Geology and Application of Clays Used in Castellon Ceramic Cluster (NE, Spain)

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Abstract

The general characteristics and technological properties of ceramic clays used in the Spanish ceramic cluster (Castellón province), have been investigated. Red clays for ceramic wall tiles and floor tiles are mainly extracted in the Valencian Community, in Villar del Arzobispo, La Yesa, Chulilla, Alcora (Más Vell) and San Juan de Moró, although there is a small proportion coming from Teruel province. An important group of clay raw materials used in the ceramic cluster of Castellón, in Spain, occurs in Permo-Triassic, Cretaceous and Tertiary sediments. These clays are intended for applications in stoneware. Clays were analyzed by X-ray diffraction, chemical composition, particle size distribution, thermal analysis and plasticity. Ceramic bodies were fired at temperatures varying from 850 to 1150ºC to determine the linear shrinkage, water absorption and flexural rupture strength.

Keywords: Ceramic clays, Technological behaviour, Economic geology, Castellón province

1. Introduction

The ceramic tile manufacturing process starts with raw materials mining. Most of these raw materials have a mineral nature, and the extractions are usually verified throughout miner tasks on site in the deposit. The quality of the clays which are used in the ceramic process are directly associated with the geologic factors and conditions of the deposits during the sedimentation stages, so the geological knowledge during mining is a basic tool which is involved directly in the quality control.

There is a close relationship between the mineralogical nature of the raw materials used in the ceramic process and the types of ceramic products manufactured. This customization is achieved thanks to the qualitative knowledge of the mineral phases which constitute the raw materials used and the mineral dynamics generated on these raw materials when they are subjected to each and every one of the industrial process step (homogenization, humidity, dry, conformation, firing, etc) by which a ceramic piece is generated. A reasonable and suitable mining plan of the ceramic minerals deposit is an excellent way to control the quality of the manufactured products (De la Fuente *et al*., 1992).

Clay's technological properties are related with their mineralogical composition, physical properties, and with their relative proportions. The knowledge of the mineralogical influence on the technological properties of clays let us improve our understanding about their behaviour and interpret accurately the variations occurring during the mining process in deposits (García-Verduch, 1973).

For instance, the clay's plasticity is one of the most important technological properties which are related to different parameters such as: organic matter content, and the amounts and types of clay minerals present (Worrall *et al*., 1953). The most disaggregated clay minerals, with major ionic exchange capability are more plastic (Holdridge, 1956). Normally, montmorillonitic minerals are most plastic, then illitics, and finally kaolinitics with a major closed structure. Inside every one of these groups, there exists significant variability of characteristics, depending upon degrees of crystallinity, crystalline structures, particle size distribution and specific surface, with a major capability to absorb water (Galan *et al*., 1974).

A significant body of literature exists on ceramic clay mineralogy and geochemistry. It is well known that industrial clays have a complex mineralogical composition, which makes the study of mineral phases present in the raw material, rather difficult. A series of transformations controlling the final properties of the ceramic products occur during the firing process of phyllosilicates and accompanying minerals like quartz, feldspar, calcite, dolomite and hematite (Gonzalez-Garcia *et al*., 1990 and Jordán *et al*., 1999, 2001). Through the ceramic process, once the crystalline structures of these minerals exceed their stability limits, they are partially decomposed while simultaneously others are being formed. The destruction of the pre-existing structure does not occur instantaneously (Jordán *et al*., 2008). The knowledge of the origin, diagenesis and physicochemical composition of the clays is essential in order to search suitable compositions when these are required for ceramic production (Sanfeliu, 1987 and Sanfeliu and Jordán. 2009).

Clay's properties are controlled by clay mineral proportion, mineral type, and chemical composition. Although, is very difficult to evaluate this influence in a quantitative way due to their complex and variables structures that largely determine their behaviour. So, the geological background conditionate all of these parameters (Weaver *et al*., 1973).

The main objective of this study is the knowledge of composition and technological behaviour of clays. They are the main raw materials used in the ceramic cluster of Castellón. The best understanding of clays: composition, mineralogy, texture, it can optimize the ceramic process. The positive results obtained in this set of preliminary tests lead us to envisage new research programs in Spain, focused on testing other raw materials on a semi-industrial scale, assessing the effective possibility of using them as ceramic raw materials in the local ceramic industry.

