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Highlights

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A study of the chemical, mineralogical and physicochemical properties of peloids prepared with two medicinal mineral waters from Lanjarón Spa (Granada, Spain)

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- Relationships of mineral medicinal water – liquid phase of peloids – CEC of peloids
- Peloid as a new medicinal product with respect to initial materials
- Studies about Lanjarón Spa, one of the main European Spas



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Research paper

A study of the chemical, mineralogical and physicochemical properties of peloids prepared with two medicinal mineral waters from Lanjarón Spa (Granada, Spain)

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ABSTRACT

We studied the interstitial liquid phase (Liq_{int}), the crystallinity of solid phase minerals (kaolinite and saponite), the cation exchange capacity (CEC) and the exchangeable bases of peloids prepared with two medicinal mineral waters (MMWs) from the springs of Lanjarón Spa (Granada, Spain). The waters employed were: “Salud V” (chloride-, sodium- and calcium-rich, bicarbonated, previously unpublished) and “El Salado” (chloride- and sodium rich, bicarbonate, calcic and ferruginous). The solid phase was a mixture of kaolin and bentonite (9:1, w:w) and maturation times of the peloids were 1, 3 and 6 months.

The physicochemical properties of the Liq_{int} of the peloid differed from those of the MMW: pH increased (from 6 to 8, approximately), Fe content decreased dramatically (from 12 to 0.03 mg l⁻¹), while potassium and bicarbonates also decreased and concentrations of other ions such as carbonates, sodium, chlorides and, especially, sulphates, increased. The effect of maturation time on Liq_{int} properties depended on the MMW employed. Kaolinite crystallinity in the peloid decreased during maturation (Hinckley Index from 0.71 to 0.52), reaching similar values in the peloids from both MMW after 6 months. On the other hand, the crystal perfection of saponite increased, revealing the existence of a process of crystallochemical aggradation towards mica due to the presence of exchangeable ions in Liq_{int}, particularly potassium.

There was a change in CEC and the exchangeable bases from the initial mineral material to the solid phase of the peloid. In the initial material the base sequence was Na⁺ > K⁺ ~ Mg²⁺ > Ca²⁺ while in the mineral phase of most of the peloids it was Ca²⁺ > Na⁺ > Mg²⁺ > K⁺. The relationship between the exchangeable bases and the Liq_{int} was demonstrated.

We demonstrate that the peloid controls and modifies the properties of the starting materials: MMW and minerals. Appears a new system of Liq_{int} – exchangeable phase – mineral phase interrelationships.

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1. Introduction

Pelotherapy is the therapeutic use of peloids, also known as medicinal muds, and has long been practised (Tateo et al., 2010) in balneotherapy, together with treatments with medicinal mineral waters (MMW) in spas (van Tubergen and van der Linden, 2002). MMW are those which, due to their special characteristics, have been officially recognised as therapeutic agents and declared to be of public interest by the relevant authorities (Maraver and Armijo, 2010). According to the World Health Organisation (WHO) and the Spanish Technical Health regulations (Torres Piles, 2005), MMW is the main therapeutic agent in medical hydrology, balneotherapy or

crenotherapy and its effects are mainly due to its particular chemical composition, unique to each spring, fountain, spa or thermal spring. These waters can be classified using various parameters: temperature, osmotic pressure, total mineralization (expressed as dry residue) or principal anion and cation contents (Armijo and San Martín, 1994; Maraver and Armijo, 2010).

Many authors currently consider pelotherapy to be a part of balneotherapy since, in spas, waters and peloids tend to be applied simultaneously (Codish et al., 2005; van Tubergen and van der Linden, 2002).

Pelotherapy is a coadjuvant curative method for the treatment of chronic illnesses or elderly persons, who tend to show significant improvement with a concomitant reduction in medication dosage (Bender et al., 2004; Codish et al., 2005). Consequently, in the last five years there has been a significant increase in the number of papers on this subject published in international scientific journals.

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The term “peloid” refers to “natural products consisting of a mixture of mineral water, including seawater and water of salt lakes, with organic or inorganic materials, formed by geological and/or biological processes and used therapeutically in the form of poultices or baths” (International Society of Medical Hydrology, 1949). Other authors have defined them as “semi-liquid therapeutic or thermo-therapeutic physical agents formed by mixing a liquid component, which may be mineral water, seawater or water from a salt lake (sulphur, sulphate, chloride, sodium, bromine waters) with a solid organic and/or inorganic component, resulting from biological and geological processes and used as therapeutic agents for local or general treatments” (Veniale et al., 2004). Naturally-occurring peloids are rare but they can be purpose-made artificially from MMW.

The water used for the peloid affects the chemical properties of the mixture through its pH, salinity and the retention or release of ions between the liquid and solid phases of the mixture (Gámiz et al., 2009). The water contributes certain trace components (iron, hydrogen sulphide, etc.) to the peloid which may give rise to some of its effects, for example, analgesia (Bender et al., 2004). Natural salt waters and brines have a high content of bromine and iodine, boron, fluorine, lithium and strontium, amongst others, (Custodio and Llamas, 2001), all of which have or may have therapeutic properties (Halevy et al., 1997). Thus, the type of MMW employed affects the type of peloid and its use (Veniale et al., 2004). However, to date, the $Li_{q_{int}}$ which bathes the peloid as an interstitial solution between the particles has not been studied and may be expected to exhibit different composition and properties (including therapeutic properties) to the original MMW used in the mixture.

The therapeutic effects of peloids also depend on the chemical and mineralogical composition of the solid phase (Carretero et al., 2006; Summa and Tateo, 1997). The phases composed of clay minerals such as bentonites and kaolins are considered the most suitable for peloid preparation due to their physicochemical properties (Carretero et al., 2007; Veniale et al., 2004, 2007). As occurs in the $Li_{q_{int}}$, the solid phase of the peloid may undergo changes in the minerals, such as modifications in the crystallinity of some phyllosilicates (saponite, illite) induced by the reactivity of the $Li_{q_{int}}$ (Carretero et al., 2007). Although these changes may affect the use of the peloid this aspect has been little studied.

One of the physicochemical properties of peloids that has been studied is the cation exchange capacity (CEC) of the solid phase. Some authors define it as the capacity of clay colloids to attract and retain positively charged ions and to exchange them with the aqueous solution surrounding the particles in accordance with chemical equilibria (Tan, 2011). Clay minerals with high CEC are usually employed in cosmetics, applied topically, to aid cleansing through absorption of toxins, bacteria and undesired skin materials (Matike et al., 2011). A high CEC value of the clay mineral particles also affects ion exchange between the clay mixture and the skin (Tateo and Summa, 2007; Tateo et al., 2009) and thus contributes to the cleansing process. Furthermore, the application of peloid can affect perspiration through the formation of an interphase in which ion exchange between the skin and the peloid takes place (Carretero et al., 2010). However, despite this, there have been few studies of these physicochemical properties of peloids.

