Psammotherapy in Porto Santo island (Madeira archipelago)

Celso de Sousa Figueiredo GOMES[(1)], João Baptista Pereira SILVA[(1)], Jorge Hamilton GOMES[(1)]

[(1)]Centro de Investigação "GeoBioTec" da FCT (Fundação para a Ciência e a Tecnologia), Departamento de Geociências,, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro (Portugal)
cgomes@ua.pt; madeirarochas@netmadeira.com

Recibido: 28-03-10
Aceptado: 20-06-10

Abstract
Psammotherapy is a practice that uses sand-baths for therapeutic purposes. Sand-baths in the biogenic carbonate sand from Porto Santo Island, in the archipelago of Madeira, constitutes a good example of the positive interaction of minerals on human health. Recent studies provided much information on relevant physical and chemical properties that could explain this sand's 200-year-long use, although on a much empirical manner, for the treatment of muscular-skeletal (rheumatic and orthopedic) diseases, such as rheumatoid arthritis, gout, osteoporosis, and fibromyalgia.
The biogenic carbonate sand from Porto Santo Island consists mainly of bioclasts of calcareous red algae (*Rhodophyta*), sand-bathing traditionally taking place in the dry sand of the transition zone beach/frontal dune, along the southern coast of the island.
Analysis of chemical data shows that Ca, Mg and Sr are the major elements of the biogenic carbonate sand from Porto Santo, elements which are bio-essential for human health. P, S, Si, Al, I, Br, F, B, V, Zn, Cu, Fe, and Se were the minor/trace elements identified in the same sand.
The average grain size of this biogenic carbonate sand is estimated at 0.200mm, all sand grain sizes ranging between 0.063mm and 0.500mm. Also, the shape of sand grains is mainly tabular or platy, an essential characteristic for a good adhesion to human skin.
In order to be therapeutically effective, sand-bathing in the biogenic carbonate sand from Porto Santo requires sand temperature to be slightly higher (40-42ºC) than body temperature (37ºC), so as to promote body sweating, an essential condition for the interaction sand/human body. The dermal absorption of the bio-essential elements liberated from sand dissolution is responsible for the healing properties of sand-bathing.

Key words: Porto Santo' island, Medical geology, Psammotherapy, Biogenic carbonate sand, Mineralogical and geochemical properties

Psammoterapia en la isla del Porto Santo (Archipiélago de Madeira)

Resumen
La Psammoterapia es una práctica que utiliza los baños arena con fines terapéuticos. Los baños en la arena biogénica carbonatada de la Isla de Porto Santo, en el archipiélago de Madeira, constituyen un buen ejemplo de la interacción positiva de los minerales en la salud humana. Estudios recientes proporcionan mucha información relevante sobre las propiedades físicas y químicas que podrían explicar el uso de estas arenas desde hace 200 años, aunque de manera empírica tanto, para el tratamiento de las enfermedades músculo-esqueléticas (reumáticas y ortopédicas), como la artritis reumatoidea, gota, osteoporosis y fibromialgia.
La arena carbonatada biogénica de la Isla de Porto Santo se compone principalmente de bioclastos de algas calcáreas rojas (Rhodophyta), el baño de arena tradicional tiene lugar en la arena seca de la zona de transición entre la playa/frontal de dunas, a lo largo de la costa sur de la isla.
El análisis de los datos químicos demuestra que Ca, Mg y Sr son los principales elementos de la arena biogénica carbonatada de Porto Santo, elementos que son bio-esenciales para la salud humana. P, S, Si, Al, I, Br, F, B, V, Zn, Cu, Fe, y Se fueron los elementos menores/elementos trazas identificados en la misma arena.
El tamaño medio de grano de esta arena biogénica carbonatada se estima en 0,200 mm, todos los tamaños de grano de arena van entre 0.063mm y 0.500mm. Además, la forma de granos de arena es principalmente tabular o laminar, característica esencial para una buena adherencia a la piel humana.
Con el fin de ser terapéuticamente eficaz, los baños de arena en la arena biogénica carbonatada de Porto Santo requieren una temperatura de la arena ligeramente superior (40-42º C) que la temperatura corporal (37º C), con el fin de facilitar la sudoración del cuerpo, una condición esencial para la interacción arena/cuerpo humano. La absorción cutánea de elementos bio-esenciales liberados desde la arena es responsable de las propiedades saludables de los baños de arena.

Palabras claves: Isla de Porto Santo, Geomedicina, Psammoterapia, Arena biogénica carbonatada, Propiedades mineralógicas y geoquímicas

REFERENCIA NORMALIZADA
Gomes CSF, Silva JBP, Gomes JH. Psammotherapy in Porto Santo island (Madeira archipelago). Anal Hidrol Med, 2011, vol. 4, 11-32.

INTRODUCTION

Minerals are fundamental constituents of the natural environment. Over the years, man has acquired experience in the existence of interactions between mine-

rals and the environment, as well as in the beneficial and hazardous effects they have upon living beings; man, other animals, and plants.

The recognition of the existence of an intimate relationship between Geology, particularly expressed by Mineralogy and Geochemistry, and human/animal health, has led to the recent development of a new field of science, Medical Geology.

The interaction of the natural environment on human health and living quality, particularly when geologic processes and geologic products are involved, currently arouses the interest of scientists, politicians and the communities.

Empirical knowledge of human health, whose practice is called Empirical Medicine or Folk Medicine, is essential to many aspects of man's life and activity. However, in regard to this subject, man's quest for rational explanations based on science and technology is hereby considered as equally essential.

As a matter of fact, with perseverance and step by step, man will be increasingly successful in understanding the interaction of minerals and other geo-resources with human health, by using the available accumulated experience and scientific information, both fundamental and applied, provided by specialists in distinctive scientific domains (chemistry, biochemistry, biology, biotechnology, mineralogy, geochemistry, hydro-chemistry, materials science, medicine, public health, pharmacy, nutrition, and others).

The use of minerals for medicinal purposes is, most probably, as old as mankind itself. Currently, there is a growing interest on health treatments using natural methods, alternative to those of conventional medicine. This is called naturotherapy, and involves distinctive natural resources and application methods[1].

