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Textural characterization of sedimentary deposits from cave of Caldeirão and interpretation of the relationship between BET area and chemical properties

Caracterização textural dos depósitos sedimentares da gruta do Caldeirão e interpretação da relação entre a área BET e propriedades químicas

Caractérisation textural des remplissages sédimentaires de la grotte du Caldeirão et interprétation de la relation entre l'aire BET et propriétés chimiques

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ABSTRACT

By means of nitrogen adsortion, the textural characterization of 19 samples removed from sedimentary deposits of a limestone cave with archaeological remains from the Medium Palaeolithic to the Present was carried out. The similarity of the isotherms gives an indication of the mineralogical continuity of the samples. The BET area is positively correlated with indicators of the samples clay content, crystalline iron oxyhydroxides, phosphates, and manganese oxyhydroxides in higher oxidation states, and negatively correlated with calcium carbonate and organic matter contents. The BET area differences between two samples core cannot be interpreted as a result of the materials age. The relationship between specific area and calcium carbonate is due to an effect of the mass and, thus, the variation of calcite along the profile is probably only a result of physical processes.

RESUMO

Dezanove amostras do depósito sedimentar de uma gruta com vestígios arqueológicos que vão do Paleolítico Médio até ao presente foram objecto de caracterização textural por adsorção de azoto a 77 K. A semelhança das isotérmicas obtidas sugere a existência de continuidade mineralógica entre as amostras. A área BET está correlacionada positivamente com propriedades que constituem indicadores do teor das argilas, com óxidos e hidróxidos de ferro cristalinos, fosfatos e óxidos e hidróxidos de manganês nos estados de oxidação mais elevados e está negativamente correlacionada com as concentrações de carbonato de cálcio e de matéria orgânica. As diferenças entre os valores da área BET correspondentes às duas colunas de amostragem não podem ser interpretadas como devidas à idade dos materiais. A relação entre a área específica e a concentração de carbonato de cálcio é devida a um efeito de massa e, portanto, a variação do teor de calcite ao longo da sequência, provavelmente, resulta apenas de processos físicos.

RÉSUMÉ

Dix-neuf échantillons du remplissage d'une grotte avec des temoins archéologiques datés du Paléolithique Moyen jusqu'à l'actualité ont été soumis à la caractérisation par adsortion d'azote à 77 K. La ressemblance des isothermes suggère l'existence de continuité mineralógique parmi les échantillons. L'aire BET montre une corrélation positive avec des indicateurs des argiles, oxyhydroxydes de fer cristallins, phosphates et oxyhydroxydes de manganèse dans les états supérieurs d'oxydation et montre une corrélation negative avec les concentration en carbonate de calcium et en matière organique. Les différences entre les valeurs de l'aire BET des deux prélèvements ne peuvent pas être atribuées à l'âge des matériaux. La relation entre l'aire spécifique et la concentration en carbonate de calcium est le resultat d'un effet de masse et, alors, la variation ou la teneur de calcite dans la séquence sedimentaire est probablement due aux processus physiques.

INTRODUCTION

In literature concerning sediments, the references to surface properties are scarce. In particular, data related to porous structure and specific surface area are not easily found (see, for instance, FORD & WILLIAMS 1989; FRIEDMAN & SANDERS 1978; RENAULT 1987).

Sedimentological properties, such as size, density and shape of particles are often use to estimate the specific geometric area. Generally, this geometric area represents only a small fraction of the totl surface area, which results mainly from the micro-fissures a the degree of aggregation of the particles. This total area can only bevaluated by adsorption methods (GREGG & SING 1982).

Although the shape of the adsorption isotherms and the specific surface area are not characteristics of any particular mineral (GRIM 1968, p.464), adsorption data can be employed to check the mineral continuity of a samples sequence.

On the other hand, because some properties such as the structure of soils and sediments and their particle size distributions may change with time as a result of chemical and physical weathering (HARDEN 1982; TORRENT & NETTLETON 1979), it might be expected that the textural parameters would also be an age index of mineralogical homogeneous soils or sediments.

With the aim of contribute to the understanding of the sedimentary history and related archaeological problems of a human occupied cave, the textural characterization of the sediments samples were performed by means of nitrogen adsortion at 77 k and the correlations of the specific surface area with chemical properties previously determined were investigated.

