Geochimica Brasiliensis, 23(3) 315-331, 2009

Geochimica Brasiliensis

CHARACTERIZATION OF CLAYS USED FOR MEDICINAL PURPOSES IN THE ARCHIPELAGO OF CAPE VERDE

Gomes, C. S. F. [1], Hernandez, R. [2], Sequeira, M. C. [1], Silva, J. B. P. [1]

[1]Research Centre "GeoBioTec" of the Foundation for Science and Technology (FCT), University of Aveiro, 3810-193 Aveiro, Portugal; cgomes@ua.pt; csequeira@ua.pt.
[2]Instituto Nacional de Investigação Agrária (INIA), Praia, Cape Verde; reglah@hotmail.com

Recebido em 04/09 e aprovado para a publicação em 06/09.

ABSTRACT

Samples taken from pieces of two clays being commercialized for medicinal purposes (alleviation of gastrointestinal problems, treatment of abscesses, furuncles and wounds, as well as of skin ailments, and cosmetic applications) by saleswomen of natural products at the public market of the town of Praia, in the island of Santiago, archipelago of Cape Verde, were submitted to several analyses, such as, granulometric analysis, mineralogical analysis, chemical analysis, cation exchange capacity and exchangeable cations, and plasticity, in order to find out any scientific justification for the applications referred to. One of the studied clay is composed of dioctahedral illite, and the other clay is composed of dioctahedral smectite, dioctahedral illite and kaolinite. Other analytical data support the capacities of the studied clays to be used as healing materials. These clays as other natural healing clays are traditionally used for internal detoxification (particularly in the gastrointestinal tract), for trauma injuries, for skin ailments and for cosmetic applications.

RESUMO

Amostras de duas argilas comercializadas para fins medicinais (alívio de afecções do foro gastrointestinal, tratamento de abcessos, furúnculos e feridas, assim como para afecções da pele e aplicações cosméticas), e vendidas numa loja de produtos naturais no mercado público da cidade da Praia (capital do arquipélago de Cabo Verde) foram submetidas a vários estudos de carácter experimental: análise granulométrica, análise mineralógica, análise química, capacidade de troca catiónica e catiões de troca, e ainda plasticidade, tendo em vista encontrar justificação científica para o seu uso empírico nas aplicações referidas. Uma argila, em termos de minerais argilosos, é composta por ilite dioctaédrica, enquanto que outra argila é composta, em termos de minerais argilosos, por esmectite dioctaédrica, ilite dioctaédrica e caulinite. Estes e os outros dados analíticos abonam a favor das capacidades curativas das argilas estudadas. As argilas estudadas revelam características semelhantes às de outras argilas naturais reconhecidas como possuindo propriedades curativas de certas afecções e que são tradicionalmente usadas para desintoxicação interna (particularmente no sistema gastrointestinal), para o tratamento de feridas externas e de diversos tipos de afecções da pele.

INTRODUCTION

Cape Verde is an Atlantic archipelago of volcanic origin that together with the archipelago of Azores, the archipelago of Madeira, and the archipelago of Canaries belong to the so-called bio-geographic archipelago of Macaronesia. The archipelago of Cape Verde is 455 km distant from the cape named Cap Vert in Senegal.

The archipelago of Cape Verde comprises ten islands and four islets, located between the meridians 22º 39' 20''W and 25º 20' 00'' W, and the parallels 14º 48' 00''N and 17º 12' 15''N. The names of the islands are as follows: Santiago, São Vicente, Maio, Santo Antão, Sal, Boa Vista, São Nicolau, Santa Luzia, Fogo and Brava.

Based on information provided by the saleslady, Clay A and Clay B would have been derived from the geographic area of Rabil, in the Boavista' island and they were sampled in a water-well. A survey of the geology of the area referred to indicates the occurrence of a complex of phonolite, extrusive igneous rock essentially consisting of alkali feldspar, alkali pyroxene and nepheline.

The town of Praia, capital of Cape Verde, is located in the island of Santiago, the main island (991km^2) of the archipelago. It was in the public market of Praia, more precisely in a shop selling natural products, that were bought by one of the authors (R.H.) two macroscopically distinctive clays, clay A and clay B, used by some inhabitants as healing materials in gastrointestinal affections, in the treatment of abscesses, furuncles and other skin ailments, as well as in cosmetic applications.

The use of clays for medicinal and cosmetic purposes is current practice in all the islands of archipelago of Cape Verde, and in other islands of the comprehensive biogeographic archipelago of Macaronesia. The authors are preparing a more comprehensive paper dealing with the typology of the heath affections, their etiology, application methodologies, and naturally with the detailed characterization of the clays.

CLAYS AND CLAY MINERALS IN MEDICAL GEOLOGY

The use of minerals for medicinal purposes is, most probably, as old as mankind itself. The therapeutic use of minerals is known since the oldest civilizations.

In Mesopotamia (3,000-2,000 BC), and in the clay plates of Nippur (~ 2,500 BC), there are written references to 125 drugs of mineral nature, the so-called medicinal *terras* or earths and minerals, particularly nitre (potassium nitrate) and halite (sodium chloride).

The medicinal *terras* mainly composed of clay were used for therapeutic purposes, including the treatment of wounds and the inhibition of haemorrhages.

In Ancient China the catalogue named Pen Ts'ao Kang Mu initiated by the emperor Shen Nung (probably in 2,700 BC) contained references to several medicinal plants and other medicines of mineral origin, such as, melanterite (hydrated iron sulphate), cinnabar (mercury sulphide), nitre (potassium nitrate), and sulphur, within others, as well as *terras*, clay rich materials, also used for medicinal purposes.

Goitre is a disease which has plagued the humans for at least several thousand years, and Sheng Nung allegedly prescribed seaweed, now known to be rich in iodine, as a treatment of the disease.

Since 1921, after iodine being recognized as a bio-essential mineral, to combat iodine deficiency in diets, iodine is incorporated in iodized common salt.

And, since September 2009, in Australia and in New Zealand, iodine will have a new source, the iodized bread, since it was found that people are cooking less they once had, now eating more processed foods which don't contain iodine.

And, since September 2009, in Australia and in New Zealand, iodine will have a new source, the iodized bread, since it was found that people are cooking less they once had, now eating more processed foods which don't contain iodine.

The oldest known book, the famous *Papyrus Ebers*, the greatest Egyptian medical document written around 1550BC from much older source material, describes some diseases and their treatment and doses, using about 500 substances generally based on minerals, such as, such as, alum (hydrate potassium and aluminium sulphate), halite (sodium chloride), copper and lead minerals, and minerals based on clays (Reinbacher, 1999).

In Ancient Egypt, Pharaoh's doctors used Nubian earth as an anti-inflammatory agent, and yellow ochre (a mixture of clay and iron oxy/hydroxides) as a cure for skin wounds and internal maladies and associated with natron (hydrated sodium carbonate) as a preservative in the mummification of cadavers.

Furthermore, Cleopatra (44-30 BC), Queen of Egypt, used mud from the Dead Sea for cosmetic purposes, for instance, facial masks (Bech, 1987; Newton, 1991; Robertson, 1996; Veniale, 1997; Reinbacher, 1999).