Examples of health treatments involving minerals include: *hydrotherapy* (the use of natural mineral water, thermal or not, for therapeutic purposes); *crenotherapy* (the medically-assisted ingestion of natural mineral water, thermal or not, for therapeutic purposes); *oligotherapy* (the use of trace elements or oligoelements as nutrition supplements for therapeutic purposes); *geophagy* (the ingestion of certain types of clay or soil, as healing materials or nutrition supplements); *peloidtherapy* or *pelotherapy* (the topical application of mud and peloids for therapeutic and cosmetic purposes); and *psammotherapy* or *arenotherapy* (the use of special sands, under the form of sand-baths, for therapeutic purposes). In the particular case of psammotherapy, special sands are currently used worldwide in therapeutic applications, particularly for the treatment of muscular-skeletal diseases.

According to Federicci[2], when marine sand is used as a therapeutic agent, it provides tonicity to the muscular and the locomotor systems. The author says that a sand-bath or psammotherapy is a 10-20 minutes application of a layer of sand, extracted from the beach down to depths not higher than 30cm. Also, the author attributes its therapeutic action to the thermal capacity of the sand.

Murgia *et al*.[3] demonstrated the efficacy of psammotherapy with the production of endogenous corticoids, the increase of glucose content, the decrease of eosinophils, and the increase of the secretion of urinary testoroids.

As a rule, sand is composed of fine grains interspersed with air. Being a porous system, it is characterized by low heat conductivity. Therefore, the sand system is able to release the heat absorbed from the sun's rays without causing burns, in spite of its high thermal gradient.

Although essentially on an empirical basis, psammotherapy has been used for the treatment of the following diseases: osteoarthritis, post-trauma conditions (fractures, sprains, etc.), extra-articular rheumatism, inflammatory rheumatism, and fibromyalgia.

Psammotherapy is a worldwide practice, well represented by the three following examples: 1. sand-baths in the biogenic carbonate sand occurring on the beaches of Porto Santo island, archipelago of Madeira; 2. sand-baths in the radioactive sand occurring on the beaches of Guarapari, state of Espírito Santo, Brazil; 3. sand-baths in the dark volcanic sand occurring in the Thermal Centers of Beppu and Ibusuki, Kyushu island, Japan, which are naturally warmed by geothermal heat.

Whenever naturotherapy involves minerals or other mineral resources, it can be named Geomedicine, or Medical Mineralogy and Geochemistry, or Environmental Medicine, or Medical Geology. Currently, Medical Geology is the recommended expression to define this globally emerging scientific discipline that comprises both fundamentals and practices. These practices involve, essentially as positive or negative conditioners of human health, minerals *s.l. (sensu latu)*, a concept that includes certain minerals *s.r. (sensu restrictu),* i.e., inorganic, natural, and crystalline solids, as well as mineral-derived macro and microelements, the oligoelements or *trace minerals*, which are present in the soil, food, waters (spring water, thermal or not, and seawater), and in the air.

The interactions of man and the environment (essentially represented by air, water and minerals) can be either beneficial or hazardous (possibly lethal). These interactions are the realm of Medical Geology, a fast-growing scientific field not only involving geoscientists and physicians, but also other specialists of public health, biology and biochemistry, environment, etiology, epidemiology, toxicology, etc[4-5-6-7-8].

Medical Geology was created about a dozen years ago to investigate and evaluate both the negative and the positive impacts on public health of these minerals *s.l. (sensu latu)*, which are present in the natural environment.

There are many publications about this subject, and within those dealing with the negative or adverse impacts, the following deserve particular mention: Nriagu[9]; Selinus & Frank[10]; Finkelman *et al.*[5]; Bowman *et al.*[6]; Appleton[11]; Derbyshire[12]; Smedley & Kinniburgh[13]; Edmunds & Smedley[14]; Fordyce[15]; Fuge[16]; Weinstein & Cook[17]; Centeno *et al.*[18]; Selinus *et al.*[19]; Gomes & Silva[1]; Bunnell *et al.*[20]; Carretero & Pozo[21] and Gomes *et al.*[22]. Several diseases are known to be caused by an exposure to an excessive dose of minerals *s.l.*, such as silicosis, asbestosis, selenosis, fluorosis, arsenicosis, manganism, saturnism, hydragyrism, berylosis, siderosis

and baritosis. Similarly, certain health problems are caused by a deficiency of bio-essential elements in food[1].

The positive or beneficial impacts are reported by various authors, such as: Galán *et al*.[23]; Robertson[24]; Novelli[25-26-27]; Veniale [28-29-30]; Lopez-Galindo & Iborra[31]; Reinbacher[32-33]; Lopez-Galindo & Viseras[34]; Carretero[35]; Carretero *et al*.[36]; Droy-Lefaix & Tateo[37]; Silva[38]; Gomes & Silva[39-1-40-41-42]; Lindh[43]; Combs[44]; Finkelman & Limpitlaw[45]; Carretero & Pozo[21]; Gomes *et al*.[46-47-22]; and Rautureau *et al.*[48]. Most of these references are related to the health benefits of clay (most probably the first mineral resource to be used by man as a healing material) and to the biological functions of bio-essential chemical elements. In the case of clay, its use is based on the specific properties of clay minerals (hydrous phyllosilicates characterized by their negative electrical charge, nanometric size, platy or fibrous-shaped particles, their ion exchange, absorption and desorption capacities, and also their chemical inertia). These properties are essential for the application of clay and clay minerals in pharmacy, pelotherapy and aesthetic medicine[1].

This paper investigates the relevant properties of the biogenic carbonate sands from Porto Santo Island, traditionally used for therapeutic purposes. Particularly focused on are the mineralogical and geochemical properties of this specific sand, so as to seek scientific arguments that could justify the decade-long empirical use of this type of sand as healing material for muscular-skeletal diseases, such as rheumatoid arthritis, osteoporosis and fibromyalgia.

Biogenic carbonate sands, similar in composition to those occurring in Porto Santo Island, also occur on other islands of the archipelago of the Azores (islands of Santa Maria and Terceira), the archipelago of the Canary Islands (islands of Gran Canaria, Fuerteventura and Lanzarote) and of the archipelago of Cape Verde (islands of Sal and Boavista). All the archipelagos referred to are part of the biogeographic archipelago of Macaronesia. However, only in Porto Santo are the biogenic carbonate sands being used for therapeutic purposes, under the form of sand-baths.

