INTERNATIONAL JOURNAL OF PHARMACY AND ANALYTICAL RESEARCH

ISSN: 2320-2831

IJPAR |Vol.4 | Issue 4 | Oct – Dec - 2015
Journal Home page: www.ijpar.com

Research Article *Open Access*

Physicochemical characterization of therapeutic peloids from the surroundings of Costa Rica Arenal Volcano

German L Madrigal Redondo[I], Rolando Vargas Zúñiga[II], Gustavo Carazo Berrocal[III], Nils Ramírez Arguedas [IV]

[I] *Doctor of Pharmacy, a Master's Degree in Intellectual Property, Associate Professor and Researcher at the Laboratory of Biopharmacy and Pharmacokinetics (LABIOFAR) of the Institute of Pharmaceutical Research (INIFAR), and the Pharmaceutical Chemistry Laboratory of the Faculty of Pharmacy University of Costa Rica, Rodrigo Facio Campus, San Jose, Costa Rica, ZipCode 11501-2060, San Jose, Costa Rica*

[II] *Doctor of Pharmacy, a Master's Degree in Intellectual Property, Professor and Researcher at the Laboratory of Biopharmacy and Pharmacokinetics (LABIOFAR) of the Institute of Pharmaceutical Research (INIFAR), and the Pharmaceutical Chemistry Laboratory of the Faculty of Pharmacy University of Costa Rica, Rodrigo Facio Campus, San Jose, Costa Rica, Zip Code 11501-2060, San Jose, Costa Rica*

[II] *Doctor of Pharmacy, M. Sc. Quality Control of Medicines, Professor and Researcher at the Laboratory of Biopharmacy and Pharmacokinetics (LABIOFAR) of the Institute of Pharmaceutical Research (INIFAR), and the Pharmaceutical Chemistry Laboratory of the Faculty of Pharmacy University of Costa Rica, Rodrigo Facio Campus, San Jose, Costa Rica, Zip Code 11501-2060, San Jose, Costa Rica*

[IV] *Doctor of Pharmacy, M. Sc. In Pharmaceutical Sciences - Director and researcher of Laboratory biopharmacy and Pharmacokinetics (LABIOFAR) of the Institute of Pharmaceutical Research (INIFAR), and the Pharmaceutical Chemistry Laboratory of the Faculty of Pharmacy University of Costa Rica, Rodrigo Facio Campus, San Jose, Costa Rica, Zip Code 11501-2060, San Jose, Costa Rica*

***Corresponding Author: German L Madrigal Redondo**

Email: generacionlcr96@gmail.com

ABSTRACT

Introduction

Costa Rica is a volcanic country, containing a variety of peloids with different physicochemical properties; also its main source of income is the tourism. Most of their abundant natural resources have not been characterized and even used yet, this need offer the opportunity to study the physicochemical characteristics of peloids near the Arenal Volcano which may be related to its therapeutic properties, despite of this is a tourist attraction area characterized by hot springs, hotels and spas, it has a low socioeconomic and industrial development, and industrialization of products would create new jobs, and promote the health and wellness tourism, producing a productive linkage.

Objective

The physicochemical characterization of the Peloids near the Arenal Volcano Costa Rica and relate them to their therapeutic properties.

Methods

Peloids were characterized by tests such as pH, rheology, density, DSC, X-ray diffraction and thermal conductivity.

Results and conclusions

Peloids where characterized primarily as kandites billaminars, with a thixotropic flow, high in Fe_2O_3 , Al_2O_3, SIO_2, Na_2O, TiO_2, ZrO_2 minerals, an acid 4,70 pH, allowing them for the formulation of masks and other anti-psoriasis and anti-acne pharmaceutical forms.

Keywords: Hot Springs, Physicochemical Properties, Cosmetics, Social Development, Microenterprise, Peloids, SMEs, link Partner Enterprise-University-Society.

