

## Characterization of peloids from different regions of Brazil

Jefferson Koyaishi Torrecilha<sup>a</sup>, Ana Paula Torres Mendes<sup>a</sup>,  
 Carolina Yume Sawamura Theophilo<sup>a</sup>, Horacio Marconi da Silva Matias Dantas Linhares<sup>a</sup>,  
 José Henrique de Paula<sup>a</sup>, Marcos Antonio Scapin<sup>b</sup>, Rafael Henrique Lazzari Garcia<sup>c</sup>,  
 Francisco Maraver<sup>d</sup>, Paulo Sergio Cardoso da Silva<sup>a,\*</sup>

<sup>a</sup> Research Reactor Center, Energy and Nuclear Research Institute (Instituto de Pesquisas Energéticas e Nucleares), Av. Prof. Lineu Prestes 2242, Cidade Universitária, CEP 05508 000, São Paulo 05508-000, Brazil

<sup>b</sup> Chemistry and Environmental Center, Energy and Nuclear Research Institute (Instituto de Pesquisas Energéticas e Nucleares), Av. Prof. Lineu Prestes 2242, Cidade Universitária, CEP 05508 000, São Paulo, Brazil

<sup>c</sup> Nuclear Fuel Center, Energy and Nuclear Research Institute (Instituto de Pesquisas Energéticas e Nucleares), Av. Prof. Lineu Prestes 2242, Cidade Universitária, CEP 05508 000, São Paulo, Brazil

<sup>d</sup> Department of Radiology, Rehabilitation & Physiotherapy, Medical Hydrology Group, Complutense University of Madrid, Plaza Ramón y Cajal s/n, Madrid 28040, Spain

### ARTICLE INFO

#### Keywords:

Natural peloid  
 Peloid characterization  
 Peloid topical application  
 Peloid therapeutic effect

### ABSTRACT

**Introduction:** Since the early days of humankind, peloids have been used for therapeutic purposes. However, the safety and efficacy of these materials for therapeutic treatments has never been regulated in most of the countries where it is commonly used.

**Materials and methods:** In this study, samples of peloids from different regions of Brazil (Águas de São Pedro, Paraty and Araxá) were characterized: mineral composition (X-ray diffractometry), physicochemical characteristics (pH, redox potential, moisture, % loss on ignition at 550 °C and 1000 °C, cooling kinetics, swelling power, specific surface area), concentration of trace elements (X-ray fluorescence, Neutron activation analysis, Graphite furnace atomic absorption spectrometry) and radiological activity (Gamma spectrometry).

**Results:** The results showed great variability in mineral composition, physicochemical characteristics, elemental concentration, concentration of activity and little variation in cooling kinetics. However, this variation is also found when comparing the results with some those presented by other authors.

**Conclusion:** This study concludes that the three peloids studied are good candidates to be used for topical application. Metals and potentially toxic elements present are in concentrations levels that are unlikely to cause risk to health.

### Introduction

Peloids have been used for therapeutic purposes since ancient times [1]. This material is composed of a mixture of solid phases (from geological or biological origin, or both, varying the number of organic substances, generally with biological metabolic activity) and liquid ones (mineromedicinal, thermal or sea water) presenting scientifically proven therapeutic and/or cosmetic properties [2–6]. Therefore, peloid is a mud, often used therapeutically, as part of pelotherapy, for therapeutic baths or spread on affected parts of the body. It consists of humus and minerals deposited naturally by geological, biological, chemical and physical processes [7]. Which peloid property is responsible for the

therapeutic treatments' effectiveness is still not exactly known today; however, some authors believe that the benefit of therapeutic treatment with this material depends on its composition (e.g., mineral, physical, chemical, organic compounds), the form of application (e.g., time and temperature) and its reactivity in the patient (e.g., ion exchange between patient skin and peloid) [3,8–23].

Although widely used, no specific regulation has been established yet for mud applications with medicinal purposes, however, there is a consensus that peloids must have almost zero toxicity since the presence of some elements, even in trace amounts, can pose a potential threat for the patient [24–28]. There is a great variability in the original composition in which natural peloids are found worldwide. Peloids composed

\* Corresponding author.

E-mail address: [jeffkoy@hotmail.com](mailto:jeffkoy@hotmail.com) (P.S.C. da Silva).

of clay, clayey silt, peat and clay are reported in Spain [16,29]; of silty clay and from biogenic origin in Turkey [30]; a mixture of different minerals in Croatia [31]; from volcanic origin in Portugal and Argentina [32,33]; composed of bentonite in Italy [34]; sandy silt sediment in Brazil, Slovenia, Montenegro, Greece and Russia [28,35–38]; clayey sediments and detrital matter in Israel [39]; from estuarine and coastal, saline and hydrothermal origin in Cuba [19,40]. The chemical variability in the mineral and organic composition peloids found entails the fact that their potential risk to human health can only be determined on a detailed, case by case, basis [26], from the physicochemical, geochemical, elemental, and radiological point of view.

The peloid effectiveness is also very important and several authors have made significant contributions to this [14,33,38,41–61], and according to Carretero [62] the number of studies of both characterization and efficiency has been growing following the increasingly complementary medicine demand.

Studies about Brazilian's clays for cosmetic purposes have been done [27,63–70], however, there are few studies about peloids, even though the application of these materials for therapeutic and esthetic treatments in spas and esthetic centers have been growing. The only studied peloid used in Brazil is the Peruíbe Black Mud (PBM), commonly used for treatment of psoriasis, peripheral dermatitis neuropathy, acne and seborrhea, myalgia, arthritis, and non-articular rheumatic processes. Silva et al. [28] showed that PBM consists of a silty-clay and fine sand material, of a pH approximately neutral, high content of fine particles, low amount of carbonate, hydrophilic character, high adsorption capacity and moderate cation exchange capacity. The PBM therapeutic activity and anti-inflammatory efficacy has also already been tested and described by Britschka et al. [42] and Gouvêa et al. [71].

Concerning the lack of regulation and the need of characterization, this study aims to present the physicochemical, geochemical, elemental and radiological characterization of three types of natural peloids commonly used in Brazil. The first one is the peloid used at the Dr. Octávio Moura Andrade Thermal SPA, located in the town of Águas de São Pedro, in São Paulo state. It is a mixture of green clay and sulfurous water, applied in patients for allergy, diabetes, asthma, intoxication, inflammation and rheumatism treatments. As it is a place with restricted access to the public, this peloid may not have anthropogenic influence. The second is found and used at the Tauá Grande Hotel Termas de Araxá, located in the town of Araxá, Minas Gerais state. This peloid is historically recognized for its therapeutic properties and is normally used to treat skin diseases, inflammation, bursitis, arthritis and osteoarthritis [72,73]. This peloid may not have anthropogenic influence as well as the ASP one. The third is found in the estuarine section of the Jabaquara Beach, located in the town of Paraty, Rio de Janeiro state. According to tradition, the original local inhabitants always had the habit of using the mud found at this place to bathe in. Nowadays, the tourists also make use of the mud bath, without access restrictions.

## Materials and methods

### Study areas

Águas de São Pedro is a touristic municipality whose main attraction is the thermal water spas existing in the town dedicated to thermalism, health, wellbeing and leisure. The town covers an area of 611 km<sup>2</sup> with a population of 36,298 inhabitants. The climate of São Pedro is Cwa (Köppen climate classification) and is characterized as mesothermic, with dry winters and hot summers [74]. Geologically, the morphostructure of the basement is part of the sandstones from the Paraná Sedimentary Basin [75]. Águas de São Pedro has three mineral water sources with different medicinal properties. Two wells are located in its territory, and the third, in the neighboring municipality, about 7 km away. The thermal waters originate from very deep sandstones and mudstones, corresponding to the Irati Formation and the deepest waters of the Paraná Basin [76]. In Dr. Octávio Moura Andrade Thermal SPA

the sulfur water is used to mature clays before applying in healing or cosmetic application.

Jabaquara Beach is located in Paraty, Rio de Janeiro state. The town has an area of 927,3 km<sup>2</sup> with almost 43,000 inhabitants. The North portion of the beach is limited by a mangrove zone where the mud occurs [77], and people can bathe in without access restrictions. For 30 years, one of the main attractions in Paraty has been the so-called “Bloco da Lama”, which consists, during the carnival period, of local residents and tourists traveling through the city covered with this mud [78]. The region is located between the sea and the Serra do Mar escarpment, a mountain chain in the Southeast region of Brazil, and presents a succession of small inlets and coastal plains where the outcrops of the crystalline basement can be seen. The sediments transported from the slopes of Serra do Mar are deposited on the beaches [79]. The rivers and channels are fed by a tropical rain regime, concentrated in the summer months. These sediments must be the main source for the mud accumulated in the mangrove.

The town of Araxá is located in the Alto Paranaíba macroregion, State of Minas Gerais, and has an area of 1166.96 km<sup>2</sup> with 78,997 inhabitants. This place is characterized by having a large reserve of niobium, apatite and plutonic rocks. The basement is made up of mineralized bodies arising from magmatic differentiation and subsequent metamorphism. Among them are carbonates formed by the supergenous enrichment of phosphate and niobium rich in calcite, barite and apatite; the glomerites, rich in phlogopite, which is a phyllosilicate composed of, among other things, potassium, magnesium and titanium; quartzites, phenites, and schists [80]. The water springs are alkaline, carbonated, sulfurous and radioactive. In Araxá, the mud used for pelotherapy is matured in two types of water. The first, with a water table interception at the terrain surface, classified as a granular, free and semi-confined aquifer system in the clayey weathered layer (2 km diameter; variable thickness, reaching up to 200 m at southern portion, close to the niobium mine). In the second, the water circulation is deep, discharging in a site dominated by slightly weathered rocks. Faults, fractures, and cracks dominate this free to semi-confined aquifer that mainly occurs in rocks surrounding the carbonatite complex [81]. In this location there is the Tauá Grande Hotel Termas de Araxá, a complex in which the mud goes through a maturation process in contact with sulfur water before being applied to patients/tourists [82].

### Samples description

The peloid from Águas de São Pedro (named ASP from now on) is composed of a mixture of the green clay and the sulfurous water, prepared a few minutes before its application. For this study, both were acquired at the Dr. Octávio Moura Andrade Thermal SPA and prepared following the instructions on the green clay container label: an unspecified portion of clay was added in a polyethylene container and, subsequently, an unspecified portion of sulfurous water was added to form a soft paste.

The peloid from Minas Gerais state (named Araxá from now on) was provided, for the study, by the Tauá Grande Hotel Termas de Araxá itself in the form it is applied to the patients, i.e., ready for use.

The peloid from Jabaquara Beach (named Paraty from now on), in the town of Paraty, is found in an open area with public access, it was manually collected with the assistance of a decontaminated polyethylene shovel and stored in a container of the same material of 1 L capacity.

Fig. 1 shows the collection regions of each sample.

### Physicochemical characterization

The pH was determined by mixing 10 ml of the wet peloid sample with 25 ml of KCl 1.0 mol L<sup>-1</sup>. The solutions were stirred for 5 min, left to stand for 1 h and then, the measurement was made [28]. The pH values were made using a Quimis pH meter. This method was applied to

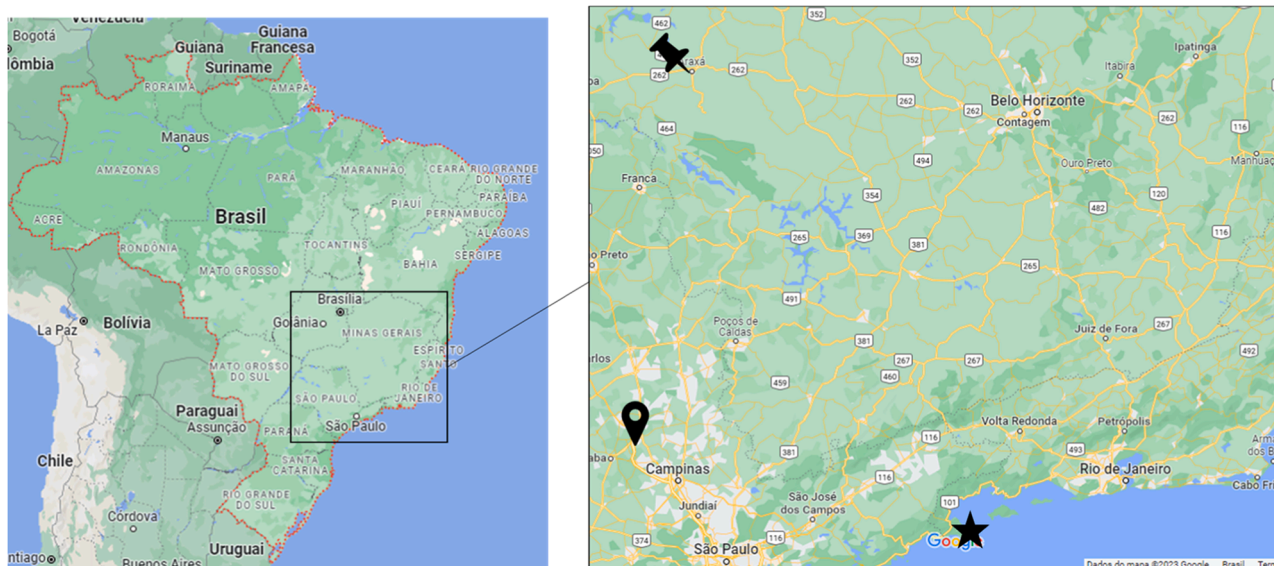


Fig. 1. Locations of the peloids: Águas de São Pedro, state of São Paulo (📍), Paraty, state of Rio de Janeiro (★) and Araxá, state of Minas Gerais (➡).

three replicates.

