Review

Not peer-reviewed version

The Scenario of Clays' and Clay Minerals' Use in Cosmetics/Dermocosmetics

Fernanda Daud Sarruf , Vecxi Judith Pereda Contreras , Renata Miliani Martinez , Maria Valéria Robles Velasco , André Rolim Baby *

Posted Date: 30 November 2023

doi: 10.20944/preprints202311.1890.v1

Keywords: clays; color cosmetics; efficacy; delivery; formulation

Review

The Scenario of Clays' and Clay Minerals' Use in Cosmetics/Dermocosmetics

Fernanda Daud Sarruf, Vecxi Judith Pereda Contreras, Renata Miliani Martinez, Maria Valéria Robles Velasco and André Rolim Baby *

Department of Pharmacy, Faculty of Pharmaceutical Sciences, University of São Paulo, São Paulo 05508-000, Brazil; fernanda.sarruf@usp.br (F.D.S.); vecxi07@hotmail.com (V.J.P.C.); remiliani03@gmail.com (R.M.M.); mvrobles@usp.br (M.V.R.V.); andrerb@usp.br (A.R.B.)

* Correspondence: andrerb@usp.br (A.R.B.)

Abstract: The use of clays in beauty care comes from ancient times, with therapeutic use since prehistory, and it is considerably relevant in the current cosmetic industry worldwide. In our review, we described types of clay and clay minerals used in cosmetics and dermocosmetics, compositions, usages as active compounds and excipients, and observations about formulation techniques. From this research, we could notice that although many scientific and specialized literature reported the characterization of clays, only some involving efficacy tests when incorporated into cosmetic products, mainly concerning haircare applications. By the exposed, our review could be considered and encouraged in the coming years to provide scientific and technical information for the cosmetic industry regarding the multifunctional use of clays and clay minerals.

Keywords: clays; color cosmetics; efficacy; delivery; formulation

---

1. Introduction

The cosmetic industry has used natural components in products since the beginning of history. The use of clays in beauty care is old, with therapeutic uses since prehistory [1–3]. Reports of treatments with "medicinal earth" mainly constituted by clay minerals are present in ancient civilizations' scriptures, such as ancient China, Egypt, and Greece [2,4]. Nowadays, there is a demand for natural ingredients by consumers, mainly for cosmetic products [5].

Minerals used for cosmetic purposes are mainly natural clay minerals due to the high cost and difficulty in industrial production. Concerning topical use, they are applied either as cosmetics or dermatological protectors [2,3], acting as adjuvant or active ingredients, and also, as a vehicle.

A cosmetic product is a preparation for external topic application (skin, hair, lips, nails) or to apply in oral cavity (teeth and mucous membranes) aiming to clean, beautify, perfume, change its appearance, correct body odors, protect and/or keep in good conditions [6–9]. According to our point of view, cosmetics and dermocosmetics can act further ahead as previously described, also contributing to the health maintenance of the consumers/patients. A broad range of cosmetic products can be formulated with clay minerals to clean, moisturize skin and treat conditions, like gynoid lipodystrophy and acne [8].

There is an important advantage in using clays for cosmetic purposes, as it is a low-cost, environmentally friendly, natural, and abundant component, which is chemically inert, easy to apply and remove, dries, and hardens fast, and presents extremely low toxicity risk when used in adequate conditions [8,10–13]. It also is used due to its high surface area, rheological properties, and excellent ion exchange capability [11,14].

Cosmetics with clays can be formulated in several forms, such as ointments, gels, creams (emulsions), and pastes. Those products must be formulated considering their adequate rheology profile (must be appropriate to maintain contact with application region) and sensory aspects (must

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 30 November 2023 doi:10.20944/preprints202311.1890.v1

be cosmetically acceptable), which are influenced by clays' physicochemical properties (e.g., particle size) [15].

Due to their composition, uses and properties, clays are very relevant in Cosmetology. In those products, clays can act either as active or as an excipient, influencing their stability, rheology, color etc. As actives, they are widely used for skin cleansing, oil reduction/control (skin and scalp), substance adsorption, antiaging, ultraviolet (UV) radiation protection (sunscreens), and ion exchange with skin, due to their color, qualitative and quantitative mineralogical composition, particle size and shape, structure, and ion exchange capacity. They can also be used in makeup products [2,15–18].

Despite the importance of clays and clay minerals in the cosmetic industry, specialized literature about this theme is thoroughly scarce. Therefore, in our review, our objective was to provide updated information concerning clays used in cosmetic products, both as active and excipient, and gathered study findings to better understand future perspectives and deficiencies in this field.

2. Clays x clay minerals

The term "clay" does not have a consensus in the specialized/scientific literature, thus being difficult to define due to the variety of materials known as "clays" and for being used in several areas, such as chemistry, mineralogy, geology etc. [19]. Therefore, clays are classified as natural inorganic rock or soil materials, composed of finely divided particles (inferior to 2 μm) with some plasticity while mixed with water and which hardens after drying. They are formed by clay minerals, organic matter, salt impurities, feldspars, and other minerals, like quartz, dolomite, calcite, iron, and/or aluminum oxides [5,6,13,14,17,19–21]. It is applied to all small-sized particles found in soils or sediments including phyllosilicates, quartz, feldspars, carbonates, sulphates, iron and aluminum oxides, humus, and other mineral and/or organic components [6,13].

Clays can be formed by one clay mineral, or (more commonly) a mixture of clay minerals with the prevalence of one. Those clay minerals give clays several properties that allow their use in many industries [13].

2.1. Types of clay

Clays for cosmetic use are produced in many colors and color difference is caused by the proportion of the minerals in each of the clays. As a raw material for cosmetic purposes, they are commercialized based on their color [14,15,17,19,20,22]. The color is mentioned during their marketing, and it is often used connected to its property. It is a visual reference for the purchaser [1].

Presence and proportion of minerals in clays interfere with their color and formulation stability [20]. Their colors also result from their crystalline structure in a certain state, being affected by composition, oxidation of structural cations, ionic charge, and ion position. Amount of water can also affect color aspect. Color can come from matter associated with clay [1].

According to Gubitosa and co-workers (2019), different clays can be found in nature depending on the presence of iron and its chemical state: clays with bivalent iron present green color; those with trivalent iron are red; and those that do not contain iron are white [5].

Rautureau and co-workers (2017) correlate color of clay minerals to the structural ions they contain. For example, white clays present Al^{3+} and Mg^{2+}; yellow clay present Fe^{3+}; red clays present Mn^{3+}, Fe^{3+}, Co^{3+} and Ti^{4+}; and green clay present Fe^{2+}, Fe^{3+}, Cr^{3+} and Ni^{2+} [1].

The clays of each color present different cosmetic attributes due to its composition, as shown in Table 1 [17,19,20]. However, literature correlating color to cosmetic use and concerning chemical and mineralogical compositions of clays for cosmetic use are very infrequent [14,22]. Matike and co-workers (2011) correlated clay colors with sunscreen ability. They mentioned that most clay soils used as UV filters corresponded to hematite's and goethite's colors, which are iron oxides. Their color is responsible for reddish and yellowish colors in clays [15].

 doi:10.20944/preprints202311.1890.v1

Table 1. Clay classification according to their color.

