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Research Article

Determination of all the Physicochemical, Mineralogical, and Sedimentological Required Parameters of Mud Deposits in the Direction of Their use for Pelotherapy, in Kefalonia and Corfu Islands, Greece

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Abstract

Pelotherapy has been used as a treatment of different diseases from medical, pharmaceutical and cosmetics fields. Mineralogical and chemical compositions and the possible toxicity of the peloids were first investigated and then compared with the existing limits in order to determine whether they have applications for pelotherapeutic treatments. The 120 studied samples were collected from natural outcrops in two islands, Kefalonia (80 samples) and Corfu (40 samples) where, in addition to the chemical and mineralogical analysis, also pH, plasticity, specific surface area and thermal analysis were determined. Grain size analysis, TOC content and depositional conditions were taken into consideration. Toxic element contents, e.g., Ni, Mo, Ga, Te, and Sr, of the peloids were higher of permissible limits, whereas the mineralogical composition mainly showed the presence of smectite, quartz, plagioclase, and some carbonate (calcite and dolomite). The temperature of the studied samples was between 23 and 26°C, pH between 8.3 and 9.6, the surface area between 6 and 26m2/gr. Thermal analysis showed gradually large weight loss from about 670°C due to calcination and decomposition of calcium carbonate $CaCO_3$. Combination of all the above results could be utilized in the direction of using the materials for pelotherapy, as they do not contain toxic elements, beyond the permissible limits their use by human.

Keywords: Mud therapy; Mineralogy; Chemistry; Toxicity; Hazardous elements; Ionian Islands; Kefalonia-Ithaca Geopark

Introduction

The therapeutic effects of peloids have been thoroughly studied, particularly in the medical fields. In pharmaceutical preparations they are also used as medicinal products as cosmetic products. The main factors that determine the nature of a peloid and its suitability for pelotherapeutic applications is low cooling rate, high absorption capacity, high Cation Exchange Capacity (CEC), good adhesiveness, ease of handling, and agreeable feeling when applied to the skin [1,2]. The use of a mineral clay for any application depends both on its type of structure and its chemical composition. Texture differences between structurally and chemically identical minerals as well affect their adsorptive and rheolog-cal properties [3-6].

The microstructure, physicochemical, mineralogical and textural characteristics of the geomaterial when applied on the skin are some of the main factors related to the treatment efficacy and health risks [7,8]. Clay minerals' type, as well as their concentration in peloids, must be examined on detail, since clay minerals affect major parameters during treatment, such as dermal absorption/adsorption, and toxicity of elements [7-9].

The requirements' definitions for safe interaction between the clay-based formulation and the skin are sustained on the increased release of ionizable elements and their disposal to percutaneous absorption. The results should, ideally, be physiologically effective during passive percutaneous absorption [10]. The solubility, molecular mass, depth of penetration, and toxicology of the clay components need to be considered in the percutaneous absorption. The Cation Exchange Capacity (CEC) and the other formulation characteristics may define the percutaneous depth efficacy that ions may reach, as well as the desirable absorption by the skin. The pain relief, the anti-inflammatory action, the range improvement of the upper limb movements, the antibacterial action, the healing action [11], and others can

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observe the success of a complete percutaneous action therein. These clay-based products are mainly used in rehabilitation programs at thermal centers and spas, being associated with musculoskeletal and tendon injuries, rheumatic pathologies, dermatological infirmities, or for aesthetic purposes and skincare. The biological and physiological mechanisms of how mud applications alleviate symptoms of several pathologies, in the dermatological and rheumatological field, are still not completely under-stood [12–17].

In Greece, there is a recognized pelotherapy, in Kavala (Krenides center). In the past, geological, ecological, biological, chemical conditions created the right environment in which healing clay matured naturally. The decay of organic matter produced carbon di-oxide, water, and nitrogen. The continuous and successive accumulation of plant organ-isms and subsequent decay gave genetically the healing material.

This paper offers a comprehensive overview of the mineralogical, geochemical, and physicochemical characteristics of the materials from natural outcrops, which humans use for many years providing a detailed perspective on their suitability for pelotherapy applications. Particularly, the trace and major elements, clay minerals, as well as pH, plasticity, surface characteristics, and thermal properties were measured. Additionally, grain size content, depositional conditions with detailed litho- and biostratigraphy, Ca-CO3 and TOC contents, also major factors for mud pelotherapy use, were presented in an academic paper submitted to other journal and is under investigation and discussed also in the present paper. As humans, use the natural materials and our study based on natural outcrops and not on existing infrastructures, it is critical to suggest the safely use of these natural materials and additionally, as some of these studied areas belongs to protected areas of the Kefalonia-Ithaca geopark it is important to find equivalent materials out of the protected areas.

Geological Setting

The Hellenic Fault and Thrust Belt dominates the External Hellenides and is mainly controlled by collision and continued convergence of the African and Eurasian plates since the Mesozoic. The most important structural control in the studied area was the contractual deformation, as suggested by the constant occurrence of evaporites throughout the thrust boundary between the Apulian platform margins and the Ionian basin. Evaporites represent the lowest detachment level of individual thrust sheets and form a major decollement level [18,19].

The Ionian Islands develop at the boundary of the Ionian basin with that of of the Apulian platform margins (former Pre-Apulian platform or zone) (Figure 1). In particular, the contact of these two different geological environments is located in North Corfu in eastern Kefalonia and in central Zakynthos. The Ionian Islands appear to have been affected by the thrust fault zone that dominates the external Hellinides and is mainly con-trolled by the collision and ongoing convergence of the African and Eurasian plates since Mesozoic times. This collision took place in the Ionian Islands region during the middle Miocene [18,19]. With the action of the Ionian thrust, which characterizes the two different geological units, foreland (progradational) basins were created at the thrust front.

From the Triassic to the Late Cretaceous, Western Greece was part of the continental part of Apulia, on the southern passive margin of the Tethys Ocean. Since the Early Jurassic (Pliensbachian) the opening of the Tethys Ocean has been associated with extensional trends and was therefore responsible for the opening of the Ionian Basin during the Late Jurassic, with the Apulian platform margins, located west of the Ionian Basin, which exceeded (Figure 2).

Based on the seismic data it was suggested that the normal faults, which affected the Mesozoic deposits, were reactivated as thrust faults during the Eocene to Miocene and further activated as normal faults during the Plio-Quaternary. In addition, it is suggested that Mesozoic normal faults and transfer faults were reactivated during the compressional regime as thrust or back-thrust faults and strike-slip faults, respectively [18,19].

