In vivo performance of a social and environmentally sustainable blend of Brazilian Kaolin

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Abstract

Background: Clays are used since ancient times for medicinal and beauty purposes and their mineral compositions depend on their geological origins. Clays originated from volcanic soil are colored and rich in minerals while clays derived from the Amazonian lateritic soil are rich in minerals and organic matter. Combining these different sources of clays opens the way to the creation of an infinite variety of clays with amazing cosmetic and aesthetic properties. This work demonstrates new skin benefits and multifunctional properties of Brazilian clays containing kaolinites, "the kaolin" for cosmetic applications.

Methods: Proof of concept clinical study: skin hydration (Corneometer™), TEWL (Tewameter™), sebum (Sebumeter™) and firmness /tensor (Cutometer™). Short term or long term of product use respectively after 4 hours or 7 days of consecutive use.

Results: The positive impact of kaolin on skin health was demonstrated such as the maintenance of hydration, protection of skin barrier function and increase of skin firmness (tensor effect). The use of kaolin was not associated with an increase in sebum secretion, a phenomenon classically observed with the use of clays and known as "rebound effect" due to the constant use of clays.

Conclusion: The positive attributes show that kaolin can be used in multifunctional formulations, even for skin care. Kaolin provides also rheological stability for the formulations and can bring benefits to the mineral make up, color cosmetic products, face products, besides sunscreens, BB creams and CC creams. New formulations and uses of kaolin can be addressed with several benefits for skin and hair care.

Keywords: kaolin, sustainable, TEWL, hydration, skin homeostasis, sebum control.

Introduction.

Clays have been used since ancient times for beauty. Medicinal purposes of clays have been evaluated also along the history, and the human being has used it for wound healing and soothing irritation on the skin.

There are several types of clays such as: montmorillonite, illite and kaolinite. Specially this last one, kaolin is a natural resource in cosmetic formulations. It has as a main characteristic, the presence of kaolinite in its structure, typical from Brazilian clays. This structure provides an interaction with water and oil in a balanced way besides absorption of greases and toxins on the skin´s surface. Brazilian clays have some special characteristics, as they are found in specific areas of the soil from different Biomes in Brazil. For example, in south of Brazil, there are colored clays originated from volcanic soil, rich in minerals and organic matter. On the other hand, there is another clay that is very particular in composition and characteristics, also very rich in minerals and organic matter, derived from the Amazonian lateritic soil – the Amazonian White Clay.

Combining the South to the North clays is possible to arrange infinite possibilities of kaolinite mineral clays. Moreover, as kaolinite mineral clays took millions of years to capture its features [1], it's very important to use these clays considering an ethical and environmentally sustainable approach. The aim of this work is to demonstrate that kaolinite clays may have multiple beneficial properties for the skin adapted for a cosmetic use.

Materials and Methods.

Panel description and formula of product assessed

In vivo proof of concept evaluation's studies aimed to measure skin properties after the use of clay minerals were performed at Beraca´s Innovation Center (Brazil). The participants were 27-62 years old, presenting a healthy skin. All participants at the beginning presented a skin free from any cosmetic or product. A written informed consent form was submitted and signed by each participant. All data were considered private, and all collected information was classified.

All measurements were done in a controlled environment (temperature of 20°C+/-2°C and relative humidity of 50%+/- 5%). The phototype skin of each participant according to the Fitzpatrick scale, was not an excluding factor. The recommendations of the Declaration of

Helsinki and the guidelines of the International Conference on Harmonization Good Clinical Practice were observed as applicable to a non-drug study.

