



Characterization of Portuguese geological materials to be used in medical hydrology

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ABSTRACT

In order to be used in therapeutics, geological materials must comply with a number of specifications. In particular, clays used as pharmaceutical raw materials must be safe. As a product to be manipulated during the manufacture of drug dosage forms, they are also required to satisfy a number of technological features, including flowability and texture. With these premises, this work aimed to characterize mineralogical, textural and technical properties of Portuguese clayey raw materials belonging to well known formations (from Upper Jurassic to Miocene in age). Some of these materials are used in particular beaches for their therapeutic properties. The present study showed that mineralogical and chemical compositions of the samples allow for their safe therapeutic application. Nevertheless, in some particular samples, it could be necessary to reduce the quartz content and coarse particles before use. Bulk samples showed better flow patterns than the <63- μm samples. For that, the use of bulk samples is preferred over separated samples. The most suitable materials for medical hydrology applications were those belonging to Freixial, Aveiro, Barracão, Luz, Xabregas and Serra de Dentro Bentonite formations.

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1. Introduction

Healing muds are dispersions composed by geological materials dispersed in salty or mineral waters (Veniale et al., 2004). These therapeutic materials are used in medical hydrology therapies because of their particular properties. These properties result from their chemical and mineralogical characteristics (Carretero et al., 2007; Gomes and Silva, 2007; Tateo and Summa, 2007; Veniale et al., 2007) as well as other synergistic mechanisms such as thermal, mechanical and biochemical factors (AAVV, 2004; De Bernardi and Pedrinazzi, 1996; Tateo et al., 2009).

To be used in therapy, geological materials must comply with a number of specifications (López-Galindo et al., 2007). Clays used as pharmaceutical raw materials must be safe (Community Directive 2001/58/EC; US Department of Labor, OSHA CFR 1910.1200). They must comply with several requisites including the accurate identification of the substance, composition, hazards identification, handling and storage, physical and chemical properties, stability and reactivity, and toxicological information. The presence of quartz and fibrous minerals has to be avoided or limited (López-Galindo et al., 2007). In addition, as natural materials, the presence of major and trace elements on these muds must be carefully controlled because of their potential hazardous or beneficial effects on health (Jobstraibizer, 1999; Minguzzi et al., 1999; Sánchez et al., 2002; Summa and Tateo, 1998; Veniale, 1999; Veniale et al., 1999, 2004).

Besides these safety requirements, the possible uses of raw clay pharmaceutical materials will depend on their technical properties, which will determine their intended or recommended final uses (EP 6th, 2007; USP, 2010). Therapeutic muds are semisolid products administered topically. Consequently, they must be optimized to satisfy a number of technological features regarding manipulation, administration and effect (Viseras et al., 2007). On the other hand, the presence of special clay minerals like kaolinite, talc, smectites, palygorskite and sepiolite is desired because of their colloidal dimensions, high specific surface area, high cationic exchange and sorptive characteristics. These well appreciated characteristics also lead to good technical properties (Carretero et al., 2007; Veniale et al., 2004). Before their dispersion in water, clay powders must flow adequately to allow their manipulation, and once dispersed in the mineral water, the resultant mud must show optimal rheological attributes that assure physicochemical stability. This avoids sedimentation of the solid phase, eases the handling and application, besides leaving a pleasant sensation when the mud is spread on the skin.

With these premises, we studied some Portuguese clayey raw materials broadly used for healing and other purposes (Gomes, 2002; Reis, 2005; Silva et al., 2003) which showed a potential therapeutic interest for thermal centers. These studies revealed the great potentialities of Porto Santo Bentonite for complementary applications in treatments of rheumatic and orthopedic disorders. Furthermore, they evidenced that some Portuguese common clays exhibited relevant technological properties for pelotherapy applications. These materials were considered in order to determine their suitability as potential components of therapeutic peloids to be used in medical hydrology treatments. In addition, we compared them with a clayey

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material commercialized in Portugal for healing and cosmetic purposes.

2. Materials and methods

The studied materials (Table 1) were collected from various Portuguese formations (Fig. 1) because of their significant amount of clayey materials (Gomes, 2002; Oliveira et al., 2002; Rebelo et al., 2005).

In the Lusitanian Basin, along the Western-Central border, clay-rich sediments from Jurassic to Pliocene age were sampled. In particular, samples L1 (Boa Viagem), L2 (Freixial) and L3 (Abadia) corresponded to clay-rich levels of Upper Jurassic formations (Alves et al., 2002; Bernardes, 1992; Kullberg, 2000; Rocha et al., 1996). Samples L4 (Torres Vedras) and L5 (Figueira da Foz) were from Lower Cretaceous formations (Dinis, 1999; Kullberg, 2000; Rey, 2003). L6 (Rodísio) and L7 (Aveiro) samples were collected from Upper Cretaceous formations (Rey, 1999; Rocha and Gomes, 2002, 2003). L8 (Barracão) was from a Pliocene formation (Barbosa, 1983). Most of the samples are currently used as raw ceramic materials (L2, L4, L5, L7 and L8) and sample L6 is used empirically on Parede Beach (Lisbon) for the recovering of bone disorders (Reis, 2005).

In the Algarve basin, along the Southern border, Lower Cretaceous sedimentary clays of the Wealdian (A1) and Luz (A2, A3) formations (Rey et al., 2006) as well as Miocene clayey materials of the Cacela (A4) formation (Cachão, 1995) were sampled. A1 is broadly used as a ceramic raw material and A2 is employed for recovering skin and bone disorders at Burgau and Luz Beaches (Gomes, 2002; Trindade, 2007).

In the Tagus Basin, Central Portugal, samples were taken from Paleogene sediments belonging to the Sarzedas (T1) formation (Cunha, 1987; Cunha and Reis, 1985), and Miocene sediments of the Torre (T2) formation (Cunha, 1996).