The Kefalonia Island appears to be affected by the action of 4-5 thrust events that cre-ated corresponding thrust basins [20]. One of these is the Aitheras-Aenos foreland basin in the front of thrust. The sediments of the basin have a surficial ap-

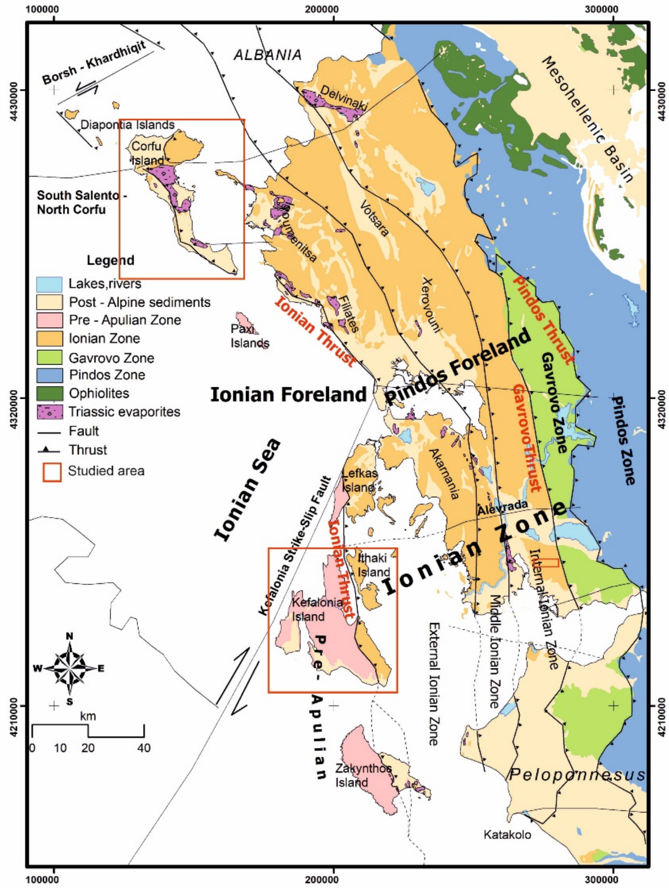

Figure 1: Geological map of Western Greece where the two research areas (Kefalonia and Corfu Islands) are marked with a red box [18,19].

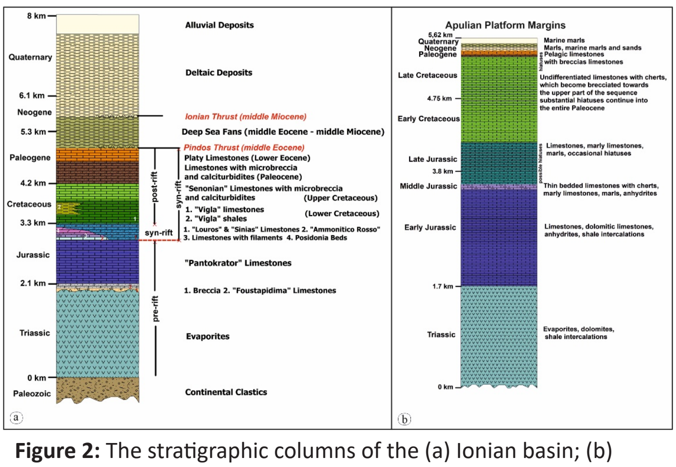

Figure 2: The stratigraphic columns of the (a) Ionian basin; (b) Apulian platform margins [18,19].

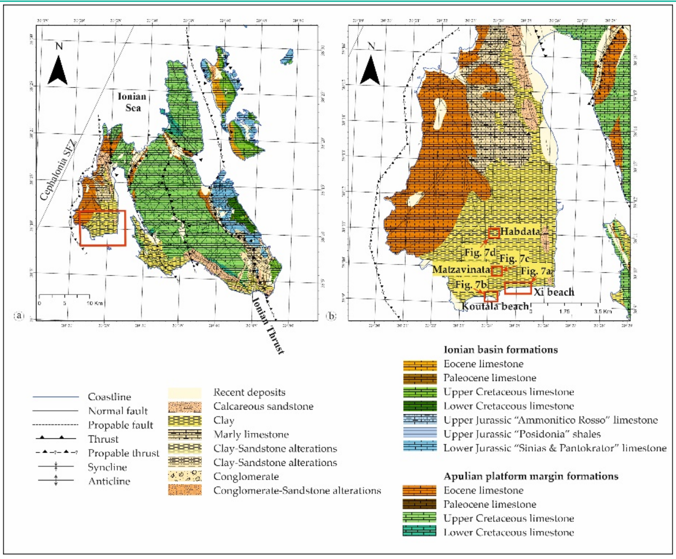

Figure 3: (a) Geological map of Kefalonia Island, where the Paliki peninsula is marked with a red frame; (b) Geological map of the Paliki peninsula [20], where the four sampling sites are marked.

pearance and outcrop out in Paliki Peninsula (Figure 3). The Miocene sediments are limited to the northern part of the Paliki peninsula while the Plio-Pleistocene sediments cover the entire south-southeast part of the peninsula with a thickness that varies (according to the IGME Geological map) from 100 to 250m.

The foreland basin in North Corfu (Figure 4) was studied in detail in terms of its sedimentological environments in which found that the deposits of the Miocene in Arillas area and the Pliocene in Agios Stefanos area were deposited in a tidal environment and the Miocene has a total exposed thickness of 100m [21].

Lobes of submarine fans, with alternations of clays and sands, north of the Agios Stefanos area, characterize the Pliocene sediments, with a total thickness of about 600m. A general shallowing trend is observed towards the northern and upper part of the sequence, indicating the uplift of the basin.

Material and Methods

Two hundred and ten samples were selected from all the studied areas to determine lithology, sedimentological environment, and the age.