INTRODUCTION

Costa Rica is a volcanic country with vast natural resources of flora, fauna and minerals. It´s main economical activity in the last year has been the ecological tourism. The segmentation of the Costa Rican Tourism has been varying over time and at this moment the field of health and wellness tourism is growing rapidly. This tourism field combines relaxation and natural therapies to enhance health and a esthetics as well as the physical and mental welfare. (1,2) The Arenal volcano has been dormant since 1958, when it erupted and two craters were formed. It is located in the province of Alajuela, Canton of San Carlos district of the Fortune; due to its recently volcanic activity it has numerous hot springs and natural peloids (volcanic muds), clays and other resources that they have been used by hotels and restaurants in the area as attractive for national and international tourism. (1,2). Despite of its reachness, the mineral resources of Costa Rica are poorly physicochemically characterized, furthermore, they have been studied by theirs physical characteristics and chemical composition, which allowed their use in therapeutic and cosmetic applications. In Costa Rica the Faculty of Pharmacy of the University of Costa Rica, founded in 1899 is the leader in research in the field of natural resources, drugs and cosmetics. Due to its volcanic nature the presence of phyllosilicates of various kinds, associated minerals such as cristobalite, quartz and tridinita,(which are polymorphic forms of silicon oxide) is common in this country.(1,2,3,4). Before starting this study some definitions must be provided for a better technical context of the investigation. According to Eduardo Besoain in its Minearología Soil Clays Treaty Clay the term clay comes from the Latin "Argilla" and the Greek "αργος" or "αργιλος" which means white, and it defines as affine material of less than 2 microns particle size, heterogeneous type, naturally occurring, consisting mainly of aluminosilicates and primary, secondary and organic components (4,5,6). The Cuban standard NCXX of specifications of uses and characterization of health interest peloids defined them as: 2.1 Peloid. Greek πηλος = mud, clay. Product formed by a mixture of mineral water including sea and salt lakes waters, with organic an inorganic materials, resulting from geological and/or biological processes, alone or together that can be used for therapeutic and cosmetic purposes (7). The classification of peloids is summarized in the following table:

Table I: Classification of peloids

Denomination	Solid	Liquid	Temperature	Mellowing
Mud or Sludge	Mineral	Sulphatated	Hyperthermal	*In situ*
		Chlorinated	Mesothermal	In tank
			Hypothermal	
Silt	Mineral	Salt lake or sea water	Hypothermal	*In situ*
Turf	Organic	Alkaline	Hiperthermal	Out door
		Sulphatated	Mesothermal	Enclosure
		Sea water	Hipothermal	
Biogleas (Baregine type or Muffe)	Organic	Sulphatated	Hipertermal	*In situ*
Other biogleas	Organic	Non sulphatated	Hiperthermal	*In situ*

Sapropeli	Mixed	Alkaline Sulphatated	Mesothermal Hipothermal Hypotermal	In situ
Gytja	Mixed	Sea water	Hypothermal	In situ

Source (6, 7, 11,15) According to the Table I, the peloid studied in this investigation fits into the category of mud or sludge. Because this product must have microbiological and sanitary conditions that allow their marketing, is necessary to form the "in situ" peloid from two natural excipients; in this case the white clay extracted from the Arenal Volcano and thermal water extracted at its original source in a 50:50 mixture by weight. (4,5,6,7)

OBJECTIVE

Characterize physicochemically a peloid composed of white clay and thermal water in a 50:50 in weight mixture of the Arenal Volcano in Costa Rica to identify its therapeutic and cosmetic properties.

MATERIALS AND METHODS

Reagents: White Clay extracted from its origin at the surroundings of the Arenal Volcano, Thermal water taken from its origin from Arenal Volcano and Kaolin 99.99 % purity Sigma Aldrich®. A comparison was made between a peloid formed by 50:50 mixture of thermal water and a Caolita used for reference and from this comparison is deduce the therapeutic and cosmetic properties.

EQUIPMENT

Instrument®pB Denver 11 pH meter, glass electrode membrane , LV DV III Rheometer Brookfield® spindle 18 and 25m, AnalisisReocal® software , stainless steel density meter, four decimal Analytical Balance, Calvet® micro calorimeter , KD2 Pro®Thermal Properties analyzer refractory furnace , X-ray diffractometer powder D -5000 SIEMENS : two circles goniometer with independent movement , X-Ray Fluorescence , Fluorescence Spectrometer SIEMENS® SRS 3000 Source anode Rh, Be window (125) Generator X -ray : 20-60 kV and mA 5-100

