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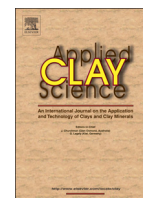
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Highlights

Assessment of three Spanish clays for their use in pelotherapy*Applied Clay Science xxx (2014) xxx – xxx*M.I. Carretero ^{a,*}, M. Pozo ^b, J.L. Legido ^c, M.V. Fernández-González ^d, R. Delgado ^d, I. Gómez ^a, F. Armijo ^e, F. Maraver ^e^a Dpto. Cristalografía, Mineralogía y Química Agrícola, Universidad de Sevilla, Prof. García González no 1, 41012 Sevilla, Spain^b Dpto. Geología y Geoquímica, Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain^c Dpto. Física Aplicada, Facultad de Ciencias Del Mar, Universidad de Vigo, Campus Lagoas-Marcosede, 36310 Vigo, Spain^d Dpto. Edafología y Química Agrícola, Facultad de Farmacia, Universidad de Granada, Campus Universitario de Cartuja s/n, 18071 Granada, Spain^e Escuela de Hidrología Médica, Facultad de Medicina, Universidad Complutense de Madrid, 28040 Madrid, Spain

- Determination of the best clay for use in pelotherapy.
- The montmorillonite and saponite were more suitable for use in pelotherapy.
- The saponite showed the best properties for use in thermotherapy.
- The kerolite-stevensite was not suitable for use in thermotherapy.

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Research Paper

Assessment of three Spanish clays for their use in pelotherapy

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ABSTRACT

The mineralogy, geochemistry and physical and physicochemical properties of three Spanish clays and their mixtures with distilled water were determined. These results were compared with the data obtained by other authors for peloids from spas in Spain and Turkey. The main clay minerals of the samples studied were montmorillonite in Clay1, saponite in Clay2 and kerolite–stevensite in Clay3. The results obtained showed that all three clays share some properties with clays already in use, but Clay1 and Clay2, that are quite rich in smectite, are more suitable when the typical smectite features are needed for therapy. The peloid from saponite was the most suitable for thermotherapy while the kerolite–stevensite sample was not suitable for the preparation of peloids for this use.

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1. Introduction

Pelotherapy is the topical use of peloids for therapeutic or cosmetic purposes (Veniale et al., 2004). A peloid is a matured mud or muddy suspension/dispersion with healing and/or cosmetic properties, composed of a complex mixture of fine-grained materials, mineral water or sea water, and, often, organic compounds from biological metabolic activity (Gomes et al., 2013). In addition to its cosmetic uses, pelotherapy is a mainly coadjuvant method for the treatment of chronic rheumatic conditions, resulting in significant improvements in clinical parameters, life quality, and need for medication (Espejo-Antúnez et al., 2013; Forestier et al., 2010). This use of pelotherapy is becoming increasingly popular and spas tend to prepare their peloids using their own mineral–medicinal water. However, the choice of solid material for peloid preparation can be difficult for the spa. Within the so-called inorganic peloids (Gomes et al., 2013), clays are the most common solid phase and require special expertise for its evaluation. As the clay supplier does not usually carry out an analysis of the clay regarding its use in pelotherapy choosing the most suitable clay can be problematic for the spa.

The first step in choosing a suitable clay is mineralogical and chemical characterization, but other properties are also important. These

include cation exchange capacity, granulometry, adsorption capacity, pH, plasticity, rheological and thermal properties (Carretero et al., 2006, 2013; Veniale et al., 2007). Others determined by some authors for peloids traditionally used in spas are percent water, solids and ash in the clay–water mixture prior to maturation, swelling, color, density, abrasiveness and instrumental texture (cohesiveness, hardness, adhesiveness and springiness) (Karakaya et al., 2010; Pozo et al., 2013). Knowledge of the microfabric at the electron microscope level is also essential, as shown recently by Gámiz et al. (2009).

Some properties related to suitability for pelotherapy have been studied in clays from Italy (Cara et al., 2000a, 2000b; Ferrand and Yvon, 1991; Summa and Tateo, 1998), Portugal (Gomes and Silva, 2001; Rebelo et al., 2010, 2011), Cape Verde (Gomes et al., 2008) and Spain (Casás et al., 2011, 2013; Legido et al., 2007; Ortiz de Zarate et al., 2010). Furthermore, some properties of peloids prepared with clays, different types of water and different maturation conditions have been studied (Carretero et al., 2007; Curini et al., 1990; Gámiz et al., 2009; Quintela et al., 2010; Sánchez et al., 2002; Tateo et al., 2010; Veniale et al., 2004). However, these studies include only some of the properties important in pelotherapy while others do not consider the modifications to these properties which occur during preparation of the clay–water mixture prior to maturation.

The aim of the present study is to characterize three Spanish clays which are available commercially for peloid preparation for possible use in spas. To this end, their mineralogy and chemistry were characterized, their microfabric studied and the physical and physicochemical properties of both the clays and the mixtures of these with distilled

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water determined. The results obtained were compared with the corresponding data for peloids already in use in spas in Spain (Pozo et al., 2013) and Turkey (Karakaya et al., 2010) to discuss their possible use in pelotherapy. The results of this research will be useful to the spas which want to prepare their own peloids with their mineromedicinal water, when they must choose the appropriate solid phase. But a study of the peloid prepared in each case will always be necessary, because their properties will be different depending on the different waters and different procedures and therefore they could have diverse therapeutical applications.

2. Materials

The clays studied were from Spanish deposits currently exploited by Süd-Chemie España and can thus be bought by any spa which deems them useful for pelotherapy. The Clay2 and Clay3 samples are from the magnesium clays of the Madrid Basin while Clay1 sample is from the bentonite deposits of Cabo de Gata (Almería).

3. Methodology

3.1. Mineralogical characterization

For the mineralogical study the clay samples were examined by X-ray diffraction analysis with a SIEMENS D-5000 instrument and DIFFRACT-AT v3.00 software. The samples ground to less than 50 μm were X-rayed from 2° to 65° 2 θ using disoriented powder and CuK α radiation with a scanning speed of 1° 20/min. The identification of clay fraction minerals (less than 2 μm) was carried out on oriented Mg²⁺-saturated samples (dry sedimented onto glass sample holders), with ethylene glycol solvation and heat-treated at 550 °C. The diagrams were between 2 and 30° 2 θ . Quantitative estimation of the mineral content was carried out using the intensity factors calculated by Schultz (1964) and Barahona (1974).

The crystallinity of the smectites was studied through measurement of the full width at half maximum peak intensity (FWHM) of the d(001) peak after treatment with ethylene glycol (approximately at 17 Å). The software used was Xpovder (<http://www.xpovder.com>). The procedure is based on the direct relationship existing between crystallinity and crystallite size (coherent diffraction domain), the latter being calculated through the Scherrer equation. Particle size is inversely proportional to the FWHM value, crystallinity thus decreasing as the FWHM value increases.

3.2. Differential thermal analysis and thermogravimetric analysis

The powdered dried sample was analyzed with a simultaneous thermal analysis system ATD/DSC/TG model Q600 by TA Instruments at a work interval of: ambient/1200 °C.

3.3. Chemical composition

The chemical analysis of the samples was carried out by Activation Laboratories Ltd., Ontario (Canada). A total of 63 elements were determined. After an acid digestion of the samples, the following techniques were used for specific elements: INNA: As, Br, Fe, Hg, Ir, Na, Sb, Sc, W; TD-ICP: Al, Ca, K, Mg, Mn, Mo, P, S, Ti, V; TD-MS: Dy, Er, Ga, Gd, Ge, Ho, In, Li, Nb, Pr, Re, Sn, Sr, Te, Tl, Tm, Y, Zr; MULT INAA/TD-ICP/TD-MS: Ag, Ni, Zn; TD-MS/INNA: Ce, Eu, Hf, La, Lu, Nd, Sm, Tb, Yb; MULT INAA/TD-ICP-MS: Ba, Co, Cr, Cs, Rb, Se, Ta, Th, U; MULT TD-ICP/TD-ICP-MS: Be, Bi, Cd, Cu, Pb.

3.4. Preparation of clay-distilled water mixtures

Prior to the preparation of the mixtures several different tests were carried out to determine the most suitable ratios of clay to distilled

water and resting times so that the mixtures were of a suitable texture for pelotherapy. The resulting paste needed to be plastic, easy to handle and not to flow when applied to the skin. This prior study established the ideal ratios and resting times as those shown in Table 1, according to macroscopic evaluations, later on translated into instrumental measurements (see Section 3.6).