Color	Present Elements / Composition [17,19]	Cosmetic Use
Yellow	Rich in silicon dioxide (SiO_2)	Rejuvenation, skin purification and hydration [17,19] Prevent bacterial infection on skin, cleansing, sunscreen, and body beautification [15] Antiaging, remineralizing, illuminating, hydration, nourishing, cleansing, tonifying, eliminates residues [4] Tensor effect, activates microcirculation and contributes to ionic balance [23]
Beige	Rich in silicon, aluminum, titanium; low in Fe and hydrated aluminum silicate content	Astringent, purifying (adsorbs oil), moisturizing and healing [19] Tissue reconstitution, purification, astringent, hydrating, remineralizing, healing, skin whitening, skin protection and oiliness absorption [17] Body beautification [15]
White	Hydrated aluminum silicate, aluminum, sulfur, iron, boron, potassium and calcium [17]	Skin whitening, healing, moisturizing and helps in oiliness removal [19] Healing, whitening, oiliness absorption, hydration [17] Anti-acne, whitening, use in skincare preparations [14] Cleansing, sunscreen, and body beautification [15] Wrinkle smoothing, whitening [4]
Grey	Rich in silica	Antiedematous, Anti-Aging, measure reduction [19] Antiedematous [17] Sunscreen, and body beautification [15]
Brown	Rich in silicon, aluminum, titanium; low iron content	Tissue reconstitution, purifying, astringent, moisturizing [17,19] Can be used for antiacne, antiaging and anticellulite cosmetic products [17] Soothing and cleansing [14] Body beautification [15]
Black	Rich in aluminum and silicon; low iron content. [19][17] Also contains titanium, aluminum and magnesium silicate, calcium and magnesium carbonate, silicon oxide, zinc, and sulfur[17]	Skin rejuvenation, whitening, healing, and oil absorption [17,19] Positive effect concerning cellulite and stretch marks [17]
Pink	Rich in Fe_2O_3 (iron oxide) and CuO (copper oxide) [19][17] Hydrated aluminum silicate[17]	Treatment of sensitive, delicate, dehydrated, tired skin, with healing and soothing action[17,19] Treatment of rosacea, localized fat, cellulite and tissue flaccidity[17] Nourishes the skin, having a depurative, cleansing, decongestant, slightly tensor, revitalizing, exfoliating, toning effect, increases elasticity, improves skin shine and smoothness, relaxing, antioxidant[4]
Green	Fe_2O_3 (iron oxide) associated with calcium, magnesium, potassium, manganese, phosphorus,	Astringent, invigorating, stimulating, drying, bactericidal, analgesic and healing action[19] Reduce skin oiliness, cleansing, and body beautification [15] Recommended for oily skin[20]

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 30 November 2023 doi:10.20944/preprints202311.1890.v1

	zinc, copper, aluminum, silicon, selenium, cobalt, and molybdenum	Treatment of oily and acneic skin, products for oily hair[17,23] Absorbent, adsorbent, purifying, pores tightening, calming, softening, repair skin cells[14] Improves blood circulation promoting toxin removal, draining, used for massage, exfoliating, emollient, oiliness control, use in acneic skin[4] Skin rejuvenation and measure reduction[17,19]
Red	Rich in Fe_2O_3 (iron oxide) and CuO (copper oxide)	Cleansing skin, sunscreen[23] Recommended for dry skin[20] Improves blood circulation, increases blood flow[4]

2.2. Structure and composition

Clays are composed by solid, liquid and gas substances – solid particles form a skeleton and the spaces between these particles is fulfilled by gas and/or liquid [17]. Mineralogic composition, particle shape (laminar or fibrous), and particle granulometric distribution are the main factors that determine clay's physicochemical properties and properties of the final product obtained [17,20]. Therefore, it is important to know these characteristics when developing a cosmetic to choose formulation components and preparation technique, culminating in a stable formulation [20]. Other characteristics that differentiate clay types are ion exchange capability, nature of the exchanged cations, specific area, dispersion viscosity, plasticity, among others [17].

Clays may be found in different types of soils due to their structure, colors and metals that compose them, which contribute to their function. Clays used in cosmetics are formed by metals, as aluminum, iron, magnesium, and titanium, which contribute to their functions [19,20].

Clay minerals are the minerals constituents of clays, which are normally crystalline and formed by hydrated aluminum silicate [19]. They contain in their composition silicon, aluminum, water, and frequently iron, alkali metals, and alkaline earth metals [17]. According to Daneluz and co-workers (2020), in general, clay minerals contain Si, Al, Fe, Ti, Mg, Ca, K, Na, phyllosilicates, oxides, carbonates, kaolinite, chlorides etc. According to the authors, these elements are important for Cosmetology due to their effect on skin – examples: hematite (Fe_2O_3) acts as pigment, opacifier, antiseptic and stimulates cell renewal; rutile (TiO_2) provides photoprotection; kaolinite provide reconstruction of skin tissues, hydration, and soothing effect; and ZnO and MgO are invigorating [18].

According to Balduíno (2016), the complexity and amount of different clay minerals in clays makes it difficult to classify them and the author considers that there are no equal clays – each one will differ in at least one property. This variability is due to varied geology formation conditions [19]. Crystalline clay minerals can be divided in two classes, which are composed by families, groups, and subgroups, as we can see on Table 2 [19].

According to Table 2, clay minerals can be divided into (a) 1:1-type layers or 1:1 structure, and (b) 2:1-type layers or 2:1 structure.

(a) 1:1-type layers or 1:1 structure is when one tetrahedral layer is bond to one octahedral layer [1,8,13,17,19].
(b) As to 2:1-type layers or 2:1 structure, it is when one octahedral layer is between two tetrahedral layers, forming a kind of "sandwich" [8,13,17,19]. These layers compose the unitary crystalline structure of the clay mineral [17].

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 30 November 2023 doi:10.20944/preprints202311.1890.v1

Table 2. Classification of clay minerals [6,13,17,19,20].

Class	Family	Group	Subgroup
Silicates with lamellar structure (phyllosilicates)	1:1-type layers	Kaolinite-serpentine	Kaolinite, halloysite, nacrite, dickite, chrysotile, antigorite, lizardite
	2:1-type layers	Smectites	Dioctahedral: beidellite, montmorillonite, nontronite
		Vermiculites	----
		Talc	Illite, celadomite, fengita, fussite, muscovite
Silicates with fibrous structure	2:1-type layers	Palygorskite- Sepiolite	Palygorskite (known as attapulgite), sepiolite

Note: The word 'bentonite' is employed for a plastic, colloidal, swelling clay consisting of a smectite mineral regardless from its origin [22].

There is also a specific third type of layer with intercalation of 2:1-type layer and an additional octahedral layer ("hydroxide layer"). This occurs in the chlorite family.

These structures are based on a perfect model. However, natural clay minerals present defects on their ions concerning nature and position, what influences their properties. Disturbed zones favor ion and molecule trapping from the external medium, thus influencing their properties [1].

The proportion of tetrahedral and octahedral layers can vary between clay minerals. The bond between those crystallin layers determines the different clay mineral structures and families they belong to (Table 2) [19].

Chemical bonds between atoms inside the layer are covalent, and therefore strong. Adjacent layers are connected parallelly one above the other by Van der Waals bonds, therefore considered weak. The space between layers is called interlayer space. This allows layers separation when submitted to excess of water or under mechanical force [19,20].

These two structure types behave differently when disperse in polar solvents [6,9,13,24]:

- 1:1-type minerals do not swell in contact with polar solvents [6,13].
- 2:1-type minerals swell in contact with polar solvents, creating structured systems with interesting rheological properties [6]. They lead typically to gels with pseudoplastic behavior. After hydration, a tridimensional net is built leading to sharply higher viscosity. When tension is applied, most of the structure breaks as shear occurs [13].

According to Moraes and co-workers (2017), 1:1 and some 2:1 clay minerals (like talc, pyrophyllite, illite, palygorskite and sepiolite) do not swell in polar solvents; chlorites swell occasionally; and smectites and vermiculite do swell. Smectites can easily swell thus forming a clay-gel with pseudoplastic behavior [24].

Tetrahedral layers are formed by an atom of silicon in the center and four atoms of oxygen in the vertices (SiO_4). Silicon atom (Si^{+4}) may be replaced by aluminum (Al^{+3}) and occasionally by iron (Fe^{+3}), causing negative charges on the faces [17,19,20].

Octahedral layers are formed by six hydroxyl groups or oxygen atoms in the vertices of an octahedron, and an atom of either aluminum (Al^{+3}), magnesium (Mg^{+2}) or iron (Fe^{+2}) in the center [19,20]. The substitution of aluminum by magnesium or iron also causes charge deficiency and the particle's surface becomes negatively charged. This is compensated by the adsorption of interlamellar cations like Na^{+} in layers' faces [20].

Therefore, most clay minerals are negatively charged on the faces (as mentioned above) and have pH-dependent charge on the edges (positive in acid or neutral solutions and may become negative with pH increase) [8,20]. The fact that clay minerals are charged is one of the main reasons for their cation exchange capacity, which is one of the aspects responsible for its use in cosmetics [8].