The clay minerals were tested in a formulation of foundation. For foundation type formulation with Brazilian kaolinite clays consisted of the placebo with the addition of 10% of kaolin in the formulation. The formulations are described as follow:

Placebo		**Clays**	
INCI name	**%**	**INCI name**	**%**
		Aqua	Up to 100
Aqua	Up to 100	Kaolin	10.0
Glycerin	4.0	Glycerin	4.0
Xanthan Gum	0.4	Xanthan Gum	0.4
Cetearyl Glucoside (and) Sorbitan Olivate	4.0	Cetearyl Glucoside (and) Sorbitan Olivate	4.0
Titanium Dioxide	5.0	Titanium Dioxide	5.0
Hydrogenated EthylHexyl Olivate and Hydrogenated Olive Oil Unsaponifiables	7.0	Hydrogenated EthylHexyl Olivate and Hydrogenated Olive Oil Unsaponifiables	7.0
Theobroma grandiflorum seed butter	2.0	Theobroma grandiflorum seed butter	2.0
Oenocarpus bataua fruit oil	2.0	Oenocarpus bataua fruit oil	2.0
Mauritia flexuosa fruit oil	1.0	Mauritia flexuosa fruit oil	1.0
Copernicia cerifera (Carnauba) Wax	2.0	Copernicia cerifera (Carnauba) Wax	2.0
Tocopheryl Acetate	1.0	Tocopheryl Acetate	1.0
Sorbitan Caprylate (and) Benzyl Alcohol	1.5	Sorbitan Caprylate (and) Benzyl Alcohol	1.5
Fragrance	0.2	Fragrance	0.2

Evaluation of skin hydration, TEWL, sebum control and skin tensor effect

Corneometer™ CM25, from Courage & Khazaka was used for determination of water content on the skin external surface, through capacitance measurement on stratum corneum. The probe measures the changes in the dielectric constant due to skin surface hydration changes observed.

Tewamater™Hex, from Courage & Khazaka, was used for TEWL (trans epidermal water loss) assessment. This probe consists of 30 pairs of sensors (evaporimeters) for determination in open chamber method of temperature and humidity´s variation, to evaluate the water loss expressed in $g/h/m^2$. TEWL and hydration were measured respectively on 8 and 7 participant's forearm after 4 hours of product application.

For skin sebum evaluation, the Sebumeter™ SM815, a photometric method, based on a sensor that measures the sebum secreted by skin was used. The total of participants enrolled in this study were 6.

Finally for tensor effect or immediate firmness through the measurement of R0 parameter, the Cutometer™ MPA 580, from Courage & Khazaka was used, that evaluates the viscoelastic properties of the skin through the principle of suction method, where the negative pressure deforms mechanically the skin. Tensor measurements were done on the hemi-face of 4 participants after a period of 7 consecutive days of product use.

All evaluations were compared to the basal level (T0) and to the Placebo (foundation without the kaolinite clays applied).

Statistical Analysis was evaluated through Prism Graph 9.2, with evaluation of average results at ANOVA test, followed by t-test evaluation for each group measured and post Dunnet test, at a significance level of $p<0.05$.

Results

Clays maintain skin hydrated

As a common sense, use of clays is conditioned to dehydration of the skin. However, it was observed on the experiments no negative impact on skin hydration. Indeed, we observed that skin hydration is maintained (figure 1).