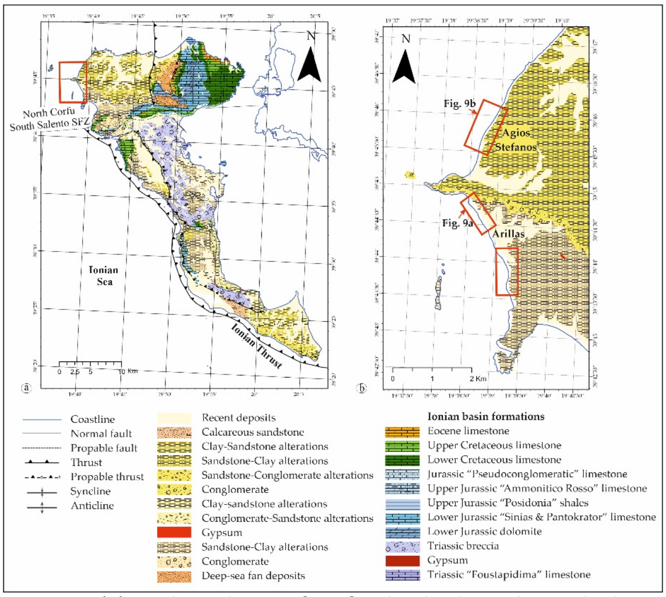

Figure 4: (a) Geological map of Corfu Island, where the studied area is marked with a red frame; (b) The study area in NW Corfu [21] where the two areas of Arillas and Agios Stefanos are located.

One hundred and twenty samples were collected from all the research areas. All samples were homogenized, dried, and then ground for 5 min in a porcelain ball mill for X-ray diffraction, chemical and mineralogical analysis.

Lithostratigraphy

The study area includes both areas in the coastal zone (Xi and Koutala in Kefalonia, Arillas and Agios Stefanos, in Corfu) and inland areas in Kefalonia (Matzavinata and Chavdata). A detailed analysis of the sedimentological features, also supported by targeted-explanatory photographs, was carried out in seven synthetic stratigraphic columns. These stratigraphic columns vary in width, ranging from 5 to 300m, and in height, ranging from 4 to 25m. Some of the stratigraphic columns show lateral continuity, extend for hundreds of meters, and are interconnected or closely spaced, with distances of less than 10 meters between them, while others are more widely separated. Data concerning the lithology and detailed thickness of each column were plotted on sedimentary lithostratigraphic columns. These detailed sections also documented grain size, sedimentary structures, and contact boundaries. In total, more than 200 mudstone samples were collected, while 5 samples were also taken from Xi beach sand. The analysis of grains larger than 63mm was performed using the sieve analysis method, while the pipette analysis method was used for grains smaller than 63mm.

Biostratigraphy

A total of 210 samples were collected from which 60 samples were selected as the most representative. From each sample, 100g of sediment were weighed, which were then dissolved in water or in a solution of water and hydrogen peroxide. Then, the wet sieving process washed the samples, where 63μ and 500μ sieves were used, followed by the drying process at 70°C. The samples were sectioned (where necessary) and with the aid of an Optica LAB20 stereoscope the microfossils identified in the sediment quantity of each sample were collected. Microfossils were divided into taxa, counted, photographed with a stereo digital camera (Optica C-B10+) and identified to genus or species level where possible.

TOC – CaCO3 Content

Geochemical analysis of 120 samples (42 samples of mud and 1 sample of sand from the Xi section, 15 samples from Chavdata, 15 samples from Matzavinata, 7 samples from Koutala-Kefalonia Island, 5 samples from Arillas north, 15 samples from Arillas South, and 20 samples from Agios Stefanos) included determining calcium carbonate ($CaCO_3$) and Total Organic Carbon (TOC) content. TOC content was measured by Rock-Eval VI analysis in the lab of "Hydrocarbons Chemistry and Technology" of School of Mineral Resources Engineering of Technical University of Crete. $CaCO_3$ analysis utilized CH_3COOH decomposition, according to Varnavas [22] method, while TOC analysis employed Rock-Eval II and VI (Delsi Inc.) analyzers under standard conditions, by utilizing ~100 mg of pulverized rock. The samples were then heated in a helium atmosphere, using a suitable oven [23-25].

XRF Analysis

The samples were ground and homogenized. Elemental analysis was then per-formed to determine major and trace elements using X-Ray Fluorescence (XRF) spectroscopy on a Bruker AXS type S4 Pioneer automatic spectrometer.

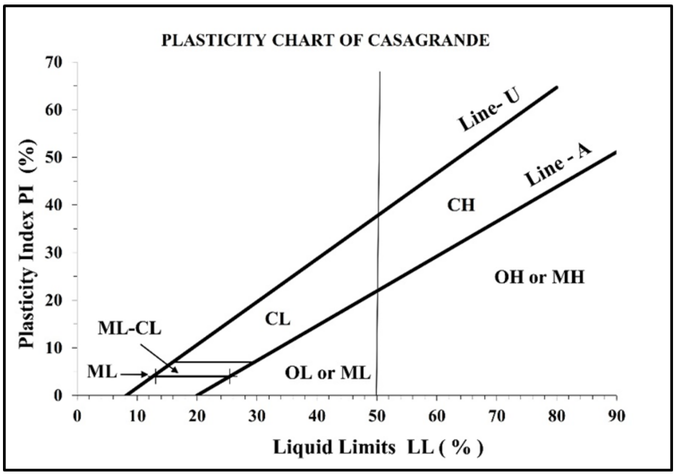

Figure 5: Plasticity diagram [27]. Abbreviations: ML-CL= Cohesive soils of clay and silt, ML=low plasticity silt, OL or ML= Organic silt or low plasticity silt plasticity, OH or MH= Organic silt or high plasticity silt, CL= Low plasticity clay plasticity, CH= Hi.

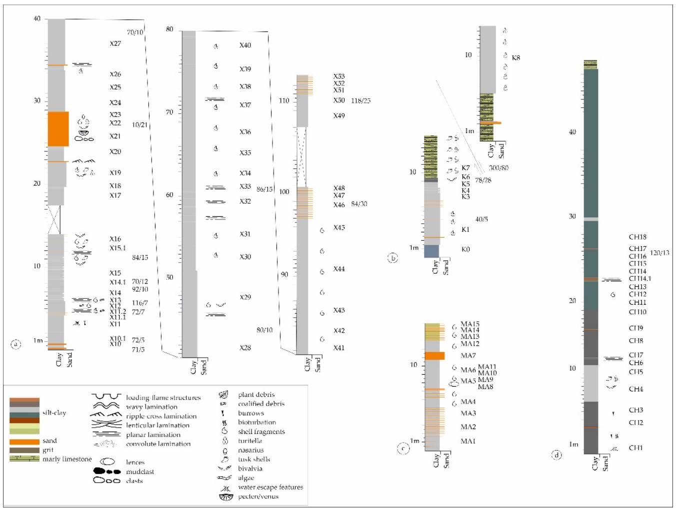

Figure 6: Lithostratigraphic columns of the studied surface appearance (a) along the Xi beach; (b) Koutala beach; (c) Matzavinata; (d) Chavdata. The numbers of the analyzed samples are also noted next to the columns.