MATERIALS AND METHODS

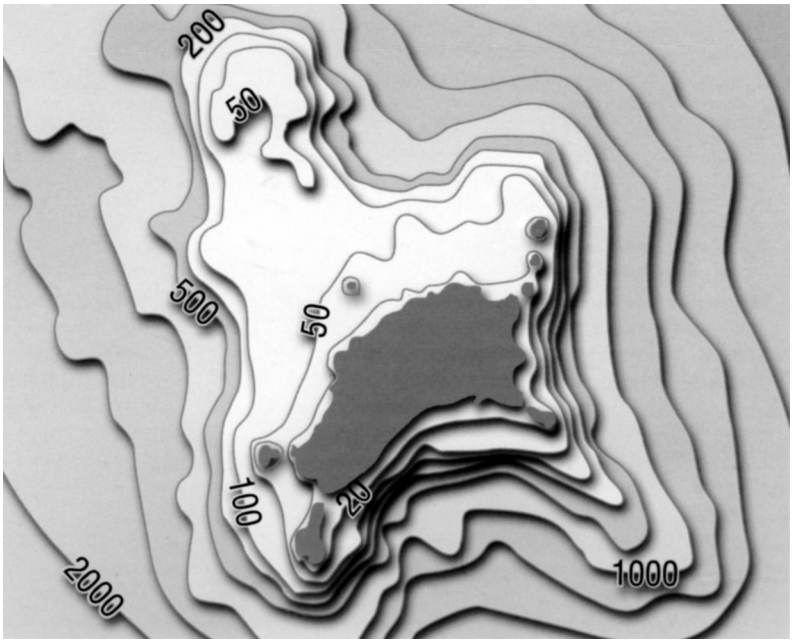
Materials and their origin

Porto Santo is a small Atlantic island of volcanic origin with a total area estimated at 42.2km^2 (10km long by 4km wide, approximately), which is part of the archipelago of Madeira, located to the west of southern Europe, between the coasts of Portugal and Morocco, and between the archipelagos of the Azores and the Canary islands.

The source of the biogenic carbonate sand that occurs on the beaches and dunes of the island was a reef that developed during the late Pleistocene, on the shallow

north-western coastal shelf of the island (Figure 1). The reef was mostly constituted by calcareous algae, symbiotically associated to corals and other organisms. The fragmentation of the calcareous exoskeletons from the organisms making the bioherm took place due to the abrasion produced by strong sea-waves, as seawater level continuously lowered during the Last Great Glaciation (LGG) and the reef became gradually exposed. At the latitude of Porto Santo, when the maximum LGG was reached, about 20,000 years ago, the mean seawater level had lowered a little over one hundred meters.

Figure 1 - Shallow coastal shelf of the northwestern coast of Porto Santo expressed by the bathymetric curves 0-100m, where the reef developed particularly



The carbonate minerals making up the sand of the beaches and dunes from Porto Santo participate in the composition of varied bioclasts (very fine fragments of calcareous algae with arborous style and calcareous exoskeletons of other organisms, which formed the huge barrier reef that is thought to have developed on the northern coast of the island about 30,000 – 35,000 years ago).

Strong-blowing trade winds provided both the transportation and the accumulation of calcareous sand grains on the beaches formed on the north coast of the island. From these beaches, the sand was transported by strong trade winds, forming

the spectacular dune deposits which can now be observed in some locations of the north littoral and of the island's interior. Additionally, sea currents transported the sand around the island and accumulated it in the open bay located on the southern coast, forming the present day 9-km long beach (Figure 2), much sought after and appreciated by tourists, and in other much smaller beaches, as is the case of Praia do Calhau, located on the eastern coast.

Figure 2 - General view of the southern coast of Porto Santo and of its excellent beach, made up mostly of biogenic carbonate sand

The biogenic carbonate samples from Porto Santo submitted to analytical studies were collected (9 samples altogether) on the frontal dune of the southern coast, since sand-baths are traditionally taken in the dry sand of the frontal dune.

Sample MPSH was collected opposite and close to Hotel Porto Santo, the first facility on the island offering a planned psammotherapy programme, to be carried out indoors, more precisely at its Geomedicine Centre. Only the analytical results of this sample are herewith disclosed, since the analytical results corresponding to the other samples show that they are very similar in composition to the one being selected.

Radiocarbon dating indicates that the age of the biogenic carbonate sand of Porto Santo is within the range 15,000-31,000 years BP.

Methods

Several analytical methods were applied to study the relevant properties of the biogenic carbonate sands, and most of the equipments used were provided by the Universidade de Aveiro.

- Grain Size Analysis was performed using a battery of ASTM sieves.
- X-Ray Diffraction Analysis was performed using an X-Ray Diffractometer from PAN analytical, X'Pert-PRO MPD, Dy 1304.
- Chemical Analysis was carried out using an X-Ray Fluorescence Spectrometer, from PAN analytical, PW 4400/40 Axios, Dy 1051.
- Bioclast Morphological Analysis and Classification was performed using a Nikon SMZ 800 binocular microscope.

Radiocarbon Dating was performed at the Laboratório de Datação por Radiocarbono do Instituto Tecnológico e Nuclear, in Sacavém, Lisbon, and at the Laboratoire du Institut Royal du Patrimoine Artistique, in Brussels.

RESULTS AND DISCUSSION

Biogenic carbonate sand: Mineralogical and geochemical properties

Recent studies[39-38-1-41-47] provided much information about the physical and chemical properties of the biogenic carbonate sand that occurs on the island of Porto Santo, in the archipelago of Madeira. Although on an empirical basis, this sand has been used for many years in the treatment of muscular-skeletal (rheumatic and orthopaedic) diseases. The referred to applications currently take place outdoors (traditional sand-baths taken in the dry sand of the transition zone between the beach and the frontal dune) and indoors, in specialized Geomedicine Clinics and in Thalassotherapy Centres.

The following properties were determined in representative samples of the biogenic carbonate sand from beach deposits and/or frontal dunes occurring in Porto Santo island: grain size and shape; bioclasts and volcaniclasts' nature and ratio; hardness; specific heat and heat diffusiveness; mineralogical and chemical composition (major, minor and trace elements); Mg/Ca and Sr/Ca ratios and chemical dissolution rate.

Figure 3 shows a binocular field of the biogenic carbonate sand (sample MPSH) from Porto Santo. The black grains correspond to titanomagnetite.