2. Castellon Ceramic Cluster

The tile and clay pavement industry is basically mainly located in the province of Castellón, in Spain. Nowadays, more than 50% of its production is exported. The manufacture of wall tiles, floor tiles and ceramic coating uses red clays as raw materials. The white body clays or ball-clays hardly reach 5% of the total amount. Other raw materials are also consumed used, such as kaolin, calcined clays, feldspars, siliceous sand, mineral pigments, etc, which are not going to be considered in this article. The focus of this paper is developed on a very prestigious sector at an international level, ranking on the top four as a world-wide producer. The production and sales data from 2003 to 2008 are shown in Table 1. In addition, in the Table 2 is showed the ceramic tile Spanish production typology (Note 1) (Note 2).

There are two types of clays consumed in this sector: red clays and white or ball clays. In order to reach the proper homogeneity, purity and particle size to get the final product quality, the previous preliminary treatment of the clays is necessary in the manufacture process. Two treatments are used:

i) a dry-via, or grinding without adding water

ii) humid-via or atomization.

The dry-via process is more frequent among Catalan companies which manufacture ceramic products processed by extrusion (face bricks, tiles), while those located in Castellón mainly use atomization processes. Atomization processes consist of pulverizing the clay suspended in water against a warm air flood. The result is microscopic spheres of clays filled with air, which are very appropriate for the dry pressing of floor tiles.(Note 3)

3. Red clays from Castellon ceramic cluster

The distribution of the main clay raw materials used in the ceramic industry in Castellon is shown in the Figure 2 as well as their classification in the Table 2. These clayish materials come from deposits of Castellón, Valencia, and Teruel provinces, and belong mostly to Permo-Triassic sediments, specifically to Saxonian and Buntsandstein facies, Cretaceous sediments of the Weald and Utrillas facies, and Tertiary sediments from Neogen (Sanfeliu, 1991, 1999). (Note 4)

The main feature of these clays and in general of all the sedimentary deposits is the heterogeneity of its mineralogy. This fact leads considerable variability of their properties at the production level. Such inconvenience can be minimized by using the homogenization systems carried out in the mine exploitations themselves, in the atomizers or in the manufacturing companies. In general, such systems consist of building up piles (backlogs) of horizontal layers made up of materials of various qualities coming from different exploitation areas (Meseguer *et al*., 2007). (Note 5)

The importance of these raw materials is their relatively proximity to the manufacturing centres, presenting as a common characteristic a high level in iron oxide content, incorporated in the mineral structure of the hematite. Consequently, these raw materials are used for manufacturing red ceramic tiles (Meseguer *et al*., 2007). The classification of these red clays is based on their cronostratigraphical origin and also their carbonate content, which is linked to the geological background of each deposit. (Table 3) (Note 6)

4. Experimental

The main deposits of red clays used in the formulation of ceramic pastes in Castellon ceramic cluster have been selected. Raw materials, 50 samples for each deposit, were oven-dried at 110ºC until constant weight. They were then ground with a hammer mill to null residue in the 630 micron control sieve, following normal practice in ceramic laboratories (Meseguer *et al*., 2009a).

The mineralogical analysis was carried out using a Siemens D-5000 diffractometer, CuKα radiation, both on powder (bulk samples) and oriented aggregates (natural and treated with ethylene glycol and heated to 550ºC for 2 h).

The chemical analysis was obtained by X- ray fluorescence (Bruker S4 Pioneer) using the conventional techniques (Meseguer *et al*., 2009b). CaCO3 content was determinated by calcimetry (Bernard method).

The Pfefferkon method was used for determined the plasticity index (PI). After moistening to obtain a shaping paste, the drying capacity of the clays was determined by using a barelattograph to trace the Bigot curve.

To simulate industrial pressing conditions, the clays were moistened by hand, mixed sufficiently and sieved (1 mm) until homogeneous agglometates were obtained with 6 % water, left to rest for 24 h and then pressed (250 Kg/cm^2, 80 x 40 x 5 mm) by using a laboratory press.

Finally, we have to take into account that there is a 15% loss during the manufacturing process due to the evaporation of the natural water and the loss of ignition.

