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



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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.

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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

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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
Group 2	AR14	Green	-	8.50	11	13	4	3	-	-	69
	AR4	Green	Softening, purifying	8.27	13	22	-	-	-	-	65
Group 3	AR12	Green	Tightening pores, skin stimulating	7.80	23	24	-	-	-	-	53
	AR15	Green	-	7.70	33	22	-	-	-	-	45
	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 K α 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°

2 θ . 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 μ m 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° 2 θ , and then examined in composite diffractograms. According to the procedures proposed by various authors (e.g. Brown and Brindley, 1980; Velde, 1995; Moore and

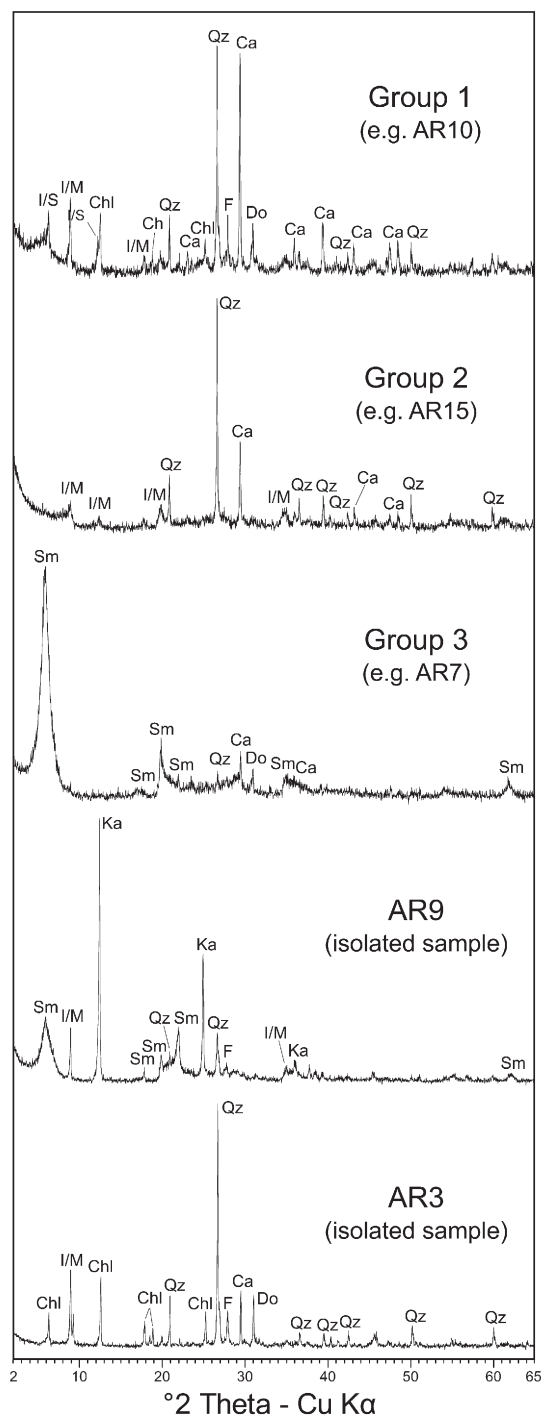


Fig. 1. Representative XRD patterns of the investigated samples (bulk compositions). Sm: smectite group, I/S: interstratified illite/smectite, Qz: quartz, I/M: illite/mica, Chl: chlorite group, Ca: calcite, F: feldspars, Do: dolomite, and Ka: kaolinite.

Table 2

Semi-quantitative results on clay minerals of the <2 μm fraction of the investigated clays, based on profile fit-derived peak areas and Biscaye's (1965) weight factors. Sm: smectite group, I/S: interstratified illite/smectite, I/M: illite/mica, Chl: chlorite group, Ka: kaolinite.