The mixtures were prepared by mixing clay and water in the correct proportions in plastic vessels. In order to achieve a good mix and to ensure that the clay particles were in contact with the water a Dynamic MF 2000 industrial mixer with a double stainless steel blade was used at 300 r.p.m. After slowly mixing all the clay and water the mixture was then beaten for 5 min to attain total homogenization. It was then left to rest for 1 to 2 days (depending on the clay, see Table 1) before determining its physical and physicochemical properties.

3.5. SEM study

To study the clays, the powdered mineral samples were fixed to aluminium sample holders using adhesive carbon tape. For the clay-distilled water mixtures the mud was placed on a specially constructed 2 cm diameter and 1 cm high cylindrical aluminium sample holder and frozen rapidly in a Reichert-Jung KF80 cryofixation system by propane immersion (T^a = 130/–140 °C). Following rapid freezing the water in the mixture is in the form of vitreous ice, preserving the relative positions of particles and spaces. The cryofixed samples were dried by lyophilization (Lyophilizer LABCONCO “Stopping Tray Dryer”, “Freeze Dry System”). The cryofixed and lyophilized samples were stored in a desiccated atmosphere (less than 20% humidity). The samples were studied freshly cut, with a fragment adhered to a sample holder using colloidal silver adhesive. Prior to observation the sample surface was metalized with a thin layer of gold, 5 to 10 nm. thick, in two orientations (Bohor and Hughes, 1971). The scanning electron microscope (SEM) used was a Hitachi S-510. The X-ray microanalysis was performed with a Röntec, 288, M-Series, Edwin energy dispersive X-ray spectrometer (EDX), connected to the SEM.

3.6. Physical and physicochemical properties

Swelling, cation exchange capacity and exchangeable cations were determined in the initial clays. In the clay-distilled water mixtures percent water, solids and ash, pH, viscosity, instrumental texture (cohesiveness, hardness, adhesiveness and springiness), thermal conductivity and thermal retentivity were all determined. Color, density, abrasiveness, granulometry, specific surface area (BET method), liquid limit, plastic limit, plasticity index and specific heat were determined for the clays and mixtures.

Swelling capacity was determined following the ASTM D 5890 method. Cation exchange capacity was determined using Tucker's method (Tucker, 1974), wherein the clay sample is saturated with 1 N ammonium chloride at pH 8.2. After which the presence of ammonium is measured using a Kjeldahl distillation apparatus and exchangeable cations (Ca²⁺, Mg²⁺, Na⁺ and K⁺) determined by atomic absorption spectrophotometry using a PerkinElmer AAnalyst 100 spectrophotometer.

Percent water, solids and ash (dry residue at 850 °C) were calculated following the methodology described by Armijo (2007), for the determination of these properties in peloids. Color was determined using the Pantone® method. The pH was measured using a HANNA instruments HI 99121 Soil pH test kit, with automatic temperature compensation.

Table 1

Ratios clay: water (w:v) for the different mixtures and rest time necessary to achieve suitable consistency for use in pelotherapy.

	Clay1	Clay2	Clay3	
Clay:distilled water proportion (w:v)	1:2	1:2.4	1:1.6	t1.5
Rest time (days)	1	1	2	t1.6

Density was determined using pycnometry (Ortiz de Zarate et al., 2010). Viscosity was determined using a Schott rotational viscometer (Cole Parmer, Vernon Hills, IL, EE.UU.), equipped with a coaxial cylindrical spindle (LCP) with a thermal jacket, following the method described by Pastoriza-Gallego et al. (2011). Abrasiveness was determined through mass loss (mg) from a bronze mesh before and after rotation of a dispersed clay using an Einleher AT100 abrasion tester.

The instrumental texture parameters were: cohesiveness, hardness, adhesiveness and springiness. These were measured using a Brookfield LFRA 4500 texture analyzer with a spherical stainless steel TA-10mmD probe following the methodology described by many authors (Armijo, 2007; Fry and Hudson, 1983; Pozo et al., 2013).

Particle size distribution of the samples was determined by photo-sedimentation, using a Micromeritics sedigraph 5100 ET, in the range 0.5 μm to 100 μm . To determine specific surface area a Micromeritics ASAP 2010 was used. The powdered sample was analyzed texturally by nitrogen adsorption at 77 K, by the single point method. The plasticity index was calculated using Atterberg limits, following the UNE 7-377-75 and UNE 103-104-93 guidelines.

The thermal properties studied in the clay-distilled water mixtures were specific heat, thermal conductivity and thermal retentivity. Specific heat was determined using a BT 2.15 SETARAM calorimeter. Simultaneous control of the thermodynamic variables, flow and temperature was achieved using a SETARAM controller and Setsoft2000 software (Casás et al., 2011). Measurements of thermal conductivity were taken using the Decagon KD2 Pro Thermal Properties Analyzer (Decagon Devices Inc., Pullman, WA, EE.UU.). This device conforms to guideline ASTM D5334 and IEEE 442-1981 regulations. The mode of action is based on the transient line heat source method (Pastoriza-Gallego et al., 2011). Thermal retentivity was calculated from the values of specific heat, density and thermal conductivity, being the product of specific heat multiplied by density, divided by thermal conductivity, and is the inverse of diffusion (Casás et al., 2013).

4. Results and discussion

4.1. Mineralogical characterization

Sample Clay1 was a bentonite of high purity, composed of more than 99% clay minerals and only traces of quartz (1%). The clay minerals were dioctahedral ($d_{(060)}$: 1.50 Å) (Table 2a, Fig. 1). The mineralogical study of the fraction of less than two microns showed the clay minerals to be exclusively smectites (Table 2b, Fig. 2). The mineralogical characterization of the main clay mineral has been described by Caballero et al. (2005) and corresponds to a montmorillonite.

Sample Clay2 was also a bentonite of high purity, consisting of 94% clay minerals and less than 5% quartz, calcite and feldspars. In this case the clay minerals were trioctahedral ($d_{(060)}$: 1.52 Å) (Table 2a, Fig. 1). The mineralogical study of the fraction of less than two microns revealed that it was composed of smectites (91%) and some illite (9%) (Table 2b, Fig. 2). The main clay mineral corresponded to a saponite, as described by Galán et al. (1986).

Sample Clay3 was composed of 98% clay minerals with traces of quartz, calcite and feldspars. The clay minerals were trioctahedral ($d_{(060)}$: 1.52 Å) (Table 2a, Fig. 1). The mineralogical study of the fraction of less than two microns showed the clay minerals to be mainly smectites (87%) although the sample also included some illite (13%) (Table 2b,

Fig. 2). The main clay mineral corresponded to a kerolite–stevensite, as reported by Martín de Vidales et al. (1991) and Pozo and Casas (1999). It should be noted that the smectites in this sample were less ordered (higher FWHM value, Table 2b) than those of the other clays.

The smectites of Clay1 and Clay2 exhibited basal spacing $d_{(001)}$ of 14.95 Å (Table 2a, Fig. 1), indicating the presence of divalent cations in the interlaminal space. This was later confirmed when the exchangeable cations were characterized, Ca^{2+} being predominant in Clay1 and Ca^{2+} and, principally, Mg^{2+} in Clay2 (see Fig. 5b). In Clay3 it was not possible to measure the basal spacing $d_{(001)}$ due to the poor crystallinity of the smectites present.

4.2. Differential thermal analysis and thermogravimetry

Sample Clay1 was characterized by two low temperature endothermic peaks at 88 °C and 160 °C, a medium temperature peak at 620 °C and a high temperature exothermic peak at 832 °C (Table 3a). The first two endothermic peaks are related to the loss of zeolitic water and the other to dehydroxylation of the clay minerals while the exothermic peak is the result of neoformation of high temperature phases. These characteristics are typical of a dioctahedral smectite (Paterson and Swaffield, 1987).

Sample Clay2 showed two endothermic peaks at 87 °C and 820 °C and an exothermic peak at 837 °C (Table 3a). The first endothermic peak is due to loss of zeolitic water and the second to dehydroxylation of the clay minerals. The exothermic peak is the result of neoformation of high temperature phases, enstatite in this case. These characteristics are typical of a trioctahedral smectite (Paterson and Swaffield, 1987).

Sample Clay3 showed a low temperature endothermic peak at 78 °C, one of medium temperature at 650 °C and a high temperature endothermic–exothermic double peak (815 °C and 831 °C) (Table 3a). The first endothermic peak is related to loss of zeolitic water, the second and third to dehydroxylation of clay minerals and the exothermic peak to neoformation of phases at high temperature, in this case, enstatite. These characteristics are typical of a trioctahedral smectite.

Total mass loss (TG) ranged from 16.84% to 19.49%, and mainly took place at less than 350 °C, as would be expected for this type of clay mineral (Brindley and Lemaître, 1987) (Table 3b).