5. Results and discussion

Clays can be classified depending on its CaCO3 content (Table 3). Table 4 shows the chemical composition of bulk samples of the deposits studied. The purpose for this was to be able to process the maximum amount of data possible in the statistical treatment of the samples.

The chemical composition (Table 4) of the samples shows a high iron content in Moró and Villar clays (> 7%), responsible for the reddish colour developed upon firing. However, the iron content in calcareous clays is low (around 4 %). Moró and Chulilla clay samples show the highest relative amount of alkalis (Na_2O + K_2O), explaining why this sample matures at relatively low temperatures. By contrast, the higher amount of carbonates in Mas Vell. Sitjar and Araya clay samples might explain the delay in the sintering process. Decarbonation is a strongly endothermic reaction that generates a high volume of gas, leading expansive reactions (Cultrone *et al*., 2004). (Note 7)

Table 5 and 6 shows the mineralogical composition of the clay samples and their ceramic characterization. (Note 8) (Note 9)

The Tertiary clays of the province of Castellón have a mineralogical composition which, shows the presence of kaolinite, chlorite and some interstratified elements in varying quantities. Other mineral phases are: montmorillonite, quartz, gypsum, calcite and feldspars. The clay fraction is made up of illite and/or kaolinite and/or chlorite and/or interstratified elements. Its mineralogical and chemical composition controls its technological properties, which in turn determine its use in manufacturing porous products (Carretero *et al*., 2002). "Arcilla de Moró" is the commercial name for one of the most widely used clays since the 70s (Jordan *et al*., 2009). It was initially used for manufacturing bricks and then for manufacturing ceramic tile bodies. An essential aspect related to this raw material is the nearness of the exploitations to the manufacturing centres. This fact represents an added advantage not only with respect to the other raw materials of the same characteristics, whether those in Villar del Arzobispo (Valencia) or in Galve (Teruel), but also to new raw materials such as the clay from Morella (Castellón). From a ceramic point of view, the "arcilla del Moró" is classified as a low carbonate content raw material (<5%), mainly used in the press manufacturing of red paste glazed stoneware. These raw materials belong to Upper-Permic (Sanfeliu *et al*., 1987). The association of minerals of the clay typical of the inferior unit and of the "arcilla de Moró" is made up of illite ± kaolinite ± chlorite ± I/S ± K/S.

The clay from Morella shows the following mineralogical composition: quartz (33%), illite (14%), sodium feldspar (7%), potassium feldspar (3%), hematite (7%), chlorite (3%) and calcite (Table 5). The technological properties of the red clays from Morella make it being very suitable for manufacturing low-porosity products –such as glazed stoneware. The balance of properties – plasticity-unfloculability-pressibility- is optimum (Sánchez *et al*., 2005). (Note 10)

6. Conclusions

As we can appreciate by mineralogy and geochemical characterization, deposits show an important heterogeneity; this fact leads to an important variability of the properties in the different materials and products. Such inconvenience has been minimized by using the homogenization systems carried out in the mine exploitations themselves, in the atomizers or in the manufacturing companies. In general, such systems consist of building up piles (backlogs) of horizontal layers made up of materials of various qualities coming from different exploitation areas.

Red clays have in general an illitic-kaolinitic nature with medium or high iron oxide content, on average higher than 3% (in weight). All studied clays seem to be easily adaptable to a correct dry pressing ceramic process. In particular, illite-kaolinite-rich samples shows the best mechanical behaviour.

The more suitable application for the Tertiary clays of the province of Castellón woud be associated to manufacture porous products. The technological properties of the red clays from Morella, Villar, or Galve make these raw materials more appropriate for manufacturing low-porosity products –glazed stoneware.

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Notes

Note 1. Production and sales of the Castellon ceramic tile industry (Spain). Sales in million € and production in million m^2. Source: Ascer.

Note 2. Spanish production typology (x $1000m^2$). Source: Ascer.

Note 3. Ceramic tile manufacturing process (source ASCER).

Note 4. Geographical distribution of the main exploitations of the red clays used in the Castellon ceramic cluster.

Note 5. Geological background of the main quarries, setting in the south-oriental portion of the Iberian mountain range (source Vera, J.A.-IGME, 2004).

Note 6. Classification of the main raw materials for red-coloured substrate used in the ceramic industry of Castellón. Castellón (Cs), Valencia (V) and Teruel (Te).