The process known as peloid maturation is necessary to improve and stabilize their therapeutic properties (Sánchez et al., 2002) and small changes in mineralogy may occur during this process (Tateo and Summa, 2007). Maturation is a process of mixing and resting with periodic shaking of the materials over a specific time period in order to homogenize and optimize the properties of the peloid while also developing some specific properties (Carretero et al., 2006; Veniale et al., 2004). These time periods can vary greatly between 30 days (Gámiz et al., 2009), 60 days (Galzigna et al., 1998) and 2 years (Veniale et al., 2004). However, much controversy surrounds the time period required to achieve maturation (Popoff,

2000). Some spas even use extemporaneous peloids (with contact between the two phases of approximately 48 h) for practical reasons (Armijo et al., 2010; Teixeira, 2011). Once again, in spite of their importance, there is few studies on peloid maturation, particularly with regard to establishing the optimum time required to ensure development of the chemical, physicochemical and mineralogical properties.

The town of Lanjarón (Granada, Spain) (Fig. 1) is located in the Sierra Nevada National Park, in the region known as Las Alpujarras, close to the Mediterranean coast. The springs are located on a large geological fault; a deep fracture resulting in contact between two distinct lithologies: the Alpujarride Complex, mainly represented in this zone by phyllitic materials (sometimes carbonated) and the Nevado-Filabride Complex, generally schistose (microschists and quartzites). The mean annual air temperature is 14.5 °C (Delgado and Ortega, 1985). Lanjarón has a world-renowned spa which uses several different springs of MMW with a range of different salinities and therapeutic properties. Although the waters of the principal springs, “Capilla”, “Capuchina”, “El Salado”, “Salud”, “Gómez” and “Agria del Río”, have been used for medicinal purposes since the 18th century no studies of these waters as a raw material for peloids have been carried out, except the spring “Salado” (i.e.: Armijo et al., 2010; Maraver et al., 2010). In addition, for some of them, no data regarding their analysis and classification have been published to date.

The aim of the present study is to investigate specific chemical, physicochemical and mineralogical properties of peloids, taking into account the type of water used in the mixture and its maturation time. The peloids were prepared with two MMW from the Lanjarón spa while the mineral composition of the solid phase was maintained constant to avoid interference by this potential variable. The MMW properties, the properties of the interstitial water extracted ($Li_{q_{int}}$) from the peloids, the crystallinity of the principal clay minerals present in the solid phase (kaolinite and saponite), the CEC and the exchangeable bases of the solid phase were studied. These topics have been little studied to date and, consequently, the present study should make a significant contribution to our knowledge of the medicinal use of peloids.

2. Materials and methods

2.1. Sampling of the medicinal mineral water (MMW)

Samples of the natural MMW were obtained from the “Salud V” and “El Salado” springs (Lanjarón spa, Granada) (Fig. 1) during October



Fig. 1. Map showing location of Lanjarón Spa.

t1.1 **Table 1**
t1.2 Sample description.

t1.3	Medicinal mineral water	Water and interstitial liquid phase		Peloid	
		Sample	Description	Sample	Description
t1.5	Salud V (Lanjarón Spa)	S0 ^a	Medicinal mineral water	S1p	Peloid with a maturation of one month
t1.6		S	Water with a maturation of one month		
t1.7		S1	Interstitial liquid phase of the peloid with a maturation of one month	S3p	Peloid with a maturation of three months
t1.8		S3	Interstitial liquid phase of the peloid with a maturation of three months	S6p	Peloid with a maturation of six months
t1.9	El Salado (Lanjarón Spa)	S6	Interstitial liquid phase of the peloid with a maturation of six months		
t1.10		E0 ¹	Medicinal mineral water	E1p	Peloid with a maturation of one month
t1.11		E	Water with a maturation of one month		
t1.12		E1	Interstitial liquid phase of the peloid with a maturation of one month	E3p	Peloid with a maturation of three months
t1.13		E3	Interstitial liquid phase of the peloid with a maturation of three months	E6p	Peloid with a maturation of six months
t1.14		E6	Interstitial liquid phase of the peloid with a maturation of six months		

t1.15 P: Solid phase of the peloid by mixing industrial kaolin: bentonite (9:1, mass:mass).

t1.16 ^a Sampling date: October 2007.

184 2007 (samples S0 and E0, Table 1) using 5 l plastic bottles which had
185 been washed with distilled water and rinsed three times with the
186 target water before filling. The following parameters were measured
187 at the sampling point: water temperature (with a digital thermometer:
188 Digi-Sense RTD PLATINUM), pH (pHmeter Crison GLP 21) and electrical
189 conductivity (conductimeter Crison GLP 31) (Table 2).

190 2.2. Peloid preparation

191 The solid phase of the peloid (sample P, Table 1) was prepared by
192 mixing industrial kaolin and bentonite (powdered materials) in the
193 proportion 9:1 (kaolin:bentonite, mass:mass) (Table 3). These are
194 pharmaceutical and cosmetic raw materials of relatively high purity
195 (kaolin: 87% kaolinite; bentonite: 94% saponite, a mineral of the
196 smectite group) previously studied by our research team (Gámiz,
197 1987; Gámiz et al., 1992).

198 The liquid/solid proportion of the peloid was 2:1 (w:w): 1000 g of
199 liquid and 500 g of solid (peloid water content was thus 66.66%).
200 With the water in relative excess this permitted maturation to take
201 place with around 2 cm of supernatant Liq_{int} always covering the
202 water-clay mixture (Veniale et al., 2004).

203 Peloid preparation commenced the day after obtaining the MMW
204 samples and was as follows: the solid phase components were mixed
205 to obtain a homogeneous powder. Water (S0 and E0, Table 1) was
206 added and the mixture stirred in a figure of eight motion with a
207 2 cm wide steel spatula until complete homogeneization. The starting
208 point for the maturation process can then begin.

209 2.3. Maturation process. Obtention of Liq_{int}

210 The samples were stored in cubic 3 l plastic containers in an open
211 atmosphere (but loosely covered to avoid possible contamination by
212 atmospheric dust) at a temperature of around 20 °C. All samples were
213 stirred and homogeneized every week during the maturation period.
214 Type, number and duration of movements applied to each sample
215 were standardized: the same 2 cm wide steel spatula was rotated 60
216 times in a figure of eight motion for 3 min for each samples. Moisture
217 content by weight was monitored to maintain the initial moisture condi-
218 tions. Addition of water was necessary in all cases employing bidistilled
219 water to maintain constant the water content of the Liq_{int}. Furthermore,
220 at the end of the maturation process the moisture content was measured
221 by oven-drying at 105–110 °C for 24 h. Maturation times were 1, 3 and
222 6 months, after which sampling was carried out (Table 1).