The redox potential (Eh) measurements were made on wet samples directly from the collection containers as fast as collected using a WTW pH/mV measure with a Mettler Toledo combined electrode.

Wet samples were treated, sequentially, by the mass difference in three different temperatures (105 °C, 550 °C and 1000 °C): (a) to determine the percent of moisture content, at 105 °C, for 24 h; (b) weight% LOI (loss on ignition) at 550 °C, for 4 h, to estimate the organic matter (OM) content and (c) the weight% LOI at 1000 °C, for 2 h, to determine the carbonate and hydroxide mass losses by employing an oven furnace [83]. This method was applied to three replicates.

The cooling kinetics determination was done following an adapted procedure described by Fernández-González et al. [3]: approximately 80 g of wet peloid was placed in a Teflon® container of approximately 75 cm<sup>3</sup> and closed with a cover of the same material with a little opening, then heated at 60 °C, placed in a water bath at 37 °C (human skin temperature) and the temperature at the center of the peloid was taken using a previously calibrated digital thermometer, at two-minute intervals, for 30 min.

Swelling power was measured by adding small portions of 0.10 to 0.15 g of material, which was gently tapped from the end of a small spatula blade into the water. Addition of similar portions was repeated at five-minute intervals until the whole sample had been added. Twenty-four hours after the last portion had been added, the volume of the peloid was measured [84]. The Foster [84] procedure was adapted by adding one more step: after the measurement, the sample was shaken with a glass stick for 5 min and left to stand for another 24 h, after which the volume was measured again. This method was applied to three replicates.

To estimate specific surface area (SSA), a titration procedure adapted from Sears [85] was used, in which 0.5 g of the peloid, dried and macerated at 100 mesh, was added to 150 ml of ultrapure water, stirred at 50 rotations per minute and its pH adjusted, measured with a pH meter, between 3 and 3.5 with HCl 0.1 mol L<sup>-1</sup>. After adjustment, 10 g of NaCl was added and this solution was titrated with standardized solution of NaOH 0.1 mol L<sup>-1</sup> at room temperature until pH 4 and then, until pH 9. This method was applied to two replicates. The SSA was calculated by using Eq. (1), where  $S$  is specific surface area (m<sup>2</sup> L<sup>-1</sup>) and  $V$  is volume (ml) used to increase the pH of the solution from 4 to 9.

$$S = 32V - 25 \quad (1)$$

#### X-ray diffractometry to mineral characterization

The peloids mineralogical components were identified by X-ray powder diffraction (XRD), using Bruker equipment, model D8 Advance, using Cu-k<sub>α</sub> radiation, 1200 W power. Diffractograms were acquired by varying the 2θ range from 4 to 60° with step size of 0.02° and 10 s per step. The crystalline phases were identified with the program Diffrac. EVA version 5.1.0.5, by Bruker, using the database PDF-2, version 2003 [28,63].

#### Elemental characterization

##### X-ray fluorescence

The chemical characterization was carried out using a wavelength dispersive X-ray fluorescence spectroscopy (WDXRF), with RIGAKU Co. spectrometer, model RIX 3000 with X ray tube, an Rh anode, a 75 μm Be window, a 60 kV maximum acceleration voltage, a scintillation detector NaI(Tl) and a flow-proportional counter. The samples were prepared in pressed pellets, adding 0.2 g powder wax to 1.8 g of sample, (analytical grade, HOECHST), this mixture was mixed and homogenized in a Mixer/Mill, then pressed using a hydraulic press. The Fundamental Parameters method was applied for the correction of the absorption/excitation effects. The methodology was evaluated using standard reference materials (SRM) 2709a San Joaquin Soil and 2711a Montana Soil 2, both from the National Institute of Standards (NIST) [28].

##### Neutron activation analysis

The instrumental neutron activation analysis (INAA) was used to determine Cl, K, Mg, Mn, Ti and V by a short irradiation period (20 s) and As, Ba, Br, Ce, Cs, Co, Cr, Cu, Eu, Fe, Hf, La, Lu, Mo, Na, Nd, Rb, Sb, Sc, Se, Sm, Ta, Tb, Th, U, Yb, Zn and Zr by a long irradiation period (8 h). For multi-elemental analysis, approximately, 60 mg and 150 mg (for short and long irradiations, respectively) of dried and crushed samples, at 100 mesh, and certified reference materials (CRM) (Estuarine

Sediment, SRM 1646a from NIST and Syenite, Table Mountain, STM-2 from United States Geological Survey (USGS)) were accurately weighed and sealed in pre-cleaned double polyethylene bags for short and long irradiations. Synthetic standards were also prepared by pipetting aliquots of standard solutions (SPEX Certiprep Inc., USA) using ultrapure water,  $18.2 \text{ M}\Omega \text{ cm}^{-1}$  at  $25 \text{ }^\circ\text{C}$  (Millipore Corporation, USA), onto small filter paper sheets. Samples and CRMs were sealed in high purity polyethylene and aluminum capsules, both manufactured especially for neutron irradiation, for short and long irradiations, respectively, and irradiated in a thermal neutron flux of  $10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ , in the IEA-R1 nuclear research reactor at Instituto de Pesquisas Energéticas e Nucleares (IPEN). Counting times were 3 min and 2 h for short and long irradiation, respectively, after the appropriate decay period for each interest nuclide (IAEA, 1990). Gamma spectrometry was performed using a coaxial Be-layer HPGe detector with 22% relative efficiency, 2.09 keV of resolution at 1.33 MeV and associated electronic devices. Spectra were acquired by a multichannel analyzer and analyzed with the aid of spectrum analysis in-house software CAX [86]. The methodology evaluations were done by cross-checking the CRMs and synthetic standards.

#### Graphite furnace atomic absorption spectrometry

For the elements Cd, Cu, Ni and Pb determination by graphite furnace atomic absorption spectrometry (GF AAS) the following procedure was followed: in approximately 200 mg of the dried and crushed peloid, at 100 mesh, were treated with concentrated  $\text{HNO}_3$ , HCl and HF in the proportion of 1:3:2 and left in digestion for 24 h. After digestion, the samples were placed in a microwave closed system for its total dissolution. The digested samples were allowed to cool at room temperature and diluted with ultrapure water. Measurements were performed by using a Perkin Elmer Analyst 800 graphite furnace atomic absorption spectrometer (Perkin Elmer, Vernon Hills, Illinois, USA). Before performing the measurements, solutions of the elements of interest were prepared from stock solutions and a  $\text{HNO}_3$  solution 0.2% (v/v) (Merck), used as a diluent, for construction of the equipment calibration curve. The same procedure was followed for marine sediment reference materials HISS-1 and MESS-3 both from the National Research Council Canada (NRCC) for verification of the methodology [28].

#### Gamma spectrometry

Activity concentrations of  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ,  $^{210}\text{Pb}$ ,  $^{228}\text{Th}$  and  $^{40}\text{K}$  were measured by gamma spectrometry with a high-pure germanium detector, GX2020, from CANBERRA. The detector was calibrated with IAEA-RGK, IAEA-RGTh and IAEA-RGU standards from the International Atomic Energy Agency (IAEA). Samples crushed at 100 mesh were placed in  $40 \text{ cm}^3$  polyethylene flasks, sealed and set apart for about four weeks, prior to the measurements, to ensure they reached the radioactive equilibrium between  $^{226}\text{Ra}$  and its short-living decay products. The  $^{226}\text{Ra}$  activity concentration was determined by taking the mean activity of three separate photopeak's of its daughter nuclides:  $^{214}\text{Pb}$  at 352 keV, and  $^{214}\text{Bi}$  at 609 keV and 1120 keV. The  $^{228}\text{Ra}$  content of the samples was determined by measuring the intensities of the 338 keV and 911 keV gamma-ray peaks from  $^{228}\text{Ac}$ . The  $^{228}\text{Th}$  activity concentration was determined by taking the mean activity of two separate photopeak's of its daughter nuclides:  $^{212}\text{Pb}$  at 238 keV and  $^{212}\text{Bi}$  at 727 keV. The activity concentration of  $^{210}\text{Pb}$  was determined by measuring the activity of its low energy peak (46.5 keV). The activity concentration of  $^{40}\text{K}$  was determined by measuring the activity of its high energy peak (1460 keV). Self-absorption correction was applied because the attenuation for low energy gamma rays is highly dependent upon the sample composition [87].

## Results

### Physicochemical characterization of the natural Brazilian peloids

The results obtained in the DRX analysis showed that the ASP peloid is mainly formed of quartz, illite and modest kaolinite and phlogopite contents (Fig. 2a). The peloid from Paraty is formed of quartz, kaolinite, illite, gibbsite and halite (Fig. 2b). In the peloid from Araxá the minerals quartz, phengite and titanium dioxide (Fig. 2c) were observed, making it the one that presents the greatest difference in its composition in relation to the others.

In Table 1 the pH, Eh, moisture, OM, LOI, SSA, and swelling before and after agitation are shown. The highest pH values, slightly alkaline, were found in Araxá sample while ASP and Paraty peloids presented the same almost neutral pH value. The redox potential values of the ASP peloid was 169.6 mV, while Paraty and Araxá showed more reducing values (-299 and -350 mV, respectively). The swelling power measurements showed different characteristics for the studied peloids. The one from ASP showed small amounts of a highly expansible suspended material with colloidal characteristics before and after the shaken process. The Paraty peloid showed no swelling, while the sample from Araxá showed high swelling power, leaving the water completely cloudy before and after shaking. The moisture content by mass were higher in Paraty peloid (14.3%), while ASP, and Araxá peloids showed an adsorbed water content of 4.7 and 4.1%, respectively. The OM content varied from 7.3 to 23.1% with the ASP peloid presenting the lowest values and the peloid of Araxá, the highest. Paraty peloid presented the intermediate value of 13.7%. Considering the weight% LOI at  $1000 \text{ }^\circ\text{C}$ , ASP, Paraty and Araxá values were 2.71%, 3.1%, 0.8%, respectively. Table 1 also shows SSA values, and it is possible to see that the ASP and Araxá peloids presented the same values ( $123 \text{ m}^2 \text{ g}^{-1}$ ) and Paraty showed the smaller ( $71 \text{ m}^2 \text{ g}^{-1}$ ).

The cooling dynamics of the peloids, explained by the variation in temperature with time, can be described as a progressive decrease in the time interval assayed, 0–30 min, although with some differences between the samples. The results of temperature with time-cooling are shown in Table 2. Using this data, the  $\Delta T$  was calculate: the accumulated decreases in temperature ( $\Delta T = T_0 - T_n$ , being  $T_0 = 60 \text{ }^\circ\text{C}$ ).  $\Delta T$  and time fit a logarithmic function ( $y = a\ln(x) + b$ ;  $y = \Delta T$ ,  $x = \text{time}$ ) with, in all cases,  $R^2 > 0.9$  (Fig. 3a, b and c). The time necessary for the decrease of  $22.5 \text{ }^\circ\text{C}$  ( $\Delta t - 22.5 \text{ }^\circ\text{C}$ ; 22.5 being 75% of the total decrease in temperature in the experiment) was calculated for each peloid by solving the equations obtained (Fig. 3a, b and c), and were ASP, 29.15 min; Araxá, 28.56 min; Paraty, 28.27 min; thus: ASP > Araxá > Paraty. The differences between maximum and minimum times were a few seconds.

### Mineralogical and elemental concentration in peloids

The concentrations of major elements, measured by WDXRF, and trace elements determined by INAA and GF AAS are given in Table 3 and Table 4, respectively. The large variability observed in mineralogical and chemical medicinal mud constitution is certainly related to its geological origin; typically, the number of major elements varies in wide ranges [88,89]. Geochemically, the values presented by the Th/U ratios in ASP, Paraty and Araxá peloids (3.2, 7.8 and 3.8, respectively). Table 6 shows concentration variations of literature reported values.