	Sample	Sm	I/S	I/M	Chl	Ka
Group 1	AR2	–	6	35	22	–
	AR5	–	5	37	21	–
	AR6	–	5	32	23	–
	AR8	–	7	35	21	–
	AR10	–	7	30	27	–
	AR11	–	5	30	24	–
	AR13	–	6	28	34	–
Group 2	AR4	–	–	66	–	–
	AR12	–	–	53	–	–
	AR15	–	–	45	–	–
Group 3	AR1	–	36	–	–	–
	AR7	81	–	–	–	–
	AR9	11	–	28	–	51
	AR3	–	–	38	35	–

Reynolds, 1997; Setti et al., 2004), the mineral identification followed standard methods and was based on the shape, position and intensity of specific reflections. Kaolinite and chlorite were distinguished using the slow scan method of Biscaye (1964) over the 004 peak of chlorite and the 002 peak of kaolinite. Where these peaks were too small to allow an accurate position, the 002 peak of chlorite and the 001 peak of kaolinite were used. This assumes that a peak position of 7.10 Å indicates chlorite and 7.16 Å kaolinite (Biscaye, 1964). Illite, smectite and mixed-layer clays were identified from diffractograms after ethylene-

glycolated and thermal dehydration treatments by referring to Reynolds (1980); Moore and Reynolds (1997) and Środoń (1980). As suggested by Kang et al. (2008), the proportions of the component layers in interstratified illite-smectites can be estimated with basal peak parameters using Reynolds' program (Reynolds, 1985). The traditional methods based on peak position (Środoń, 1980) and the peak intensity (saddle/peak method of Inoue et al., 1989) have been used for comparison. The 7 Å reflection in the dry samples, which disappeared after heating to 550 °C, was attributed to kaolinite. The 10 Å reflection, which was not affected by chemical treatment or heating, indicated the presence of illite.

For the semi-quantitative analyses of the bulk sample composition, the relative abundance of minerals was estimated from the heights of the main reflections. According to Setti et al. (2004), the following peaks and correction factors (CF) were used for the estimation: quartz (4.26 Å), CF 1; calcite (3.03 Å), CF 0.4; alkali feldspar (3.24 Å), CF 0.9; plagioclase (3.18 Å), CF 0.5; mica (10 Å), CF 2.8; chlorite (7 Å), CF 2.8; and smectite (15 Å on the glycolated sample), CF 6.5. Semi-quantitative analyses of the clay fraction were performed on glycolated samples by measuring the integrated peak areas of the main basal reflections: smectite at 17 Å, illite at 10 Å and kaolinite/chlorite at 7 Å. The values of the peak areas were converted into relative concentrations using the weighting factors of Biscaye (1964). The methods of Biscaye (1965) and Thorez (1976) were then used to evaluate the degree of crystallinity. This approach was tested using kaolinite and pyrophyllite internal standards, and the results agreed with each other well (confidence level for the correlation coefficient = 0.9). The overall error rate for any particular clay with this method is unknown, but repeated tests indicated that it was internally consistent. However, as reported

