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## *A Clay Odyssey*



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## Fibrous clay minerals as lithostratigraphic markers in a Tertiary continental deposit (Malpica do Tejo, Portugal)

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Fibrous clays are very common in the Iberian Peninsula, especially in the Tagus Tertiary Basin in several stratigraphic levels of deposits of Palaeogene age. We report here on a sedimentary profile located in a small tectonic basin (Castelo Branco, Eastern Portugal) in which the sediments, mainly feldspar and quartz, are detrital. A lithostratigraphic scheme is proposed for this region based mainly on statistically distinct clay mineral suites. The statistical approach was useful in differentiating among several lithostratigraphic levels, and their classification based on mineralogical parameters. This leads to a better clarification of the variables that discriminate the units, emphasising the importance of the clay mineralogical associations, especially palygorskite in the Palaeogene levels.

### 1. INTRODUCTION

The first sedimentological studies done on the Portuguese Tagus Tertiary basin were those of Carvalho (1967, 1968, 1969), in which palygorskite was shown to be associated with smectite at several stratigraphic levels of deposits attributed to the Palaeogene. In Portugal, palygorskite occurs almost always in a Tertiary context, being mainly associated with montmorillonite and more rarely with illite and kaolinite (Carvalho, 1964; Carvalho and Alves, 1970; Grade and Moura, 1981). Dias (1998) presented the “state of the art” concerning fibrous clay minerals in the Portuguese deposits with respect to the geological contexts as well as the main mineralogical associations.

In this paper, a sedimentary record of a Portuguese Tertiary deposit located in Beira Baixa is presented. In this deposit, the presence of palygorskite is important as a lithostratigraphic marker (Dias, 1998; Dias and Prates, 1997), and as a means for testing statistical analysis of the mineralogical parameters. These deposits fill two small tectonic basins, Sarzedas and Castelo Branco, and are mainly detrital, conglomerates rich in feldspar and quartz, sandstones or silty-sandstones. The studied profile is located in the Castelo Branco basin. The basement is a “schist-greywacke complex” dated from Precambrian-Cambrian, intruded in some places by the granite plutons of Castelo Branco and Penamacor, by the Pre-Hercynian of Salvaterra do Extremo, Zebreira and Segura, and also by veins of quartz, pegmatite, aplite, microgranite and basic rocks. Some higher upper units are covered with a “raña” deposit (Plio-Quaternary), which consists of a red fanglomerate of quartzite pebbles.

## 2. MATERIALS AND METHODS

Several lithostratigraphic sections have been analysed and thirty-six representative samples have been collected of the different beds of the Tertiary sediments of the studied profile, in Malpica do Tejo, south of Castelo Branco. Powdered samples were analysed by X-ray diffraction (bulk rock prepared as unoriented aggregates; <2µm fractions prepared as oriented aggregates under ambient conditions, after solvation with ethylene-glycol and after heating to 550°C). Semi-quantitative mineralogical contents were obtained according to Schultz (1964), Barahona (1974) and Galan (unpublished, for fibrous clay minerals). Multivariate data analysis (cluster analysis, R-mode factor analysis, and discriminant function analysis) of the mineralogical data has been carried out.

## 3. RESULTS AND DISCUSSION

According to Dias (1998) two mineralogical patterns (Table 1) can be defined for the bulk sample: 1 - quartz, phyllosilicates and goethite associated with the upper stratigraphic units and 2 - quartz, phyllosilicates, feldspars (K feldspars and Ca-Na feldspars), dolomite and sometimes calcite associated with the middle to lower stratigraphic units. In the clay-size fraction, four units were defined (Table 1): A - an upper unit in which kaolinite is associated with illite; B - downwards, one unit in which smectite is associated with illite and kaolinite; C - other unit with palygorskite associated with illite; and D - in the basement (closer to the schists) smectite associated with palygorskite and illite.

Table1: Lithostratigraphic units defined in the Malpica do Tejo region according to mineralogical parameters (Dias, 1998).