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 30 November 2023 doi:10.20944/preprints202311.1890.v1

Based on charge, clay minerals can also be classified as cationic (most abundant) and anionic clay minerals (uncommon to be found) [8].

High repellent potential in layers' surfaces contributes to increasing the space among them, causing water penetration in the interlayer space. Therefore, some clay minerals (mainly smectites) have an expansive structure where all layer surfaces are open for hydration [20].

Several characterization techniques may be used to identify clay components, behavior, and structure. As examples, we can mention X-ray diffraction, X-ray fluorescence, scanning electronic microscopy, thermal analysis, and Fourier transform infrared spectroscopy. These techniques allowed to verify that most clay minerals are hydrated aluminum silicates, which present defined crystalline structure and may contain non-clay materials, organic and inorganic substances, adsorbed cations, organic matters, and soluble salts. These components interfere with mineralogical composition and properties of each clay [17].

3. Demands for cosmetic use

Among 4,500 minerals known until today, only around 30 are used in pharmaceutical and cosmetic industries (including kaolin, talc, smectites, and fibrous clays) due to safety and requirements they must fulfill. They must be submitted to a series of purification treatments to meet strict Pharmacopeia specifications. To be proper for cosmetic use, both as active and as excipients, they must [4,6,8,12–14,17,19,24,25]:

- Fulfill chemical requirements - stability, purity, and chemical inertia.
- Fulfill physical requirements - texture, water content, particle size (must present fine granulometry) and pH compatible with the region of application.
- Fulfill toxicological requirements - zero or extremely low toxicity, be safe and microbiological purity. The high absorption capacity of clays may cause them to accumulate potentially toxic trace elements, what must be verified.

Concerning chemical and physical properties, they should have:
(a) high surface area (which contributes to adequate rheology);
(b) high absorption and adsorption capacity;
(c) high cationic exchange capability;
(d) favorable colloidal dimension;
(e) high refraction index and heat retention
(f) low hardness (must be soft to apply on skin);
(g) astringency'
(h) low toxicity;
(i) chemical inertia;
(j) pleasant colors;
(k) and neutral odor.

Therefore, the most used clay minerals in this segment are smectites (montmorillonite, saponite and hectorite), fibrous clay minerals (palygorskite and sepiolite), kaolinites and talc [4,5,12,19]. Clay minerals' high adsorption capacity allows them to adsorb toxins, impurities, oiliness, secretion, bacteria, and viruses. High cationic exchange capability may offer vital chemical elements to the organism that are present in minerals, such as sulfur, phosphorus, sodium, potassium, magnesium, copper, iron, zinc, and manganese [4].

Natural deposits of those clay minerals are rarely pure and may present chemical composition variation. They are composed of two or more clay minerals mixed with variable amounts of non-clay materials (for example quartz, feldspars, carbonates, oxides, amorphous materials, and organic matter). Thus, before its use, clay raw materials are treated to increase and achieve quality patterns. The physical and chemical treatments to which clays are submitted may include desiccation, pulverization, bleaching, magnetic separation, size fractionation, chemical modification, and drying, among others. In some cases, it is necessary to remove specific associated substances that exceed

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 30 November 2023 doi:10.20944/preprints202311.1890.v1

Pharmacopoeia requirements or modify appropriate properties (e.g., quartz, heavy metals, dolomite) [8,9,12,24].

According to Silva (2011), the most important clay properties for their usage choice are mineralogical composition, particle shape and granulometric distribution, plasticity, mechanical resistance, linear drying retraction, compaction, thixotropy, reactive surface (absorption, ionic exchange, swelling), low toxicity, therapeutic and viscosity dispersion [17]. Also, they must be easy to apply and remove, and dry quickly in contact with skin [17]. By the exposed, besides the several positive properties of clays to be considered for the cosmetic industry, it is not trivial the obtaining a clay ingredient, regarding the relevant characteristics. Commercially available clays for cosmetic use must include the following information: substance identification (mineralogical and chemical composition); hazard identification; handling and storage; stability; reactivity; toxicology; and physicochemical properties [14].

Despite the abundance of clay minerals in nature, some have been synthetized to allow obtaining purer raw materials with homogeneous structure and composition, as well as lower contaminations, thus meeting industrial requirements. Also, they can be enriched with mineral elements, such as Zn, Co and Ni [8]. Also, clay minerals can be modified to improve performance and expand their applications. Modifications can be chemical alteration to promote surface reactivity (homoionic clays), interaction with organic substances to improve hydrophobicity (organoclays) and incorporation into polymers to create clay-polymer composites [8,9].

4. Important considerations when formulating clays-containing cosmetics

When formulating cosmetics with clays, parameters such as particle size and shape/morphology, temperature, pH, agitation time, and speed, as well as other formulation ingredients may influence product stability and clays' dispersion in the medium [9,20]. Formulation's pH is also important, concerning the effect and product safety on the skin – ideally, it should be compatible with skin's value (slightly acid) in cleansing and beautification cosmetics, for example [15].

When preparing a face mask, for example, clay hydration (dispersion in water) is a critical step. It involves incorporation, powder humectation, and fragmentation of agglomerates. This step is affected by temperature, pH value, and agitation parameters (speed and time), as well as product composition. The stability of this dispersion may be affected by interactions between clay particles and between those particles with the liquid. The use of humectants (propylene glycol and glycerin, for instance), for example, helps retain water in the formulation and avoids its dehydration, thus enhancing product stability and improving product use [20].

When laminar clays are dispersed in polar solvents, a rigid network is formed by face-to-face and face-to-edge interactions. Also, laminar silicate gels are sensitive to electrolytes, which may influence the formed structure. As to fibrous clays, they form a 3D structure in water composed of interconnecting fibers, and they retain their stability in the presence of electrolytes in high concentrations [6,24].

Another important aspect is their swelling property. As previously mentioned, high repellent potential in layers' surfaces contributes to increasing the space between them, causing water penetration in the interlayer space. Therefore, when they are dispersed in aqueous medium, the solvent is trapped between those layers by solvation. Swelling involves the separation of those layers until reaching balance [20]. However, some clay gels may contract upon standing, expelling interstitial liquid (syneresis) [9].

Swelling is a required property to achieve high viscosity systems. Smectite gels can swell by absorbing liquids and increasing volume, and the resulting material presents thixotropic behavior. Bentonite can swell to, approximately, 12 times its volume except in the presence of organic solvents [9,24]. Clay's swelling degree can be influenced by several factors, such as present clay mineral types (expansive or non-expansive); addition of electrolytes (may increase interaction between particles); and the presence of other hydrophilic substance that will compete with clay for water [20].

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 30 November 2023 doi:10.20944/preprints202311.1890.v1

The formation of gel clays is influenced by the type of mineral and preparation technique. For example, the simple addition of water to bentonite does not lead to gel formation. To jellify it, bentonite must be sprinkled on hot water and the dispersion must rest for 24h with occasional stirring after the clay has become wetted. Bentonite may also be dispersed in water after being triturated with glycerin or being previously mixed with a powder, like ZnO. To achieve dispersion in cold water, high-speed mixing equipment is required to enable swelling [9]. Another relevant factor to consider is that formulated products should have adequate consistency to be suitable for cosmetic use. Viscosity must allow product application, and it must allow product to remain in contact with the application area at least until achieving the desired effect. As far as concentration is concerned, the amount of clays applied to the formulation may vary from a small proportion until almost the total final mass [9].

5. Properties in cosmetic products for skincare and haircare

5.1. Minerals

There are several minerals used as active ingredients in cosmetic products (Table 3). Their activity depends on their physical and physicochemical properties, as well as their chemical composition [25]. Minerals with high refraction index and good light scattering properties, like oxides, can be used in photoprotective formulations. Those with high sorption capacity and large surface areas may be used in powders, and emulsions. The ones with proper hardness can be used as abrasives in toothpastes [8,25]. Those with antiseptic properties (for example, borax, zincite, and goslarite, among others) are highly astringent, and astringency is controlled by their concentration. They may be incorporated in liquid (lotions) and solid formulations (powder) and can be used in deodorants/antiperspirants. They are toxic in high concentrations, so one should avoid continuous application on extensive skin areas or application on damaged skin [25].

