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PHYSICOCHEMICAL CHARACTERIZATION, ELEMENTAL SPECIATION AND HYDROGEOCHEMICAL MODELING OF SANTA LUCÍA PELOID USED FOR THERAPEUTIC USES

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ABSTRACT

Santa Lucía peloid is a sediment, extracted from salt mines, used in pelotherapy in Cuban primary health care services. Therefore, in addition to classical quality control analyses of total metal concentrations in sediments, speciation and complementary analyses are required to understand potential geochemical element availability for their use in human health.

The present study was conducted to characterize the Santa Lucía peloid, based on the total metal content and geochemical speciation of major elements and transition metals (Cr, Cu, Fe, Ni, Mn, Pb and Zn), using a sequential extraction procedure and inductively couple plasma emission techniques. In order to predict the distribution of majoritarian and trace elements in different geochemical fractions, the physicochemical parameters, the particle size (electronic microscopy), mineralogy (X-ray diffraction), and the hydrogeochemical models (Pourbaix phase diagrams) were used. The results showed that the predominant cation was Na with high mobility and exchange capacity; meanwhile most of the trace elements studied (Cr, Pb, Ni) in this investigation appeared in the less mobile fractions, which suggested low availability in the sediment, under the studied conditions. The findings were useful to predict the behavior of the metals regarding solubility, potential motility and availability in the sediment, and it was concluded that most of the metals are strongly retained in the peloid and that sediment was considered as non-polluted, according to USEPA normative.

Keywords: Peloid, Trace elements, Pelotherapy, Sediment, Santa Lucía

INTRODUCTION

Peloids are multi-component systems which consist of mineral water and clay minerals, organic matter and organo mineral complexes that are applied in healing procedures [1]. Peloids can be formed by the interaction of geo materials with mineral waters over long periods of time in a natural environment or can be formulated in an artificial maturation process focused in a product with suitable properties for the treatment of specific pathologies [2].

During the last decades, several investigations have been done to get insights on the chemical composition and biological mechanism of action of peloids for the significance in their correct application and use in the treatment called Pelotherapy [2]. Tendencies of the chemical studies in peloids have been related with the determination of chemical species (organic and inorganic compounds with biological activities); changes in maturation process; determination of

physicochemical and rheological properties of peloids, organic contaminants and toxic elements (As, Cd, Hg, Pb Se, Tl, etc.); and the establishment of standard criteria for the certification of the quality and suitability of the peloids devised for specific therapies [2]-[4].

In particular, mobile and/or exchangeable toxic elements (e.g. Fe, Mn, Cu, Zn, Pb, Cr, As, Cd, Hg), are of special concern, since they can be scavenged by the skin sweat [4]. These metals have therefore become important discussion issues in the “certification” of the quality of sediments for therapeutic uses [2]. However, there are only a few comprehensive studies related to the presence and availability of these metals in peloids, despite being a key knowledge to understand the possible beneficial and/or dangerous effects to human health [2], [4]. Particularly, there is a need for studies related to the geochemical composition of peloids used in balneotherapy due to the risk of heavy metals in peloids, the interaction between metals and other components of the peloid matrix, and with the

human biomembranes, with possible re-adsorption through the skin [2].

Besides the total content, metals can be partitioned into different chemical forms that are associated with a variety of organic and inorganic phases, depending on chemical and geological conditions [2], [5]. Thus, speciation analysis of metallic elements and mineralogical studies might provide useful information regarding the potential mobility and bioavailability of a particular element, which consequently can offer a more realistic estimation of its effects [5].

In Cuba, there is still a great reserve of natural peloids, used in pelotherapy. The profuse resources are related with coastal and salt mine (brine) sediments due to a wide distribution through the island coastal line. Santa Lucía peloid is a sediment extracted from “El Real” salt mine, located in Santa Lucía locality, in Camaguey Province, Cuba, at 20° 52' 03" of north latitude and 90° 22' 20" west longitude. This peloid has been used in pelotherapy for many years, mainly associated with Cuban primary health care centers and services, for the routinely treatment of inflammatory (osteoarthritis, rheumatoid arthritis, bursitis) and dermatological (eczemas, psoriasis, cutaneous seborrhea and mycosis) processes. As far as the actual knowledge, there are no reports of operational speciation and geoavailability of metals in this peloid; either or studies on its relation with the physicochemical and geological conditions, to predict the metallic elements mobility and establish the inorganic quality for its use in pelotherapy.