### Radiological characterization

The activity concentrations obtained for  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ,  $^{228}\text{Th}$ ,  $^{210}\text{Pb}$  and  $^{40}\text{K}$  as well as worldwide soil activity concentrations [90] are summarized in Table 6. The ASP peloid presented the highest activity concentrations for all radionuclides, except for  $^{210}\text{Pb}$  for which the higher value was found in the Paraty peloid. The absorbed dose rate (D) is related to the risk due to the amount of radiation deposited in the body per unit of time resulting from terrestrial gamma emitters. The absorbed

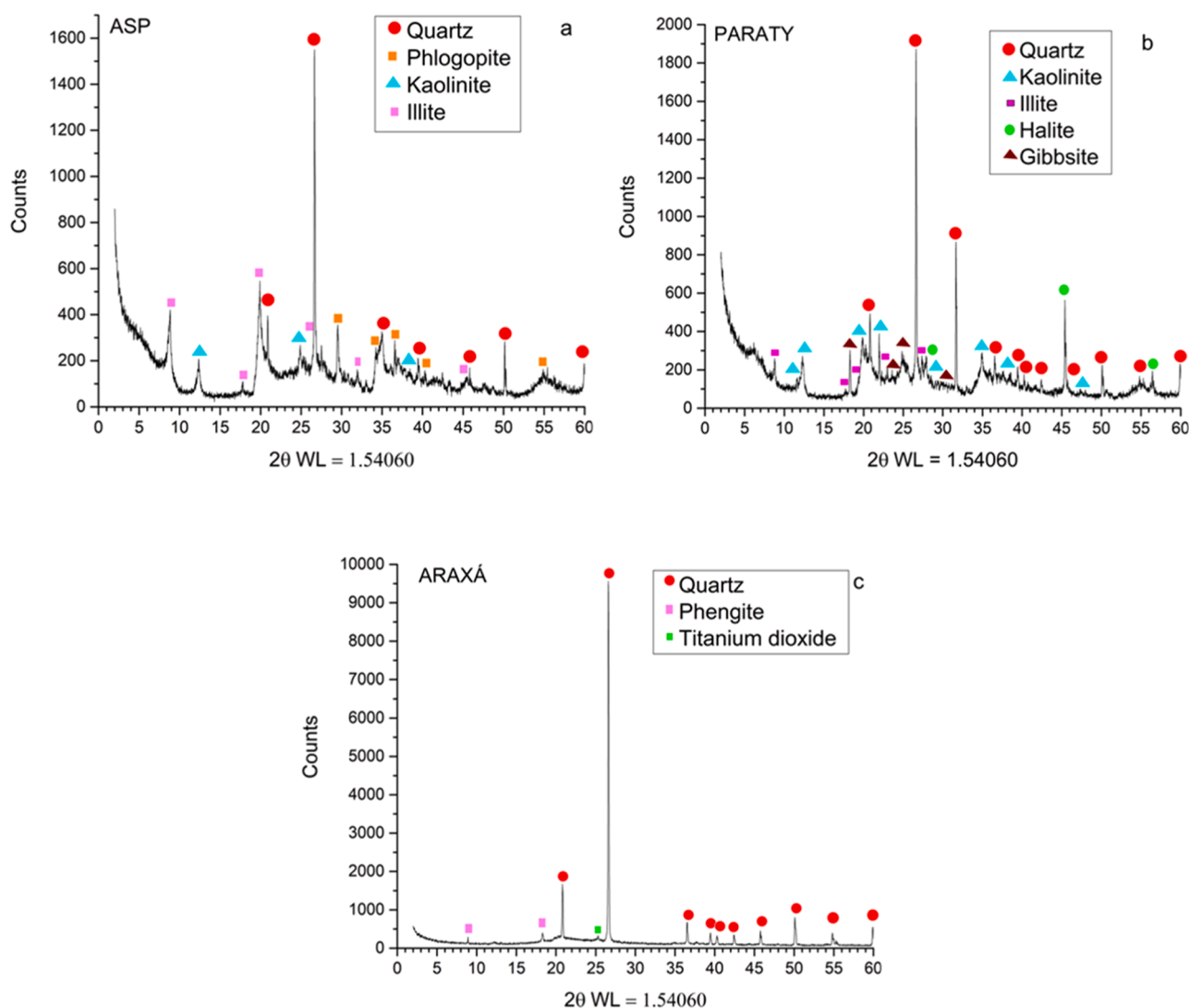


Fig. 2. Minerals composition of ASP (a), Paraty (b) and Araxá (c) peloids obtained by DRX.

dose rate ( $D$ ) ( $\text{nGy h}^{-1}$ ) can be derived from the measured activity concentrations and from the following conversion factors, according to UNSCEAR [90] and Al-Zahrani [91], shown in Eq (2), where  $A_{Ra}$ ,  $A_{Th}$ , and  $A_K$  are the defining activities of  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$ , and  $^{40}\text{K}$  in  $\text{Bq kg}^{-1}$  and their corresponding dose conversion factors:

$$D = 0,462A_{Ra} + 0,604A_{Th} + 0,0417A_K \quad (2)$$

The absorbed dose rate results for ASP, Paraty and Araxá peloids were 101, 48 and 49  $\text{nGy h}^{-1}$ , respectively. The annual effective dose ( $D_{\text{eff}}$ ) ( $\text{mSv y}^{-1}$ ) was calculated to estimate a dose received by a patient who spends 80% of the total hours of a year applying this peloid to his body (Eq. (3))

$$D_{\text{eff}} = D \times 8760 \times 0.8 \times 0.7 \times 10^{-6} \quad (3)$$

The equation used was according to UNSCEAR [90] and Al-Zahrani [91], where  $D$  is the absorbed dose rate ( $\text{nGy h}^{-1}$ ), 0.7 is the dose conversion factor  $\text{Sv Gy}^{-1}$  and 8760 are the total hours in a year. The results of the  $D_{\text{eff}}$  showed that the ASP peloid (worst case), in this very conservative scenario would deliver an annual effective dose of 0.5 ( $\text{mSv y}^{-1}$ ).

## Discussion

### Comparison between the peloids

The pH values may influence the availability of the chemical elements adsorbed in the mineral grains that compose the mud and a small change in this parameter may affect ionic exchange properties during skin contact [28,92], and the values may vary depending on the peloid composition. For peloids, no pH range is recommended by any regulation but a range of 4 to 8 is advisable in order to avoid skin irritations [35] and the pH values measured are within this range.

It is believed that an important aspect within the general characterization of a peloid is the determination of its Eh. This characteristic is believed to be related to its antioxidant action [93], in addition to being a parameter of great importance to determine whether or not a peloid is matured or ready for use [19]. According to the Cuban Norm for Specifying Peloids [94], one of the parameters to be observed for a peloid to be considered matured is that its Eh is below -100 mV. The Cuban norm establishes the specifications for peloids intended for human use, meeting the requirements of the country's health and mining authorities and the Eh values determined in this work will not cause health problems.

The oxidant Eh value shown by the ASP peloid can be justified by the little or no maturation time that this peloid passes before topical use.

**Table 1**

Physicalchemical parameters obtained for ASP, Paraty and Araxá peloids, peloids and pharmaceutical clays studied by some authors.

	This study			Peloids								Pharmaceutical clays				
	ASP	Paraty	Araxá	[30]	[31]	[29]	[19]	[28]	[35]	[40]	[36]	[38]	[116]	[117]	[92]	[63]
pH	7.31 ± 0.09	7.31 ± 0.04	8.5 ± 0.1	7.94 to 9.90	7.6	–	7.35 to 7.61	6.9	7.93 to 8.52	6.79 to 7.61	6.23	7.46 to 8.04	8.7–10.2	8.5 to 10.5	7.36 to 9.48	3.6 to 7.8
Eh (mV)	169.6	–299	–350	–340 to 160	–	–	–337 to –220	–	–	–413 to –320	–	–125 to 46	–	–	–	–
Moisture (%)	4.7 ± 0.3	14.3 ± 0.6	4.1 ± 0.1	–	–	–	–	12 to 73	44 to 50	–	–	–	–	–	–	0.97 to 5.01
Organic matter (%)	7.3 ± 0.2	13.7 ± 0.4	23.1 ± 0.3	–	8.2	–	–	3.6 to 20	–	2.7 to 5.3	–	–	–	–	–	2.07 to 8.02
Loss on ignition (%)	2.71 ± 0.06	3.1 ± 0.8	0.8 ± 0.03	–	26	–	–	0.4 to 3.0	–	–	–	–	–	–	–	0.31 to 8.07
SSA (m <sup>2</sup> g <sup>–1</sup> )	123 ± 16	71 ± 8	123 ± 16	38.5 to 66.46	7.5	6 to 97	–	–	–	–	–	–	–	–	196 to 710	–
Swelling (before agitation) (ml g <sup>–1</sup> )	CPS	NOT	TOTAL	–	1.64	–	–	NOT	–	–	–	–	12 to 27	8 to 35	4 to 36	–
Swelling (after agitation) (ml g <sup>–1</sup> )	CPS	NOT	TOTAL	–	–	–	–	25 of SPC	–	–	–	–	–	–	–	–

CPS = colloidal particle suspension

**Table 2**

Cooling of peloids over 30 min. Starting temperature (T0), 60 °C.

Time (min)	T Reading (°C)		
	ASP	Paraty	Araxá
0	60	60	60
2	55.8	55.5	56
4	51.8	51.8	52.1
6	49.1	48.9	49.2
8	46.7	46.5	46.7
10	44.9	44.7	44.8
12	43.4	43.2	43.4
14	42.2	41.9	42.1
16	41.2	41	41.1
18	40.4	40.2	40.3
20	39.7	39.6	39.7
22	39.3	39.1	39.1
24	38.8	38.7	38.7
26	38.5	38.3	38.4
28	38.2	37.9	38.1
30	38	37.7	37.9

The reductant values observed in the Paraty and Araxá peloids are probably justified by the maturation time, since they are directly obtained from their environment of natural formation (Table 1).

According to Veniale et al. [95] the release–exchange of mobile elements between the skin sweat and peloid depends on the amount of swelling clay minerals. Paraty peloids do not present any observed swelling probably due to the ionic strength provided by the sea water in which it was naturally matured, different from what occur with the ASP and Araxá peloids, which showed high swelling.

According to Glavaš et al. [35], generally, the moisture values in peloids can reach up to 80% and high moisture values cause increases in the values of specific heat capacity and thermal conductivity, however, also cause decreases in viscosity values. The moisture values measured showed that ASP and Araxá are similar, while Paraty ones is almost three times higher.

The study of the organic matter content (OM) in medicinal muds is important since it may be related to its therapeutic properties and the

effectiveness of treatment involving peloids may be closely related to this parameter due the metabolic activity of microorganisms [62, 96–100], in addition to being inversely related to abrasiveness [2]. A peloid consists of a geological part composed of a mixture of clay, water and an organic part that provides biological metabolic activity [29]. Different compositions of the OM that composes the peloid contribute to the way in which chemical elements are linked to it, such as humic acids, lipids, carbohydrates, proteins and hydrogen sulfide which usually is produced by prokaryotic breakdown of organic matters [101]. The smaller value of ASP OM in comparison to Paraty and Araxá peloids must be related to the maturation time and the collection site of each one of them.

Loss on ignition at 1000 °C was mainly related to carbonate content in the sample and certain volatile non-carbon components such as gypsum, sulfide minerals, and dehydration of metallic oxyhydroxides [102]. The LOI results are in agreement with the Al<sub>2</sub>O<sub>3</sub>, CaO, Cl<sup>–</sup> and Fe<sub>2</sub>O<sub>3</sub> results obtained in FRX analysis, in which LOI values in ASP and Araxá are probably due to the loss of coordinate hydroxyls and for Paraty the loss of coordinate hydroxyls and chloride.

The specific surface area (SSA) may be directly related to the content of OM in the peloid, since clay guarantees conditions for the absorption of organic compounds [103] and cation exchange capacity (CEC) [104, 105]. The literature reports that a high SSA value is one of the properties for beneficial effects in therapeutic skin treatments [105–107] and, according to Carretero and Pozo [105], it favors the anti-inflammatory and anesthetic effect in topical application. ASP and Araxá peloid showed the same values of SSA while Paraty peloid is smaller, maybe because of sea water maturation.

The cooling rate values obtained in this study show little difference between the peloids and indicates that they are appropriated to use in therapeutic treatment according to providing their low rate of heat loss [29,71,108].

Elemental characterization shows great variation in the concentration of many elements. This was expected, as each peloid has different types of maturation and are from different places. The concentrations of trace elements vary across a wide range. Concentration of Br and Na in the Paraty peloid was higher than the other ones, it is justified because of

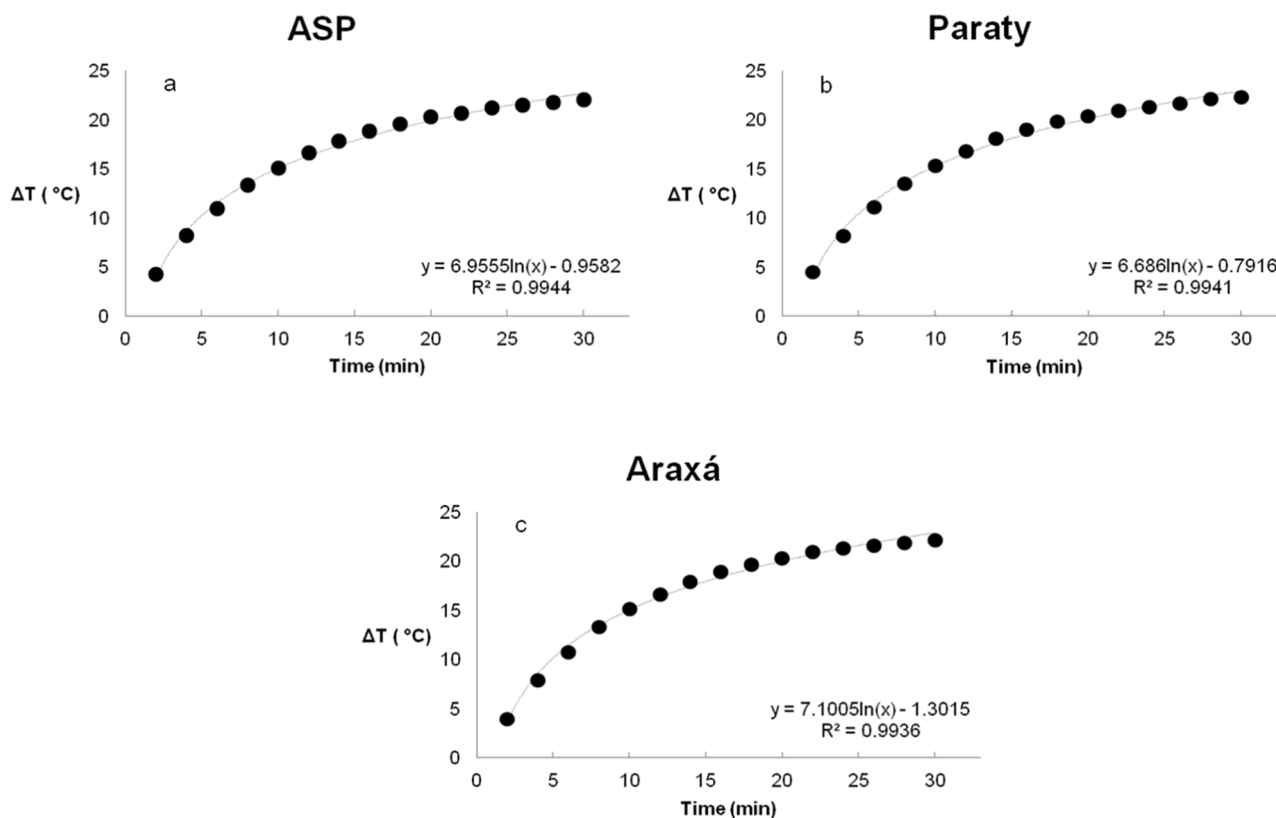


Fig. 3. Variation of temperature,  $\Delta T$ , with time ( $\Delta T = T_0 - T_n$ ;  $T_0 = 60$  °C) and ( $x = \text{time}$ ;  $y = \Delta T$ ).

