Applied Clay Science 99 (2014) 131–143

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

Assessment of three Spanish clays for their use in pelotherapy

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

ARTICLE INFO

Article history:
Received 11 March 2014
Received in revised form 17 June 2014
Accepted 18 June 2014
Available online 5 July 2014

Keywords:
Bentonites
Characterization
Physicochemical properties
Pelotherapy

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.

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; Fernández-González et al., 2013; 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

* Corresponding author at: Dpto. Cristalografía, Mineralogía y Química Agrícola, Facultad de Química, Universidad de Sevilla, C/Prof. García González no 1, 41012 Seville, Spain. Tel.: +34 954 556327; fax: +34 954 557140.
E-mail address: carre@us.es (M.I. Carretero).

http://dx.doi.org/10.1016/j.clay.2014.06.022
0169-1317/

properties of both the clays and the mixtures of these with distilled 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° 2θ using disoriented powder and CuKα radiation with a scanning speed of 1° 2θ/min. The identification of clay fraction minerals (less than 2 μm) was carried out on oriented Mg^{2+}-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° 2θ. 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 Xpowder (http://www.xpowder.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 macrospopic 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 "Stoppering 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 rule. *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* (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) determined by atomic absorption spectrophotometry using a PerkinElmer AAnalist 100 spectrophotometer.

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
Rest time (days)	1	1	2