Note 7. Chemical composition (% weight) of main Red-clays used in the ceramic industry of Castellón.

Note 8. Mineralogical composition (% weight) of main Red-clays used in the ceramic industry of Castellón.

Note 9. Ceramic characterization of some of the main Red-Clays used in the ceramic industry of Castellón. Legend: * Pfefferkorn; ** pressure 250 kg/cm^2

Note 10. Permo-triassic clay deposit from Sant Joan de Moró, Castellón.

Table 1. Production and sales of the Castellon ceramic tile industry (Spain). Sales in million € and production in million m^2 (Source: Ascer.)

	2003	2004	2005	2006	2007	2008*
Production	583.4	595.5	609.2	608.4	584.7	494.7
Domestic sales	1,379	1,5	1,609	1,799	1,871	1,46
Exports	1,939	1,977	2,041	2,183	2,295	2,211
Total sales	3,318	3,477	3,65	3,982	4,166	3,671

Table 2. Spanish production typology (x $1000m^2$) (Source: Ascer.)

Production	2002	2003	2004	2005	2006	2007
Extruded	19.073	18.955	19.482	19.800	19.924	20.900
% total production	*3,1%*	*3,2%*	*3,3%*	*3,3%*	*3,3%*	*3,6%*
Porcelain tiles	48.187	59.527	73.964	94.675	113.534	116.207
% total production	*8,0%*	*10,2%*	*12,4%*	*15,5%*	*18,7%*	*19,9%*
Wall tiles	236.324	233.356	234.989	238.132	242.054	239.956
% total production	*49,9%*	*40%*	*39,5%*	*39,1%*	*39,8%*	*41%*
Glazed floor tiles	302.116	271.562	267.066	256.593	232.887	207.637
% total production	*49,9%*	*46,5%*	*44,8%*	*42,1%*	*38,3%*	*35,5%*
Red body clays	493.370	458.775	453.349	447.794	431.458	400.552
% total porcelain tiles	*81,5%*	*78,6%*	*76,1%*	*73,5%*	*70,9%*	*68,5%*
Ball clays or white body clays	112.330	124.625	142.151	161.406	176.942	184.148
% total production	*18,5%*	*21,4%*	*23,9%*	*26,5%*	*29,1%*	*31,5%*

Table 3. Classification of the main raw materials for red-coloured substrate used in the ceramic industry of Castellón. Castellón (Cs), Valencia (V) and Teruel (Te)

DENOMINATION	% weight	ORIGIN		
		Permo triassic	Cretaceous	Tertiary
Low carbonate content clays	< 5	Sant Joan de Moró (Cs)	Morella (Cs) Villar (V) Higueruelas La Yesa (V) Galve (Te)	
Medium carbonate content clays	5-15		Chulilla (V)	
High carbonate content clays	> 15			Mas Vell Sitjar Araia (Cs)

Table 4. Chemical composition (% weight) of main Red-clays used in the ceramic industry of Castellón

Red Clay	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	L.O.I.
Moró	60,2	19,2	7,69	1,79	0,84	0,35	4,95	0,85	4,6
Villar	57,5	21,9	7,66	0,62	1,44	0,44	3,55	1,09	6,3
Galve	59,4	23	5,98	1,24	1,19	0,24	3,41	0,62	5,6
Chulilla	54,7	20,1	6,41	2,41	2,85	0,14	4,65	0,94	7,8
Mas Vell	43,7	15	4,84	13,2	2,5	0,26	4,48	0,56	15
Sitjar	31,1	13,4	4,39	23,6	1,36	0,2	3,67	0,26	21,7
Araya	31,1	14,3	4,24	22,8	1,72	0,16	3,83	0,62	21,8

Table 5. Mineralogical composition (% weight) of main Red-clays used in the ceramic industry of Castellón

Red Clay	Kaolinite	Illite	Quartz	Carbonates	Feldspars	Fe&Ti compounds	Chlorite	Others
Moró	18	26	42	4	2	7	-	1
Villar	19	22	39	3	8	7	-	2
Galve	22	21	35	3	8	7	3	1
Chulilla	10	24	34	11	8	6	5	1
Mas Vell	10	18	28	31	8	4	-	1
Morella	15	14	33	3	10	7	3	-