Miocene clayey sediments were also collected from another Tertiary basin, the Sado basin, located at Setúbal Peninsula. They included two samples belonging to the Xabregas (S1) and Penedo (S2) formations (Antunes et al., 1992; Cotter, 1956; Romariz and Carvalho, 1961; Zbyszewski, 1967; Zbyszewski et al., 1965). Both of them are used at Costa da Caparica and Mecó Beaches for the treatment of skin diseases and aesthetic purposes (Gomes, 2002; Reis, 2005).

In the Hercynian Massif, at Alentejo region, clayey materials with a completely different origin were sampled. In this zone, common clay deposits are restricted to Palaeozoic altered schists occurrences, which are associated to marbles and dolomites of the Moura-Ficalho volcano-sedimentary complex (O1) (Oliveira et al., 1991). On the other hand, bentonites resulting from the alteration of Benavila's quartz diorites are

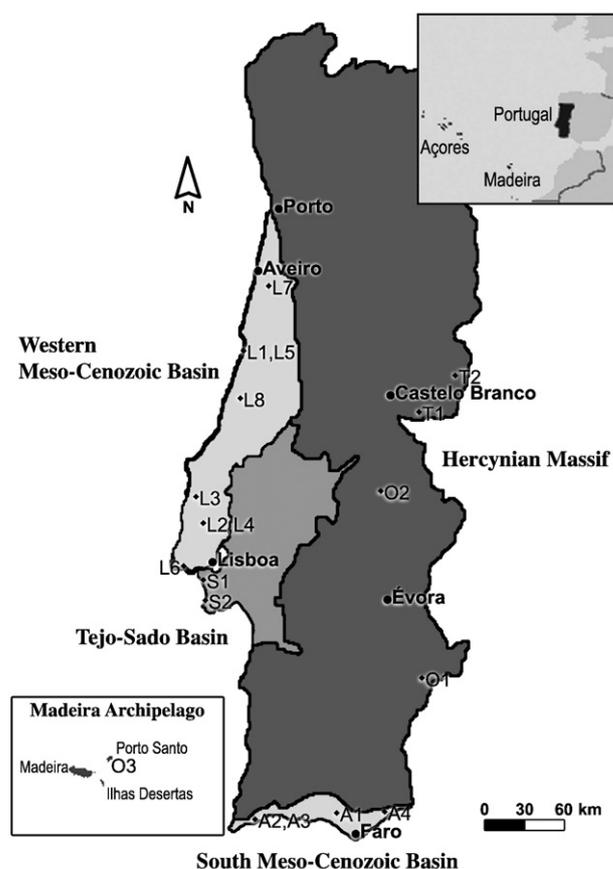


Fig. 1. Location of the samples.

located in one of the most important bentonite deposits in Portugal (Gomes, 2002), in the Avis Region (O2) (Dias et al., 2004).

In Madeira archipelago, sample O3 was collected from a large bentonite deposit located at the Serra de Dentro (Porto Santo Island). This deposit originated from the alteration of Miocene submarine tuffs and breccias (Silva, 2003). The material from this deposit is commonly used for complementary treatments of rheumatic and orthopaedic affections (Gomes and Silva, 2001).

For each of the formations described above, about 5 kg of representative materials was taken. A commercial green clay was also studied for comparative purposes. This clay is sold in many Portuguese stores for internal and external use in the treatment of multiple affections and is manufactured by PROVIDA® Natural Products. Samples were wet sieved (63 µm mesh) and the clay fraction (<2 µm) was separated by sedimentation according to Stokes law and dried at 60 °C.

2.1. Mineralogy and geochemistry

The mineralogical composition was determined by X-Ray Powder Diffraction (XRPD) using a Philips® X-Pert diffractometer with Cu K α radiation. Random powder diffraction was used on silt-clay fraction, and air-dried/ethylene glycol solvated oriented-aggregates of the clay fractions were prepared on glass slides. All oriented clay fractions were submitted to thermal treatments (300 and 500 °C). The diffraction data were analyzed using the XPOWDER® computer program (Martín-Ramos, 2004). For mineral quantification, the quantitative option of the XPOWER program was used considering the chemical analysis of major elements. Furthermore, the calculated structural formulae of the clay minerals were used as supplementary control data (López-Galindo et al., 1996). The experimental error was $\pm 5\%$.

Table 1
Description of the samples.

	Age	Sample	Formation
Lusitanian Basin	Upper Jurassic	L1	Boa Viagem
		L2	Freixial
		L3	Abadia
	Lower Cretaceous	L4	Torres Vedras
		L5	Figueira da Foz
	Upper Cretaceous	L6	Rodísio
			L7
Algarve Basin	Pliocene	L8	Barracão
	Lower Cretaceous	A1	Wealdian
		A2	Luz
		A3	Luz
Tagus/Lower-Tagus Basin	Miocene	A4	Cacela
	Paleogene	T1	Sarzedas
		T2	Torre
	Miocene	S1	Xabregas
		S2	Penedo
Alteration Products	Palaeozoic	O1	Ficalho
	Paleogene	O2	Benavila
	Miocene	O3	Serra Dentro
Commercial product		O4	Provida® green clays

Table 2
Mineralogical composition of the samples (in mass %).