SAMPLES

The samples were taken from cave of Caldeirão (Tomar, Portugal) a limestone cave with sedimentological sequence of more than 6 m and showing signs of human occupation corresponding at least to the last 30 thousand years (ZILHÃO 1985, 1987. n.d.a., n.d.b.).

Two cores, D and E, collected by F. REAL (Departamento de Arqueologia, Instituto Português do Património Cultural, Lisboa) and J. ZILHÃO (Instituto de Arqueologia, Faculdade de Letras, Lisboa), were analyzed.

Core D, 162 cm deep, contains: the superficial layer A/B/C-D with archaeological remains of all ages from Neolithic to the Present (samples D1 to D5); the Ea Neolithic layer (samples D6 and D7); and the Magdalenian and Solutrean layer Eb (10,700 to 14,450 years Before Present on the bases of ^{14}C data). Core E, 87 cm deep, contains a non-specified Upper Paleolithic layer K (earlier than 27,600 years Before Present) (samples E1 to E3) and, separated by a stratigraphical discontinuity from the K layer, the Mousterian (?) L (samples E4 to E7) and M layers (samples E8 and E9) (CRUZ n.d.a., n.d.b.; ZILHÃO 1987, n.d.a., n.d.b.). The two cores are separated from each other by about 2.5 m, either horizontally or vertically (see CRUZ 1988, Fig.2, and CRUZ 1989a, Fig.1).

Calcite and quartz are the principal mineralogical species which are identified in the X-ray diffraction patterns (CRUZ 1989b).

EXPERIMENTAL PROCEDURES AND RESULTS

Tecniques and BET area values

For each sample a fraction with grain size smaller than 2 mm has been ground in an agate mortar and dried at 378 K.

Adsorption measurements were performed in a conventional volumetric apparatus.

Six subsamples of sample D3 had been subjected to outgassing under various conditions and the isotherms were determined (Fig.1). The specific surface areas for these subsamples obtained with the BET equation varied between 22.8 and 25.9 m^2g^{-1}, with a standard deviation of 4.4 % (Table 1). The remaining samples were outgassed for 90 minutes at 473 K. All the isotherms are of type II of IUPAC classification (Sing *et al.* 1985). the linear range of BET plots occurs for relative pressure between 0.05 and 0.3. The evaluation of specific surface area and *c* parameter has been made with the points in this range (Table 2).

Four samples (D7, D10, E5 and E8) were treated with the sodium acetate / acetic acid 1 M buffer at pH 5 to remove carbonates. After this treatment the adsorption isotherms for the non-carbonate fraction were determined too (Table 3).

Relationship between BET area and chemical properties

Of the samples properties previously determined (see CRUZ 1988, 1989a, 1989b, n.d.d.), the specific area is positively correlated with potassium and aluminum contents in the fraction obtained by hot hydrochloric acid dissolution (Fig.2), which are an indicator of the clay content of the samples, with crystalline iron oxyhydroxides (Fig.3), with phosphates and, in a less extent, with manganese oxyhydroxides in higher oxidation states. In cases of potassium, aluminum, iron and manganese, this correlation agrees with the fact that, generally, both clays and oxyhydroxides are compounds with high values of specific surface area (GRIM 1968; BORGGAARD 1982; BARROW *et al.* 1988; JENNE 1968, p. 343).