In Ancient Greece the so-called *terras*, effectively corresponding to clays, after being mixed with water were utilized, under the form of patches, to heal skin affections. *"Bolus Armenus"*, red clay found in the mountain caves of Cappadocia, ancient Armenia, present-day Turkey, was famous medicinal clay.

Other well-known curative clays are the so-called *terras*, derived from the alteration of volcanic rocks, from the Greek islands Lemnos, Chios, Samos, Milos, and Kimolos. Among these the *terra sigillata* of Lemnos' island deserves particular mention. After processing, this white, astringent, and absorptive clay is made into disks appearing coins, and afterwards stamped with the goat image, representing the goddess Diana or Artemis. It was usual the ingestion of these types of *terras*.

On the other hand, the *terra* or clay from Kimolos' island was identified as Ca^{2+}-smectite (Robertson, 1986).

The first classifications of medicinal *terras* are due to Hippocrates (460-355 BC) and to Aristotle (384-322 BC). Aristotle reports the ingestion of *terras*, soils or clays, by man with therapeutic or religious purposes. Later, Marco Polo described how in his travels he saw Muslim pilgrims cured fevers by the ingestion of "pink earth".

Dioscorides in his book *De Materia Medica* (60 AC) reports the healing properties of certain minerals and chemical substances utilized in the preparation of medicines and cosmetics. Pliny the Elder (23-79 AC) in his book *Natural History* describes the use of clays, particularly those occurring around Naples and being related with the alteration of volcanic ash, to heal stomach and intestinal problems.

Galeno (131-201 AC), a Greek doctor, describes the medicinal *terras* being used, for instance, for gastrointestinal affections, and indicates their therapeutic properties, their organoleptical characteristics and properties, and how to recognize them.

The rubbing of clays onto parts of the body for therapeutic purposes has been known for very long time. Romans in dedicated buildings called *balnea*, erected around thermal springs, took advantage of benefits for health and wellbeing of water-bath and clay or fango.

During the Bizantine Empire the use of the so-called *medicinal terras* or *earths* has proceeded.

Avicena (980-1037) and Averroes (1126-1198) encouraged the use of medicinal mud, and have classified various types of mud.

Paracelsus (1493-1541) has used minerals for the preparation of drugs, and created a branch of Chemistry named Iatrochemistry, that preceeded the actual Pharmacology, aimed at the study and use of chemical substances for therapeutic purposes.

Georgius Agricola in his book De Re Metallica (1556) reports certain minerals that after being dissolved or dispersed in water could counteract lethal effects of certain poisons of mineral origin (oripiment and realgar, both arsenic sulphides) and heal some diseases.

During the Renaissance were issued the first texts of the so-called *Pharmacopoeias*, namely the Pharmacopeia of Valence (1601) and the Pharmacopeia Londinensis (1618). Besides the drugs, these texts classify and describe regulations of various minerals for medicinal uses.

Clay and mud have been used by humans, since prehistoric times, as healing natural material improving health and enhancing general well-being. Indeed, particular types of clay and mud are still used worldwide as therapeutic agents.

However, only in the last two decades researchers have tried to explain the scientific backing of the relevant properties, application methodologies, health benefits and contraindications of healing clay and mud. There is no doubt that the informed use of the right clays (each, and every clay, is unique, and different clays may respond in the body differently), either internally or externally, can accomplish healing.

Certain types of clay and mud could be externally applied in the form of cataplasms or poultices, patches or clay-mud baths for the treatment of arthro-rheumatic, muscular and other inflammatory ailments, as well as coatings for the alleviation of dermatological affections, such as psoriasis, acne, and seborrhoea.

Also, certain clays and clay minerals could be orally taken in the form of pills, powders, and emulsions to serve as gastrointestinal protectors, laxatives, and anti-diarrhoeic, while other types have found applications in aesthetic medicine, notably as ingredients of dermocosmetics and dermopharmacy formulations.

Particular types of clays and clay minerals (kaolinite, smectite, palygorskite, and sepiolite) can enter as active principles or as excipients in the formulations of several medicines or drugs.

About these subjects several scientific articles have been published in the last two decades, some of them deserving particular mentions:

Among the numerous papers and reviews on the role of clays in Geomedicine which have appeared over recent years, the following are of general interest and relevance: Letizia (1975), Galán et al. (1985), Ferrand and Yvon (1991), Barbieri (1996), Yvon and Ferrand (1996), Novelli (1996), Veniale and Setti (1996), Veniale (1996, 1997, 1999), Cara et al. (1996, 1999, 2000a, 2000b), Lopez-Galindo and Iborra (1996), Veniale et al. (1999), Bettero et al. (1999), Gorgoni et al. (1999), Jobstraibizer (1999), Minguzzi et al. (1999), Sánchez et al.(2000 a,b), Lopez-Galindo and Viseras (2000), Carretero (2002), Carretero et al. (2006), Gomes and Silva (2006), Carretero and Pozo (2007), Ferrell (2008), and Williams et al. (2008).

The historical and technical aspects of the beneficial effects of clays in medicine has been described by Bech (1996), while the beneficial effects and hazardous effects of clay minerals upon human health are the topics of excellent reviews by Carretero (2002), Carretero et al. (2006), and Gomes and Silva (2006).

Ferrell (2008) mentions that edible earths for medicinal and spiritual purposes were sold openly in markets, for instance, in Mexico, in New Mexico, (under the form of capsules), in Guatemala (under the form of tablets), and in Nigeria (under the form of discs and rough blocks). Vermeer and

Ferrell (1985) report the use in Nigeria of "eko" for anti-diarrhoeal purposes.

According to Ferrell (2008) the direct consumption of the so-called "edible earths" for medicinal and spiritual purposes occurs worldwide and is deeply rooted in "the so-called "folk medicine" and religion. This is the case in Chimayo, New Mexico, where close to the Sanctuary clay is extracted from a pit and ingested for spiritual healing by the peregrines. The author has investigated the mineralogical composition of 22 samples of healing clays from New Mexico, North America and other regions of the world, and he did find out how varied are the clays being consumed: either monomineralic clays essentially consisting of kaolinite or smectite; or complex polymineralic mixtures of illite, kaolinite, smectite, and chlorite or vermiculite.

The chemical composition, mean particle size, particle size distribution, cation exchange capacity, nature of exchangeable cations, specific surface area, specific heat and heat diffusivity, are properties of natural clays that are considered relevant to their use in Geomedicine.

According to Gomes and Silva (2001; 2006) the clay or mud used as healing material must have fine grain size, have high specific surface area, high specific heat, and high adsorption and absorption capacities, while its cooling rate or heat diffusiveness should be low. Also clay or mud should also be easy to handle, and give a pleasant sensation when applied directly on to the skin.

According to Droy-Lefaix and Tateo (2006), within the properties referred to, high adsorptive capacity is the most important property, when clay or mud is used as healing material, for instance, of gastrointestinal illnesses, promoting the adsorption of microbes, viruses, or their toxins, and the modification of the mucus lining reinforcing the natural defences of both stomach and intestine tissues.