Table 6. Ceramic characterization of some of the main Red-Clays used in the ceramic industry of Castellón. Legend: * *Pfefferkorn; ** pressure 250 kg/cm^2*

CLAY TYPE	Upper fraction 63µm (%)	Plasticity *	LC1150ºC	Apparent Density**
MORÓ	7,5	14-16	3,5	2,14
MADROÑO	3	20-23	7,5	1,99
GALVE	4,5	21-22	5,7	2,04
MORELLA	6	18-19	6	1,98
LA YESA fundente	2	23	8,5	1,93
LA YESA refractaria	4,5	19	2,9	2,02
CAMPILLO (Mas vell)	6	18-20	1,5	1,95

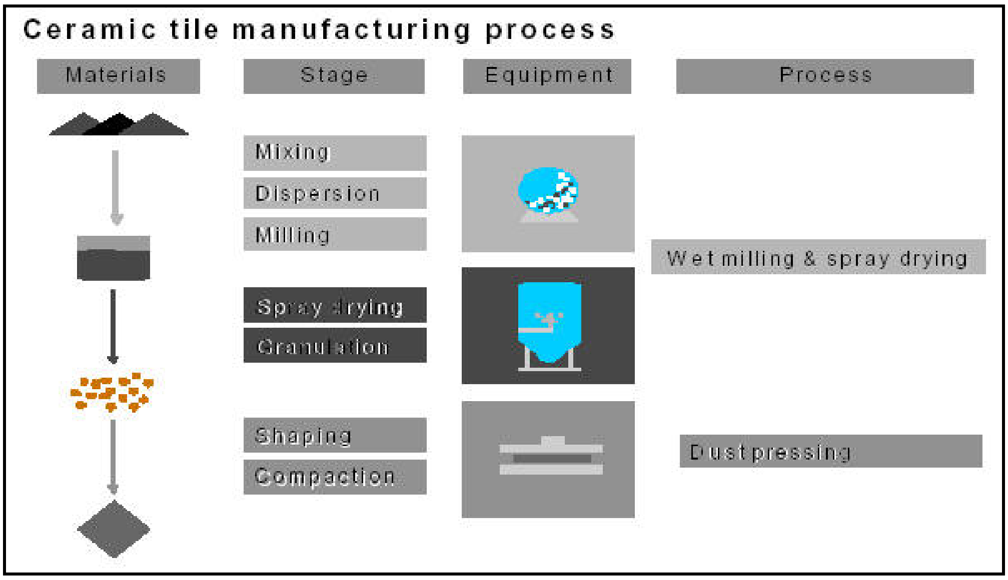

Figure 1. Ceramic tile manufacturing process (Source: ASCER)

