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Minerals and clay minerals in medical geology

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Abstract

Medical geology is an emergent field of science that for some authors deals with the relationships between the geological environment and health problems in humans, animals and plants. Chemical elements, minerals, rocks, soils, water and air are the essential components of the geologic environment. Both quality and quantity of these components condition very much the living quality and the life duration, due to the beneficial and hazardous effects they have upon organisms, man, other animals, and plants. Medical geology is a multidisciplinary scientific field shared by specialists of distinct areas and scientific domains, such as earth sciences, environmental sciences, medicine, public health, biology, biochemistry, chemistry, pharmacy, nutrition, and others. Certain diseases are attributed to several minerals *sensu latu* (concept that includes the minerals *sensu restrictu* considered as natural, inorganic and crystalline solids, the so-called oligoelements or trace minerals, the biominerals and mineral resources such as natural mineral water), naturally or humanly derived. Within minerals, clay minerals, the essential constituents of clays, are omnipresent at the earth surface where organisms live, and due to their specific properties they can interact, positively as a rule, with them. Some clay minerals are being used, either as active principles (gastrointestinal protectors, laxatives, antidiarrhoeaics), or as excipients (inert bases, emulsifiers, lubricants) in certain medicines. Also they participate in formulations used for topical applications in both dermopharmacy and dermocosmetics.

Keywords: Minerals; Trace minerals; Biominerals; Clays; Clay minerals; Medical geology

1. Medical geology

Man created in nature dependant on it for his survival and pleasure and the natural environment are two very complex entities made up of many components and variables, which are not yet fully identified and the interaction is still far from being satisfactorily understood.

Chemical elements, minerals, rocks, soils, water and air are the essentials of the natural environment, and over the years man has progressively accumulated experience regarding the interactions between these components, as well as the beneficial and hazardous effects they have upon organisms: man, other animals, and plants. Empirical knowledge related to human health, the practice of which is called "*Empirical Medicine*", is essential in many aspects of man's life and activity. Man quest for rational explanations based on science and technology.

Step by step, man increased his knowledge of the interaction between minerals and other geo-resources (such as soil, spring, sea and underground water) and human health by using the accumulated experience and scientific information, both fundamental and applied, provided by specialists of distinct areas and scientific

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domains (chemistry, biochemistry, biology, biotechnology, mineralogy, geochemistry, hydrochemistry, materials science, medicine, public health, pharmacy, nutrition, and others).

The recognition that an intimate relationship exists between the environment, particularly the geologic materials and processes and human/animal health, has led to the recent development of a new field of science called *Medical Geology* (Finkelman et al., 2001; Selinus, 2002; Bowman et al., 2003; Selinus, 2004; Bunnell, 2004; Centeno et al., 2005; Selinus et al., 2005). The last mentioned reference corresponds to the book entitled "*Essentials of Medical Geology: Impacts of the Natural Environment on the Public Health*". In our opinion it is an excellent book containing vast and very relevant information, however essentially limited to the negative effects of some geologic resources and processes on human health. However, clays and clay minerals, considered as being the first materials used by man for therapeutic purposes have not received much treatment in the book. The several topics dealt with in the book were classified into four main sections: Environmental Biology; Pathways and Exposures; Environmental Toxicology, Pathology and Medical Geology; Techniques and Tools.

Taking into account the foreseen scope of the expression *Medical Geology* we consider it as far of being perfect as Bunnell (2004) has considered too. This author rather prefers the expression *Geology and Public Health*.

On the one hand, the term *Geology* refers to a scientific area with a scope not limited to chemical elements and minerals, which apparently are the main intervening or conditioning factors on human/animal health. Geology is the study of the Earth in terms of its development as a planet since its origin, and includes the history of its life forms, the materials of which it is made and processes that affect these materials. How could, for instance, plate tectonics and geological mapping have direct influence on human living quality? However, minerals and chemical elements (either natural or anthropogenic) have direct impacts (benefits and risks) on human health, the reason why both geochemical and mineralogical surveys of soils, sediments and waters are of paramount importance.

On the other hand, the term *Medical* refers to the scientific area *Medicine*, having a scope not exclusively limited to the identification and interpretation of the impacts of both chemical elements and minerals on human/animal health. As a matter of fact, *Medicine* is based on three interdependent basic pillars: *scientific information*, *diagnosis* and *therapeutic*.

Anyhow, the emerging scientific field of Medical Geology, according to the authors who have introduced this expression, deals with the impacts of the natural environment on public health, such as: 1) exposure to toxic levels of trace elements, such as, arsenic, cadmium, lead, uranium and mercury; 2) deficiency of essential trace elements; 3) exposure to mineral dusts; 4) exposure to radioactivity and radon.

Centeno et al. (2005) consider Medical Geology as a complement of Environmental Medicine since it deals with the impacts of geological materials and processes on human and animal health. These same authors point out that the practitioners of Medical Geology should be involved in the following tasks: 1) to identify the environmental causes of known health problems and, in collaboration with biomedical/public health researchers, to seek solutions to prevent or minimize these problems; 2) to identify geochemical anomalies in soils, sediments, and waters that may impact on health; 3) to reassure the public when there are not warranted environmental health concerns deriving from geo-materials and processes; 4) to assess the beneficial health effects of geo-materials and processes.

The terms *Geomedicine and Environmental Geochemistry* have been traditionally used. According to Selinus et al. (2005) Ziess, in 1931, was the first who introduced the term *Geomedicine*, and considered it synonymous with *Geographic Medicine*, which he defined as "*a branch of medicine where geographical and cartographical methods are used to present medical research results*".

Some decades later, Läg (1990) in Norway redefined the term *Geomedicine* as the "*science dealing with the influence of ordinary environmental factors on the geographic distribution of health problems in man and animals*". It was in Nordic countries, particularly in Norway, that research in Geomedicine was most considered and developed. Läg (1990), a soil scientist, mentions a working group "Soil Science and Geomedicine" within the framework of the International Union of Soil Science. More recently, Gomes and Silva (2001) have used the term *Geomedicine*, too. Presently, the term *Geomedicine* is being deferred by the expression *Medical Geology*, an emerging scientific field dealing with the impacts of the natural environment on public health.

The expression *Environmental Medicine* is also employed, according to Fowles et al. (2005), for studies how environment affects health, including the practice to minimize any adverse effects. For instance, it has been estimated that over 80% of all cancers are environmentally induced, and this estimation includes cancers from smoking, dietary carcinogens, and exposure to polluted air and water, in addition to cancers due to cosmic and solar radiation.

Yushkin (2004) considers the importance, in modern mineralogy investigations, of two new research lines: *Environmental Mineralogy* (section of Mineralogy addressed to the investigation of the mineralogical factors of environment having negative effects, mineral induced pathogenesis, on human health) and *Medical Mineralogy* (section of Mineralogy addressed to the determination of medicinal properties of minerals and opportunities of application of minerals in therapeutic preparations, as they occur in nature, after being submitted to beneficiation treatments, or as components of drugs).

