technological restrictions; and a lower unit with a much greater potential. A small set of parameters has been identified which differentiate the typological units. These parameters allow a realistic estimation to be made of the ceramic properties of any clay layer sampled in the study area. It is anticipated that with minor field work and sampling, the typological column can also be used in adjacent areas.

Keywords Typological column · Mapping · Clays · Raw material · Classification · Ceramics

Résumé La cartographie des ressources en argiles dans les dépôts cénozoïques de la région de Tábua (centre du Portugal) a été réalisée, en même temps que la caractérisation chimique, minéralogique et technique de dix-sept échantillons d'argile. L'étude a été entreprise pour mettre en relation les unités lithostratigraphiques et la typologie des matières premières concernant l'industrie céramique. La séquence sédimentaire comprend deux unités présentant des caractéristiques différentes pour l'industrie céramique : une unité supérieure, avec des argiles qui présentent des contraintes techniques et une unité inférieure avec un potentiel beaucoup plus important. Un petit ensemble de paramètres a été identifié, permettant de différencier les unités typologiques. Ces paramètres permettent une estimation réaliste des propriétés de n'importe quelle couche d'argile de la région intéressant l'industrie céramique. On pense que des travaux limités de terrain et d'échantillonnage permettraient d'étendre ces conclusions à d'autres régions voisines.

Mots clés Colonne typologique · Cartographie · Argiles · Matières premières · Classification · Céramiques

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Introduction

One of the main concerns of the ceramic industry is to obtain a permanent supply of raw material and maintain quality-controlled stocks in order to ensure the consistent quality of the final products. To meet these needs, besides mapping the locations of raw materials it is essential to know their mineral composition, textural properties and technological parameters.

Establishing a detailed lithological column helps the better identification of favourable layers. The typological column corresponds to a broader concept compared with the lithostratigraphical or lithological column, in that it goes beyond identifying the lithofacies and offers a first assessment of the suitability of the raw materials for use in ceramics, based on a range of values related to its compositional and technological properties (Carvalho et al. 2000).

This study demonstrates how a typological classification of common clays can help in the exploitation planning and management of the resource as well as contributing to improved field work and mapping. The deposits studied are the common or red firing clays which occur in the Cenozoic continental sediments of the Tábua region, where an active ceramics industry based on the production of structural clay products has been established since the beginning of the twentieth century. At present there are two working plants processing some 90,000 t of local clays per year.

The Tábua region is in central Portugal and is part of the extensive Mondego planation surface (Ferreira 1978), where the exploitation of red firing clays is a traditional activity, albeit not as centralised or intensive as in other parts of the country where this resource is exploited. Red firing clay manufactured products represent about 80 % of the total ceramics produced in Portugal (Gomes 2002). The Cenozoic deposits of the Tábua region consist of two unconformable clayey sequences, which are frequently difficult to discriminate in the field. However, they have different compositions and therefore different applications in the ceramics industry.

Geological setting

The geology of the study area (Fig. 1) consists of continental fluvial and alluvial fan deposits of Cenozoic age, unconformably overlying the metasediments of the Pre-Cambrian to Lower Cambrian Beiras Group (Sousa and Sequeira 1987–1989; Silva et al. 1987–1989) and the Variscan granitoid basement rocks. In the study area, the Cenozoic sediments are siliciclastic and comprise the Coja Formation and the Serra de Sacões Group (Soares et al. 1983; Cunha 1992, 1999; Pais et al. 2012).

The Coja Formation (Middle Eocene to Lower Chattian) rests above the Variscan basement and comprises two members separated by a disconformity:

(a) the Monteira member occupies an upper stratigraphic position and includes gravels, arkoses and clays. Although usually <4 m thick, in the study area it has a maximum thickness of about 8 m.
(b) the underlying Casalinho de Cima member is not always represented but where present consists of tabular beds of massive coarse arkoses.

The Serra de Sacões Group is ascribed to the upper Tortonian to Gelasian (Cunha 1999), or even to the earliest Pleistocene. This mainly conglomeratic succession covers most of the study area and includes three formations—the Campelo Formation, Telhada Formation and Santa Quitéria Formation.