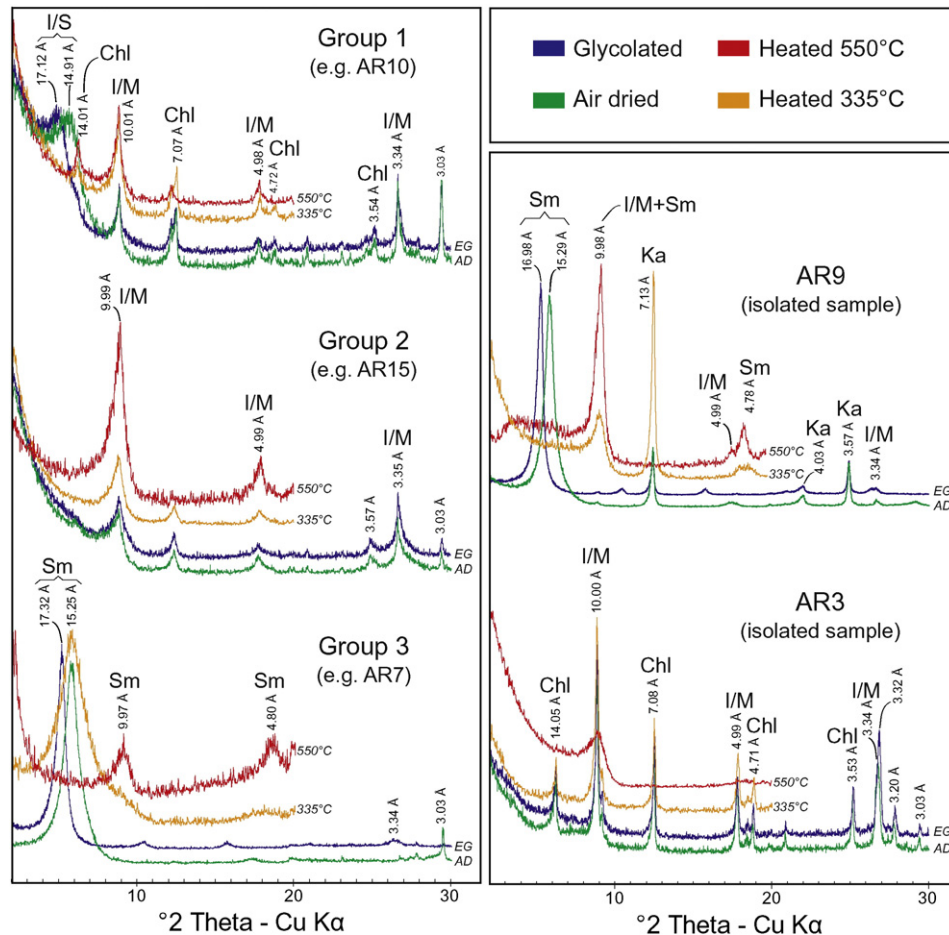


Fig. 2. Representative XRD patterns of the investigated samples (<2 μm clay fraction). Sm: smectite group, I/S: interstratified illite/smectite, I/M: illite/mica, Chl: chlorite group, and Ka: kaolinite.

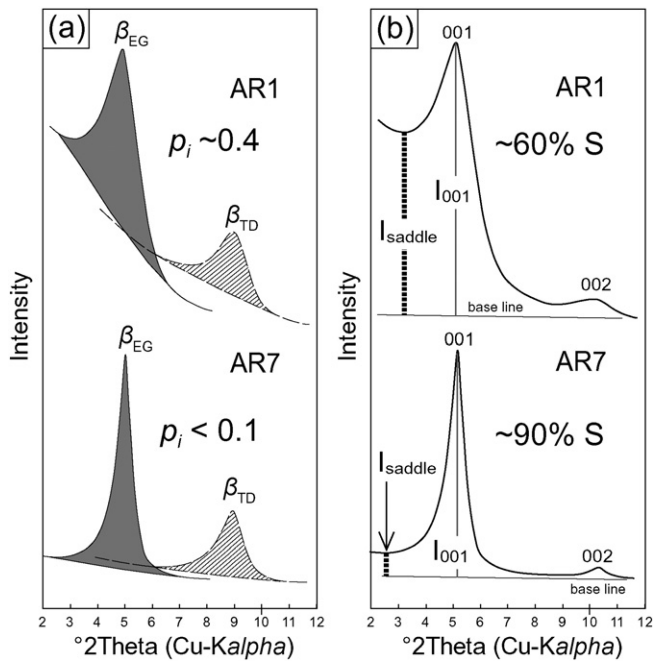


Fig. 3. (a) Variation of the first-order peak profiles for the ethylene-glycolated (EG) and thermal-treated (TD) samples of the Group 3. p_i : proportion of the interstratified illite layers, β : integrated peak widths, assuming linear backgrounds. (b) Estimation of the saddle/001 peak intensity ratio for the analyzed Group 3 samples. The intensity was approximated by the peak height from the base line. S: smectite layer percentage in illite/smectite interstratified minerals.

by Moore and Reynolds (1997), the error rate for XRD-derived results is estimated to be around 10%.

3. Results and discussion

3.1. Mineralogical composition of the bulk sample

The results of the bulk mineralogical analyses of the studied samples, as well as their color, suggested uses and pH, are reported in Table 1, with their X-ray patterns presented in Fig. 1.

The samples are divided into five groups based on type and association of clay minerals, as described in more detail later. In terms of bulk composition, all of the samples are characterized by the presence of a significant non-clay fraction (from ~11 to ~64%) that is represented by calcite, dolomite, quartz, feldspars and gypsum.

Calcite is generally the most abundant non-clay phase (~13–24%, excluding three samples). Dolomite is present in ~73% of the total samples, but its content is generally low (~4–12%). Quartz is always present as a common constituent of clays (~3–13%), and its levels are comparable (~23%, AR12), or higher (~33%, AR15), than the calcite content in two samples (Fig. 1). Feldspar is a minor component of clay, and its content is generally very low in our samples (~2–8%), which contain both alkali feldspars (orthoclase and microcline) and plagioclase feldspars. Gypsum is very rare, and was detected in only two samples in low (~3%, AR1) or significant (~35%, AR2) amounts. One sample (AR9) also contains cristobalite (~6%).