Sample	L1	L2	L3	L4	L5	L6	L7	L8	A1	A2	A3	A4	T1	T2	S1	S2	O1	O2	O3	O4
Quartz	17	32	26	29	30	23	28	12	27	36	7	50	20	36	29	37	15	2	1	10
K-Feldspar	2	4	8	5	2	3	4	2	4	2	8	1	3	2	5	2	–	1	–	–
Na-Plagioclase	1	1	6	1	1	1	2	1	2	1	1	10	1	2	7	12	18	–	–	–
Anortite	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	7	21	–
Calcite	25	–	7	–	–	1	1	–	–	–	12	–	3	–	6	5	12	4	4	46
Dolomite	–	1	1	–	–	–	–	–	–	1	–	–	–	–	–	–	–	4	–	10
Gypsum	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	2
Anhydrite	–	–	–	–	–	1	–	–	–	1	–	–	–	–	–	–	–	–	–	–
Siderite	–	1	–	–	–	–	–	1	–	–	–	–	–	–	–	–	3	1	–	–
Fe Oxide/Hydroxide	4	4	5	15	11	5	4	2	7	8	10	1	2	3	3	2	3	5	9	2
Anatase	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	2	–
Hornblende	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	3	–	–
Cristobalite	–	–	–	–	–	–	–	–	–	–	–	3	–	–	2	–	–	1	–	–
Kaolinite	18	22	8	28	36	18	22	63	20	4	11	8	7	10	20	5	22	16	–	10
White micas (Illite)	23	34	31	22	20	48	34	15	35	47	50	17	17	20	21	27	21	3	10	10
Palygorskite	–	–	–	–	–	–	–	3	–	–	–	–	–	35	20	–	–	–	–	–
Smectite	10	–	–	–	–	–	5	–	5	–	1	10	7	5	10	7	13	40	53	9
Chlorite	–	–	8	–	–	–	–	–	–	–	–	–	5	2	–	2	–	–	–	–
I-S	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	5	–	–

The chemical composition of major, minor and trace elements of the <63- μm fraction was determined by XRF and flame-photometric methods, using a Philips PW1404 X-ray fluorescence spectrometer and a Coring 400 flame photometer (for Na and K).

Transmission electron microscopy (TEM) was preferentially used to obtain the structural formulas of the identified clay minerals. Observations and microanalyses were performed on several individual clay mineral microparticles and the average compositions of these clay minerals were calculated. Analyses were conducted using a PHILIPS CM 20 TEM/STEM fitted with an EDAX energy dispersive X-ray detector operated at 100 Å beam diameter and a 200 × 1000 Å scanning area.

2.2. Granulometry, morphology and microtexture

The grain size distribution was determined by an X-ray beam particle size analyzer (Micromeritics® Sedigraph 5100), which measures the gravity-induced settling rates of different particles (0.5–250 μm diameter) in a liquid with known properties.

Clay particles morphology data were obtained using a Leo 1430 VP Scanning Electron Microscope (SEM) equipped with an Oxford Instruments INCA 350v.18 microanalysis system using X-Ray dispersive energy system (EDS).

2.3. Flow properties

As indirect method for flow characterization, the common pharmacopoeias propose the measurement of bulk density (EP 6th, 2007; USP, 2010). By using the apparatus described in the European Pharmacopoeia (EP 6th, 2007), and following the proposed methodology, 30 g of each powder sample (total and <63 μm fraction) was introduced in a 250-mL cylinder and the corresponding bulk volumes were measured. Then, by using the mechanical tapping device, the powder was tapped at a constant velocity so that the initial bulk density (d_0) was reduced depending of the number of taps (d_{10} , d_{500} and d_{1250}). The measured bulk volumes and corresponding densities were used to calculate compressibility Carr index and Hausner ratio, both used to quantify powder flow (Wells and Aulton, 2007).

3. Results and discussion

3.1. Mineralogical composition

The mineralogical composition of the <63- μm samples is shown in Table 2. The sediments of the Lusitanian Basin (samples L1–L8) were

rich in quartz, white micas and kaolinite independently of their age. Detrital tectosilicates (quartz, K-feldspar and plagioclases) accounted for about a third of the total composition, and calcite was only significant in L1 and, into a lesser extent, in L3. With regards to clay minerals, kaolinite was rich in the Lower Cretaceous and Pliocene sediments, where it reached 63% of the bulk composition. White micas were always present with noticeable quantities (between 15% and 48%), having a high crystallinity according to the Kübler's index of the white micas (Kübler, 1967), in the Jurassic samples. Smectites were only detected in L1 and L7, chlorite in L3 and palygorskite in L8, but they represented 8% or less of the bulk composition. Fe-oxides were also found in low to moderate amounts.

Concerning Algarve basin Cretaceous sediments (samples A1–A3), they were rich in illite¹ and, to a lesser extent, in quartz and Fe-oxides. Carbonates were only significant in sample A3 and kaolinite content was highly variable (from <5% up to 20%). This mineralogical composition was different in the Miocene sample (A4) where detrital tectosilicates accounted for 61% of the bulk composition, and smectite was well represented (10%). Also, this was the only sample containing cristobalite.

The samples of the Tagus (T1 and T2) and Sado (S1 and S2) basins showed similar quantities of feldspars and high amounts of quartz. Carbonate and Fe-oxides contents were very low (Veniale et al., 2007). Concerning the clay minerals, illite appeared in lower amounts when compared with the above mentioned sequences. It showed better crystallinity in S2 (Fig. 2) while S1 showed significant quantities of kaolinite in the bulk sample. The presence of palygorskite in T1 and T2, reaching up to 35% of the bulk sample, should be mentioned. These results were in agreement with previous studies (Dias, 1998; Dias et al., 1997). Smectites (ranging from 5% to 10%) and chlorites (<5%) were identified in all sediments, with exception of S1 which did not contain chlorite.

In the altered products (O1–O3), in contrast to the sediment samples, low contents of quartz were observed. K-feldspars were almost absent, and plagioclases showed significant amounts (18% of Na-plagioclase in O1 and 21% anortite in O3). Carbonates were detected in all these samples and were particularly well represented in O2 (16%). Fe-oxides were found in all samples, and amphibole was identified in O2. Smectites were present in the alteration products of Palaeozoic rocks but only reached high content (40–53%) in the Tertiary samples, one of which (O2) contained the only illite–smectite mixed layer mineral. Illite was present in highly variable amounts (3–

¹ The term "illite" is referred as a non-expandable dioctahedral aluminous mica-like mineral occurring in the <4- μm clay size fraction.