Recent research and publications on Medical Geology reduce the range of this scientific field to the relationship between the geochemistry of geo-materials and human health, and focus on the negative effects caused by the chemical properties of *minerals s.l.* (*sensu latu*) on the environment, clearly neglecting the positive or negative effects of their physical properties. It should be clarified that the concept of *mineral s.l.* employed in this publication includes (i) the concept of *minerals s.r.* (*sensu restrictu*), adopted, for instance, in Earth Sciences and Materials Sciences to designate a natural inorganic solid, generally crystalline, (ii) the concept of minerals, adopted, for instance, in Biochemistry, Medicine, Pharmacy and Nutrition to designate an inorganic chemical element in the environment or in the human body. In the last situation the expressions *mineral salts* and *macronutrients* are used when the chemical element occurs in relatively high or major quantity (expressed in mg g^{-1}). The expressions *trace minerals*, *oligoelements* and *micronutrients* are used when the chemical element occurs in minor or trace quantity (expressed in μg g^{-1}).

In this text the concept of *mineral s.l.* comprises mineral resources such as mineral water and natural or mineral gases (such as, volcanic gas and radon), the so-called biominerals formed inside the organism as the result of biological or cellular activity (Skinner, 2000), and chemical products of human activities derived from mineral resources such as combustion of mineral oil or derived products and coal, or firing of mineral raw materials used for the production of ceramics, glass and cement, all of which are able to interact with the human body.

The direct relationship between Geochemistry and human/animal health (Bowman et al., 2003) is widely demonstrated. Since Geology is a basic science, very broad in terms of goals, it simply cannot be reduced to the fundamental and applied study of the geochemistry of *minerals s.l.*

In medical terms, the assessment of both the positive and negative effects of *minerals s.l.* requires further research by *in vivo* and *in vitro* experiments and well-planned and systematized epidemiological studies. In fact, medical diagnosis and treatment of environmentally induced diseases also require further research and development.

It follows that expressions such as *Geomedicine*, *Minerals and Health*, *Georesources and Health*, or *Geology and Public Health* would be more appropriate than the expression *Medical Geology*. This expression, in spite of being more or less suitable do describe the discipline, increasingly deserves good acceptance within the international scientific community as it is easy to use and remember, and is accessible to general public and policy-makers (Bunnell, 2004).

The study of the hazardous effects of *minerals s.l.* on human health involves, as a rule, specialists of Epidemiology and Toxicology. Epidemiology refers to the study of disease occurrence in populations. Data on their prevalence and incidence will only be useful if associated with explicable variables that may relate to genetics, lifestyle, age, gender, occupation, environment, etc. (Nielsen and Jensen, 2005). Toxicology refers to the study of poisons and to the response of the body to xenobiotics.

As mentioned before, most of the scientific publications on the subject Medical Geology emphasizes the hazards on human health due to *minerals s.l.* neglecting their benefits. Very recently, Gomes and Silva (2006) published a bilingual (Portuguese and English) book entitled *Os Minerais e a Saúde Humana: Benefícios e Riscos/Minerals and Human Health: Benefits and Risks* that presents a fair balance of both positive and negative effects of minerals on human health.

2. Minerals as conditioners of human health

Man and minerals (here considered as natural inorganic solids, generally crystalline) are chemical systems having in common, in their composition, the major chemical elements oxygen, hydrogen, carbon, nitrogen, the so-called *mineral salts* sulfur, phosphorous, sodium, potassium, magnesium, and some others called *oligoelements* or *micronutrients* or *trace minerals* such as Fe, Cu, Zn, Se, Mn, I, F which are essential both to life and to the formation of minerals. Hence, considering their physical and chemical properties, minerals can be essential to keep human health in good shape, but in certain circumstances, deficiency or excess of minerals can be factors of human disease generation.

Minerals s.l. being present in the environment where man lives can interact, either positively or negatively with the human body. Although being essential to human health, some chemical elements in macro or micronutrients can be good, toxic or lethal, depending on the individual dosage.

Non-essential chemical elements can also be tolerable, toxic or lethal, depending on the dosage too. This principle was established long ago. According to Paracelsus (1493–1541 AC) "*all substances are poisons*; *there is none which is not a poison*; *the right dose differentiates a poison and a remedy*". Fig. 1 shows the Periodic Table distinguishing essential from toxic elements as well as those considered as essential and toxic.

The intake of minerals and non-toxic or toxic chemical elements by food, water, soil (through geophagy) or dust takes place either by ingestion, inhalation or dermal absorption (Fergusson, 1990). The sources and intake pathways of minerals and non-toxic or toxic chemical elements are shown in Fig. 2. Ingestion is the most common pathway of exposure for the general people, whereas inhalation and dermal sorption are significant in certain occupational settings (Adriano, 2001).

The dose/functional response curve for a specific element (Fig. 3) may differ from organism to organism but the sequence: deficiency, ideal concentration, and toxicity is always the underlying principle(Bowman et al., 2003).

Many health problems are related to dietary deficiencies of certain essential chemical elements. Life style, particularly dietary, is an important environmental factor that decisively conditions the human health. There is an old aphorism "*We are what we eat*" that expresses this fact very well. Combs (2005) reports several examples of geologic impacts on nutrition. For instance, iodine (I) is one essential trace element in human nutrition. According to Nordberg and Cherian (2005), both the United Nations Organization (UNO) and the World Health Organization (WHO) estimated that one billion people are at risk of iodine deficiency disorders (IDD), 211 million with goitre (enlargement of the thyroid gland), 5.1 million with severe cognitive and neuromotor deficiency, and many more with less severe neuropsychological defects. Iodine deficiency can lead to the so-called hypothyroidism whereas the excess of iodine intake can lead to the so-called hyperthyroidism responsible for the cancer of the thyroid (Fuge and Jonhson, 1986; Fuge, 1996, 2005). The total I content in the human body is estimated at 20–50 mg, and around 20% of this are found in the thyroid. The main source of I is food, particularly marine food, vegetables, meat and eggs. In developed countries the major sources of I are presently milk, butter and cheese, due to the addition of I to cattle fodder. Humans may also obtain I by inhalation, particularly in coastal areas. Iodine concentration in soil and water determines the I contents in food; rich organic soils and alkaline clay-rich soils contain higher I concentrations.

Dietary deficiencies and excesses with repercussion on human health involve other essential chemical elements characterized by specific functions such as Ca, Mg, K, Na, Fe, Zn, Cu, F, and Se (Nieboer and Sanford, 1984; Lindh, 2005a,b; Combs, 2005). The deficiency of these elements can cause health problems.