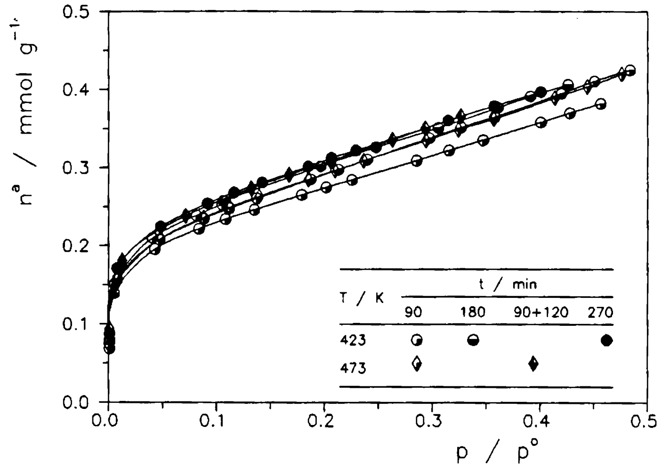

Fig. 1 - Adsorption isotherms of nitrogen at 77 K on D3, outgassed in different conditions of temperature and heating time.
Isotérmicas de adsorção de azoto a 77 K para diferentes sub-amostras da amostra D3 desgaseificadas sob várias condições.
Isothermes d'adsorption de l'azote à 77 K pour différents sous-échantillons de l'échantillon D3 soumis à plusieurs conditions de dégazéification.

However, the specific surface area is not correlated with amorphous iron compounds, which, in general, has higher specific area values than the crystalline compounds (BORGGAARD 1982; DAVIS & LECKIE 1978).

On the other hand, the specific surface area is negatively correlated with the carbonate fraction (Fig.4) and properties related with organic matter (Fig.5).

Analysis of isotherms

The 19 isotherms, based on 200 experimental points, are, in a first approximation, superposable by a simple scale adjustment of the adsorbed amounts, even under quite low relative pressures. The curve shown in fig.6 was obtained by dividing, for each sample, the adsorbed amounts by the amount adsorded at $p/p^o = 0.3$.

The small scattering at low pressures, besides being due to the experimental incertainty, is explained by the fact that the experimental isotherms correspond to different values of the *c* parameter (between 60 and 164), which is related to the isotherm shape, specially at relative pressures lower than ~ 0.2. However the *c* values (shown on Table 1) are not quit reproducible, which explains to some extent that the C parameter is not correlated with other samples properties. On the other hand, considering the difficulties generaly existing in the interpretation of *c* parameter (GREGG & SING 1982), the scattering in Fig. 6 should be ignored.

TABLE 1

Results of preliminary experiments with D3 sample

Subsamples	Outgassing		*n*	BET parameters	
	T / K	*t* / min		a_S/ m^2 g^{-1}	*c*
D3-1	423	90	7	22.8	97
D3-2	423	90	2	24.9	86
D3-3	423	90	7	24.0	70
D3-4	423	180	3	25.5	79
D3-5	423	270	6	25.9	83
D3-6	473	90	7	23.8	79
D3-6	473	90+120	6	24.8	90

n : number of points

TABLE 2

Results of the analysis of the adsorption isotherms of nitrogen at 77K

Samples	n	BET parameters	
		a_S/ m^2 g^{-1}	c
D1	9	19.4	60
D2	7	23.7	71
D3	7	23.8	79
D4	8	22.9	105
D5	9	27.0	77
D6	10	28.6	102
D7	9	25.0	89
D8	10	24.3	90
D9	10	23.4	122
D10	9	23.5	92
E1	6	40.9	88
E2	9	35.7	94
E3	9	38.1	164
E4	9	42.4	77
E5	9	43.6	131
E6	10	41.1	98
E7	9	37.2	132
E8	10	36.9	95
E9	7	35.8	138

n: number of points

TABLE 3

Results of the analysis of decarbonated samples

Samples	n	BET parameters		$a(CaCO_3)$	$a_{S'}$ (calculated)
		a_S/ m^2 g^{-1}	c	m^2 g^{-1}	m^2 g^{-1}
D7	10	31.6	138	3.1	36.1
D10	10	27.8	129	5.6	36.4
E5	10	35.6	86	9.8	45.9
E8	9	41.4	173	0.5	42.0

n: number of points

$a(CaCO_3)$: eq. [1]

a_S (calculated) : eq. [2]