According to Aufreiter et al. (1997) besides these beneficial effects clay or mud can supply nutritional mineral supplements (e.g. Fe, Cu). These and other elements (e.g. Ca, Mg, Na, K…) fixed in a reversible mode at the surfaces of clay minerals, depending on their electric charge and cation exchange capacity, can become available too as nutritional supplements.

The adsorptive capacity of clay or mud is directly related with grain size and surface area, as well as with electric charge and ion exchange capacity, these two properties depending on clay minerals typology. The kind of clay mineral consumed and the pH of the system can determine whether the mineral nutrients are supplied or depleted from the body by adsorption or desorption from the clay surface (Diamond, 1999).

Recent investigations found out the antibacterial and bactericidal properties of some clay, based on experiments carried out by Williams et al. (2004), Ma'or et al. (2006) and Haydel et al. (2008), showing the ability to kill a broad spectrum of pathogenic bacteria. One of these bacteria is *Mycobacterium ulcerans* which causes the skin common chronic disease named *Buruli ulcer*, mostly endemic in much of central and western Africa. Treated with special clay of bentonite type the skin lesions or wounds became gradually less grave due to skin tissue regeneration.

In terms of typology natural healing clays can be classified into three main groups: swelling green clays (rich in smectite, closely related to bentonite, bearing dioctahedral Fe^{2+}, alkaline pH, intermediate electric charge, high specific surface area, and high sorption), illite clays (white, near white or green, high electric charge, intermediate specific surface area, high cation exchange capacity, and high sorption), kaolinite clays (white, low electric charge, low specific surface area, low cation exchange capacity, and low sorption), and fibrous clays bearing either palygorskite or sepiolite (white or near white, low electric charge, high specific surface area, intermediate cation exchange capacity, and high sorption).

Clays are pelitic or lutitic geomaterials. Particular types of clay and mud are used worldwide in the form of both mud baths and hot cataplasms or patches of *peloids*. The associated treatments are therefore called *mudtherapy* or *peloidtherapy* (or *pelotherapy*, abbreviated).

Peloids are made of mixtures of clay or mud and thermal spring water or sea water. They are applied at an initial temperature of ~ 50 ºC (i.e., higher than human body temperature), and left until the temperature decreases to ~36 ºC). The process lasts about 20 minutes, depending upon the characteristics (texture, composition, specific heat and heat diffusiveness) of the clay/mud paste which is wrapped in a permeable tissue.

Geophagy or geophagia can be defined as the deliberate eating or ingestion of earth, soil, or clay. In certain countries and regions some communities still practise geophagy for therapeutic and religious purposes, or even to relieve famine.

The first reference to geophagy was made by Aristotle (*in* Mahaney et al., 2000). Not only men but other animals (herbivore mammals such as gorillas and chimpanzees, reptiles and birds) eat earth. In general, humans have preference for soils bearing a significant amount of clay and, sometimes, iron oxides/hydroxides. In fact, in certain regions of Africa and South America, people select soils from special sources such as termite mounds.

In the last two decades geophagy has deserved much interest from researchers (Abrahams and Parsons, 1996; Ziegler, 1997; Geissler, et al.1998; Geiss; Krishnamani and Mahaney, 2000; Mahaney et al. 2000; Wilson, 2003; Abrahams, 2005; Ferrell, 2008). The papers by Wilson (2003) and Abrahams (2005) are excellent reviews on geophagy.

According to Wilson (2003) some hypotheses have been proposed to account for geophagy:1) adsorption of toxic or unpalatable plant compounds;2) anti-diarrhoeal effects;3) antacid effects;4) countering enteric parasites;5) supplementation of mineral elements;6) countering famine;7) social, cultural, religious factors.

In regards with soil bearing clay the healing effects may be explained in terms of the adsorptive power of the clay minerals (e.g., kaolinite, illite, smectite, sepiolite, palygorskite), and associated minerals (e.g., quartz, feldspar, mica, calcite, dolomite, goethite) which are present in the ingested earth, soil, or clay.

Because of their very small particle size (often <1μm), large specific surface area, and negative layer charge, clay minerals (hydrous phyllosilicates) have a large propensity for adsorbing and retaining extraneous cations and molecules. Some clay minerals, notably smectites, can also intercalate a wide range of small and polymeric organic compounds (Theng, 1974, 1979; Lagaly, 1999).

Smectite bearing clays, the so-called green healing clays, are widely used in pelotherapy due to their high swelling, plasticity, specific surface, and cation exchange capacity.

The heat liberated by clay/mud pastes, after being properly warmed up and placed in contact with the human body, reduces both arthicular and muscular inflammations. This phenomenon can be monitored by thermography. Simultaneously, the heat-induced opening of pores in the skin promotes the absorption into both extra-and intra-cellular fluids of essential major and minor elements (e.g., Si, Ca, Mg, Fe, P, S, Sr, Zn and Cu) which are required for good health.

Cation exchange between the main exchangeable cations existing in the paste (such as, Ca^{2+}, Mg^{2+}) and the main exchangeable cations eliminated by the human body (such as, K^+, Na^+), regulated by the prevailing concentration gradient is likewise promoted by heat.

Nevertheless, the interaction between clay/mud and the human body, particularly the pathways of the ions or molecules going into the body, is still not well understood, and requires a great deal of systematic research based upon adequate clinical tests.

Clay or mud particles are commonly smaller than bacteria. When coated or encapsulated by clay particles, bacterial cells lose activity and can be eliminated. Clays with smectite and palygorskite as major constituents are commonly and widely used for the treatment of intestinal disorders.

According to Reinbacher (1999) anti-diarrhoea formulations sold in the USA contain about 75% palygorskite, while in Germany the clay mineral used in formulations of comparable efficacy consists of kaolinite.

Kaolinite, smectite, palygorskite, and sepiolite incorporated in pharmaceutical and animal feed formulations, can adsorb certain chemical compounds as well as toxins, bacteria and viruses. When taken internally, these minerals give protection to the lining of the stomach and intestines. Applied externally, clay or mud is used in the treatment of skin diseases, such as psoriasis, seborrhea and acne, as well as rheumatic ailments, arthropathies, post-traumatic conditions and muscular dislocations.

In Europe it is possible to find pharmaceutical formulations based upon specific clay minerals, such as kaolinite and smectite (more precisely dioctahedral smectite). Kaolinite is also a constituent of facial masks, used for toning the underlying skin. Pastes made of clay/mud from thermal springs containing sulphurous thermal water, green sulphurous algae and vitamins E and PP are also used in facial masks. Those pastes produced in Terme di Répole, Italy, are recommended as skin-nourishing, anti-wrinkle products.

There seems to be growing interest in treatment by natural means as an alternative to conventional medicine. It is the so-called naturotherapy which involves distinctive methodologies, such as: phytotherapy, hydrotherapy, mudtherapy, thermotherapy, etc.

Naturotherapy involving minerals or other geologic resources (e.g., sea water and thermal spring water) may be called 'Geomedicine' (Gomes and Silva, 2001).

Naturopathologists believe that good health depends upon three main factors: structural, biochemical and emotional. Minerals, particularly those associated with clay and mud, would be included in the second group because they participate in biochemical interactions.