Fluorine (in the form of fluoride) can stimulate the formation of healthy bones, and it is demonstrated that doses of fluoride in the range 0.7–1 mg L^{-1} in drinking water can reduce dental caries. However, doses of fluoride >1.5 mg L^{-1} can cause dental and skeletal fluorosis. This disease can also be caused by fluorine

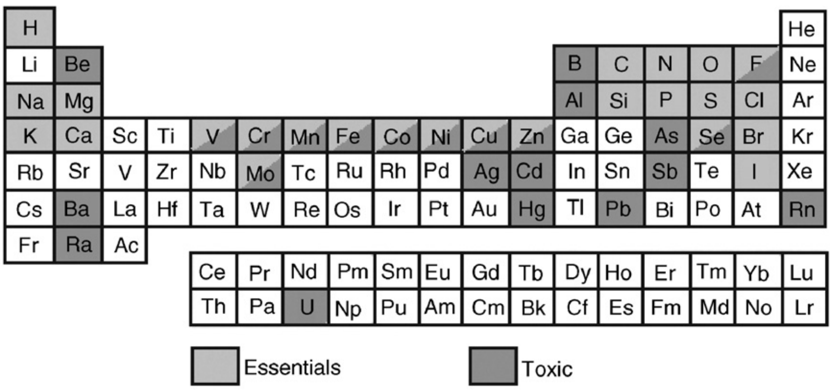

Fig. 1. Essential, toxic and essential/toxic chemical elements. From BGS–UK.

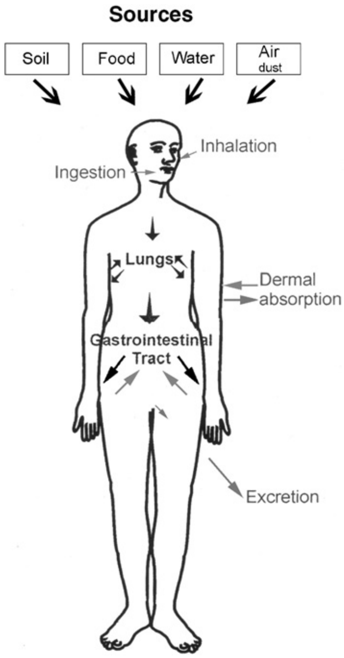

Fig. 2. Sources, intake pathways, and uptake of minerals s.l. by the human body. Adapted from Fergusson (1990).

volatilized from the domestic burning of mineralized coal and briquettes. Coal contains As-bearing pyrite, and the clay used in the manufacture of briquettes contains F-bearing clay minerals (illite, mica and vermiculite are the clay minerals bearing higher contents of F replacing structural OH groups).

Centeno et al. (2002, 2005) mention that more than 10 million people in Guizhou Province, China, suffer of fluorosis and arsenicosis by inhalation of indoor air polluted by arsenic and fluorine due to the combustion of high-arsenic and fluorine coals. In China and in other countries, such as India, Bangladesh, Vietnam and Mexico, serious health problems for millions of people are attributed to high concentrations of As in drinking water (Kinniburgh and Smedley, 2001).

Selenium is a trace element in soils which possess protecting anti-oxidant functions. According to Fordyce (2005) the range of Se concentrations between (<11 μg/day) and toxicity (>900 μg/day) is narrow. If soils are deficient in Se, people who use the vegetables cultivated on these soils can get some health problems such as juvenile cardiomyopathy or heart muscle disease (Keshan disease) and muscular anomalies in adults (Kaschin–Beck disease).

To be in good shape, the body requires the maintenance of *minerals* (here considered as inorganic chemical elements) in concentrations in adequate balance. These *minerals* can interact with each other and with other nutrients. Caution is required when the intake of one mineral is excessive because it can lead to deficiency of other minerals or nutrients.

The exposure, and more importantly, the *bio-availability* (the amount or fraction of the element which is actually available for uptake) depends on several factors such as concentration in the source, particle size and the specific physical and chemical properties of the contaminant itself.

Adriano (2001) and Alloway (2005) emphasize the bio-availability and risk of some trace elements (metals) present in terrestrial environments. According to Bowman et al. (2003) the elements may be present at toxic or deficient levels in the environment but may not pose a direct risk to health. For instance, thorium (Th) when bound in zircon ($ZrSiO_4$) by isomorphous substitution of Zr is not dangerous as it is not in free ionic state.

Minerals s.l. are essential to every living being that inhabits the surface of the earth. We humans depend on the environment not only in spatial terms but also for all our sustenance, and are therefore beginning to understand our advances towards defining our own environment (Skinner, 1997, 2000; Skinner and Berger, 2003).

Hochella (2002) and Hochella and Mazen (2005) emphasizes the role of minerals in Environmental Sciences, and naturally on human health, particularly due to their interaction with the atmosphere and with surface and ground waters, conditioning the chemical composition of water from springs and aquifers. On one hand, the *minerals s.l.* present in soil, groundwater and in the atmosphere (mineral dust, emissions from volcanic and anthropogenic activities, and radon) play an important role in promoting an untold number of gastro-intestinal, muscular–skeletal, respiratory and dermatological diseases. On the other hand, the therapeutic use of *minerals s.l.* in diseases of the alimentary tract, of the urinary tract, of metabolism, of the muscular–skeletal system, of the respiratory system,

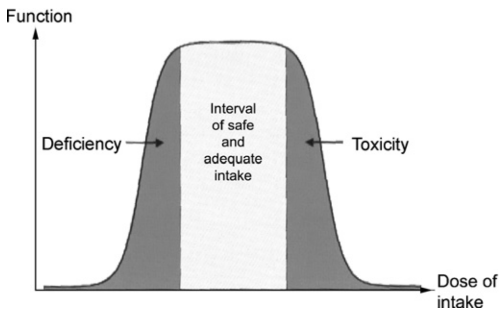

Fig. 3. Dose versus functional response. From Lindh (2005a,b).

of the circulatory system, and of the dermal system is an old practice.

The medicinal use of minerals is most probably as old as mankind itself. There are references to the use of "medicinal earths" (clay/mud) in Mesopotamia, Ancient Egypt and Ancient Greece, to cure wounds and soothe skin rashes. For instance, in Ancient Greece Hippocrates (460–377 BC), regarded as the Father or Founder of Medicine, reported interesting information about *medicinal earths* in his book "*On Airs, Waters, and Places*", and so did Aristotle (384–322 BC) who dedicated part of his life to biological research. Hippocrates reports the negative effects (corrosive, caustic, etc.) of arsenic minerals, much later identified as orpiment (As_2S_3) and realgar (As_2S_2), at that time extensively used as therapeutic agents. Recently, and according to the International Agency for Research of Cancer (IARC), arsenic and arsenic-containing compounds are considered as human carcinogens (IARC, 1987).