The Mhos hardness of the biogenic carbonate sand from Porto Santo, measured after the extraction of the magnetic grains, is 3, a value that corresponds to the hardness of calcite and is much lower than the value 7, which corresponds to the hardness of quartz sand, current in continental European beaches. Also, the bio-

genic carbonate sand from Porto Santo exhibits a yellowish or golden-like color, which explains why Porto Santo is known as the island of the "golden beach". This sand is also characterized by its very fine grain. Around 95% of the sand grain size lies within the range 0.250mm-0.125mm. All grains of sand have sizes within the range 0.063mm-0.500mm.

Figure 3 - Bioclasts and volcaniclasts in a specimen of biogenic carbonate sand (MPSH) from Porto Santo; seen in black are titanomagnetite grains

Another fundamental characteristic of the biogenic carbonate sand of Porto Santo, highly relevant in terms of traditional therapeutic applications, is the predominant tabular shape of its particles (mainly tiny fragments of calcareous algae).

Associated to the yellowish-brownish grains of calcium carbonate, a small amount of dark lithic grains (most of them magnetic) occur, on average not higher than 2% in the sand from beaches, and less than 1% in the sand from dunes. The lithic grains are derived from the erosion of the volcanic rocks (basalt, trachyte and tephra) of Porto Santo.

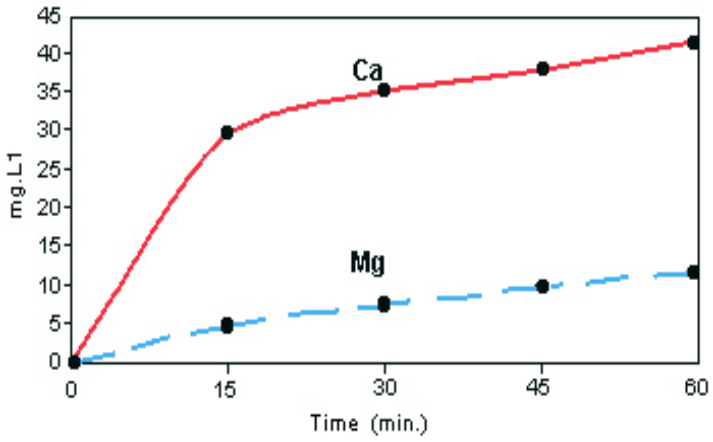
Figure 4 shows the dissolution curves for Ca and Mg, corresponding to the interaction of the biogenic carbonate sand from Porto Santo with an acid solution (pH=5.5) which replicates human sweat.

Whereas Ca/Mg ratio in the bulk sample of Porto Santo is about 20 (see Table I), Ca/Mg ratio shown in the dissolution curves is around 4. This means that Mg related with Mg-calcite enters into solution more rapidly than Ca.

Dissolution rates were determined at laboratory temperature (ca.20ºC), whereas in sand-baths the dissolution of sand by human sweat takes place at twice the temperature of the laboratory. Also, in sand-baths the sweat is being renewed, which

explains that the dissolution kinetics would be different from the one verified in the laboratory.

Figure 4- Dissolution curves for Ca and Mg formed when the biogenic carbonate sand interacts with the acid human sweat (experiences were carried out at laboratory temperature, i.e. around 20ºC).



According to Morse & Arvidson[49], the temperature, the crystalline structure and the chemistry, as well as the grain size, shape and porosity of the calcium carbonate species (Mg-calcite, aragonite and calcite) might influence the dissolution kinetics.

Table I - Chemical analysis of major elements (in %) in the biogenic carbonate sand (sample MPSH) from Porto Santo. Fe_2O_3- corresponds to total iron content; I.L. (ignition loss) was obtained by heating to 1100ºC, for 1 hour.

	SiO_2	Al2O3	TiO2	Fe2O3	MnO	CaO	MgO	K2O	Na2O	I.L.
MPSH	1.40	1.05	0.20	0.80	0.10	53.10	2.50	0.31	0.50	41.40

The studies we have carried out using XRD analysis on the dissolution residues of the biogenic carbonate sand from Porto Santo indicate that as the dissolution progresses, the content of Mg-calcite diminishes.

Figure 5 shows the X-ray diffraction pattern corresponding to the studied sand.

Three forms of calcium carbonate were identified in all samples: calcite, Mg-calcite and aragonite, their relative contents varying from sample to sample.

Calcium (Ca), magnesium (Mg), and strontium (Sr) are quantitatively important chemical elements present in the biogenic carbonate sand (see Table I and Table II), which are important in terms of health applications.

Figure 5 - X-Ray Diffraction patterns showing the type of carbonate minerals present in the biogenic carbonate sand (sample MPSH) of Porto Santo.

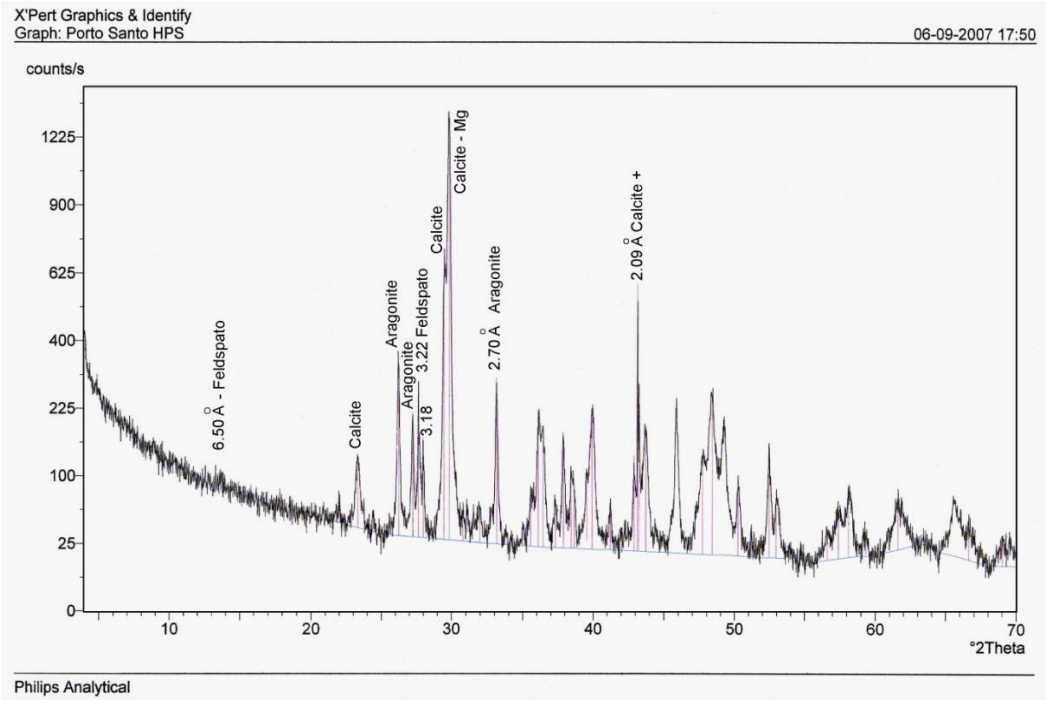


Table II - Chemical analysis of minor and trace elements (in ppm), mostly essential to life, making up the biogenic carbonate sand (sample MPSH) from Porto Santo