(a) In the Tábua region, the Campelo Formation (upper Tortonian to Messinian) is the most common unit comprising gravels that grade upwards to predominant silty-clays.
(b) The Telhada Formation (uppermost Messinian to Zanclean) unconformably overlies the Campelo Formation and is less common. It has an intense red colour, which results from the iron oxides in the clay matrix which penetrate into the nucleus of the phyllite/metagreywacke or milky quartz clasts.
(c) The Santa Quitéria Formation (uppermost Zanclean to Gelasian) is rarely found in the study area.

The studied sedimentary sequences belong to the Campelo and Coja Formations. The fine sediments that make up these sequences vary in thickness by up to some 15 m and are frequently intercalated with sands and/or gravels layers, usually <2 m thick.

Methodology

Field work involved mapping of the Cenozoic lithostratigraphic units at a scale of 1:10,000. This included the identification, assessment and positioning of the main clayey layers within the lithological sequence, recording information on its suitability for different ceramic purposes. To accomplish this, sediment samples were collected and characterized in terms of chemical, mineralogical and technological properties in order to establish the relationships between the lithological column and the properties of the sampled layers.

With the geometric, textural, compositional and technological information acquired, it was hoped to distinguish useful indicators to identify the locations and elevations of the main clay bodies within the sequences. This information is important because, in addition to the difficulties inherent in the mapping of the clay-rich bodies, due to the sedimentary veneer uncertainties occur regarding their stratigraphic correlation and structural interpretation. Finally, it was hoped to propose a series of threshold values for a few selected parameters which would distinguish the typological units.

To accomplish these tasks, 17 different clayey raw materials belonging to the Campelo Formation (samples C1, C2, C3, C4, C5, C6, C7) and to the Monteira Member (samples M1, M2, M3, M4, M5, M6, M7, M8, M9, M10), with a potential for the formulation of ceramic blends, were collected (Fig. 2). Due to the absence of outcrops, all samples belonging to the Coja Formation were collected in

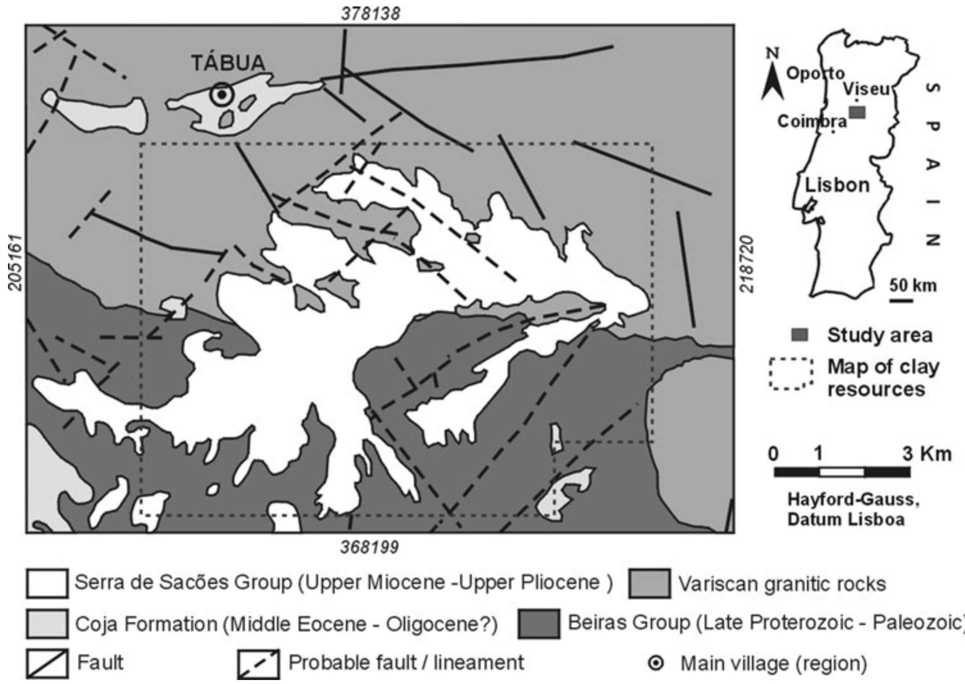

Fig. 1 Geological map of the study area (modified from Cunha 1992)