The present study was conducted to characterize the Santa Lucía peloid, based on the total metal content and geochemical speciation of major elements and transition metals (Cr, Cu, Fe, Ni, Mn, Pb and Zn), using a sequential extraction procedure and inductively couple plasma emission techniques. In order to predict the distribution of majoritarian and trace elements in different geochemical fractions, the physicochemical parameters, the particle size (electronic microscopy), mineralogy (X-ray diffraction), and the hydrogeochemical models (Pourbaix phase diagrams) were used.

MATERIALS AND METHODS

Field methodology

Surface samples of the peloid (20-40 cm) were collected directly in the “El Real” salt mine, 50 m away from the coastal line. A composite sample was prepared from 10 different subsamples. “In situ” measurements of pH, oxidation–reduction potential (Eh), electric conductivity (EC), temperature and dissolved oxygen in the peloid samples were carried out using a HANNAHI-8424 pH/Eh meter, a WTW

LF197 conductimeter with internal temperature probe and a HANNA HI 914 oxymeter, respectively.

Sediment samples were sealed in clean polyethylene containers, placed in a cooler at 4 °C, and transported to the laboratory immediately for further analysis.

Laboratory methodology and hydrogeochemical modeling

The sequential extraction method followed a modified Tessier diagram [6], to obtain five different fractions: (i) exchangeable (EXC), (ii) bound to carbonates (CARB), (iii) bound to easily reducible oxides (Fe/Mn oxide-bound fraction) (ERO), (iv) bound to organic matter and sulfide (MO), and (v) residual (R-RES). Total metal concentration (digestion using HNO₃ (65%) and HClO₄ (60%)(3:1.5)) and sequential extraction procedures used in this study were previously described by Suárez [2]. The final extracts were analyzed using an inductively coupled plasma optical emission spectrometer (ICP-OES, Varian: 730-ES Optical Emission Spectrometer) to determine metals commonly present in sediments (Cu, Cr, Fe, Mn, Ni, Pb and Zn). Total metal concentrations were compared with results obtained from the sequential extraction procedure of the sediment samples. Quality control was assured by the analysis of triplicate samples and standard reference materials with recoveries ranged from 86 to 116% and analytical precision better than 10%.

The Pourbaix phase diagrams were used as hydrogeochemical model to predict the dominant aqueous species of each metal and sulfur in the sediment, defined by the Eh and pH values [7].

Solid phase analysis (XRD, SEM-EDS, particle size)

Bulk mineralogy was determined by X-Ray Diffraction (XRD) using PANalytical X'Pert PRO X Ray Diffractometer with Cu K α radiation. Analyses were performed in a 2 θ range of 5 to 90° at a scan rate of 0.02° s⁻¹. Phase identification was carried out by comparison with the Joint Committee of Powder Diffraction Standard 2007 Data Base. Mineral semi-quantification was estimated by the Reference Intensity Ratio (RIR) method using the X'pert High Score Plus software.

For the Scattering Electronic Microscopy (SEM), the peloid samples were observed using a scanning electron microscope Phillips XL 30, EE.UU. The particle size was determined using at least 10 different areas of each sample microphotography; and the image processing was obtained by the ImageJ IJ 1.46r software. The obtained data was classified by the International System of Texture of Soils and Sediments [39], and the normalized

classification of soils attending to different normatives (DIN (4022), British, ASTM) [8].

Sediment quality assessment

In the present work, the peloid was considered and evaluated as a generic sediment, using standard quality guidelines (USEPA, 1977) [9] to establish chemical inorganic quality criteria, since it was not possible to find in the literature any specific requirements regarding metal content in peloids.

Elemental results are then compared with background concentrations to determine if the metal content in the analyzed peloid represents a natural concentration or a contamination value. These background values are used for the calculation of the contamination factor (Cf) and the contamination degree (Cd) calculated as described in [2], [10].

The mobility factor (MF), as the relation of the content in the more labile fractions against all the fractions determined [10], were calculated as Eq. (1).

$$MF = \frac{(EXC + CARB)}{(EXC + CARB + ERO + MO + R - RES)} * 100 \quad (1)$$

RESULTS AND DISCUSSION

Physicochemical, elemental characterization

The results obtained for physicochemical parameters show very low (negative) oxidation–reduction (Eh) potential ($-0.413 \pm 0.002V$) and anoxic conditions with rather neutral pH values (6.79 ± 0.02). The main aspect is that electric conductivity (EC) is high with values of 120.86 ± 0.03 mS/cm due to the salinity contributed by sea water. Both EC and Eh values show extreme geochemical conditions of the peloid and they can have a decisive effect in the chemical and biological reactions which are responsible for the properties of the peloid, since they can affect metal mobility due to changes in metal-binding capacity of humic materials, metal sulfide formation (or sulfide oxidation), and changes in Fe/Mn-oxyhydroxides [4], [12].