METHODS

Three samples of the natural peloid were compared with the reference peloid that was formulated with caolin and thermal water (50:50), both formulations were used to measure pH and specific gravity. For pH, the instrument was calibrated and verified with certified 4.0, 7.0 and 10.0 buffers. About 15 grams of the mixture were used to measure pH. For specific gravity empty pycnometer was weighed on the analytical balance, then the pycnometer fill with distilled water, and finally fills with the mixture (8). All determinations were measure at 25 ° C. For the rheological tests, a ramp of speeds were used from 5 rpm to 50 rpm, six-speed measurements were repeated at returning ramp, the spindles used were 16 and 28 and a R18 container; the working temperature was 22 °C. The data were analyzed by Reocal® software (8). The organic elemental analysis (N,C,H,S): This determination requires the sample in an oven at 1000 ° C, the resulting gases are driven through helium reactants which reduce the number of gaseous species in the resulting mixture of combustion. Then they pass through a gas chromatograph with thermal conductivity detector (TCD) that measure N_2, CO_2, H_2O and SO_2 (9). Weight loss test was performed by drying of three samples in a refractory oven at 110 ° C for 24 hours and weighed by difference on an analytical balance. The cooling curve calorimeter test was carried at 200 ° C at a rate of 10 ° per minute, and cooled at the same rate; the sample was placed in an aluminum capsule. The heat capacity was obtained from a microcalorimeter cell with a volume of 10 cm^3 connected to a Phillips PM2535 multimeter. Three samples were measured by Thermal conductivity, an assay method for transient heat source 25 ° C ASTM D5334 were performed (8,9). Semi-quantitative X-ray fluorescence analyses (Fquant) of elements atomic weight were more than boron. Source with Rh anode, Be window (125) X-ray generator: 20-60 kV, mA and 5-100 Collimators: 0.46; crystals analyzers: LiF (z> 23) LiF . The method was used the reflective powers method (8,9) X-ray diffraction conditions: Temperature, 25 ° C; filter of Nickel. The anodes were copper (Kα,λ1,54 A°) and molybdenum (Kα , λ 0,73 A °) The sample holder was of polimetacrilate. The analysis was continuous to 0,1° per second in a range of 3 ° to 40 ° 2θ. The detector was a gas with photodiodes. Three samples were weighed about 8 to 10 mg by sample. (8,9)

RESULTS

In the table below it is shown the crystalline phases identified in the sample of white clay obtained from the Arenal Volcano, with X-ray diffraction.

Table II: Composition of Crystalline Phases identified in the white clay of the Arenal Volcano in Costa Rica

Crystalline phase	Halloysite	Cristobalite	Quartz	Microcline	Albita / Anorthite
Class	Silicate			Silicate	Silicate
Subclass	Phyllosilicate	SIO_2	SIO_2	Tectosilicate	Tectosilicate
Formula	$Al_2Si_2O_5(OH)_4$	SIO_2	SIO_2	$KAlSi_3O_8$	$NaAlSi_3O_8$
% Semiquantitative	63.1	30.9	1.6	2.1	2.3