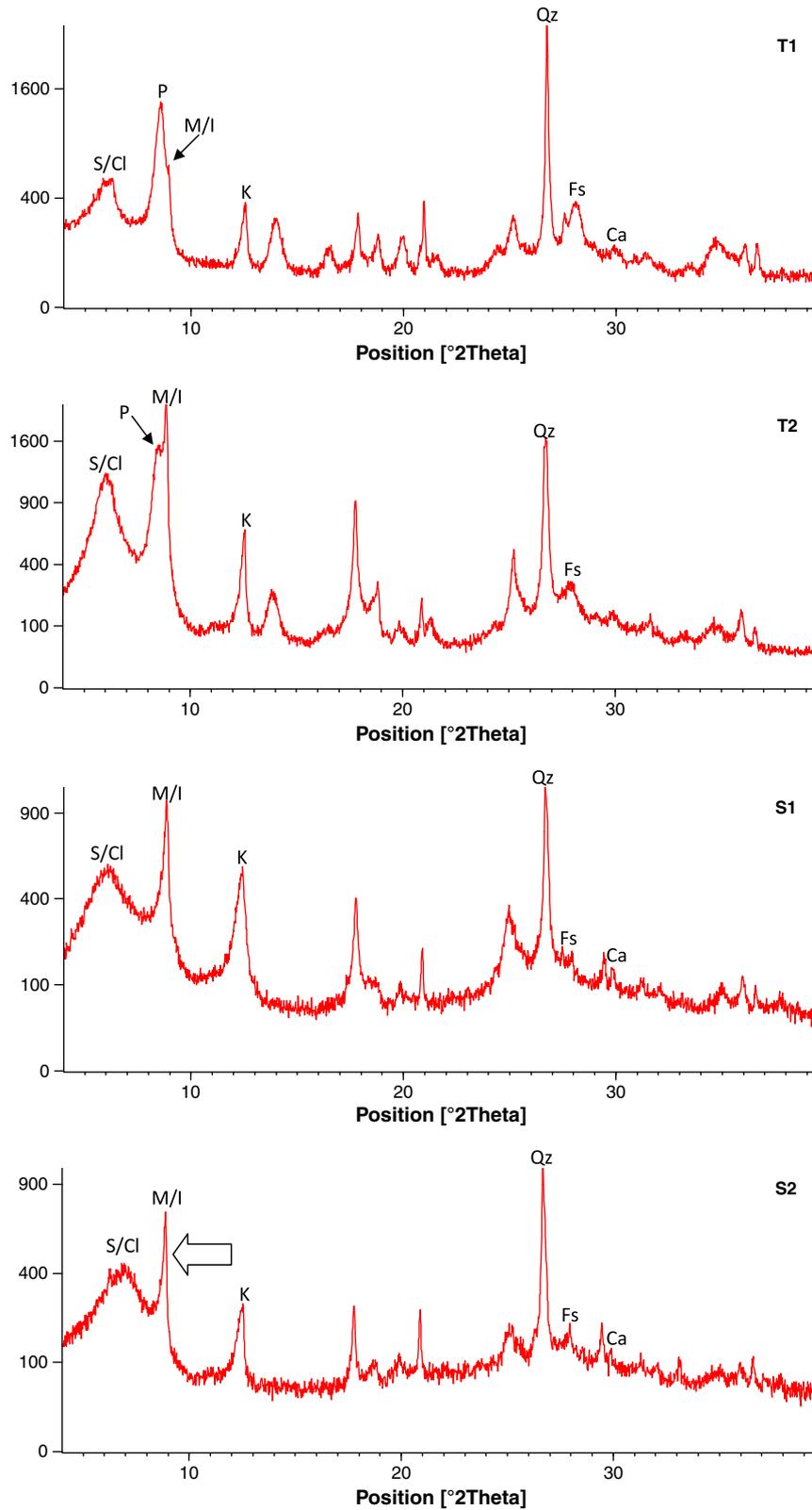


Fig. 2. XRD patterns of air-dried oriented aggregates from Tertiary samples, with mica/illite showing better crystallinity in sample S2. [Legend: Qz = Quartz; Fs = Feldspars; M/I = Mica/Illite; K = Kaolinite; Ca = Calcite; S/Cl = Smectite/Chlorite; P = Palygorskite.]

21%), and kaolinite, not always present, appeared both in Palaeozoic and Tertiary alteration products.

The commercial product (O4) was very rich in carbonates (46% calcite, 10% dolomite), and presented similar contents of quartz,

kaolinite, illite and smectite (about 10%). Lesser quantities of gypsum and Fe-oxides were also present.

The average structural formulas for the identified clay mineral particles are shown in Table 3. From the mineralogical point of view,

Table 3
Average structural formulas of the identified clay mineral particles.