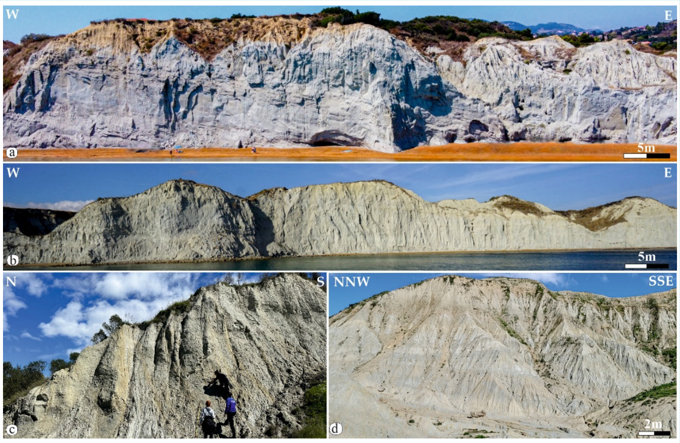

Figure 7: Panoramic pictures of (a) the Xi beach section; (b) the Koutala beach section; (c) the Matzavinata section; and (d) the Chavdata section.

XRPD Analysis

The analysis of the samples was done by the X-ray diffractometry method of the samples in an automatic X-ray diffractometer, type PANAlytical X' Pert Pro with a copper lamp and a graphite monochromator. A semi-quantitative determination of their mineralogical components was made using the X-ray diffractometry method. Then the clay fraction of the samples was separated. To distinguish minerals with close constants the following was applied: a. Treatment of fraction preparations with ethylene glycol vapors for the identification of expanded clay minerals and b. Pyrolysis the fraction preparations to distinguish chlorite from vermiculite and establish the presence of kaolinite. The XRF and XRPD analysis of the 120 samples took place in H.S.G.M.E. (Hellenic Survey of Geology & Mineral Exploration) labs.

pH Determination

The determination of pH was carried out dry samples, using an electronic parameter type CONSORT C835 at the Minerals and Rocks Research laboratory of department of Geology, University of Patras. Before the measurement, the following procedure was followed to prepare the samples where 10g of each sample was placed in 50ml polyethylene bottles and added 25ml deionized water. The sediment-water mixture was then stirred for 60 minutes in an Edmund Buhler shaker and then the sample was left to stand for 60 minutes. Before measuring the pH, the sample was stirred for 10 seconds using a magnetic stirrer and the pH was measured at room temperature.

Plasticity Determination

The plasticity was determined by calculating the Atterberg limits [26] (hydraulic limit and plastic limit) and using the Casagrande [27] hydrousity apparatus. The plasticity index (Ip) was calculated from the numerical difference between the hydration and plasticity limits. The water limit (LL) is defined as the water content where the sediment changes from the plastic state to the aqueous state. The Plasticity Limit (PL) is defined as the percentage of water needed for the sediment to pass from the plastic state to the solid state. The results were shown in the diagram Casagrande plasticity, used to classify sediments. The diagram, as shown in Figure 5, contains two axes with the water limit and the plasticity and based on line "A" and the vertical line corresponding to LL=50%, the chart is divided into four regions.

Surface Area Determination

The specific surface area of the studied samples from all studied areas was deter-mined using the N2 Quantachrome NOVA 2200E BET Surface Area Analyzer porosimeter and applying the adsorption theory [28]. After drying the samples at 105°C, they were then degassed at 70°C overnight and then we measured the specific surface area, obtaining isotherms with a range of points for P/Po from 0.05-0.3.

Thermal Analysis

The samples were analyzed by using a thermogravimetric analyzer type TG Q500 (TA Instruments) Thermogravimetric Analyzer, at the Minerals and Rocks Research Laboratory of Department of Geology, University of Patras. Approximately 30 mg of sample was thermally analyzed at rate heating 10oC min-1 and in a temperature range from ambient temperature to 900oC under continuous nitrogen flow.

Results

Following the results of all the parameters which are used for the analytical evaluation of the clays.

Lithostratigraphy

Kefalonia island: In the area of Lixouri, the studied sediments reach 800 meters and consist of clay, marls and limestones alternating with sandstones. South of Lixouri, the marls are characterized by the intercalation of limestone layers, which reach a total thickness of about 300m (Figure 6). These deposits are interpreted as lacustrine or marine sediments. More specifically, the studied desposits from the marine phase that is evident in the west and southwest of the island, is composed by marls and sandstones 300m thick, followed by a series of Pleistocene deposits 600m thick (Figure 7). These Pleistocene rocks were deposited in a shallow marine basin that received significant clastic material from fluvial sources, the main source being the Aenos thrust front.

The average composition consists of 3.46% sand, 57.80% silt, and 38.74% clay.

Corfu island: In the coastal area of Arillas (Figure 8), an extensive Miocene sequence is out-cropped, with approximately 1km in length, extending to the cape of Agios Stefanos (Figure 9a), marking the Miocene-Pliocene boundary. Stratigraphically, the lower deposits (South Arillas section) exhibit shifts between episodes of low and high energy, primarily featuring silt and sand, respectively. In the northern part of the beach area there is a sequence characterized by alternating layers of sand and silt, with an average thickness of approximately 15m. These rhythmites are characterized by flat, parallel-laminated bedding, with alternating deposition of muddy materials, showing a tidal environment. On the coastal area of Agios Stefanos (Figure 8, 9b), there are two distinct phases of the Pliocene. Slightly thicker sandy layers and a higher sand/mud ratio characterize the first phase, with a total thickness of about 20 m. This phase is characterized by distinct gradation structures and wavy lamination, with variations in grain size indicating circularity. The second phase is notable for the predominance of sandy layers in rhythmic alternation with thin layers of gray mud. The sandy layers show a wavy layer and the presence of "hummocky" cross-stratification. Total sequence was interpreted as a tidal environment [29-31]. The average composition consists of 9.32% sand, 54.75% silt, and 35.94% clay.

Biostratigraphy

Planktonic foraminifera have been utilized for dating the succession due to their high abundance and their capability to facilitate interregional correlation. The biostratigraphic results were evaluated in relation to the stratigraphic position of the samples and the sections. A table of the estimated ages in each studied sequence is presented (Table 1).