Unit	Clay Mineralogical Association	Bulk Sample Mineralogical Association
A	KT (+ ILL)	1) Qz (+Phyllosilicates + Goethite)
B	SM (+ ILL + KT)	2) Qz (+Phyllos. + Felds ± Calc ± Dol)
C	PAL + ILL	2) Qz (+Phyllos. + Felds ± Calc ± Dol)
D	SM (+ PAL + ILL)	2) Qz (+Phyllos. + Felds ± Calc ± Dol)

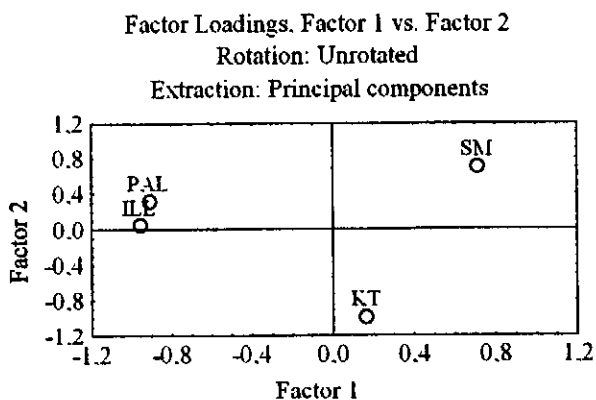


Figure 1. R-mode factor analysis of the mineralogical composition of the clay fractions.

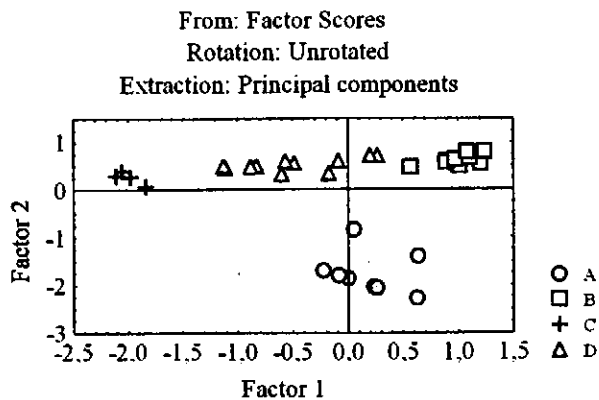


Figure 2. Factor scores of the mineralogical composition of the clay fractions.

The application of R-mode factor analysis (Figure 1) to the mineralogical composition of the clay fractions allow some interesting observations to be made: 1) smectite is positively weighted on factor 1 relative to palygorskite and illite; 2) kaolinite is negatively weighted on factor 2; and 3) there is a correlation between palygorskite and illite.

Considering the factor scores resulting from the application of R-mode factor analysis to the mineralogical composition of the clay fractions, it is important to highlight the clear differentiation obtained between the four groups defined according to the prevailing mineralogical association shown in Table 1 (Figure 2).

The application of R-mode factor analysis (Figure 3) to the mineralogical composition of the bulk samples, stresses the contribution of goethite with quartz to define one group and dolomite and feldspars another group (both groups explained by factor 1). Calcite and phyllosilicates plot in opposition, explained by another factor (factor 2).

Considering the factor scores resulting from the application of R-mode factor analysis to the mineralogical composition of the bulk sample (Figure 4), two groups are clearly defined, corresponding respectively to groups 1 and 2 of Table 1, although four samples are detached from the others, due to their higher amounts of calcite, or for sample 10B, higher amount of phyllosilicates. Two samples of group 1 plot close to group 2 as a result of their amounts of feldspars, in general absent in that group.

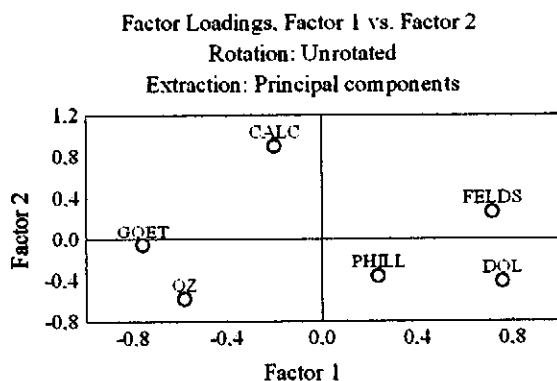


Figure 3. R-mode factor analysis of the mineralogical composition of the bulk samples.

