



**POTENTIALITIES FOR THERAPEUTIC PURPOSES OF THE BIOGENIC
CARBONATE SAND OCCURRING IN SOME ISLANDS OF THE MACARONESIA'
ARCHIPELAGO BASED ON THEIR UNIQUE CHEMICAL AND PHYSICAL
PROPERTIES**

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ABSTRACT

Minerals are fundamental constituents of the natural environment. As a rule, minerals can have both negative and positive impacts on human health. However, the research that has been carried out worldwide, for obvious reasons, emphasizes more the hazardous effects than the beneficial effects. This paper deals with the relevant properties for therapeutic uses of biogenic carbonate sand that occurs in certain islands of the comprehensive biogeographic archipelago of Macaronesia which includes the archipelagos of Azores, Madeira, Canaries and Cape Verde. The paper discloses the results of the investigation carried out on that type of sand, particularly focused on its mineralogical and geochemical characterization, seeking scientific arguments able to justify the empirical use during many decades in the island of Porto Santo, archipelago of Madeira, of the sand as healing material for muscular-skeletal diseases, such as: rheumatoid arthritis, osteoporosis and fibromyalgia.

RESUMO

Os minerais são constituintes fundamentais do ambiente natural. Em regra, os minerais podem ter impactos tanto negativos como positivos na saúde humana. Contudo, as investigações desenvolvidas em todo o mundo dão preferência aos efeitos nocivos dos minerais sobre os efeitos benéficos. O presente trabalho trata das propriedades relevantes para usos terapêuticos da areia carbonatada biogénica que ocorre em certas ilhas da ampla região biogeográfica denominada arquipélago da Macaronésia que reúne os arquipélagos dos Açores, da Madeira, das Canárias e de Cabo Verde. São divulgados os resultados das investigações levadas a efeito neste tipo de areia, focadas em particular na sua caracterização mineralógica e química, procurando encontrar os argumentos científicos que possibilitem a justificação para a utilização, de modo empírico e durante muitos anos, na Ilha do Porto Santo, arquipélago da Madeira, da areia que sob a forma de banho de areia tem efeitos benéficos em doenças dos sistemas muscular e esquelético, tais como: artrite reumatóide, osteoporose e fibromialgia.

INTRODUCTION

Natural environment and man who has been created in it and used it for his survival and pleasure are two very complex entities made up of many components and variables, which are not yet entirely identified, and whose interaction is still far from being satisfactorily understood.

Chemical elements, minerals, rocks, soils, waters and air are the essentials of the natural environment.

Over the years, man has acquired experience about the existence of interactions between these components, as well as about the beneficial and hazardous effects they have upon living beings, man, other animals, and plants.

Empirical knowledge related to human health, which practice is called "*Empirical Medicine*", is essential in many aspects of man life and activity. However, in regard with this subject, man quest for rational explanations based on science and technology is considered equally essential. As a matter of fact, with perseverance, step by step, using the available accumulated experience, and the scientific information, both fundamental and applied, provided by specialists of distinctive scientific domains (chemistry, biochemistry, biology, biotechnology, mineralogy, geochemistry, hydro-chemistry, materials science, medicine, public health, pharmacy, nutrition, and others), man could be better and better succeeded in what concerns, for instance, the understanding of the interaction of minerals and other geo-resources with the human health.

The use of minerals for medicinal purposes is, most probably, as old as mankind itself.

Presently there is a growing interest on health treatments using natural means, alternative to those of the conventional medicine. It is the so-called *naturomedicine*, which involves distinctive natural resources and application methods. Examples of

health treatments involving minerals are: *hydrotherapy*, *crenotherapy*, *mudtherapy*, *peloidtherapy* or *pelotherapy*, *psammotherapy* or *arenotherapy*, and *oligotherapy*".