Recent developments in molecular biology and biotechnology, as well as in the new field of pharmacogenetics, further indicate that every human being has a unique genetic and physiologic make-up, and hence would react differently to the same pharmaceutical agent. The implications of this concept are both complex and intriguing since an individual patient would require a particular, 'tailor-made' treatment. Similarly, individual patients might be expected to react differently to naturotherapy. A certain treatment may be totally ineffective, or even may produce negative effects. However, damages arising from naturotherapy would not be as serious as those caused by conventional medicine.

MATERIALS AND METHODS

Clay A displays pretty white colour and softness; it appears to be fine grained and shows easy slaking into water providing a milky dispersion.

Clay B displays beige colour; comparatively to Clay A it appears to be coarser and shows difficult and partial slacking into water.

Grain size distribution and mean grain size were determined in an apparatus Sedigraph 5100 manufactured by Micromeritics, based on X-ray diffusion by the fine grains. Previous to grain size distribution analysis test clay samples were slacked in distilled water and passed through an ASTM sieve with openings of 0.63µm.

The mineralogical composition was determined on total samples and on the less than 63µm and 2µm separates, by X-Ray Diffraction (XRD) using a Philips X' Pert diffractometer and monochromatic Cu Kα radiation. The chemical composition, comprising major, minor, and trace elements, was determined by X-Ray Fluorescence (XRF) using a Pan Analytical Aχios spectrometer.

Cation Exchange Capacity (CEC) was determined on natural samples of Clay A and Clay B, using the ammonium acetate method. Plasticity was determined using the Casagrande method.

RESULTS AND DISCUSSION

Clay A is extremely fine grained; particles median diameter was estimated at 0.25µm, and particles modal diameter was estimated at 0.24µm.

The cumulative curve relating the cumulative mass finer (in %) *vs.* equivalent spherical diameter (e.s.d.) (in µm) shows that 85% (in mass) of particles have e.s.d. less than 1µm, about 60% (in mass) of particles have e.s.d. less than 0.3µm, and about 10% (in mass) have e.s.d. less than 0.1µm. This last class of particles could be classified as colloidal particles.

The outlines of the frequency curve point out, either to the almost complete *in situ* argillization of the source rock (assumed to be phonolite), or to some human preparation and concentration of the altered source rock.

Figures 1A and 1B show for Clay A and Clay B, respectively, the histograms relating the frequency of mass population (% in interval) *vs.* equivalent spherical diameter (in µm).

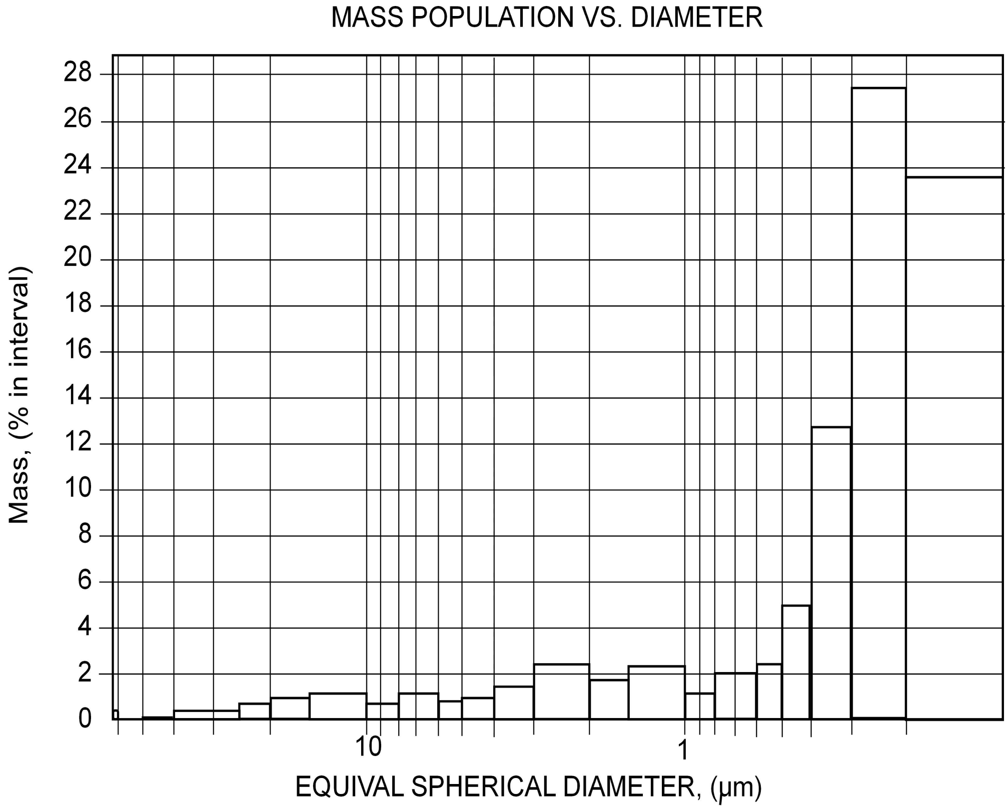
Clay B, in comparative terms, is much coarser than clay A; its median diameter was estimated at 0.75µm, and its modal diameter was estimated at 4.16µm.

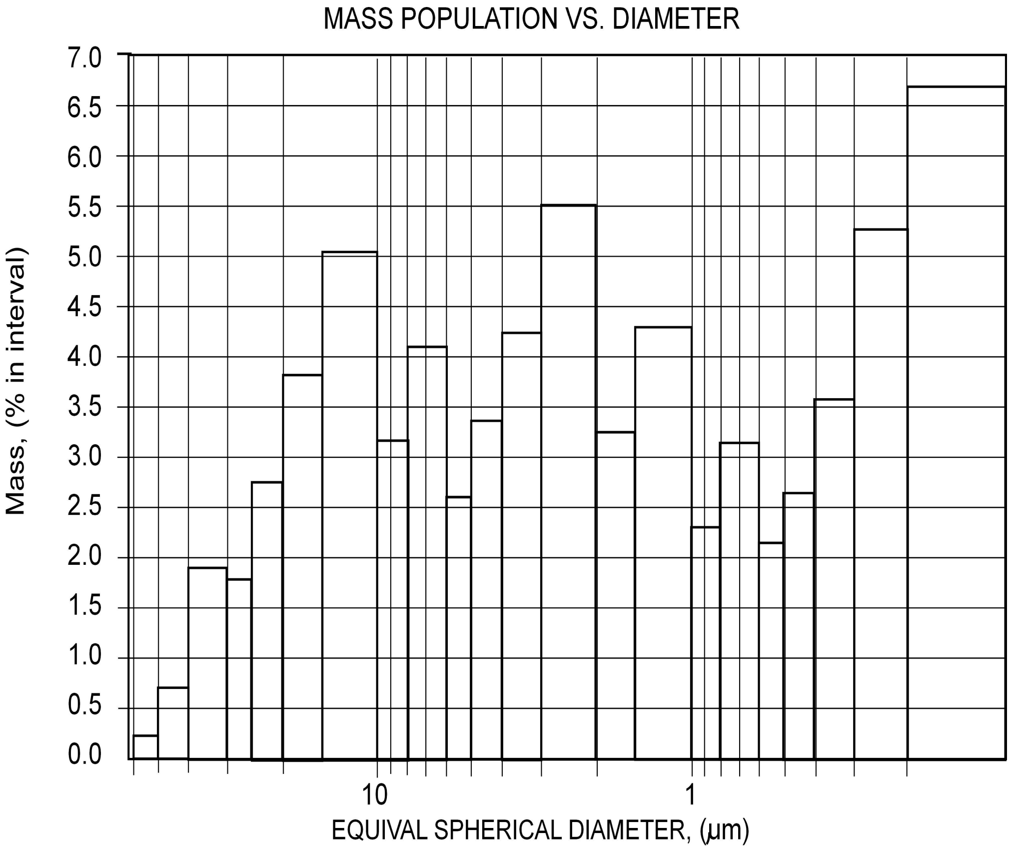
The cumulative curve relating mass finer (in %) *vs.* equivalent spherical diameter (e.s.d.) (in µm) shows that about 53% of particles have e.s.d. less than 1µm, and about 27% of particles have e.s.d. less than 0.15µm.