Minerals can be used as antibacterial agents depending on high sorption properties, large surface area, mineral content (release minerals that are toxic to bacteria), pH and oxidation state, and structure. The structure must ease the sorption of nutrients and/or disrupt bacterial envelope and/or impair bacterial metabolites' efflux. In general, the antibacterial effects from minerals come from the exchange of their soluble constituents toxic to bacteria [8].

Table 3. Minerals used as actives in cosmetic formulations.

Group	Mineral	Cosmetic use	Other relevant characteristics
Oxides	Rutile (TiO_2)	Physical UV filter, protection against visible light, dermatological protector	High refraction index
	Zincite (ZnO)	Physical solar filter, UV filter, protection against visible light, dermatological protector, antiseptic	High refraction index
Carbonates	Calcite ($CaCO_3$)	Abrasive and polishing agent in toothpastes	Non-toxic, proper hardness to be used in toothpastes
	Hydrozincite ($Zn_5(CO_3)_2(OH)_6$) and Smithsonite ($ZnCO_3$)	Dermatological protector	High sorption capacity
Sulphates	Epsomite ($MgSO_4.7H_2O$) and Mirabilite ($Na_2SO_4.10H_2O$)	Bathroom salt	High water-solubility
	Chalcanthite ($CuSO_4.5H_2O$), Zincosite ($ZnSO_4$) and Goslarite ($ZnSO_4.7H_2O$)	Antiseptic	High astringent capacity

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 30 November 2023 doi:10.20944/preprints202311.1890.v1

	Alum ($KAl(SO_4)_2 \cdot 12H_2O$)	Antiseptic and deodorant	High astringent capacity
Chlorides	Halite (NaCl) and Sylvite (KCl)	Bathroom salt	High water-solubility
Phyllosilicates	Smectites (montmorillonite, saponite, hectorite), Talc	Dermatological protector, cosmetic creams, powders, and emulsions, makeup products	Opacity and high sorption capacity
	Kaolinite	Dermatological protector, cosmetic creams, powders, and emulsions, face masks, makeup products, anti-inflammatory	Opacity and high sorption capacity, heat retention capacity
	Palygorskite, Sepiolite, Mica (Muscovite)	Cosmetic creams, powders, and emulsions	Opacity and high sorption capacity
Others	Sulphur (S)	Antiseptic, keratolytic reducer	High astringent capacity
	Greenockite (CdS)	Keratolytic reducer	Reacts with cysteine in keratinocytes
	Borax ($Na_2B_4O_7.10H_2O$)	Antiseptic	High astringent capacity
	Niter (KNO_3)	Desensitizing agent in toothpastes	Non-toxic, high water-solubility

Adapted from Carretero and Pozo (2010) [25]; Moraes et al. (2017) [24].

Although kaolinite has a low cation exchange capacity and relatively small surface area compared to other groups, it can still absorb small substances such as proteins, bacteria, and viruses, justifying its use in cosmetics [24].

Minerals with high sorption capacity (kaolinite, talc, smectites) can be applied in dermatological protectors, which are solid or semisolid compositions that protect skin against external agents, exudations, and liquid excretions. Those minerals adhere to the skin, forming a film that provides mechanical protection against external agents, as well as take up skin exudations. They also produce a water-poor medium unfavorable to bacterial growth and sorb bacteria, viruses, grease, and toxins, thus presenting some antiseptic activity [2,3,13,25]. Also, minerals used in deodorant formulations can eliminate gases responsible for bad odor [6]. The mentioned properties could also allow those minerals to be used in antipollution cosmetics, which is an increasingly used and desired claim in the market in skin and haircare products. In that case, minerals could be applied on skin to protect it against pollutants from the environment, which favor skin aging process. This is a field that should be explored in future research.

Minerals with high refraction index and that also scatter light (rutile and zincite) are suitable as UV filters in photoprotective formulations. Their effectiveness as filters also depends on their stability against degradation by UV radiation. Natural rutile is not used; rutile's synthetic analogous (synthetic TiO_2) is used instead. Synthetic TiO_2 is a white powder with a high refraction index that reflects UV radiation and presents good photostability. Its light-scattering property depends on particle size – bigger particles (around 230 nm) scatter visible light, while smaller particles (around 60 nm) scatter UV rays and reflect visible light [8,25]. As synthetic TiO_2 may give a white appearance on the skin due to bigger particle distribution, currently it has been used in very small particle sizes to avoid this undesirable effect. Fifty nm is considered an optimum particle size to provide good photoprotection without being white on the skin [25].

Regarding toothpastes, minerals can be used as desensitizing agents for sensitive teeth (niter), or as abrasive/polishing agents (calcite). Niter releases K^+ ions when dissolving in contact with saliva, which act on nerve endings in the dentine to inhibit pain sensation [25].

Clay minerals with opacity and high sorption capacity (for example, palygorskite, sepiolite, kaolinite, smectites, and talc) are applied to cosmetic compositions (solid and semisolid) as opacifiers,

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 30 November 2023 doi:10.20944/preprints202311.1890.v1

mattifiers, and for imperfection coverage. They also form a protective film on the skin, adsorb excessive oiliness and toxins, and increase adherence to the preparation [6,13,25]. Talc is widely used in a diversity of applications in cosmetic products. It is odorless and can be micronized to ideal particle size, becoming a white powder. As it absorbs grease, it can be incorporated into makeup face products as a mattifier and/or oil control component [24]. Talc is also widely used in children's cosmetics for its sorption and fluidity properties to absorb humidity and sweat in the diaper's zone. It cleans, deodorizes, lubricates skin surfaces, and acts as an antiseptic. It also keeps skin folds lubricated avoiding friction [6,13]. Micas are used in makeup cosmetics, like lipsticks and eyeshadows due to their high reflectance and iridescence. They are also applied to moisturizers to provide luminous effect on skin [13,24,25].

5.2. Clays

Clays' use depends on the type of clay mineral (mineralogical composition), type of layer (clay structure), and chemical composition. Also, differences in texture may affect rheological properties and adsorption capacity, even among identically structured clays [6,14]. Application temperature also affects their use. When using clay minerals as facial masks, they can be applied directly on the skin at room temperature. However, when used to treat acne, it is advisable to apply at higher temperatures, as the heat increases perspiration and opens pilosebaceous orifices, thus favoring efficacy [11]. On inflamed areas, the application temperature should be lower than body temperatures, so that the mixture of water and clays will cool the inflamed treated area, acting as an anti-inflammatory agent [2].

Clays' properties related to cosmetic applications in general are related to surface (surface area, charges, cation exchange capacity, etc.), rheological (thixotropy, viscosity, etc.), physical (color, particle size, and shape, opacity, reflectance), mechanical [8,15,26], and functional properties. Clays used in cosmetics have functional properties, such as adsorption of skin secretions, dirt, oiliness, sweat, toxins, bacteria and viruses (which comes from their high cation exchange capacity); rejuvenating; skin cleansing; slight physical exfoliation; carrying of active substances; antiseptic; healing and regenerative; astringent; lifting effect; whitening; moisturizing; contribution in the improvement of inflammatory processes of boils, acnes and ulcers [2–4,8,10,15,17,19,20,27].

As examples of cosmetic products that may contain clays, we can mention exfoliants, masks, sunscreens, soaps, shampoos, toothpastes, deodorants, makeups (foundations, eye shadows, lipsticks etc.), and facial skincare products, among others [4,5,26]. According to Velasco and co-workers (2016), "clays are mostly used in face masks due to their high absorbency levels on skin surface, such as greases, toxins and even bacteria and viruses". They are also used for cleansing and lifting effect. Still, there are few studies concerning impact of clay masks on skin biomechanical properties [22]. Face masks can contain more than 25% of solid phase dispersed in liquid and are applied on the skin during 10 to 25 min in a layer of 1 to 2 mm thick. After water evaporation, the mask hardens and contracts, causing mechanical tension, slight physical exfoliation and astringency [13,20].

Another important characteristic that allows clays to be used in cosmetics is their detergent property. Some clays behave like detergents when wet with water, as well as remove impurities, what makes them an excellent choice for products, like soaps and shampoos [5]. That property also enables their use as emulgents or emulsifiers [26].