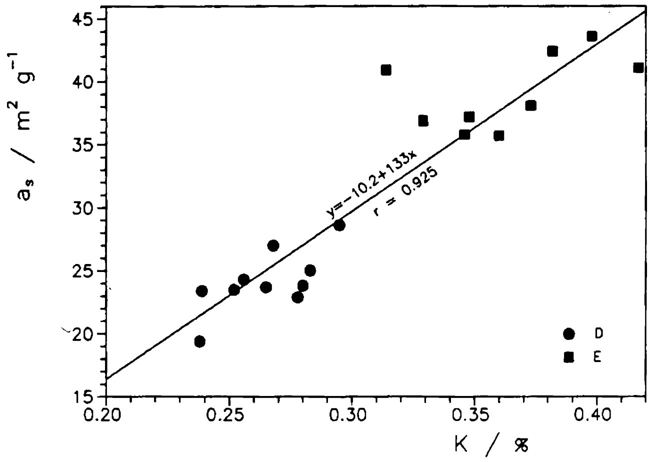

Fig. 2 - Specific surface area versus potassium content of the fraction of the samples extracted by hot concentrated hydrochloric acid.
A área superficial específica em função da concentração de potássio extraído por ácido clorídrico concentrado, a quente.
Aire superficielle spécifique en fonction de la concentration du potassium dans la fraction extraite avec l'acide chlorhydrique concentré, à chaud.

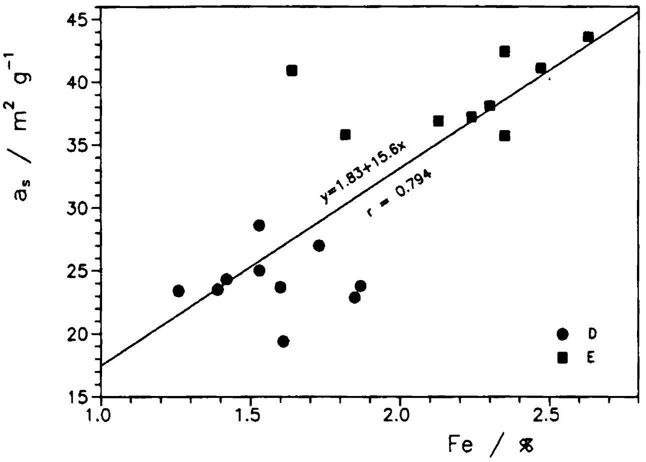

Fig. 3 - Specific surface area versus crystalline iron oxyhydroxides contents of the samples.
A área superficial específica em função da concentração de óxidos e hidróxidos cristalinos de ferro.
Aire superficielle spécifique en fonction de la concentration des oxyhydroxides de fer cristallins.

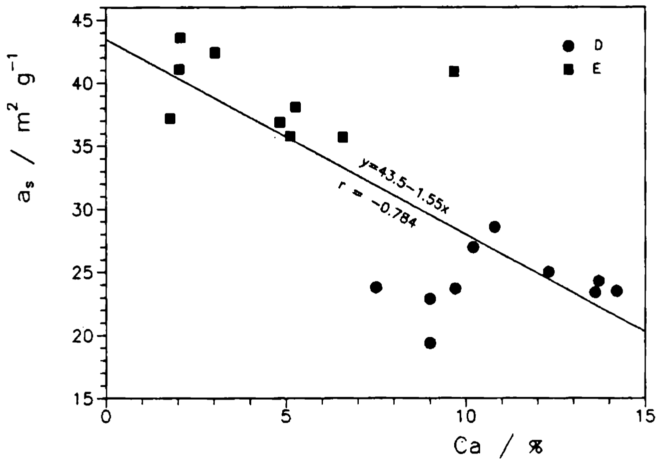

Fig. 4 - Specific surface area versus calcium concentration of the samples.
A área superficial específica em função da concentração de cálcio das amostras.
Aire superficielle spécifique en fonction de la concentration du calcium dans les échatilons.

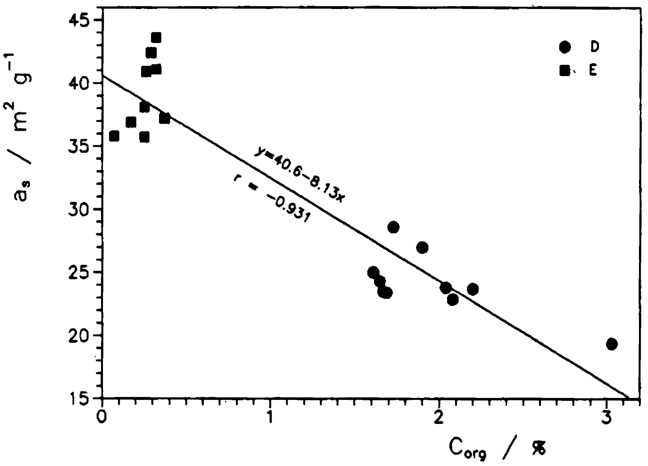

Fig. 5 - Specific surface area versus organic carbon content of the samples.
A área superficial específica em função da concentração de carbono orgânico das amostras.
Aire superficielle spécifique en fonction de la concentration du carbone organique dans les échantillons.