The tri-modal frequency curve shows no particle classification indicating that the argillization of the source rock took place *in situ*.

Many particles of clay minerals have sizes which are commonly smaller than bacteria sizes, and because of their extremely small particles (particularly those with e.s.d less than 0.1µm) bacteria cells can be encapsulated and in consequence they can loose activity and be eliminated. Also, smectite particles are able to adsorb certain chemical compounds as well as toxins, bacteria, and viruses.

Within clay minerals, smectite is the clay mineral characterized by the smallest particles and great adsorption and absorption capacities, reason why smectite is widely used for the treatment of intestinal disorders. When taken internally, smectite and other clay minerals showing very fine particles can provide protection to the lining of the stomach and intestines.

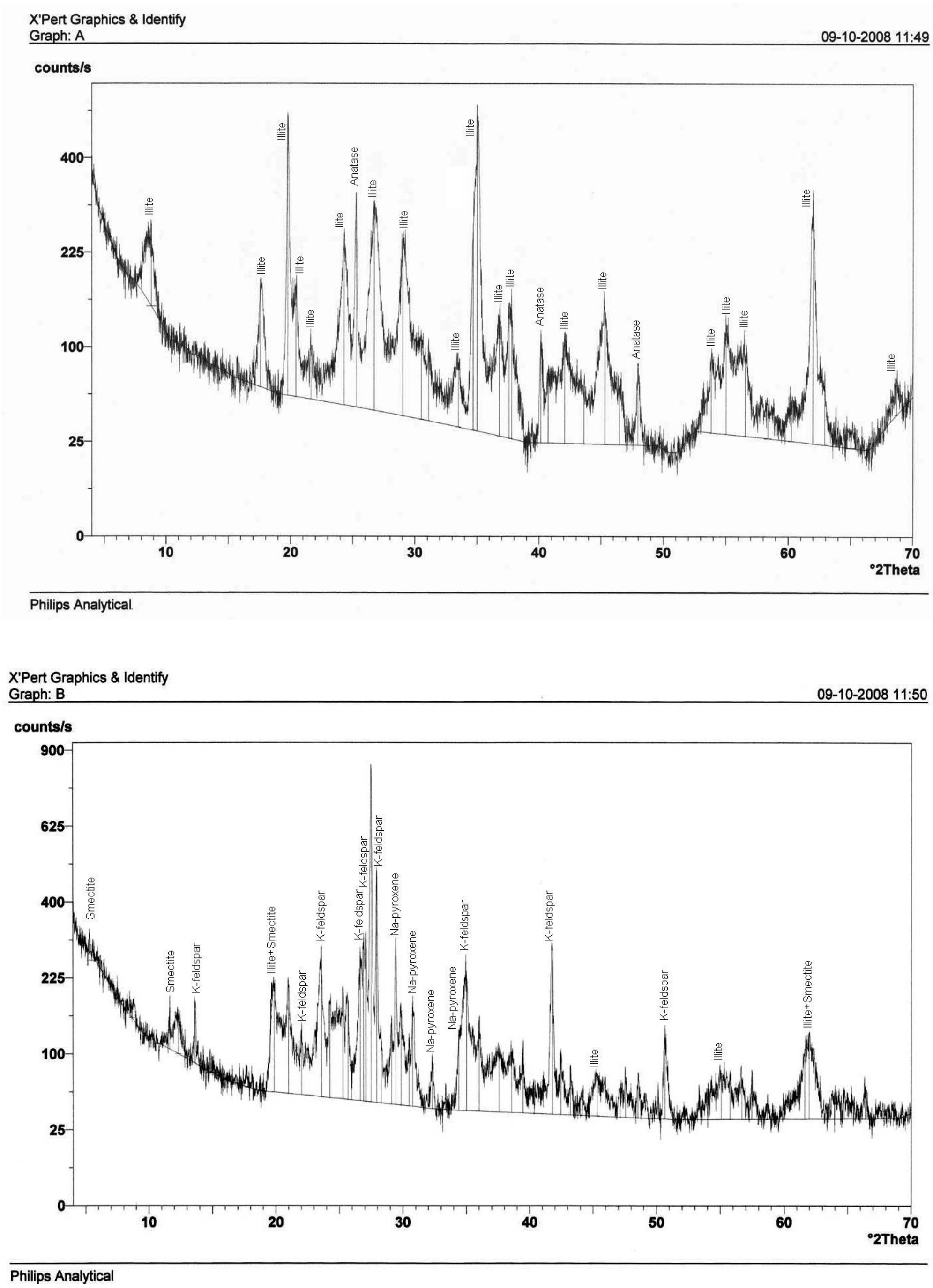




Figures 1A and 1B: Frequency curves corresponding to Clay A and Clay B showing the respective particle size distribution patterns;

Palygorskite, a fibrous clay mineral, also enters in anti-diarrheal formulations of certain medicines, mainly due to its very high capacity of liquids sorption (Reinbacher, 1999).