In conceptual terms, some of the referred to processes which involve mineral resources deserve some particular comments:

Crenotherapy is a term much used in France, which is derived from the Greek word *krine* that means spring, corresponding to the therapeutic utilization of spring water in *Thermal Resorts* and *Spas*, under the form of drink, bath, shower, pulverisation, inhalation and mud-bath;

Oligotherapy corresponds to a complementary therapy based on *oligoelements*, certain metals or metalloids, such as, Fe, Cr, Ni, Co, Mn, Mg, Se, P, S, I, F, Cu, Zn and Li, present as traces in the human body, but indispensable to its correct performance due to the catalytic role of enzymatic functions, and their deficiency or excess can lead to pathologic situations. The deficiency in *oligoelements* is caused, as a rule, by inadequate diets. In very small concentrations, in order to avoid toxicity risks, and under the form of soluble salts, the *oligoelements* in the ionic state can be administered, either orally or percutaneously.

It matters to add that *peloidtherapy* or *pelotherapy* (for short) implies the topical application of *peloids*, made of clay or mud deposited in thermal springs and shallow seas, which have been submitted to an industrial processing called *maturation*. The famous black mud (rich in humic acid) from the inland sea called Dead Sea whose hypersaline water, comparatively to standard sea water, are enriched in minerals such as, magnesium, potassium, sodium, bromine and iodine, is known for their healing properties for psoriasis sufferers and patients with rheumatic complaints. Those minerals and the humic acid are considered essential healing elements of the mud. *Pelotherapy* is the act

of smearing oneself, onto an affected area, with *peloids* of clay or mud, or having a practitioner to do smearing for you. In case the patient is placed in a full body steamer the opening of skin pores lets the active principles of the *peloid* go into the body.

Some special sands are being used worldwide in therapeutic applications (*psammotherapy*), particularly for the treatment of muscular-skeletal diseases, under the form of sand-bath. There are the cases, for instance, of the biogenic carbonate sand from Porto Santo' island, Madeira archipelago, of the radioactive sand from Guarapari beaches, Espirito Santo, Brasil, and of the dark volcanic sand from the Thermal Centres of Beppu and Ibusuki, Kyushu island, Japan, naturally warmed up by the 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*.

Presently, *Medical Geology* is the recommended expression to define a globally emerging scientific discipline that comprises the essentials and practices which involve, essentially as positive or negative conditioners of human health, certain minerals *s.l.(sensu lato)*, concept that includes certain minerals *s.r. (sensu restrictu)*, i.e., certain inorganic, natural, crystalline solids, and certain mineral derived macro and microelements, the so-called oligoelements or *trace minerals*, which are present in soil, in food, and in certain waters (spring water, thermal or not, and seawater).

The interactions of man and the environment (air, water and minerals) can be either beneficial or hazardous (eventually lethal). These interactions are the realm of Medical Geology, a fast-growing scientific field that not only involves geoscientists but also medical, public health, biological, environmental, and other scientists.

Geomedicine, expression that has preceded for some decades the expression Medical Geology, is defined as the relation between natural environmental factors and health. In addition to the composition of rocks, minerals, soils, and water, it considers too factors related to climate, ozone and natural radiations, and deals with human as well as with animal health. Therefore the aim of Geomedicine is more comprehensive than the aim of Medical Geology.

Medical Geology a discipline created about a dozen of years ago is being essentially dedicated to the impacts in public health of deficiency and toxicity of trace elements exposure, for instance, of arsenic, lead, cadmium, mercury, fluorine, selenium, iodine, and radon. There are many publications about these subjects, and within them the following deserve particular mention: Nriagu (1998); Finkelman et al. (1999); Selinus & Frank (2000); Finkelman et al. (2001); Smedley & Kinniburgh (2005); Bowman et al. (2003); Edmunds & Smedley (2005); Fordyce (2005); Fuge (2005); Selinus et al. (2005); Gomes & Silva (2006); and Bunnell et al. (2007).

However, the positive or beneficial effects of the natural environment, particularly of certain chemical elements (some of those aforementioned and others, as well as certain minerals, such as, clay minerals and special clays, special sands, natural mineral waters (thermal or not) are reckoned by various authors, such as: Robertson (1996); Novelli (1996, 1998, 2000); Veniale (1996, 1998); Reinbacher (1999, 2003); Carretero (2002), Carretero et al.(2006); Droy-Lefaix & Tateo (2006); Gomes & Silva (2006, 2007).