223 The Liq_{int} of the peloid were extracted by suction (approx.
224 100 kPa). Controls were also prepared with the MMW used in the
225 study (samples S and E, Table 1), undergoing a similar maturation
226 process of one month but without a solid phase.

227 2.4. Analysis of the Liq_{int}

228 For the MMW, the Liq_{int} and the controls the following analyses
229 were performed: electrical conductivity; pH; dry residue content
230 (DR), in an oven at 110 °C; carbonate and bicarbonate content, by
231 tritration with hydrochloric acid; chlorides and sulphates by ionic chro-
232 matography (Dionex, DX300); and calcium, magnesium, sodium, potas-
233 sium, iron and silicon by atomic absorption spectrophotometry.

t2.1 **Table 2**
t2.2 Water and interstitial liquid phase parameters.

t2.3	Sample ^a	S0 ^b	S	S1	S3	S6	E0 ^b	E	E1	E3	E6
t2.4	Electric conductivity (20 °C) (mS cm ⁻¹)	2.35	2.06	3.07	2.76	2.67	5.98	5.23	5.92	5.37	5.68
t2.5	pH ^c	5.6	8.0	8.2	7.7	7.9	6.4	8.0	8.2	8.0	7.9
t2.6	Solid residue (110 °C) (g l ⁻¹)	1.50	1.45	1.92	1.74	2.09	3.93	3.56	3.64	3.56	3.55
t2.7	Chloride (mg l ⁻¹)	644	621	669	675	710	1577	1650	1775	1560	1704
t2.8	Sulphate (mg l ⁻¹)	47	45	226	254	239	133	140	322	295	274
t2.9	Carbonate (mg l ⁻¹)	0	120	270	210	180	0	150	240	240	120
t2.10	Bicarbonate (mg l ⁻¹)	366	61	30.5	61	61	732	122	61	61	122
t2.11	Calcium (mg l ⁻¹)	108	61	30	21	39	261	97.6	190	65	74
t2.12	Magnesium (mg l ⁻¹)	22	21	13	10	22	70	44.3	60	44	51
t2.13	Sodium (mg l ⁻¹)	366	366	703	685	703	884	1165	1269	1202	1202
t2.14	Potassium (mg l ⁻¹)	40	37	13	9	14	110	102	28	27	37
t2.15	Iron (mg l ⁻¹)	10.00	0.03	0.05	0.05	0.03	12.00	0.21	ND	ND	0.05
t2.16	Silicon (mg l ⁻¹)	14.13	13.00	8.33	2.68	0.33	26.71	23.47	4.89	3.86	0.94

t2.17 ND = not detected.

t2.18 ^a Sample nomenclature in Table 1.

t2.19 ^b Sampling temperature: S0 = 19 °C; E0 = 24 °C.

t2.20 ^c Measured at the sampling point.

Table 3
General characteristics of the minerals (solid phase) used to prepare the peloids.^a

Materials	Characteristic											
	Provenance	Purification/pretreatment	Texture	Colour (common term)	Munsell Colour	pH _{H2O}	pH _{KCl}	pH _{NaF}	OM (%)	SSA (m ² g ⁻¹)	Granulometry	Mineralogy (XRD)
Kaolin C-6A	Explotaciones Cerámicas Españolas S.A. (Burela, Lugo, Spain)	Washed kaolin. Very fine powder	Very slippery and soft	White, slightly yellowish	10YR 8/1 (White)	4.7	3.8	9.2	0.87	55.82	Fine sand (200–20 μm) = 10%; silt (2–20 μm) = 48%; clay (<2 μm) = 42%	K = 87% (presence of halloysite); Qz = 7%; FdK = 3%; K-mica = 3%; traces of IM
Bentonite 1	Tolsa S.A. (Madrid, Spain)	Very fine powder	Soft, although a little rough due to hardened clay aggregates	Dark green	5Y 7/2 (Pale grey)	10.4	9.6	9.9	0.78	506.43	Fine sand (200–20 μm) = 3.7%; silt (2–20 μm) = 5.9%; clay (<2 μm) = 90.4%	Sa = 94%; Qz = 2%; Il = 4%

Abbreviations: OM = organic matter; SSA = specific surface area; K = kaolinite; Qz = quartz; FdK = potassium feldspars; K-mica = muscovite; IM = interstratified minerals; Sa = saponite; Il = illite.

^a Adapted from Gámiz (1987) and Gámiz et al. (1992).

2.5. Measurement of crystallinity by X-ray diffraction

Crystallinity was measured for the most abundant clay minerals, kaolinite and saponite, in the solid phases of the peloid and for kaolin and bentonite initials (raw materials) by Philips PW 1730 diffractometer, using Cu K α radiation with a scanning speed of 1° 2 θ /min. The process was as follows: the sample (approx. 20 cm³) underwent dialysis with distilled water to eliminate excess salts. One part was then dried and ground (<50 μm) to obtain disoriented powder diagrams (using a holder filled from the side after Niskanem, 1964). Another part of the sample was used to prepare oriented aggregates of the clay fraction (<2 μm) by drying the suspension on a glass slide (approximately 3.3 mg cm⁻²) after clay extraction by depletion following Stokes' law. These were air dried after treatment with ethylene glycol (Brown and Brindley, 1980).

The Hinckley index for kaolin (Hinckley, 1963) was estimated in the disoriented powder diagrams. This provides an approximate, total and empirical measure of crystallinity under the working conditions recommended by Hughes and Brown (1979). For the saponite, the crystallinity is a measure of the lattice ordering and crystallite size, and is expressed as the integral breadth of the smectite 1.65 nm peak. The integral breadth is the width of the rectangle (in $\Delta^{\circ}2\theta$), which has the same height and area as the measured peak. It was measured in oriented aggregate diagrams treated with ethylene glycol (Ehrmann et al., 2005).

2.6. Study of the cation exchange capacity (CEC) and exchangeable bases

This was carried out on the solid phases of the peloids, after extraction of the Liq_{int}, and on the initial solid phase (sample P).

The exchangeable bases were quantified by macerating the samples in ammonium acetate, centrifuging and then measuring them by atomic absorption in the supernatant (MAPA, 1994; Rhoades, 1982) and were sodium and potassium, and calcium and magnesium

The CEC was determined by washing the samples used to establish the exchangeable bases with ethanol and then leaching the ammonium with sodium (sodium acetate), centrifuging and measuring the ammonium in the supernatant using the method of Bouat and Crouzet (MAPA, 1994).