Table 3

Elemental concentrations, in percentage, for ASP, Paraty and Araxá peloids obtained by FRX.

Elements	ASP	Paraty	Araxá
Al <sub>2</sub> O <sub>3</sub>	18 ± 1	11 ± 1	10 ± 1
As <sub>2</sub> O <sub>3</sub>	<0.006	<0.006	<0.006
Br	<0.035	<0.035	<0.035
CaO	4.4 ± 0.5	0.86 ± 0.09	0.24 ± 0.02
Cl	0.19 ± 0.02	12.1 ± 0.9	<0.01
Co <sub>2</sub> O <sub>3</sub>	<0.020	<0.020	<0.020
CuO	0.017 ± 0.002	<0.012	<0.012
Fe <sub>2</sub> O <sub>3</sub>	10.2 ± 0.9	9.5 ± 0.9	1.8 ± 0.2
MgO	3.4 ± 0.4	1.9 ± 0.2	0.108 ± 0.008
MnO	0.19 ± 0.02	0.23 ± 0.03	0.022 ± 0.002
Na <sub>2</sub> O	0.23 ± 0.03	18.1 ± 0.9	2.5 ± 0.2
Nb <sub>2</sub> O <sub>3</sub>	<0.003	<0.003	<0.003
NiO	0.017 ± 0.002	0.014 ± 0.002	0.026 ± 0.002
K <sub>2</sub> O	5.1 ± 0.6	2.2 ± 0.3	1 ± 0.2
P <sub>2</sub> O <sub>5</sub>	0.61 ± 0.06	0.25 ± 0.03	0.45 ± 0.05
PbO	<0.003	<0.003	<0.003
Rb <sub>2</sub> O <sub>3</sub>	0.019 ± 0.002	0.024 ± 0.003	<0.010
SO <sub>3</sub>	0.58 ± 0.06	1.21 ± 0.09	1.5 ± 0.2
SiO <sub>2</sub>	46 ± 1	26 ± 1	57 ± 1
SrO	0.015 ± 0.002	0.012 ± 0.002	<0.010
TiO <sub>2</sub>	1.02 ± 0.09	1.12 ± 0.09	1.8 ± 0.2
Y <sub>2</sub> O <sub>3</sub>	<0.003	<0.003	0.002 ± 0.001
ZnO	0.02 ± 0.002	0.017 ± 0.002	<0.011
ZrO <sub>2</sub>	0.006 ± 0.001	0.006 ± 0.001	0.015 ± 0.002

its marine origin and its anthropic activity may justify the higher concentration of As and Cd, since this peloid is found in a public place.

Among the multiple characteristics presented by the peloids it is of fundamental importance to determine the levels of radioactive elements due to natural radionuclides that are normally associated with the clays [109–111]. Natural radionuclides, when found in high activity concentrations, may cause many health problems after long-term exposure,

e.g. chronic lung diseases, leukemia and bone, kidney and pancreatic cancers [112].

The ASP peloid presented activity concentrations of <sup>226</sup>Ra, <sup>228</sup>Ra, <sup>228</sup>Th and <sup>40</sup>K higher than the other ones, while Paraty showed higher ones only for <sup>210</sup>Pb. One of the concerns regarding the use of mud and clays in general, in pelotherapy, is the radiation dose that can be received by patients because the former contains natural radionuclides. For the analyzed samples the activity concentrations found are within the background range for soils and sediments [113] indicating that no radiological risk are associated with them.

#### Comparison with literature peloid values

Considering the mineralogy results, the presence of halite in Paraty peloid is justified because this peloid was collected directly from the beach it is formed. The same was also observed for the Perufbe black mud (PBM) characterized by Silva et al. [28] and other peloids produced after seawater interaction [16,114,115]. The amount of kaolinite in Paraty and ASP composition may also contribute to the therapeutic activity since this clay mineral is generally found in medicinal peloids such as PBM and peloids characterized by Fernández-González et al. [17], Pozo et al. [29] and Jalil et al. [33].

The pH values found in this study were within the values measured in different clays used for pharmaceutical purposes in Patagonia [116], Egypt [117], Iran [92], and Brazil [28] (3.6–10.2) and peloids used in spas in Turkey [30], Brazil [28], Slovenia [35], Cuba [40] and Montenegro [36] (6.23–9.9). As observed in Table 1, generally, the pH values are in a wide range, varying from 4 – 10, certainly being applied to different types of diseases.

Considering the reduction potential, the Paraty peloid was within the range of the values reported by Karakaya [30] (-340 mV to 160 mV) and Fedorov [38] (-125 mV to 46 mV) and the values of Araxá were lower. Paraty and Araxá peloids Eh values are more reductant than PBM values reported by Gouvêa [108] (-200 mV) and Araxá's values are more

**Table 4**Elemental concentrations, in mg kg<sup>-1</sup>, for ASP, Paraty and Araxá peloids obtained by INAA and GF AAS (\*) and parameters EP, USP, NHPD, SQG TEC, SQG PEC, ISQG, and PEL.

Elements	ASP	Paraty	Araxá	EP, USP	NHPD	SQG TEC	SQG PEC	ISQG	PEL
As	4.9 ± 0.1	11.3 ± 0.2	1.5 ± 0.1	<8	–	9.79	33	7.24	41.6
Ba	672 ± 30	307 ± 14	170 ± 9	1300	–	–	–	–	–
Br	9.9 ± 0.1	244 ± 1	6.2 ± 0.1	–	–	–	–	–	–
Ca (%)	2.54 ± 0.06	0.84 ± 0.02	0.54 ± 0.02	–	–	–	–	–	–
Cd*	0.1161 ± 0.0007	0.31 ± 0.03	0.349 ± 0.004	3	–	0.99	4.98	0.7	4.2
Ce	88 ± 2	156 ± 4	82 ± 2	–	–	–	–	–	–
Co	20.6 ± 0.1	12.8 ± 0.1	2.55 ± 0.03	–	5	–	–	–	–
Cr	107 ± 1	86.8 ± 0.9	116 ± 1	1100	–	44.3	111	52.3	160
Cs	13.8 ± 0.1	6.2 ± 0.3	3.23 ± 0.04	–	–	–	–	–	–
Cu*	46.6 ± 0.6	10 ± 0.2	15 ± 2	–	–	–	–	–	–
Eu	0.99 ± 0.01	1.38 ± 0.01	0.694 ± 0.004	–	–	–	–	–	–
Fe (%)	5.31 ± 0.03	4.78 ± 0.04	0.718 ± 0.004	–	–	–	–	–	–
Hf	3.08 ± 0.02	3.04 ± 0.02	12.01 ± 0.08	–	–	–	–	–	–
K (%)	2.7 ± 0.3	1.16 ± 0.07	0.33 ± 0.04	–	–	–	–	–	–
La	49.9 ± 0.8	92.3 ± 1.2	39.1 ± 0.6	–	–	–	–	–	–
Lu	0.29 ± 0.01	0.28 ± 0.01	0.32 ± 0.01	–	–	–	–	–	–
Mg (%)	<LD	1.3 ± 0.3	0.21 ± 0.03	–	–	–	–	–	–
Mn	3350 ± 85	1159 ± 20	77 ± 2	–	–	–	–	–	–
Na (%)	0.241 ± 0.004	2.001 ± 0.03	1.101 ± 0.02	–	–	–	–	–	–
Nd	37 ± 2	62 ± 1	28 ± 1	–	–	–	–	–	–
Ni*	96 ± 1	44.3 ± 0.2	108.9 ± 0.5	–	–	–	–	–	–
Pb*	21 ± 1	74 ± 0.3	10.7 ± 0.9	<50	–	35.8	128	30.2	112
Rb	216 ± 3	86 ± 3	15 ± 0.3	–	–	–	–	–	–
Sb	0.64 ± 0.02	0.23 ± 0.02	0.51 ± 0.02	–	5	–	–	–	–
Sc	10.99 ± 0.04	8.83 ± 0.03	4.47 ± 0.02	–	–	–	–	–	–
Se	1.26 ± 0.1	1.07 ± 0.06	1.5 ± 0.05	–	–	–	–	–	–
Sm	6.8 ± 0.2	8.75 ± 0.02	4.6 ± 0.1	–	–	–	–	–	–
Ta	1.55 ± 0.09	1.11 ± 0.04	2.4 ± 0.1	–	–	–	–	–	–
Tb	0.6 ± 0.1	1.31 ± 0.02	0.67 ± 0.01	–	–	–	–	–	–
Th	17.3 ± 0.7	21 ± 1	9.96 ± 0.4	–	–	–	–	–	–
Ti	0.47 ± 0.09	0.42 ± 0.04	0.45 ± 0.09	–	–	–	–	–	–
U	5.5 ± 0.1	2.7 ± 0.1	2.6 ± 0.1	–	–	–	–	–	–
V	72 ± 9	108 ± 5	40 ± 4	–	–	–	–	–	–
Yb	2.3 ± 0.1	2.4 ± 0.1	2.3 ± 0.1	–	–	–	–	–	–
Zn	182 ± 4	103 ± 2	43 ± 1	–	–	121	459	124	271
Zr	203 ± 7	153 ± 8	432 ± 8	–	–	–	–	–	–

reductant than peloids from Cuba reported by Muñoz [19] (from -337 mV to -220 mV) and Rizo [40] (-413 mV to -320 mV). Although it is believed that a negative redox potential is necessary for the healing properties of peloids, the values presented in Table 1.

The results obtained in the swelling tests showed that the Paraty peloid is similar to PBM studied by Silva [28], it can be justified because both are matured with sea water, however, ASP and Araxá peloids showed values different than reported to Iborra et al. [116] and Modabberi et al. [92] with colloidal particle suspension for ASP and total swelling for Araxá one.

The moisture content is generally related to the number of hydration sites [118] and this value is highly dependent of the peloid origin varying from 0.97% (kaolinite) [63] to 73% (quartz and feldspar) [28]. The values found in the peloids presented in this work are closer to the lower limit of this range and the Paraty peloid should be the one with the highest number of hydration sites.

It is known that clays used for pharmaceutical purposes are autoclaved in order to sterilize them, thus losing part of the OM, therefore, it is natural that pharmaceutical clays have a lower OM than peloids, but this is not a rule, as shown by the peloids from ASP and Paraty when compared with the results presented by Silva [63] which showed similar values (2.07–8.02%). However, the OM amount in the Araxá peloid is slightly higher than PBM reported by Silva [28] (3.5–20%), but all values from this study are higher than the peloids from Cuba studied by Rizo et al. [40] (2.7–5.3%).

When comparing the SSA, the ASP and Araxá peloids presented value higher than the peloids reported by Karakaya et al. [119] (38.5–66.46 m<sup>2</sup> g<sup>-1</sup>) and smaller than pharmaceutical clays reported by Modabberi [92] (196–710 m<sup>2</sup> g<sup>-1</sup>). The peloids studied by these authors contain large amounts of illite and kaolinite that may contribute to the reduction

of SSA values, and this is noticeable in peloids from Paraty that showed a smaller SSA than ASP and Araxá peloids and the results are within the values reported by Pozo [29] (6–97 m<sup>2</sup> g<sup>-1</sup>).

To be used as therapeutic and cosmetic products, clays, in general, have to be completely characterized as for the impurity content, such as trace elements [28]. As there is no established official regulation about the chemical composition of peloids, both in raw material and matured form, to be used in pelotherapy, the obtained results were compared to consensus-based sediment quality guidelines (SQGs) to provide a reliable basis for assessing sediment quality conditions in aquatic ecosystems as reported by MacDonald [120]. These SQGs are used in numerous applications, including the design of monitoring programs, the interpretation of historical data, the assessment of the need for detailing sediment quality, the conduct of corrective investigations, ecological risk assessments and the development of remediation objectives for sediment quality. SQG values also used were, the threshold effect concentration (TEC), below which adverse effects should not occur, and the probable effect concentration (PEC), above which adverse effects can occur frequently. The levels of elements found were also compared with values from European Pharmacopeia (EP) and United States Pharmacopeia (USP), which recommends values for some elements in pharmaceutical clays [121,122]; Canadian Natural and Non-prescription Health Products (NHPD) which recommend values for topical products [123]; and ISQG and PEL values, which correspond to the provisional standard of quality and level of probable effect for marine sediments according to the Canadian Council of Ministers of the Environment [124].