DISCUSSION

Mineralogical continuity

The plot in Fig. 6 suggests that the samples have a quite similar pore structure pattern. This can be easily explained if the component materials with higher contribution to the specific area value are the same in the samples. They differ only in quantity and eventually in the size and shape of the particles.

As a matter of fact, the chemical properties previously determined (see Cruz 1988; 1989a, n.d.b.) and the X-ray diffraction spectra shown a continuity among samples of core D and E exists, they don't imply a mineralogical discontinuity among the two cores because those differences may only reveal different proportions of the samples mineralogical components.

Besides, the identical chemical speciation of elements such as magnesium, calcium, manganese, iron and aluminum in cores D and E (CRUZ n.d.b.) supports the conclusion of mineralogical continuity suggested by the adsortion data.

Relationship between BET area and calcium carbonate

The decrease of the surface area with the increase of the calcium carbonate content, shown by Fig.4, can be interpreted as the result of the frequently low specific area of calcite (AMRHEIN & SUAREZ 1987; HOUSE 1981; MUCC *et al.*1989) or as the result of the cementation action of calcite, which can lead to the filling of the narrower pores of the samples or to the increase of the mean particle size (FRIEDMAN & SANDERS 1978; BORRERO *et al.*1988). The first hypothesis is supported by the quantitative importance of calcite in samples (ranging from to 4 to 34%) and implied that the relationship is induced by other variables - a common problem in closed data set (DAVIS 1986).

The apparent surface area of the calcium carbonate, $a\{CaCO_3\}$,

$$a\{CaCO_3\} = a_s\{\text{sample}\} - a_s\{\text{decalcified sample}\}\ (1 - CaCO_3/100),\ [1]$$

determined for some samples is positive (Table 3), exactly the contrary that it would be if the removal of carbonate from samples exposed new surfaces which were not acessible due to the cemention (BORRERO *et al.*, 1988). Besides, the specific surface area value calculated for the non-carbonate fraction,

$$a_s\{\text{decalcified sample}\}^{\text{calculated}} = = a_s\{\text{sample}\}/\ (1 - CaCO_3/100),\ [2]$$

is, in the four samples, equal or greater than the value obtained for the decalcified samples (Table 3). This is equally interpreted as an evidence of the non-exposure of the new surfaces by the decalcification process. These results suggest that the effect of the calcium carbonate content on the specific surface area is due, above all, to a mass effect, *i. e.*, to an indirect effect of other minerals.

Because the calcium carbonate content is highly correlated with the potassium and aluminum contents in the fraction obtained by hot hydrochloric acid dissolution and with the iron concentration in the crystalline oxyhydroxides fraction, but with a negative value, the indirect effect revealed by the calcium carbonate may be attributed, above all, to the variation of the samples minerals with high specif surface area values.

Organic matter effect on specific surface area

The organic carbon concentration, which decrease with depth as a result of the mineralization process (CRUZ 1988, 1989a), is correlated with the specific area (Fig.5). This agrees with the low specific surface area of some types of organic matter and with the fact that this matter can be a cementation agent in a manner similar to that of the calcite (BURFORD *et al.*1964; JAMBU *et al.* 1987; OLSON & JONES 1988; VICENTE & ROBERT 1981).

Considering the two cores separately, the mentioned relationship between the two properties is found in core D but in core E the specific surface area increases with the organic carbon content. However, in core E the trend is weaker and, on the other hand, the organic carbon concentration is very small and, so, its influence on other samples properties is much poorer. This trend in core E is probably due to an indirect effect of other samples components.

The BET area and the samples age

At first sight, the variation of the specific surface area from core D (24.2 ± 2.5 m^2g^{-1}) to core E (39.1 ± 3.0 m^2g^{-1}) suggests that it can be interpreted as a result of the age of materials.