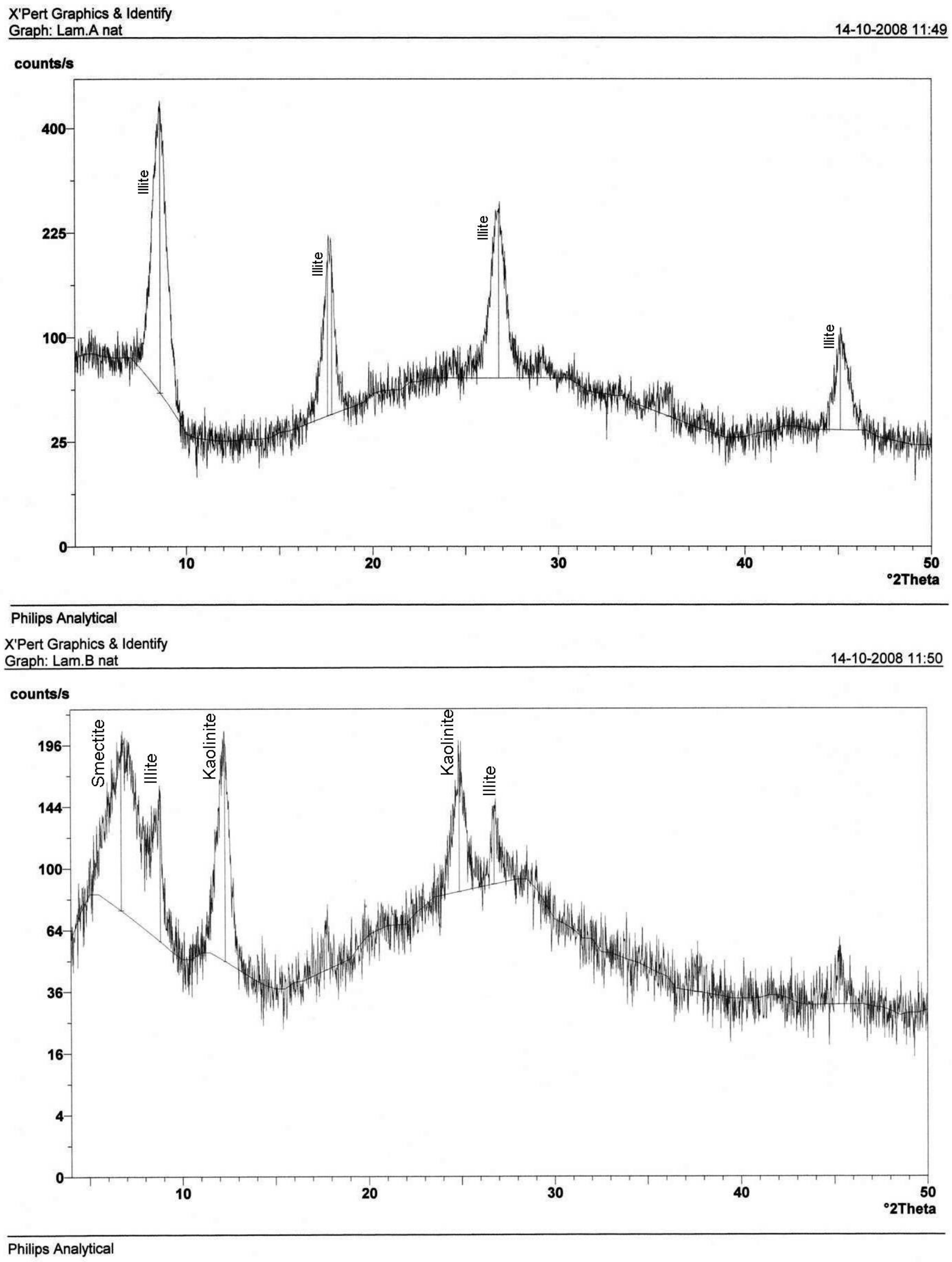
Figure 2A displays the X-ray diffraction pattern of Clay A corresponding to a total powder sample, in the natural state and non-oriented, whose interpretation indicates an almost monomineralic composition based on dioctahedral illite and anatase.



Figures 2A and 2B: X-ray diffraction patterns of non oriented total samples corresponding to Clay A and Clay B.

Figure 2B displays the XRD pattern of Clay B corresponding to a total powder sample, in the natural state and non-oriented whose interpretation indicates the following composition: dioctahedral illite, dioctahedral smectite or diosmectite, kaolinite, K-feldspar, Na-pyroxene and anatase.

Figures 3A and 3B show de X-ray diffraction pattern of oriented aggregates (O.A.), in the natural state, of the less than 2μm fractions (clay fraction) of Clay A and Clay B; the expansive component (smectite) of Clay B becomes much more evident.



Figures 3A and 3B: X-ray diffraction patterns of oriented aggregates (O.A), in the natural state, of the less than 2μm fractions (clay fraction) of Clay A and Clay B.

Chemical composition, comprising major, minor, and trace elements were determined by X-Ray Fluorescence (XRF).

Table I shows the contents (in weight %) of major and minor elements existent in Clays A and in Clay B.

Table I: Chemical composition (in weight %) of the medicinal Clay A and Clay B from Cape Verde.

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	MgO	CaO	K_2O	Na_2O	I.L.
Clay A	50.33	28.07	3.09	2.21	0.09	1.62	0.28	7.63	0.65	5.9
Clay B	51.40	24.14	3.69	1.17	0.03	0.72	2.52	6.66	1.61	8.0

Table II: Contents (in ppm) of the trace element existent in Clay A and in Clay B.

	V	Cr	Cu	Zn	Sr	Mo	Br	As	I	Se
Clay A	110	2	11	158	40	23	11	7	3	1
Clay B	107	63	14	156	325	2	20	1	18	1

Table II shows the contents (in ppm) of the trace element existent in Clay A and in Clay B.

Besides the elements referred to in table II other elements have been analysed, their contents being expressed in ppm too:

Clay A: Ni -2; Cd -2; Ba -70; Ga -104; Rb -279; Zr -2,753; Ce -1,356; La -562; Pb -9; Th -47; U -13; Hf -63;

Clay B: Ni -6; Cd -1; Ba -247; Ga -43; Rb -136; Zr -1,172; Ce -208; La -173; Pb -19; Th -23; U -5; Hf -23.

The relatively high concentration of rare earths in both clays deserves to be emphasized. This fact points out to a common source of the clays, weathering of an alkali igneous rock.

Clay A relatively to Clay B indicates deeper argillization of the source rock. It looks like that both clays have been collected in the same area from the same or similar source rock. However, in case of both clays have been collected in the same well, most probably Clay A would have been in a position near to the ground surface relatively to Clay B. The higher content of TiO_2, under the form of anatase, in Clay A relatively to Clay B, is an argument in favour of this assumption, due to the reckoned low mobility of Ti in weathering profiles.

Cation Exchange Capacity (CEC) of Clay A is 50meq/100g, whereas CEC of Clay B after being ground to less than 0.063 μm is 60meq/100g.

Plasticity index of Clay A was estimated at 30, whereas the Plasticity index of Clay B after being ground to less than 0.063 μm was estimated at 35.

CONCLUSIONS

The obtained analytical data corresponding to the two commercial healing clays, Clay A and Clay B from the Boavista' island, Cape Verde' archipelago, show the existence of great affinities between both clays, in terms of genesis, and of mineralogical and chemical properties.

Nevertheless, the referred two clays show significant differences in regards with clay mineral assemblages. Clay A is almost monomineralic, being essentially constituted of dioctahedral illite. Clay B has a more complex clay minerals assemblage, consisting of dioctahedral illite, dioctahedral smectite or diosmectite and kaolinite.

Both clays display physical and chemical properties that could justify their use via oral, particularly for the healing of gastrointestinal affections, essentially based on their high sorption capacities.

REFERENCES

Abrahams, P.W. (1997) Geophagy (soil consumption) and iron supplementation in Uganda, Tropical Medicine and International Health, 2, 617-623.

Abrahams, P.W. & Parsons, J.A. (1996) Geophagy in tropics: a literature review, The Geographical Journal, 162, 63-72.

Abrahams, P.W. & Parsons, J.A. (1997) Geophagy in tropics: an appraisal of three geophagic materials, Environmental Geochemistry and Health, 19, 19-22.