The peloid from Araxá presented values of total Cr higher than those compared to TEC, PEC and the ISQG index, however, some clays and peloids studied by other authors (Table 5) presented similar values. The

**Table 5**  
Concentration variations, in mg kg<sup>-1</sup>, of literature reported values.

Elements	[108]		[63]		[63]		[89]		[88]		[135]		[37]	
	MAX	MIN	MAX	MIN	MAX	MIN	MAX	MIN	MAX	MIN	MAX	MIN	MAX	MIN
As	35.2	4.8	2.4	0.6	21	2.5	15.6	1.8	39	2.5	5.5	1.9	14.1	9.3
Ba	516	166	1894	160	736	95	359	25	799	147.7	831	254	315	222
Br	148.8	32.7	6	1.28	5.4	0.5	–	–	554.7	1.9	–	–	–	–
Cd	0.49	0.003	0.053	0.006	0.105	0.016	0.2	<0.1	0.5	0.1	0.4	0.1	–	–
Ce	73	32	165	26	161	20	–	–	–	–	98.1	25.8	57.3	45.2
Co	10.7	3.81	48	1.7	17.4	2.5	19.2	5	16.8	4	13	8	20.3	8.7
Cr	69	30	144	18	92	4.4	101	16	68.2	14.6	–	–	220	98
Cs	5.5	1.8	3.7	0.78	11	4.2	–	–	–	–	14	0.6	–	–
Eu	1.64	0.51	5.7	0.09	2.54	0.58	–	–	–	–	1.89	0.49	–	–
Hf	7.9	2.7	15	6	14.9	2.1	–	–	–	–	15.3	3.7	3.8	2.1
La	34.7	16.5	153	4.64	68	12.4	–	–	43.1	13.7	48.3	13	28	21
Lu	0.36	0.1	1.17	0.08	0.91	0.2	–	–	–	–	0.55	0.1	–	–
Nd	40.9	12.4	120	3	77	14	–	–	–	–	50.5	11.2	–	–
Pb	30.8	12.4	36	6.7	121	16	13.4	8.1	37.5	8.5	36.3	15.8	15	11
Rb	86	40	135	7	179	44	–	–	–	–	34.7	9.4	107	62
Sb	0.51	0.13	0.4	0.09	2	0.4	0.5	0.1	4.3	0.1	0.4	0.1	–	–
Sc	12.35	4.9	28.6	6.4	13.8	1.6	–	–	14	3	32	13	–	–
Sm	8	2.6	33.8	0.53	12.4	2.4	–	–	–	–	10	3.5	–	–
Ta	0.99	0.1	–	–	–	–	–	–	–	–	1.2	0.3	–	–
Tb	0.6	0	3.1	0.11	2.1	0.25	–	–	–	–	1.17	0.28	–	–
Th	10.3	5.2	11.4	3.4	21	4.3	–	–	12.8	4.8	22.6	7.7	8.8	6.8
U	4.4	2.9	3.1	0.8	5.2	2.7	–	–	–	–	4.8	1.4	–	–
Yb	1.8	0.6	6.4	0.3	5.1	1	–	–	–	–	3.66	0.72	–	–
Zn	129	36	546	37	314	67	–	–	160.4	33.1	89	13	84	62

\* Pharmaceutical clay.

finding of toxic effects following dermal exposure suggests that Cr is absorbed through the skin, although information on the absorbed percent is limited and penetration of Cr through skin has been studied in animals and humans, previously analyzing biopsies from skin or evaluating the “disappearance measurement” of isotopes of Cr in salt formulations [125–127]. Also, in Table 4 it is possible to note that elements like As, Co, Cr, Pb and Zn are higher in ASP and Paraty peloids compared to the indices EPUSP, NHPD, SQG, PEC and ISQG, but few quantitative studies on the absorption of these potentially toxic elements in humans, after dermal exposure, were found. Arsenic measured in Rhesus monkeys [128] indicates less than 7% of absorption, after 24 h. Skin exposure to inorganic Pb has shown that the absorption was only 0.06% during 1 month of exposure to soluble inorganic salt of this metal [129]. However, some exposure may occur from cosmetics [130]. Although occurring, the skin absorption of Co and Zn can, also, be considered negligible [126,131]. Even with the values of the elements described above, they are in agreement with those reported in the literature.

Geochemically, the values presented by the Th/U ratios in ASP, Paraty and Araxá peloids (3.2, 7.8 and 3.8, respectively), are close to the theoretical value of 3.5–4.0 [132]. The values of the Th/U ratios were related to the redox environment in the clay deposit. Under reduction conditions U mainly exists as U<sup>4+</sup>, much less mobile than its oxidized form U<sup>6+</sup> [133], therefore, the lower value of the Th/U ratio may be due to the higher oxidizing potential of ASP. In comparison with the Upper Continental Crust (UCC), the ASP and Paraty peloids are enriched with the heavy rare earth elements (HREE), this is also noted for peloids from Araxá, except for the elements Sm and Eu (Eu was noted as slightly depleted). In relation to light rare earth elements (LREE), enrichment was noted only for the element Tb in the Paraty peloid.

For the three peloids Ni is enriched when compared with the UCC. Peloids from ASP presented enrichment in Al, Br, Cs, Cu, Fe, Mn, P, Rb, Sb, Se, Th, Ti, U, and Zn and depletion in Hf and Na while Araxá is enriched in Br, Cd, Hf, Sb, Se, Ti, Zr and depleted in Al, Ba, Ca, Cu, Fe, K, Mn, Na, Pb, Rb, Sc and Zn. This discrepancy in the elementary concentrations shows the geochemical difference among the peloids. In general, these values are in good agreement with the literature for most elements.

Considering the radioactive elements, the values obtained in this work are slightly different (higher, in general) than worldwide soil

activity concentrations according to UNSCEAR [113] and compared with data (Table 6) the concentrations of the radionuclides are within the range and it is important to note that the data values vary widely. The values of <sup>228</sup>Ra and <sup>228</sup>Th in UNSCEAR [113] is considering in balance with the <sup>232</sup>Th.

With the calculated absorbed dose rate, it is possible to note that the ASP value is almost two times higher than the world average for soil (58 nGy h<sup>-1</sup>) [113]. Nevertheless, it is also reported that globally the absorbed dose can be found up to 10 times the average value [113].

Considering that the time of application of peloids to patients is around 20 min a day, if this patient undergoes treatment every day for a year, the estimated dose would be 0.009 mSv y<sup>-1</sup> (ASP), this value can be considered negligible, taking into account the value of 1 mSv per year, recommended for activities that can provide an excess dose above background, the reported as safe by UNSCEAR [113]. The annual effective dose of all radiation sources, including medical, in the environment is estimated at about 3.3 mSv [134].

## Conclusions

This study presented the characterization of different peloids from different locations in Brazil, i.e., town of Águas de São Pedro, in the State of São Paulo, town of Araxá, in the State of Minas Gerais, and town of Paraty, in the State of Rio de Janeiro. Comparisons were made among then and with other well-known peloids registered in literature.

Considering the physical-chemical characteristics, the pH, MO and SSA are in agreement with values found for peloids around the world, swelling power varied from no swelling, for the Paraty peloid, to high swelling, for the Araxá peloid. An important characteristic generally considered for peloids classification is the Eh. Among the analyzed samples, the peloids from ASP showed oxidant character while the other two presented reductant values. The reductant character is normally associated with the organic matter content and the maturation time, nevertheless, globally, both oxidant and reductant peloids are used for healing purpose.

The elemental concentrations found indicated that possible toxic effects are unexpected from the topical application of the three analyzed peloids. The determined elements presented a wild range of concentrations, as expected, reflecting the geochemical differences in their

**Table 6**

Activity concentrations, in Bq/kg, for the ASP, Paraty and Araxá peloids and literature reported values obtained by gamma spectrometry.

	ASP	Paraty	Araxá	[134]	[27]	[136]*	[28]	[119]	UNSCEAR [113]
<sup>226</sup> Ra	51 ± 8	20 ± 4	31 ± 5	–	27–54	58–168	11–23.3	–	32
<sup>228</sup> Ra	68 ± 32	40 ± 18	50 ± 24	259	64–92	–	17.5–44.2	9.94–401.64	45
<sup>210</sup> Pb	39 ± 9	268 ± 6	154 ± 7	–	144–252	–	18–32	–	35**
<sup>228</sup> Th	72 ± 23	44 ± 15	40 ± 14	–	40–111	–	–	–	45
<sup>40</sup> K	883 ± 52	360 ± 23	114 ± 8	219	76–1146	211–996	353–542	64.82–1698.60	412

\* clay used in cosmetic.

\*\* UNSCEAR [90].

origins and mineralogical composition. Quartz, illite and kaolinite appears as the main phases in the ASP and Paraty peloids. In Araxá peloid, besides quartz, a small amount of phenguite, from the mica group, was found. In general, the elemental concentrations values are within the range reported in literature for most elements in peloids of different origins. Considering the radioactive content, the results showed that no radiological risk can be expected from their topical use.

This study concludes that the three peloids studied are good candidates to be used for topical application. Metals and potentially toxic elements present are in concentrations levels that are unlikely to cause risk to health, however, to reinforce this conclusion, a clinical study of these three peloids is suggested as well as studies on the production of artificial peloids may be necessary considering that the reserve of peloids spread around the world is a finite resource.

#### Ethical statement

All data are reported in references.

#### Authors' contributions

Jefferson Koyaishi Torrecilha: The corresponding author. Prepared all samples and experimental reagents for analysis and executed all experimental process (except X-ray fluorescence and X-ray diffraction), discussed and concluded the results, wrote the paper.

Ana Paula Torres Mendes: Supported with Neutron activation analysis

Carolina Yume Sawamura Theophilo: Supported with Graphite furnace atomic absorption spectrometry

Horacio Marconi da Silva Matias Dantas Linhares: supported with study of cooling kinetics

José Henrique de Paula: supported with Neutron activation analysis

Marcos Antonio Scapin: made the X-ray fluorescence (XRF) analysis.

Rafael Henrique Lazzari Garcia: made the X-ray diffraction (XRD) analysis.

Francisco Maraver: Assisted to corrections. Supported with tables, figures and references. Formated the paper.

Paulo Sergio Cardoso da Silva: Coordinated the project.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgments

This study was funded by Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) (no grant number).

#### References

- [1] M.I. Carretero, Clays in pelotherapy. A review. Part I: mineralogy, chemistry, physical and physicochemical properties, *Appl. Clay Sci.* 189 (2020), 105526, <https://doi.org/10.1016/j.clay.2020.105526>.
- [2] C. Gomes, M.I. Carretero, M. Pozo, F. Maraver, P. Cantista, F. Armijo, J.L. Legido, F. Teixeira, M. Rautureau, R. Delgado, Peloids and pelotherapy: historical evolution, classification and glossary, *Appl. Clay Sci.* 75–76 (2013) 28–38, <https://doi.org/10.1016/j.clay.2013.02.008>.
- [3] M.V. Fernández-González, J.M. Martín-García, G. Delgado, J. Parraga, M. I. Carretero, R. Delgado, Physical properties of peloids prepared with medicinal mineral waters from Lanjarón Spa (Granada, Spain), *Appl. Clay Sci.* 135 (2017) 465–474, <https://doi.org/10.1016/j.clay.2016.10.034>.
- [4] A. Fioravanti, M. Karagülle, T. Bender, M.Z. Karagülle, Balneotherapy in osteoarthritis: facts, fiction and gaps in knowledge, *Eur. J. Integr. Med.* 9 (2017) 148–150, <https://doi.org/10.1016/j.eujim.2017.01.001>.
- [5] J. Drobnik, A. Stebel, Central European ethnomedical and official uses of peat, with special emphasis on the Tolpa peat preparation (TPP): an historical review, *J. Ethnopharmacol.* 246 (2020), 112248, <https://doi.org/10.1016/j.jep.2019.112248>.
- [6] M.L. Mourelle, C.P. Gómez, J.L. Legido, Microalgal peloids for cosmetic and wellness uses, *Mar. Drugs* 19 (2021), <https://doi.org/10.3390/md19120666>.
- [7] D. Vadjla, M. Bujak, R. Což-Rakovac, M. Roje, L. Čizmek, A. Horvatić, E. Svetličić, J. Diminić, S. Rakovac, D. Oros, J. Zucko, A. Starcevic, Bioprospecting for microorganisms in peloids—extreme environment known for its healing properties, *Front. Mar. Sci.* 9 (2022), <https://doi.org/10.3389/fmars.2022.822139>.
- [8] G. Nappi, M.M. Masciocchi, S. De Luca, P. Calcaterra, I.G. Carrubba, Le mufte termali solfuree nel trattamento de la psoriasi cutanea, *Med. Clin. Termale* 34 (1996) 7–18.
- [9] S. Bellometti, M. Poletto, C. Gregotti, P. Richelmi, F. Bertè, Mud bath therapy influences nitric oxide, myeloperoxidase and glutathione peroxidase serum levels in arthritic patients, *Int. J. Clin. Pharmacol. Res.* 20 (2000) 69–80.
- [10] S. Cara, G. Carcangiu, G. Padalino, M. Palomba, M. Tamanini, The bentonites in pelotherapy: thermal properties of clay pastes from Sardinia (Italy), *Appl. Clay Sci.* 16 (2000) 125–132, [https://doi.org/10.1016/S0169-1317\(99\)00050-2](https://doi.org/10.1016/S0169-1317(99)00050-2).
- [11] S. Cara, G. Carcangiu, G. Padalino, M. Palomba, M. Tamanini, The bentonites in pelotherapy: chemical, mineralogical and technological properties of materials from Sardinia deposits (Italy), *Appl. Clay Sci.* 16 (2000) 117–124, [https://doi.org/10.1016/S0169-1317\(99\)00049-6](https://doi.org/10.1016/S0169-1317(99)00049-6).
- [12] A.M. Beer, A. Grozeva, P. Sagorchev, J. Lukanov, Comparative study of the thermal properties of mud and peat solutions applied in clinical practice, *Biomed. Tech.* 48 (2003) 301–305.
- [13] G. Argenziano, M. Delfino, N. Russo, Mud and Bath Therapy in the acne cure, *Clin. Ter.* 155 (2004) 121–125.
- [14] S. Codish, M. Abu-Shakra, D. Flusser, M. Friger, S. Sukenik, Mud compress therapy for the hands of patients with rheumatoid arthritis, *Rheumatol. Int.* 25 (2005) 49–54, <https://doi.org/10.1007/s00296-003-0402-4>.
- [15] E. Gámiz, J.M. Martín-García, M.V. Fernández-González, G. Delgado, R. Delgado, Influence of water type and maturation time on the properties of kaolinite- saponite peloids, *Appl. Clay Sci.* 46 (2009) 117–123, <https://doi.org/10.1016/j.clay.2009.07.016>.
- [16] M.I. Carretero, M. Pozo, J.A. Martín-Rubí, E. Pozo, F. Maraver, Mobility of elements in interaction between artificial sweat and peloids used in Spanish spas, *Appl. Clay Sci.* 48 (2010) 506–515, <https://doi.org/10.1016/j.clay.2010.02.016>.
- [17] M.V. Fernández-González, J.M. Martín-García, G. Delgado, J. Parraga, R. Delgado, A study of the chemical, mineralogical and physicochemical properties of peloids prepared with two medicinal mineral waters from Lanjarón Spa (Granada, Spain), *Appl. Clay Sci.* 80–81 (2013) 107–116, <https://doi.org/10.1016/j.clay.2013.06.011>.
- [18] M.V. Fernández-González, M.I. Carretero, J.M. Martín-García, A. Molinero-García, R. Delgado, Peloids prepared with three mineral-medicinal waters from spas in Granada. Their suitability for use in pelotherapy, *Appl. Clay Sci.* 202 (2021), <https://doi.org/10.1016/j.clay.2020.105969>.
- [19] M.S. Muñoz, C.M. Rodríguez, A.G. Rudnikas, O.D. Rizo, M. Martínez-Santos, E. Ruiz-Romera, R.F. Castillo, A.P.G. Juan, N.V. Martínez-Villegas, D.B. Padilla, R. H. Díaz, P. González-Hernández, Physicochemical characterization, elemental speciation and hydrogeochemical modeling of river and peloid sediments used for therapeutic uses, *Appl. Clay Sci.* 104 (2015) 36–47, <https://doi.org/10.1016/j.clay.2014.11.029>.
- [20] C. Morer, C.F. Roques, A. Françon, R. Forestier, F. Maraver, The role of mineral elements and other chemical compounds used in balneology: data from double-blind randomized clinical trials, *Int. J. Biometeorol.* 61 (2017) 2159–2173, <https://doi.org/10.1007/s00484-017-1421-2>.
- [21] I. Gálvez, S. Torres-Piles, E. Ortega, Effect of mud-bath therapy on the innate/ inflammatory responses in elderly patients with osteoarthritis: a discussion of