	Sr	P	V	S	Zn	Cu	Ni	Co	Cr	Se
MPSH	590	40	15	20	10	6	4	5	9	25

Ca essentially enters the composition of calcite (stable); Mg essentially enters the composition of Mg-calcite (meta-stable), and Sr essentially enters the composition of Sr-aragonite (meta-stable).

All this chemical data was obtained after separation of magnetic minerals. The content of magnetic minerals determined in the studied samples of the biogenic carbonate sand from the frontal dune existent in the southern coast varies within the range 1-2%.

Magnetic separation with a simple magnet can separate titanomagnetite and most of the plagioclase (since it contains inclusions of iron oxides), minerals associated to carbonate minerals.

Biogenic carbonate sand: Therapeutic assets and methodologies

Figure 6 and Figure 7 show the sand-bathing facilities of the former and the current Geomedicine Centre of Hotel Porto Santo.

Figure 6 - Sand-bath facilities at the pilot Geomedicine Clinic of Hotel Porto Santo, in Porto Santo

The grain size of the biogenic carbonate sand from Porto Santo is very fine, and due to their tabular shapes most sand grains become stuck to the skin (Figures 8 and Figure 9) after sand-bathing (like breadcrumb), and so they should remain for some minutes until the skin dries.

This peculiar shape of the sand grains provides a firm adhesion to the parts of the human body involved in sand-bathing; and such firm adhesion allows a better and more lasting interaction between the carbonate particles and the human sweat being exuded, since in the sand-bath, sand is dry and warm.

The sand used in sand-bathing for medicinal purposes, either outdoors or indoors in specialized clinics, must be dry and warmed to a temperature of 40-42ºC, i.e., a little above the normal body temperature of 37ºC; outdoors, in the natural environment, that temperature is normally attained at the interface body/sand, when a 5cm-thick layer of sand is used to cover the parts of the body under treatment.

Figure 7 - Sand-bath facilities at the current Geomedicine Clinic of Hotel Porto Santo, in Porto Santo

Figure 8 - The biogenic carbonate sand becomes firmly adhered to the sweated body like a breadcrumb

The biogenic carbonate sand from Porto Santo, more precisely the dry sand from the transition zone between the beach and the frontal dune, possesses thermal properties characterized by their singularity, such as specific heat and heat diffu-

siveness. In fact, the sand behaves as a good heat reservoir (at the surface it can reach temperatures as high as 65ºC, i.e., scalding temperatures).

Figure 9 - Detail of a foot showing the biogenic carbonate sand adhered to the skin

During sand-bathing, the human body receives and stores heat, and the acid sweat (pH variable within 4.1 and 6.5, depending on the person) being produced reacts with the carbonate sand (calcium carbonates are soluble in acid solutions) rich in fragments of calcareous algae, liberating in the ionic form, Ca^{2+}, Mg^{2+}, Sr^{2+}, P^{+5} and the other existing cations, which are freed at the surface of the skin and can be absorbed through it. The surface of the human body of a normal adult is estimated at about1.5 m^2. Also, it is known that in 1cm^2 of skin there are, in average, 1 metre of blood capillary vessels, 4 metres of nervous fibres, 3 millions cells, 100 sweat-producing glands and 15 sebaceous glands, besides 100 to 500 sensorial receptors. Therefore, in practical terms, the skin corresponds to a communication structure between the surrounding environment represented by the adjacent body tissues, and the cerebrum maintained in continuous functioning through the nervous cells.

In the case of the Porto Santo sand-baths, if the temperature of the sand is above body temperature, the sweat formed dissolves the carbonates of the sand. The chemical elements liberated increase their concentration in the liquid phase, meanwhile formed at the interface sand/body. After the sand-bath, and before sand removal with a sea-bath or a shower, it is fundamental to dry the body in order to allow the sorption through the skin of the chemical elements existing in the referred to liquid phase.

The carbonate particles that make up the sand, particularly the fragments of calcareous algae which are relatively unstable under acidic conditions, are partially

dissolved by the perspiration liquid that becomes particularly enriched in Ca, Mg, Sr, and other chemical elements. As was said before, these elements become free and available to pass through the epidermis and to be absorbed into dermis cells.

Ca is an important chemical element present in sea water and in other natural systems, considered of paramount importance for human health; in fact, Ca under the ionic form Ca^{+2} , is essential for the functional integrity of both muscular and nervous systems, and for a normal cardiovascular function.

Also, it is well-established that calcium therapy simultaneously with vitamin D therapy increases the capacity for calcium absorption. Ca is, in quantitative terms, the major component of Porto Santo biogenic carbonate sand, whose grains are made essentially of $CaCO_3$ bearing Mg^{+2} and Sr^{+2}, a compound that in acid solutions (pH <7) easily dissociates into the ions Ca^{+2}, Sr^{+2}, $Mg^{+2}$and CO_3^{-2}.

Mg is another significant chemical element that exists in sea water and other natural systems, such as certain soils and spring waters, and which is equally very important for human health. Under the form of Mg^{+2}, it produces well-known effects, based on animal experimentation or tests "*in vivo*". It decreases cardiovascular pathologies, because it plays an important role in the metabolism of fats, by reducing the athroma plaque that causes atherosclerosis.

Mg content increases as the content of Mg-calcite increases, Mg-calcite content being directly dependent upon the content of bioclasts of calcareous Rhodophyceae algae.

Some edible vegetables and fruits, such as melon and watermelon, cultivated in soils developed on the biogenic carbonate sand of Porto Santo are particularly rich in Ca, Sr and Mg[1]. Several other beneficial effects are attributed to the element Mg: anti-stress, anti-oxidant, cardio-protector, anti-infectious, anti-inflammation, and re-mineralizing.