4.3. Chemical composition

The concentrations of the most abundant elements in the clays studied (Table 4) were in agreement with the results obtained in the mineralogical study and confirmed that Clay1 was an aluminium bentonite (6.37% Al) and that Clay2 and Clay3 were composed of magnesium smectites (10% and 13% Mg, respectively). The most abundant trace elements in the three clays were Ba, Li and Sr (>50 ppm). Of particular note is the higher concentration of Ba, Li and Rb in Clay2 and Clay3 and of Br, As, V and U in Clay3 with respect to the other clays. Furthermore, Clay1 showed higher values of Sr, Sn, Sb, some heavy metals (Pb, Zn, Ni) and the majority of the rare earths, compared to the other two clays studied (Table 4).

4.4. SEM microfabric

The SEM study of Clay1 and Clay2 revealed particles with pseudospherical shape and size between 30 μm to 40 μm (Fig. 3), which, in the case of the Clay2, exhibited a more pseudorounded surface (Fig. 3c). When examined closely these shapes appeared as sheet aggregates, sometimes indistinguishable from one another (Figs. 3b and d). Elemental analysis with EDX revealed that these laminae were principally composed of Si and Al in the aluminium bentonite and of Si and Mg in the magnesium bentonite, in agreement with the mineralogical and chemical characterization performed on these samples.

SEM Clay3 appeared to form larger pseudorounded aggregates (from 60 μm to 80 μm) (Fig. 3e) than those of the other samples.

Table 2a

Mineralogical composition of total sample and basal spacings $d_{(001)}$ and $d_{(060)}$ (CM: clay minerals, Q: quartz, Ca: calcite, Fd: feldspars).

Sample	CM %	Q %	Ca %	Fd %	$d_{(060)}$	$d_{(001)}$
Clay1	99	1	—	—	1.50	14.95
Clay2	94	2	1	3	1.52	14.95
Clay3	98	1	1	<1	1.52	—

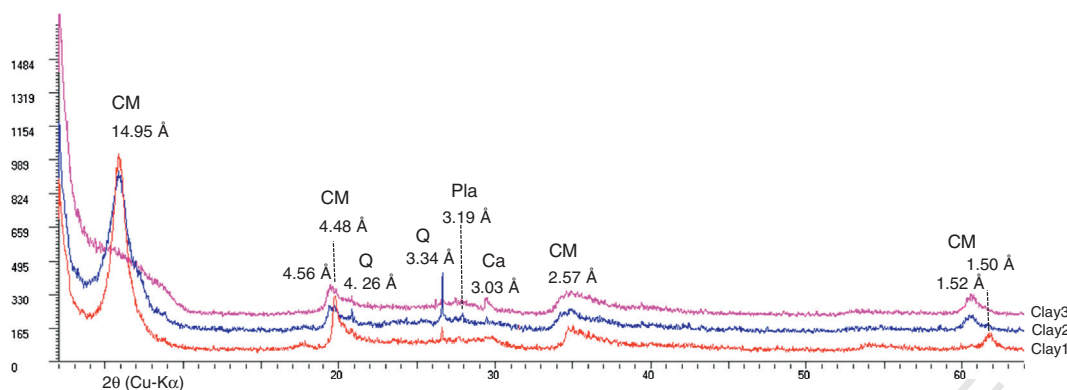


Fig. 1. XRD randomly powder diagrams of the clays studied. CM: clay minerals, Q: Quartz, Pla: plagioclase, Ca: calcite.

These aggregates were also formed of laminae similar to those of the other clays but appeared to be more compact (Fig. 3f). The results of EDX analysis were similar to those of Clay2, revealing that they were mainly composed of Si and Mg, once again corroborating the mineralogical and chemical study.

When Clay1 and Clay2 were mixed with distilled water the smaller laminae forming the pseudorounded aggregates were dispersed, separating and creating an organized structure. Thus, in the clay/water pastes, it was possible to observe a fabric composed of small laminae (<5 μm), joined together in a type of net to form a disperse porous system (Fig. 4). The fabric, particularly in the aluminium bentonite mixture, showed preferential directions for particle organization within the space (Fig. 4a). The laminae were joined face to face or, sometimes, face to edge, in larger aggregates (20 μm–30 μm). The fabric type is close to “honeycomb” or “house of cards” and could even be called “reticulated” in some zones (Fig. 4b). In the magnesium bentonite mixtures the laminae were less pronounced, the resulting fabric appearing less structured, although the porous system could still be detected (Fig. 4c). Detailed examination of the sample revealed that the smaller particles took on filamentous bacillar form, joined together by larger laminar particles, creating larger aggregates with spaces of up to 15 μm (Fig. 4d). These fabrics described in Clay1 and Clay2 are characteristic of smectites (Tessier, 1984).

The mixtures of Clay3 with distilled water exhibited a very different type of fabric to those described for the other mixtures. This was much more closed (less pores) and did not appear to have attained its maximum organization (Fig. 4e) because the small laminae were hardly dispersed and there were still large aggregates and pseudorounded forms reaching 30 μm. It was also possible to observe smaller particles of laminar habit joined face to face in larger aggregates of 15 μm to 20 μm (Fig. 4f).

These results are supported to a large extent by those from the granulometry (see Table 5), since Clay1 and Clay2 had a higher percentage of clay fraction particles than Clay3, with Clay1, having a more structured fabric, being the most clayey. On preparing the mixture the differences in fraction <2 μm content were visible in the fabric.

The ultrastructure (fabric) of the clay dispersions can be related to the mechanical properties which are important when the peloid is applied (Vali and Bachman, 1988). Well-structured fabrics increase viscosity or springiness, both of which are favorable properties for topical therapeutic application. It might also be supposed that the well-structured

fabrics (Clay1, Clay2) favor adsorption processes due to the greater number of active surfaces of the small laminae of the clay minerals.

4.5. Physical and physicochemical properties of the clays and mixtures

4.5.1. Swelling

The swelling values of the three clays (Table 5) were all low although that of Clay1 (5 ml/g) was slightly higher than that of Clay2 (4.5 ml/g) while both were considerably higher than that of Clay3 (2.5 ml/g). These low values are related to the presence of Ca²⁺, or of Ca²⁺ and Mg²⁺, in the interlayer space of the smectites (see Fig. 5b). The lower swelling capacity of Clay3 is related to the lower crystallinity of the smectites of which it is formed (Martín de Vidales et al., 1991). However, the swelling values of the three clays could increase when the peloids are prepared if the mineral–medicinal water is rich in sodium since a cation exchange of Ca²⁺ or of Ca²⁺ and Mg²⁺ for Na⁺ would take place during the maturation process, as reported by Carretero et al. (2007), as the swelling of a sodium smectite is greater than that of a calcic smectite (Koch, 2002).

4.5.2. Cation exchange capacity and exchangeable cations

Of the three clays studied, Clay1 showed the greatest cation exchange capacity (CEC), followed by Clay2 (Table 5, Fig. 5a). These values agree with the mineralogy. Of the exchangeable cations, Ca²⁺ was the most abundant exchangeable cation in Clay1, and Mg²⁺, and, to a lesser extent Ca²⁺ predominated in the other two clays. Concentrations of Na⁺ and K⁺ were practically inappreciable in the three clays (Fig. 5b). These results agree with the basal spacing d₍₀₀₁₎ values of the smectites which indicated the presence of divalent cations in the interlaminal space (see Tables 2a, 2b and Fig. 1).

4.5.3. Percent water, solids and ash

The percent water indicates the quantity of water required to form a peloid with a suitable consistency for its application. The mixtures prepared with Clay1 and Clay2 showed higher percent water, and, within these, the mixtures prepared with magnesium bentonite had slightly higher values (Table 5). This is due to this sample having a higher liquid limit value and greater plasticity. As would be expected, the variation in percent water for the different mixtures was also reflected in the values for percent solids (Table 5). The three mixtures all showed low values (between 24.7 and 37.9%) of ash (dry residue at 850 °C).

4.5.4. Color

The original clays were all of different colors. Sample Clay3 was darker than the others (bluey gray, Pantone® 7534), which were light gray (Pantone® 7528 for Clay1, and Pantone® 7527 for Clay2) (Table 5). As expected, the color changed when the clays were mixed with distilled water. In Clay1 the color became slightly darker (gray, Pantone® 7535). For Clay2 the mixtures became darker than those of Clay1,

Table 2b

Mineralogical composition of the fraction < 2 μm of the clays and crystallinity index of the smectites (FWHM), (Sm: smectites).