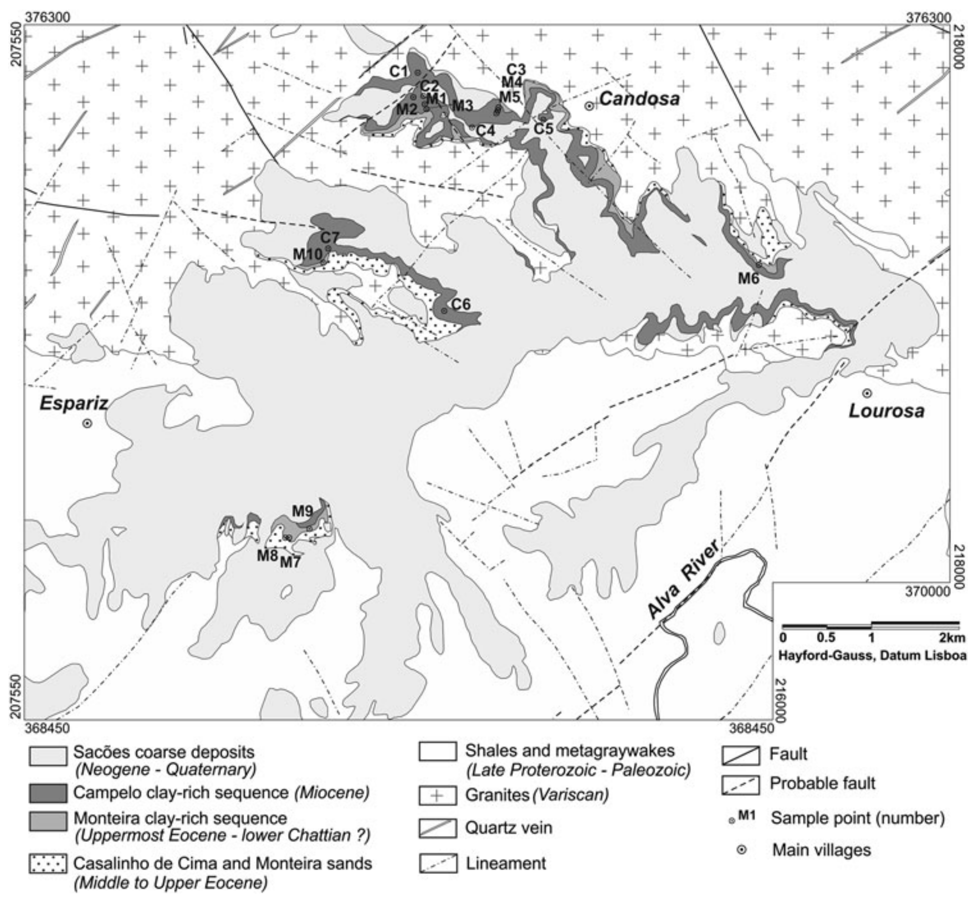

Fig. 2 Map of clay resources in the Tábua region and sample points location

clay pits. The analytical tests on samples were performed in the LNEG laboratory and are described by Lisboa (2009).

Mineralogical analysis was made by X-ray diffraction carried out on a Philips diffractometer, PW1820 goniometer with a cobalt 2,700 W bulb (PW2256/20). The data