Several pathologies were also attributed to minerals, some related to mineral processing, particularly to metallurgical works. Galen (129–199 AC), a Greek physician who became famous in Rome, wrote many books, and reaffirmed the potential danger of mining activities when he observed acidic fumes associated to copper production (cited *in* Lindberg, 1992). Health problems due to metal toxicity, for instance lead and cadmium poisoning, have occurred since ancient times, in many parts of the world where mineral processing (smelting and refining of mineral ores and ore concentrates) for metal production was carried out. Lead, mercury and arsenic poisoning, called *saturnism* or *plumbism*, *mercurosis* or *hydrargyrosis* and *arsenicosis*, was common among the Romans (Nriagu, 1983, 1989, 1996, 1998). Hong et al. (1994) speculate about the contribution of these types of poisoning, particularly the one caused by lead, to the Fall of the Roman Empire. We know today that it was common for Romans to store wine in lead containers. More than 2000 years ago, healing and hazardous properties of minerals have been reported in ancient Chinese and Indian texts. Since then, particularly in more recent times, researchers have continued investigating the specific properties of minerals, for instance, clay/mud and clay minerals, both in their natural state and after beneficiation by means of chemical and physical processes, as well as the therapeutic advantages of final products.

Some special clays and clay minerals are being used both in external and in internal treatments as mentioned, for instance, by Carretero (2002), and Carretero et al. (2006), as well as some special sands reported, for instance, by Gomes and Silva (2001, 2006) and some special spring waters, the so-called mineral–medicinal waters as mentioned, for instance, by George (2001), and by Gomes and Silva (2006).

Minerals and the human body have in common most of the chemical elements found in the Periodic Table. All chemical elements except the so-called *trans*-uranium elements are present in the environment and therefore can be found in minerals. Some elements are mineral forming, others can participate in mineral structures isomorphously replacing mineral forming elements.

In the natural environment where man lives, minerals and chemical elements are omnipresent. Therefore, interactions are expected to condition the living quality, highly determined by the health state. Both quality and quantity of chemical elements change with the nature of the geologic materials (granite, basalt, limestone, schist, shale, clay, etc.). The concentration of some elements depends, for instance, on the acidic or basic character of igneous rocks. Several elements, especially heavy metals, tend to be concentrated or enriched in rocks rich in clay minerals and organic matter, for instance, in black shales.

As a matter of fact, the intimate relationship between natural environment and health cannot be limited to the hazardous or negative effects of *minerals s.l.* (These include certain chemical elements, particularly certain heavy metals and metalloids and certain *minerals s.r.* existent in the environment). The positive effects of *minerals s.l.* on the human health are acknowledged since antiquity. Mineral resources such as special clays, muds and special sands, thermal spring water or just mineral water have been and are still being used as curative or healing materials, in thermal resorts, thalassotherapy centers and spas (Melo, 1971; Novelli, 1996; Veniale, 1996, 1998, 1999; Novelli, 2000; George, 2001; Gomes and Silva, 2001; Carretero, 2002; Gomes, 2003, Gomes and Silva, 2003; Lee, 2004; Yushkin, 2004; Gomes, 2005; Gomes and Silva, 2005, 2006; Carretero et al., 2006). For instance, the practice of using mineral spring water to prevent or cure disease goes back 50,000 years to the Bronze Age. Water is the essence of life, and spring/thermal spring water has been used since antiquity, in the Mediterranean basin, even before the Roman "*balnea*", associated to living quality, culture and tradition.

There are several types of mineral water, depending on the presence of the main chemical anions (sulfate, chloride, bicarbonate, silicate, fluoride) and cations (calcium, magnesium, sodium, potassium). Both the physical and chemical properties of mineral waters condition their therapeutic functions.

Medical Hydrology is the comprehensive designation for the whole science dealing with the several factors comprising the medicinal use of water in all situations. *Hydrotherapy* is the scientific use of water as a therapeutic agent and treatment of disease in various ways and in various gradations of temperature from ice to steam. *Balneotherapy* is the science of baths and bathing, including their effects in the treatment of disease. "*Crénotherapie*" (a French term) is the internal administration (oral consumption) of mineral water in the treatment of diseases of the metabolism, of the alimentary or digestive tract, of the liver, of the epidermis, of the urinary tract, of the circulatory system, and of the respiratory system.

Water quality changes with natural factors, time, and human activities. Toxicity of both surface and underground waters could be provided by certain metals of natural or anthropogenic origin (such as As, Pb, Zn, Cr, and Cu), fertilizers and pesticides.

Air carries always aerosols of dispersed fine mineral particles such as quartz, feldspar, mica, clay minerals, etc. (Guthrie, 1992; Buseck et al., 2000; Derbyshire, 2005). Mineral–atmosphere interactions taking place in the lower 10–15 km of the earth atmosphere (the so-called troposphere) affect very much the atmospheric chemistry, the climate and human health (Guthrie, 1992; Guthrie and Mossman, 1993; Bencko and Vostal, 1999; Hochella, 2002). Wind and volcanic eruptions are important sources not only of mineral dust which can be transported over thousands of kilometers (Ross et al., 1993; Santaren and Alvarez, 1994; Chisholm, 1994; Prospero, 1999a,b, 2001; Pósfai and Molnár, 2000; Weinstein and Cook, 2005) but also of toxic gases, which can cause injuries and health problems. Trace metals (some of them are toxic like Pb, Cd, Cu, Zn, As, Se) are abundant in the plumes of degassing volcanoes (Hinkley et al., 1999; Garret, 2000). The pathways and biotoxicity mechanisms of the health effects caused by trace elements carried in natural dusts (sources include volcanoes and dust storms) are described by Cook et al. (2005).

Inhalation of mineral aerosol particles and their deposition in human pulmonary alveoli can cause health problems dependent on composition and size and shape of the particles. Silicate particles <5 µm with acicular shape, as a rule, penetrate deeper into the lungs and cause *silicosis* or *asbestosis* than particles >5 µm. The disease caused by crystalline silica particles (particularly quartz) belongs to the group of *silicotic diseases* which are occupational hazards mostly related to activities when people are exposed to crystalline silica dust such as extraction and transformation of minerals, cutting dressing of natural stone, tunnel works in roads and railways, smelting of mineral ores for metal concentration, fragmentation and pulverization of siliceous rock, and preparation of raw materials for the manufacture of ceramics and glass. Depending on the dose and duration of exposure, *silicotic diseases* are classified into three classes: *chronic*, *accelerated* and *acute*.

The further disease is mainly caused by a group of fibrous silicates called asbestos (Stanton et al., 1981; Skinner et al., 1988; Wagner, 1997; WHO, 1997; van Oss et al., 1999; Skinner, 2000; Kohyama, 2005; Nolan et al., 2005). Asbestos were recognized in 1960 by the World Health Organization (WHO) as potentially carcinogenic, being banned only few years afterwards from important industrial applications (for instance, asbestos cement and lining of pipes where fluids circulated to heat buildings) in which they were used for their fire-resistant and thermal insulation properties. However, these days various asbestos substitutes (man-made mineral fibers, such as titanium oxide whiskers) are being used over a wide range of industrial applications, raising concern about the safety of workers exposed to these fibers in occupational environments. Evidence for potential biological effects is being assessed through *in vivo* and *in vitro* experiments (Ishihara, 2001).

To understand the processes and mechanisms of the benefits and hazards on human health due to minerals *s.l.*, further *in vivo* and *in vitro* investigations are required. Recently, a research team from the University of Chicago reported in *The Proceedings of the National Academy of Sciences*, that asbestos fibers fixed to the lung tissue promote the production of a protein known as the "alfa-factor of tumor necrosis". This protein promotes the formation of another one named NF-kB having the function to protect from death the cells damaged by the fibers, which instead of dying undergo division leading to malign tumors.