Total Organic Carbon Content (TOC) and Calcium Carbonate (CaCO3)

Laboratory analysis of TOC shows that the ratio ranges from 0.10% to 0.77%. The average percentage of Corfu (TC) samples is 0.30% and the average percentage of Kefalonia (TK) samples is 0.33%.

Laboratory analysis of calcium carbonate (CaCO3) shows that the ratio ranges from 12.22% to 39.27%. The average percentage of the Corfu (TC) samples is 30.90% and the average percentage of the Kefalonia (TK) samples is 24.60%.

XRF Analysis

Twenty-one (21) rare elements were studied (Li, Be, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Mo, Ag, Cd, Te, Ba, Pb, U, Bi) of which 14 out of 21 elements are considered toxic [(Be, Cr, Co, Ni, Cu, Zn, As, Mo, Ag, Cd, Te, Ba, Pb, Bi) 32], but 6 out of 14 elements are considered low toxicity [(Cr, Ni, Cu, Mo, Ag, Ba) 33].

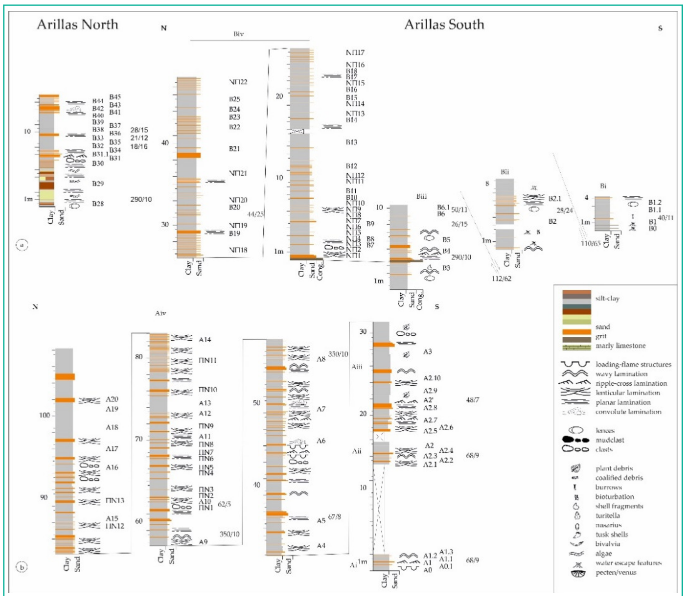

Figure 8: Lithostratigraphic columns of the studied surface occurrences along the beaches (a) Arillas beach from north to south; (b) Agios Stefanos beach. The numbers of the analyzed samples are also noted next to the columns.

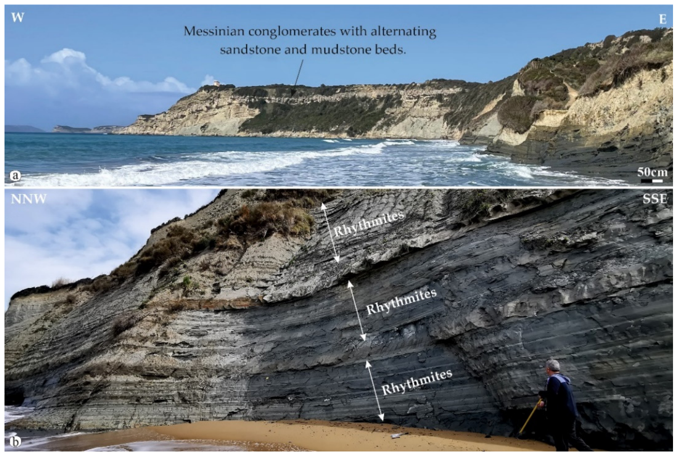

Figure 9: (a) Photograph of the Northern part of Arillas bay; (b) Photograph of the Agios Stefanos section showing sandstone-mudstone alterations.

It should also be mentioned that the contents of the above 21 rare elements in outcropped clay sediments were also considered for the comparative investigation [34].

Of the twenty-one rare elements analyzed in detail, the results depending on the studied area, showed 16 to 18 elements (Li, Be, V, Cr, Mn, Co, Cu, Zn, As, Rb, Ag, Cd, Ba, Pb, U, Bi) to be within the permitted limits of their use. Specifically, 9 to 11 rare elements (Be, Cr, Co, Cu, Zn, As, Ag, Cd, Ba, Pb, Bi), out of 14 toxic elements are within the permissible limits, with values well below the upper limits (Table S1: Chemical analysis).

It is worth mentioned that all samples are within the permissible toxicity limits for their use, for the elements considered toxic [33].

Some of the above rare elements (Cu, Co, Fe, Mn or Zn), can be dangerous for humans and can cause certain diseases [35]. Therefore, the results show that they have no harmful toxic elements beyond the permissible limits.

In detail Nickel (Ni) appears in almost all studied samples (115 out of 120 analyzed) beyond the permissible limits of which are 40-90 mg/Kg or 60 mg/Kg respectively [32,33].

Specifically, in the areas of Xi, Koutala, Matzavinata and

Chavdata, in Kefalonia Island, in a total of 80 samples out of 120, Ni ranges from 70 to 190mg/kg, with the highest values in Chavdata. On the contrary, in the areas of Arillas and Agios Stefanos, in Corfu Island (40 samples out of 120), the values range from 170-240mg/kg, quite increased compared to the previous areas.

The Ni content, in almost all analyzed samples, was greater than the required limit. Allergic contact dermatitis is also frequently caused by Ni chloride and sulfate. Ni is a natural component of soil in concentrations ranging from 4 to 80 ppm [36].

Furthermore, while Nickel has values beyond the permissible limits, it seems that as it is reported under the code NC: Natural clay [37], nickel is within the limits since natural clay reaches values of 324 units, while the analyzes of samples had values mostly below 200 units.

Strontium (Sr), for the Arillas beach is beyond the limits, according to the CHC: Commercial use of clay, it has a limit of 696 units, that is, well above the values measured in the samples.

Gallium (Ga) shows values beyond the upper allowed limits in 16 out of 120 samples (7 from Xi, 1 from Chavdata, 6 from Agios Stefanos and 2 from Arillas).

Molybdenum (Mo) appears beyond the limits in 54 of 120 with increased concentrations mainly in Arillas beach.