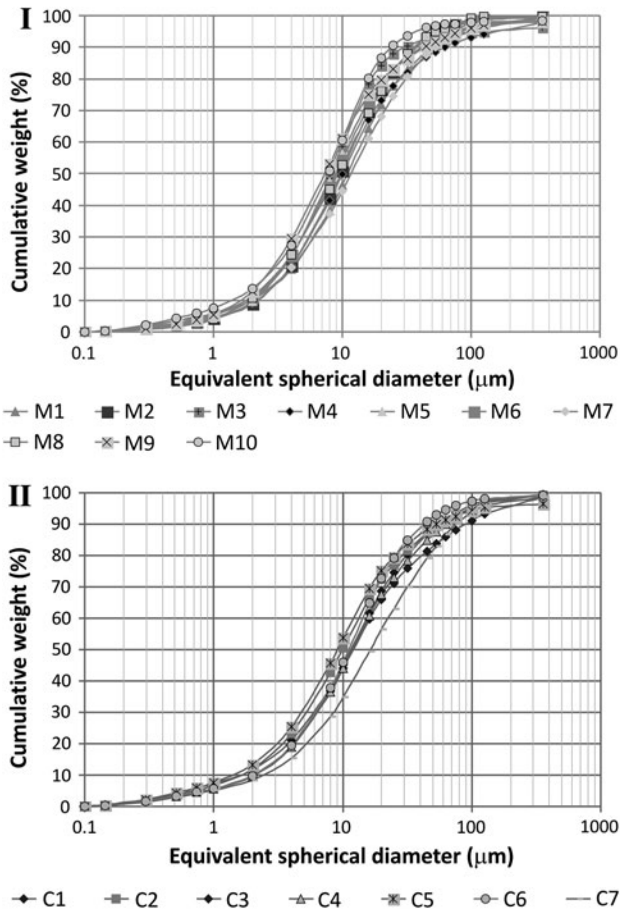

Fig. 3 Grain-size cumulative curves of the samples collected in Tábua region. I - Monteira group; II - Campelo group

were processed with the PW1877 Automatic Powder Diffraction program version 3.6 h (operating conditions: potential 40 kV, current intensity 40 mA). The relative abundance of minerals present was estimated semi-quantitatively by the reflective power method (Schultz 1964; Thorez 1976; Brindley and Brown 1980). For the chemical analysis, bulk samples were analyzed for their major elements by X-ray fluorescence spectrometry on fused discs using a Philips PW 2404 equipped with Rh tube and monochrometer. Tube voltage and current were 40 kV and 60 mA, respectively. Loss on ignition (LOI) was determined by heating at 1,050 °C for 1 h. The pH was determined by the method of selective electrodes in accordance with internal procedures, based on standard LNEC E203 (1967) using a Sentron 2001 pH System meter (calibration at 20 °C). Two measurements were made per sample: the first after 1 min and the second after a 15 min interval in order to ensure the pH had stabilized.

To assess the technological affinities of the samples, the parameters considered were: grain size, plasticity index, bending strength, shrinkage green/dry, total shrinkage at 900 °C and water absorption capacity at 900 °C. Concerning colour, the reddish intensity (parameter *a** CIE Lab) was also considered a discriminating parameter in the Tábua region.

The particle size distribution was undertaken using a Coulter LS130 laser granulometer following DIN 4022-1 (1987). The plasticity index was calculated on the basis of the Atterberg limits following the Portuguese Standard NP-143 (1969). Bending strength was estimated based on ASTM C 689/93 (1993), according to the LNEG laboratory standard procedures, using a Zwick Z010 tensiometer with a 2 kN load cell. The operating conditions were: 10 cm spacing between support blades and loading speed of 10 mm/min. After firing at 900 °C the procedure was based on ASTM C 674/88 (1988), with the same operating conditions of the green to dry test, but with a 10 kN load cell. Dry and fired linear shrinkage were obtained based on ASTM C 326/82 (1982). Determination of water absorption followed the LNEC E216 (1968) specification.

Results and discussion

The major lithostratigraphic units mapped in the Tábua region are those comprising the basement (shales and metagreywackes, granites and quartz veins) and the sedimentary cover. The latter consist of informal units organized, from top to the bottom, in four main lithofacies associations (Fig. 2):

- *Sacões coarse deposits* predominantly gravelly and sandy facies, interbedded with silty-clayey lenses. This lithofacies corresponds to the Telhada and Santa Quitéria formations, but also to the slope deposits which veneer most of the other deposits.
- *Campelo clay-rich sequence* comprises silts and clays of the Campelo Formation, predominantly reddish or brown in colour, sometimes with sandy intercalations, overlying a basal gravel.
- *Monteira clay-rich sequence* predominantly consisting of greyish or yellowish silt and clay beds. This sequence comprises the upper part of the Monteira Member.
- *Casalinho and Monteira sands*—in the few areas where it occurs, this lithofacies is relatively thin and comprises feldspathic sands, which correspond to the Casalinho de Cima Member and the lower part of the Monteira Member.