Topical formulations using clays as active components, like facial masks, applied to skin during a certain period trigger a flow that transports metabolic products, cell particles and bacterial toxins out of the skin to adhere to the clay. Besides, clay particles absorb excess of sebum, impurities and skin exudates, cleanse pores and improve blood flow, thus enhancing oxygen and nutrients' supply to skin [2,6,28].

The absorption capacity of cutaneous exudates may be related to particles' porosity – porous particles from minerals with large surface area can adhere to the skin, forming a film with mechanical protection and oil retention properties [21]. Meier and co-workers (2012) studied the efficacy of facial masks with clay and jojoba oil against mild acne. The results showed that the proposed treatment reduced acne lesions, such as papules, pustules, and comedones. For the study, participants used the

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 30 November 2023 doi:10.20944/preprints202311.1890.v1

product 2-3 times a week for 6 weeks with 15-20min contact per application and further removal. Lesions were counted before and after treatment for comparison [28].

As clays have high absorption power, they can adhere to the skin and form a pellicle that protects against external chemical and physical agents [5,10]. This property is important for the retention of skin oiliness, contributing to skin regenerating (healing) potential [21]. Due to their capacity to eliminate excessive oiliness and toxins from the skin and healing properties, they are considered effective against several dermatological conditions, such as ulcers, furunculosis, psoriasis, chronic eczemas, and acne [2,27].

As they are rich in sulphidric acid, they present bactericide, fungicide, and healing properties [4]. High amounts of silicon mean that it can be used for skin hydration and reconstruction [27]. Clays with high sorption capacity may be used in cosmetics as opacifier, mattifier and skin imperfection coverage [5]. Massage practices with clays suspended in liquid vehicles explore their slight abrasive effect for physical exfoliation of the skin. This property is also used in shampoos and soaps. For toothpastes, clays can also be used as abrasives, as well as for their properties of impurity absorption [1].

They may also be used as physical filters in photoprotective formulations [10,15,16]. To be used as filters, they must have a high refraction index and optimal light dispersion properties [26]. This property is also affected by particle size. Small particle sizes allow better skin coverage, reducing the intensity of UV radiation reaching the skin [15].

Besides, they are capable to invigorate tissues, activate microcirculation, present lifting effect, soften skin, and reduce oiliness due to absorption properties [17].

As clays are rich in iron, silicon, magnesium, titanium, and potassium, they present antibacterial, antiseptic, and regenerative efficacy, contribute to cell renewal, absorb impurities, and activate microcirculation, therefore being suitable to be used as active compounds for numerous cosmetic products. The importance of those minerals in Cosmetology stems from their assumed effects on skin – e.g.,: iron is antiseptic and catalyzes cell renewal; silicon helps reconstruct skin tissues and hydrates skin; zinc and magnesium are invigorating; potassium acts on circulation and tissue invigoration; titanium is used as UV filter [17,21]. Therefore, they have been successfully used in haircare and hair-therapy through application protocols on scalp in patients with seborrheic dermatitis, psoriasis, dandruff and seborrhea [5,29]. In those cases, clays may be associated with essential oils for synergic effect to clean, nourish and revitalize the scalp [23].

The application of clays on scalp (for example as hair treatment masks) allows to remove dead cells (slight physical exfoliation); stimulates local cutaneous microcirculation (thus nourishing the scalp); eliminates impurities, dirt, excessive oiliness and toxins by adsorption; and also acts as a seborregulator [23,29]. Damazio and Makino (2017) [23] published several hair-therapy protocols with clays associated to essential oils to treat different scalp conditions, for example:

- Treatment for scalp affected with dandruff and seborrhea - after cleaning the scalp with a neutral shampoo, apply a hair mask on the scalp composed of 10 mL of the same shampoo, 3 drops of peppermint (*Mentha piperita*), 3 of lemon (*Citrus limon*) and 3 of petitgrain (*Citrus aurantium*) essential oils and 5 g of yellow clay thoroughly mixed; then, cover with plastic film and leave for 20 minutes. Rinse completely after that and apply hair conditioning [23].
- Protocol for chemically treated hair (bleached, straightened, for instance) - after cleaning the scalp with a neutral shampoo, apply a hair mask on the scalp composed of 10 mL of the same shampoo, 3 drops of lavender (*Lavandula angustifolia*), 3 of chamomile (*Chamomilla recutita*) and 3 of copaiba (*Copaifera langsdorffii*) essential oils and 5 g of white clay thoroughly mixed; then, cover with plastic film and leave for 20 minutes. Rinse completely after that and apply hair conditioning [23].

Clays incorporated in cosmetics protect the skin against external damaging agents, like UV radiation, acting as a physical barrier and increasing sun protection factor (SPF) [6]. This is improved by its high surface area, which allows effective skin coverage. Therefore, when applied to sunscreens, this property offers a great advantage. Still, the magnitude of UV protection depends on its mineralogical composition [10,27,30], as well as the type of the vehicle.

Studies showed that smectite and kaolinite clays incorporated into sunscreens were effective in reflecting/scattering/absorbing UV radiation between the wavelengths of 250 to 400 nm. This is probably related to their composition, as clays' UV protection capability was shown to depend on iron oxides' concentration among their components; the higher the amount of iron oxides (Fe_2O_3) in the minerals, the better the protection against UV rays [10,16].

Clays were also found to contain other physical protectors, such as titanium dioxide (TiO_2), zinc oxide (ZnO), and silicon oxide (SiO). The amount of these protectors in clay's composition may also present a positive effect on clay's photoprotective efficacy [10,16]. Also, clays' particle size was shown to influence their photoprotective efficacy [16]. On the other hand, clays containing higher iron concentrations present stronger colors, affecting the final product aspect [10].

Dusenkova and co-workers (2015) researched the use of Latvian illite clays in sunscreens. They proved them effective in improving protection due to high iron content, mentioning the advantage of clay's brown color which allows its use as a pigment in facial sunscreens [30]. Hoang-Minh and co-workers (2010) assessed UV protection of several types of clays (some types of kaolins, bentonites, among others), discussing the influence of mineralogical parameters on photoprotective efficacy. According to the authors, clays have UV protection potential due to absorbing or reflecting radiation, which could be influenced by particle size and chemical composition. They measured UV transmission of cream samples containing clays by Analytik Jena AG Specord 50 photometer. They found that samples had different levels of UV transmission, which varied across UVA and UVB spectral ranges. They concluded that hematite (Fe_2O_3) content of clay minerals significantly affected the samples' UV protection behavior. They observed different patterns of relations between Fe_2O_3 content and photoprotection efficacy, comparing expandable and non-expandable clay minerals, which could be explained by their arrangement in the cream samples. Therefore, UV protection of clay minerals was found to be dependent on their hematite content and expandability [31].

Not only clays are used in cosmetics as actives but also as excipients. In that case, they are added to formulations to improve stability, and rheology, as thickening or suspending agents, and to carry active substances, allowing the development of formulations with active controlled liberation [1,13,17,20]. Their functionality depends highly on particle morphology and surface electric charge [1].

6. Clays used as excipients

Excipients are components incorporated into formulations to improve the physicochemical characteristics of the active substances and improve/allow the formulation process [8].

Clays into cosmetics can be used as excipients for solid, liquid, and semisolid samples based on their properties. Among those properties, we can mention high adsorption and swelling, high cation exchange capacity, large surface area, water miscibility and hydration ability, dispersity, thixotropy, opacity and color [8,18,32]. They can be used as lubricants, grease absorption agents, carriers, inert bases, protectors, heat release controllers, and so on [5].

Clay minerals dispersed in polar solvents tend to form gels with characteristics between solid and liquid, whose rheological behavior differ depending on the type of clay mineral used, concentration, and presence of other molecules/ions in the composition [9,13]. It can be dilatant (less frequent), pseudoplastic or thixotropic. As they form a tridimensional structure that is easily deformed and rearranged, they are usually incorporated into semisolid cosmetic preparations, like dental gels or mascara. This is because those formulations need to be easily deformed as a liquid during application, and then restore to their initial shape (more solid) at rest [13,24].