OCCURRENCES OF BIOGENIC CARBONATE SAND IN CERTAIN MACARONESIA' ISLANDS

Recent studies (Gomes & Silva, 2001; Silva, 2003; Gomes & Silva, 2006; Gomes & Silva, 2007) have provided much

information about the relevant physical and chemical properties for therapeutic applications of the biogenic carbonate sand occurring in the island of Porto Santo belonging to the archipelago of Madeira, which has been used for many years, in an empirical way, in the treatment of muscular-skeletal (rheumatic and orthopaedic) diseases.

The referred to applications are taking place, either outdoors using the traditional way under the form of sand-bath in the dry sand of transition zone between the beach and the frontal dune, or indoors in specialized Geomedicine or Thalassotherapy Clinics.

The biogenic carbonate sand of Porto Santo has been considered to be derived from the dismantling, during the Last Great Glaciation, of a reef existent and mainly constituted of calcareous Rhodophyceae algae which had great development in north-eastern coast of the island. Dating of the sand using the radiocarbon method provided ages within the range 31,000-15,000 BP (Gomes & Silva, 2001).

Gomes & Silva (2001), Silva (2003) and Gomes & Silva (2006, 2007) report the specific properties, particularly the granulometric, morphological, thermal and chemical properties of the biogenic carbonate sand of Porto Santo, properties that could justify their interest for therapeutic purposes.

The results of the research being carried out led the authors to find consistency and credibility, both in the application methods and in the health benefits reported in several historical records.

Biogenic carbonate sands similar in composition to the ones occurring in Porto Santo island (Figure 1) also occur in some other islands that belong to the archipelago of Azores (islands of Santa Maria and Terceira), to the archipelago of Canaries (islands of Gran Canaria, Fuerteventura and Lanzarote) and to the archipelago of Cape

Verde (islands of Sal and Boavista – Figure 2). All the archipelagos referred to are included in the so-called biogeographic archipelago of Macaronesia.



Figure 1: General view of the southern coast of Porto Santo island and its excellent beach.



Figure 2: Chaves' dune, Boavista island, Cape Verde archipelago.

PROPERTIES OF THE BIOGENIC CARBONATE SAND INTERESTING FOR THERAPEUTIC APPLICATIONS

Properties such as grain size and shape, bioclasts and volcanoclasts nature (Figure 3) and ratio, specific heat and heat diffusiveness, mineralogical and chemical composition (major, minor and trace elements), Mg/Ca and Sr/Ca ratios and chemical dissolution rate, have been determined in representative samples of the biogenic carbonate sand from beach deposits and/or frontal dunes occurring in certain Atlantic volcanic islands belonging to the archipelagos of Azores, Madeira,

Canaries and Cape Verde.

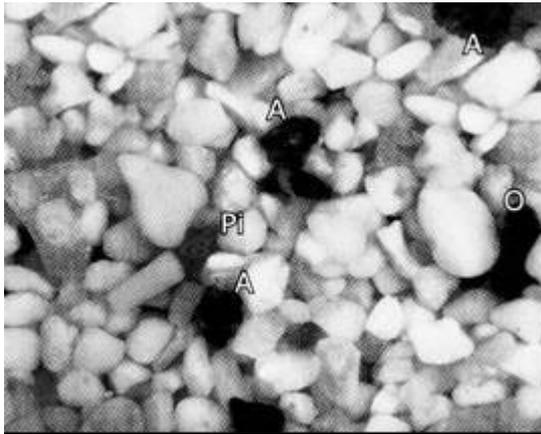


Figure 3: Bioclasts and volcanoclasts from a sample of Porto Santo beach sand.

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

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



Figure 4: Sand-bath facilities in the former Clinic of Hotel Porto Santo, in Porto Santo' island, Madeira' archipelago.

During sand-bath (Figure 4) human body receives and stores heat (sand temperature is within the range 40-42°C), and the acid (pH = 4.1-6.5) sweat being produced reacts with the carbonate sand 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 becoming free at the skin surface can be absorbed through it. It is known that the surface of the human body of a normal adult is estimated at about 1.5 m^2 . Also, it is known that in 1 cm^2 of skin there are, in average, 1 metre of bloody capillary vessels, 4 metres de nervous fibres, 3 millions of cells, 100 glands sweat producers and 15 sebaceous glands, and 100 to 500 sensorial receptors. Therefore, in practical terms, the skin corresponds to a communication structure between the surrounding environment, other body tissues, and the cerebrum maintained in continuous functioning due to the nervous cells.