Elemental content analysis of major and minor elements of Santa Lucía showed that Ca, Na, Mg, and K are the main cations that contribute to sediment composition, and are also responsible for the high values of electric conductivity (Fig. 1). The concentration of these four major elements was found in the range of 190-61680 mg·kg⁻¹. These cations are present in the sediment as result of the lithological contribution (terrigen-carbonated deposits and sands with composition rich in carbonates, gypsum and halite) and also the salts coming from the concentrated sea water. Other metals (Cr, Cu, Ni, Pb and Zn) appeared at lower concentrations (5.20-25.4 mgkg⁻¹) (Fig. 1) as a result

of lithological origin from the geochemical cycle in the ecosystem [2].

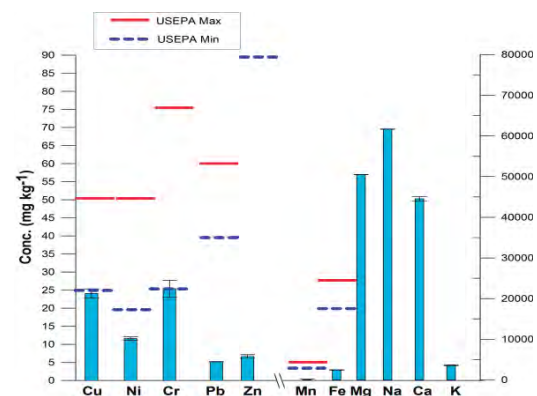


Fig. 1 Metal concentration in mg/Kg.

Solid phase analysis (XRD, SEM-EDS, particle size)

Table 1 shows the granulometric or particle size analysis obtained by SEM. The results demonstrate that the main sizes are related with fine sand distribution (near 60%) followed with a distribution as silty particle size (30%).

This distribution corresponds with the coastal environment, with high percent of sand and low percent of clay (Table 1). Therefore, these results indicates that the retention of transition metals in the sediment is poor (it is reported that clayed materials with lower sizes (2 μ m and < 63 μ m) favor the retention and cation exchange having higher specific superficial area) [13]. Therefore, the distribution of the particle size may play an important role in the geoability, mobility and finally bioability of the metals showing Santa Lucía peloid, in this case, less retention capacity of metals than other peloids reported in literature [4], [13].

Bulk XRD analysis shows a homogeneous composition dominated by gypsum and halite. Phyllosilicates contribution (clayed material), in concordance with particle size analysis, is not high or significant. Other precipitated minerals in low magnitude are calcite as well as quartz, common in terrestrial crust (Table 2).

The use of theoretical Pourbaix Eh–pH phase diagrams in hydrogeochemical modeling, contributes to understand the potential mobility of metals. As can be seen in Fig. 2, the reducing conditions determine that all the metals are situated in the lower zone of water stability, corresponding to sub-aqueous sediment accumulations and in the so-called “euxinic” environments of poorly ventilated marine water bodies or organic-rich brines pools [14].

Table 1 Granulometric analysis

Classification	%	Classification	%	
Clay	12.08	Fine	60.59	
Silt	27.13	Sand	Thick	0.2

Table 2 Mineralogical composition

Mineral	%	Mineral	%
Phyllosilicates	10	Calcite	8
Halite	29	Pyrite	5
Gypsum	44	Quartz	4

Hydrogeochemical modeling

In the case of the major elements, Na and K are predicted in their monovalent soluble species meanwhile Mg and Ca are described to be present in their divalent species and also $MgHCO_3^+$ and $CaHCO_3^+$ species with the same behavior than reported in [2]. For the trace elements (Fig. 2 a–h), the Pourbaix Eh–pH diagrams predicts that all elements, with exception of Cu ($Cu(s)$), are in their soluble form (Cr, Fe and Pb forming metal(OH)ⁿ⁺ species and Zn, Mn and Ni soluble divalent cations). These results predict a low retention of transition metals in the peloid in agreement with the findings of the particle size analysis and mineralogy.

The sulfur species were also modeled due to the relevance for metal mobility in highly reductive environments. In the case of sulfur species (S), it is predicted to appear in the form of H_2S .