Sample	Sm	Illite	FWHM
Clay1	100	—	1021
Clay2	91	9	1161
Clay3	87	13	1581

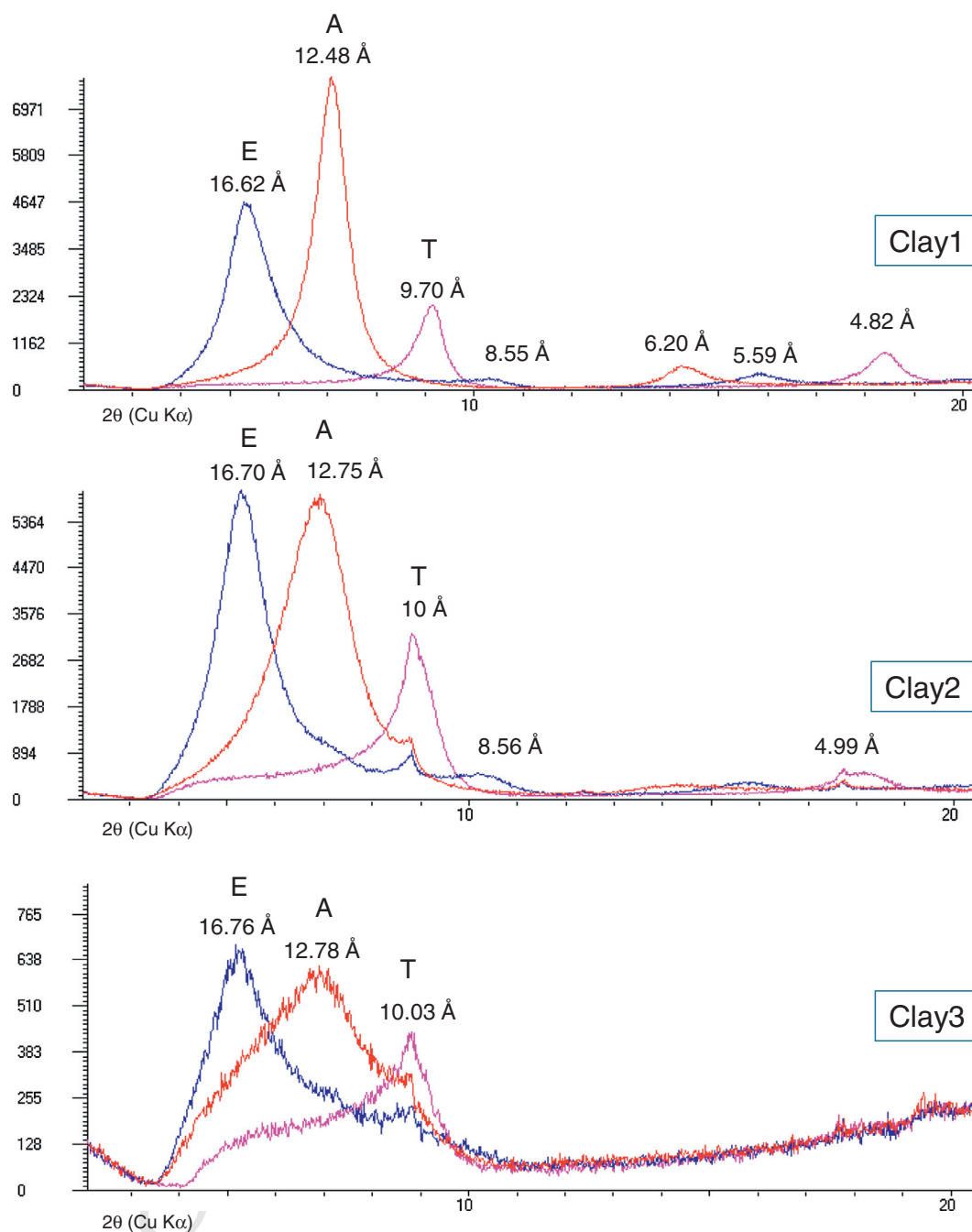


Fig. 2. XRD diagrams of clay fraction oriented samples, previously Mg²⁺ saturated. A-air dried. E-solvated in ethylene glycol atmosphere. T-heated to 550 °C.

390 becoming dark gray (Pantone® 7497). The mixtures for Clay3 were dark
391 brown (Pantone® 7504) (Table 5).

392 4.5.5. pH

393 The pH values of the mixtures prepared with each of the three clays
394 were similar, between 8.4 and 8.9 (Table 5).

t8.1 Table 3a

t8.2 Results of differential thermal analysis (DTA) of the clays.

t8.3	Sample	T °C	T °C	T °C
t8.4	Clay1	88 (-) 160 (-)	620 (-)	832 (+)
t8.5	Clay2	87 (-)	820 (-)	837 (+)
t8.6	Clay3	78 (-)	650 (-)	815 (-) 831 (+)

4.5.6. Density

395 The densities of the three clays were quite similar, with Clay3 having
396 the highest (2360 kg/m³), followed by Clay2 (2230 kg/m³) and then
397 Clay1 (2160 kg/m³). These slight differences may be related to
398

Table 3b

Results of thermogravimetric analysis (TGA) of the clays.

Sample	Total mass loss	Partial mass loss	Partial mass loss	Partial mass loss
Clay1	19.49	14.90 (<350 °C)	3.84 (350–725 °C)	0.76 (725–1095 °C)
Clay2	18.02	12.20 (<200 °C)	3.44 (200–700 °C)	2.38 (700–1095 °C)
Clay3	16.84	8.98 (<200 °C)	5.38 (200–700 °C)	2.52 (700–1095 °C)

Table 4
Chemical composition of the clays studied, range of variability of Spanish (Carretero et al., 2010) and Turkish peloids (Karakaya et al., 2010). a) main elements (%), b) trace elements (ppm).

	Clay1	Clay2	Clay3	Detection limit	Spanish peloids range	Turkish peloids range
a)						
Al	6.37	2.53	1.58	0.01	3.58–12.24	6.24–19.78
Ca	1.03	0.80	1.35	0.01	2.27–26.48	0.89–29.69
Mg	4.79	10.00	13.00	0.01	0.98–22.35	1.65–9.95
Fe	2.12	1.90	1.01	0.01	1.70–5.24	3.10–7.28
Na	0.70	0.36	0.19	0.01	1.86–4.34	0.53–3.39
K	0.57	0.94	0.61	0.01	0.57–2.57	0.97–2.93
Ti	0.1	0.2	0.1	0.01	0.22–0.55	0.35–0.85
Mn	0.0208	0.0261	0.0275	0.0001	0.021–0.608	0.05–0.19
P	0.014	0.020	0.020	0.001	n.d.	0.06–0.20
S	0.01	<0.01	0.02	0.01	0.06–2.37	n.d.
b)						
Ag	<0.05	<0.05	0.40	0.05	<6	<0.1–0.1
As	17.4	27.6	43.2	0.5	4.4–29.6	5.1–62.6
Ba	107	186	148	1	148–799	110–1153
Be	2.0	1.8	0.8	0.1	n.d.	1.0–5.0
Bi	0.2	0.4	0.2	0.1	<1–3.3	<0.1–0.7
Br	5.2	4.8	10.3	0.5	1.9–554.7	n.d.
Cd	<0.1	0.1	0.7	0.1	<10	0.1–0.2
Ce	61.3	36.3	18.3	0.1	29.2–76.3	n.d.
Co	2.8	5.8	2.8	0.1	4.0–16.8	9.1–54.5
Cr	25	34	22	1	14.6–68.2	61.6–547.4
Cs	4.11	5.90	3.05	0.05	<6–28.5	3.6–39.8
Cu	10.9	15.8	6.1	0.2	11.5–52.3	12.4–32.2
Dy	5.2	2.5	1.2	0.1	n.d.	n.d.
Er	2.5	1.3	0.6	0.1	n.d.	n.d.
Eu	0.72	0.45	0.22	0.05	n.d.	n.d.
Ga	19.4	10.0	5.2	0.1	5.9–16.3	7.9–18.2
Gd	5.6	3.0	1.4	0.1	n.d.	n.d.
Ge	0.2	0.2	0.2	0.1	1.1–1.5	n.d.
Hf	3.8	1.5	0.9	0.1	<2.87–4.5	2.1–7.2
Hg	<1	<1	<1	1	n.d.	0.02–0.15
Ho	1.0	0.5	0.2	0.1	n.d.	n.d.
In	0.1	<0.1	<0.1	0.1	n.d.	n.d.
Ir (ppb)	<5	<5	<5	5	n.d.	n.d.
La	36.8	24.4	13.5	0.5	14.9–43.1	n.d.
Li	95.2	247.0	196.0	0.5	n.d.	n.d.
Lu	0.46	0.27	<0.05	0.05	n.d.	n.d.
Mo	2	1	<1	1	<1–4.4	0.2–1.2
Nb	9.2	7.9	3.8	0.1	4.2–10.7	8.0–26.7
Nd	24.6	16.9	8.0	0.1	11.6–32.6	n.d.
Ni	13.9	7.9	4.4	0.5	3.4–50.8	27–67.1
Pb	25.7	11.4	10.0	0.5	10.9–37.5	6.9–38.2
Pr	6.6	4.3	2.2	0.1	n.d.	n.d.
Rb	38.5	57.5	42.8	0.2	35.5–120.5	38.7–175.1
Re	<0.001	0.002	0.003	0.001	n.d.	n.d.
Sb	1.7	0.8	1.3	0.1	<2.37–4.3	<0.1–1.2
Sc	10.8	7.9	3.8	0.1	2.6–11.5	7–12
Se	<0.1	<0.1	<0.1	0.1	<1–1.6	<0.5–0.7
Sm	6.4	4.4	2.3	0.1	<7.23–8.6	n.d.
Sn	8	4	2	1	<2.10–2.3	n.d.
Sr	163.0	98.4	70.3	0.2	87.3–187.9	214.3–1540.4
Ta	0.9	0.8	0.3	0.1	<2.47–3.8	0.6–3.3
Tb	<0.5	<0.5	<0.5	0.5	n.d.	n.d.
Te	<0.1	<0.1	<0.1	0.1	n.d.	n.d.
Th	14.0	9.5	5.1	0.1	<1.50–12.8	n.d.
Tl	0.07	0.41	0.31	0.05	<1.60	<0.1–1.6
Tm	0.3	0.2	<0.1	0.1	n.d.	n.d.
U	3.0	8.0	19.2	0.1	<1.20–18.4	1.0–6.3
V	23	43	86	2	31.6–90.9	55–95
W	<1	<1	<1	1	<2.21–4.3	0.6–3.6
Y	22.2	12.9	6.6	0.1	8.9–22.7	13.3–32.3
Yb	2.1	1.2	0.6	0.1	n.d.	n.d.
Zn	57.7	45.4	22.5	0.5	33.1–160.4	33–56
Zr	128	47	32	1	75.3–130.2	67.3–274.5