3.2. Mineralogical composition of the clay fraction

The results of mineralogical analyses on the clay fraction are reported in Table 2. The X-ray patterns of the air-dried, ethylene-glycolated and heated clay fraction are illustrated in Fig. 2.

The behavior of the mineral reflections under natural conditions (air-dried, ethylene glycolated and heating to 335 °C and 550 °C) defines a very diverse set of clay minerals represented by illite, smectites, interstratified illite/smectite, kaolinite and chlorites. Based on the type (and association) of the clay minerals, the studied samples can be divided into five groups.

Group 1 is the most represented (53% of the total samples) and has a clay fraction formed by prevailing illite + chlorites, with subordinate interstratified illite/smectite. Group 2 (20% of the total samples) is entirely composed of illite, whereas Group 3 (16% of the total samples) is made up of almost pure smectite (AR7) and interstratified illite/smectite (AR1). Meanwhile, Groups 4 and 5 correspond to isolated samples that have a clay fraction composed of kaolinite + illite + smectites (AR9) and illite + chlorites (AR3), respectively.

Illite is present among the clay minerals in almost all the investigated samples (except Group 3), ranging from ~27% to ~65%, with an average of ~38%. It is the only clay mineral in Group 2. In some samples, on heating to 550 °C, the (001) peak of illite shows a slight collapse, suggesting that expandable layers could also be present. In most of the samples, the sharp peaks of illite indicate that the illites are generally well-crystallized. Kaolinite is only present in one sample (AR9, ~51%), whereas chlorites are present in Groups 1 and 4. Quartz is probably also present in very small amounts in the separated clay fraction.

The presence of interstratified minerals in some of the studied clays (Group 1 samples and AR1 sample of Group 3) is indicated by either the presence, in their diffraction patterns, of an ancillary low-angle tail, shoulder or minor peak, or separate 10 and 17 Å peaks. In order to estimate the nature of these phases, we simulated the XRD patterns of the two samples of the Group 3 (AR1 and AR7), in which the clay fraction was significant (e.g. >10%) and the reflection was better developed,

Table 3
Trace-element content (ppm) of the investigated clays. For the details of the analytical methods, detection limits, relevant errors and standard deviation, see Roselli et al. (2015). *bdl*: below detection limit.

	Sample	Ni	Cu	Zn	As	Br	Rb	Sr	Ba	La	Ce	Nd	Pb	U	Th	
Group 1	AR2	75.6	29.6	75.8	3.1	6.1	108	453.2	356.2	20	49.2	27.9	19.9	3.25	9.7	
	AR5	88.4	28.1	79.1	3.9	5.3	110	458.7	379.3	17.2	48.2	26	19.1	2.92	6.94	
	AR6	89.5	30	78.6	3.4	5.5	109	464.8	382.4	19.3	46.6	28.4	18.8	3.75	6.97	
	AR8	86.3	33.2	78.8	4.5	3.7	107	450.7	400.1	24	56	28.4	18.7	5.34	8.29	
	AR10	128	37.6	83.6	3.2	2.8	114	453.3	481	21.2	53.4	37.9	20	2.55	8.17	
	AR11	105	31.1	79.6	3.9	4.4	112	453.8	436.2	18.9	52.4	27.3	19.4	2.98	7.32	
	AR13	155	32.8	82.1	5.8	1.9	111	452.2	497.7	23.8	56.2	32.7	18.5	2.31	8.02	
	AR14	170	35.9	83.8	5.3	1.9	112	457.5	539.8	26.6	57.3	33.4	19	2.49	8.37	
	Group 2	AR4	35.8	27	140.9	29.6	<i>bdl</i>	494	139.9	366.9	16.2	45.2	23.5	36	2.84	9.12
		AR12	38.9	25.7	86.2	10	<i>bdl</i>	139	291.3	451.4	33.1	76.1	30.3	23.5	4.73	9.71
AR15		31.4	22.5	75.8	9.4	<i>bdl</i>	128	250	461.8	34.7	76.5	36.9	20.8	3.78	7.68	
Group 3	AR1	10.3	12.8	30.7	2.4	13.9	36.7	303	214.7	4.6	23.3	<i>bdl</i>	10.8	7.41	1.9	
	AR7	13.1	24.3	63.6	11.5	1.1	39.8	116.1	872	30.2	58	30.6	11.4	6.19	8.83	
	AR9	10.3	8	224.2	36.8	2.1	66.7	86.2	1589	48.9	78.6	33	65.4	3.37	13.4	
	AR3	50.5	44.4	84.7	13.1	2.8	101	115.4	331.3	33.5	71.4	35.4	23.8	1.22	7.2	