It is assumed that Mg in diets increases bone density and activates an enzyme that favours the incorporation of Ca in bones. In fact, Mg enters, in very small amounts, the composition of hydroxyapatite, the biomineral that makes up the bones, and is continuously reabsorbed and redeposited in the bone tissues. People suffering from osteoporosis appear to present Mg deficiency. Osteoporosis, the degeneration and loss of bone mass, usually associated with older and less active individuals, has led people to consume food and drink that has added calcium and vitamin D (needed for proper calcium uptake). However, these supplements appear to be insufficient to preserve bone integrity, so it has been put forward that other oligoelements, such as Mg, Sr, F and Si, could play essential roles.

MgO contents between 2.5-4% are also to be found in the biogenic carbonate sand of Porto Santo, the highest MgO values correspond to sands with lowest aragonite content and with highest magnesium bearing calcite or Mg-calcite content. As a rule, in the studied biogenic carbonate sands, Mg content increases as sand dating values, determined by radiocarbon, decrease.

Strontium (Sr) is also an important chemical element present in seawater and in other natural systems that is equally important for human health. Sr^{+2} has an ionic radius 132 pm (picometer), which is much higher than the ionic radius of Ca^{+2}, 99pm. Therefore, Sr^{+2} more easily get into the more-open structure of aragonite, than into the more closed or dense *calcite* structure. Both aragonite and calcite are distinctive natural forms or polymorphic forms of the chemical compound $CaCO_3$. When relatively high concentrations of Sr^{+2} enter the aragonite structure, this structure becomes much more stable than in relatively low concentrations. A higher content of Sr^{+2} in the aragonite structure stabilizes it for longer, before the inversion of the unstable aragonite structure into the stable calcite structure takes place.

In Porto Santo, the Sr content lies within the range 1,800-2,500mg/kg for older biogenic carbonate dune sand, and within the range 2,500-3,500mg/kg for more recent biogenic carbonate beach and dune sand. As a rule, in the studied biogenic carbonate sands, Sr content increases as sand dating values decrease.

Human bones and teeth are made of bioapatite, a biomineral composed of calcium phosphate, whose structure is close to the structure of the mineral hydroxylapatite and can accommodate OH, CO_3, F, Si, Mg and Sr.

As said before, Sr can stabilize the unstable structure of aragonite for a longer period of time. Similarly, Sr could make the structure of bioapatite forming the bones more stable, preventing the loss of bone mass that causes osteoporosis. In nature, where Sr concentrations are high, discrete apatite minerals form, such as strontium hydroxyapatite $(Ca, Sr)_5 (PO_4)_3 (OH)$. Although to our knowledge, it is not considered an essential element for human health, strontium is always present in bones, in very small contents (parts per million).

Recently, a pharmaceutical for the treatment of osteoporosis was developed and commercialized, whose active principle is an organic compound-bearing Sr, strontium ranelate, which decreases bone re-absorption. This pharmaceutical won the Galien 2005 prize, which awards both innovation and investigation in the pharmaceutical industry.

As said before, a healthy mineralized skeletal and dental system requires a good nutritional diet that includes calcium, phosphorous, magnesium, strontium, fluorine and silicon. Fluorine is found in relatively high contents (2-4mg/l) in Porto Santo spring water, dental fluorosis, a disease causing mottle teeth, being common among the residents of the island. Silicon is another element found in spring water in relatively high contents, its main source being hyaloclastite tuff occurring in large outcrops.

Among the minor chemical elements, phosphorous (P), sulphur (S), and iodine (I) are significantly represented in the biogenic carbonate sand of Porto Santo (see Table II).

Phosphorous (P), for instance, is considered essential for the integrity of cellular structures and for many catabolic processes, because it controls the enzymatic activity and it is important for the liberation of oxygen to human body tissues.

Sulphur (S) is a bio-essential element, and a component of enzymes and other key proteins. Iodine (I) is another bio-essential element. A low intake of iodine can cause IDD (Iodine Deficiency Disorders), the most common of these disorders being goitre and cretinism. IDD are closely related to geography, that is, with the geographic location of populations. Iodine is much more abundant in the sea, along the seashore and in areas close to the sea, than inland.

In Porto Santo treatments involving sand-bathing are addressed to people suffering from rheumatoid arthritis, fibromyalgia and osteoporosis. This last disease remained for long almost unknown (as it is a silent disease, without symptoms), and its consequences were not well-established.

In regards to osteoporosis, an epidemiological comparative study[50] carried out by specialists in orthopaedics from the Hospital of Funchal, who assist patients from the islands of Madeira and Porto Santo, indicated that bone density was higher in patients from Porto Santo than in patients from Madeira.

For 5 years those specialists undertook a survey on fractures of the neck of the femur. This survey took various factors into account, such as age, gender, and diet (particularly the chemical composition of drinking water).

The stronger bones of the inhabitants of Porto Santo may result from the association of Ca to Mg, Sr, P, and F, elements which occur in high or significant contents in drinking water and edible vegetables and fruits in Porto Santo, combined with a higher Ca absorption, allowed by vitamin D.

Since most vitamin D comes from the incidence of solar radiation on the skin, the absorption of Ca is facilitated in Porto Santo. The number of hours (average values) of sunshine in Porto Santo are as follows: 233 in May, 211 in June, 230 in July, 245 in August, 215 in September, and 186 in October.

Psammotherapy or arenotherapy using biogenic carbonate sand is a very energetic application, and thus requires attentive medical surveillance. Sand-bathing is not recommended to people suffering from either cardio-vascular problems or from low blood pressure. It should also be mentioned that a minimum of 14 baths is recommended to patients.

Health Programmes carried out at the Geomedicine Clinics of Porto Santo are frequented mostly by groups of patients (about 20 per group) of Nordic origin. They are assisted by a medical team consisting of one doctor and one nurse. As a rule, the resulting medically-recognized health benefits last for at least 10-12 weeks.

Finally, various formulations, corresponding to analgesic gels and dermocosmetic creams with exfoliating properties, respectively containing dissolved biogenic carbonate sand from Porto Santo and certain grain size fractions of this special sand, have been or are currently being developed[40-51].

CONCLUSIONS

This paper discloses relevant analytical data that could explain the traditional use for therapeutic purposes of the biogenic carbonate sands from Porto Santo.