399 mineralogical differences between them, namely the presence of calcite, feldspars and illite in Clay2 and Clay3 but not in Clay1. In all cases the densities of the mixtures were lower than those of the original clays (Table 5) since distilled water is less dense than clay and the density of the mixture is thus between the two. The variations in density of the different mixtures are thus correlated with percent water values so that the higher the percent water the lower the

density and vice-versa, as can be seen in the mixtures prepared with Clay2 and Clay3, respectively.

4.5.7. Viscosity

The viscosity values for the mixtures prepared with each clay and distilled water were very similar (20 Pa.s–25 Pa.s, Table 5), although that of Clay3 was slightly higher than the other two.

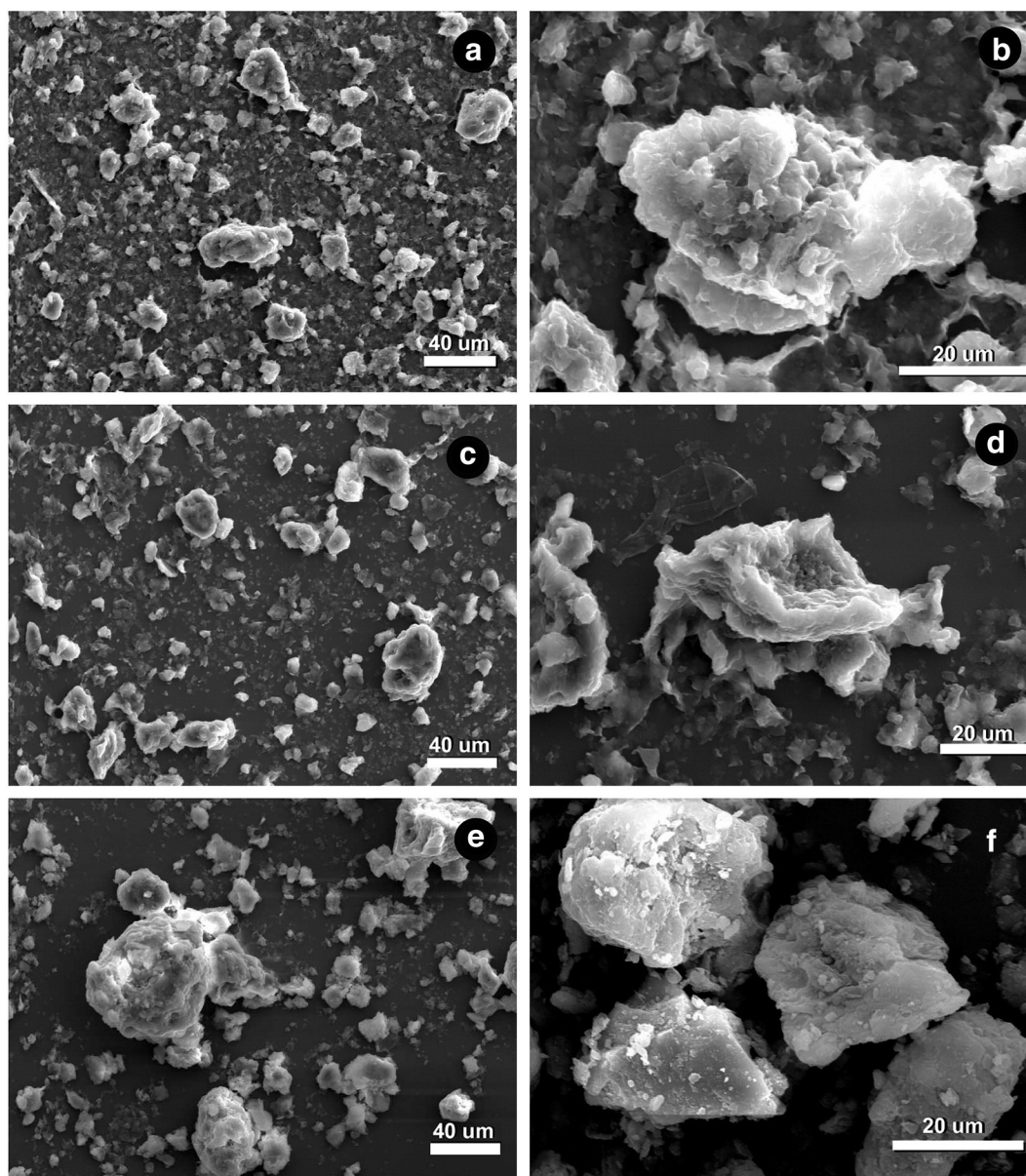


Fig. 3. SEM images of the clay samples: a and b, Clay1. c and d, Clay2. e and f, Clay3.

4.5.8. Abrasiveness

Samples Clay1 and Clay2 showed similar very low values for abrasiveness while that of Clay3 was slightly higher (Table 5). These low values are due to the mineralogical composition and particle size distribution of these clays. They have a low content of non-clay minerals (hard minerals: <2% quartz and <3% calcite or feldspars) while the sand fraction is almost inappreciable (<1.6%).

Abrasiveness values hardly changed when the mixtures were prepared. The slight decrease observed may be due to modification of the microfabric during preparation of the mixtures (see Figs. 3 and 4) and modification of the granulometry toward smaller particles (increase in the clay fraction) (see Figs. 6 and 7).

4.5.9. Instrumental texture

The cohesiveness of the mixtures was similar. Values for Clay3 were lower than for Clay2, which were, in turn, lower than for Clay1 (Table 5). These small differences are related to the presence of non-clay minerals and that of illite, highest in Clay3 (see Tables 2a, 2b). The presence of these minerals results in slightly weaker cohesive forces.

The adhesiveness of the mixtures was quite similar, ranging from 137 g.s to 164 g.s. The springiness was also similar for the three clays studied, ranging from 17.77 mm to 18.85 mm (Table 5). The values for hardness ranged from 19.7 g to 15.2 g (Table 5). The low hardness values of the mixtures are consistent with the low values of abrasiveness and are thus related to the low proportion of hard minerals and sand fraction in the samples.

4.5.10. Granulometry

The original clays were characterized by a high percentage of silt fraction (particularly in Clay3 with 91%) and a very low percentage of sand fraction (<1.6%, Table 5, Fig. 6a), the latter being extremely important for its use in pelotherapy (Carretero et al., 2006, 2013; Veniale et al., 2007). The three clays showed a wide range of particle sizes (Fig. 7a). The particle size distribution of Clay1 and Clay2 was bimodal, with maxima around 10 μm and 3 μm. However, the particle size distribution of Clay3 was very narrow, with a maximum around 15 μm. With regard to the clay fraction, Clay1 showed the highest percentage of particles <2 μm, with Clay3 having the lowest (Table 5).