Due to the tabular shape of most sand grains, they become stuck to the skin after sand-bathing, and they should remain as so during some minutes till the skin gets dry.

The carbonate particles that make up the sand, particularly the algae fragments which are relatively more unstable under acidic conditions, are partially dissolved by the perspiration liquid that becomes particularly enriched in Ca, Mg, Sr, and other elements. As was said before, these elements become free and available to pass through the epidermis and to be absorbed into dermis cells.

Mg content increases as far as the content of Mg-calcite increases, Mg-calcite content being directly dependent upon the content of bioclasts of calcareous Rhodophyceae algae. Sr enters into the composition of aragonite and its content decreases as far as the sand age increases.

Ca it is an important chemical element that exists 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 the normal cardiovascular function. Also, it is well established that calcium therapy in simultaneous 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 of calcite (CaCO_3), a mineral that in acid solutions ($\text{pH} < 7$) dissociates easily into the ions Ca^{+2} , Sr^{+2} , Mg^{+2} and CO_3^{-2} .

Mg is another important chemical element that also exists in significant contents in sea water and other natural systems such as certain soils and spring waters, being 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*": reduces cardiovascular pathologies, reducing the artroma plaque that causes atherosclerosis, since it has an important role in the metabolism of fats or lipides.

Soya, cereals, nuts and other fruits (such as melon and watermelon) are rich in Mg. To this element several other beneficial effects are attributed too: 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. Effectively, Mg participates in very small amounts in the composition of hydroxyapatite, the biomineral that makes the bones, being continuously resorbed 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, and it is being considered that other oligoelements, such as Mg, Sr, F and Si could play an essential role.

MgO contents also are comprised between 2.5-4% in the biogenic carbonate

sand of Porto Santo. Higher MgO values correspond to sands having lower values of aragonite content but higher magnesium bearing calcite or Mg-calcite content.

Strontium (Sr) is also an important chemical element existing in seawater and in other natural systems that is equally important for human health. Sr^{+2} has an ionic radius 132 pm (picometer) that is much higher than the ionic radius of Ca^{+2} , 99pm. Therefore, Sr^{+2} more easily gets into the *aragonite* more open structure, 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 Sr^{+2} enters in relatively high concentrations into the aragonite structure, this structure becomes rather more stable than when Sr^{+2} enters in relatively low concentrations into the aragonite structure; an higher content of Sr^{+2} in the aragonite structure allows its longer lasting before taking place the inversion of the unstable aragonite structure to the stable calcite structure.

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

As it was said before Sr can stabilize for longer time the unstable structure of aragonite. Similarly Sr could turn more stable the structure of bioapatite forming the bones, preventing the loss of bone mass that causes the disease osteoporosis. Where, in nature, Sr concentrations are high, discrete apatite minerals form, such as strontium-hydroxyapatite, $(\text{Ca,Sr})_5 (\text{PO}_4)_3 (\text{OH})$. Although not being considered an essential element for human health, strontium is always present in bones, in very small contents (parts per million).

Recently a medicine was developed and commercialized for the treatment of osteoporosis, whose active principle is an

organic compound bearing Sr, strontium ranelate that decreases bone re-absorption. Such medicine won the Galien 2005, a prize that awards both innovation and investigation in the pharmaceutical industry.

In Porto Santo, Sr contents are 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 was 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 content (2-4mg/l) in the water of springs from Porto Santo, the disease dental fluorosis causing mottle teeth being common within the residents of the island. Silicon is other element found in spring water in relatively high content, the main source being hyaloclastite tuff occurring in large outcrops.

Within 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 being a component of enzymes and other key proteins.

Iodine (I) is another bio-essential element. The so-called Iodine Deficiency Disorders (IDD) have common occurrence within the population of many regions of the world. Humans need Iodine because of the thyroid gland. Iodine's role in this gland is to synthesize and store the hormones thyroxine and 3,5,3'-triiodothyronine (Lindh, 2005). Thyroid hormones are important for the normal growth and development, since

they control the metabolism of carbohydrates, proteins, lipids, and vitamins.