The sand from Porto Santo beaches is mainly composed of three calcium carbonates: calcite (calcium carbonate), magnesian-calcite (calcium carbonate showing partial substitution of magnesium for calcium) and aragonite (calcium carbonate showing partial substitution of strontium for calcium).

The deposits of biogenic carbonate sand in Porto Santo present very small variations, for instance, in terms of grain size, mineralogical composition, chemical composition, and bioclasts nature (higher or lower content of fragments of calcareous algae).

Experience has shown that the most interesting characteristics of the sand to be used for therapeutic purposes are as follows: a) highest content of grain size within the range of 0.125-0.250mm; b) highest content of tabular shaped grains; c) lowest content of volcaniclasts and of ferromagnetic minerals; d) highest content of carbonate minerals; e) highest content of calcareous algae bioclasts; f) highest content of Mg-calcite; g) highest contents of Sr, P, S, I, and F.

It has also been found that parameters e), f) and g) are maximized in the sand whose age, as determined by the radiocarbon method, is the lowest. Currently, in the case of Porto Santo Island, such sand occurs in the beaches and in the dunes that constitute the frontal dune system, occurring, particularly, in the southern coast of the island.

REFERENCES

1. GomesCSF, Silva JBP. Os Minerais e a Saúde Humana: Benefícios e Riscos/Minerals and Human Health: Benefits and Risks, In: Gomes, C. & Silva, J. (editors), 2006, 300p.
2. Federicci PC. Sabia, limi e alghe nella talassoterapia. *In* Gualterotti (ed.), Proceedings of the I World Thermalism Congress on Progress in Medical Hydrology, Climatology and Thalasotherapy, Lido di Lesolo, Venezia, 1980.
3. Murgia A. Hipótesis sul le mecanismo d´aczione della psammoterapia. *In* In Gualterotti (ed.), Proccedings of the I World Thermalism Congresso on Progress in Medical Hydrology, Climatology and Thalasotherapy, Lido di Lesolo, Venezia, 1980.
4. Berger A, Selinus O, Skinner C. Medical Geology: An Emerging Discipline, Episodes, 2001, 24 (1).
5. Finkelman RB, Skinner CW, Lumlee GS, Bunnell JE. Medical Geology, Geotimes, 2001, 46 (11), 20-23.

6. Bowman CA, Bobrowsky P T, Selinus O. Medical Geology: New Relevance in the Earth Sciences, Episodes, Journal of International Geoscience, 2003, 26, 4, 270-278.
7. Bunnell JE. Medical Geology: Emerging Discipline on the Ecosystem-Human Health interface, EcoHealth, 2004, 1, 15-18.
8. Selinus OS. Medical Geology: An emerging speciality, Terrae, 2004, 1 (1), A1-A8.
9. Nriagu J O. Tales told in lead, Science, 1998, 281, 1622-1623.
10. Selinus O, Frank A. Medical Geology. *In*: Moller, L. (ed.), Environmental Medicine, Joint Industrial Safety Council, Stockholm, Sweden, 2000, 327p.
11. Appleton JD. Radon in air and water, *In*: Selinus O, Alloway B, Centeno JA, Finkelman RB, Fuge R, Lindh U, Smedley O (editors). Essentials of Medical Geology, Elsevier, 2005, 227-262.
12. Derbyshire E. Natural aerosolic mineral dusts and human health, *In*: Selinus O, Alloway B, Centeno JA, Finkelman RB, Fuge R, Lindh U, Smedley O (editors). Essentials of Medical Geology, Elsevier, 2005, 459-480.
13. Smedley P, Kinniburgh DG. Arsenic in groundwater and the environment, *In*: Selinus O, Alloway B, Centeno JA, Finkelman RB, Fuge R, Lindh U, Smedley O (editors). Essentials of Medical Geology, Elsevier, 2005, 263-299.
14. Edmunds M, Smedley P. Fluoride in natural waters: occurrence, controls and health aspects, *In*: Selinus O, Alloway B, Centeno JA, Finkelman RB, Fuge R, Lindh U, Smedley O (editors). Essentials of Medical Geology, Elsevier, 2005, 301-329.
15. Fordyce F. Selenium deficiency and toxicity in the environment, *In*: Selinus O, Alloway B, Centeno JA, Finkelman RB, Fuge R, Lindh U, Smedley O (editors). Essentials of Medical Geology, Elsevier, 2005, 373-415.
16. Fuge R. Soils and iodine deficiency, *In*: Selinus O, Alloway B, Centeno JA, Finkelman RB, Fuge R, Lindh U, Smedley O (editors). Essentials of Medical Geology, Elsevier, 2005, 417-433.
17. Weinstein Ph, Cook A. Volcanic emissions and Health, *In*: Selinus O, Alloway B, Centeno JA, Finkelman RB, Fuge R, Lindh U, Smedley O (editors). Essentials of Medical Geology, Elsevier, 2005, 203-226.
18. Centeno JA, Finkelman RB, Selinus O. Medical Geology: Impacts of the natural environment on human health, XIV Semana de Geoquimica/VIII Congresso de geoquímica dos Países de Língua Portugueses, 2005, 1, 15-22.
19. Selinus O, Centeno J, Finkelman R, Fuge R, Lindh U, Smedley P (editors). Essentials of Medical Geology: Impacts of the Natural Environment on Public Health, Elsevier Academic Press, 2006, 1024p.
20. Bunnell JE, Finkelman RB, Centeno JA, Selinus O. Medical Geology: A Globally Emerging Discipline, Geologica Acta, 2007, 5, 3, 273-281.
21. Carretero I, Pozo M. Mineralogía Aplicada: Salud y Medio Ambiente, Thomson ed., Madrid, España, 2007, 406p.