3. Results

3.1. Analysis of the MMW and Liq_{int}

The values of dry residue obtained from the samples of MMW, S0 and E0 (Table 2), were higher than 1 g/l (1.5 g/l for "Salud V" and 3.93 g/l for "El Salado"), showing that these are highly mineralized waters (according to the classification of Maraver and Armijo,

2010). This is confirmed by the electrical conductivity results, 2.35 mS/cm and 5.98 mS/cm, respectively.

The temperature of both waters during sampling was below 35 °C (19.8 °C for S0 and 26.1 °C for E0). They can thus be classified, from a balneotherapeutic perspective, as "hypothermal" (Maraver and Armijo, 2010). However, from the point of view of Schoeller (1962) (Custodio and Llamas, 2001), both waters would be classified as "hyperthermal".

The pH determined at the spring of samples S0 and E0, was 5.6 and 6.4, respectively. These values are considerably lower than those for the waters after one month of maturation (pH around 8), samples S and E, and those of the Liq_{int} extracted from the peloids (between 7.7 and 8.2), samples S1, S3 and S6 and E1, E3 and E6 (Table 2).

According to their ion contents, both the medicinal mineral sample (S0) and the control (S) from "Salud V" are "sodium chloride-rich, calcic and bicarbonated waters" (Fig. 2, Tichel's classification, recommended for these types of water by Custodio and Llamas, 2001). The sample S0 can also be classified as "ferruginous" due to its iron content of 10 mg/l (Maraver and Armijo, 2010). After one month sample S could no longer be considered "ferruginous" since iron content had decreased to 0.03 mg/l but was "carbonated" (Tichel), exhibiting a high concentration of carbonates. Most of the ion contents (except the carbonates, which showed a large increase) decreased from S0 to S (matured for one month).

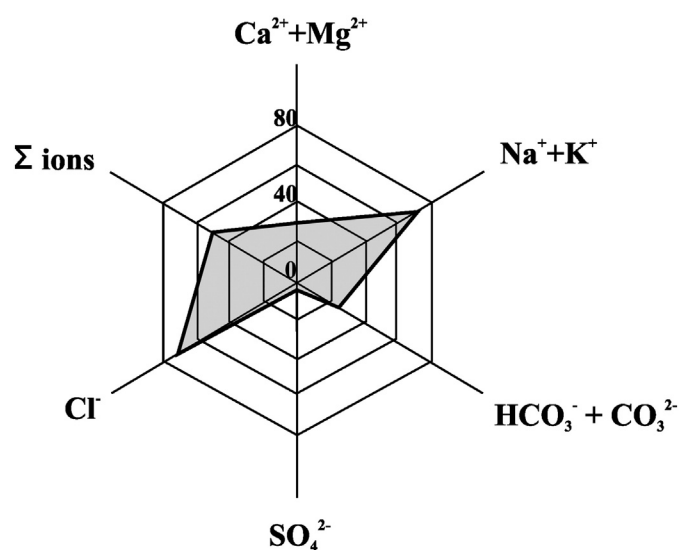


Fig. 2. Tichel diagram of mineral-medical water "Salud V", sample S0. Cations and anions are in %; ion sumatory is in meq l⁻¹.

Table 4Linear correlation matrix for medicinal mineral water parameters and interstitial liquid phase of the peloid parameters: r values ($n = 10$).

	CE	pH	RS	Chloride	Sulphate	Carbonate	Bicarbonate	Ca	Mg	Na	K	Fe ^a	Si	Anions	Cations
t4.4	CE (mS cm ⁻¹)		0.9888	0.9805					0.9218	0.9049				0.9963	0.9820
t4.5	pH					0.8536	-0.8157					-0.9448			
t4.6	RS (g l ⁻¹)			0.9746					0.9240	0.8995				0.9879	0.9803
t4.7	Chloride (mg l ⁻¹)								0.9119	0.9159				0.9744	0.9813
t4.8	Sulphate (mg l ⁻¹)														
t4.9	Carbonate (mg l ⁻¹)						-0.8196								
t4.10	Bicarbonate (mg l ⁻¹)							0.7721							
t4.11	Ca (mg l ⁻¹)								0.8352						
t4.12	Mg (mg l ⁻¹)													0.9331	0.8768
t4.13	Na (mg l ⁻¹)													0.8923	0.9519
t4.14	K (mg l ⁻¹)												0.9004		
t4.15	Fe (mg l ⁻¹)														
t4.16	Si (mg l ⁻¹)														
t4.17	Anions (mg l ⁻¹)														0.9787
t4.18	Cations (mg l ⁻¹)														

t4.19 Statistical significance: $r > 0.7646$, $p < 0.01$ (**); $r > 0.8721$, $p < 0.001$ (***)t4.20 ^a $n = 8$, statistical significance: $r > 0.8343$, $p < 0.01$ (**); $r > 0.9249$, $p < 0.001$ (***)

The MMW of “El Salado” (E0) was classified as “chloride- and sodium-rich, calcic, bicarbonated and ferruginous”, as found by Maraver and Armijo (2010). The control (E) was classified as “chloride- and sodium-rich and bicarbonated” but not “calcic” or “ferruginous” since, during maturation, the contents of most of the ions decreased, including calcium and iron, and, to a lesser extent, bicarbonates, magnesium, potassium and silicon. Furthermore, over time, other ions such as carbonates appeared in the solution while chlorides, sulphates and, particularly, sodium increased.

When the water comes into contact with its mineral phase and becomes part of the peloid as the Liq_{int}, notable changes in composition occur. In the Liq_{int} of the samples of “Salud V” (S1, S3 and S6) iron (from 10 mg/l to 0.03–0.05), potassium and bicarbonates decreased while other ions such as carbonates, sodium (concentration doubled) and, especially, sulphates and chlorides increased. Thus, all the Liq_{int} S1, S3 and S6 were classified as “sodium- and chloride-rich, carbonated and bicarbonated”.

Similarly as has occurred in the “Salud V” samples, the Liq_{int} of the peloids of “El Salado” (E1, E3 and E6), showed differences with respect to the original water: higher concentrations of anions such as chlorides, sulphates and carbonates and of cations such as sodium, while iron or potassium again decreased. They were classified as “chloride- and sodium-rich” except for E1, which could also be classified as “calcic” since the proportion of this cation was greater than 20% (Custodio and Llamas, 2001).

The effect of maturation time on the physicochemical properties of the Liq_{int} depended on the MMW used. There was a general tendency for concentrations of most of the ions (chlorides, bicarbonates, calcium and magnesium) to increase in the Liq_{int} of the “Salud V” peloids after 6 months maturation (S6), although some of these

ions (calcium, magnesium, sodium and potassium) showed a slight decrease between one (S1) and three months (S3). Carbonates decreased gradually from S1 to S6. However, in the Liq_{int} of the peloid samples of “El Salado”, the opposite tendency was observed for most ions: concentrations decreased towards the end of maturation (E6) (sulphates and carbonates) or at the third month (E3) (chlorides and calcium-concentration halved-, magnesium and sodium), later stabilizing or even increasing (E6).