Tellurium (Te) occurs in 39 out of 120 samples out of bounds and mainly refers to the areas of Chavdata, Matzavinata and Arillas. Tellurium (Te) has mild toxicity, but its compounds are (more) toxic and must be handled carefully.

It is indicated that only Ni should be tested in the direction of causing skin diseases. Analyses-applications of the use of the material must be done in collaboration with dermatologists to see if allergies are caused.

XRPD Analysis

The results from the one-hundred twenty analyzed samples (Table S2: Main elements) of the present investigation showed variations of the main elements in their concentrations: SiO_2: 32-47, Al_2O_3: 9-13, Fe_2O_3: 5-7.5, MgO: 3.5-6.5, CaO: 14-30, Na_2O: 0.5-1.70, K_2O: 2-3, TiO_2: 0.55-0.75, P_2O_5: 0.08-0.17, MnO: 0.09-0.17. SiO_2 ranges between 32% and 47% of the total sample percentage and Al_2O_3 ranges from 9-13%. The percentage of Fe_2O_3 varies between 5% and 7.5%. As in the analyzes [9], for known peloids in use in 18 pelotherapy centers in Turkey, also in the present research it appears that SiO_2 exhibits a strong to moderate positive correlation with some or most of the major oxides e.g. with Al_2O_3, TiO_2, K_2O, Na_2O, and P_2O, while showing a negative correlation with CaO. This correlation indicates that the main minerals from which materials are derived, were formed by silicate minerals while the MgO and F_2O_3 content of the samples is associated with non-silicate minerals or partially with Fe-rich smectite minerals. The ratio of Na_2O/CaO oxides in the samples is well below 1.0 and resembles the corresponding ratio of CHC.

The mineralogical compositions showed similarities with the analyzed samples of the present investigation (Table S3: Mineralogical composition). Clay minerals range from 5-31%. It is observed the lowest percentages in the samples from Xi beach in Kefalonia (5-13%), while the samples from Agios Stefanos beach in Corfu have a better composition (18-31%). Smectite ranges from 1-6%, with the highest values at Agios Stefanos beach and the lowest in Xi beach with valued of 1-2%. Quartz ranges from 24-40%. The highest percentages were found on Xi beach with 40% and the lowest on Agios Stefanos beach with 24%. Also, calcite ranges from 19-40%. The lowest percentages were found in the samples from Xi beach (19%) while the highest percentages were found in the samples from Arillas beach (40%). Moreover, dolomite ranges from 1-6%. The highest percentage was found in Xi beach with 6% and then in Koutala beach with 5%, while the rest of the areas showed values of 4%. Finally, plagioclase ranges from 14-23%. The beaches of Xi (17-23%) and Koutala (17-21%) have the highest valued, while the rest of the areas have considerably lower values (14%).

pH Determination

The limits were determined based on the Soil Survey Staff manual [38] are: 7.4-7.8= Slightly alkaline, 7.9-8.4= Moderately alkaline 8.5-9.0= Strongly alkaline, >9 ,00= Very Strongly alkaline.

Kefalonia island: The pH measurements of samples from the Xi Beach site showed that it ranges from 7.8 to 9.6 and by extension is classified as slightly alkaline to very strongly alkaline sediments based on the manual [38]. Twenty-one (21) samples have a moderately alkaline pH, nineteen samples (19) are characterized as strongly alkaline, one sample (X29) as slightly alkaline and one (X45) as a very strongly alkaline precipitate. The samples from the Kefala beach are mostly characterized as moderately alkaline. Two samples (K1 and K8) have very strongly alkaline pH, while one (K0) strongly alkaline. In addition, the measurements of the pH of the samples from the Matzavinata location showed that it ranges from 8.4 to 9.5 and by extension; they are characterized as moderately alkaline to very strongly alkaline sediments. Most samples have a strongly alkaline pH. Five samples (MA3, MA8, MA9 and MA14) are characterized as very strongly alkaline and one sample (MA15) as moderately alkaline. Furthermore, twelve samples from Chavdata have a very strongly alkaline pH, while the remaining six are characterized as strongly alkaline (Table S4: pH determination).

Corfu island: The pH measurements of Arillas beach showed in the majority of them strongly alkaline, except for four (B5, B22, B31 and B41) which are characterized as moderately strongly alkaline while the pH measurements of Agios Stefanos samples is mostly characterized as moderately alkaline, except for three (A8, A11 and A17) which are strongly alkaline (Table S4: pH determination).

Plasticity Determination

Kefalonia island: Twenty samples in Xi beach, based on the calculation of water limit and plasticity index, are mainly characterized as low plasticity clays (Figure S1: Plasticity chart, Table S5: Plasticity determination). Only four (4) are projected in the field of high plasticity clays (samples X13, X14, X16 and X34), while the rest in the field of low plasticity silts. Half of the samples are considered suitable for therapeutic use [39]. The rest (X18, X19, X21, X23, X26, X27, X28, X30, X31, X32, X35, X37, X38, X39, X40, X41, X44, X45, X46, X48 and X49), due to the low limits of water content, calculated below 41wt%, are not considered suitable. Four of the eight samples in Koutala beach are characterized as low plasticity clays, while two (K1 and K6) are promoted in the low plasticity silt sector (Figure S1: Plasticity chart, Table S5: Plasticity determination). One sample (K5) is characterized as highly plastic clay. All samples are considered suitable, except for two [(K1 and K6) 39].

The samples from the Matzavinata area, based on the calculation of the water limit, the plasticity index, and their projection on the Casagrande plasticity diagram, are mainly characterized as clays of low plasticity. Only two (samples MA10 and MA15) are characterized as highly plastic clays (Figure S1: Plasticity chart, Table S5: Plasticity determination). For the values set in the plasticity index and water limits, most samples are considered suitable for therapeutic use [39].

Most of the samples from the Chavdata area are characterized as low plasticity clays, while only two are projected in the field of high plasticity clays (samples X3 and X9). Finally, sample X5 is shown in the field of low plasticity muds, while X12 is shown in the field of high plasticity muds (Figure S1: Plasticity chart, Table S5: Plasticity determination). All samples, except one (X12) are considered suitable for therapeutic use [39].

Corfu island: The sediments from Arillas beach are mostly characterized as low plasticity silts, except for one (B41) which is projected on the low plasticity clays. Most samples are considered suitable for therapeutic use, except for three [B7, B12 and B17, (Figure S2: Plasticity chart, Table S5: Plasticity determination) 39].