Abrahams, P.W. (2005) Geophagy and the involuntary ingestion of soil, *In*: Selinus, O., Alloway, B., Centeno, J. A., Finkelman, R. B., Fuge, R., Lindh, U., Smedley, O. (editors), Essentials of Medical Geology, Elsevier, 435-458.

Aufreiter, S.; Hancock, R.G.; Mahamey, W.C., Stambolic-Robb, A.; Sanmugadas, K. (1997) Geochemistry and mineralogy of soils eaten by humans, International Journal of Food Sciences and Nutrition, 48, 293-305.

Barbieri, P. (1996) Validitá terapeutica dei fanghi delle Terme di Salice. Atti Conv. Argille Curative (Veniale, F., ed.), Gruppo Italiano AIPEA, Salice Terme PV (Italy), Tipografia Trabella, Milano, 13-15.

Bech, J. (1996) Aspectos históricos y técnicos de las arcillas de uso medicinal, *In*: IX Simp. Grupo Especializado de Cristalografia, La Cristalografia y la Industria Farmacêutica, Ed Reales Soc. Esp. Física y Química, Univ. Granada, 15-17.

Bettero, A.; Marcazzan, M.; Semenzato, A. (1999) Aspetti reologici e tensiometrici di matrici fangose di impiego termali e cosmético, Proposta di un protocollo per la loro qualificazione, Atti Simposio "Argille per fanghi peloidi termali e per trattamenti dermatologici e cosmetici", Montecatini Terme. Mineralogica e Petrografica Acta XLII, 277-286.

Browne, J.E.; Feldkamp, J.R.; White, J.L.; Hem, S.L. (1980) Characterization and adsorptive properties of pharmaceutical grade clays, Journal Pharmaceutical Science, 69, 816-823.

Cara, S.; Carcangiu, G.; Ligas, P.; Padalino, G.; Palomba, M.; Tamanini, M.; Uras, I. (1996) Possibilità di impiego dele bentoniti sarde nel campo delle argille sanitarie. Atti Conv. Argille Curative (Veniale, F., ed.), Gruppo Italiano AIPEA, Salice Terme PV (Italy), Tipografia Trabella, Milano, 103-117.

Cara, S.; Carcangiu, G.; Tamaniini, M. (1999) Proprietà termiche dei fanghi termali bentonitici: proposta di una metodologia speditiva per un controllo di qualità. Atti Simposio "Argille per fanghi peloidi termali e per trattamenti dermatologici e cosmetici", Montecatini Terme. Miner. Petrogr. Acta XLII, 299-305.

Cara, S.; Carcangiu, G.; Padalino, G.; Palomba, M.; Tamanini, M. (2000a) The bentonites in pelotherapy: chemical, mineralogical and technological properties of materials from Sardinia deposits (Italy), Applied Clay Science, 16, 117-124.

Cara, S.; Carcangiu, G.; Padalino, G.; Palomba, M.; Tamanini, M. (2000b) The bentonites in pelotherapy: thermal properties of clay pastes from Sardinia (Italy), Applied Clay Science, 16, 125-132.

Carretero, M. I. (2002) Clay minerals and their beneficial effects upon human health: a review, Applied Clay Science, 21, 155-163.

Carretero, M. I.; Gomes, C.S.F.; Tateo, F. (2006) Clays and Human Health, In: Handbook of Clay Science, Bergaya, F., Theng, B., Lagaly, G. (editors), Elsevier, Amsterdam.

Carretero, M.I. & Pozo, M. (2007) Mineralogia Aplicada: Salud y Médio Ambiente, Thomson Editores, España, 406p.

Cornejo, J. (1990) Las arcillas en formulaciones farmaceuticas, *In*: Galán, E., Ortega, M. (editors), Conferencias de IX y X Reuniones de la Sociedad Española de Arcillas, 51-68.

Diamond, J.M. (1999a) Dirty eating for healthy living, Nature, 400, 120-121.

Diamond, J.M.; Bishop, K.D.; Gilardi, J.D. (1999b) Geophagy in New Guinea birds, Ibis, 141,181-193.

Droy-Lefaix, M.T. & Tateo, F. (2006) Clays and clay minerals as drugs, In: Handbook of Clay Science (editors, Bergaya, F., Theng, B. K.G., and Lagaly, G.), 743-753, Developments in Clay Science, 1, Elsevier, Amsterdam.

Ferrand, T. & Yvon, J. (1991) Thermal properties of clay pastes for pelotherapy, Applied Clay Science, 6, 21-38.

Ferrell, R.E. (2008) Medicinal Clay and Spiritual Healing, Clay and Clay Minerals (in press).

Galán, E.; Liso, M.J.; Forteza, M. (1985) Minerales utilizados en la Industria Farmaceutica, Bol. Soc. Esp. Min., 369-378.

Geissler, P.W. (1998) Geophagy, iron status and anaemia among pregnant women on the coast of Kenya, Transactions of the Royal Society of Tropical Medicine and Hygiene, 92, 549-553.

Geissler, P.W. (2000) The significance of earth-eating: social and cultural aspects of geophagy among Luo children, Africa, 70, 653-682.

Gomes, C. & Silva, J. (2001) Beach sand and bentonite of Porto Santo Island: Potentialities for applications in Geomedicine, Gomes, C. & Silva, J. (editors), O Liberal, Câmara de Lobos, Madeira, 60 p.

Gorgoni, C.; Bertolani, M.; Ghittoni, A.G.; Pallante, P. (1999) Comoposizione, radiottivitá, mineralogia e reologia dei fanghi delle Salse Emiliane, Abstracts Book of Simposio "Argille per fanghi peloidi termali e per trattamenti dermatologici e cosmetici", Montecatini Terme, Gruppo Italiano AIPEA.

Haydel, S.E.; Remineh, C.M.; Williams, L.B. (2008) Broad-spectrum in vitro antibacterial activities of clay minerals against antibiotic-susceptible and antibiotic-resistant bacterial pathogens, Journal of Antimicrobial Chemotherapy (in press).

Hermosin, M.C.; Cornejo, J.; White, J.L.; Hem, S.L. (1981) Sepiolite, a potential excipient for drugs subject to oxidative degradation. J. Pharm. Sci., 70, 189-192.

Jobstraibizer, P. (1999) Definizione mineralogica e chimica del fango termali e per trattamenti dermatologici e cosmetici, Montecatini Terme, Mineral. Petrogr. Acta XLII, 317-327.

Johns, T. & Duquette, M. (1991) Detoxification and mineral supplementation as functions of geophagy, American Journal of Clinical Nutrition, 53, 448-456.

Krishnamani, R. & Mahaney, W.C. (2000) Geophagy among primates: adaptive significance and ecological consequences, Animal Behaviour, 55,899-915.

Lagaly, G. (1999) Introduction: from clay mineral-polymer interactions to clay mineral-polymer nanocomposites, Apllied Clay Science, 15, 1-9.

Letizia, G. (1975) La fango-balneoterapia sulfurea in ortopedia e traumatologia, Clinica Termale, 28.

Lopez-Galindo, A. & Iborra, C. (1996) Usos farmaceuticos de arcillas especiales (sepiolita e palygorskita). Atti Conv. "Argille Curative", Veniale, F. (editor), Gruppo Italiano AIPEA, Salice Terme (PV), Italy, Tipografia Trabella, Milano, 45-53.