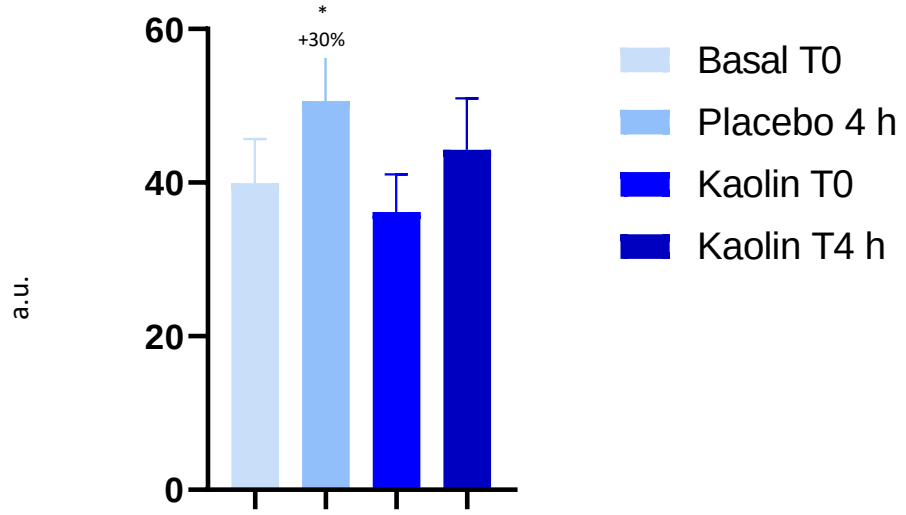

Figure 1 : Measurement of skin hydration before and after 4 hours of application of a placebo foundation or 10% kaolin Clays containing foundation on the forearms (Corneometer™). Data are presented as mean ± SD. Statistical significance using Student's t-test (paired data) was calculated at each study time in comparison to T0 (* Significance p value at $p<0.05$). n= 7 participants

Clays reinforce skin barrier function

Before, each TEWL measurement, the foundation formula was removed, and the measure was immediately performed. The figure 1 shows that skin barrier function is reinforced with the use of kaolin clays. Indeed, the TEWL is significantly reduced with the use of Kaolin clays product. The results are better and significantly different from the Placebo, with a decrease on TEWL in 22% when compared to the basal level (T0) (figure 2). Placebo presented a decrease of 11% when compared to T0.

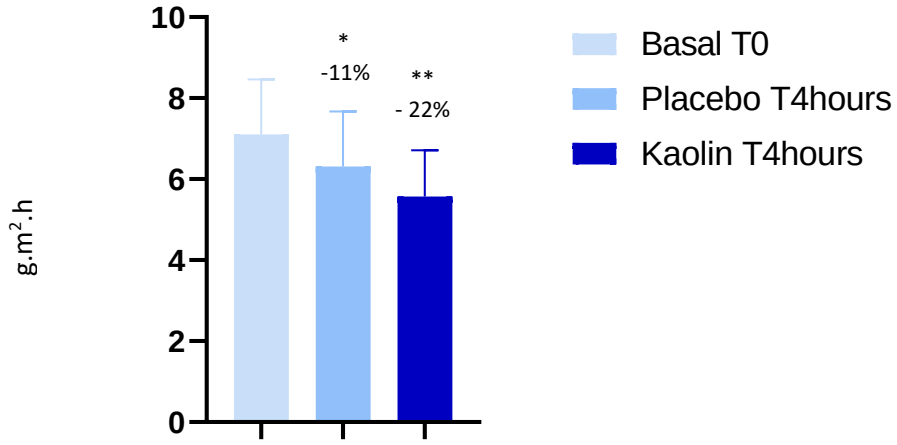

Figure 2: Measurement of TEWL before and after 4 hours of application of a Placebo foundation or 10% kaolin Clays containing foundation on the forearms (Tewameter). Data are presented as mean ± SD. Statistical significance using Student's t-test (paired data) was calculated at each study time in comparison to T0 (* Significance p value at p<0.05; **p=0.0005 when compared to Basal T0). n= 8 participants

Clays provide a skin tensor effect

The figure 3, shows the skin tensor effect provided by kaolinite clays applied in hemi face at 10% in a liquid foundation formula. Indeed, after 7 days of consecutive use a statistically significant decrease in R0 parameter was observed by -13% in comparison to untreated skin (basal level T0). The lower the R0, the higher the firmness of the skin is. In contrast and as expected the Placebo foundation has no effect on skin firmness. These results related to R0 parameter can explain the sensation of tensor effect observed after an application of a clay mask, for example, but also the sensation that skin appear to be firmer after the product application and its removal.