The correlation matrix corresponding to the set of variables for the MMW (S0, S, E0, E) and the Liq_{int} (S1, S3, S6, E1, E3, E6) (Table 4), can be considered as proof of the internal coherence of the results obtained. The good correlation of the summations of ions and cations, both between each other and with the total salts present (dry residue) should be noted. These summations also correlate with the principal cations, such as sodium and magnesium, and the principal anions, such as chlorides. The expected linear correlation Cl⁻ vs Na⁺ ($n = 10$, $r = 0.9159$, **) (Fig. 4) exhibits a slope of 0.598, close to the atomic proportions Na⁺/Cl⁻ (0.65), since these ionic species in solution are in equilibrium with the NaCl.

3.2. Mineral crystallinity

3.2.1. Kaolinite

The Hinckley Index (HI) values obtained for the kaolinite of all the peloid samples (between 0.52 and 0.65; Table 5) are within the range of natural kaolinites. According to the bibliography (Hinckley, 1963), the values considered as high (kaolinites with fewer defects) are close to 1.0, while those below 0.5 are considered low; the kaolinites of the present study have medium values.

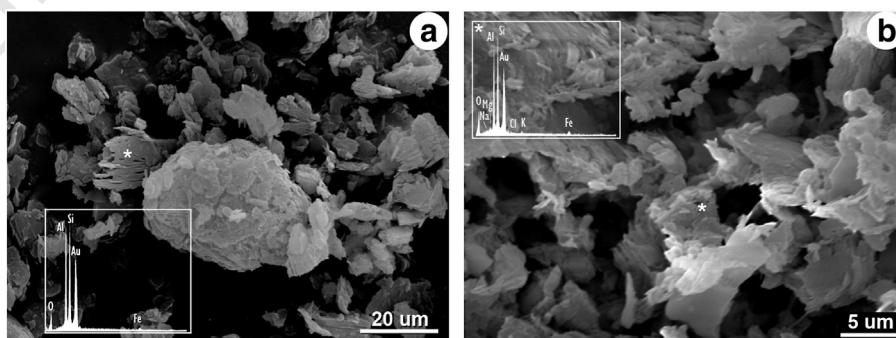


Fig. 3. SEM images and X-Ray microanalysis a) General vision of Kaolin C6A. A kaolinite stack can be seen (*) with characteristic microanalysis. b) SEM image of E1p (laminar mineral particles with characteristic microstructure) with X-Ray microanalysis.

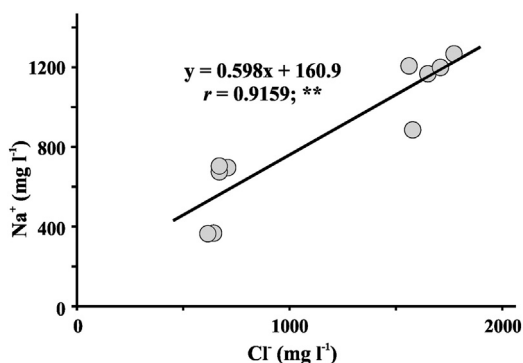


Fig. 4. Relationship between chlorides and Na^+ contents in the interstitial liquid phase of the peloids.

The HI value for the kaolinite of the initial kaolin, 0.70, decreased in all the peloid samples after maturation: slightly, in the “Salud V” samples (S1p, 0.64; S3p, 0.65 and S6p, 0.63), and more notably in those from “El Salado” (E1p, 0.52; E3p, 0.60 and E6p, 0.58). In other words, crystalline perfection decreased during the maturation process, particularly in the “El Salado” samples.

The effect of maturation time on HI varied slightly according to MMW. In the peloids prepared with “Salud V” HI values hardly changed while they increased slightly between one and three months and later hardly changed in those from “El Salado”.

3.2.2. Saponite

The Integral Breadth (IB) crystallinity values of the saponites ranged from 1.06 to 1.26 $\Delta^{\circ}2\theta$ (Table 5). According to Ehrmann et al. (2005), the IB value is the inverse of the crystallinity and the categories for saponite are: “highly crystalline” (IB < 1.0 $\Delta^{\circ}2\theta$), “well crystalline” (IB between 1.0 and 1.5 $\Delta^{\circ}2\theta$), “moderately crystalline” (IB between 1.5 and 2.0 $\Delta^{\circ}2\theta$) and “poorly crystalline” (IB > 2.0 $\Delta^{\circ}2\theta$). In the present study both the original saponite and those that underwent maturation can be classified as “well crystalline”.

In the peloids IB values decreased with respect to those of the initial solid phase. Thus, there was an increase in crystallinity and an improvement in crystalline perfection from the initial saponite. However, there was a very slight increase in IB in the peloid from “Salud V” with 6 months maturation (P: 1.24, S6p: 1.26).

Simple observation revealed no clear relationships between IB and MMW nor maturation time. Although IB values of the saponites of the S peloids increased at 6 months whereas those of E peloids gradually decreased these were relatively minor variations.

3.3. CEC and exchangeable bases

The CEC values of the peloid solid phase were always below 10 $\text{cmol}_+ \text{kg}^{-1}$ (Table 6) and the evolution of these values from the initial mineral phase to the end of the maturation period was the same for the two MMW studied. The CEC of the solid phase decreased slightly during peloid preparation from 9.4 cmol_+/kg (P) to 8.2 $\text{cmol}_+ \text{kg}^{-1}$ (S1p) and 8.9 $\text{cmol}_+ \text{kg}^{-1}$ (E1p). There was a tendency to increase with maturation time, attaining similar values to the

Table 6

Cation exchange capacity (CEC) and exchangeable bases of the solid phases of the peloids.^a

	P	S1p	S3p	S6p	E1p	E3p	E6p
CEC ($\text{cmol}_+ \text{kg}^{-1}$)	9.4	8.2	8.9	9.3	8.9	8.9	9.4
Ca^{2+} ($\text{cmol}_+ \text{kg}^{-1}$)	5.1	6.6	5.6	7.3	7.6	5.5	4.5
Mg^{2+} ($\text{cmol}_+ \text{kg}^{-1}$)	5.5	6.2	5.7	5.5	6.1	5.8	5.2
Na^+ ($\text{cmol}_+ \text{kg}^{-1}$)	8.4	5.7	5.6	6.2	7.0	6.5	7.8
K^+ ($\text{cmol}_+ \text{kg}^{-1}$)	5.6	0.4	0.4	0.6	0.7	0.7	0.8

^a Sample nomenclature in Table 1.

initial mineral phase after 6 months: 9.3 $\text{cmol}_+ \text{kg}^{-1}$ in S6p and 9.4 $\text{cmol}_+ \text{kg}^{-1}$ in E6p.