- recent results and a pilot study on the role of the innate function of monocytes, *Int. J. Biometeorol.* 64 (2020) 927–935, <https://doi.org/10.1007/s00484-019-01748-4>.
- [22] F. Maraver, F. Armijo, M.A. Fernandez-Toran, O. Armijo, J.M. Ejeda, I. Vazquez, I. Corvillo, S. Torres-Piles, Peloids as thermotherapeutic agents, *Int. J. Environ. Res. Public Health* 18 (2021) 1–17, <https://doi.org/10.3390/ijerph18041965>.
- [23] X. Tian, Y. Zhang, H. Li, Y. Jiao, Q. Wang, Y. Zhang, N. Ma, W. Wang, Property of mud and its application in cosmetic and medical fields: a review, *Environ. Geochem. Health* 44 (2022) 4235–4251, <https://doi.org/10.1007/s10653-022-01228-6>.
- [24] A. López-Galindo, C. Viseras, P. Cerezo, Compositional, technical and safety specifications of clays to be used as pharmaceutical and cosmetic products, *Appl. Clay Sci.* 36 (2007) 51–63, <https://doi.org/10.1016/j.clay.2006.06.016>.
- [25] G. Gerencsér, E. Murányi, K. Szendi, C. Varga, Ecotoxicological studies on Hungarian peloids (medicinal muds), *Appl. Clay Sci.* 50 (2010) 47–50, <https://doi.org/10.1016/j.clay.2010.06.022>.
- [26] M. Mattioli, L. Giardini, C. Roselli, D. Desideri, Mineralogical characterization of commercial clays used in cosmetics and possible risk for health, *Appl. Clay Sci.* 119 (2016) 449–454, <https://doi.org/10.1016/j.clay.2015.10.023>.
- [27] P.S.C. Silva, S.M.B. Oliveira, L. Farias, D.I.T. Fávoro, B.P. Mazzilli, Chemical and radiological characterization of clay minerals used in pharmaceuticals and cosmetics, *Appl. Clay Sci.* 52 (2011) 145–149, <https://doi.org/10.1016/j.clay.2011.02.013>.
- [28] P.S.C. Silva, J.K. Torrecilha, P.F. de M. Gouvea, M.F. Máduar, S.M.B. Oliveira, M.A. Scapin, Chemical and radiological characterization of Perufe Black Mud, *Appl. Clay Sci.* 118 (2015) 221–230, <https://doi.org/10.1016/j.clay.2015.09.016>.
- [29] M. Pozo, M.I. Carretero, F. Maraver, E. Pozo, I. Gómez, F. Armijo, J.A.M. Rubí, Composition and physico-chemical properties of peloids used in Spanish spas: a comparative study, *Appl. Clay Sci.* 83–84 (2013) 270–279, <https://doi.org/10.1016/j.clay.2013.08.034>.
- [30] M.Ç. Karakaya, N. Karakaya, Ş. Sarçođlan, M. Koral, Some properties of thermal muds of some spas in Turkey, *Appl. Clay Sci.* 48 (2010) 531–537, <https://doi.org/10.1016/j.clay.2010.02.005>.
- [31] G. Mihelčić, G. Kniewald, G. Ivanišević, R. Čepelak, V. Mihelčić, N. Vdović, Physico-chemical characteristics of the peloid mud from Morinje Bay (eastern Adriatic coast, Croatia): suitability for use in balneotherapy, *Environ. Geochem. Health* 34 (2012) 191–198, <https://doi.org/10.1007/s10653-011-9434-y>.
- [32] A. Mateus, M.R. Carvalho, J.C. Nunes, J.M. Carvalho, Influence of wall-rock alteration and fluid mixing mechanisms in the chemistry of thermal fluids and mud-pool sediments at Caldeiras da Ribeira Grande (S. Miguel Island, Azores), *Environ. Earth Sci.* 73 (2014) 2809–2831, <https://doi.org/10.1007/s12665-014-3439-7>.
- [33] M.E.R. Jalil, M. Sanchez, M. Pozo, C.O. Soria, L. Vela, N. Gurnik, M. Baschini, Assessment of natural and enhanced peloids from the Copahue thermal system (Argentina): effects of the drying procedure on lidocaine adsorption, *Appl. Clay Sci.* 196 (2020), 105751, <https://doi.org/10.1016/j.clay.2020.105751>.
- [34] M. Centini, M.R. Tredici, N. Biondi, A. Buonocore, R. Maffei Facino, C. Anselmi, Thermal mud maturation: organic matter and biological activity, *Int. J. Cosmet. Sci.* 37 (2015) 339–347, <https://doi.org/10.1111/ics.12204>.
- [35] N. Glavaš, M.L. Mourelle, C.P. Gómez, J.L. Legido, N.R. Šmuc, M. Dolenc, N. Kovač, The mineralogical, geochemical, and thermophysical characterization of healing saline mud for use in pelotherapy, *Appl. Clay Sci.* 135 (2017) 119–128, <https://doi.org/10.1016/j.clay.2016.09.013>.
- [36] M. Bigovic, M. Roganovic, I. Milasevic, D. Djurovic, V. Slavic, M. Kosovic, M. Vlahovic, S. Perovic, A. Perovic, V. Kastarovic, Z. Potpara, M. Martinovic, S. Pantovic, Physico-chemical characterization of igalo bay peloid (Montenegro) and assessment of the pollution of potentially toxic elements in the sampling area, *Farmacia* 68 (2020) 560–571, <https://doi.org/10.31925/farmacia.2020.3.24>.
- [37] P. Lampropoulou, P. Petrounias, A. Rogkala, P.P. Giannakopoulou, E. Gianni, S. Mantzoukas, I. Lagogiannis, N. Koukouzas, S. Hatziantoniou, D. Papoulis, Microstructural and microbiological properties of peloids and clay materials from Ixouri (kefalonia island, greece) used in pelotherapy, *Appl. Sci.* 13 (2023), <https://doi.org/10.3390/app13095772> (Switzerland).
- [38] Y.A. Fedorov, D.N. Gar'kusha, R.G. Trubnik, N.A. Latushko, D.A. Ruban, Coastal peloids as geological heritage: evidence from the Taman Peninsula (Southwestern Russia), *Water* 11 (2019), <https://doi.org/10.3390/w11061119> (Switzerland).
- [39] M.D. Kamitsou, V. Sygouni, D.G. Kanellopoulou, K. Gardikis, P.G. Koutsoukos, Physicochemical characterization of sterilized muds for pharmaceuticals/cosmetics applications, *Environ. Geochem. Health* 40 (2017) 1449–1464, <https://doi.org/10.1007/s10653-017-0066-8>.
- [40] O.D. Rizo, M.S. Muñoz, P.G. Hernández, N.M. Villegas, C.M.M. Rodríguez, C. D. López, A.G. Rudnikas, R.H. Díaz, P.A. Gramatges, J. de J.B. Cossío, K.D. A. Rodríguez, J.R.F. Castillo, D.B. Padilla, Caracterización de peloides nacionales de uso terapéutico mediante técnicas nucleares y conexas, *Anal. Acad. Cienc. Cuba* 10 (2020) 1–16.
- [41] A.M. Beer, H.E. Junginger, J. Lukanov, P. Sagorchev, Evaluation of the permeation of peat substances through human skin *in vitro*, *Int. J. Pharm.* 253 (2003) 169–175, [https://doi.org/10.1016/S0378-5173\(02\)00706-8](https://doi.org/10.1016/S0378-5173(02)00706-8).
- [42] Z.M.N. Britschka, W.R. Teodoro, A.P.P. Velosa, S.B.V. de Mello, The efficacy of Brazilian black mud treatment in chronic experimental arthritis, *Rheumatol. Int.* 28 (2007) 39–45, <https://doi.org/10.1007/s00296-007-0371-0>.
- [43] F. Cozzi, M. Podeswiadek, G. Cardinale, F. Oliviero, L. Dani, P. Sfriso, L. Punzi, Mud-bath treatment in spondylitis association with inflammatory bowel disease - a pilot randomized clinical trial, *Joint Bone Spine* 74 (2007) 436–439.
- [44] F. Cozzi, B. Raffener, V. Beltrame, L. Ciprian, A. Coran, C. Botsios, E. Perissinotto, E. Grisan, R. Ramonda, F. Oliviero, R. Stramare, L. Punzi, Effects of mud-bath therapy in psoriatic arthritis patients treated with TNF inhibitors. Clinical evaluation and assessment of synovial inflammation by contrast-enhanced ultrasound (CEUS), *Joint Bone Spine* 82 (2015) 104–108, <https://doi.org/10.1016/j.jbspin.2014.11.002>.
- [45] D. Evcik, V. Kavuncu, A. Yeter, I. Yigit, The efficacy of balneotherapy and mud-pack therapy in patients with knee osteoarthritis, *Joint Bone Spine* 74 (2007) 60–65, <https://doi.org/10.1016/j.jbspin.2006.03.009>.
- [46] A. Fioravanti, L. Cantarini, M.R. Bacarelli, A. de Lalla, L. Ceccatelli, P. Bardi, Effects of spa therapy on serum leptin and adiponectin levels in patients with knee osteoarthritis, *Rheumatol. Int.* 31 (2011) 879–882, <https://doi.org/10.1007/s00296-010-1401-x>.
- [47] A. Fraioli, A. Serio, G. Mennuni, F. Ceccarelli, L. Petracchia, M. Fontana, M. Grassi, G. Valesini, A study on the efficacy of treatment with mud packs and baths with Sillene mineral water (Chianciano Spa Italy) in patients suffering from knee osteoarthritis, *Rheumatol. Int.* 31 (2011) 1333–1340, <https://doi.org/10.1007/s00296-010-1475-5>.
- [48] M.L. de Gois da Silva, A.C. Fortes, A. da Rocha Tomé, E.C. da Silva Sfilho, R.M. de Freitas, J.L. Soares-Sobrinho, C.M. da Silva Leite, M.F. de La Roca Soares, The effect of natural and organophilic polygorskite on skin wound healing in rats, *Braz. J. Pharm. Sci.* 49 (2013) 729–736, <https://doi.org/10.1590/S1984-82502013000400012>.
- [49] R. Forestier, C. Genty, B. Waller, A. Françon, H. Desfour, C. Rolland, C.F. Roques, J.L. Bosson, Crenobalneo therapy (spa therapy) in patients with knee and generalized osteoarthritis: a post-hoc subgroup analysis of a large multicentre randomized trial, *Phys. Rehab. Med.* 57 (2014) 213–227, <https://doi.org/10.1016/j.rehab.2014.03.001>.
- [50] N.A. Fortunati, A. Fioravanti, G. Seri, S. Cinelli, S. Tenti, May spa therapy be a valid opportunity to treat hand osteoarthritis? A review of clinical trials and mechanisms of action, *Int. J. Biometeorol.* 60 (2016) 1–8, <https://doi.org/10.1007/s00484-015-1030-x>.
- [51] F. Cozzi, P. Galozzi, L. Ciprian, E. Zanatta, P. Polito, F. Oliviero, M. Carrara, L. Punzi, Mud-bath treatment of seronegative spondyloarthritis: experience at the Euganean Thermal Area, *Int. J. Biometeorol.* 64 (2020) 937–941, <https://doi.org/10.1007/s00484-019-01761-7>.
- [52] C. Hou, L. Liang, X. Chu, W. Qin, Y. Li, Y. Zhao, The short-term efficacy of mud therapy for knee osteoarthritis: a meta-analysis, *Medicine* 99 (2020) e19761, <https://doi.org/10.1097/MD.00000000000019761> (Baltimore).
- [53] M. Király, E. Kóvári, K. Hodosi, P.V. Bálint, T. Bender, The effects of Tiszasüly and Kolop mud pack therapy on knee osteoarthritis: a double-blind, randomised, non-inferiority controlled study, *Int. J. Biometeorol.* 64 (2020) 943–950, <https://doi.org/10.1007/s00484-019-01764-4>.
- [54] D. D'Angelo, D. Coclite, A. Napoletano, A.J. Fauci, R. Latina, S. Gianola, G. Castellini, K. Salomone, F. Gambalunga, F. Sperati, L. Iacorossi, P. Iannone, The efficacy of balneotherapy, mud therapy and spa therapy in patients with osteoarthritis: an overview of reviews, *Int. J. Biometeorol.* 65 (2021) 1255–1271, <https://doi.org/10.1007/s00484-021-02102-3>.
- [55] F.D. Güneri, F.B.E. Forestier, R.J. Forestier, S.S. Karabulut, F. Karaarslan, M. Z. Karagülle, M. Karagülle, Peloidotherapy in rheumatoid arthritis: a pilot randomized clinical trial, *Int. J. Biometeorol.* 65 (2021) 2171–2180, <https://doi.org/10.1007/s00484-021-02181-2>.
- [56] S. Hamed, A.M. Almalaty, H.S. Alkhatib, The cutaneous effects of long-term use of Dead Sea mud on healthy skin: a 4-week study, *Int. J. Dermatol.* 60 (2021) 332–339, <https://doi.org/10.1111/ijd.15304>.
- [57] F. Karaarslan, H. Yilmaz, H.E. Akkurt, S. Gül, S. Kardeş, Effectiveness of peloid therapy in patients with chronic low back pain: a single-blind controlled study, *Int. J. Biometeorol.* 65 (2021) 1799–1809, <https://doi.org/10.1007/s00484-021-02137-6>.
- [58] G. Mennuni, M. Fontana, C. Perricone, S. Nocchi, R. Rosso, F. Ceccarelli, A. Fraioli, A meta-analysis of the effectiveness of mud-bath therapy on knee osteoarthritis, *Clin. Ter.* 172 (2021) 372–387, <https://doi.org/10.7417/CT.2021.2343>.
- [59] C. Munteanu, M. Rotariu, G. Dogaru, E.V. Ionescu, V. Ciobanu, G. Onose, Mud therapy and rehabilitation - scientific relevance in the last six years (2015 –2020) Systematic literature review and meta-analysis based on the PRISMA paradigm, *Balneo PRM Res. J.* 12 (2021) 1–15, <https://doi.org/10.12680/balneo.2021.411>.
- [60] V.R. Tuulik, M. Kumm, V. Tuulik, A. Veraksits, T. Päll, The therapeutic effect of Värksa mud and Värksa mineral water baths on the overuse pain and muscle tension syndromes in the working age population, *Environ. Geochem. Health* 44 (2022) 2101–2110, <https://doi.org/10.1007/s10653-021-00951-w>.
- [61] Y.A. Fedorov, D.A. Ruban, Geoheritage resource of small mud lakes in the semi-arid environments of the Russian South, *Resources* 8 (2019), <https://doi.org/10.3390/resources8020075>.
- [62] M.I. Carretero, Clays in pelotherapy. A review. Part II: organic compounds, microbiology and medical applications, *Appl. Clay Sci.* 189 (2020), 105531, <https://doi.org/10.1016/j.clay.2020.105531>.
- [63] P.S.C. Silva, M.F. Máduar, M.A. Scapin, R.H.L. Garcia, J.P.M. Martins, Radiological assessment of pharmaceutical clays, *J. Radioanal. Nucl. Chem.* 307 (2016) 2035–2046, <https://doi.org/10.1007/s10967-015-4404-y>.
- [64] M.G. Silva-Valenzuela, C.M. Matos, L.A. Shah, F.M.S. Carvalho, L.J. Sayeg, F. R. Valenzuela-Díaz, Engineering properties of kaolinitic clay with potencial use in drugs and cosmetics, *Int. J. Mod. Eng. Res.* 3 (2013) 163–165.
- [65] M. das G. Silva-Valenzuela, M.M. Chambi-Peralta, L.J. Sayeg, F.M. de S. Carvalho, S.H. Wang, F.R. Valenzuela-Díaz, Enrichment of clay from Vitoria da Conquista