In these environments, the salinity is such that the water is no longer solvent and the thermodynamic conditions preclude the use of the PHREEQC software with conditions described [2], and a special database must be designed for the environments of the samples.

Metal speciation in Santa Lucía peloid

Although total metal content can be used as a preliminary approach to evaluate quality and suitability of peloids for therapeutic uses, chemical speciation is of supreme importance to elucidate possible mechanisms of distribution and mobility in these complex systems. In peloids, no matter the total content, elements can only cause a positive or toxic response in biological systems, if they are mobile and available and can interact with sweat and biological barriers (skin or mucous membranes).

The analysis of the different fractions obtained after sequential extraction showed the distribution of the species according to their affinity with the different phases (Fig.3 a and b). In general, the major elements are distributed in the leachable fractions (EXC, CARB and ERO). This behavior is

due to the high solubility of the elements of the alkaline and alkaline-earth metal groups.

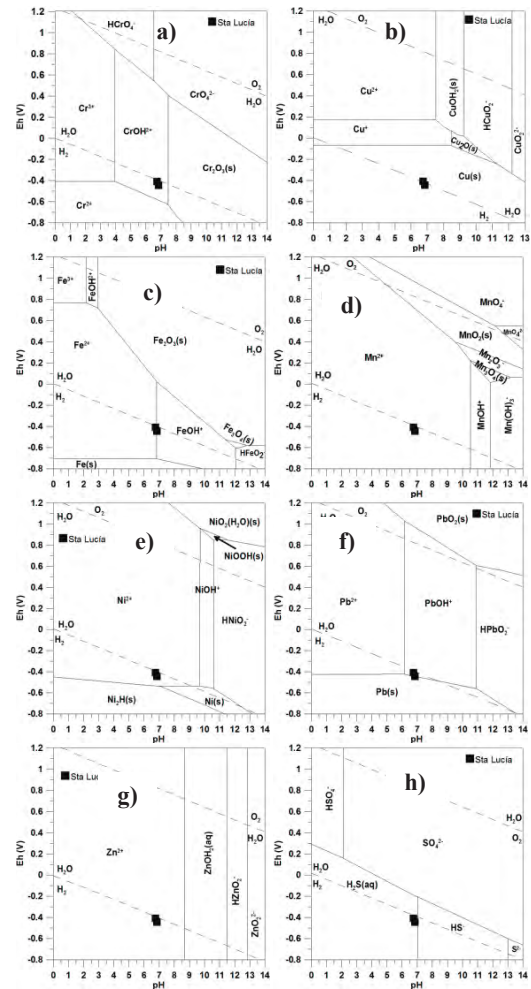


Fig. 2 Pourbaix Eh–pH diagrams of the transition metals (Cr (a), Cu (b), Fe (c), Mn (d), Ni (e), Pb (f), Zn (g)) and sulfur (h) speciation in RSD and PSD sediments.

For transition metals, shown in Fig. 3b, the main distribution is associated to ERO, MO and R-RES fractions, with the exception of Mn with 67% in the CARB fraction. The percentages of metals in the ERO fraction are of 22%, 15%, 77% and 10 % for Cr, Pb, Cu, Ni, respectively. Those values were higher than those obtained for another Cuban peloid (San Diego de los Baños), where the mentioned metals are linked in the less mobile fractions (MO and R-RES) and ERO fraction percentages were lower than 10% [2]. The results show that these transition metals in Santa Lucía peloid are less retained than in San Diego peloid, as predicted with the hydrogeochemical modeling and their particle size and mineralogical composition.

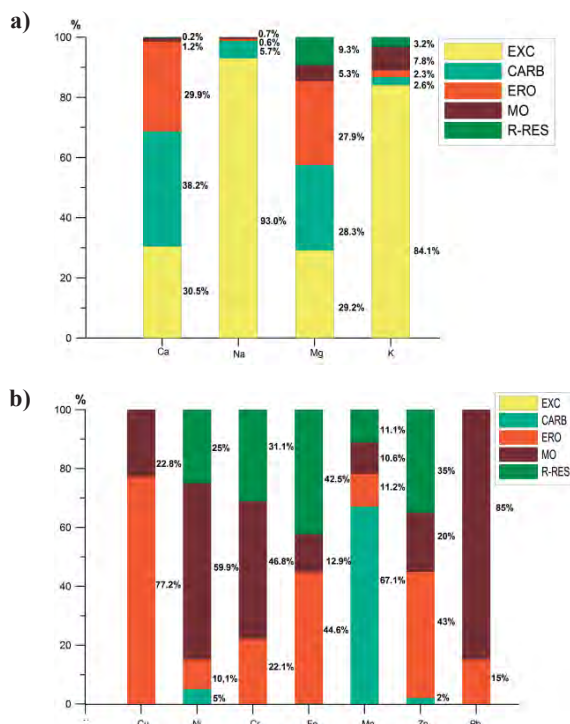


Fig. 3 Distribution of majoritarian (a) and trace (b) metals in the different extraction fractions.