In addition, nine samples from Agios Stefanos beach are characterized as low plasticity clays and eleven as low plasticity silts (Figure S2: Plasticity chart, Table S5: Plasticity determination). Most of the samples are considered suitable for therapeutic use, except for two [(A1 and A14) 39].

Specific Surface Area determination (Table S6: Specific Surface Area Determination)

Kefalonia island: Samples from Xi beach show a range of specific surface area values from 6 to 24 m2/gr. Samples X20, X22 and X26 gave the smallest measurements, while X14, X16 and X38 gave the highest. In Kefalas beach five samples have been measured, from which it appears that approximately the same conditions prevail as the samples from Xi beach, with variations in the specific surface area from 9 to 25m2/gr. The specific surface area of the fourteen analyzed samples from the Matzavinata area ranges from 9 to 19 m2/gr. Sample MA1 has the lowest and MA3 the highest value. Finally, the specific surface area values for the fifteen analyzed samples from Chavdata area show higher than the previous two areas and average 23 m2/gr.

Corfu island: Regarding the Corfu Island and specifically the Arillas beach, nineteen samples seem to have a larger specific surface area than those of Agios Stefanos, since the majority of them have more than 20 m2/gr. In Agios Stefanos beach, the thirteen measured samples showed a trend and an average of the specific surface at 17 m2/gr.

Thermal Analysis

In Kefalonia Island, part of the samples from the Matzavinata area gradually begins a large weight loss from about 670°C. This is due to calcination and decomposition of calcium carbonate CaCO3 [40, 41]. This is reflected in both the Thermogravimetric Analysis (TGA) plots (Figure S3) and the differential thermal analysis (Figure S4) obtained by calculating the first derivative of the weight loss. Similarly, the same is observed in some of the samples from Xi Beach, such as those from the Matzavinata area.

In Corfu Island, the samples from Agios Stefanos beach (Figure S5, S6) show a large weight loss from about 670 °C. This is due to the calcination and decomposition of calcium carbonate CaCO3.

Discussion

Lithostratigraphy

The research locations include both coastal (Xi and Kefalas in Kefalonia, Arillas and Agios Stefanos in Corfu) and inland areas in Kefalonia (Matzavinata and Chavdata). In total, more than two-hundred clay samples were collected, while five sand samples were also taken from Xi beach.

In detail, sediments in Kefalonia Island are interpreted as lacustrine or shallow marine sediments. More specifically, the studied deposits from the marine phase that is evident in the west and southwest of the island, is composed by marls and sandstones 300m thick, followed by a series of Pleistocene deposits 600m thick. Pleistocene sediments were deposited in a shallow marine environment that received significant clastic material from fluvial source that was the Aenos thrust front.

Miocene Arillas and Pliocene Ag. Stefanos sequences, in Corfu Island, interpreted as tidal deposits, with the Miocene/Pliocene boundary extending to the cape of Agios Stefanos.

Comparison of the two Islands outcrops showed that tidal deposits with rhythmites (alternating mudstone and sand stone beds) characterize Corfu Island, whereas Kefalonia Island is characterized by shallow marine homogenous sequence with rare thin interbedded sandstones.

Finally, grain size analysis showed that studied deposits from both Islands consist of lower than 10% sand, and so on all the studied samples are considered suitable for therapeutic use. A detailed work on the lithostratigraphy of the same research is carried out [42].

Biostratigraphy

A total of two-hundred ten samples were collected from all studied outcrops and showed that five sections are of Pliocene-Pleistocene age, whereas Arillas beach is of Miocene age and specifically Tortonian with Messinian age. In terms of environment, the deep sea seems to dominate according to the oceanicity index but this of shallow marine conditions according to the benthic foraminifera. A detailed work on the biostratigraphy of the same research is carried out [42].

TOC and CaCO3 Content

Both TOC (ranges from 0.10% to 0.77%) and CaCO3 (ranges from 12.22% to 39.27%) contents showed that are out of limits, as the accepted TOC contents is be-tween 2-5% and CaCO3 must be less than 10%. Therefore, it seems, and is in accordance with the rest results, that both parameters influenced and reduced the plasticity behavior. A detailed work on the TOC and CaCO3 content, their relationship of the same research is carried out [42].

XRF Analysis

It is indicated that the samples do not contain toxic elements, beyond the permissible use limits by humans. An exception is the element Nickel (Ni), which, however, is considered to be of low toxicity, since it mainly causes skin diseases manifested by skin rash. This reaction usually occurs between 12 and 48 hours after exposure to Nickel (Ni). The skin can become red, dry and itchy, and sweating can make an allergic reaction to nickel (worst condition). Nickel (Ni) allergy can be treated with OTC medications. However, allergy testing is recommended and if the results show that allergies are caused then the material must be processed to remove Nickel by chemical processes.

Therefore, it is proposed to produce two types of material where the basic type will not be processed at all, while the second type will be processed with the removal of Nickel and will be indicated "for sensitive skin".

Kefalonia island: The Xi beach presents loaded samples only in terms of Nickel (Ni) and Molybdenum (Mo) (almost 50%), while in a few samples, in specific horizons; limits were also exceeded in Gallium (Ga) and Tellurium (Te).

The Koutala beach presents the best conditions since only Nickel (Ni) shows in-creased values and these not too high (90-135), which means it can be used without any processing.

The Matzavinata area, apart from Nickel (Ni), which has quite low values (70-120) and beyond the limits in 11 of the 15 samples, also shows increased Tellurium (Te) values in almost all the analyzed samples, but with values of 2 and a limit of <1. Increased value in Molybdenum (Mo) showed a sample but it is in a certain horizon (at the roof of the sequence) and therefore its use can be avoided by removing from the sediments to be used the upper 3m.

The Chavdata area, apart from Nickel (Ni), which has quite low values (100-190) and all samples beyond the limits, also shows increased Tellurium (Te) values in almost half of the samples but with values of 2 and a limit of <1, and increased values of Molybdenum (Mo) in 3 of the 15 samples which, however, are in a specific horizon (at the base of the sequence) and therefore its use can be avoided.

Corfu island: The Arillas beach presents 5 out of 21 rare elements, Nickel (Ni), Gallium (Ga), Strontium (Sr), Molybdenum (Mo), Tellurium (Te), values that are beyond the permissible limits, and for this reason it is proposed to reject the specific area for extended use or only in places where the rare elements are absent.