The samples were collected in the fine facies of the Monteira Member and Campelo Formation (Monteira and Campelo clay-rich sequences). The main results can be summarised as:

(a) The samples show a marked homogeneity in grain size distribution, with a high silt component (Shepard

Table 1 Average mineralogical (bulk samples and clay fraction) and chemical compositions (bulk samples), color CIE Lab (raw samples and after firing at 900 °C) and pH after 1 and 15 min, of upper and lower sequences

Group	Bulk sample						<2 µm fraction				
	Sm/Sm-Int	Illite/mica	Kaol	Qtz	Felds	Hem	Sm/Sm-Int	Illite/mica	Kaol	Qtz	Hem
Campelo											
x	–	35	24	37	2	2	1	44	52	2	1
sd	1	5	4	6	1	1	3	6	6	1	–
Monteira											
x	10	35	15	34	5	1	26	39	29	6	–
d.p.	6	6	6	7	2	1	14	7	12	5	–

Group	SiO_2	Al_2O_3	Fe tot	MnO	CaO	MgO	Na_2O	K_2O	TiO_2	P_2O_5	L.O.I
Campelo											
x	64.68	18.29	6.03	0.03	0.04	0.44	0.24	2.65	1.09	0.09	6.28
sd	2.04	1.09	0.60	0.01	0.01	0.13	0.10	0.27	0.11	0.02	0.47
Monteira											
x	61.89	17.90	5.95	0.05	0.09	1.26	0.28	3.06	0.88	0.06	8.43
sd	3.67	2.54	1.08	0.05	0.04	0.39	0.14	0.49	0.07	0.02	1.07

Group	$pH_{1'}$	$pH_{15'}$	L*	*a**	*b**	$L^*_{900\ °C}$	$a^*_{900\ °C}$	$b^*_{900\ °C}$
Campelo								
x	5.20	5.04	62.29	25.21	32.57	58.04	30.26	29.40
sd	0.69	0.59	2.27	2.86	3.16	1.77	1.59	1.80
Monteira								
x	5.89	5.67	74.65	8.35	22.95	58.45	24.14	27.64
sd	0.64	0.63	5.57	7.16	6.76	4.66	4.67	1.72

x average, *sd* standard deviation, *Sm/Int* smectite and interstratified clay minerals, *Kaol* kaolinite, *Qtz* quartz, *Felds* feldspars, *Hem* hematite

1954). They are poorly sorted, although the samples from the Monteira sequence (Fig. 3a) are slightly better sorted than those from the Campelo sequence (Fig. 3b).

(b) Average mineralogical compositions (Table 1) indicate quartz as the major mineral in both groups of samples. Feldspars and hematite occur in minor amounts, though the alkali feldspar content is higher in the lower group. Regarding clay minerals, the samples of the Campelo sequence have a significant kaolinite content and expansive clay minerals are virtually absent. The phyllosilicates in the Monteira samples are predominantly illite/mica with kaolinite as well as smectite and interstratified clay minerals. In the clay fraction the mineralogical composition indicates an increase in kaolinite in the near surface zone.

(c) The chemical analysis shows a high silica content and a relatively low alumina content (Table 1). The major elements content correlates with the mineralogical composition, as indicated by the higher MgO content in the lower group of samples which can be related to the presence of smectite and interstratified clay minerals. Loss on ignition values reflect the clay mineral composition and the presence of hydroxides. All samples show an acid pH compatible with red firing clays (Table 1).

These sequences can be divided into two typological units in terms of potential raw materials for ceramics (Fig. 4):

(a) the Campelo typological unit, consisting of clays which could present some problems for the manufacture of ceramics;

(b) the Monteira typological unit with a higher potential for use in the ceramics industry.