Other health problems might be due to metal toxicity. Poisoning by lead, mercury and arsenic can be lethal. *Selenosis*, *fluorosis*, *manganism*, *beryllosis*, *siderosis* and *baritosis* are other diseases attributed to the excessive intake and uptake of Se, F, Mn, Be, Fe, and Ba-minerals (Gomes and Silva, 2006).

The human body produces compounds crystal-chemically analogous to *minerals s.r.*, the so-called *biominerals*, formed through cellular activity. Well-known are the so-called *stones* formed in kidneys, bile and bladder vesicles (Driessens and Verbeeck, 1990; Duce, 1995; Mann, 2000; Skinner, 2005).

We may ingest or inhale mineral or other particles from the environment, and the body reacts, producing often mineralized tissues around these interlopers (Skinner et al., 1988). The inhaled particles (for example, asbestos particles) are *minerals*; the reaction products formed in the mineralized tissues are *biominerals*.

Naturopathologists believe that good health mainly depends on structural, biochemical and emotional factors. Naturally, the biochemical factors are those which are closely related to *minerals* considered as natural chemical products, reason why the interactions of minerals *s.l.* with human health deserve to be dealt with in this publication.

Every day the human body produces the essential nutrients that make life possible. Human body is like a factory producing skin, muscles and bones, and feeding the red globules or erythrocytes which transport nutrients and oxygen to the cells all over the body. To accomplish these goals, the human body requires raw materials, the *vitamins* (organic micronutrients, lipid-soluble like A, D, E, K, or water-soluble like B and C), and the so-called *minerals* (here considered as inorganic chemical elements) or *mineral elements* which are obtained through food or nutritional supplements.

Certain minerals (such as Zn, Se, and Mg minerals) as well as certain enzymes and vitamins (such as A, C, E) are examples of anti-oxidants, substances which are able to protect the organism from oxidation processes constantly being in progress. Oxygen essential for life can also be a source of toxicity. Many of its harmful effects are attributed to *free oxygen radicals* which are highly unstable, rapidly react with neighboring molecules, and initiate a harmful process called *oxidative stress*.

Table 1
Specific functions of most essential mineral salts and trace minerals

Ca	Essential for developing and maintaining healthy bones and teeth; assists in blood clotting, muscle contraction and nerve transmission; helps reduce risk of osteoporosis
Mg	Activates over 100 enzymes and helps nerves and muscles function
K	Regulates heartbeat, maintains fluid balance and helps muscles contraction
Fe	Essential for red blood cells formation and function; important for brain function
Cr	Aids in glucose metabolism and regulates blood sugar
Co	Promotes the formation of red-blood cells
Cu	Promotes the formation of red blood cells and connective tissue; acts as a catalyst to store and release iron to help form haemoglobin; contributes to central nervous system function
I	Needed by the thyroid hormone to support metabolism
P	Works with Ca to develop and maintain strong bones and teeth; enhances the use of other nutrients
S	Needed for muscle protein and hair; its deficiency results in degeneration of collagen, cartilage, ligaments, and tendons
Se	Essential component of a key anti-oxidant enzyme, needed for normal growth and development
Zn	Essential component of more than 200 enzymes involved in digestion, metabolism, reproduction and wound healing
Mo	Contributes to normal growth and development
F	Essential for bones and teeth; Ca by itself cannot build bone
Si	Essential for normal bone growth, and for proper integrity of the skin

The organism produces anti-oxidants that neutralize the effects of free radicals constantly formed as a natural consequence of metabolism. However, the exposure to risk factors (such as tobaccoism, sedentarism, obesity, stress, etc.) determines an exacerbated production of free radicals making the body's natural defences insufficient. This justifies the need of taking anti-oxidant *minero-vitaminic* supplements.

Vitamins and *minerals* can interact. For instance, vitamin D makes the body able to extract Ca from food, at the intestinal level, instead of extracting it from bones; also, vitamin C helps Fe sorption, but obstructs Cu assimilation, another essential micronutrient.

Minerals can be divided into two main groups: *mineral salts* and *trace minerals*. Human body requires higher amounts of the so-called *mineral salts* (for instance, Ca, Mg, Na, K, P, and S), than of the *trace minerals* (for instance, Fe, Si, F, Cu, Zn, Mn, Se, Mo, Cr, and I). They are added in formulations of medicines, not in their elementary form but as inorganic or organic salts (potassium chloride, magnesium sulfate, potassium iodide, chromium chloride, sodium molybdate, nickel sulfate, sodium metasilicate, sodium metavanadate, sodium selenate, dibasic calcium phosphate and ferrous fumarate), or as other chemical compounds (cupric oxide, zinc oxide, magnesium oxide and silicon dioxide).

Table 1 contains the specific functions of most of mineral salts and trace minerals. Within the *mineral salts*, Na, Cl, and K are responsible for maintaining the adequate equilibrium of intra-cellular and extra-cellular electrolytes in the human body. Also, Ca, P, and Mg are fundamental for good state and performance of bones. On the other hand, S helps to stabilize protein structures.

Within the *trace minerals*, Fe is essential for the transport of oxygen all over the body; Zn helps blood coagulation and stimulates immunological answer; and Cu contributes for the formation of diverse enzymes required for several functions, production of energy, anti-oxidation, synthesis of hormone named *adrenaline*, formation of conjunctive tissue, and Fe metabolism and formation of haemoglobin, the pigment of *erythrocytes* that transports the oxygen (Lindh, 2005a,b).

However, interactions between mineral salts and trace minerals produce beneficial or adverse situations. An example of such interactions is related to the osteoporosis disease. Osteoporosis was a not very well-known disease for a long time, mainly for lack of investigation and for being a silent disease, with no symptoms, so its consequences were not fully identified. After the age of 50, one in every three women and one in every eight men will suffer a bone fracture as consequence of osteoporosis. This is a generalized bone disease characterized by a decrease of bone mass or bone density due to changes in bone structure. Unlike what many people think, osteoporosis is not only the lack of Ca in the bone. Ca is an important component but not exclusive. P, Mg, Sr, F, and Si are other constituents. Sr, for instance, is a relatively large cation that contribute to the stabilization of the calcium phosphate (hydroxyl apatite) structure in the bone, similarly to the stabilization of calcium carbonate (aragonite) by Sr. Recently, a pharmaceutical was developed with strontium ranelate as the active principle. The clinical tests have been performed with women suffering from post-menopausal osteoporosis (reported in the New England Journal of Medicine) and confirm that the drug contributes for bone formation and simultaneously decreases bone re-absorption.