Lopéz-Galindo, A. & Viseras, C. (2000) Pharmaceutical applications of fibrous clays (sepiolite and palygorskite) from some circum-mediterranean deposits, *In*: Gomes, C. S. F. (ed.), 1st Latin American Clay Conference, Funchal, Madeira, Associação Portuguesa de Argilas (APA), 1, 258-270.

Mahaney, W. C.; Milner, M.W.; Mulyono, H.; Hancock, R.G.V.; Aufreiter, S.; Reich, M.; Wink, M. (2000) Mineral and chemical analyses of soils eaten by humans in Indonesia. International Journal of Environmental Health Research, 10, 93-109.

Ma'or, Z.; Henis, Y.; Along, Y.; Orlov, E.; Sorensen, K.B.; Oren, A. (2006) Antimicrobial properties of Dead Sea black mineral mud, International Journal of Dermatology, 45,504-511.

Mascolo, N.; Summa, V.; Tateo, F. (1999) Characterization of toxic elements in clays for human healing use, Applied Clay Science, 15, 491-500.

Minguzzi, V.; Morandi, N.; Tagnin, S.; Tateo, F. (1999) Le argille curative in uso negli stabilimenti termali emiliano-romagnoli: verifica della comosizione e delle propietá. Atti Simposio "Argille per fanghi peloidi termali e per trattamenti dermatologici cosmetici", Montecatini Terme. Miner. Petrogr. Acta, XLII, 287-298.

Novelli, G. (1996) Applicazioni medicali e igieniche delle bentoniti, Atti Conv. "Argille Curative", 25-44, (Veniale, F. ed.), Gruppo Italiano AIPEA, Salice Terme (PV), Italy, Tipografia Trabella, Milano.

Novelli, G. (2000) Bentonite: a clay over the centuries, Incontri Scientifici, V Corso di Formazione "Metodi di Analisi di Materiali Argillosi", Fiore, S. (editor), Gruppo Italiano AIPEA, 263-304.

Reinbacher, W.R. (1999) A brief history of clay in medicine, Clay Minerals Society News, 11, 1, 22-23.

Robertson, R.H.S. (1986) Fuller´s Earth: A History of Calcium Montmorillonite, Mineralogical Society (occasional publication), 421p, Volturna Press, Hythe, Kent, UK.

Robertson, R.H.S. (1996) Cadavers, choleras and clays, Mineralogical Society Bulletin,113, 3-7.

Sánchez, C.; Parras, J.; Carretero, M.I.; Barba, P. (2000a) Aplicaciones terapéuticas de las arcillas de Santa Cruz de Mudela (Ciudad Real). In: Pascual, J (ed.), Integración Ciencia-Tecnologia de las Arcillas en el Contexto Tecnológico-Social del Nuevo Milenio. Sociedad Española de Arcillas, 31-40.

Sánchez, C.; Parras, J.; Carretero, M.I.; Barba, P. (2000b) Behaviour of matured illitic-smectitic clays for pelotherapy. In: Gomes, C. S. F. (ed.), 1st Latin American Clay Conference, Funchal, Madeira, Associação Portuguesa de Argilas (APA), v.2, 317-321.

Sánchez, C.; Parras, J.; Carretero, M.I. (2002) The effect of maturation upon the mineralogical and physicochemical properties of illitic-smectitic clays for pelotherapy. Clay Minerals, 37, 3, 457-463.

Summa, V. & Tateo, F. (1998) The use of pelitic raw materials in thermal centres: mineralogy, geochemistry, grain size and leaching test: examples from the Lucania area (southern Italy), Applied Clay Science, 12, 403-417.

Tateo, F. & Summa, V. (2007) Element mobility in clays for healing use, Applied Clay Science, 36, 64-76.

Tateo, F.; Summa, V.; Gianossi, M.L.; Ferrero, G. (2006) Healing clays: Mineralogical and geochemical constraints on the preparation of clay-water suspension (“argillic water”), Applied Clay Science, 33, 3-4.

Theng, B.K.G. (1974) The chemistry of clay-organic reactions, Wiley, New York, 343 p.

Theng, B.K.G. (1979) Formation and properties of clay-polymer complexes, Elsevier, Amsterdam, 362p.

Torrescani, C. (1990) Utilizzo del fango termale sulfureo nel tratattamento della cute seborreica, Comestici Derm., 30, 59-71.

Ueda, H. & Hamayoshi, M. (1992) Sepiolite as a deodorant material: an ESR study of its properties, Journal of Materials Science, 27, 4997-5002.

Veniale, F. (1996) Argille Curative: Antefatti, fatti e misfatti, *In*: Atti Convegno “Argille Curative”, 1-11, Veniale, F. (editor), Salice Terme (PV), Gruppo Italiano AIPEA, Tipografia Trabella, Milano.

Veniale, F. (1999) Le argille nelle terapie curative: dalla leggenda all´empirismo, fino ai tempi moderni, Atti Simposio “Argille per fanghi peloidi termali e per trattamienti dermatologici e cosmetici”, Montecatini Terme, Miner. Petrografica Acta, XLII, 263-265.

Veniale, F. & Setti, M. (1996) L´argilla di Pontestura (AL): Potenzialità d´impiego nella formulazione di fanghi peloid. Atti Conv. "Argille Curative", 139-145, (Veniale, F. ed.), Gruppo Italiano AIPEA, Salice Terme (PV), Tipografia Trabella, Milano.

Veniale, F.; Setti, M.; Soggetti, F.; Lofrano, M.; Troilo, F. (1999) Esperimenti di maturazione di geomateriali argillosi com acqua sulfurea e salso-bromo-ionica per la preparazione di fanghi peloidi termali e per trattamenti dermatologici e cosmetici, Montecatini Terme, Miner. Petrogr. Acta, XLII, 267-275.

Vermeer, D.E. & Ferrell, R.E. (1985) Nigerian geophagical clay: A traditional antidiarrheal, Science, 227, 634-636.

Viseras, C. & López-Galindo, A. (1999) Pharmaceutical applications of some Spanish Clays (sepiolite, palygorskite, bentonite): Some pre-formulation studies, Applied Clay Science 14, 69-82.

Williams, L.B.; Holland, M.; Eberl, D.D.; Brunet, T.; Brunet de Courrsou, L. (2004) Killer Clays! Natural antibacterial clay minerals, Mineralogical Society Bulletin, 139, 3-8.

Wilson, M.J. (2003) A review of clay mineralogical and other characteristics of geophagic materials ingested by animals and man, Applied Study of Cultural Heritage and Clays, Pérez-Rodriguez, J. L. (editor), Consejo Superior de Investigaciones Científicas, Madrid, 301-326.

Yvon, J. & Ferrand, T. (1996) Preparation ex-situ de peloides, Proprietés thermiques, mecaniques et d´exchange, Atti Conv. "Argille Curative", (Veniale, F., editor), Gruppo Italiano AIPEA, Salice Terme (PV), Tipografia Trabella, Milano, 67-78.

Ziegler, J.L. (1997) Geophagy: a vestige of palaenutrition, Tropical Medicine and International Health, 2, 609-611.