The Campelo unit is made up of quartz and illite/mica-kaolinite phyllosilicates. The silt content is lower and the sand fraction higher than in the Monteira unit. An important consideration is the colour; the Campelo clays are generally darker and more red than the Monteira clays (see also Table 1).

The Monteira unit includes quartz as well as illite/mica-kaolinite and smectite. This is a distinguishing characteristic as swelling clays are scarce or absent in the upper unit. The kaolinite content is also lower than in the Campelo unit.

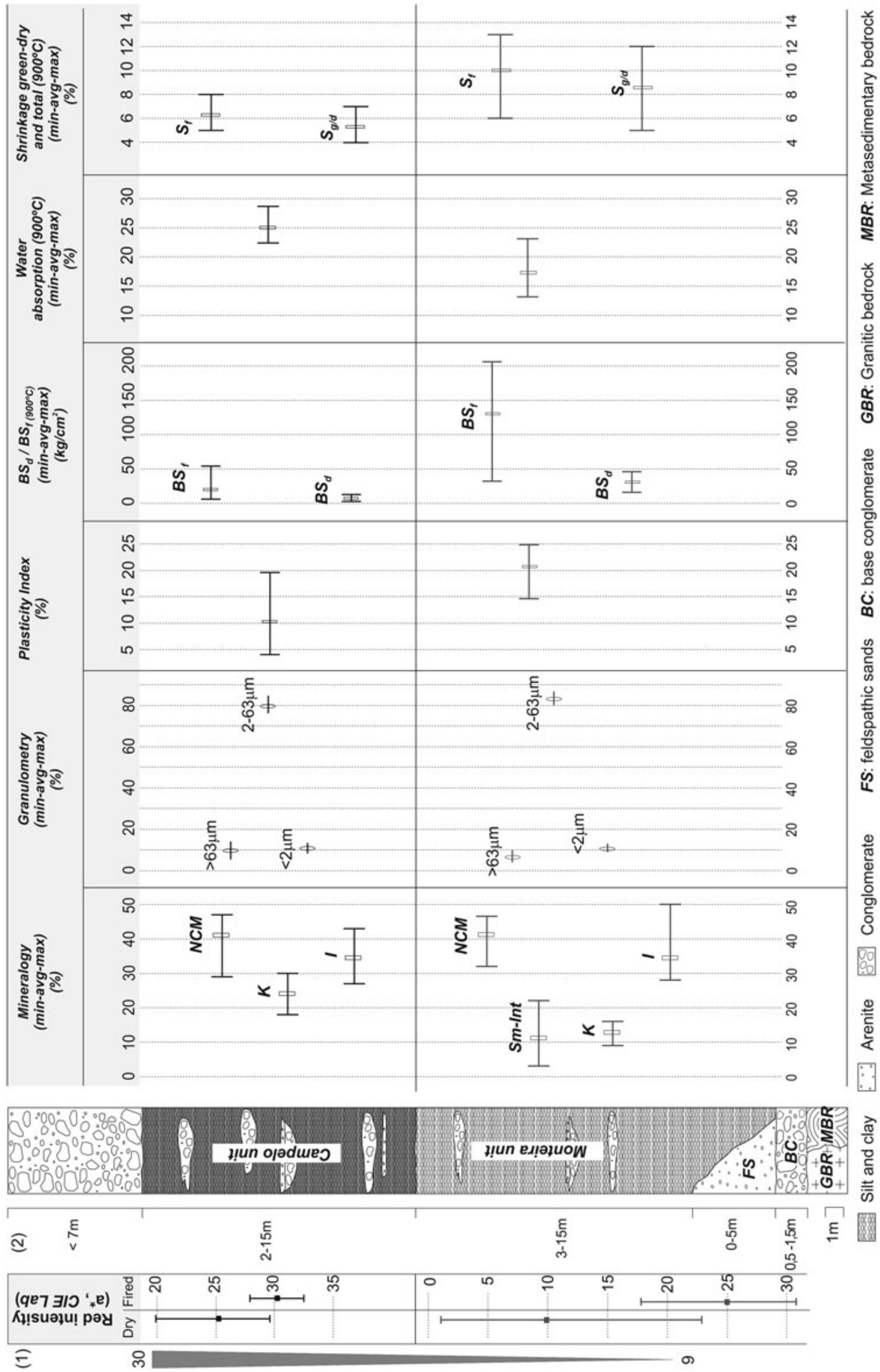

Fig. 4 Typological column for the Tábua region. (1) kaolinite concentration tendency according to its relative position in the sedimentary column, with semi-quantitative maximum and minimum observed values; (2) visible thickness, maximum and minimum. NCM -non clay minerals; I - illite/mica; K - kaolinite; Sm-Int - smectite and interstratified clay minerals; BS - bending strength, dry (d) and after firing at 900 °C (f); S - shrinkage green-dry (g/d) and total (t)

Table 2 Reference values for ceramic blends used in common ceramic product manufacturing and mineralogical composition type for hollow brick manufacture (Gomes 2002; Martins 2007)

Parameters	Brick	Vaulted brick	Tile	Mineral	%
BS_d	45–50 kg/cm^2	50–60 kg/cm^2	70–90 kg/cm^2	Quartz	30–40
S_d (max value)	5 %	5 %	6 %	Illite/mica	20–30
Drying cicle	24–48 h	24–36 h	48 h	Calcite/dolomite	0–25
Firing temp.	900 ± 50 °C		1,000 ± 50 °C	Chlorite	0–10
BS_f	≥100 kg/cm^2	≥130 kg/cm^2	≥160 kg/cm^2	Kaolinite	0–15
S_t	5–6 %			Smectite	0–20
Water absorption	10–17 %		Max 10 %	Feldspar	5–10
				Fe oxides, hydroxides	5–10

The technological parameters reflect the particle size distribution and chemical–mineralogical composition. Both units have high water absorption and variable plasticity, fired bending strength and shrinkage; particularly the latter two in the Monteira unit. On average, the Campelo group of samples show higher water absorption while plasticity and BS values (dry and fired) are low. The Monteira unit has a higher green to dry and total shrinkage.