Walter Willet, a teacher of Nutrition at the Harvard School of Public Health, mentions (*in* Underwood, 1979) the interesting *Calcium Conundrum or Paradox*. In fact, if bones require Ca, then people who ingest a lot of Ca-rich products should have extra-strong bones. However, why are hip fractures uncommon in Singapore, where adults do not drink milk, and are frequent in Scandinavian countries where diets heavily include dairy? It looks like that the absorption of Ca from diets does not work by itself but depends on other factors and not only on the Ca intake.

In humans, the primary uptake or absorption of mineral elements takes place in the gastro-intestinal track, predominantly in the duodenum and in the first part of the jejunum.

Vitamins, *mineral salts* and *trace minerals* are essential to maintain healthy the immunological system, to maintain mental and physical mentality, and to confer a healthy aspect to skin, hair and nails. In order to assess the health status of the human body, the analysis of minerals in the blood is difficult and expensive. On the other hand, one urine sample can reveal what the body is eliminating, not what it is storing.

H, C, N, O, Na, Mg, Ca, P, S, Cl, K, Mn, Fe, Cu, Zn, and Se are considered *essential elements* to all animals and vegetation. H, O, C, and N make up just over 96% of the human body mass, reason why they are called *major elements*. Na, K, Ca, Mg, P, S, and Cl make up 3.78% of the body mass and they are called *minor elements or minor minerals*, their concentration is expressed in mg g^{-1}. The remaining elements and others (about 70) are called *trace elements or trace minerals*, their concentration being expressed in μg g^{-1}. The World Health Organization (WHO, 2002) considers the trace elements: Fe, Zn, Cu, Cr, I, Co, Mo, and Se, essential to human health. According to Lindh (2005a,b) an element is essential if: 1) it is present in living tissues at a relatively constant concentration; 2) it provokes similar structural and physiological anomalies in several species when removed from their organisms; 3) these anomalies are prevented or cured by the supplementation of the element. For the World Health Organization (WHO) "*an element is considered essential to an organism when the reduction of its exposure below certain limit results consistently in a reduction in a physiologically important function, or when the element is an integral part of an organism structure performing a vital function in the organism*".

Concerning the uptake of elements, the biological ecosystems are dependent on the geo-sphere (Williams, 2005). The environment cannot be separated from the overall chemical systems of life and its evolution.

Mineral elements are initially taken up by plants, and from these they are transferred to animals. Both *minerals s.r.* and *minerals s.l.* are orally supplied as formulations of medicines and nutritional supplements or re topically applied as formulations in *balneotherapy*, *dermopharmacy* and in *dermocosmetics*.

Nowadays, it is accepted that good health is very much dependent on an equilibrated diet and the beneficial effects of food rich in anti-oxidants. In all biological systems formation of free radicals is very much influenced by a non-equilibrated diet particularly rich in animal anti-oxidants are provided by vitamins such as vitamin A, particularly found in dark green vegetables and fruits, vitamin C, particularly found in certain fruits, vitamin E, particularly found in cereals, nuts, vegetable oil, and fish oil, by certain enzymes (such as *catalase*), and by certain minerals such as Se, Zn, and Mg.

However, it can happen that a certain treatment involving natural products, minerals included, shows no effect at all. In case of possible negative effects, and in comparative terms, damages due to treatment with natural products would not be as serious as those that rely on conventional medicines (Gomes and Silva, 2001).

Recent developments in molecular biology and biotechnology as well as in the new field of *Pharmacogenetics* 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*" or personalized treatment. Similarly, individual patients might be expected to react differently to health treatments using natural means, the so-called *naturotherapy*, which involves distinct processes and methods such as *phytotherapy*, *algotherapy*, *hydrotherapy*, *mudtherapy*, *peloidtherapy* or *pelotherapy*, *balneotherapy*, *thermotherapy*, *oligotherapy*, and "*crenotherapy*".

There are no inoffensive pharmaceuticals or medicines. However, the benefits of taking medicines overcome the risks they can cause, particularly if the medical recommendations inherent to any treatment are strictly followed.

Taking two or more medicines simultaneously may cause beneficial or harmful effects. The harmful effects, currently called interactions, could not be noticed by the patient. One medicine can reduce or cancel the efficacy of another medicine. This is why it is important that doctors and pharmacologists should know all medicines which are taken by the patient, in order to raise their positive effects and reduce their toxicity.

3. Clay minerals in medical geology

3.1. Essential properties of clay minerals and the origin of life

Clay minerals are formed at the interface of the earth crust, hydrosphere and atmosphere, that is, in the same environment where man lives. Among the particulate materials existing at or near the Earth's surface, nanoparticles of clay minerals, iron or manganese oxy-hydroxides, and organic colloids possess strong metal retention power (adsorption and absorption) due to their very large surface areas, which in the case of clay minerals reaches values of around 800 $m^2 g^{-1}$. Thus, nanoparticles control the mobility, destination and bio-availability of metals (such as As, Cu, Ni, Cu, Hg, and Zn) in soil, air and water environments. In the specific case of clay minerals, both their small particle size and their negative electric charge intervene in metal retention. Oxy-hydroxide particles also have an electric charge (as a rule, globally positive).

Clay minerals are important constituents of soils which are essential to life, in general, and to human health, in particular. Clays are the result of chemical processes taking place at or near the earth surface and are essentially formed at the interfaces of the earth crust with the atmosphere, the hydrosphere and the biosphere. Clay minerals occur everywhere, in rocks of all types (Pédro, 1994; Moll, 2000), dispersed in atmospheric aerosols (Sanfeliu et al., 2002), and dispersed in water from oceans, seas, lakes, lagoons, and rivers (Gomes, 1987).

"*Clay minerals, the most abundant and chemically active components of the surface mineral world, are the key to understanding the links between nature (life), its substrate (essentially silicates), and a mastery of the total ecosystem by man*" (Velde, 1995). Velde (1995) also noted that clay habitat coincides in general with the man habitat, and that clay acts as a filter and substrate for life.

Bernal (1949) and Goldschmidt (1952) were independently the pioneers proposing that clay minerals, acting as catalysts may have played an important role in pre-biotic synthesis. Miller (1953, 1957) reports experiments on the preparation of smallest organic molecules such as simplest amino acid glycine. Cairns-Smith (1971, 1982, 1985, 1988, 2003) and Cairns-Smith and Hartman (1986) developed interesting experiments and theories about the emergence of life from inorganic materials. In a recently published paper, Cairns-Smith (2005) considers that the driving force for the transition from geochemistry to biochemistry was natural selection operating, in the earliest stages, on inorganic materials, and the hydrothermal submarine systems were increasingly invoked as appropriate sites for "*the origin of life*" (Holm, 1992; Russell and Hall, 1997).

The evolution of life from seawater could be supported by the similarity of the compositions of seawater, human body serum, and human red cells, in terms of free cations and anions such as calcium, magnesium, potassium, sodium, chloride, bicarbonate and phosphate (Lindh, 2005a,b).

Clays and clay minerals formed in terrestrial or deep-sea vent hydrothermal systems rich in iron and manganese sulfides and unstable silicates, are microcrystalline and have specific properties such as layer charge, high specific surface area, high ion exchange capacity, and high adsorption capacity. They would be the appropriate substrate for bacteria and enzymes.