- (Brazil) for applications in cosmetics, *Appl. Clay Sci.* 155 (2018) 111–119, <https://doi.org/10.1016/j.clay.2018.01.011>.
- [66] J. da S. Favero, J. Parisotto-Peterle, V. Weiss-Angeli, R.N. Brandalise, L.B. Gomes, C.P. Bergmann, V. dos Santos, Physical and chemical characterization and method for the decontamination of clays for application in cosmetics, *Appl. Clay Sci.* 124–125 (2016) 252–259, <https://doi.org/10.1016/j.clay.2016.02.022>.
- [67] J. da Silva Favero, V. dos Santos, V. Weiss-Angeli, L.B. Gomes, D.G. Veras, N. Dani, A.S. Mexias, C.P. Bergmann, Evaluation and characterization of Melo Bentonite clay for cosmetic applications, *Appl. Clay Sci.* 175 (2019) 40–46, <https://doi.org/10.1016/j.clay.2019.04.004>.
- [68] B.M.A.B. Buriti, J.S. Buriti, I.A. Silva, J.M. Cartaxo, G.A. Neves, H.C. Ferreira, Characterization of clays from the State of Paraíba, Brazil for aesthetic and medicinal use, *Cerâmica* 65 (2019) 78–84.
- [69] J. Daneluz, J. da S. Favero, V. dos Santos, V. Weiss-Angeli, L.B. Gomes, A. S. Mexias, C.P. Bergmann, The influence of different concentrations of a natural clay material as active principle in cosmetic formulations, *Mater. Res.* 23 (2020) 1–11, <https://doi.org/10.1590/1980-5373-MR-2019-0572>.
- [70] A.K.L.C. Lopes, S. do N. de Carvalho, J. di P. dos S. Sousa, L.M.A. Meirelles, Development and characterization of peel-off masks based on attapulgite Desarrollo, *Res. Soc. Dev.* 9 (2020), e397985820, <https://doi.org/10.33448/rsd-v9i8.5820>.
- [71] P.F.M. Gouvêa, Z.M.N. Britschka, C. de O.M.S. Gomes, N.G.T. de Queiroz, P.A. V. Salvador, P.S.C. Silva, Evaluation of the use of sterilized and non-sterilized perube black mud in patients with knee osteoarthritis, *Int. J. Environ. Res. Public Health* 18 (2021) 1–11, <https://doi.org/10.3390/ijerph18041666>.
- [72] F.F. Oliveira, A.R. Baby, C.A.S.O. Pinto, T.M. Kaneko, M.V.R. Velasco, Caracterização física, físico-química e química da turfa, lama sulfurosa e fango visando sua aplicação cosmética, *Latin Am. J. Pharm.* 27 (2008) 403–409.
- [73] T. de Araxá, TERMAS DE ARAXÁ. Disponível em: <http://termasdearaxa.com.br/terapias-lama/>. Acesso em: 19 jan. 2021., (2021).
- [74] M. Neves, J.A. Di Lollo, Rainfall Erosivity in the Municipality of São Pedro-SP: analysis Between 1960-2020, *Soc. Nat.* 34 (2022), <https://doi.org/10.14393/sn-v34-2022-64608>.
- [75] C.C. Montibeller, G.R.B. Navarro, A. Zanardo, R. Rohn, C. Del Roveri, R.R. da Rocha, F.T. da Conceição, Geochemistry of siltstones from the Permian Corumbataí Formation from the Paraná Basin (State of São Paulo, Brazil): insights of provenance, tectonic and climatic settings, *J. South Am. Earth Sci.* 102 (2020), <https://doi.org/10.1016/j.jsames.2020.102582>.
- [76] A. da Silva Bellettini, A.P. Viero, A.C.B. Neto, Hydrochemical and contamination evolution of Rio Bonito aquifer in the Carboniferous region, Paraná Basin, Brazil, *Environ. Earth Sci.* 78 (2019), <https://doi.org/10.1007/s12665-019-8625-1>.
- [77] A.B. Pinheiro, A.L.C. Da Silva, T.G. Pereira, J.A.B. Neto, Coastal erosion and flood susceptibility in Paraty, Southeast Brazil Erosión Costera Y Susceptibilidad A Inundaciones En Paraty, Sureste De Brasil, *Revista Geografica de Chile Terra Australis.* 57 (2021) 111–128. doi:10.23854/07199562.2021571esp.Pinheiro111.
- [78] Paraty, PARARY, 2023.
- [79] A.L.C. Silva, J. da C.A. Gralato, T.C.F. Brum, C.P. Silvestre, É.C.da S. Baptista, A. B. Pinheiro, Dinâmica de praia e susceptibilidade às ondas de tempestades no litoral da Ilha Grande (Angra dos Reis-RJ), *J. Hum. Environ. Trop. Bays* 1 (2020) 9–44.
- [80] J.M. Braga, J.C. Biondi, Geology, geochemistry, and mineralogy of saprolite and regolith with Nb, P, Ba, REEs (+Fe) in mineral deposits from the Araxá alkali-rbonatic complex, Minas Gerais state, Brazil, *J. South Am. Earth Sci.* 125 (2023) 1–35. <https://ssrn.com/abstract=4360614>.
- [81] D.M. Bonotto, F. de Oliveira Thomazini, Comparative study of mineral and surface waters of Araxá spa, Minas Gerais State, Brazil, *Environ. Earth Sci.* 78 (2019), <https://doi.org/10.1007/s12665-019-8539-y>.
- [82] M.B.B. Rocha, J.S. Hildor, The physical environment mapping and characterization of the Municipal District of Araxá, Minas Gerais, using geoprocessing techniques, *Educação Tecnol.* 13 (2008) 3–13. <http://www.almg.gov.br>.
- [83] W.E. Dean, Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition: comparison with other methods, *J. Sediment. Petrol.* 44 (1974) 242–248.
- [84] M.D. Foster, Geochemical studies of clay minerals: II. Relation between ionic substitution and swelling in montmorillonites, *Am. Mineral.* 38 (1953) 994–1006.
- [85] G.W. Sears, Determination of specific surface area of colloidal silica by titration with sodium hydroxide, *Anal. Chem.* 28 (1956) 1981–1983, <https://doi.org/10.1021/ac60120a048>.
- [86] G.S. Zahn, L.S. Junqueira, F.A. Genezini, CAX and Xsel: a software bundle to aid in automating NAA spectrum analysis, *Braz. J. Radiat. Sci.* 7 (2019) 1–7, <https://doi.org/10.15392/bjrs.v7i2a.565>.
- [87] N.H. Cutshall, L.H. Larsen, C.R. Olsen, Direct analysis of <sup>210</sup>Pb in sediment samples: self-absorption corrections, *Nucl. Instrum. Methods Phys. Res.* 206 (1983) 309–312.
- [88] A. Quintela, D. Terroso, E.F. da Silva, F. Rocha, Certification and quality criteria of peloids used for therapeutic purposes, *Clay Miner.* 47 (2012) 441–451, <https://doi.org/10.1180/claymin.2012.047.4.04>.
- [89] R. Sánchez-Espejo, C. Aguzzi, P. Cerezo, I. Salcedo, A. López-Galindo, C. Viseras, Folk pharmaceutical formulations in western Mediterranean: identification and safety of clays used in pelotherapy, *J. Ethnopharmacol.* 155 (2014) 810–814, <https://doi.org/10.1016/j.jep.2014.06.031>.
- [90] UNSCEAR, Annex B exposures from natural radiation sources, New York, 2000.
- [91] J.H. Al-Zahrani, Estimation of natural radioactivity in local and imported polished granite used as building materials in Saudi Arabia, *J. Radiat. Res. Appl. Sci.* 10 (2017) 241–245, <https://doi.org/10.1016/j.jrras.2017.05.001>.
- [92] S. Modabberi, A. Namayandeh, A. López-galindo, C. Viseras, M. Setti, M. Ranjbaran, Characterization of Iranian bentonites to be used as pharmaceutical materials, *Appl. Clay Sci.* 116–117 (2015) 193–201, <https://doi.org/10.1016/j.clay.2015.03.013>.
- [93] M. Oláh, Á. Kocz, J. Fehér, J. Kálmánchzey, C. Oláh, G. Nagy, T. Bender, The effect of balneotherapy on antioxidant, inflammatory, and metabolic indices in patients with cardiovascular risk factors (hypertension and obesity)-A randomised, controlled, follow-up study, *Contemp. Clin. Trials* 32 (2011) 793–801, <https://doi.org/10.1016/j.cct.2011.06.003>.
- [94] CUBA, MINSAP (Ministerio de Saúde Pública de Cuba) - Norma Cubana de Especificações de Pelóides. 1998. Disponível em: <[www.sld.cu/galerias/doc/sitios/mednat/norma\\_cubana\\_peloides.doc](http://www.sld.cu/galerias/doc/sitios/mednat/norma_cubana_peloides.doc)> Acesso em: 27 set. 2017., (2017) 2017.
- [95] F. Veniale, A. Bettero, P.G. Jobstraibizer, M. Setti, Thermal muds: perspectives of innovations, *Appl. Clay Sci.* 36 (2007) 141–147, <https://doi.org/10.1016/j.clay.2006.04.013>.
- [96] T. Setnescu, I. Bancuta, R. Setnescu, R. Bancuta, A. Chilian, M. Bumbac, E. D. Chelăreşcu, O. Culicov, M. Frontasyeva, Characterization of some therapeutic muds collected at different sites in Romania, *Revue Roum. Chim.* 58 (2013) 599–610.
- [97] J. Demay, S. Halary, A. Knittel-Obrecht, P. Villa, C. Duval, S. Hamlaoui, T. Roussel, C. Yéprémian, A. Reinhardt, C. Bernard, B. Marie, Anti-inflammatory, antioxidant, and wound-healing properties of cyanobacteria from thermal mud of balnear-les-bains, France: a multi-approach study, *Biomolecules* 11 (2021) 1–21, <https://doi.org/10.3390/biom11010028>.
- [98] B. Gris, L. Treu, R.M. Zampieri, F. Caldara, C. Romualdi, S. Campanaro, N. La Rocca, Microbiota of the therapeutic Euganean thermal muds with a focus on the main cyanobacteria species, *Microorganisms* 8 (2020) 1–23, <https://doi.org/10.3390/microorganisms8101590>.
- [99] N. Martínez-Villegas, M. Suárez Muñoz, P. González-Hernández, C. Melián Rodríguez, J. Barrios Cossio, R. Hernández Díaz, J.R. Fagundo Castillo, A. Golen Rudnikas, C. Díaz López, A. Pérez-Gramatges, O. Díaz Rizo, Inorganic and organic characterization of Santa Lucía salt mine peloid for quality evaluations, *Environ. Sci. Pollut. Res.* 27 (2020) 15944–15958, <https://doi.org/10.1007/s11356-019-04790-2>.
- [100] R.M. Zampieri, A. Adessi, F. Caldara, A. Codato, M. Furlan, C. Rampazzo, R. De Philippis, N. La Rocca, L.D. Valle, Anti-inflammatory activity of exopolysaccharides from *Phormidium* sp. ETS05, the most abundant cyanobacterium of the therapeutic euganean thermal muds, using the zebrafish model, *Biomolecules* 10 (2020), <https://doi.org/10.3390/biom10040582>.
- [101] E. Odabasi, M. Turan, H. Erdem, F. Tekbas, Does mud pack treatment have any chemical effect? A randomized controlled clinical study, *J. Altern. Complement. Med.* 14 (2008) 559–565, <https://doi.org/10.1089/acm.2008.0003>.
- [102] J.I. Santisteban, R. Mediavilla, E. López-Pamo, C.J. Dabrio, M.B.R. Zapata, M.J. G. García, S. Castaño, P.E. Mastrfré-Alfaro, Loss on ignition: a qualitative or quantitative method for organic matter and carbonate mineral content in sediments? *J. Paleolimnol.* 32 (2004) 287–299.
- [103] R.M.A. Cessa, L. Celi, A.C.T. Vitorino, J.O. Novellino, E. Barberis, Área superficial específica, porosidade da fração argila e adsorção de fósforo em dois latossolos vermelhos, *Rev. Bras. Cienc. Solo* 33 (2009) 1153–1162, <https://doi.org/10.1590/s0100-06832009000500009>.
- [104] E.I. Unuabonah, K.O. Adebowale, B.I. Olu-Owolabi, L.Z. Yang, L.X. Kong, Adsorption of Pb (II) and Cd (II) from aqueous solutions onto sodium tetraborate-modified Kaolinite clay: equilibrium and thermodynamic studies, *Hydrometallurgy* 93 (2008) 1–9, <https://doi.org/10.1016/j.hydromet.2008.02.009>.
- [105] M.I. Carretero, M. Pozo, Clay and non-clay minerals in the pharmaceutical and cosmetic industries Part II. Active ingredients, *Appl. Clay Sci.* 47 (2010) 171–181, <https://doi.org/10.1016/j.clay.2009.10.016>.
- [106] A. Lopez-Galindo, C. Viseras, *Pharmaceutical and cosmetic applications of clays*, F. Wypych, K.G. Satyanarayana. *Clay Surfaces: Fundamentals and Applications*, Elsevier Ltd, 2004, pp. 268–289.
- [107] M.I. Carretero, C.S.F. Gomes, F. Tateo, Clays and human health, F. Bergaya, B.K. G. Theng, G. Lagaly. *Handbook of Clay Science*, Elsevier Ltd, 2006, pp. 717–741, [https://doi.org/10.1016/S1572-4352\(05\)1024-X](https://doi.org/10.1016/S1572-4352(05)1024-X).
- [108] P.F. de, M. Gouvêa, Avaliação Clínica Em Pacientes Portadores De osteoartrite, *Tratados Com a Lama Negra De perube, Caracterização química, Radiológica e Estabelecimento De Protocolos De Boas Práticas Para a Obtenção e Eso Deste Pelóide*, Universidade de São Paulo, 2018.
- [109] J. Nikolov, N. Todorovic, T.P. Pantic, S. Forkapic, D. Mrdja, I. Bikit, M. Krmar, M. Veskovik, Exposure to radon in the radon spa Niška Banja, Serbia, *Radiat. Meas.* 47 (2012) 443–450, <https://doi.org/10.1016/j.radmeas.2012.04.006>.
- [110] V. Ramasamy, M. Sundarajan, G. Suresh, K. Paramasivam, V. Meenakshisundaram, Role of light and heavy minerals on natural radioactivity level of high background radiation Area, Kerala, India, *Appl. Radiat. Isot.* 85 (2014) 1–10, <https://doi.org/10.1016/j.apradiso.2013.11.119>.
- [111] M.R. Calin, I. Radulescu, A.C. Ion, L. Capra, E.R. Almasan, Investigations on chemical composition and natural radioactivity levels from salt water and peloid used in pelotherapy from the Techirghiol Lake, Romania, *Environ. Geochem. Health* 42 (2020) 513–529, <https://doi.org/10.1007/s10653-019-00382-8>.
- [112] H. Taskin, M. Karavus, P. Ay, A. Topuzoglu, S. Hidiroglu, G. Karahan, Radionuclide concentrations in soil and lifetime cancer risk due to gamma radioactivity in Kırklareli, Turkey, *J. Environ. Radioact.* 100 (2009) 49–53, <https://doi.org/10.1016/j.jenvrad.2008.10.012>.
- [113] UNSCEAR, Sources and effects of ionizing radiation, in: *Unsclear 2010 Report*, New York, 2010. 10.18356/97887b8d-en.