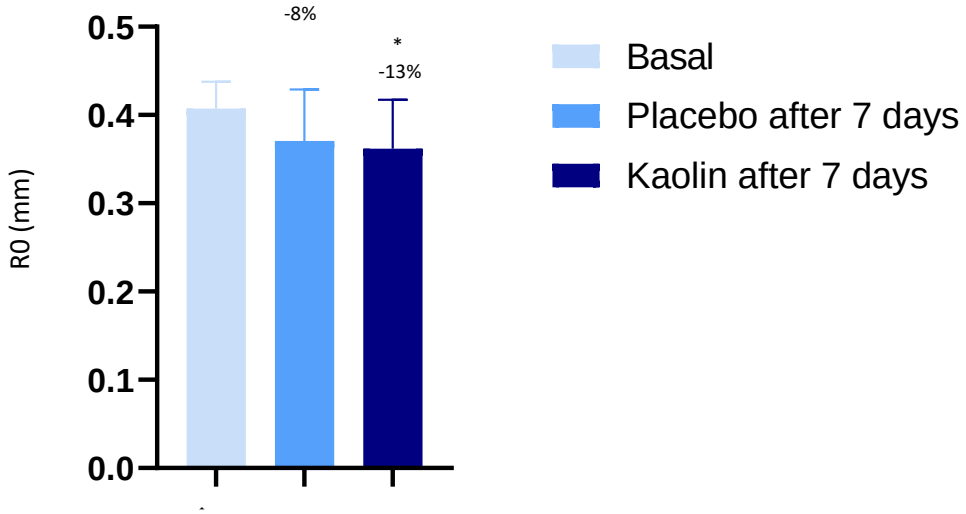

Figure 3: Measurement of R0 before and after 7 days of application of a Placebo foundation or 10% kaolin Clays containing foundation on the forearms (cutometer). Data are presented as mean ± SD. Statistical significance using Student's t-test (paired data) was calculated at each study time in comparison to T0 (* Significance p value at p<0.05). n=4 participants.

Clays maintain skin homeostasis (sebum control)

Finally, even with the constant use of the kaolinite clays, we observed a maintenance of the skin homeostasis. The sebum level is balance neither overproduced nor decreased. We didn't observe the rebound effect usually observed as a result of constant use of clays (Figure 4).

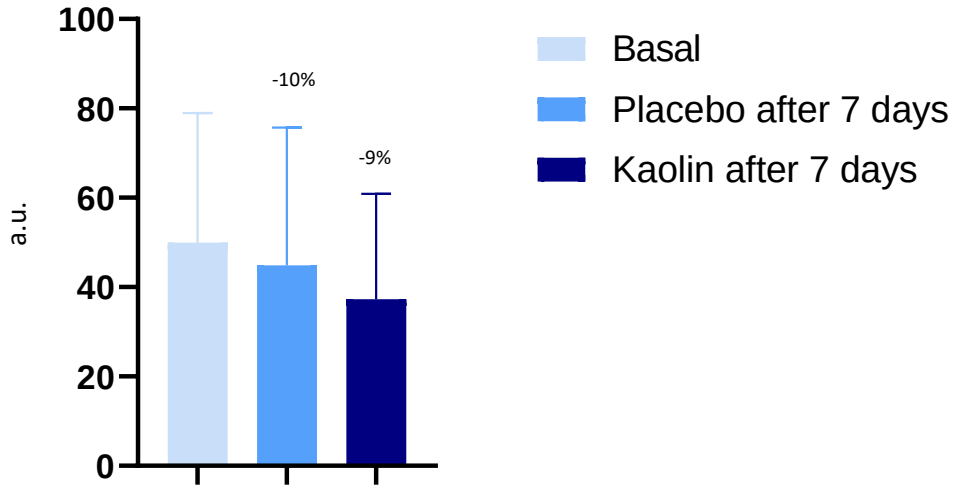

Figure 4: Average values of oiliness comparatively to the BASAL level on time 0 and after the period of 7 days with the continuous use of liquid base containing KAOLIN composition applied at 10%. n=6 participants.