Age	Clay mineral	Formula
Lusitanian Basin	Upper Jurassic	White micas Beidellite (Si _{3.19} Al _{0.81})O ₁₀ (Al _{1.57} Mg _{0.20} Fe _{0.30})OH ₂ (K _{0.49} Ca _{0.05} Na _{0.03} Mg _{0.09}) (Si _{3.50} Al _{0.50})O ₁₀ (Al _{1.41} Mg _{0.28} Fe _{0.40})OH ₂ (K _{0.22} Ca _{0.05} Na _{0.06} Mg _{0.06}) · nH ₂ O
	Lower Cretaceous	White micas (Si _{3.07} Al _{0.93})O ₁₀ (Al _{1.83} Mg _{0.03} Fe _{0.16})OH ₂ (K _{0.47} Na _{0.06} Mg _{0.17})
	Upper Cretaceous	White micas Beidellite (Si _{3.28} Al _{0.72})O ₁₀ (Al _{1.51} Mg _{0.24} Fe _{0.33})OH ₂ (K _{0.46} Ca _{0.02} Mg _{0.11}) (Si _{3.48} Al _{0.52})O ₁₀ (Al _{1.39} Mg _{0.36} Fe _{0.37})OH ₂ (K _{0.33} Ca _{0.03} Mg _{0.07}) · nH ₂ O
Algarve Basin	Lower Cretaceous	White micas Beidellite (Si _{3.27} Al _{0.73})O ₁₀ (Al _{1.54} Mg _{0.23} Fe _{0.30})OH ₂ (K _{0.45} Ca _{0.03} Na _{0.09} Mg _{0.08}) (Si _{3.44} Al _{0.56})O ₁₀ (Al _{1.40} Mg _{0.27} Fe _{0.42})OH ₂ (K _{0.37} Ca _{0.03} Mg _{0.06}) · nH ₂ O
	Miocene	White micas Beidellite (Si _{3.22} Al _{0.78})O ₁₀ (Al _{1.86} Mg _{0.04} Fe _{0.16})OH ₂ (K _{0.28} Na _{0.03} Mg _{0.17}) (Si _{3.47} Al _{0.53})O ₁₀ (Al _{1.46} Mg _{0.22} Fe _{0.39})OH ₂ (K _{0.22} Ca _{0.02} Mg _{0.13}) · nH ₂ O
	Tagus Basin	Paleogene
Sado Basin Alteration Products	Miocene	Beidellite (Si _{3.54} Al _{0.46})O ₁₀ (Al _{1.64} Mg _{0.27} Fe _{0.18})OH ₂ (K _{0.20} Ca _{0.04} Mg _{0.09}) · nH ₂ O
	Paleozoic	Palygorskite (Si _{7.62} Al _{0.38})O ₂₀ (Al _{1.86} Mg _{1.83} Fe _{0.27})OH ₂ (K _{0.19} Ca _{0.02} Mg _{0.05}) · 4H ₂ O
	Paleogene	Beidellite (Si _{3.58} Al _{0.42})O ₁₀ (Al _{1.30} Mg _{0.40} Fe _{0.43})OH ₂ (K _{0.23} Ca _{0.08} Mg _{0.03}) · nH ₂ O
	Miocene	White micas Montmorillonite (Si _{3.11} Al _{0.89})O ₁₀ (Al _{1.70} Mg _{0.13} Fe _{0.22})OH ₂ (K _{0.50} Na _{0.13} Mg _{0.13}) Si ₄ O ₁₀ (Al _{1.32} Mg _{0.44} Fe _{0.33})OH ₂ (K _{0.01} Ca _{0.11} Na _{0.03}) · nH ₂ O (Si _{3.65} Al _{0.35})O ₁₀ (Al _{1.29} Mg _{0.50} Fe _{0.36})OH ₂ (K _{0.05} Ca _{0.07} Na _{0.23}) · nH ₂ O

the *a priori* most convenient samples to be used in future medical hydrology applications should be L2, L6, L8, A3, T1, S1, O2 and O3, because they have reasonable clay mineral contents, usually around 50–60% in the <63- μ m fraction.

3.2. Granulometry and micromorphology

Grain size distribution of bulk sediments is shown in Fig. 3. In the Lusitanian basin sediments, significant quantities (30–40%) of sand-sized particles were found in L1, L3 and L5. Jurassic samples were rich in silt-sized particles while Cretaceous and Pliocene sediments were rich in clay-sized particles. This fine fraction accounted for almost 80% of samples L7 and L8. In the Algarve basin sediments, only samples A2 and A3 showed an important clay-sized fraction (around 60%), while the Miocene sample, the richest in quartz, presented almost 80% of silty particles. Tagus and Sado basins sediments were very poor in clayey particles and sandy fraction was particularly significant (around 60%) in T2 and S2. With reference to alteration products, all samples were quite rich in sand particles, representing more than 60% of their bulk composition in samples O2 and O3. The commercial product was rich in silty particles (54%) but still had a notable content of sandy particles (17%).

Veniale et al. (2007) points out that a suitable peloid must have at least 70–80% of clay sized particles. In addition, studies (Armijo and Maraver, 2006) showed that the majority of Spanish Thermal Centres apply peloids with about 57–70% of particles sized between 2 and 20 μ m. In this sense, the best Portuguese materials without mechanical grinding were L2, L4, L7, L8, A2 and A3. Concerning samples O2

and O3, its application is only advisable if the sand sized particles were previously separated.

All samples showed highly variable morphologies. Many particles were disposed in aggregates with heterogeneous shape and size. The Lusitanian sediments were the most heterogeneous ones, showing large aggregates (> 100 μ m) and less particles of smaller size (Fig. 4A). These aggregates were composed of small platy particles (usually <2 μ m), which sometimes acquired a more flocculated appearance (Fig. 4B). The Algarve basin sediments showed more homogeneous and pseudospherical aggregates (with size usually not exceeding 100 μ m, Fig. 4C), while in the Tagus sediments large aggregates were rare and associated with fibrous palygorskite particles (Fig. 4D). In the Sado sediments, aggregates were of small size, generally <50 μ m. The alteration products showed quite distinct morphologies. They were mainly composed of large angular aggregates (200–500 μ m, Fig. 4E) made up of planar smectite particles (Fig. 4F).

3.3. Chemical composition

The contents of major elements are shown in Table 4 and, as expected, they showed a direct relationship with the mineral composition. Samples were rich in SiO₂ representing, in average, about 50–60% of the bulk composition. Al₂O₃ was around 15–20% (except L8, the richest in kaolinite, and O4, the richest in calcite). The Fe₂O₃ content was highly variable, as a direct function of the amounts of Fe-oxides. MgO was below 3%.