The sequence of quantities of exchangeable bases in the initial raw mineral (sample P) was $\text{Na} > \text{K} \sim \text{Mg} > \text{Ca}$. The introduction of MMW to prepare the peloid substantially modified the sequence with potassium becoming the least abundant base. In most cases (S1p, S6p and E1p), calcium was the most abundant cation, between 6.6 and 7.6 $\text{cmol}_+ \text{kg}^{-1}$ followed by sodium, with the highest concentrations in the peloids with water from “El Salado” (E1p, E3p and E6p), ranging from 6.5 to 7.8 $\text{cmol}_+ \text{kg}^{-1}$. Regardless of water type and maturation time the least abundant exchangeable base in all the peloids studied was potassium with concentrations below 0.8 $\text{cmol}_+ \text{kg}^{-1}$.

4. Discussion

4.1. Evolution of the Li_{int}

The classification (Tickel system) of the two MMW used for peloid preparation (Table 2) in terms of their composition and properties showed certain similarities. Sample E0, “El Salado”, is “chloride- and sodium-rich, bicarbonated, calcic and ferruginous”, as also found by Maraver and Armijo (2010). We have classified sample S0, “Salud V”, previously unstudied, as “sodium chloride-rich, calcic, bicarbonated and ferruginous” as it shows an iron concentration of 10 mg/l. Fig. 2 shows the Tickel diagram for this water. The most abundant ions in this sample were chlorides and sodium, S0, although the classifications of S0 and E0 are similar, their characteristics are ordered differently.

Both waters are also classified as “hypothermal” (classification terms from Maraver and Armijo, 2010) since temperature ranged from 19.8 °C (“Salud V”) to 26.1 °C (“El Salado”), but from the point of view of the Schoeller’s criterion, they are classified as “hyperthermal” (Custodio and Llamas, 2001). At the moment of sampling both MMW were around pH 6. Differences in mineralization were more evident, the electrical conductivity (20 °C) of “El Salado” (5.98 mS cm^{-1}) being almost three times higher than that of “Salud V” (2.35 mS cm^{-1}).

The loss of the characteristics of water recently emerged from a spring by the samples S0 and E0 is clear when they are compared to the control samples S and E, respectively. Both mineral waters became more basic (increase in pH) on contact with the atmosphere and over time (one month) as they increase in carbonates. This must be due to loss of CO_2 , which contributes to the increase in pH (around or greater than 8), causing transforming of bicarbonates to carbonates. Some of these carbonates in solution must have been precipitated as calcium carbonate as there was a significant decrease in calcium in both S and E. The oxidation and precipitation of soluble iron may also be involved in the increase in pH. The soluble iron decreased drastically in both waters from the moment of sampling at source to the end of the one month of storage.

These changes suggest that patients should receive treatment with MMW at spring in order to obtain the full benefit of its therapeutic properties. In this case, waters with a moderately acidic pH and with soluble iron contents of 10 mg/l will be administered orally to treat hypochromic anaemia and as a tonic, since they produce regeneration of

Table 5
X-ray diffraction (XRD) indices of kaolinite and saponite.^a

	Initial materials ^b	S1p	S3p	S6p	E1p	E3p	E6p
Kaolinite Hinckley Index (HI)	0.71	0.64	0.65	0.63	0.52	0.60	0.58
Integral Breadth (IB) of saponite ($\Delta^{\circ}2\theta$)	1.24	1.17	1.06	1.26	1.19	1.14	1.09

^a Sample nomenclature in Table 1.

^b Values of the X-ray diffraction indices of initial kaolinite and saponite.

Table 7
Linear correlation matrix for interstitial liquid phase of the peloid parameters and CEC and exchangeable bases of the solid phase of the peloids (n = 6).

	CE	pH	RS	Chloride	Sulphate	Carbonate	Bicarbonate	Ca	Mg	Na	K	Fe	Si	Anions	Cations	Δ Anions	Δ Cations	CEC	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺			
CE (mS cm ⁻¹)																									
pH	0.9832																								
DR (g l ⁻¹)		0.9942																							
Chloride (mg l ⁻¹)			0.9892																						
Sulphate (mg l ⁻¹)				0.9892																					
Carbonate (mg l ⁻¹)					0.9782																				
Bicarbonate (mg l ⁻¹)						0.9782																			
Ca (mg l ⁻¹)							0.8412																		
Mg (mg l ⁻¹)								0.8412																	
Na (mg l ⁻¹)									0.9699																
K (mg l ⁻¹)										0.9699															
Fe (mg l ⁻¹)											0.9243														
Si (mg l ⁻¹)												0.9243													
Anions (mg l ⁻¹)													0.9745												
Cations (mg l ⁻¹)														0.9745											
Δ Anions (mg l ⁻¹)															0.9868										
Δ Cations (mg l ⁻¹)															0.9977										
CEC (cmol+ kg ⁻¹)																0.9977									
Ca ²⁺ (cmol+ kg ⁻¹)																	0.9166								
Mg ²⁺ (cmol+ kg ⁻¹)																		0.9654							
Na ⁺ (cmol+ kg ⁻¹)																			0.9654						
K ⁺ (cmol+ kg ⁻¹)																				0.9654					
Anions (mg l ⁻¹)																									
Cations (mg l ⁻¹)																									
Δ Anions (mg l ⁻¹)																									
Δ Cations (mg l ⁻¹)																									
CEC (cmol+ kg ⁻¹)																									
Ca ²⁺ (cmol+ kg ⁻¹)																									
Mg ²⁺ (cmol+ kg ⁻¹)																									
Na ⁺ (cmol+ kg ⁻¹)																									
K ⁺ (cmol+ kg ⁻¹)																									

Statistical significance: r > 0.9172, p < 0.01 (**); r > 0.9741, p < 0.001 (***)

red blood cells and stimulate erythropoiesis (Maraver, 2004; Torres Piles, 2005). According to these authors, the iron in these ferruginous waters is in ferrous form, resulting in increased bioavailability and requires moderately acidic conditions in order to be stable.

The Liq_{int} extracted from the peloids also showed differences in composition and properties when compared to the original MMW (both for the samples from “Salud V”, SO, and those from “El Salado”, EO). The pH of the Liq_{int} was slightly alkaline, which would lead to a change in possible chemical reactions at skin level. Application of the peloid rather than the MMW would modify the acid equilibrium of the skin, which has a pH between 4.2 and 5.9 (Eberlein-König et al., 2000; Takigawa et al., 2005). These slightly alkaline Liq_{int} of the peloids would produce effects at skin level; This is the reason why alkaline waters are often used to treat a variety of cutaneous disorders (Tateo et al., 2010).