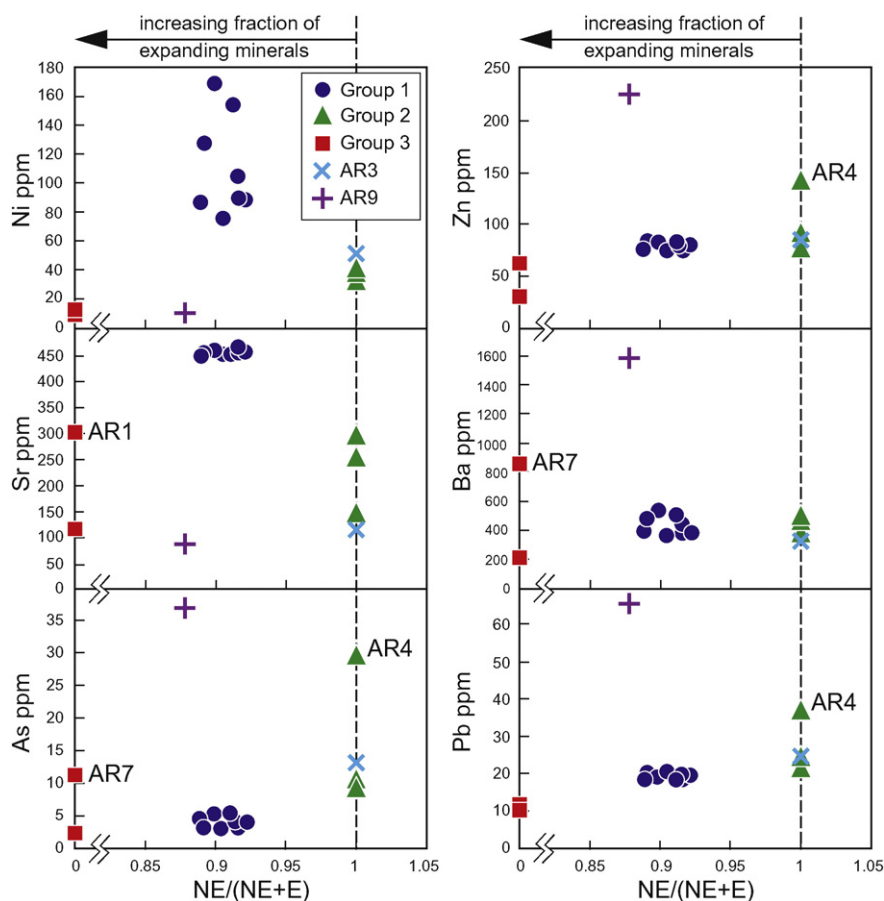


Fig. 4. Selected trace elements vs mineralogical composition diagrams of the investigated clays. NE: non-expanding minerals, E: expanding minerals.

using basal peak parameters. Working on the ethylene-glycolated and thermal dehydrated samples, the procedure resulted in a best fit of a mixed-layer illite/smectite with a proportion of interstratified illite layers (p_i) of ~0.4 for AR1 sample, while AR7 sample is coherent with an almost pure smectitic composition ($p_i < 0.1$; Fig. 3a). Results obtained indicate a random mixed-layer illite/smectite with ~60% smectite for AR1 and a smectite-dominated mixed-layer (illite/smectite with ~90% smectite) for AR7 (Fig. 3b).

X-ray powder diffraction analyses indicate that none of the samples are pure clays, with them instead being characterized by the presence of a significant non-clay fraction dominated by calcite and quartz and, to a limited extent, dolomite, feldspars and gypsum. Unlike reports in literature, which state that the clay minerals used in pharmaceuticals and cosmetics are only smectites, palygorskite, kaolinite and talc, our studied samples have a clay fraction composed of a very diverse set of clay minerals represented by illite, smectites, interstratified illite/smectite, kaolinite and chlorites. Moreover, it should be noted that there is great uncertainty regarding the use of color as a “compositional term” for clays. The Group 1 samples, which were composed of interstratified illite/smectite + illite + chlorites, are available on the market as “green clays”, as are the Group 2 samples, which are only made up of illite. AR1 is a “brown clay” and AR7 a “white clay”, but they contain the same clay mineral (interstratified illite/smectite). Furthermore, AR9 is also a “white clay”, but includes kaolinite + illite + smectite.