The content of trace elements could be classified into three categories (Table 5). “Class 1” included Cd, Pb and As, elements that

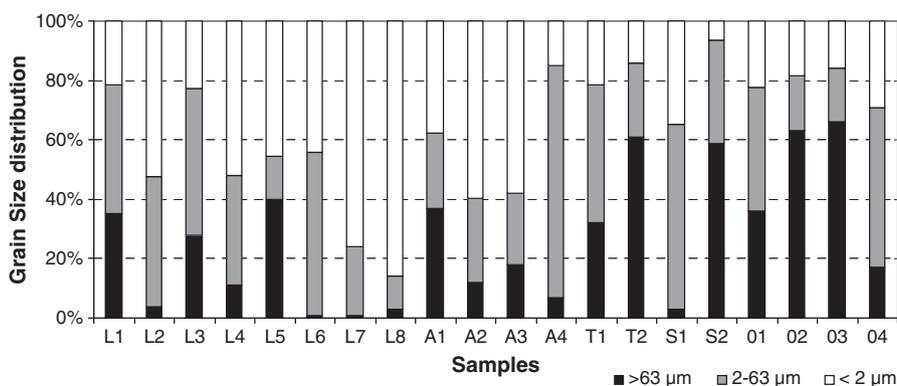


Fig. 3. Grain size distribution of the bulk samples.

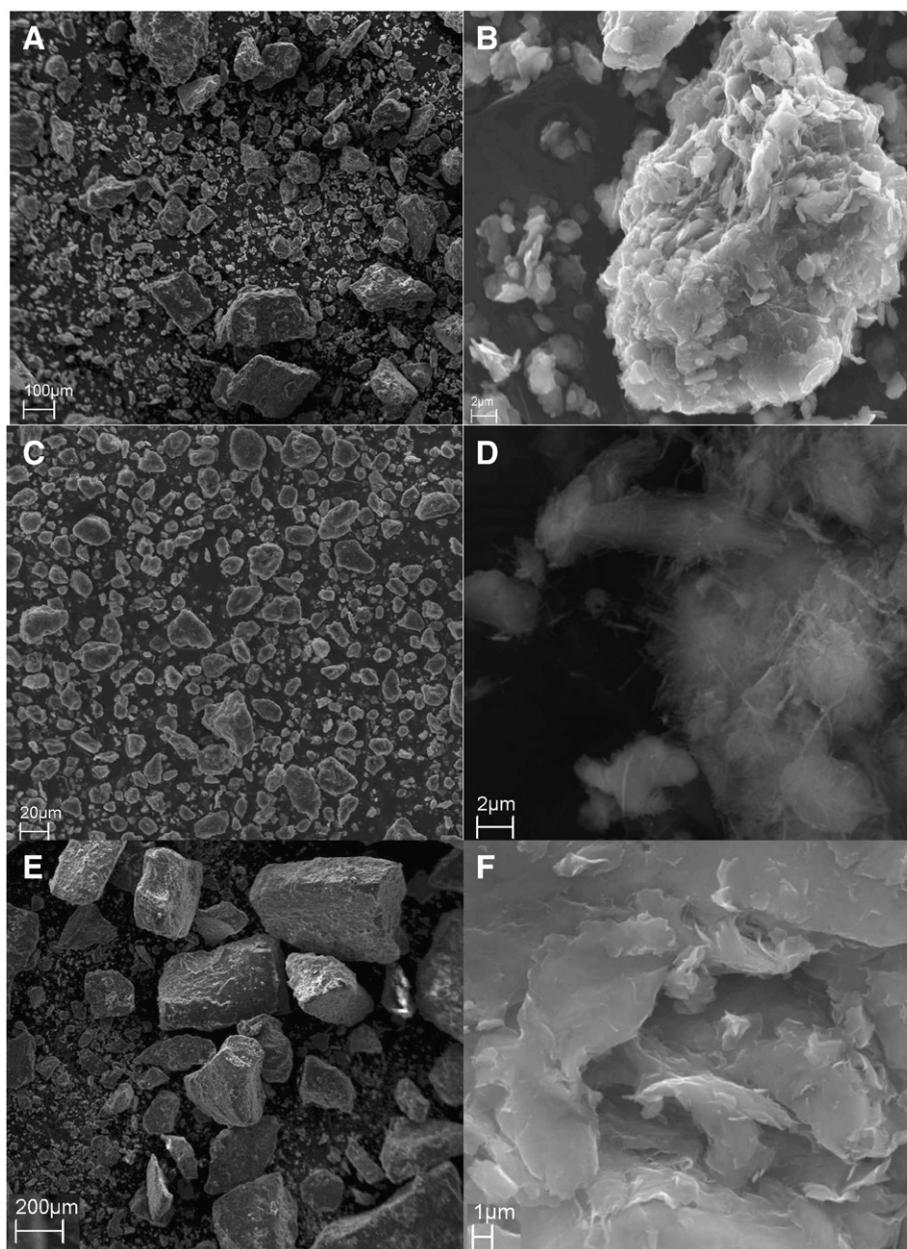


Fig. 4. SEM microphotographs of the samples. (A) General view of large aggregates in sample L3. (B) Detailed image of particles in a large aggregate of sample L8. (C) General view of pseudospherical aggregates in sample A2. (D) Detailed image of an aggregate with fibrous palygorskite particles in sample T1. (E) General view of angular big aggregates in sample O3. (F) Detailed image of planar smectite particles in sample O2.

should be essentially absent because they are known as human toxicants or environmental hazards (USP, 2010). “Class 2” included Mo, Ni, V, Cr, Cu and Mn, elements that should be limited in pharmaceuticals and have less toxicity than those present in “Class 1” (USP, 2010). “Other metals” included elements which may also be present as impurities in cosmetic products (e.g. Ba, Se, Zn and Sb). Even though Zn has no significant toxicity (EMEA, 2008), Sb is included as an element of primary toxicological concern in cosmetics together with Pb, As, Cd and Hg (Health Canada, 2009). In the case of Se and Ba, in spite of their less significant toxicological properties and risks, no impurity limits were developed for cosmetics (Health Canada, 2009). Tl and Te were also included as elements that are not allowed in cosmetic products, including clays and peats for pelotherapy (European regulation n.85/391/CEE,86/179/CEE and 86/199/CEE).