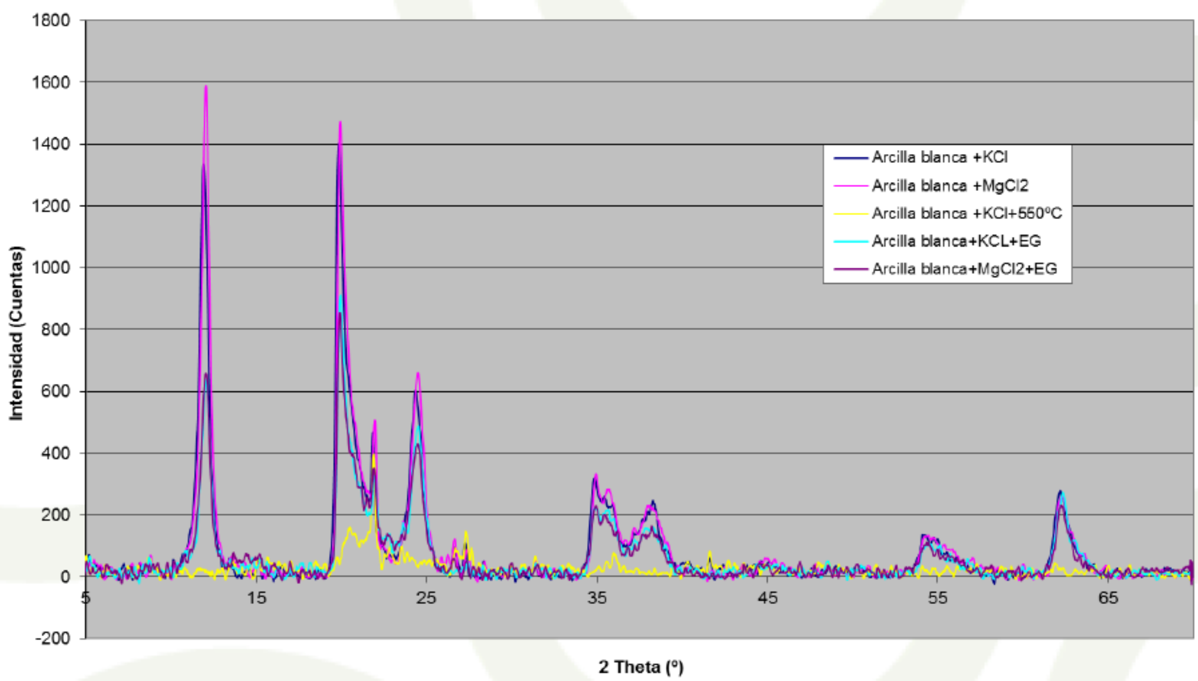


Figure 1: shows the diffractogram of the white clay from Arenal Volcano

Angulo 2 θ. Figure 1. X -ray diffraction pattern of white clay from Arenal Volcano Costa Rica. Source 9.

The composition of the main elements of the organic compounds in the sample of white clay of the Arenal volcano is shown in Table III.

Table III: Elemental composition (CHNS) in the sample of white clay of the Arenal Volcano

Sample	% Nitrogen	% Carbon	% Hidrogen	% Sulfur
White clay	< 0,07	<0,07	1.79	<0,30

Source 9.

The analyses of inorganic compounds by X-ray fluorescence obtain in a sample of white clay Arenal Volcano shown in the table IV.

Table IV: Chemical analysis by X-Ray Fluorescence of the sample of white clay from Arenal Volcano Costa Rica

Compound or element	% wt in the sample
LOI	13.75
Na_2O	0.11
MgO	0.071
Al_2O_3	35.9
SiO_2	43.3
P_2O_5	0.038
SO_3	0.049
Cl	0.025
K_2O	0.296
CaO	0.082
TiO_2	0.697
MnO	0.07
Fe_2O_3	5.014
CuO	0.005
ZnO	0.022
Rb_2O	0.0019
SrO	0.0164
ZrO_2	0.110
BaO	0.4

Loss on ignition (LOI). Source 9.

The sample color was light gray, with a humidity of 13 % which is fine to the touch. The pH was determined at 25 °C by triplicate, comparing two formulations of peloids 50:50 by weight of white clay and thermal water with reference formulation. The results are shown in Table V.

Table V. Results of pH from peloids and thermal water of the study

Sample/pH	Thermal water	Peloids of White clay (50:50)	Peloids of kaolin (50:50)
1	8.15	4.84	6.28
2	8.20	4.64	6.24
3	8.30	4.82	6.28
Average	8.22 ± 0.08	4.77 ± 0.11	6.27 ± 0.02

Source 10.

The next table, Table VI, compares specific gravities between white clay: thermal water 50:50 and peloid of caolita: thermal water 50:50 measured by pycnometry.

Table VI: Results of peloids specific gravity and thermal water of the study

Sample/pH	Peloids of White clay (50:50)	Peloids of kaolin (50:50)
1	1.4268	1.4429
2	1.4195	1.4509
3	1.4234	1.4468
Average	1.4232 ± 0,0036	1.4468 ± 0,0040

Source 10.

The thermal conductivity data are shown below, in the Table VII.

Table VII: Determination of Thermal Conductivity white clay formulation (50:50)

Clay sample	%H_2O	□(W/mK) a 25°C
M1	35	0.97
M2	43	0.87
M3	35	0.93
Average	37.67±4.62	0.92±0.05

Source 9.

Determination of the heat capacity determined at 25 ° C the results are shown in the Table VIII.

Table VIII: Determination of heat capacity white clay formulation (50:50)

Clay sample	% H_2O	Cp (J/KgK) a 25°C
M1	35	2160
M2	43	2260
M3	35	2065
Average	37.67±4.62	2262±98

Source 9.