They are often used to stabilize emulsions or suspensions, increase their viscosity, modify systems' rheological behavior, carry active substances, and are used as adsorbents or absorbents [5,18,26,32]. To improve the stability of suspensions, clays may be used as agents to delay sedimentation. The same is applied to emulsions [32], to avoid phase separation in a short period of time. Stabilization of those formulations occurs because of the gel-forming capacity of clay minerals and due to their presence on interface boundaries, which occurs because of their colloidal size, surface charges, and high surface areas [9].

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 30 November 2023 doi:10.20944/preprints202311.1890.v1

In semisolid cosmetics, clay minerals may be used as excipients for two main reasons: to stabilize dispersed systems and to modify rheology. This is related to the presence of charge on their surface, their colloidal dimension, and their capacity to form different structures when dispersed in polar media [9,32]. Also, clay minerals are adsorbed and act as a physical barrier in the interface, thus preventing stability issues, like flocculation and coalescence, as well as acting as an emulsifier [13,20].

Clay minerals may also be used to formulate Pickering emulsions. In Pickering emulsions, colloidal solid particles (colloidal surfactants) act as stabilizing agents in the interface between two liquid phases. It is possible to formulate stable emulsions using only solid particles as emulsifiers, and some clay minerals may be used with this aim. The characteristics of the obtained Pickering emulsions will depend on the properties of the chosen solid particles [33–35].

Ashby and Binks (2000) studied emulsions stabilized by laponite (synthetic smectite clay with uniform particle size) [33]. Lu and co-workers (2014) prepared Pickering emulsions with fibrous palygorskite clay particles, which formed a three-dimensional network to stabilize the formulation [36]. Kpogbemabou and co-workers (2014) formulated oil-in-water Pickering emulsions stabilized using three different phyllosilicates - kaolin, halloysite, and palygorskite [37].

Clay minerals' fine texture and plasticity ease the application of makeup products and increase their durability over the skin. Their oil control property also improves makeup's water resistance without making the skin dry. As they provide excellent coverage, sorption, and adhesion, they have been used in facial treatments to hide imperfections and fine lines [8].

Phyllosilicates may have several functions as excipients in cosmetics, such as: thickening or suspending agents, binders, anti-caking agent, emulgent, adherent, diluent, lubricant, and stabilizers in emulsions. They can also be used to facilitate the incorporation of hydrophobic actives in formulations, as they enable their dispersion [13]. In Table 4, we listed different uses of clays as excipients in cosmetics/dermocosmetics.

Table 4. Uses of clay as excipients in cosmetic formulations [3,6,9,13,18,32].

Clay type	Use as excipient
Kaolinite	Emulsifying agent (creams and pastes), suspending and anticaking agent (in liquid formulations), thickening agent
Talc	Emulsifying agent (creams and pastes), suspending and anticaking agent (in liquid formulations)
	Secondary emulsifying agent in makeup products (as it remains in the interface between water and oil phases) Diluent and lubricant in powder formulations; can ease cosmetic powder compaction (e.g., face powders); diluent for pigments in makeup formulations
	Filler, absorbent, protection agent in formulations like creams and pastes
Bentonite* and purified bentonite	Emulsifying agent (creams, ointments, and gels), suspending and anticaking agent (in gels, emulsions, pastes, and suspensions), improve formula stabilization (due to surface electronic charges that promote repulsion between particles and avoid formation of aggregates)
	Rheological additive in toothpastes
	Emulsion stability additive
	Thickener in topical suspensions
	Thickener, suspending and thixotropy agent in liquid makeup products
Magnesium Aluminum Silicate	Emulsifying agent (creams, ointments, and gels), suspending and anticaking agent (in gels, emulsions, pastes, and suspensions), improve formula stabilization (due to surface electronic charges that promote repulsion between particles and avoid formation of aggregates)
	Rheological additive, gelling agent. Can be applied to pigment suspensions
Magnesium	Suspending and anticaking agent

doi:10.20944/preprints202311.1890.v1

trisilicate	Gelling in non-polar organic solvents in antiperspirants, lotions, suntan products, nail lacquers, lip products
Smectites	Emulsifying agent, thickening agent, suspending and anticaking agent
	Some smectites (e.g., mixture of montmorillonite and saponite) are used as thickening or gelling agents in cosmetic gels**
	Smectites can be mixed with pigments to dilute them – this mixture can be used in makeup products (10-25% pigments) or incorporated in emulsions (3-10% pigments)
Palygorskite	Emulsifying agent, thickening agent, suspending and anticaking agent in topical suspensions, pastes, creams, etc.
Vermiculite	Diluent and binder, emulsifying agent, thickening agent, anticaking agent, flavor corrector, carrier of active compounds
Hectorite	Thickener, suspending and thixotropy agent in lotions, shampoos, and liquid makeup products
Synthetic hectorite	Viscosity agent in toothpastes and shampoos
	Thixotropy in toothpastes, emulsions, and shampoos
	Suspending agent in liquid makeup products

*Used at 0.5 – 5.0% (w/w) as suspending agent. Its gelling properties are reduced by acids and increased by bases [32]. **Used at 1.0-2.0% (w/v) to slightly increase viscosity and 10.0% (*w/v*) for accentuated increase [13].

7. Clays used as delivery systems

Excipients, including clay minerals, can be used in formulations to target active release [38]. Currently, clays have been explored as active ingredient/drug delivery systems. They can be used as vectors to transport substances to their targets in our organism, thus benefiting pharmaceutical and cosmetic industries [1]. They can interact with formulation components and affect bioavailability by influencing on actives' liberation and stability [3,6,13].

Clay minerals can be used as auxiliary components to maintain the active dose in the treated area due to viscosity increase, better skin-adhesivity, and active concentration on the treated site [6]. Clay minerals can interact with organic molecules by different mechanisms, such as hydrophobic interactions (kaolinites, smectites, and others with neutral sites), hydrogen bonding (clays with oxygen surfaces), cation exchange (smectite, vermiculite, illite) etc. Based on these interactions and on their swelling properties, clay minerals are effective in delaying and targeting drug release, as well as in improving solubility. So, they can be interesting to increase active stability and alter drug delivery patterns, creating extended and/or site-specific delivery systems [38].

One example of clays used as delivery system in cosmetics is in sunscreens. In those products, clays improve the stability of organic UV filters, as well as they allow slowing the filters' release, avoiding close contact with the skin, therefore, preventing cutaneous reactions and allergies, and improving water resistance [3,5]. Sepiolite and smectites are capable of forming complexes with organic UV absorbers enabling their use in sunscreens. This allows the use of lower concentrations of active components [2], which contributes to improving formulation efficacy and safety.

Another example is the combination of vitamins (e.g., B and C) and antioxidants with clay minerals to deliver these actives to the skin for cosmetic purposes [8].

Halloysites have been used in nanotechnology due to their tubular morphology, which allows their use as drug carriers in the dermatological field. Its nanotubular structure can accommodate active molecules inside, enabling controlled delivery of substances to the target area [24].

8. Clays and clay minerals used in spas and aesthetic medicine

Clay minerals, mainly smectites and kaolinite, are widely used in spas and aesthetic medicine in geotherapy, pelotherapy and paramuds, even before the industry started incorporating them in cosmetic products [2,3,24]. Polymineralic clays are also used [3].

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 30 November 2023 doi:10.20944/preprints202311.1890.v1

Geotherapy corresponds to clay minerals mixed with water and applied directly on the skin, as a layer. It is used mainly as facial treatment against boils, acne, ulcers, seborrhea, blackheads, and spots, among others. In spas, when the treated area is extensive, it can be applied as mud baths, where the whole area is immersed in the mixture [2,3].

Pelotherapy consists of clay minerals mixed and matured with sea or salt-lake water, or minero-medicinal water resulting in a peloid [2]. Carretero (2020) recently wrote a review about clays in pelotherapy (should be read for further information). The article mentions a new definition of a peloid: "a peloid is a maturated mud or muddy suspension (more precisely, a muddy dispersion) with healing and/or cosmetic properties composed of a complex mixture of fine-grained materials (mineral and/or organic), with mineral water, seawater, salt-lake water, and commonly organic compounds from biological metabolic activity" [39,40]. The maturing process alters some clay minerals' properties, thus improving their efficacy; it cools more slowly, decreases grain size, increases plasticity, and improves absorption capacity. It is normally applied on the skin for 20-30 min in layers covered with an impermeable material to preserve the heat. This causes vasodilatation and perspiration, favoring its effect [2]. However, depending on the purpose, it can also be applied cold [3].