However, if such an explanation was applied, each of the cores would also show an increase of the specific area with depth. Besides, as there are other important discontinuities in the cores, that interpretation would also implies a discontinuity in the surface area values of core D (between Ea and Eb layers) and core E (between K and L layers).

As neither of this is verified (Table 4), the relationship between BET area and depth is interpreted as due to the covariance between depth and organic carbon and calcim carbonate contents and not with the age.

We have attempt to remove this influence by calculating the surface area relatively to the compounds that are positively correlated with the BET area (potassium, manganese, iron, aluminum and phosphorus in oxide form) instead of the all samples. However, the values obtained are not at all correlated with the stratigraphical position of the samples.

Because the differences in the organic carbon content in the assemblage of all samples, this fact may be related with the organic matter effect on the BET area, which, probaby is very important. However in the samples of core E, which have a small content of organic carbon, the BET area values calculated for those compounds with high specific areas are also not correlated with depth.

These results show that the variations of the specific surface area is not related with the materials age and, as a consequence, suggest that the sediments of Caldeirão cave have not been subject to chemical weathering - which agree with the evidence provided by several chemical properties (CRUZ 1989b, 1990, n.d.b.).

TABLE 4

Specific surface area as a function of the statigraphical layer

Layers	a_s/ m^2 g^{-1}			
	Average	Standart deviation	Minimum	Maximum
A/B/C-D	23.4	2.7	19.4	27.0
Ea	26.8	2.5	25.0	28.6
Eb	23.7	0.5	23.4	24.3
K	38.2	2.6	35.7	40.9
L	41.0	2.8	37.2	43.6
M	36.3	0.8	35.8	36.9

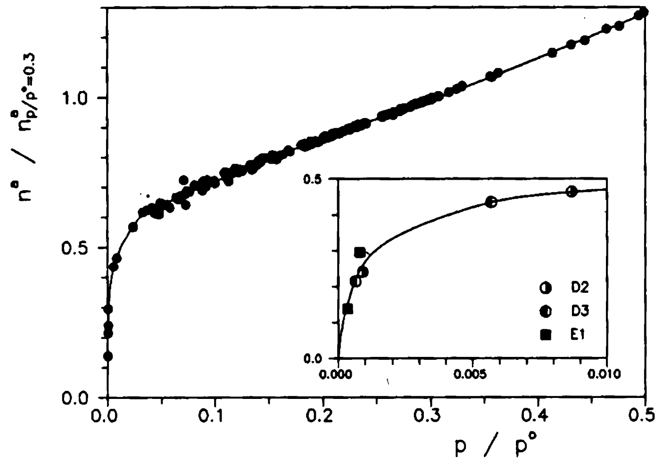

Fig. 6 - Reduced isotherm for the adsorption of nitrogen at 77 K on the samples (using as normalizing factor the amount adsorbed at $p/p^0 = 0.3$).
Isotérmicas de adsorção de azoto a 77 K reduzidas tomando como unitária a quantidade adsorvida a $p/p^0 = 0.3$ para cada uma das amostras.
Isothermes d'adsorption de l'azote à 77 K réduites (adsorption à $p/p^0 = 0.3$ égal à l'unite).

CONCLUSIONS

The similarity of the adsortion isotherms shows a mineralogical continuity between core D and core E, although they are separate from each other by some thousand years and the configuration of the inside of the cave has considerably changed (for example, the floor has been rise several meters). Rigorously, the results show only the continuity concerning the materials that effectively contribute to the specific area. Nevertheless, they disclose a group of geoecological factors which was maintained relatively constant during the last 30 thousand years.

The interpretation of the relationship between the specific area and the calcium carbonate has implications in the explanation of the geochemical and sedimentological results. If this association is due, above all, to an effect of mass and not to the cementation action of calcite, the variations of the calcium carbonate content along the profile cannot be interpreted in terms of dissolution and precipitation actions *in situ*. On the contrary, these variations should be explained mainly through mechanical actions of fragmentation and disaggregation.

This conclusion, on the other hand, agrees with the other evidences that the cave sediments have not been subject to chemical weathering.

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