Discussion

Clays have been used since the Antiquity, as mentioned by occidental medicine [2,3] in historical texts as Hippocratic Corpus [2]. Natural clays minerals are used for health protection and treatment in cosmetic formulations, pharmaceutical formulations, spas and for aesthetic treatments, providing cleaning, emulsification, beautifying and detox effect [1,2,4,10]. The properties of clays are related to high specific area, adsorption capacity, rheological properties, chemical inertness, and low toxicity [2,3,4,7].

Some specific clays are part of pharmacopeias (as bentonite, magnesium trisilicate, magnesium aluminum silicate, attapulgite) and they are part of inorganic excipients [2]. As excipients, clays minerals can be used as emulsifiers, thickeners, lubricants, agents that aid disintegration and carriers, bringing increase in stability and viscosity of formulations [2,4]. They can also be used as active substance, such as gastrointestinal protectors, osmotic oral laxatives, and dermatological protectors [4]. The use of clays is related to anti-inflammatory effect (example in pelotherapy, use of hot muds), and wound healing properties [2]. Moreover, natural clays can be used as delivery system, or scaffolds for tissue engineering and special clays have also antimicrobial effect [2,3].

The main minerals related to clays are, for example, kaolinite, montmorillonite, beidellite, nontronite, illite, vermiculite, besides others [4]. Kaolinite is from the name Kau-Ling, that means high ridge [1], composed of flexible sheets of triclinic crystal, with a diameter of 0,2 - 12µm and a density of about 2.1-2.6 g/cm^3, with a lower cation exchange capacity (figure 5). However, the rate of exchange reaction is fast, and it adsorbs small substances.

The main functional groups are hydrogens (present in octahedral sheets, SiO_4) that binds oxygen (present in tetrahedral sheet, Al_2O_6). Kaolinite has several trace elements present on mineral structure that is dependent of the geological history. Kaolin formation is due to the rock transformation due to the effects of climatic factors or weathering. Specially in Amazon, the primary kaolinite was formed along millions of years under tropical climate conditions, bringing a special characteristic of the material. Kaolin is available in the environment and respirable dust concentrations in kaolin mining is lower than 5 mg/m^3, providing a safe material, with lower toxicity for aquatic species. Kaolin clays are highly biocompatible materials, with low or no toxicity.

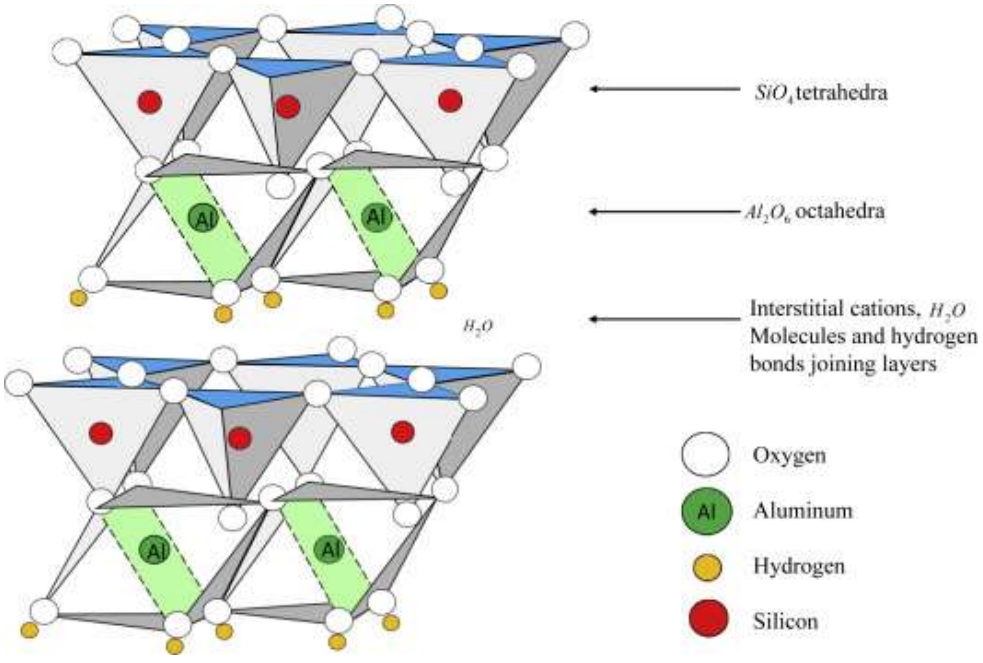

Figure 5: Structure 1:1 of Kaolinite. Source: Science Direct, Advanced Powder Technology, 2017.