Paramuds consist of a mixture of paraffin with an inorganic material which is usually clay. They are applied hot for 20-30 min in layers covered with an impermeable material to preserve temperature. This therapy moisturizes skin and enhances penetration of other active substances, as pores are dilated, and superficial circulation is stimulated. All these actions are due to the provided heat [2,3,39]. The presence of paraffin allows paramuds not to adhere to the skin, so they can be conveniently removed after treatment. However, it has reduced efficacy since, unlike peloids, there is no exchange between paramuds and skin apart from heat exchange [39].

Those approaches are used in spas for their properties of (1) high sorption capacity – to eliminate the excess of grease and toxins from the skin; (2) high cation exchange capacity – to enable the exchange of nutrients; (3) rheology – must be adequate to enable the formation of a consistent paste with good plastic properties for easy application and skin adhesion; (4) grain size - ideally must be small and soft for application to be pleasant; (5) cooling index/heat retention capacity – in some therapies they are applied hot to treat dermatological conditions; and (6) adequate pH – must be compatible to the skin to avoid irritation [2,3].

Among those properties, we can highlight high cation exchange capacity, which is presented mainly by peloids containing clays with smectites (minerals sensitive to ion exchange). This property enables ion exchange with minero-medicinal water, modifying the composition of the liquid part of the peloid, thus enhancing bioavailability of ions to the treated skin [39].

Geotherapy and pelotherapy can be applied as face masks (mainly in beauty treatment), cataplasms (applied on small areas), or mud baths (on extensive areas), depending on the treatment area. They can be applied hot (40-45°C) or cold, depending on the aims. Paramuds are always applied hot (40-45°C) and as cataplasms [3].

In beauty treatment, geotherapy, pelotherapy and paramuds should be applied hot for the following reasons: (1) it allows to moisturize the skin since perspiration cannot evaporate during therapy application due to the impermeable material, thus remaining retained on the skin; (2) it increases cutaneous absorption of active ingredients; (3) it stimulates local circulation and acts as anti-inflammatory; and (4) it improves cutaneous cleaning and treatment of dermatological conditions (as acne, ulcers, and seborrhea) since it increases perspiration and sebaceous secretions, as well as opens pilosebaceous orifices, thus improving clay mineral's sorption properties and, therefore, efficacy [2,3,11].

9. Conclusions

A review of clays and clay minerals used in Cosmetology was carried out. They can be used in several types of cosmetics and dermocosmetics, both as active ingredients and/or as excipients, due to their several properties, like sorption, cation exchange capacity, physical exfoliation, and swelling, among others. However, most specialized literature justifies their efficacy based most on theories, and only some proved efficacy using specific assays to demonstrate cosmetic attributes. Most papers that showed efficacy tests concerning clays used in photoprotection used comparative in vitro spectrophotometric methodologies, which are not the accepted for product registration in industry, for instance. As far as haircare is concerned, scarce literature was found. Therefore, we believe our review, as organized with the discussed issues, could be considered in the coming years in the cosmetic field to provide information for the related industry.

Author Contributions: Conceptualization, F.D.S. and A.R.B.; methodology, F.D.S., V.J.P.C. and A.R.B.; formal analysis, A.R.B.; investigation F.D.S. and V.J.P.C.; resources, A.R.B. and M.V.R.V.; writing—original draft preparation, F.D.S. and A.R.B.; writing—review and editing, F.D.S., R.M.M. and A.R.B.; visualization, M.V.R.V. and A.R.B.; supervision, A.R.B.; project administration, F.D.S. and A.R.B.; funding acquisition, M.V.R.V. and A.R.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Process 303862/2022-0); Coordenação de Aperfeiçoamento de Pessoal de Nível Superior-Brasil (CAPES, Finance Code 001); and PrInt USP – PAME (call 15/2023).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: The data presented in this study are available upon request from the corresponding author.

Data Availability Statement: Data sharing not applicable.

Acknowledgments: F.D.S. is highly thankful to the Conselho Nacional de Desenvolvimento Científico e Tecnológico, CNPq, for the doctorate scholarship. R.M.M. acknowledges deeply the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior-Brasil, CAPES, for the doctoral scholarship. A.R.B. is extremely thankful to the Conselho Nacional de Desenvolvimento Científico e Tecnológico, CNPq, for the Research Productivity Scholarship, and to the PrInt USP/CAPES Program.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Rautureau, M.; Figueiredo Gomes, C. de S.; Liewig, N.; Katouzian-Safadi, M. *Clays and Health*; Springer International Publishing: Cham, 2017; ISBN 978-3-319-42883-3.
2. Carretero, M.I. Clay Minerals and Their Beneficial Effects upon Human Health. A Review. *Appl Clay Sci* **2002**, *21*, 155–163, doi:10.1016/S0140-6736(00)90347-7.
3. Carretero, M.I.; Gomes, C.S.F.; Tateo, F. Chapter 11.5 Clays and Human Health. In *Developments in Clay Science*; Elsevier, 2006; Vol. 1, pp. 717–741.
4. Nardy, B.C. Caracterização Do Material Pelítico Utilizado Para Fins Terapêuticos, Cosméticos e de Higiene Pessoal No Vale Do Capão, Chapada Diamantina, Bahia [Trabalho de Conclusão de Curso] 2018, 81.
5. Gubitosa, J.; Rizzi, V.; Fini, P.; Cosma, P. Hair Care Cosmetics: From Traditional Shampoo to Solid Clay and Herbal Shampoo, A Review. *Cosmetics* **2019**, *6*, 1–16, doi:10.3390/cosmetics6010013.
6. López-Galindo, A.; Viseras, C. Pharmaceutical and Cosmetic Applications of Clays. *Interface Science and Technology* **2004**, *1*, 267–289, doi:10.1016/S1573-4285(04)80044-9.
7. Agência Nacional de Vigilância Sanitária - ANVISA Resolução Da Diretoria Colegiada RDC Nº 7, de 10 de Fevereiro de 2015 2015.
8. Ghadiri, M.; Chrzanowski, W.; Rohanizadeh, R. Biomedical Applications of Cationic Clay Minerals. *RSC Adv* **2015**, *5*, 29467–29481, doi:10.1039/c4ra16945j.
9. Viseras, C.; Aguzzi, C.; Cerezo, P.; Lopez-Galindo, A. Uses of Clay Minerals in Semisolid Health Care and Therapeutic Products. *Appl Clay Sci* **2007**, *36*, 37–50, doi:10.1016/j.clay.2006.07.006.
10. Costa, J.T.C. da Preparação de Protetores Solares Com Argila: Análise Da Eficácia in Vitro Da Propriedade Fotoprotetora [Masters Dissertation] 2015, 83.
11. Baby, A.R.; Velasco, M.V.R.; Zague, V.; Dario, M.F.; Nishikawa, D.O.; Pinto, C.A.S.O.; Almeida, M.; Henrique, G.; Trossini, G.; Carlos, A.; et al. Characterization and Short-Term Clinical Study of Clay Facial Mask. *Journal Of Basic and Applied Pharmaceutical Sciences* **2016**, *37*, 1–6.