Low intake of iodine can cause IDD, 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. As a rule, Iodine concentration in soils decreases as far as the distance to the sea increases. Iodine deficiency in diets can be combated with iodine supplementation, through the so-called iodized salt, since salt is a good of generalized use by people.

In Porto Santo treatments involving sand-bathing are addressed to people suffering from rheumatoid arthritis, fibromyalgia and osteoporosis, the last disease being considered for long time as a little known disease (a silent disease, without symptoms), since its consequences were not well established.

In regards with osteoporosis an epidemiological and comparative study (Rodrigues et al., 1988) carried out by specialists in orthopaedics from the Hospital of Funchal, who assist patients from the islands of Madeira and Porto Santo, indicates that bone density was higher in patients from Porto Santo than in patients from Madeira.

During 5 years those specialists undertook a survey of fractures of the neck of the femur. The survey took into account various factors, such as, age, gender, and diet (particularly the chemical composition of the 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 of vitamin D comes from the incidence of solar radiation on the skin, the absorption of Ca is easier in Porto Santo characterized by its significantly higher insolation (number of sunny days per year) comparatively to Madeira (Gomes and Silva, 2006).

Figure 5 shows the X-ray diffraction patterns corresponding to selected samples of biogenic carbonate sand collected in certain sites and islands of the Macaronesia' archipelago. In the X-ray diffraction patterns it is possible to clearly distinguish Calcite and Mg-calcite and to

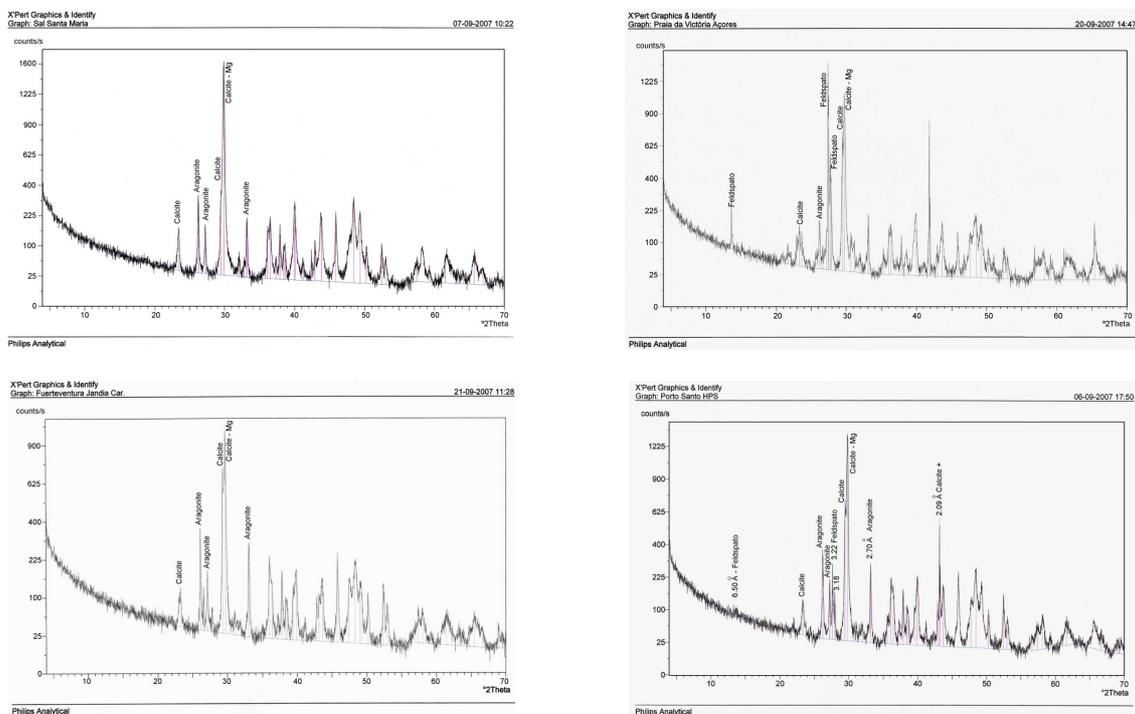


Figure 5: X-Ray Diffraction patterns showing the type of carbonate minerals present in the studied sands: a - Praia de Santa Maria, Sal' island, Cape Verde' archipelago (CVSM); b - Praia da Victória, Terceira' island, Azores' archipelago (ATPV); c - Playa de Jandia, Fuerteventura, Canaries' archipelago (CPJA); d - Praia do Hotel do Porto Santo, Porto Santo' island, Madeira' archipelago (MPSH).

