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Note

Mineralogical characterization of commercial clays used in cosmetics and possible risk for health

Michele Mattioli [a,*], Liliana Giardini [a], Carla Roselli [b], Donatella Desideri [b]

[a] Department of Earth, Life and Environmental Sciences, University of Urbino, Via Cà le Suore 2/4, 61029 Urbino, Italy
[b] Department of Biomolecular Sciences, University of Urbino, P.zza Rinascimento 6, 61029 Urbino, Italy

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ABSTRACT

The present study was carried out to determine the suitability of 15 clay samples used for cosmetic purposes. The mineralogical composition of both the bulk sample and the clay fraction was determined by X-ray powder diffraction, and the bulk chemical composition was also obtained by energy-dispersive polarized X-ray fluorescence spectrometry, with particular focus to the trace elements to assess the possible risk for health.

The bulk mineralogical composition of the studied clay samples is characterized by the presence of a significant non-clay fraction made up of calcite and quartz, with minor dolomite, feldspars, and gypsum. The clay fraction is composed of illite, smectites, interstratified illite/smectite, kaolinite and chlorites in variable amounts and diverse associations. The most represented samples are green clays which are composed of interstratified illite/smectite + illite + chlorites, with considerable amounts of Ni and Sr, while the other green samples are composed of illite only and are enriched in As. The almost pure smectite samples (both brown and white in color) are depleted of almost all trace elements and, therefore, represent the most suitable samples for commercialization. In contrast, the white kaolinite-rich sample is notably enriched in Zn, As, Ba and Pb, and is thus the most potentially hazardous product for human health.

1. Introduction

Clays are fine-grained (normally <2 μm) natural rock or soil materials composed of one or more clay minerals with lesser quantities of other minerals and/or organic products such as quartz, feldspars, carbonates, sulfates, Fe and/or Al oxides, and humus (Guggenheim and Martin, 1995). In the field of health, clay minerals and clays are extensively used for pharmaceutical (treatment) or cosmetic (care and beauty) purposes, because of their high specific surface area, optimum rheological characteristics and excellent ion exchange capability (Summa and Tateo, 1998; Carretero, 2002; Carretero et al., 2006; Tateo et al., 2006; Choy et al., 2007; López-Galindo et al., 2007; Viseras et al., 2007).

The use of a particular clay for any specific application depends on (i) its mineralogical composition, i.e. the type of clay mineral, (ii) the structure of the clay mineral (1:1 or 2:1 layer type), and (iii) its chemical composition. The different types of cations in the octahedral sheet, as well as the isomorphic substitutions in the octahedral and tetrahedral sheets, can generate different mineral phases, giving rise to varied technical behavior (Grim, 1968; Velde, 1995). For example, because of their structural and chemical characteristics, both kaolinite and talc show minimal layer charges, presenting low cation-exchange capacities. In contrast, smectites are characterized by octahedral and tetrahedral substitutions and high ion-exchange capacities (Bergaya et al., 2006). Moreover, textural differences between structurally and chemically identical clay minerals also affect their adsorptive and rheological properties (Lagaly, 1989; Murray and Keller, 1993; Viseras, 1997; Yebra, 2000).

To be suitable for pharmaceutical or cosmetic applications, clays must comply with a number of chemical (stability, purity, chemical inertia), physical (texture, water content, particle size) and toxicological (toxicity, safety and microbiological purity) requirements (López-Galindo and Viseras, 2004; López-Galindo et al., 2007; Tateo and Summa, 2007; Viseras et al., 2007). Specifically, they must have zero or very low toxicity. This is regulated in the European Community by EC Regulation 1223/2009, which is a simplification of Community Directives 76/768/EEC and 2001/58/EC. In addition, the Occupational Safety and Health Administration (US Department of Labor, OSHA CFR 1910.1200) establishes the safety information that must accompany different commercial products. In the case of clays, this must include: an accurate identification of the substance (i.e. mineralogical and chemical compositions); information on ingredients, hazard identification, handling and storage, physical and chemical properties, stability, and reactivity; and toxicological data. It should be noted that the high adsorption capacity of clays can lead to the accumulation of trace elements, some of

* Corresponding author.
E-mail address: michele.mattioli@uniurb.it (M. Mattioli).

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Table 1
Semi-quantitative percentages of mineral of the investigated clays (bulk compositions). Qz: quartz, Ca: calcite, Do: dolomite, F: feldspars, Gy: gypsum, Cr: cristobalite, CF: clay fraction.

	Sample	Color	Uses	pH*	Qz	Ca	Do	F	Gy	Cr	CF
Group 1	AR2	Green	Absorbent, adsorbent, purifying	7.74	7	16	8	3	3	–	63
	AR5	Green	Absorbent, adsorbent	7.85	8	15	9	5	–	–	63
	AR6	Green	Tightening pores, skin stimulating	8.30	13	15	8	4	–	–	60
	AR8	Green	–	7.84	8	16	8	5	–	–	63
	AR10	Green	Absorbent, adsorbent, purifying	8.11	9	14	6	7	–	–	64
	AR11	Green	Purifying, calming	8.36	11	15	7	8	–	–	59
	AR13	Green	Absorbent, repairing skin cells	8.50	7	15	5	5	–	–	68
	AR14	Green	–	8.50	11	13	4	3	–	–	69
Group 2	AR4	Green	Softening, purifying	8.27	13	22	–	–	–	–	65
	AR12	Green	Tightening pores, skin stimulating	7.80	23	24	–	–	–	–	53
	AR15	Green	–	7.70	33	22	–	–	–	–	45
Group 3	AR1	Brown	Soothing, cleansing, detoxifying	*nd*	9	5	12	3	35	–	36
	AR7	White	Skin care preparations, powders	*nd*	6	6	7	–	–	–	81
	AR9	White	Acne problems, blemishes	*nd*	3	–	–	2	–	6	89
	AR3	Brown	–	8.16	9	4	9	5	–	–	72

* pH values are from Roselli et al. (2015).

which may be regarded as potentially toxic (Mascolo et al., 1999; Gomes and Silva, 2007; López-Galindo et al., 2007; Carretero and Pozo, 2009; Silva et al., 2011).