The analyzed trace elements exhibited normal values for sediment samples (Carretero and Pozo, 2007). However, when compared with the known abundances of sediments on Earth's Crust (Turekian and

Wedepohl, 1961), some anomalies were detected for As (samples A1 and T1) and Cr (sample O2). The natural abundance of As in the Earth's Crust is about 1.8 ppm (De Stefano et al., 2010), being higher when associated with sulphur minerals in soils (Carretero and Pozo, 2007). As S was not detected in A1 and T1, the As anomaly in these samples was linked to the surrounding lithology. The content of Cr (sample O2) was in agreement with the values presented by basaltic magmatic rocks (2–600 ppm) and was attributed to the origin of the sample O2 in the Eruptive Rocks of Benavila formation.

To discuss the exposure limits on the basis of toxic chemicals present in pharmaceuticals and cosmetics, the term “Permitted Daily Exposure” (PDE) was used. This term was recently chosen to better define, on a chronic basis, the pharmaceutically maximum acceptable exposure to an element that is unlikely to produce any adverse health effect. The presented limits of trace elements were according to those currently defined as acceptable for pharmaceuticals and cosmetics (Health Canada, 2009; EMEA, 2008; USP, 2010).

Table 4
Major and trace elements composition of the samples.

Samples		L1	L2	L3	L4	L5	L6	L7	L8	A1	A2	A3	A4	T1	T2	S1	S2	O1	O2	O3	O4	
Major elements (%)	SiO ₂	41.72	57.95	56.01	50.11	50.10	56.00	59.95	47.29	58.35	57.23	44.81	76.98	58.46	64.16	62.79	67.28	53.00	44.74	46.65	23.93	
	Al ₂ O ₃	14.58	22.23	16.90	18.70	22.70	20.21	19.54	26.23	19.63	18.72	17.26	11.96	15.49	14.93	16.80	12.56	21.10	13.23	16.81	9.40	
	Fe ₂ O ₃	8.67	4.33	6.82	17.65	14.70	6.73	5.14	3.70	7.02	10.09	11.85	2.41	4.98	5.49	5.30	4.60	5.80	7.96	11.82	4.07	
	MgO	1.57	1.76	2.30	1.11	0.40	1.93	2.81	0.87	2.08	1.16	1.42	0.63	6.01	3.47	1.60	1.45	2.59	5.60	3.33	2.42	
	CaO	14.86	0.27	4.21	0.14	0.10	0.86	0.80	0.10	0.40	0.57	6.93	0.09	2.09	0.32	1.77	3.38	3.03	10.00	6.33	29.03	
	Na ₂ O	0.15	0.31	0.72	0.29	–	0.62	0.66	0.24	0.36	0.20	0.08	1.58	0.17	0.22	0.95	1.53	2.11	0.24	1.83	0.01	
	K ₂ O	3.15	4.42	3.60	3.56	2.80	5.05	4.35	2.74	4.68	4.90	6.26	1.87	1.93	2.92	3.74	2.73	3.32	0.48	1.35	1.47	
	TiO ₂	1.03	1.09	0.77	1.17	1.30	0.87	0.75	1.03	1.09	1.40	1.33	1.14	0.70	0.91	0.87	1.12	0.70	0.62	3.10	0.45	
	P ₂ O ₅	0.08	0.04	0.11	0.08	0.10	0.06	0.08	0.01	0.03	0.02	–	0.02	0.03	0.13	0.06	0.12	0.02	0.02	0.11	1.13	0.04
	SO ₃	0.03	●	●	●	●	1.00	–	●	–	0.03	0.04	–	–	●	–	●	0.14	●	●	1.03	
	LOI	13.90	7.20	8.10	6.70	7.80	7.10	5.90	17.80	6.30	5.40	10.00	3.30	10.10	7.00	6.10	5.20	8.30	16.80	7.40	28.30	
	Trace elements (ppm)	Component limit																				
As		15	24	4	2	12	9	47	53	4	105	12	17	*	80	27	*	*	18	5	*	*
Cd		5	*	*	*	*	*	*	35	–	11	–	*	7	4	*	–	17	6	–	–	4
Pb		10	28	27	31	18	66	55	53	52	55	13	17	36	55	21	33	50	38	5	4	14
Sb		5	*	*	*	*	*	10	–	*	14	*	*	–	8	*	–	14	–	–	–	*
Component limit																						
Cr		250	55	79	68	104	85	196	66	79	113	109	94	81	75	71	195	66	36	401	79	65
Cu		2500	14	22	14	35	42	24	10	18	35	16	15	9	14	50	16	13	7	18	90	8
Mn		2500	*	*	*	*	*	152	195	*	307	*	*	83	314	*	161	152	332	*	*	151
Mo		250	1	1	1	1	1	3	*	1	4	1	1	–	2	1	2	–	–	–	1	2
Ni		250	29	38	38	40	20	41	29	34	42	31	38	11	30	37	28	19	10	57	3	22
V		250	115	187	146	149	142	115	114	198	170	146	180	61	103	140	88	57	63	98	188	62
Component limit																						
Ba		n.a	437	463	567	397	401	261	252	344	376	715	279	266	290	438	361	250	786	309	504	120
Se		n.a	*	*	*	*	*	16	7	*	3	*	*	–	3	*	–	12	–	–	–	1
Zn		13,000	73	69	150	76	48	33	27	66	82	76	62	*	43	117	87	3	66	35	99	27
Tl		n.a	*	*	*	*	*	51	17	*	–	*	*	17	2	*	4	–	–	–	–	*
Te		n.a	*	*	*	*	*	16	9	*	6	*	*	32	–	*	–	31	16	–	–	*

* Below detection limit.