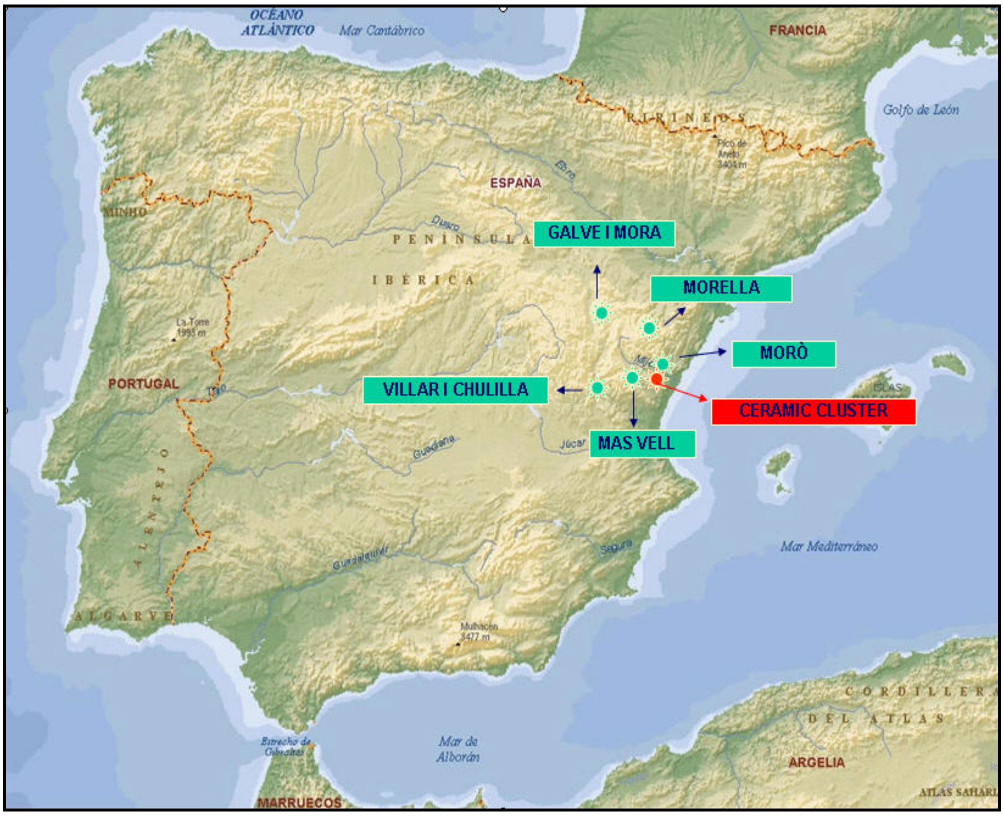

Figure 2. Geographical distribution of the main exploitations of the red clays used in the Castellon ceramic cluster

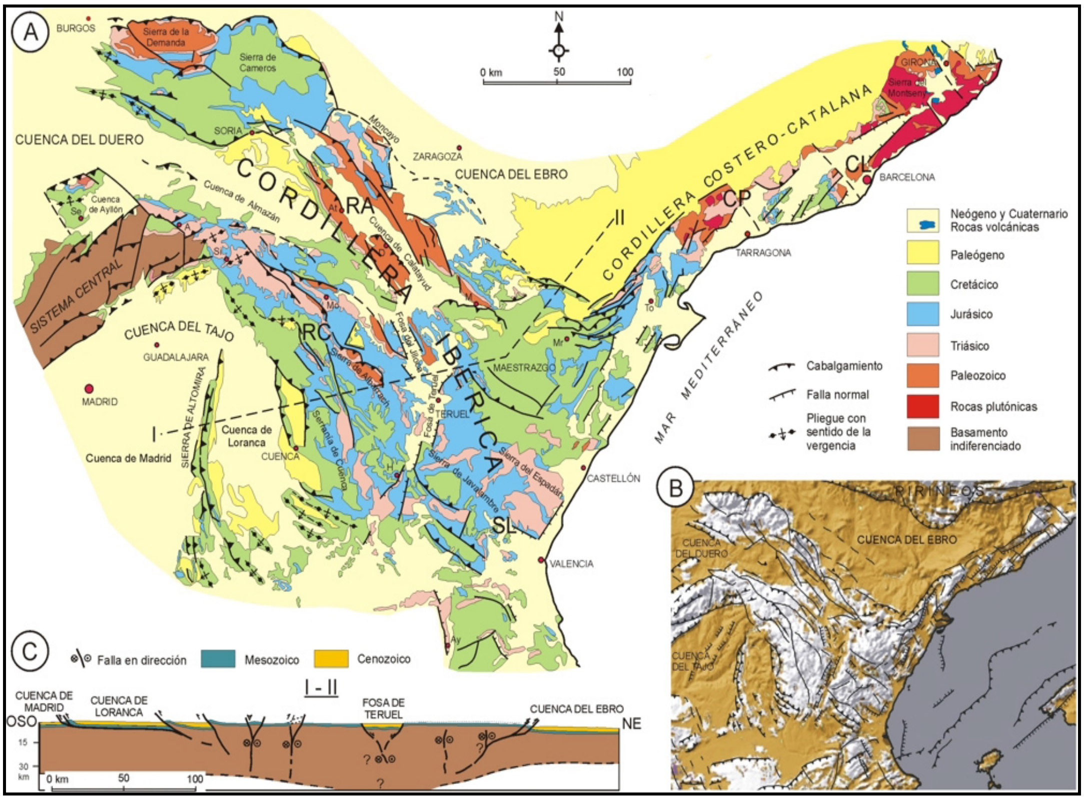

Figure 3. Geological background of the main quarries, setting in the south-oriental portion of the Iberian mountain range (Source: Vera, J.A.-IGME, 2004)

Figure 4. Permo-triassic clay deposit from Sant Joan de Moró, Castellón