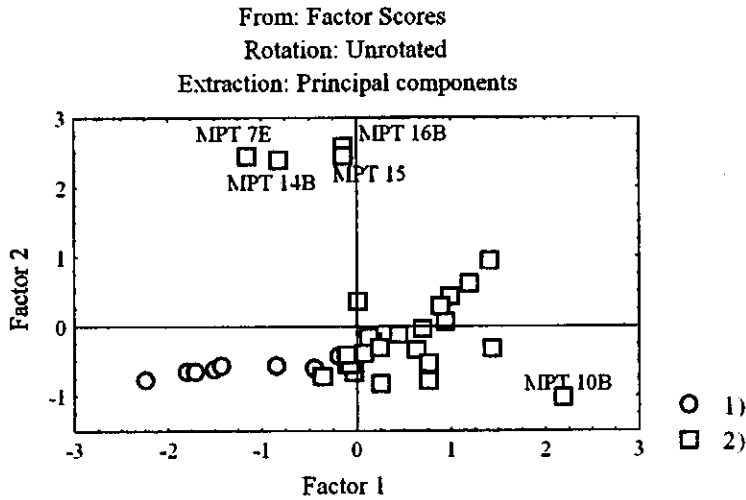


Figure 4. Factor scores of the mineralogical composition of the bulk sample.

Regarding the discriminant analysis results, it is important to notice that the groups previously defined through the mineralogical patterns of the clay fractions (and also distinguished by factor analysis) are now clearly confirmed, by Wilks' Lambda parameter (Table 2), which is very close to zero, as well as by Correlations Variables - Canonical Roots (Pooled-within-groups correlations) and classifications of cases (Figure 5 and Tables 3 and 4).

Table 2: Discriminant Function Analysis for the mineralogical composition of the clay fraction. Wilks' Lambda: .00412 approx.  $F(12,74)=43.223$   $p < .0000$

	Wilks' Lambda	Partial Lambda	F-remove (3.28)	p-level	Toler.	1-Toler. (R-Sqr.)
SM	.004415	.931989	.681093	.571026	.015426	.984574
PAL	.004571	.900327	1.033270	.392985	.046992	.953008
ILL	.004519	.910568	.916683	.445516	.031957	.968043
KT	.004734	.869333	1.402869	.262655	.026776	.973224

Figure 5. Discriminant function analysis of the clay fraction mineralogy.

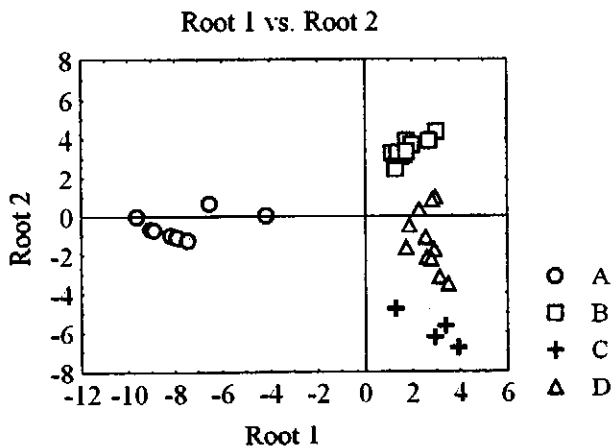


Table 3: Factor Structure Matrix – Clay fraction

Correlations Variables - Canonical Roots. (Pooled-within-groups correlations)

	Root 1	Root 2	Root 3
SM	.410296	.888525	.175690
PAL	.338766	-.809295	.225071
ILL	.102340	-.588814	-.381699
KT	-.913830	-.053155	.091114

Table 4: Classification Matrix – Clay fraction

Rows: Observed classifications. Columns: Predicted classifications

	Percent Correct	A p=.22857	B p=.34286	C p=.11429	D p=.31429
A	100.0000	8	0	0	0
B	100.0000	0	12	0	0
C	100.0000	0	0	4	0
D	100.0000	0	0	0	11
Total	100.0000	8	12	4	11

It is important to emphasize that no incorrect cases of classification occur as shown in the classification matrix, which shows the number of cases that were correctly classified according to their mineralogical pattern (clay fraction). Therefore 100 % of all cases are correctly classified (Table 4). Root 1 seems to discriminate unit A from all the other units (B, C and D). Root 2 discriminates unit C from unit B (Figure 5). Discriminant function analysis was useful to determine which variables discriminate the previous defined units. Kaolinite distinguishes unit A, smectite distinguishes unit B, and palygorskite unit C (Table 3).