When comparing the average values obtained for water absorption, bending strength and retraction with the corresponding technological properties' reference values (Table 2) it can be seen that for structural clay products (brick, vaulted brick and tile), most clays of the Campelo unit do not satisfy the values required except for shrinkage. These materials therefore have limited potential for the manufacture of brick, vaulted brick and masonry, unless blended with fine and plastic clays. The Monteira clays generally satisfy the required values for water absorption and fired bending strength, although dry bending strength values are frequently below the accepted minimum value and total retraction is high for ceramics manufacture hence again the clays require appropriate blending.

Conclusion

Mapping the common clay resources in the Tábua region resulted in the identification of two clay-rich sequences and corresponding typological units with a distinct ceramics potential. The laboratory characterization of the clays was a crucial part of the exercise.

A small set of parameters with major significance for differentiating the typological units was selected. In the Tábua region:

- The Campelo unit shows minor (≤5 %) occurrences of smectite or interstratified clay minerals with smectite. From a ceramic viewpoint, the water absorption is high, generally >22 %, and the raw colour parameter *a** is ≤20 %;
- The Monteira unit is characterized by the presence of smectite or interstratified clay minerals with smectite. Water absorption is usually <22 % and the raw colour parameter *a** is ≤20 %.

The study has shown that some common tests for characterization of clays allow clay layers to be placed in the proposed typological units, which demonstrate properties important to their use in the ceramics industry. Knowing both the lithological and typological sequence, the relative position in the sedimentary column of any clay-rich material sampled in the region can be estimated and a preliminary characterization made of the material from a ceramics viewpoint. This is a major advantage in areas such as the present one, because:

(a) clay layers are covered by younger deposits and are rarely exposed, such that mapping is very difficult;
(b) the textural similarity between layers makes it difficult to distinguish the sequences;

As the study area is part of a broader area where the lithostratigraphical sequence is quite similar, it is likely that this classification will be applicable to adjacent areas, although this should be confirmed with some minor field work and a sampling study.

Finally, the typological column is a contribution to the sustainable exploitation of clay raw materials deposits, taking into account the needs of ceramic producers.

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