Increases and decreases in ionic contents were also observed. The former can be attributed to the contributions of chlorides, sulphates and sodium from the solid phase to the Liq_{int} or even, in the case of increase of carbonates, can not be ruled out the capture of CO₂ from the atmosphere. Precipitation or ion exchange mechanisms which remove ions (iron, calcium, potassium or silicon) from the Liq_{int} should also be considered. These changes in composition once again suggest that the therapeutic action must also change. It should be remembered that MMW (and, by extension, the Liq_{int}) performs different actions affecting metabolic and organ functions (Armijo and San Martín, 1994), depending on the ions present and their concentrations. For example, sodium chloride-rich waters improve cellular trophism, tissue repair and scar formation and are often used to treat rheumatic conditions (Armijo and San Martín, 1994).

The six months of the maturation process also leads to changes in the composition of the Liq_{int}. The behaviours and processes involved would be similar to those mentioned for the passing of MMW to Liq_{int}: precipitation and release or capture from the solid phase. Thus, during maturation, the therapeutic effects of the peloid due to the ions of the Liq_{int} must change slightly.

Statistical analysis provided information regarding the differences detected between the waters and the Liq_{int}. We calculated the correlation matrix, which included the data for the Liq_{int} and the exchange complex excluding the MMW (Table 7). Comparison with the matrix for all waters + Liq_{int} (Table 4) showed almost all the same correlations, although, in the Liq_{int}, the correlation coefficients tended to be higher. This was thus a case of two somewhat different populations of variables, since, when studied together, the correlation decreased. As before (see results, 3.1), the problem was studied by analyzing the variables Cl⁻ and Na⁺ (Fig. 4). Differences were found between the population of waters and that of the Liq_{int}. The slope of the regression line (significance <1%, **) in the population of waters (0.679), very close to the atomic proportion Na⁺/Cl⁻ (0.65), is of interest as the species in solution reflect the proportion in NaCl. On the other hand, this value for the Liq_{int} (significance <1 per thousand, ***) was lower, 0.526. The reason for there being two populations may be that in the Liq_{int} the equilibria established by ionic exchange due to the presence of the solid phase in the medium must be added to the chemical equilibrium Na/Cl in the solution. Possible proof of this is the correlation between Na_(Liqint) and Na_(exchangeable), 10% significance (linear) (r = 0.7586) and 5% significance (logarithmic) (r = 0.8857). The positive significant relationships between the concentrations of Liq_{int}-K and exchangeable sodium (**) and exchangeable potassium (**) (Table 7) should also be noted.

4.2. Evolution of the solid phase

The mineralogical changes occurring during maturation in the solid phase of the peloids were estimated using the crystallinity measurements of the most abundant minerals, kaolinite and saponite. This was because the initial mineral phase had a constant mineralogical

composition (proportion of the different mineral phases) for all the samples, the timescale of the study was not sufficiently long and the geochemical conditions of the peloid not sufficiently extreme for this composition to change significantly.

The HI, which determines the quantity of defects in the structure empirically and globally (Guggenheim et al., 2002), was used to assess the crystallinity of the kaolinite (Table 5). Crystalline perfection decreased during maturation, reaching a similar level in the peloids from both waters after six months, although slightly lower in the samples from “El Salado”. The increase in defects in the kaolinite of the peloid during maturation may be due to the particles with lesser defects being the largest, in the form of vermicular stacks or pseudo-hexagonal crystals (Delgado et al., 1994). During peloid preparation and maturation, both of which involve mechanical stirring of the sample and the particles (described in Methods), these packets and crystals must be broken into smaller individual particles with more defects. Evidence for this hypothesis is that the kaolinite stacks were detected in the mineral (Fig. 3a) but not in the peloids, which were always composed of laminar particles (Fig. 3b).

MMW also appears to affect the HI of the kaolinite since the peloids with the less crystalline kaolinite were those from “El Salado”. It is thought that the more saline water from this spring (Table 2) disperses the particles more, leading to more defects.

In terms of therapeutic applications, the decrease in crystallinity of the kaolinite may increase its ability to delay the release of drugs adsorbed onto the peloid (Delgado et al., 1994), another benefit of the maturation process.

Regarding the crystallinity of the saponite, the widespread decrease in IB in the peloids (increase in crystalline perfection, Ehrmann et al., 2005) from the mineral sample (P) can be attributed to the presence of cations such as potassium (and, to a lesser extent, sodium, calcium and magnesium) in relatively significant quantities in the interstitial medium (Liq_{int}) of the peloids from both waters (Table 2). These cations must enter the interlayer spaces of the saponite where they stabilize the structure and increase crystalline perfection, making the saponite closer to mica. This process, known as aggradation (Pédro, 1987) has been described in soils treated with potassium fertilizer (Velde and Barré, 2010). However, in the specific literature for peloids, the opposite process has been described, whereby crystalline perfection decreases in the saponites during maturation (Sánchez et al., 2002). We believe that this case is due to the water employed (ferruginous, bicarbonated and sulphate-rich), which may have degraded the clay minerals. The waters “Salud V” and “El Salado” are chloride- and sodium-rich, calcic, bicarbonated and ferruginous, although the iron content soon decreases in the water and would not act on the minerals (Table 2).

The maturation process brings about differences in the evolution of crystallinity in the kaolinite and saponite, depending on the MMW employed (Table 4). A most precise interpretation would require further studies with more variables and samples than the present study.

4.3. Solid phase/Liq_{int} interaction

The decrease in CEC from mineral sample P to the solid phases of the peloids, S1p and E1p, matured for one month (Table 6), could be explained by hypotheses based on the ionic exchange phenomena between the solid phase and the water and the aggradation process of the saponite mentioned previously. Some exchange positions of the saponite may have been blocked more or less irreversibly by cations such as potassium from the water, fixed in the interlaminar space of the saponite. This would aggragate towards mica, as suggested by the crystallinity measurements, thus reducing CEC. The CEC of mica is lower than that of a smectite-saponite (Tan, 2011).

The decrease in potassium in the Liq_{int} of S1p and E1p compared to the MMW, S0 and E0, respectively (Table 2), would tend to support

this hypothesis. The exchangeable potassium from the initial mineral phase itself (P) would be responsible for the aggradation, being irreversibly fixed in the saponite, shown by its sharp decrease in the peloids compared to P. For example, from P to S1p exchangeable potassium decreased from 5.4 cmol₊/kg to 0.4 cmol₊/kg (Table 5). Further proof of aggradation, statistical in this case, is the negative correlation (significance < **) between the peloid CEC and the concentration of silicon in the Liq_{int} (Table 8). When aggradation of the saponite layer towards mica occurs the silicon in the crystalline layer must decrease leading to an increase in the soluble silicon of the Liq_{int}: the crystallochemical exchange involved to tetrahedral sheet in the structural formula would be Si_{3.7}Al_{0.3} → Si₃Al releasing Si, which goes into solution).