Table 5: Discriminant Function Analysis – Bulk sample

Wilks' Lambda: .34540 approx. F (6.28)=8.8443 p< .0000

	Wilks' Lambda	Partial Lambda	F-remove (1.28)	p-level	Toler.	1-Toler. (R-Sqr.)
GOET	.393261	.878289	3.880159	.058824	.717435	.282565
QZ	.361125	.956447	1.275026	.268407	.000687	.999313
FELDS	.364175	.948436	1.522271	.227533	.001255	.998745
CALC	.364094	.948649	1.515649	.228520	.000845	.999155
DOL	.383239	.901258	3.067680	.090812	.224640	.775360
PHYLL	.362261	.953448	1.367087	.252171	.000756	.999244

Table 6: Classification Matrix – Bulk sample

Rows: Observed classifications. Columns: Predicted classifications

	Percent Correct	1) p=.22857	2) p=.77143
1)	75.0000	6	2
2)	100.0000	0	27
Total	94.2857	6	29

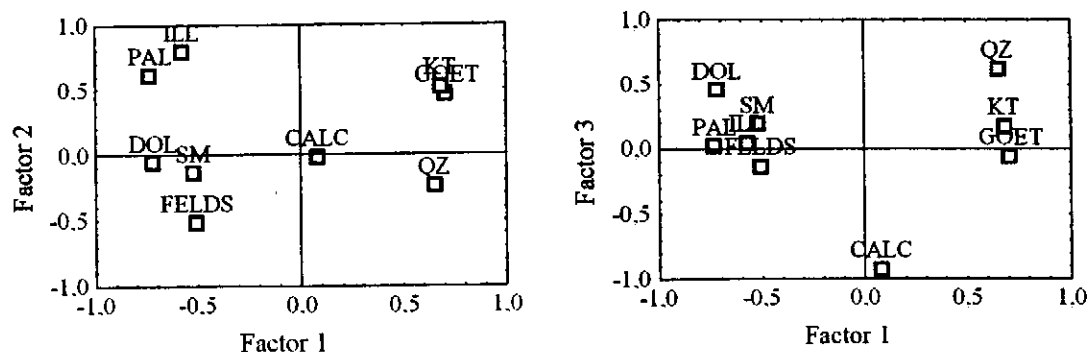


Figure 6 - R-mode factor analysis of the mineralogical composition of the global samples (with redistribution of phyllosilicates contents by kaolinite, illite, palygorskite and smectite).

Applying the discriminant analysis to the bulk sample mineralogy, the classification into two groups is mostly correct, although not with the same accuracy as obtained for the clay fraction. This is indicated by the higher Wilks' Lambda parameter (Table 5) and by the case classifications (Table 6), being 94 % of all cases correctly classified, 75 % of the samples of group 1 correctly classified, as well as 100 % of group 2. The samples from group 1, which appear distinct, correspond to those samples in Figure 4 that plotted close to group 2 (due to the presence of feldspars). Although some samples plotted distinctly away from the others in figure 4 due to differences in calcite or phyllosilicate content, these do not support this statistical approach. Nevertheless, the higher values of Wilks' Lambda parameter for bulk samples relative to the clay fraction, indicate less discrimination between groups. It was not possible to present an x-y plot, because only one canonical root was extracted.

The application of R-mode factor analysis (Figure 6) to the mineralogical composition of the global samples (bulk sample with redistribution of phyllosilicate content by kaolinite, illite, palygorskite and smectite) allows some interesting observations to be made: 1) Factor 1 shows kaolinite, goethite and quartz positively weighted and dolomite, smectite, feldspars, palygorskite and illite negatively weighted; 2) Factor 2 shows illite and palygorskite correlated and positively weighted but feldspars negatively weighted; 3) calcite is negatively weighted in factor 3.

Considering this global sample, it is clear that these statistical analysis allow, as a first step, to differentiate two main groups, directly connected to the previously defined 1 (units A and B) and 2 (units C and D) for the bulk sample.

Combining the results obtained in all these statistical analysis of the mineralogical data (clay fraction and bulk sample), we propose the subdivision of Palaeogene sediments of Malpica do Tejo (Castelo Branco Basin) not in four but only in three main units: A, B and C, subdividing unit C, in C2 (previous C) and C1 (previous D), based on their clay mineralogical features. The differentiation observed in the clay fraction, related to the association of palygorskite with illite in what is now subunit C2, as well as the behaviour of all the other minerals, lead us to the assumption that subunit C2 can be interpreted as an evolutionary products of subunit C1.