Table IX: Thermal Retentivity determination white clay formulation (50:50)

Clay sample	% H_2O	Cp (s/m^2) a 25°C
M1	35	3.9×10^{6}
M2	43	$3,7 \times 10^{6}$
M3	35	$3,6 \times 10^{6}$
(Average)	37.67±4.62	$3.73 \times 10^{6} \pm 0.15 \times 10^{6}$

Source 9

In the Figure 2 shows the cooling curve of white clay: thermal water 50:50

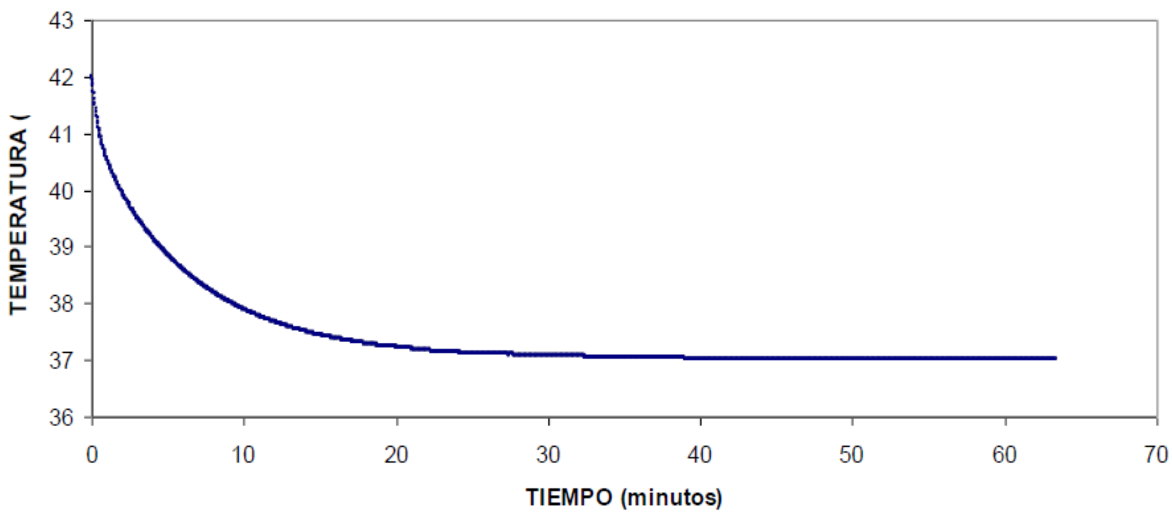


Figure 2: Cooling curve of clay and thermal water of the Arenal volcano in Costa Rica. Source 9

The figures from the results of the rheological study of peloids composed of white clay and reference formulation (kaolite with thermal water in a proportion of 50:50) are shown in the following figures.