Notwithstanding this, and despite several articles in literature on the use of clay minerals in health sciences, very little information is available about the mineralogical and chemical composition of the clays used for pharmaceutical and cosmetic purposes. In this study, a selection of clays, which are commercially available on the market for cosmetic purposes, have been studied with the aim of determining their mineralogical and chemical composition. It is relevant to note that these products are only characterized (and commercialized) based on their color (white, green and brown), and there is no information about their composition and the origin of clay fraction. Furthermore, their bulk chemical compositions have been used to investigate whether there is any correlation between clay mineralogy and chemistry, with emphasis on the trace elements that are prohibited in cosmetic concentrations (EC Regulation 1223/2009). The main objective of this study is to give scientific information on clays used in cosmetics, and possible risk for health.

2. Materials and methods

Analyses were carried out on 15 clay samples purchased from local stores (Table 1). Most of the clays were contained in 0.5 kg sacks. About 0.5 kg of each sample was weighed and dried in an oven at 30 °C for 24 h. The dried samples were then weighed and homogenized.

The mineralogical analyses were carried out using a Philips X'Change PW 1830 diffractometer (Cu Ka radiation). Randomly-oriented powders were prepared by gently hand crushing the bulk samples. The powders were then side loaded into an aluminum holder to examine the unoriented powder (bulk composition), and were subsequently analyzed at a 0.02° step with a counting time of 1 s/step from 2° to 60° 2θ. The analytical conditions were a 35 kV accelerating potential and a 30 mA filament current. All major peaks were indexed in the refinement, and quartz served as an internal standard. Successively, the <2 μm clay fraction was extracted by crushing, dispersing and a two-stage centrifuging, according to Moore and Reynolds (1997). Oriented clay mounts were prepared and analyzed under air dried conditions, ethylene glycolated, heated to 335 °C, and then further heated to 550 °C for 2 h. The mounts were analyzed in a 0.02° step, with a counting time of 1 s/step from 2° to 30° 2θ, and then examined in composite diffractograms. According to the procedures proposed by various authors (e.g. Brown and Brindley, 1980; Velde, 1995; Moore and

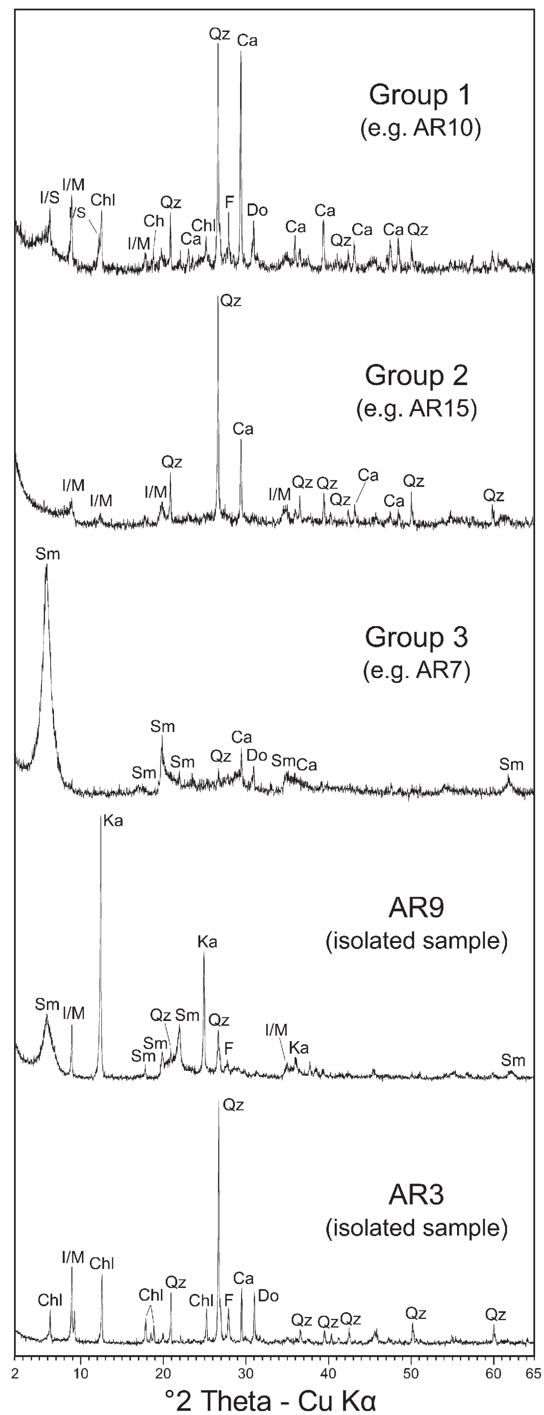

Fig. 1. Representative XRD patterns of the investigated samples (bulk compositions). Sm: smectite group, I/S: interstratified illite/smectite, Qz: quartz, I/M: illite/mica, Chl: chlorite group, Ca: calcite, F: feldspars, Do: dolomite, and Ka: kaolinite.