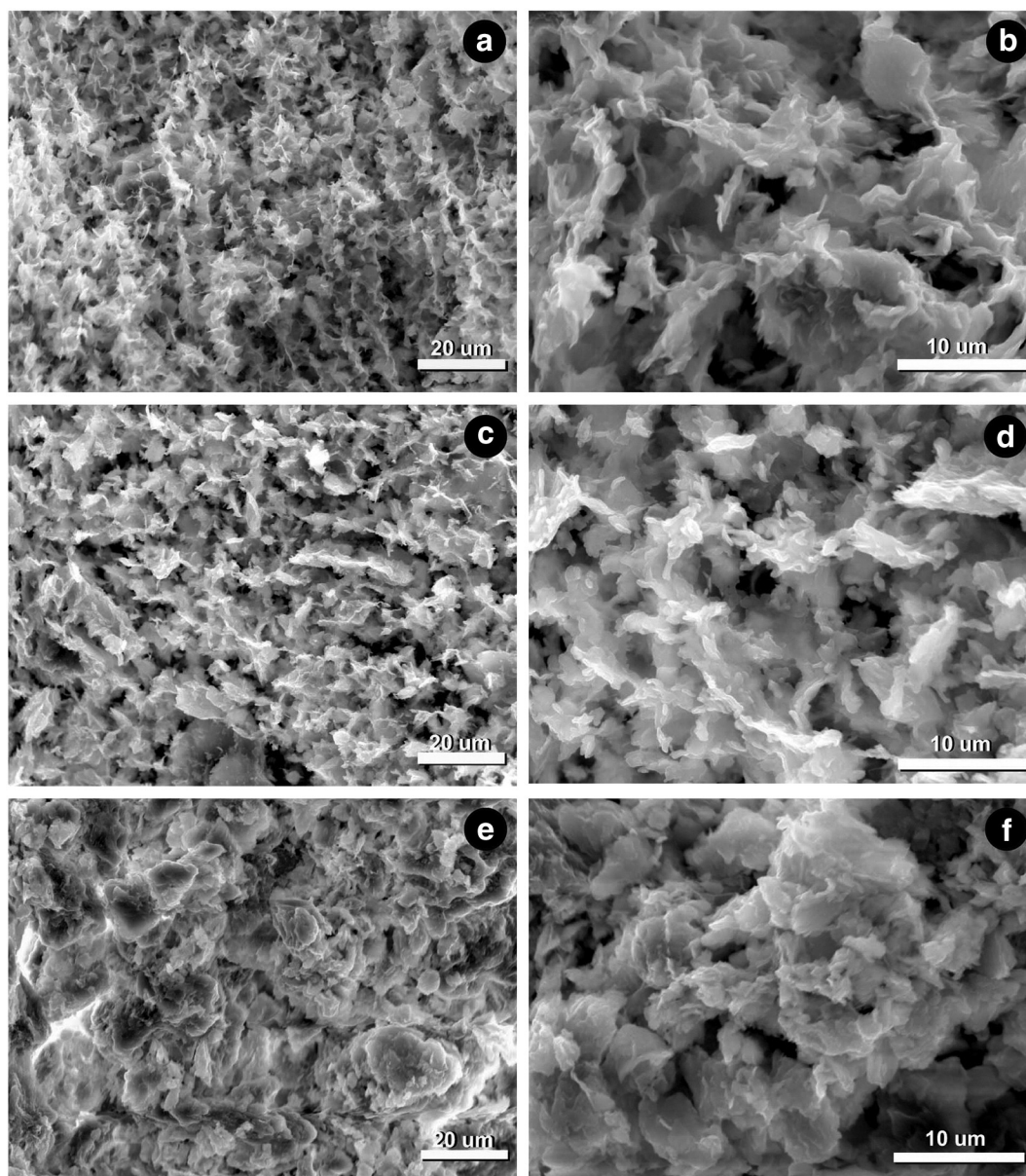


Fig. 4. SEM images of the clay-distilled water mixtures. a and b, Clay1. c and d, Clay2. e and f, Clay3.

On preparing the mixtures of Clay1 and Clay2 with distilled water the clay fraction increased considerably (Table 5, Fig. 6b) and the particle size distribution tended toward smaller particles (Fig. 7b). Very little granular modification was observed in the Clay3 mixture (Table 5, Fig. 6b), although there was a slight change in the particle size distribution toward smaller sizes (Fig. 7b). These modifications are related to variations in the microfabric of the clays on preparing the mixtures and were observed in the SEM study (see Figs. 3 and 4).

4.5.11. Specific surface area (BET)

The BET values of the clays were within the range for clays with similar mineralogy studied by other authors (Legido et al., 2007; Martín de Vidales et al., 1991). When the clays were mixed with distilled water BET values hardly changed, the small differences observed are related to variations in the method of measurement.

4.5.12. Plasticity index

The plasticity index of Clay1 and Clay2 was much higher than that of Clay3, due mainly to the higher value of the liquid limit (Table 5) related

to a higher percentage of the clay fraction and the concomitant higher water absorption capacity. This is shown by Clay1 and Clay2 requiring a greater percentage of water to achieve a consistent mixture.

After preparation of the mixtures the plasticity index increased slightly from that of the original clays due to an increase in the liquid limit since the plastic limit remained practically constant (Table 5). The increase in liquid limit is due to the increase in the clay fraction, with modification of the microfabric and in particle size distribution toward smaller sizes produced during preparation of the mixtures, which would favor higher water absorption capacity.

4.5.13. Thermal properties

The specific heat values of the clays studied were very similar (between 865 J/kg.K and 894 J/kg.K) and of a similar order to those of similar clays studied by other authors (Carretero and Pozo, 2009; Legido et al., 2007). However, in the mixtures with distilled water the specific heat of Clay3 (2850 J/kg.K) was lower than that of Clay1 and Clay2 (3230 J/kg.K y 3340 J/kg.K, respectively) due to the Clay3 mixture requiring less water (see Table 5). As the specific heat of distilled water

t5.1 **Table 5**

t5.2 Physical and physicochemical properties of the clays, their mixtures with distilled water and the peloids used in Spanish spas. (–) Not determined (*) data from Pozo et al., 2013.

t5.3	Raw materials			Mixtures			Spanish peloids(*)
t5.4	Clay1	Clay2	Clay3	Clay1/distilled water	Clay2/distilled water	Clay3/distilled water	Range
t5.5	Swelling capacity (ml/g)	5	4.5	2.5	–	–	–
t5.6	CEC (cmol(+)/kg)	91.2	49.5	24.8	–	–	11–112
t5.7	Water content (%)	–	–	–	70.64	73.90	59.98
t5.8	Solids content (%)	–	–	–	29.36	26.10	40.02
t5.9	Ash content (%)	–	–	–	27.50	24.70	37.89
t5.10	Color Pantone®	7528	7527	7534	7535	7497	7504
t5.11	pH at 25 °C	–	–	–	8.9	8.6	8.4
t5.12	Density (Kg/m ³) at 25 °C	2160	2230	2360	1200	1180	1320
t5.13	Viscosity (Pa.s at 25 °C)	–	–	–	25	25	20
t5.14	Abrasiveness (mg)	7.7	11.9	29.3	7.2	11.2	26.2
t5.15	Cohesiveness	–	–	–	0.97	0.90	0.86
t5.16	Hardness (g)	–	–	–	15.17	17.83	19.67
t5.17	Adhesiveness (g.s)	–	–	–	137	163	164
t5.18	Springiness (mm)	–	–	–	18.85	17.77	18.32
t5.19	BET (m ² /g)	101	185	250	99	190	244
t5.20	Liquid limit (%)	130	156	94	143	206	107
t5.21	Plastic limit (%)	49	48	58	52	51	59
t5.22	Plasticity index (%)	81	108	36	91	155	48
t5.23	<i>Granulometry</i>						
t5.24	Sand (2 mm–63 μm) (%)	0.8	1.1	1.6	0.0	0.9	1.0
t5.25	Silt (63–2 μm) (%)	73.0	85.8	91.0	53.7	56.2	88.1
t5.26	Clay (<2 μm) (%)	26.2	13.2	7.4	46.3	42.9	10.9
t5.27	<i>Thermal properties</i>						
t5.28	Specific heat (J/kg.K)	865	892	894	3230	3340	2850
t5.29	Thermal conductivity (W/m.K a 25 °C)	–	–	–	0.720	0.710	0.790
t5.30	Thermal retentivity (10 ⁶ s/m ²)	–	–	–	5.38	5.55	4.76
t5.31							2970–3800
t5.32							0.40–0.53
							5.59–8.71

483 (4178 J/kg.K) is much higher than that of the clays, the more water in
 484 the mixture the higher its specific heat.