Another interesting observation is that CEC increased progressively during maturation in both samples, S and E, eventually attaining the same values as P. Maturation regained the initial CEC of the mineral phase, a process that requires a more detailed study.

The principal exchangeable bases, calcium, magnesium, sodium and potassium (Table 6) are of interest in this study. The sequence of quantities changed from the original mineral material (P) to the mineral phase of the peloids. In P it was Na > K ~ Mg > Ca while in most of the the mineral phases it was Ca > Na > Mg > K. The peloid thus causes other changes in the mineral phase as well as in the crystallinity.

The exchangeable bases are important as they are potentially exchangeable in human sweat and can thus reach the skin. This process would also involve the Liq_{int} of the peloid.

However, in order to evaluate this process it is first necessary to consider the mean composition of human sweat: Ca²⁺, <1 mg/l, Mg²⁺, <1 mg/l, Na⁺, 1870 mg/l, K⁺, <1 mg/l (calculated using the European regulation EN 1811:1998 + A1:2008). It is also necessary to compare (in similar concentration units) sweat composition, the Liq_{int} (Table 2) and the exchange complex (Table 5), leading to the creation of Table 8, which normalizes all quantities to cmol₊/l.

According to Table 8, the concentration of sodium is highest in sweat, meaning that the sodium in the sweat would be captured by the peloid and either incorporated into the Liq_{int} by diffusion or into the solid phase by ionic exchange. The opposite is true of calcium, magnesium and potassium, which were always more concentrated in the Liq_{int} and as exchangeable bases than in sweat. The peloid

Table 8
Content of calcium, magnesium, sodium and potassium in the human sweat, medicinal mineral waters, interstitial liquid phase of the peloids and in the solid phase of the peloids.

Sample ^a	Ca ²⁺ (cmol ₊ l ⁻¹)	Mg ²⁺ (cmol ₊ l ⁻¹)	Na ⁺ (cmol ₊ l ⁻¹)	K ⁺ (cmol ₊ l ⁻¹)
Human sweat ^b	<5 × 10 ⁻³	<8.3 × 10 ⁻³	8.13	<2.56 × 10 ⁻³
S0	0.54	0.18	1.59	0.10
S	0.31	0.17	1.59	0.10
S1	0.15	0.11	3.05	0.03
S3	0.11	0.08	2.97	0.02
S6	0.20	0.18	3.05	0.04
S1p ^c	3.30	3.10	2.85	0.20
S3p ^c	2.80	2.85	2.80	0.20
S6p ^c	3.65	2.75	3.10	0.30
E0	1.31	0.58	3.84	0.28
E	0.49	0.36	5.06	0.26
E1	0.95	0.49	5.51	0.07
E3	0.33	0.36	5.22	0.07
E6	0.37	0.42	5.22	0.10
E1p ^c	3.80	3.05	3.50	0.35
E3p ^c	2.75	2.90	3.25	0.35
E6p ^c	2.25	2.60	3.90	0.40

^a Sample nomenclature in Table 1.

^b Calculated amounts following European standard EN 1811:1998 + A1:2008.

^c Exchangeable bases (in cmol₊ l⁻¹) = cmol₊ kg⁻¹ × 500 (g peloid)/1000 (cm³ medicinal mineral water).

would thus be a potential supplier of these cations and responsible for the sedative effects mentioned previously (magnesium and potassium) and anti-inflammatory effects (calcium) (Armijo and San Martín, 1994).

Table 8 also shows that, with the exception of sodium, concentrations in the exchangeable base complex are at least ten times greater than in the Li_{int} . A similar phenomenon was observed on comparison of the MMW with the exchange complex although the differences in concentrations were smaller. Consequently, the exchange complex cations could constitute a reservoir which would increase the effect on the skin of the cations from the Li_{int} or the water on the skin, even though the exchangeable cations are less available. Matike et al. (2011) suggested that clay mineral materials with $\text{CEC} < 15 \text{ cmol}_+/\text{kg}$ could have a low absorption capacity and cannot absorb ions from the skin, although they may be able to supply ions to the skin, depending on their concentration in the soils. They concluded that at high CEC values ion exchange from the skin to the clay minerals mixture and release of ions to the skin can occur during application (of the peloid), facilitating skin cleansing and providing a refreshing sensation. For these authors the peloids from the present study with $\text{CEC} < 15 \text{ cmol}_+/\text{kg}$, would not be especially valuable as skin cleansing agents although they could be a source of ions.

When peloid is applied to the skin, there are therefore three inter-related environments: 1) solid phase (with exchange complex), 2) Li_{int} and 3) skin will result in the establishment of more intense, complete and permanent (effective) equilibria for supplying cations to the skin than just the application of mineral–medicinal water. The statistically significant relationships between Li_{int} and exchange complex for some cations (Table 7) has already been discussed.

Finally, Table 8 shows how maturation times do not result in relevant differences in the behaviour described and those that do appear are subordinate to the influence of MMW type. In the peloids from “Salud V” concentrations in both the Li_{int} and the exchange complex generally increased with maturation while there was more disparity in the peloids from “El Salado”.

5. Conclusions

The properties of the initial MMW underwent significant changes on its incorporation into the peloid and becoming the Li_{int} . This will act in a different way to the MMW and will also have different therapeutic properties.

The peloid is seen to be a complex system of interrelationships in terms of the soluble cations, which can potentially be supplied to the patient's skin. These cations are mainly found in the Li_{int} bathing the mineral particles but closely related to the exchange cations on the mineral surface. As the solid phase of the peloid has an ionic exchange phase it becomes active, a reservoir of available ions which enhance the action of the peloid. This is not only restricted to cations but extends to polar pharmacologically active substances which can be sorbed in the peloid in ionic exchange positions of the mineral phase. These substances later pass from the exchange complex to the Li_{int} of the peloid and thence to the skin.

The peloid causes changes to the mineral phase used in its preparation. The relative quantities of the exchangeable cations change and the starting minerals of the peloid, kaolinite and saponite, are also modified, depending on MMW type and maturation time. In the other hand, the kaolinite evolves towards lower degrees of crystallinity while the saponite undergoes the opposite process, aggradating towards mica, in this case by interrelation with the Li_{int} and the exchange complex, probably capturing K for this from both media.

The number of cases studied makes it difficult to draw detailed conclusions regarding the role of MMW type in the properties of the peloid. This is also true of maturation time although both are proven to have an effect.

In conclusion, the peloid controls and modifies the properties of the initial materials: MMW and minerals. Peloid is thus a new product in which new properties can develop and be employed in alternative therapies to those currently in use.

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