Table I: Chemical analysis of major elements (in weight %) of biogenic carbonate sand from some islands of the Macaronesia' archipelago.

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	MnO	MgO	CaO	K ₂ O	Na ₂ O	I.L.
MPSH	1.40	1.05	0.20	0.80	0.10	53.10	2.50	0.31	0.50	41.40
ATPV	3.25	1.30	0.90	1.10	0.15	50.10	1.95	0.25	0.35	39.05
CPJA	2.60	1.10	0.95	0.75	0.20	50.05	2.05	0.30	0.40	39.50
CVSM	0.60	0.25	0.08	0.46	0.05	53.30	2.70	0.25	0.65	42.20

Table II: Chemical analysis of minor and trace elements (in ppm), mostly essential to life, making the biogenic carbonate sand from some islands of the Macaronesia' archipelago.

	Sr	P	V	S	Zn	Cu	Ni	Co	Cr	Se	I	As
MPSH	590	40	15	20	10	6	4	5	9	25	60	5
ATPV	490	35	12	18	5	7	6	8	12	15	30	3
CPJA	610	30	10	15	8	8	7	9	13	18	50	5
CVSM	760	35	8	22	12	3	3	4	6	20	55	2

determine in quantitative terms, the ratios Calcite/Mg-calcite.

On the other hand, Tables I and II contain the relevant chemical data corresponding to the same samples.

Both mineralogical and chemical data were obtained after separation of magnetic minerals. The contents in magnetic minerals of the biogenic carbonate sands (in the natural state) MPSH, ATPV, CPJA and CVSM were estimated at 2.0%, 16%, 8% and 1.0% in weight, respectively. Magnetic separation with a simple magnet can separate titanomagnetite and most of the plagioclase (since it contains inclusions of iron oxides), minerals associated with carbonate minerals.

MPSH - Sand from Praia do Porto Santo; collected in the frontal dune right in front of Hotel Porto Santo, Porto Santo' island, Madeira' archipelago.

ATPV - Sand from Praia da Victória, Terceira' island, Azores' archipelago; collected in the beach.

CPJA - Sand from Playa de Jandia, Fuerteventura' island, Canaries' archipelago; collected in the beach.

CVSM - Sand from Praia de Santa Maria, Sal' island, Cape Verde' archipelago; collected in the frontal dune.

CONCLUSIONS

This paper discloses the results provided by a comparative study being carried out on biogenic carbonate sands occurring in certain beaches from Terceira' island (Azores' archipelago), Porto Santo' island (Madeira' archipelago), Fuerteventura' island (Canaries' archipelago), Sal and Boavista' islands (Cape Verde' archipelago).

The obtained analytical results allowed us to put forward a classification of the most adequate sands to be used for therapeutic applications, either in the form of sand-bathing indicated for the treatment of muscular-skeletal affections, or in the form of cream and gel made of blends with other minerals and/or drugs interesting for the treatment of dermatological and rheumatic affections.

Sand relevant properties interesting for its use in balneotherapy (sand-bath), as well as in the preparation of dermocosmetics and dermopharmacy formulations, are as follows:

- . Grain size within the range 0.125mm-0.250mm; in all the studied sands most (>90%) of grain size is within this interval; clay and silt fractions should be eliminated in case they exist; sand micronization is required whenever it is incorporated in dermocosmetics and dermopharmacy formulations;

- . Tabular grains (as a rule, they mostly correspond to calcareous algae) content, the highest the best;

- . Carbonate minerals total content, the highest the best; to be beneficial to health, in most of the applications, it is important that sand could easily be soluble in weak acids (like human sweat);

- . Mg-calcite content, the highest the best;

- . Sr, P, S, I, and F contents, the highest the best.

Based on the properties referred to, the biogenic carbonate sand from the islands of Porto Santo (Madeira' archipelago) and Sal (Cape Verde' archipelago) are those which appear to show the best characteristics and potentialities for the treatment of rheumatic diseases.

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