● Not determined.

Table 5
Powder flow characterization of the samples.

<63 μm				Total		
	Carr (%)	Hausner	Flow	Carr (%)	Hausner	Flow
L1	32	1.5	Poor	28	1.4	Poor
L2	24	1.3		22	1.3	
L3	32	1.5		31	1.5	
L4	29	1.4		25	1.3	
L5	33	1.5		19	1.2	Fair
L6	35	1.5	Very poor	31	1.5	Poor
L7	24	1.3	Poor	33	1.5	
L8	24	1.3		20	1.3	Fair
A1	29	1.4		18	1.2	Fair
A2	20	1.3	Fair	31	1.4	Poor
A3	20	1.3		24	1.3	Poor
A4	29	1.4	Poor	22	1.3	Fair-Poor
T1	23	1.3		19	1.2	Fair
T2	26	1.4		15	1.2	Good
S1	24	1.3		25	1.3	Poor
S2	35	1.5	Very poor	30	1.4	
O1	29	1.4	Poor	23	1.3	
O2	25	1.3		27	1.4	
O3	22	1.3	Fair poor	14	1.2	Good
O4	29	1.4	Poor	27	1.4	Poor

Concerning “Class 1”, the As content was below the detection limit of the used technique in a few samples (A4, S1, S2, O3 and O4) but, when present, was acceptable for cosmetic usage and was in agreement with the PDE in samples L4, L5 and A2. The studied samples presented no high risk of toxicity since dermal exposure to As contributes <1% of the exposure from ingestion (US FDA, 2003). Pb was always present in variable quantities, of acceptable toxicity mainly in samples O2 and O3, and was closer to the limits for cosmetic usage in samples L4, A2, A3 and O4 (Health Canada’s Natural Health Products Directorate). The other samples also showed low toxicity since the Pb content in sediments usually ranges between 30 and 300 ppm (De Stefano et al., 2010). Cd was frequently below the detection limits and, when detected, was acceptable in samples T1, O1 and O4.

With regards to “Class 2”, all studied samples (except the Cr anomaly) presented acceptable PDE concentrations. In “Other metals” category the Zn content was tolerable, also in accordance with typical values for clays/shales, and the Sb content was in agreement with cosmetic usage limits. When detected, the remaining elements showed quantities not exceeding 20 ppm.

In conclusion, except for A1, T1 and O2, the studied materials exhibited normal to low toxic element concentrations. Therefore, they showed a low risk of toxicity if a dermal application is intended, and were considered safe.

3.4. Powder flow properties

Table 5 shows the powder flow properties of the samples. Carr indexes of the <63- μm fractions were >23% (poor flow powders) and decreased in most of the corresponding bulk samples (fair-poor flow powders). The Hausner indexes ranged between 1.2 and 1.5 in both the bulk samples and the <63- μm fraction.

Table 6
Suitability of the samples for medical hydrology treatments.

	L1	L2	L3	L4	L5	L6	L7	L8	A1	A2	A3	A4	T1	T2	S1	S2	O1	O2	O3	O4
Mineralogy	◊	○	■	■	◊	○	◊	○	◊	■	○	■	○	◊	○	■	◊	○	○	■
Granulometry	■	○	■	○	■	○	○	○	■	○	○	■	■	■	◊	■	■	◊	◊	■
Chemistry	○	○	○	○	○	○	○	○	■	○	○	○	■	○	○	○	○	■	○	○
Flowability	◊	◊	◊	◊	◊	■	◊	◊	◊	○	○	◊	◊	◊	◊	◊	◊	◊	○	◊
Overall suitability	◊	○	■	◊	◊	◊	○	○	■	◊	○	■	■	◊	○	■	◊	◊	○	■

○ Advisable; ◊ Advisable with limitations; ■ Not Advisable.

Some samples showed distinct behavior. The <63- μm fractions of two Algarve basin samples (A2 and A3) showed fair flow properties and one total bentonitic sample (O3) showed good flow. On the other hand, samples L6 and S2 showed the highest Carr Index values and were considered very poor flow powders. Thus, the samples should be used as bulk as possible to avoid problems during their manipulation. In some cases, they would need addition of coadjutants to improve the flow properties.

4. Conclusions

Table 6 shows the suitability of the studied samples for medical hydrology applications. The Lusitanian basin samples (L1 to L8) presented advisable properties and some limitations because of the small amounts of the clay fractions and the clay mineral content. L2 and L8 showed mineralogical and chemical composition, optimal for the preparation of peloids. L7 also presented an advisable composition even if high quartz content should be reduced. L6, currently used for traditional treatments at Parede Beach, had good compositional parameters but the flow properties should be improved.

Regarding the Algarve samples (A1 to A4) only those from the Luz formation were advisable (A2 and A3) if the quartz content of sample A2 is reduced. The results confirmed the actual therapeutic utility of these clays at Burgau and Luz beaches and guaranteed their mineralogical and chemical safety.

Tertiary samples (T1 to S2) presented unsuitable characteristics due to their high content in sand-sized particles. Only S1 was considered suitable but the therapeutic use of sample S2 at Meço Beach was not favored considering the obtained data.

Samples O1 to O3 (alteration products) showed also advisable properties with limitations. O3 was the most suitable product due to its good flow properties whereas O2 (with similar flow behavior) is not advisable before its bioavailability is tested. The commercial product (O4) was safe but presented a very high content of carbonates that, due to their abrasivity, could cause some discomfort during application.

It can be concluded that samples L2, L7, L8, A3, S1 and O3 presented good compositional, safety and technological properties to be used in medical hydrology treatments.

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