485 The thermal conductivity values of the mixtures with Clay1 and
 486 Clay2 and distilled water were very similar and slightly lower than
 487 that of the Clay3 mixture (Table 5). This is due to the greater quantity
 488 of water required for the first two mixtures, since, the higher the per-
 489 centage of water the lower the thermal conductivity since the thermal

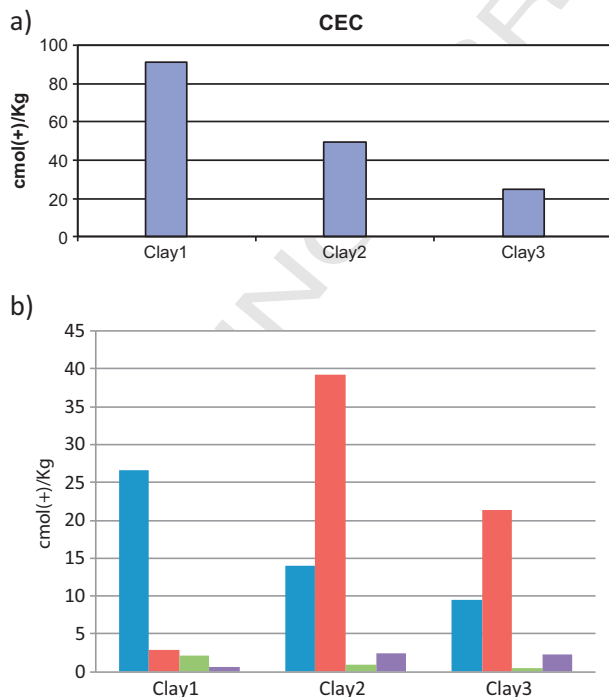


Fig. 5. CEC (a) and exchangeable cations (b) of the clays studied.

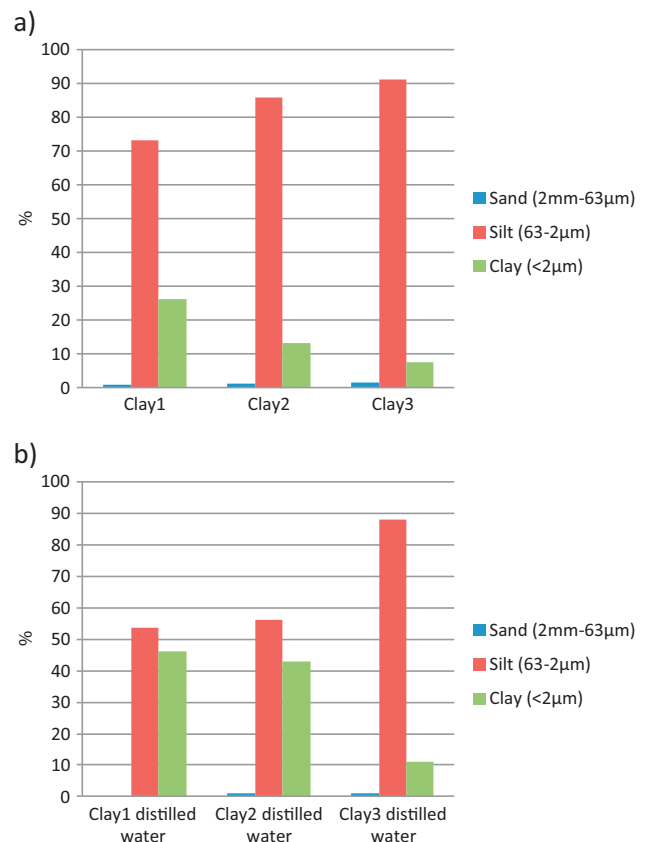


Fig. 6. Granulometry of the samples studied (a) and of their mixtures with distilled water (b).

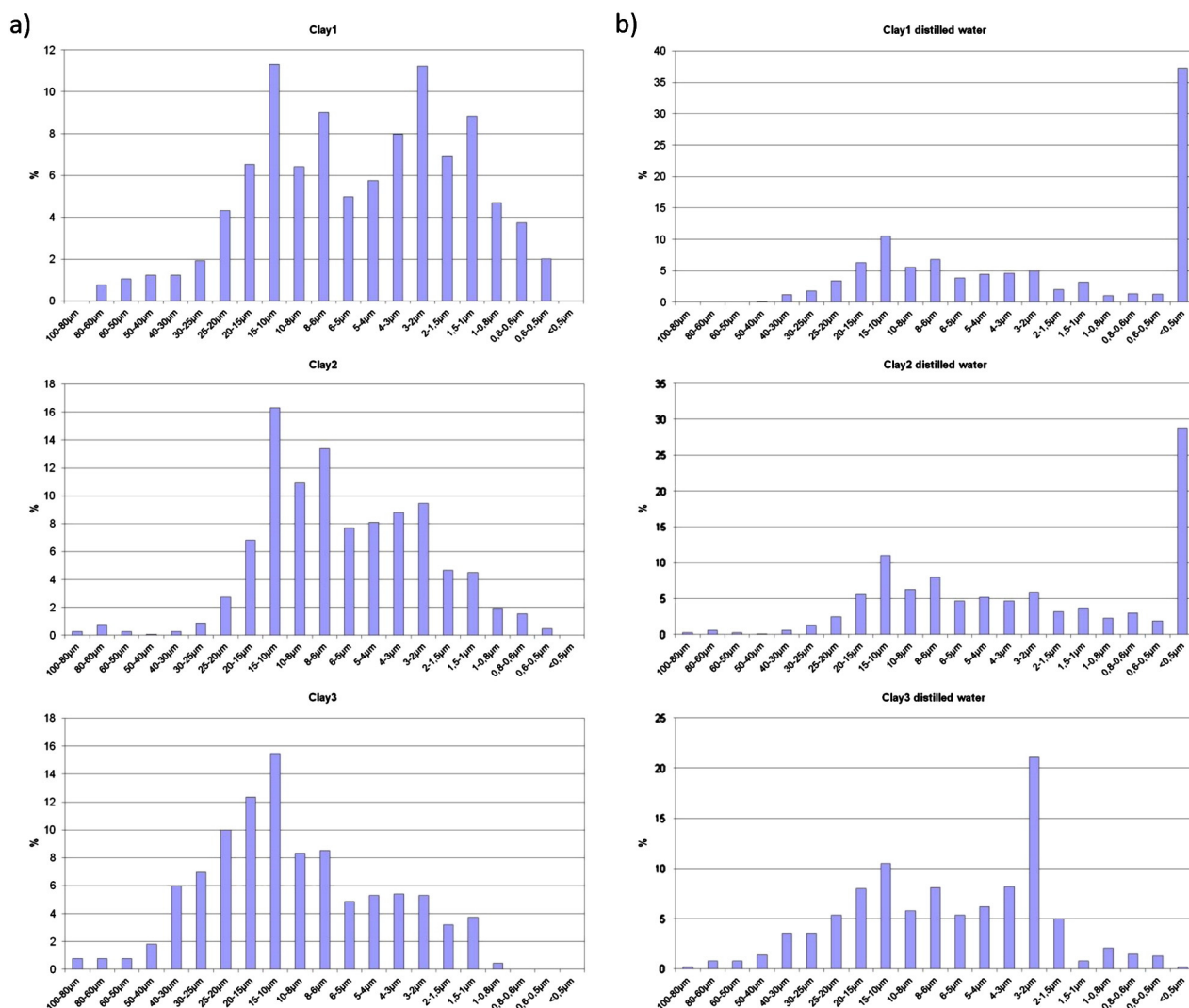


Fig. 7. Particle size distribution of the samples studied (a) and of their mixtures with distilled water (b).

conductivity of water (around 0.6 W/mK) is much lower than that of the clays (around 1.3 W/mK).

Finally, as the previous data would suggest, the thermal retentivity values of the mixtures with Clay1 and Clay2 and distilled water were higher than that for the Clay3 mixture. Of the first two, Clay2 had a slightly higher thermal retentivity value (Table 5).

4.6. Comparison with peloids used in spas

The data obtained for the mixtures were compared with those previously reported for peloids used in five spas in Spain (Carretero et al., 2010; Pozo et al., 2013) and seven in Turkey (Karakaya et al., 2010) to determine their suitability for use in pelotherapy.

The mineralogical composition of the sample is directly related to its chemical composition and physical and physicochemical properties. The peloids from the Spanish and Turkish spas varied greatly in their mineralogical composition. The peloid from Archena (Spain) is monomineral (bentonite) while all the others are polymineral, with the principal clay minerals being smectites, illite and kaolinite in varying proportions. These mineralogical variations will affect the properties of the peloids, but, since they are currently used in spas, they can be used for reference values in the present study.