12. Silva-Valenzuela, M. das G.; Chambi-Peralta, M.M.; Sayeg, I.J.; de Souza Carvalho, F.M.; Wang, S.H.; Valenzuela-Díaz, F.R. Enrichment of Clay from Vitoria Da Conquista (Brazil) for Applications in Cosmetics. *Appl Clay Sci* **2018**, *155*, 111–119, doi:10.1016/j.clay.2018.01.011.
13. Daré, R.G.; Estanqueiro, M.; Amaral, M.H. dos A.R.; Truiti, M. da C.T. Significância Dos Argilominerais Em Produtos Cosméticos. *Revista de Ciencias Farmaceuticas Basica e Aplicada* **2015**, *36*, 59–67.
14. Mattioli, M.; Giardini, L.; Roselli, C.; Desideri, D. Mineralogical Characterization of Commercial Clays Used in Cosmetics and Possible Risk for Health. *Appl Clay Sci* **2016**, *119*, 449–454, doi:10.1016/j.clay.2015.10.023.
15. Matike, D.M.E.; Ekosse, G.I.E.; Ngole, V.M. Physico-Chemical Properties of Clayey Soils Used Traditionally for Cosmetics in Eastern Cape, South Africa. *International Journal of Physical Sciences* **2011**, *6*, 7557–7566, doi:10.5897/ijps11.1249.
16. Ng'etich, W.K.; Mwangi, E.M.; Kiptoo, J.; Digo, C.A.; Ombito, J.O. In Vitro Determination of Sun Protection Factor on Clays Used for Cosmetic Purposes in Kenya. *Chemistry and Materials Research* **2014**, *6*, 25–31.
17. Silva, M.L. de G. da Obtenção e Caracterização de Argila Piauiense Paligorsquita (Atapulgita) Organofilizada Para Uso Em Formulações Cosméticas [Masters Dissertation] 2011, 106.
18. Daneluz, J.; da Silva Favero, J.; dos Santos, V.; Weiss-Angeli, V.; Gomes, L.B.; Mexias, A.S.; Bergmann, C.P. The Influence of Different Concentrations of a Natural Clay Material as Active Principle in Cosmetic Formulations. *Materials Research* **2020**, *23*, doi:10.1590/1980-5373-MR-2019-0572.
19. Balduino, A.P.Z. Estudo Da Caracterização e Composição de Argilas de Uso Cosmético [Masters Dissertation] 2016, 55.
20. Zague, V. Desenvolvimento e Avaliação Da Estabilidade Física e Físico- Química de Máscaras Faciais Argilosas [Masters Dissertation] 2007, 160.
21. Favero, J. da S.; Parisotto-Peterle, J.; Weiss-Angeli, V.; Brandalise, R.N.; Gomes, L.B.; Bergmann, C.P.; dos Santos, V. Physical and Chemical Characterization and Method for the Decontamination of Clays for Application in Cosmetics. *Appl Clay Sci* **2016**, *124–125*, 252–259, doi:10.1016/j.clay.2016.02.022.
22. Velasco, M.V.R.; Zague, V.; Dario, M.F.; Nishikawa, D.O.; Pinto, C.A.S.O.; Almeida, M.M.; Trossini, G.H.G.; Coelho, A.C.V.; Baby, A.R. Characterization and Short-Term Clinical Study of Clay Facial Mask. *Revista de Ciencias Farmaceuticas Basica e Aplicada* **2016**, *37*, 1–6.
23. Damazio, M.G.; Makino, R. de F.L. *Terapia Capilar: Uma Abordagem Inter e Multidisciplinar*; 1st ed.; RED Publicações: São Paulo, 2017; ISBN 978-85-69225-04-1.
24. Moraes, J.D.D.; Bertolino, S.R.A.; Cuffini, S.L.; Ducart, D.F.; Bretzke, P.E.; Leonardi, G.R. Clay Minerals: Properties and Applications to Dermocosmetic Products and Perspectives of Natural Raw Materials for Therapeutic Purposes—A Review. *Int J Pharm* **2017**, *534*, 213–219, doi:10.1016/j.ijpharm.2017.10.031.
25. Carretero, M.I.; Pozo, M. Clay and Non-Clay Minerals in the Pharmaceutical and Cosmetic Industries Part II. Active Ingredients. *Appl Clay Sci* **2010**, *47*, 171–181, doi:10.1016/j.clay.2009.10.016.
26. Viseras, C.; Carazo, E.; Borrego-Sánchez, A.; García-Villén, F.; Sánchez-Espejo, R.; Cerezo, P.; Aguzzi, C. Clay Minerals in Skin Drug Delivery. *Clays Clay Miner* **2019**, *67*, doi:10.1007/s42860-018-0003-7.
27. Misiņa, S.M.; Tretjakova, R.; Kodors, S.; Zavorins, A. Lake Zeiļu Clay Application Induced Changes in Human Skin Hydration, Elasticity, Transepidermal Water Loss and PH in Healthy Individuals. *Cosmetics* **2020**, *7*, 1–9, doi:10.3390/cosmetics7030051.
28. Meier, L.; Stange, R.; Michalsen, A.; Uehleke, B. Clay Jojoba Oil Facial Mask for Lesioned Skin and Mild Acne-Results of a Prospective, Observational Pilot Study. *Forsch Komplementarmed* **2012**, *19*, 75–79, doi:10.1159/000338076.
29. de Limas, J.R.; Duarte, R.; Moser, D.K. A Argiloterapia: Uma Nova Alternativa Para Tratamentos Contra Seborreia, Dermatite Seborreica e Caspa 2018, 17.
30. Dušenkova, I.; Kusiņa, I.; Mālers, J.; Bērziņa-Cimdiņa, L. Application of Latvian Illite Clays in Cosmetic Products with Sun Protection Ability. *Vide. Tehnologija. Resursi - Environment, Technology, Resources* **2015**, *1*, 28–32, doi:10.17770/etr2015vol1.203.
31. Hoang-Minh, T.; Le, T.L.; Kasbohm, J.; Gieré, R. UV-Protection Characteristics of Some Clays. *Appl Clay Sci* **2010**, *48*, 349–357, doi:10.1016/j.clay.2010.01.005.
32. Favero, J. da S.; dos Santos, V.; Weiss-Angeli, V.; Gomes, L.B.; Veras, D.G.; Dani, N.; Mexias, A.S.; Bergmann, C.P. Evaluation and Characterization of Melo Bentonite Clay for Cosmetic Applications. *Appl Clay Sci* **2019**, *175*, 40–46, doi:10.1016/j.clay.2019.04.004.
33. Ashby, N.P.; Binks, B.P. Pickering Emulsions Stabilised by Laponite Clay Particles. *Physical Chemistry Chemical Physics* **2000**, *2*, 5640–5646, doi:10.1039/b007098j.

doi:10.20944/preprints202311.1890.v1

34. Sun, Z.; Yan, X.; Xiao, Y.; Hu, L.; Eggersdorfer, M.; Chen, D.; Yang, Z.; Weitz, D.A. Pickering Emulsions Stabilized by Colloidal Surfactants: Role of Solid Particles. *Particuology* **2022**, *64*, 153–163, doi:10.1016/j.partic.2021.06.004.
35. Yang, Y.; Fang, Z.; Chen, X.; Zhang, W.; Xie, Y.; Chen, Y.; Liu, Z.; Yuan, W. An Overview of Pickering Emulsions: Solid-Particle Materials, Classification, Morphology, and Applications. *Front Pharmacol* **2017**, *8*, 1–20, doi:10.3389/fphar.2017.00287.
36. Lu, J.; Tian, X.; Jin, Y.; Chen, J.; Walters, K.B.; Ding, S. A PH Responsive Pickering Emulsion Stabilized by Fibrous Palygorskite Particles. *Appl Clay Sci* **2014**, *102*, 113–120, doi:10.1016/j.clay.2014.10.019.
37. Kpogbemabou, D.; Lecomte-Nana, G.; Aimable, A.; Bienia, M.; Niknam, V.; Carrion, C. Oil-in-Water Pickering Emulsions Stabilized by Phyllosilicates at High Solid Content. *Colloids Surf A Physicochem Eng Asp* **2014**, *463*, 85–92, doi:10.1016/j.colsurfa.2014.09.037.
38. Aguzzi, C.; Cerezo, P.; Viseras, C.; Caramella, C. Use of Clays as Drug Delivery Systems: Possibilities and Limitations. *Appl Clay Sci* **2007**, *36*, 22–36, doi:10.1016/j.clay.2006.06.015.
39. Carretero, M.I. Clays in Pelotherapy. A Review. Part I: Mineralogy, Chemistry, Physical and Physicochemical Properties. *Appl Clay Sci* **2020**, *189*, 105526, doi:10.1016/j.clay.2020.105526.
40. Gomes, C.; Carretero, M.I.; Pozo, M.; Maraver, F.; Cantista, P.; Armijo, F.; Legido, J.L.; Teixeira, F.; Rautureau, M.; Delgado, R. Peloids and Pelotherapy: Historical Evolution, Classification and Glossary. *Appl Clay Sci* **2013**, *75–76*, 28–38, doi:10.1016/j.clay.2013.02.008.