3.3. Relationships between mineralogical composition and bulk chemistry

The healing use of clay is widespread, but often little is known about the mineralogical and chemical compositions of the raw materials. This is surprising if we consider that natural materials are highly variable and could be very rich in dangerous or toxic minerals and/or trace chemical

elements. On the basis of chemical data reported in a companion paper (Roselli et al., 2015), we tried to compare the mineral compositions of the studied samples with their bulk chemistry (Table 3 and Fig. 4), with the main focus on the trace elements that are prohibited in cosmetic concentrations (EC Regulation 1223/2009).

First of all, it is important to note that all of the investigated clays contain variable amounts of these prohibited trace elements. In particular, the samples with significant fraction of expanding minerals seem to show the higher contents. The eight samples of Group 1 have a very homogeneous chemical composition according to the similar mineralogy of their clay fraction. They have the highest Sr (450–465 ppm) content, whereas they have intermediate Zn (75–84 ppm), Ba (356–540 ppm) and Pb (18–20 ppm) contents, and low levels of As (3–6 ppm). The only exception is represented by Ni, which shows a significant variation within this group, ranging from 75 to 170 ppm. The samples containing a non-expanding phase (illite, Group 2) have comparable Ni (31–39 ppm) and Pb (21–36 ppm) contents, but they are distinct in terms of Ba (330–450 ppm), Sr (140–290 ppm), Zn (75–140 ppm) and As (9–30 ppm) contents. The highest amounts of Zn, As and Pb are related to the illite-richest AR4 sample. Comparable behavior is shown by the two smectite-bearing samples of Group 3, which have very similar Ni (31–36 ppm), Zn (31–63 ppm), As (2–11 ppm) and Pb (10–11 ppm) contents and significantly different levels of Sr (116–303 ppm) and Ba (215–872 ppm). As regards the two isolated samples, AR3 has a chemical composition comparable with that of the Group 2 samples, whereas AR9 has a bulk chemistry that is very different from that of all the other studied samples. It is characterized by the highest contents of Zn, As, Ba and Pb, and the lowest amounts of Ni and Sr.

According to the chemical limitations reported in EC Regulation 1223/2009 (EC, 2009), the EU Pharmacopoeia of 2011 and the US Pharmacopoeia of 2009 in the field of health (U.S. Pharmacopoeia 32-NF 27,

2009), great attention needs to be paid to the amounts of some metals, when present. This is true of both those traditionally considered as toxic (As, Sb, Cd, Co, Cu, Pb, Ni, Zn, Hg, Se, Te, Tl, Ba), and other less dangerous elements (Li, Rb, Sr, Cr, Mo, V, Zr, REE). Most of the clay samples examined in this study contain relatively high amounts of some trace elements, which can be related to: (i) adsorption by the clay minerals, (ii) impurities in the structure of the micas and clay minerals, or (iii) possible contamination during the manufacturing and commercialization processes. More specifically, some of the studied samples contain trace elements, concentration of which is significantly higher than the allowable limits (e.g. Zn and Ba) or even contain chemical elements (e.g. As, Ni and Pb) that, according to EC Regulation 1223/2009, are prohibited in cosmetics.

4. Concluding remarks

This study has investigated the mineralogical and chemical composition of some clays used in cosmetic applications. X-ray powder diffraction analyses indicate that none of the samples is a pure clay being characterized by the presence of a significant non-clay fraction dominated by calcite and quartz, and to a minor extent by dolomite, feldspars and gypsum. The clay fraction is composed of a very diverse set of clay minerals represented by illite, smectites, interstratified illite/smectite, kaolinite and chlorites. The most common samples are green “mixed” clays composed of interstratified illite/smectite + illite + chlorites, with considerable amounts of Ni and Sr. The green illite-bearing samples are enriched in As, while the smectite-bearing samples (both brown and white in color) are depleted in almost all the trace elements. They are therefore the most suitable samples for commercial purposes. In contrast, the white kaolinite-rich sample is the most enriched in Zn, As, Ba and Pb, and is thus the most potentially hazardous product.

These results show that the natural clays available on the market vary considerably in their mineralogical and chemical compositions. This means that their potential risk to human health can only be determined on a detailed, case by case basis.

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