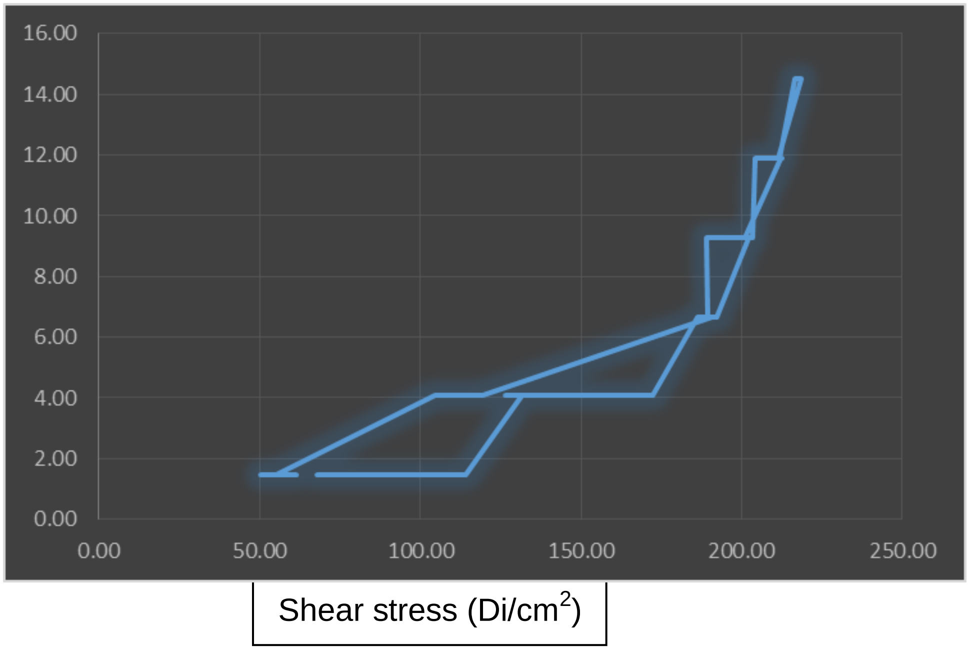


Figure 3: Rheological study of Peloid White clay: thermal water 50:50. Source 10

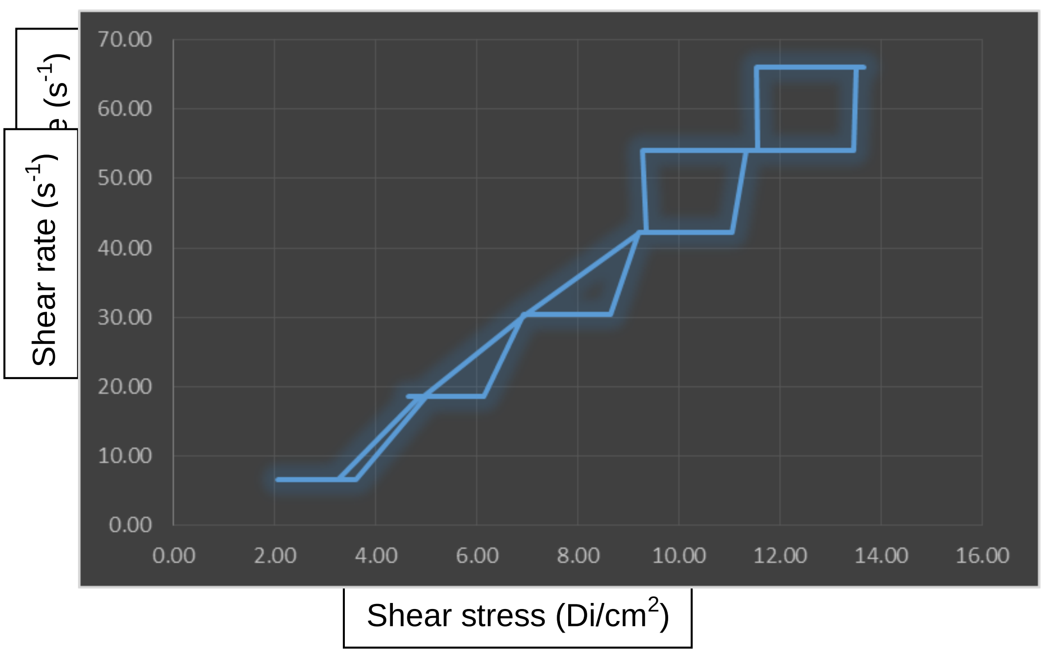


Figure 4: Rheological study of Peloid Kaolita: thermal water 50:50. Source 10

According to the figures 3 and 4, for both peloids the fluid behavior is mainly plastic thixotropic, but the formulation of the white clay:thermal water 50:50 has more thixotropic behavior, the kaolita:water 50:50 is closer to a Newtonian fluid behavior (11).

DISCUSION AND CONCLUSIONS

The characteristic X-ray diffraction patterns were found for the phyllosilicates of dioctaedric bilaminar, more specifically: the band 7.3 and 3.6 suggests the presence of Canditas when the sample is brought to 550 ° C, at this temperature it loses the band 7 A wich confirms the presence of halloysite and not Kaolita. There aren't peaks at 14 A, therefore, the presence of vermiculites, chlorites, smectites are discarded, not found reflections correspond ding to carbonates. The presence of reflection to 4.04 A demonstrates the presence of cristobalite and the lack of quartz or tridymite. (4.9). Rheological testing, pH measurement and specific gravity were the tests performed to differentiate between caolitas and hallosyte. These results are presented before in the Tables V and VI and Figures 3 and 4. These information allows to differentiate between caolitas and halloysite because the laminar triclinic system in the case of caolitas allows a higher water absorption capacity if it is compared with the tubular hexagonal system of the halloysite. The white clay peloid shows a lower density because of its compactation and water absorption, and an acid pH which helps to protect the skin. (4,9,10,12). The presence of a high content of cristobalite which has a cubic crystal structure provides a good abrasion which makes it ideal for an exfoliative skin treatment. The combination of a hexagonal structure, with a high water absorption capacity, and a cubic structure allows a gentle exfoliation because of the presence of water and the classic small particle size of clays with plastic action on the skin. Especially the thixotropic plastic flow found in the essay performed confirms the good application characteristics of peloid on weak skin such as in elderly or in children. Another important feature that differences the halloysite from the kaolinite is that the layers overlap in an disorderly manner in the first type, unlike to the caolita which is an orderly one. This also allows the incorporation of water into the spaces between layers making a greater capacity of absorption (4,11,13).