Concerning bacteria, interesting investigations have been carried out on the scientific domain of microbial ecology of hydrothermal systems, on which life on earth could have been initiated.

The relationships between Geology and Biology are the goal of Geobiology, the science that understands the earth as a system, and life as part of it. In space and time, life influences earth development, and earth's changing environment moulds life (Noffke, 2005). On the other hand, the interactions between Geology or Geo-sciences and the Ecology are the goal of a scientific area called Geo-ecology, which particularly highlights the interactions between man and the ecosystems.

According to Hazen (2005a,b), the investigations carried out on the origin of life lead to the conclusion that minerals must have played key roles in virtually every phase of life emergence, catalyzing the synthesis of key biomolecules, and selecting, protecting and concentrating these molecules. They jump-started metabolism, and they may even have acted as first genetic systems.

Ferris et al. (1988) and Ferris (2005) consider that catalysis was essential for the formation of the biopolymers required for the origin of the first life, and that montmorillonite, a clay mineral formed by the weathering of volcanic ash deposited in ancient seas and in submarine volcanic vents, may have played a central role in the evolution of life as montmorillonite adsorbing organic compounds is able to catalyze a variety of organic reactions critical to the scenarios of life's origins. Ferris experimentally found that RNA (ribonucleic acid) molecules bind efficiently to clay minerals and that montmorillonite can catalyze the formation of longer molecules (oligomers), thus lending support to the RNA world hypothesis.

Ferris (2005) has found that montmorillonite having alkali and alkaline earth metal ions as exchangeable cations is catalytically more active than montmorillonite with iron and other transition metal ions as exchangeable cations. He elaborated the theory that life based on RNA precedes current life which is based on DNA (desoxy ribonucleic acid) and proteins.

As a final note, the approaches to the origin of life on earth, only based on geochemical and mineralogical criteria, are criticized by other researchers (Towe, 2005; Hazen, 2005a,b) who acknowledge the non-existence of an "*integrated*" scenario for the origins of life. They consider that criteria of other nature have not been taken into account such as the effect of the enhanced ultraviolet radiation (UVB) that the young Sun would have provided to the primordial surface environments of the earth, at that time without the ozone screen, and the fact that the Archean deep oceans were saturated in dissolved iron of hydrothermal origin which provided the formation of extensive banded formations of iron ores.

The controversy still persists between the Creationist theory and the Naturalist or Darwinist theory. Very recently, Morris (2005) and Hazen (2005a,b) made contributions to the continuity of the discussion about the origin of life.

3.2. Clay minerals and human health

Man has used since antiquity, in an empirical manner, clay, mud or clayey soil for therapeutic purposes, either ingesting it, or applying it topically in the form of patches, cataplasms or mud-baths. Clay minerals are ubiquitous mineral resources, therefore of easy access. Presently, there is much scientific information on the assets or properties of these materials that justify their incorporation in pharmaceutical formulations and cosmetics (Wai and Banker, 1966; Hermosin et al., 1981; Cornejo, 1990; Gámiz et al., 1992; Ueda and Hamayoshi, 1992; Lopez-Galindo and Iborra, 1996; Novelli, 1996; Galán, 1998; Galán et al., 1985; Novelli, 1998; Viseras and López-Galindo, 1999; Jobstraibizer, 1999a,b; Lopéz-Galindo and Viseras, 2000; Tateo et al., 2001; Lopez-Galindo et al., 2005) as well as regarding their application in pelotherapy, mudtherapy, or fangotherapy (Torrescani, 1990; Ferrand and Yvon, 1991; Veniale, 1996; Veniale and Setti, 1996a,b; Barbieri, 1996; De Bernardi and Pedrinazzi, 1996; Yvon and Ferrand, 1996; Cara et al., 1996, 1997; Summa and Tateo, 1998; Cara et al., 1999; Gorgoni et al., 1999; Minguzzi et al., 1999; Morandi, 1999; Tolomio et al., 1999; Bettero et al., 1999; Cara et al., 2000a,b; Sánchez et al., 2000a,b; Tolomio et al., 2002; Veniale et al., 2004; Cerezo et al., 2005). Also, there is much information regarding the processing or maturation that is required for the improvement of mud or fango properties (Galzingna et al., 1995, 1996; Galzingna and Bellometti, 1999; Galzingna et al., 1999; Veniale et al., 1999; Gomes, 2002; Sanchez et al., 2002; Veniale et al., 2004; Viseras et al., 2005; Garcés et al., 2005).

Specific properties of clay minerals such as the nanometer size and thin platy or fibrous shapes, the negative electric charge, and high adsorption and absorption capacities justify the therapeutic uses referred to. Also, these and other properties justify the use of clay minerals for improving environmental quality which is fundamental for the living quality of man and other organisms as they can act as catalysts for potentially benign chemical processes.

Due to the properties referred to, particularly the surface properties, clay minerals and other colloidal minerals (oxides, hydroxides and oxy-hydroxides of Fe, Mn and Al) constitute environmental factors of paramount importance since they can control the bioavailability, ecological effects, biogeochemical cycles, and distribution of trace metals and metalloids in ecosystems (Jackson, 1998; Sparks, 2005). As we know heavy metals and metalloids have critically important biological effects, both beneficial and harmful. According to Jackson (1998) trace elements in natural waters and soil solutions can be readily taken up from solution by clay minerals and other colloidal minerals, the efficiency of the phenomenon depending on the properties and concentrations of the reactants and on environmental factors that affect the forms of the elements and the surface properties of the colloids. The process involves: 1) sorption by clay minerals, oxides and clay–oxide–humic complexes; 2) co-precipitation with oxides; 3) complexing by organic matter. Among the clay minerals, montmorillonite and vermiculite are those that exhibit higher adsorption capacities.

In aquatic and terrestrial ecosystems clay minerals and other colloidal minerals can act as sinks and secondary sources of trace metals and metalloids with important biological consequences as they can limit or prevent their uptake and bio-availability by organisms. The binding and release of trace metals and metalloids by colloidal particles limiting the biological uptake provides the control of the nutritional and toxic effects of the trace metals and metalloids to the benefit or detriment of the organisms.

The surface properties of clay minerals and other colloidal minerals allow them to function as catalysts in many organic reactions (Malla et al., 1991; Sun Kou et al., 1992) and the role on pollution prevention and reduction. For instance, clay-liners have revealed great importance in the case of landfills to avoid migration of toxic metal ions and organic pollutants into neighboring soil, groundwater, and surface water. Also, the use of clay to remove metal ions from wastewater is another important field of application (Sharma et al., 1991; Gupta et al., 1992). A further application is the remediation of polluted environments such as rivers, lakes and lagoons, where toxic metals from both natural and artificial sources become concentrated, either in fine-grained bottom sediments, or in dispersed particulate matter (Rudd and Turner, 1983; Parks and Hamilton, 1987).