Specialized literature reports that in low salinity environments, the main factor controlling metal distribution is pH, meanwhile in cases with high salinity the distribution of metals is influenced by pH, EC and salinity, the last two intimately related [15] [16]. The trace metals at high salinity can be easily exchanged by alkaline metal and the saturation of the cationic exchange capacity of the sediment can occur. This phenomenon can decrease the retention and storage of trace metals in sediment matrix, as reported for Pb (II), Cu (II), Cd (II) and Cr (III) [12], [15]. These mechanisms are also conditioned by the high particle size that provides small specific superficial area causing low retention of trace metals.

On the other hand, Mn is the more labile trace element with more of 67% in the CARB fraction. This behavior of Mn in sediments has been reported in the interaction with solutions with high NaCl concentration originating that Mn solubility arises due to the exchange reactions of this cation with Ca and Na, which preclude the sorption reaction of Mn over the ERO particles (Fe/Mn oxides), although other mechanisms as the formation of complexes with Cl^- y SO_4^{2-} have been proposed [16], [17].

Despite the difference in the behavior of trace elements in Santa Lucía peloid, in comparison with other reported peloids, under the studied conditions,

still Cr, Ni and Pb are highly immobilized (MO and R-RES (78-85%)). The literature reports that Cr, Ni and Pb, showed a high affinity for the organic matter. Lead has been mostly distributed in MO fraction and is reported to form strongly bounded complexes with the organic matter, and that slighted alkaline pH inhibits the mobility of this element [2]. Ni and Cr, are mostly located between MO and R-RES phases and it is reported that for Ni is expected that brusque changes in sediment conditions would lead to a slight redistribution between the MO and ERO fractions as observed in the sequential extractions [2]. Also the same behavior is reported for Cr, with the variation of salinity (higher salinity makes Cr less bounded to MO) [2].

Quality assessment

Due to the therapeutic use of peloids, a further analysis of the concentration values of transition metals regarding possible contamination was made by comparing with the limits reported by the USEPA (Fig. 1). It can be seen that the concentration values for all the sediments were below the minimum limit reported by the USEPA, so the peloid can be considered as non-polluted. Also using the background of the marine sediments for terrestrial crust can be considered with low contamination factor (Cf) and low degree of contamination (Cd). Meanwhile the FM index shows that all the elements exhibit low mobility with the exception of Mn (Table 3).

Special care should be paid to the chemical equilibrium and distribution of trace metals, as well as to the conditions of application of the peloid, because, despite the results obtained for FM index, Santa Lucía trace metals exhibit lower retention than the obtained for San Diego de los Baños peloid, mostly related with oxido-reduction changes (ERO fraction). Particular is the case of Mn species that are highly soluble and mobile, and can increase its bioavailability; however the dermal absorption of this metal is considered minimal and not a risky exposition pathway in normal conditions [2].

Table 3 Contamination factor (Cf), contamination degree (Cd) and FM index for trace elements

Element	(Cf)	FM
Cr	0,28	0,00
Cu	0,09	0,00
Fe	0,04	0,20
Mn	0,03	67,15
Ni	0,05	5,00
Pb	0,06	0,00
Zn	0,04	2,00
(Cd)	0,56	

CONCLUSIONS

The results showed that the major cations were Na, Ca, Mg and K, and that Na was the predominant element with high mobility and exchange capacity. Some of the trace elements studied in this investigation (Cr, Pb, Ni) appeared in the less mobile fractions, but the effect of salinity and particle size are observed with the displacement of a percentage of all the elements distribution toward the ERO fraction. Even so, still the results based in the FM index suggest low availability in the sediment, under the studied conditions. Also the peloid is considered as non-polluted, according to USEPA normative and not contaminated in relation with the background levels of marine sediments. The findings were useful to predict the behavior of the metals regarding solubility, potential mobility and availability in the sediment, and it was concluded that most of the metals are strongly retained in the peloid.

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