With regard to chemical composition, in pelotherapy it is important to know the concentrations of elements which are beneficial (Ca, Mg, Na, K, Fe, amongst others) or potentially toxic (Hg, As, Cu, Cr, Pb, Zn,

Co, Ni, Cd, Sb, Ba, V, U) present in the peloid since both can pass through the skin of the patient during treatment. The concentration of these elements in the peloid will depend on their concentration in the mineral-medical water and the solid phase (generally clay) used to prepare the peloid. Several authors have described the presence of essential and/or potentially toxic elements in peloids used in spas (Carretero et al., 2010; Karakaya et al., 2010) and in clays with potential for use in pelotherapy (Carakaya et al., 2000a, 2000b; Gomes and Silva, 2001; Vreca and Dolenc, 2005; Williams et al., 2008). However, when considering a potentially useful clay, the concentration of a particular element in the clay or peloid is not as important as its bioavailability, that is, the concentration of the element which could enter the body of the patient during application of the peloid. Many authors have studied the mobility of essential and/or potentially toxic elements in clays for human healing (Kikouama et al., 2007, 2009; Mascolo et al., 1999, 2004; Szántó and Papp, 1998; Szántó et al., 1999; Tateo and Summa, 2007; Tateo et al., 2001, 2006) and the behavior of peloids has been subjected to leaching tests (Carretero et al., 2010; Summa and Tateo, 1998, 1999; Tateo et al., 2009).

The clays in the present study showed similar or sometimes much lower values for trace elements (Cr, Ba, Cs, Ni, Sr, Zr) than those for thermal muds used in some spas in Turkey (see Table 4). The values for trace elements in the three clays were similar to those for peloids currently in use in Spanish spas while those for harmful or potentially toxic elements were lower (or similar in the case of As in sample

Clay3) (see Table 4). Thus, with regard to chemical composition, all three clays could be used for the preparation of peloids. However, as mentioned previously, the chemical composition of each mineral–medicinal water employed should also be considered. This would be added to that of the clay. Furthermore, the bioavailability of the potentially toxic elements is particularly important and lixiviation tests should be carried out in each case.

Although the *microfabric* of peloids used in spas was not studied by other authors the best organized samples (Clay1 and Clay2) would be the most suitable for peloid preparations, as it was indicated before (see epigraph 4.4).

With regard to *physical and physicochemical properties*, the greater the *swelling capacity* of a peloid the greater its absorption capacity and, thus, the better its behavior from a therapeutic point of view (Carretero et al., 2006, 2013; Veniale et al., 2007). Swelling was low in the three clays studied, as is the case of peloids normally used in spas (Karakaya et al., 2010). However, swelling values can increase, depending on the type of mineral–medicinal water used to prepare the peloid.

The CEC values of the studied clays were within the range of the peloids already used in spas, which ranged from 11 cmol(+)/kg to 112 cmol(+)/kg for Spanish spas and 9.2 cmol(+)/kg to 32.2 cmol(+)/kg for those in Turkey (Karakaya et al., 2010).

With respect to the *exchangeable cations*, it is vital to know the concentration and type of exchangeable ions in a peloid from a therapeutic point of view since these may be bioavailable and can reach the skin of the patient through their sweat during application. However, the type and concentration of exchangeable ions will vary according to the type of mineral–medicinal water used for the mixture as there will be a cation exchange during the maturation process. It is therefore not possible to determine the most suitable clay for peloid preparation in terms of exchangeable ions.

Percent water of the peloids used in Spanish spas ranges widely (31.43% to 76.64%). The values for the mixtures in the present study fell within this range (Table 5). The mixtures with Clay1 and Clay2 showed similar values to that of the peloid from the spa of Archena (76.6%) while that of Clay3 was similar to that of the peloid from the spa of Caldas de Boí (56.7%). The values for *percent ash (dry residue at 850 °C)* for the three mixtures were similar to those of the peloids from Archena (23.31%) and Caldas de Boí (22.73%).

Color does not affect the therapeutic activity of a peloid but does affect its organoleptic properties. The peloids used in Spanish spas vary greatly in color, from black (Caldas de Boí) to yellowy gray (Archena) or dark yellow (Lo Pagan), passing through brownish gray (El Raposo) or brown (Arnedillo) (Pozo et al., 2013). However, peloids should show lightish or pastel tones since these are more appealing to patients.

The *pH* values for the three clays were similar to those from Turkey (between 7.73 and 9.90, Karakaya et al., 2010) and all three would thus be suitable. Values for *density* were within the range for the peloids used in Spanish spas (see Table 5), once again showing that all three would be suitable with regard to this property.

Values for *viscosity* were highest for sample Clay3. This should be taken into consideration when choosing the method of application as a low viscosity is preferable for application with a brush while a higher viscosity is better for a poultice or cataplasm.

Values for *abrasiveness* for Clay1 and Clay2 were similar to those of the peloid used in Archena, and much lower than those for the other Spanish peloids (see Table 5). Abrasiveness was slightly higher for Clay3, which showed a value similar to that of the peloid from Caldas de Boí (44.8 mg), much lower than those of other Spanish peloids, with the exception of that from Archena (7.2 mg). In terms of pelotherapeutic application, low abrasiveness is recommended since this will be more comfortable for the patient (Carretero et al., 2006, 2013; Veniale et al., 2007).

In terms of *instrumental texture*, values for cohesiveness for the mixtures were slightly higher (between 0.86 and 0.97) than those for

the Spanish peloids (between 0.50 and 0.80). With regard to adhesive-ness, all the mixtures showed much lower values than those of the Spanish peloids, which ranged from 2491 g.s to 7102 g.s. During therapeutic application the peloid must adhere to the skin, but not so well that removal would be difficult. Values for hardness were much lower than those of the Spanish peloids (between 132 g and 462 g, see Table 5). Finally, springiness values were within the range of the Spanish peloids.

In terms of *granulometry*, the best peloid should contain a high percentage of the fine fraction (<2 µm). However, the three clays studied, together with their mixtures with distilled water had a high silt fraction content. Nonetheless, this is also true of the Spanish peloids (see Table 5) and the Turkish thermal muds (Karakaya et al., 2010). Consequently, the three clays could be used for the preparation of peloids, with Clay1 and Clay2, especially the former, being the most suitable.

Comparison of the data for *specific surface area* revealed that the three clays studied had higher values than those for Spanish (see Table 5) and Turkish peloids (Karakaya et al., 2010). A high specific surface area results in a greater absorption/adsorption capacity.

With regard to *plasticity*, this should be high (but not excessively so) to facilitate application of the peloid (Carretero et al., 2006, 2013; Veniale et al., 2007). The plasticity indices of the mixtures with Clay1 and Clay2 were higher than those of the Turkish thermal muds (Karakaya et al., 2010) and from the Spanish spas (except for Archena: 227%). The Clay3 mixture showed similar values to all the Turkish and Spanish peloids (except that of Archena).

When *thermal properties* were compared, values of specific heat for the mixtures of Clay1 and Clay2 were similar to those of the Spanish peloids (between 2970 J/kg.K and 3800 J/kg.K) while that of Clay3 was slightly lower. In thermotherapy, peloids with high specific heat values are the most suitable since the higher the specific heat of a peloid, the better its thermal behavior (Casás et al., 2013).

Comparison of thermal conductivity and thermal retentivity revealed that the mixtures prepared with the three clays and distilled water showed higher and slightly lower values respectively than those of the Spanish peloids (see Table 5). Thermal retentivity is a thermal property reflecting the capacity of a peloid to retain heat. It is directly related to specific heat and inversely related to thermal conductivity. Peloids with low thermal conductivity and consequently high thermal retentivity are most suitable for thermotherapy as they transmit heat poorly, that is, they retain heat well. Thus, Clay1 and Clay2, particularly the latter, would be more suitable than Clay3, concerning these properties. Overall, Clay2 would be most suitable for peloid preparation for thermotherapy. Clay3 could be discounted since none of the values for its thermal properties were within the range of the Spanish peloids.

5. Conclusions

The main clay minerals of the samples studied were different. Montmorillonite was predominant in Clay1, saponite in Clay2 and kerolite–stevensite in Clay3. The studied clays had levels of harmful trace elements which were lower than or similar to those for peloids used in spas in Spain and Turkey. The mixtures prepared with the clays and distilled water had similar physical and physicochemical properties to the Spanish and Turkish peloids, except in the case of thermal properties, where values for the kerolite–stevensite sample fell outside the range of values for these spas. Values for the saponite sample were closest to those for the spas. Although all three clays would be suitable for peloid preparation, Clay1 and Clay2 would be preferable. For use in thermotherapy, saponite would be most suitable while kerolite–stevensite should not be used.

Acknowledgments

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