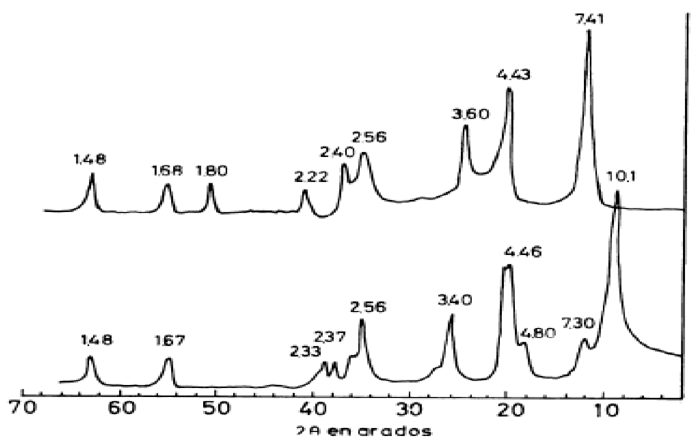
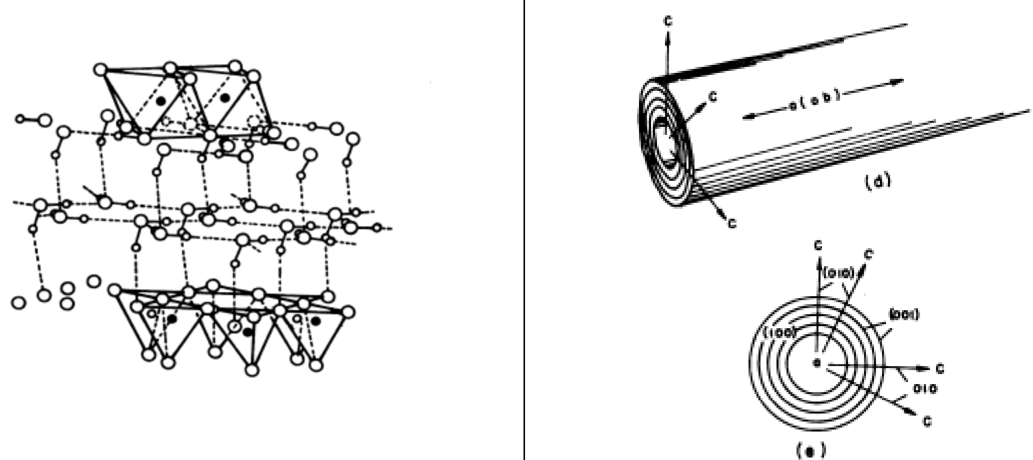


Figure 5: Comparison of X-ray diffractograms of hydrated halloysite below and metahalloysite above. Source4

Since halloysite is mainly as its hydrated form it has a great ability to dissolve Fe_2O_3, thus high presence of iron oxide II is explained by this characteristic, which is the third compound predominant in the clay analyzed. The presence of iron oxide II gives more advantages to the clay peloids because it gives them an important antioxidant capacity, which is very beneficial for the skin (4, 14). According to the diffraction test seems to dominate the metahalloysite form containing 2 waters of hydration, and the least amount endelita or hydrated halloysite with 4 waters of hydration, this primarily by a preponderance of reflection to 7 instead of reflection to 10.01 A (4.9). The presence of a low content of titanium dioxide is characteristic of young Canditas, the halloysite has a higher cationic exchange capacity than caolita, it makes more useful in the treatment of skin cleansing, halloysite has a capacity of exchange of 10 to 40 meq / g while the caolita only 3 to 5 meq / g. The cationic exchange capacity increases when decreasing the particle size; with sizes of less than 50 microns is reached to 200 meq / g (4,15,16). Halloysite clay of the volcano contains more iron oxide II than commonly reported; besides the surface area of the halloysite is higher than kaolinite. The first has a surface area of 60 m^2 / g, while the kaolinite has a surface area of from 15 to 50 m^2 / g depending on their crystallinity. (4,15,16). From the thermal analysis was found that the peloid has low thermal conductivity, which is explained by high amount of water and this also explains the high heat capacity of the peloid which is twice the dry clay, and high thermal retentivity making keeps the temperature up quickly and gives good thermal therapeutics properties. See table VII, VIII and figure 2 (9.14).