They are used on dry and sensitive skin as they can re-mineralizing, absorb toxic substances and nourish the skin [7]. Kaolinite type protects the skin against external physical and chemical agents, with refreshing action, gentle antiseptic action, absorbance of greases and toxins and are recommended to treat cutaneous inflammation process, as seborrheic dermatitis, psoriasis, chronic eczema, and acne, besides the uses for hair care as anti-dandruff and anti-seborrheic (for example, minerals with high content of sulphur) [10]. In addition, some Brazilian clays (kaolinite type mainly) were evaluated in cosmetic formulations, for example in the application of gel (at 1, 3 and 5%), providing a non-Newtonian fluid with pseudoplastic behavior [8], and easy to formulate with.

Specially in Brazil, the kaolin clays extracted from a sustainable environmental approach were studied. The organic soil is removed properly and is reserved. After clays extraction occurs reorganization of the area extracted with the use of the soil previously extracted and reserved and planting of native species in the area, or even a formation of lake with clean water and fish, promoting environmental recovery.

This process occurs properly with the inclusion of environmental metrics and certifications, such as Fair for Life and For Life, that ensure the proper process for the extracted area recovery, besides the fair trade and social organization. Important key elements for a responsible approach to use clays as a cosmetic ingredient, are several, such as: proper prices for the clays extracted; fomenting a good interaction between people and communities who are involved in the extraction and environmental recovery.

Regarding physico-chemical aspects about the Brazilian kaolin, the phyllosilicate structure provides a small surface area (10 – 20 m^2/g) that brings an interaction with skin surface mainly through its mineral composition, and action through adsorption and absorption of excess of water and oil in a balanced way. This process can impact positively also in the NMF (Natural Moisturizing Factors) of the skin and keep the skin hydration. The kaolinite clay and its very fine particle structure (usually less than 10μm) provides an impact on the skin surface, protecting it against external environment through a subsequent decrease of trans epidermal water loss (TEWL). These properties might explain the results observed in our study. A tensor effect was observed also in all participants, as a result of immediate impact on the skin, according to the constant use of the foundation containing 10% of kaolin in the formulation.

The proper decrease of R0 observed in the experiment was significantly higher even when compared to the Placebo, providing firmness. Interestingly, our results confirm those published by Velasco *et al* in 2016 on Brazilian clays. This team studied the impact of clays (formulated at 30%) on face's skin biomechanical properties (firmness and elasticity). They mentioned that participants naturally felt a mechanical tension of the face after the mask removal [9]. Finally, even with the continuous use, it was observed that there was no impact like over sebum production or huge skin dryness, even with the constant kaolin use, that allows to affirm that Brazilian kaolin provides a balanced way to keep the skin homeostasis.

Conclusion.

Thanks to its several positive attributes demonstrated in this proof-of-concept study, kaolin clays can be considered as a multifunctional ingredient through its capacity to interact with the skin, maintain its hydration to reinforce skin barrier function, to improve skin firmness by providing a tensor effect. Besides their sebum control properties and their unique color, clays can be used also in makeup formulation.

Kaolin can be used in multifunctional formulations, even for skin care. Kaolin provides also rheological stability for the formulations and can bring benefits to the mineral make up, color cosmetic products, face products, besides sunscreens, BB creams and CC creams.

Acknowledgments.

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Conflict of Interest Statement. None.

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