The discriminant analysis performed with the mineralogical composition of the global sample (after redistribution of phyllosilicates contents by kaolinite, illite, palygorskite and smectite) became useful for a proposal of dividing in mineralogical units the Palaeogene

deposits of Castelo Branco, confirming the proposed division into three main groups (Figure 7).

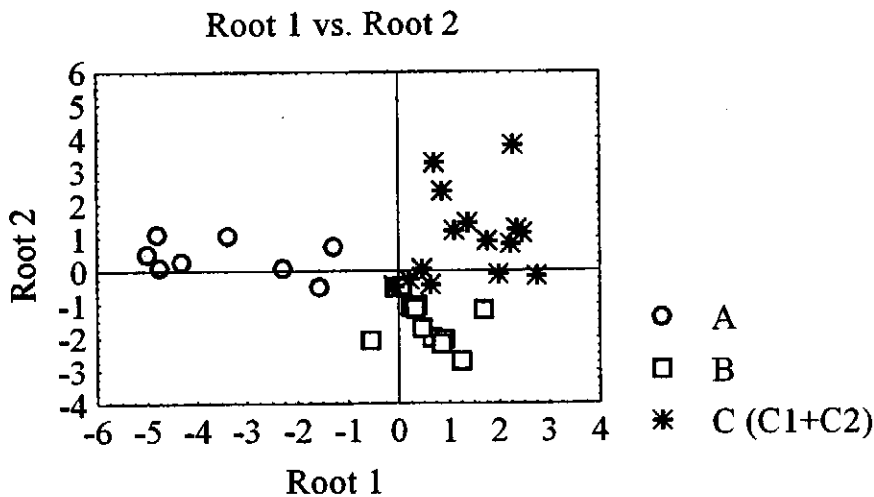


Figure 7 – Discriminant function analysis of the global sample (after redistribution of phyllosilicates contents by kaolinite, illite, palygorskite and smectite).

Table 7: Factor Structure Matrix – Global sample  
Correlations Variables - Canonical Roots. (Pooled-within-groups correlations)

	Root 1	Root 2
GOET	-.443290	.045739
QZ	-.364925	-.156205
FELDS	.302531	-.261611
CALC	.117714	.102591
DOL	.237710	-.016252
SM	.265991	-.371426
PAL	.286839	.583956
ILL	.137508	.513872
KT	-.620503	.167000

Root 1 discriminates group A from groups B and C, and root 2 discriminates group B from group C. Looking at which variables discriminates each one of the defined groups, goethite associated with quartz and kaolinite discriminates group A, whereas feldspars, dolomite and smectite, in opposition to palygorskite and illite, discriminate group B (Table 7).

Table 8  
Lithostratigraphic units defined in the Malpica do Tejo region according to mineralogical vs statistical parameters, considering fingerprints minerals of each unit

Unit	Subunit	Mineralogical Association (clay fraction crossed within bulk sample)
A		kaolinite + goethite + quartz
B		feldspars + smectite + dolomite + (calcite)
C	C2	palygorskite + illite + (+ calcite + feldspars + dolomite)
	C1	smectite + feldspars + palygorskite + illite + dolomite + calcite



Table 8 synthesise the results of the application of multivariate data analysis to mineralogical data of clay fractions and bulk samples, emphasising minerals fingerprints of each defined unit. Therefore, mineralogical patterns became quite useful to lithostratigraphic differentiation, namely the clay minerals suites combined with the bulk rock ones. Some mineral fingerprints were defined for each unit/subunit, emphasising the role of palygorskite as the main lithostratigraphic marker in the Palaeogene deposit of Malpica do Tejo. This means that only unit C (C1 and C2) are Paleogene in age and units A and B are younger.

#### 4. CONCLUDING REMARKS

A lithostratigraphic scheme for the Tertiary deposits of Castelo Branco region (Beira-Baixa, Portugal) is proposed based mainly on the clay mineral suites. Statistical analysis was useful in differentiating the several lithostratigraphic levels. The sample's classification considering mineralogical parameters allowed a better clarification of which variables discriminate the previously defined units. The clay fraction is the best feature for differentiating between lithostratigraphic levels, emphasising the role of kaolinite for Pliocenic levels and of palygorskite for Palaeogene ones. Three main units were proposed, unit A in a Quaternary context and the other two (B and C) in a Tertiary context.

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