22. Gomes CSF, Silva JBP, Silva EAF. Alvorada e Desenvolvimento da Geologia Médica em Portugal. Encontro Internacional de Termalismo e Turismo Termal & III Fórum Ibérico de Águas Engarrafadas e Termalismo, Furnas, Açores, 2009, 237-252.
23. Galán E, Liso MJ, Forteza M. Minerales utilizados en la industria farmacéutica, Bol. Soc. Esp. Min. 1985, 369-378.
24. Robertson RHS. Cadavers, Choleras and Clays, Bulletin Mineralogical Society, U.K, 1996, 113, 3-7.
25. Novelli G. Applicazioni Medicali e Igieniche delle Bentoniti, Atti. Conv. "Argille Curative", Veniale (Editor), Gruppo Italiano AIPEA, Salice Terme (PV), Tipografia Trabella, Milano, 1996.
26. Novelli G. Applicazioni Cosmetiche e Medicaliu delle Argille smectiche, Cosmetic News, 1998, 122,350-357.
27. Novelli G. Bentonite: A Clay over the Centuries, Incontri Scientifici, V Corso di Formazione "Metodi di Analisi di Materali Argillosi, Gruppo Italiano AIPEA, 2000, 263-304.
28. Veniale F. Argille Curative: antefatti, fatti e misfatti (Healing Clays: Previous facts, facts and wrong facts) In: Proceedings of the Mediterranean Clay Meeting, Lipari, Mineralogica e Petrographica Acta, XXXV-A, 1996, 13-44.
29. Veniale F. Applicazioni e Utilizzazioni Medico-Sanitarie di Materiali Argillosi (Naturali e Modificati), *In*: Morandi N, Dondi M (editors). Argille e Minerali delle Argille: Guida alla Definizione di Charatteristiche e Proprietá per gli Usi Industriali, Corso di Specializzazione, Gruppo Itaiano AIPEA, Rimini, Italy, 1997, 205-239.
30. Veniale F. Le argille nelle terapie curative: dalla leggenda all'empirismo, fino al tempi moderni, In: Atti Simposio "Argille per faghi peloidi termai e per trattamenti dermatologici e cosmetici", Montecatini terme, Mineralogica et Petrographica Acta XLII, 1999, 263-265.
31. Lopez-Galindo A, Iborra C. Usos farmacêuticos de arcillas especiales (sepiolia y palygorskita. Atti Conv. "Argille Curative" (Veniale F editor) Gruppo Italiano AIPEA, Salice Terme (PV), Italy, Tipografia Trabella, Milano, 1996, 45-53.
32. Reinbacher WR. Brief History of Clay in Medicine, Clay Minerals Society News, 1999, 11 (1), 22-23.
33. Reinbacher WR. Healing Earths: The Third Leg of Medicine, 25, 1st Books Library, Bloomington, U.S.A, 2003, 141-144.
34. Lopez-Galindo A, Viseras C. Pharmaceutical applications of fibrous clays (sepiolite and palygorskite) from some circum-Mediterranean deposits, *In:* Gomes C editor. 1st Latin American Clay Conference, Funchal, Madeira, Associação Portuguesa de Argilas (APA), 2000, 1, 258-270.
35. Carretero I. Clay Minerals and their beneficial effects upon human health: a review, Applied Clay Science, 2002, 16, 125-132.

36. Carretero I, Gomes C, Tateo F. Clays and Human Health, Handbook of Clay Science. In: Bergaya F, Theng B, Lagaly G (editors). Developments in Clay Science, 2006, 1, 717-741.
37. Droy-Lefaix MT, Tateo F. Clays and Clay Minerals as Drugs, Handbook of Clay Science. In: Bergaya F, Theng B, Lagaly G (editors). Developments in Clay Science, 2006, 1, 743-752.
38. Silva JBP. Areia de Praia da ilha do Porto Santo: Geologia, Génese, Dinâmica e Propriedades justificativas do seu interesse Medicinal, Madeira Rochas (editor), Funchal, Madeira, 2003, 344p.
39. Gomes CSF, Silva JBP. Beach sand and bentonite of Porto Santo' island: Potentialities for Applications in Geomedicine, Madeira Rochas-Divulgações Científicas e Culturais (editor), Funchal, Madeira, 2001, 60p.
40. Gomes CSF, Silva JBP. Products based on Clay and Sand with interest for Balneotherapy, Clay Science, 12, Supplement 2, 2006b, 228-232.
41. Gomes CSF, Silva JBP. Minerals and Clay Minerals in Medical Geology, Applied Clay Science, Elsevier, 2007, 36, 4-21.
42. Gomes CSF, Silva JBP. Pelóides: Tipologia, Propriedades, Preparação e Funções, Encontro Internacional de Termalismo e Turismo Termal & III Fórum Ibérico de Águas Engarrafadas e Termalismo, Furnas, Açores, 2009, 219-230.
43. Lindh U. Biological functions of the elements, *In*: Selinus O, Alloway B, Centeno JA, Finkelman RB, Fuge R, Lindh U, Smedley O (editors). Essentials of Medical Geology, Elsevier, 2005.
44. Combs G F.Geological Impacts on Nutrition, *In*: Selinus O, Alloway B, Centeno JA, Finkelman RB, Fuge R, Lindh U, Smedley O (editors). Essentials of Medical Geology, Elsevier, 2005, 161-178.
45. Finkelman RB, Limpitlaw U. Health benefits of geologic materials and geologic processes, International Journal of Environmental Research and Public Health, 2006, 3, (4), 278-283.
46. Gomes CSF, Hernandez R, Sequeira MC, Silva JBP. Characterization of clays used for medicinal purposes in the archipelago of Cape Verde, Geochimica Brasiliensis, 2008, 22 (3), 315-331.
47. Gomes CSF, Silva JBP, Sequeira MC, Gomes JH. Potentialities for therapeutic purposes of the biogenic carbonate sands occurring in some islands of the Macaronesia' archipelago based on their unique chemical and physical properties, Geochimica Brasiliensis, 2008, 22 (3), 332-343.
48. Rautureau M, Liewig N, Gomes C, Katouzian-Safadi M. Argiles et Santé: Propriétés et Thérapies, Lavoisier (editeur), Paris, 2010, 201p.
49. Morse JW, ArvidsonRS. The dissolution kinetics of major sedimentary carbonate minerals, Earth Science Reviews, 2002, 58, 51-84.
50. Rodrigues M, Branco J, Menezes V, Costa Neves L, Jardim Fernandes J, Viana de Queiroz M. Estudo retrospectivo de 5 anos sobre as fracturas do colo

do fémur no arquipélago da Madeira, Relatório Interno do Serviço de Ortopedia do Centro Hospitalar do Funchal, 1988, 43p.

51. Santos D, Amaral MH, Padilha M, Andreani T, Pena-Ferreira MR, Silva JBP, Gomes CSF. Development of exfoliating formulations containing biogenic carbonate sand from Porto Santo island, Madeira archipelago, Skin and Formulation, 3rd Symposium, Versailles, 2009.