The interactions between clay minerals and organic molecules have been investigated by many authors, especially by Theng (1974), Lagaly (1984), and Yariv (2001).

Many researchers proceed in investigating the natural properties of clay/mud and clay minerals, the beneficiation of these properties after submitting the materials to certain chemical and physical treatments, and the therapeutic advantages of the obtained products. Much information regarding the use of different minerals, particularly clay minerals, for medicinal purposes is referred to by several authors such as Robertson (1986), Bech (1996), Robertson (1996), Novelli (1996), Veniale (1996), Veniale (1997), Veniale (1998), Reinbacher (1999), Novelli (2000), Carretero (2002), and Reinbacher (2003).

Among the many papers which have been published in recent years, the review of Carretero (2002) deserves a particular reference. This paper systematically emphasizes the beneficial effects of clay and clay minerals on human health, both as external or topical applications (cataplasms, mud-baths, cosmetics, etc.), and as internal or oral applications (incorporated in the formulations of many pharmaceuticals or medicines, as *active principles* or as *excipients*). The paper also mentions some few risks that can be attributed to clay minerals. A very recent paper of Carretero et al. (2006) discusses in comprehensive way both the positive and negative effects of clays and clay minerals on human health.

Other field of research is the beneficiation of such natural properties after submitting the materials to certain chemical and physical treatments, and the therapeutic advantages of the obtained products. In the particular case of thermal mud, another field of research is mud recycling that should consider microbiological studies as well as sterilization studies not affecting the relevant mud proprieties.

Geophagy, the deliberate intake or ingestion of soil or clay by man or other animals (may be to compensate dietary deficiencies), is an old and generalized practice still taking place, these days, in some regions of the world (Mahaney et al., 2000; Wilson, 2003a,b; Abrahams, 2005). Various hypotheses have been put forward to explain such practice, and one of them is the supplementation of mineral nutrients to compensate dietary deficiencies.

Several diseases have been attributed to human intake of polluted air and water. Dispersed in the air-borne dust, minerals or mineral derived industrial products, particularly those that could be classified as *nanominerals* like clay minerals, can cause serious problems to the respiratory system. For instance, the clinical effects of inhalation of clay minerals as well as the pathological effects of exposure to clays have been a matter of concern of several researchers (Wagner et al., 1987; Gibbs, 1990; Wagner, 1990; Gibbs et al., 1992; Gibbs and Pooley, 1994; Wagner et al., 1998). According to Wagner et al. (1998) the vast majority of clay dusts are innocuous and only produce deleterious health effects if the exposure is intense and long lasting.

3.3. Clay-based formulations designed for topical applications in balneotherapy, dermopharmacy and dermocosmetics

We have been trying, in the last 2 years, to design and develop clay-based products, in the form of creams, ointments or lotions with balsamic or curative properties, which could be used for topical applications in balneotherapy, dermopharmacy, and dermocosmetics. Attempts were made to take advantage of the relevant specific properties previously identified of natural resources (climate, sea water, spring water, bentonite and biogenic carbonate sand) occurring in the island of Porto Santo that belongs to the Madeira archipelago (Gomes and Silva, 2001; Silva, 2003; Gomes and Silva, 2006). Porto Santo, rather appreciated by very many tourists, has been considered as a natural health resort due to the healing assets of their natural resources, utilized in thalassotherapy centers and spas.

One of the products being developed is based on blends of bentonite of Porto Santo (/Madeira archipelago) and biogenic carbonate sand of Porto Santo. In the formulation of the product the following components intervene: the bentonite clay fraction (grain size <2 μm) which had been previously separated; biogenic carbonate sand finely milled; glycerin of pharmaceutical grade; lanolin; lemon juice/citric acid (pH conditioner, since the pH of the final product should be slightly acidic), and perfume. Bentonite acts as the plastic and bonding agent in the final product. Biogenic carbonate sand is the active component and the pH conditioner is responsible for the dissolution and corresponding liberation of Ca, Mg, Sr and other elements existent in the sand, making them available for sorption through the skin passing into the extra-cellular matrix (basic and vital mean for the cells). These biochemical and biophysical parameters (for instance, pH and Eh) can be changed. All cellular metabolic and catabolic chemicals circulate in this matrix. The heat provided by an infrared lamp facilitates the sorption of the chemical elements already referred to, since it promotes the body sweating, basic condition for cation exchange reactions.

A further product has been developed based on bentonite gel and an extract containing all relevant chemical elements present in the biogenic carbonate sand of Porto Santo. It can be topically applied as healing gel in the treatment of certain rheumatic diseases.

Another product that is being experimentally developed for eventual topical applications is based on blends of the following ingredients: amorphous biogenic silica extracted from a quite pure diatomite from Rio Maior (central Portugal), mud from the fumaroles (solfataras) field of Furnas Lake (S. Miguel island, Azores), refined bentonite from Porto Santo island, lanoline, glycerin of pharmaceutical grade (increases the bio-adhesivity), sodium hydroxide (pH conditioner), and perfume. Biogenic silica is the active component and the selected pH conditioner is responsible for the liberation of silicon (Si) making it available to be absorbed through the skin. Silicon (Si) is considered to be an essential chemical element in the human body. Silicon is one of the most common chemical elements participating in the composition of the geo-materials that make the earth crust, in quantitative terms following oxygen, and is a highly productive mineral (silicates) forming element. Diatom cell walls (frustules) are made of amorphous silica (opal-A). To be more easily absorbed and assimilated by the human body, Si should be part of organic derived materials. For instance, Silicium-R contains silicon+ licopene, recently developed and commercialized by Vichy Laboratories, which has been considered as a skin regenerator and strengthener. Another product, named Arthrosilium, is produced by Bodywell (Switzerland). It is known that the Si content in the human body decreases with the age. Silicon is considered to be fundamental for the synthesis of collagen (protein making up the white fibers or collagen fibers of skin, cartilage, and all connective tissue) fibers needed for the regeneration of articulator cartilage's (Smit, 2004), reason why osteo-articular and muscular affections can be ameliorated through treatments using products based on bionic silica. Treatments based on products having anti-inflammatory properties are fundamental in the treatment of osteo-articular and muscular–skeletal affections.

Organic silicon is an active component that participates, for instance, in the formulation of some anti-homotoxic homeopathic medicines, such as Zeel®.

Specialists consider that the bio-availability of chemical elements could be higher when they enter into the formulations in organic forms. In the case of silicon *Equisetum L.* could be used as a source of organic silicon, which is considered very important for preservation of cartilage and connective tissues and thus for the trophism of bones. In human bones a tiny amount of Si replaces P, and there is evidence that Si can improve bone strength. Yamada et al. (2003) found that in the human vertebral column the Si/Ca ratio in the lumbar vertebra is twice the Si/Ca ratio in the cervical vertebra. This finding suggests that Si is biokinetically compatible with Ca from bones, and the Si/Ca ratio increases along the backbone to the sacral direction. Thus, Si may contribute to increasing the vertebra strength as a response to compensate the higher compression due to gravity.

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