- [114] F. Veniale, E. Barberis, G. Carcangiu, N. Morandi, M. Setti, M. Tamanini, D. Tessier, Formulation of muds for pelotherapy: effects of "maturation" by different mineral waters, *Appl. Clay Sci.* 25 (2004) 135–148, <https://doi.org/10.1016/j.clay.2003.10.002>.
- [115] M.I. Carretero, M. Pozo, C. Sánchez, F.J. García, J.A. Medina, J.M. Bernabé, Comparison of saponite and montmorillonite behaviour during static and stirring maturation with seawater for pelotherapy, *Appl. Clay Sci.* 36 (2007) 161–173, <https://doi.org/10.1016/j.clay.2006.05.010>.
- [116] C.V. Iborra, G. Cultrone, P. Cerezo, C. Aguzzi, M.T. Baschini, J. Vallés, A. López-Galindo, Characterisation of northern Patagonian bentonites for pharmaceutical uses, *Appl. Clay Sci.* 31 (2006) 272–281, <https://doi.org/10.1016/j.clay.2005.11.002>.
- [117] A. Abdel-Motelib, Z.A. Kader, Y.A. Ragab, M. Mosalamy, Suitability of a Miocene bentonite from North Western Desert of Egypt for pharmaceutical use, *Appl. Clay Sci.* 52 (2011) 140–144, <https://doi.org/10.1016/j.clay.2011.02.012>.
- [118] A. Banin, A. Amiel, A correlative study of the chemical and physical properties of a group of natural soils of Israel, *Geoderma* 3 (1970) 185–198.
- [119] M.Ç. Karakaya, M. Doğru, N. Karakaya, H.C. Vural, F. Kuluöztürk, S.Ş. Bal, Radioactivity concentrations and dose assessments of therapeutic peloids from some Turkish Spas, *Clay Miner.* 50 (2015) 221–232, <https://doi.org/10.1180/claymin.2015.050.2.06>.
- [120] D.D. MacDonald, C.G. Ingersoll, T.A. Berger, Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems, *Arch. Environ. Contam. Toxicol.* 39 (2000) 20–31, <https://doi.org/10.1007/s002440010075>.
- [121] EP, "European pharmacopeia," 2011. doi:10.1016/s0003-0465(16)31141-7.
- [122] USP 36 – NF31, 2013. United States Pharmacopoeia 36 and National Formulary 31. US Pharmacopoeial Convention, Rockville, MD (USA)., (2013) 2013.
- [123] NHPD, 2018. Natural and non-prescription health products. Disponível em: <[www.healthcanada.gc.ca/nhp](http://www.healthcanada.gc.ca/nhp)> Asseso em dez. 2017, (2018) 2018.
- [124] CCME, Canadian sediment quality guidelines for the protection of aquatic, *Environ. Conserv.* (2002).
- [125] B. Baranowska-Dutkiewicz, Absorption of hexavalent chromium by skin in man, *Arch. Toxicol.* 47 (1981) 47–50.
- [126] J. Peterson, M. MacDonell, L. Haroun, F. Monette, Radiological and chemical fact sheets to support health risk analyses for contaminated areas, 2007.
- [127] F.L. Filon, F. D'Agostin, M. Crosera, G. Adami, M. Bovenzi, G. Maina, *In vitro* percutaneous absorption of chromium powder and the effect of skin cleanser, *Toxicol. Vit.* 22 (2008) 1562–1567, <https://doi.org/10.1016/j.tiv.2008.06.006>.
- [128] R.C. Wester, H.I. Maibach, L. Sedik, J. Melendres, M. Wade, *In vivo* and *in vitro* percutaneous absorption and skin decontamination of arsenic from water and soil, *Fundam. Appl. Toxicol. Toxicol. Sci.* 20 (1993) 336–340, <https://doi.org/10.1093/toxsci/20.3.336>.
- [129] J.L. Stauber, T.M. Florence, B.L. Gulson, L.S. Dale, Percutaneous absorption of inorganic lead compounds, *Sci. Total Environ.* 145 (1994) 55–70, [https://doi.org/10.1016/0048-9697\(94\)90297-6](https://doi.org/10.1016/0048-9697(94)90297-6).
- [130] R.M. Al-Ashban, M. Aslam, A.H. Shah, Kohl (surma): a toxic traditional eye cosmetic study in Saudi Arabia, *Public Health* 118 (2004) 292–298, <https://doi.org/10.1016/j.puhe.2003.05.001>.
- [131] F.L. Filon, G. Maina, G. Adami, M. Venier, N. Coceani, R. Bussani, M. Massiccio, P. Barbieri, P. Spinelli, *In vitro* percutaneous absorption of cobalt, *Int. Arch. Occup. Environ. Health* 77 (2004) 85–89, <https://doi.org/10.1007/s00420-003-0455-4>.
- [132] R.L. Rudnick, S.M. McLennan, S.R. Taylor, Large ion lithophile elements in rocks from high-pressure granulite facies terrains, *Geochim. Cosmochim. Acta* 49 (1985) 1645–1655, [https://doi.org/10.1016/0016-7037\(85\)90268-6](https://doi.org/10.1016/0016-7037(85)90268-6).
- [133] C. Carvalho, R.M. Anjos, R. Veiga, K. Macario, Application of radiometric analysis in the study of provenance and transport processes of Brazilian coastal sediments, *J. Environ. Radioact.* 102 (2011) 185–192, <https://doi.org/10.1016/j.jenvrad.2010.11.011>.
- [134] G. Manic, S. Petrovic, M. Vesna, D. Popovic, D. Todorovic, Radon concentrations in a spa in Serbia, *Environ. Int.* 32 (2006) 533–537, <https://doi.org/10.1016/j.envint.2005.12.002>.
- [135] M.T. Baschini, G.R. Pettinari, J.M. Vallés, C. Aguzzi, P. Cerezo, A. López-Galindo, M. Setti, C. Viseras, Suitability of natural sulphur-rich muds from Copahue (Argentina) for use as semisolid health care products, *Appl. Clay Sci.* 49 (2010) 205–212, <https://doi.org/10.1016/j.clay.2010.05.008>.
- [136] A. Papadopoulos, K. Giouri, E. Tzamos, A. Filippidis, S. Stoulos, Natural radioactivity and trace element composition of natural clays used as cosmetic products in the Greek market, *Clay Miner.* 49 (2014) 53–62, <https://doi.org/10.1180/claymin.2014.049.1.05>.