The Agios Stefanos beach, although it shows exceeding limits in 5 of the 21 rare elements, but only in characteristic horizons, it can be used but avoiding the horizons where the analyzes showed exceeding the limits in Gallium (Ga), Strontium (Sr) and Tellurium (Te).

XRPD Analysis

It is given that it is needed as much clay mineral content as possible in the clay, and of these the most desirable is the presence of montmorillonite, due to the high C.E.C. and the plasticity that imparts to the mature clay. The content limits proposed by [43,7] range between 30-40%.

In the analyzed samples the clay minerals range from 5-31%. The lowest percentages are observed in the samples from Xi beach [Kefalonia island (5-13%)], compared to the samples from Agios Stefanos beach [Corfu Island (18-31%)]. Smectite ranges from 1-6%, with the highest values at Agios Stefanos beach and the lowest in Xi beach with values 1-2%.

Correlating the results of the elemental determination of the main elements with those of the X-ray analysis to determine the mineralogical composition of the samples, the uniformity and compositional similarity of all the samples is easily established.

Their composition is mainly siliceous as they consist of SiO2 at a rate of ~40%, while the participation of CaO (~25%), Al2O3 (~15%) and Fe2O3 (~5%) is notable. Also, the main mineralogical phases are calcite, quartz, and plagioclase while the clay phases and dolomite complete the composition. The separation techniques of the clay fraction showed the participation of chlorite, illite and kaolinite in all samples. The only sample that differs visually (color), elementally and clearly mineralogically from the rest is X71. This sample is light red-brown in color and has a carbonate composition, while no clay minerals participate in its composition.

In sample X71, which is from the "red sand" on the beach, quartz almost disappears (as in the main elements SiO2), while the percentage of calcium is more than doubled (as in the main elements CaO), reinforcing the view of the negative correlation between them, which emerged for the main elements, and confirms their main connection with silicate minerals, which apparently dissolve during their surface exposure and contact with sea-water, and consequently remove the clay minerals.

Finally, it should be noted the presence of pyroxene and amphibolite, magmatic minerals, show the source of origin of the materials, which apparently come from rocks that were affected by the penetration of magma towards the earth's surface, but without the manifestation of volcanic activity.

pH Determination

The natural pH of the skin is around 5, while to avoid skin irritations a pH value between 9 and 10.5 is recommended for the use of the clays in pelotherapy centers, while there are no special specifications for the common clays.

The fact that in the present research the pH was measured with values of 8.1-9.6 shows that the sediments are suitable for use.

Plasticity Determination

Plasticity is an indicator of the mud's ability to be molded into various shapes. The increase in the water holding capacity of the mud results in an increase in its heat capacity, thus improving its thermal action. The plasticity limit results in our samples were 17-48 (PL). Therefore, most samples were classified as low plasticity soils but close to the high plasticity limits.

Specific Surface area Determination and Thermal Analysis

These two factors are affected by the mineralogical composition of the material and in particular the clay minerals, for this reason the measured values are considered marginally below the limits. Correlating the above two parameters with the quality of the material, is suggested that the result of maturing a clay with thermometallic water is the creation of therapeutic clay, i.e., the creation of a material of perfect mixing and uniform dispersion of the solid phase within the liquid at a rate of 50 + 5% w /w which brings together the advantages of each phase. The high specific gravity of the clay (1.4-1.6 g/mL) allows the human to float effortlessly during total immersion, while at the same time reducing muscle spasm, facilitating movement. The simultaneous presence of solids and water in the clay also aims to improve its thermal behavior for a better thermal therapeutic effect. Water with its high specific heat increases the heat capacity of the clay, while solids as poor conductors of heat reduce the thermal conductivity of the clay increasing heat retention. Therefore, through the permeability of the skin and with ion exchange processes, the clay provides the human body with trace elements and compounds with a pharmacodynamic effect.

Conclusions

It is the first time for such extensive sampling and analysis of natural exposed mud-stones for pelotherapy use. The evaluation of the quality of the materials in four areas of Kefalonia (Xi and Koutala beaches, Matzavinata and Chavdata inland areas) and two areas in Corfu (Arillas and Agios Stefanos beaches) is completed with all the proposed measurement - analysis - determination procedures. A total of 10 parameters were laboratory and tested in one-hundred twenty samples.

From the combination of all the above laboratory analyzes as described and interpreted, it is suggested that almost all the areas could be utilized in the direction of using the materials for pelotherapy because they do not contain toxic elements, beyond the permissible limits their use by human, although some of the parameters showed out of limits values e.g. TOC and $CaCO_3$ content.

An exception is the element Nickel (Ni), which, however, is considered to be of low toxicity, since it mainly causes skin diseases manifested by skin rash and can be treated with OTC drugs or with further processing and removal, if deemed necessary that causes allergies. Ni ratio limits are reported for the free Ni element and not for the Ni oxides, and must therefore be considered.

The only area that should be rejected for use of that of Arillas beach, because of many toxic element's presence (in relation to the other areas) and high sand beds ratio (rhythmites of sand/mud beds). It should be noted that all areas have Pliocene sediments while the Arillas beach has Miocene sediments.

Considering human activity with the use of materials for pelotherapy and the results for biological activity [44], which they considered safe for Xi Beach, it must be emphasized that a careful evaluation of the materials is required.

For the maturation of the material for pelotherapy, organic matter should be added during the preparation of the material (to increase the participation of the organic matter > 2%) to reinforce the material in the direction of maturation. However, the fact that the material is already being used shows that it can be used in its current state, but obviously this application has a limited application.

The samples were studied for plasticity, pH, specific surface area and mass change with increasing temperature and showed they can be used for therapeutic use as they are and without any intervention. However, to improve plasticity, montmorillonite could be added as its presence increases the plasticity and specific surface area of the material.

Regarding the pH determination, based on the specifications of the international as-sociation of pharmacology, that of smectites is recommended which is 9-10.5, the studied samples are either within their limits of use or very close to them.

In conclusion, five from six studied areas and their materials could be used as they are without any processing, although they have small chances of affecting skin diseases and lower values than the required plasticity. With a little processing, on a case-by-case, all indicators can be improved, producing materials that are within their limits of use, for all the parameters required to consider a material suitable - ideal for mud therapy.

The attempt to protect geosites of Kefalonia-Ithaca geopark, like this of Xi, new locations are highlighted with equivalent materials, these of Koutala, Matzavinata and Chav-data areas, where there are huge amounts of muds for pelotherapy use and the development of spa.

Author Statements

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