(A) (B)

Figure 6 (A): Structure of a hydrated halloysite with water in the interlayer space.
(B) Tubular phase and cross section of the tubular structure of the halloysite. Source 4

Both halloysite as metahaloisitas have a tubular structure as indicated above and shown in Figure 6.As shown in both figures (3 and 4) the type of flow is thixotropic plastic nevertheless plastic characteristic is more pronounced in the peloid clay since its yield point is higher, also at low shear it shows greater thixotropy, needing a greater shear it has increased adhesion between the particles, because the caolita presents a triclinic laminar structure, while halloysite shows a hexagonal tubular structure, although both have a bilaminar meta-structure. Caolita flows with less effort while halloysite has more grip this can be an advantage when formulating cleaning or exfoliating products (4, 9, 11,14).

CONCLUSIONS

In conclusion the properties of white clay of the volcano are useful as therapeutic and cosmetic clays, their main properties are high water absorption due to the presence of halloysite structures partially disordered between layers and tubular formation of crystal structures, high capacity exfoliating due to the presence of silicon dioxide in cubic shape (cristobalite), antioxidant capacity by the presence of iron oxide II in high concentration, high cationic exchange capacity, which allows a deep cleaning of the skin, acid pH of 4.77 which protects the acid mantle of the skin, gives protection against infection and useful in delicate skin like children and the elderly one, in add with the thixotropic plastic flow this permits good extensibility with soft massage on the skin and exfoliation and higher lubrication at time of application. Its high heat capacity, high thermal retentivity, and low thermal conductivity allows peloids formed to be useful in therapeutic massages or thermo masks including facial massage and body wraps, scrubs or detoxifying. Their good thermal and rheological properties along with the other already mentioned makes the peloids formed with the white clay and water of Arenal Volcano offer a high quality of therapeutic and cosmetic use.

REFERENCES

[1]. Tristán, J. F. Baratijas de Antaño. San José: s.n., 1925.
[2]. López Porras, K. Oportunidades para cosméticos y productos de cuidado personal en la Unión Europea. San José: Editorial Promotora de Comercio Exterior, Ministerio de Comercio Exterior Costa Rica, 2013.
[3]. Fumero, P. Centenario de la Facultad de Farmacia de la Universidad de Costa Rica 1897-1997. San José: Editorial Universidad de Costa Rica, 1998.
[4]. Besoain, E Minearología de Arcillas y Suelos de Costa Rica. San José Costa Rica. Instituto Interamericano de Cooperación de Agricultura, 1985.
[5]. Romero, J.F. Características de las aguas minerales y fangos, Uso y control de la Calidad de estos Recursos. [En línea] [Visualizado el: 13 de diciembre de 2013.] http://www.sld.cu/galerias/pdf/sitios/rehabilitacion-bal/peloides_romero.pdf.
[6]. Mourelle Mosqueira, M. L. Aspectos Físicos y Químicos del Termalismo. [En línea] [Visualizado el: 13 de diciembre de 2013.]
[7]. Normalización, Oficina Nacional de. NC XX Norma de Especificaciones y Caracterización de Peloides. La Habana, Cuba: s.n., 1998.
[8]. Vargas, R, Madrigal, G, Fonseca L, Berrocal L. Manual de Prácticas de Laboratorio de Fisicoquímica Farmacéutica II. San José Editorial Universidad de Costa Rica, Universidad de Costa Rica, 2009 y Anexos 2014..
[9]. Peloides Termales S.L Informe Analítico Agua Mineralo medicinal y Arcilla Blanca Costa Rica. Vigo, Universidad de Vigo España, 2013.
[10]. Instituto de Investigaciones Farmacéuticas. Informe analítico. Agua Mineralo medicinal y Arcilla Blanca Volcán Arenal, Costa Rica San José Costa Rica ,2014.
[11]. Faulí, I y Trillo, C. Farmacia Galénica. Madrid: Ediciones Luzán S.A., 1993.
[12]. Romero, J, Reyes G, Llerena, M, Marzán, R, Capitulo VII Peloides Mineralo medicinales, En línea] [visualizado el: 13 de diciembre de 2014.]
[13]. Martini, M. Introducción a la Dermofarmacia y Cosmetología. Zaragoza: Editorial Acribia S.A., 2005.
[14]. Wilkinson, J y Moore, R. Cosmetología de Harry. Madrid: Editorial Díaz de Santos S.A., 1990.
[15]. García, E, Suarez, M, Las arcillas: Propiedades Usos.[En línea] [visualizado el: 13 de diciembre de 2014.] http://www.uclm.es/users/higueras/yymm/arcillas.htm. 2014
[16]. Bolger, R. "Industrial Minerals in Pharmaceuticals". Industrial Minerals. Agost