Chemical analysis and *in vitro* UV-protection characteristics of clays traditionally used for sun protection in South Africa

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None declared.

SUMMARY

Clays have been used in southern Africa as photoprotectants by the indigenous people. Typically two types of clay are used: one white in colour and the other red. In this work the two clays were identified and characterised, and their *in vitro* SPF values measured. The clays afford a low SPF but offer broad spectrum protection. No cutaneous side-effects from the use of these clays is known. Further consideration should be given to the potential use of clays in sunscreen preparations.

Key words

clay, UV protection, chemical analysis, African women, South Africa, sunscreen

In hot, sunny climates as experienced in Durban, South Africa, photoprotective measures are required all year round to prevent erythema, irrespective of photoskin type (1). Indigenous African women, particularly those from rural areas, use local clay material for photoprotection and decorative purposes. These women follow a subsistence lifestyle and are outdoors for many hours each day, gardening, fetching wood and water, cooking, and performing other chores. They also lack the means to purchase commercial sunscreen products. Although these women typically present with Fitzpatrick skin types 5 and 6, for which skin cancer is less common, photoprotection is important to prevent hyperpigmentation disorders such as melasma.

Clay minerals are widely used in the pharmaceutical industry for a variety of purposes in oral and topical applications, as excipients and in aesthetic medicine (2). They have been used since ancient times (2), so it is not surprising that they form part of the heritage in southern Africa. Recently, the UV protective capacity of clays was reported (3).

Two clays are typically used: one white in appearance and the other red. The white clay is known locally as *umcaku* (isiZulu/isiXhosa), and the red as *ibomvu* (isiZulu/isiXhosa). The women mix the clay (100 g) with water (125 cm^3) and glycerine (20 cm^3) to produce a paste which is applied to the face. The clays are used individually with some women preferring one over the other. The distinct appearance of patients wearing these clays is shown in Figure 1. Since very little is known of the composition and UV efficacy of these clays, it was of interest to undertake a study thereof.

Methods

White and red clay samples were obtained from the local riverbank next to Inanda district in Durban. Informal traders, who are predominantly black women, buy 5 kg clay balls from the river traders and sell them at the local Durban market.

The clays were characterised by means of X-ray fluorescence, X-ray powder diffraction, Fourier transform infrared spectroscopy, transmission electron microscopy, and thermogravimetric analysis. Particle-size analysis was performed on a Malvern Mastersizer 2000 instrument which employs laser light scattering.

In order to estimate the UV-protective efficacy of the clays in their natural state, they were subjected to the *in vitro* SPF testing procedure, as developed by Diffey and Robson (4), on an Optometrics SPF 290 Analyser. For this test the clays were applied to Transpore tape at an application density of 2 mg cm^{-2}.

Results

X-ray fluorescence was used to determine the chemical composition of the clays. The results are presented as weight percentages of the oxides in Fig. 1a. The major constituents of the clays were oxides of silicon and aluminium. In the case of the red clay, iron oxide was also present, which is consistent with the hue of the clay. A small percentage of titanium dioxide was also present in both clays. The main impurities were K_2O, MgO, Na_2O, P_2O_5, Cr_2O_3 and MnO. The loss on ignition (LOI) was 10.58 and 24.46 wt% for white and red clay respectively. The mass loss is mainly due to the removal of structural water and organic substances.

The energy-dispersive X-ray spectrometry analysis spectra also confirm the presence of the major oxides (see Fig. 1b).

The phases of the oxides present were investigated by means of powder X-ray diffraction (Figure 1c). The white clay consisted predominantly of kaolinite and quartz (as evidenced by the peaks at 3.52, 4.37 and 4.17 Å for kaolinite and 3.31 and 4.28 Å for quartz). The red clay instead contained kaolinite, quartz and haematite (peaks at 2.72, 2.55 and 1.81 Å). The presence of these phases was confirmed by Fourier transform infrared spectroscopy (Figure 1d). Further confirmation that the major component of these clays was kaolinite was obtained from thermogravimetric analysis (Figure 1e). The exotherm at 507 °C in the case of the white clay and 481 °C in that of the red clay correspond to loss of structural hydroxyl groups due to the transformation of kaolinite ($Al_2Si_2O_5(OH)_4$) to metakaolinite ($Al_2Si_2O_7$). The mass loss below 100 °C is due to dehydration (removal of moisture). The mass losses between dehydration and dehydroxylation are due to the presence of the iron oxides, particularly for the red clay. Kaolin deposits have been reported in Inanda (the source of the clays) and the nearby Ndwedwe region (5).

The microstructure of the two clays, as observed by transmission electron microscopy and scanning electron microscopy, can be seen in Figures 1f and 1g respectively. The white clay appears as platy particles that have the typical kaolinite pseudo-hexagonal shape. The red clay is less regular in morphology.

The white clay sample showed a broad, dispersed particle-size distribution, whereas the red clay showed a bimodal distribution (Fig. 1h). In the case of the white clay, 50% of the particles (by volume) had a diameter smaller than 12.463 μm. For the red clay the value was 14.630 μm. Using the classification of clay ≤ 2 μm, silt = 2-63 μm and sand = 63-2000 μm, the fractions in the white clay were 9.9%, 58.9 % and 31.2% respectively. For the red clay the corresponding figures were 11.5%, 68.4% and 20.1% respectively. That the white clay had a greater fraction of "sand" is in keeping with a larger SiO_2/Al_2O_3 ratio (theoretical value for kaolinite is 1.16), indicative of a high quartz content. The fact that the clay particles are mostly in the micron range accounts for the visible appearance of these clays when applied to the skin. Modern sunscreen formulations that contain metal oxides do so in a micronized form in which the particles have diameters in the nanometer range and appear almost invisible but have good UV blocking ability.

The white clay displayed an estimated SPF of 3.6, a UVA/UVB ratio of 0.9 and a critical wavelength of 388 nm. The red clay had an estimated SPF of 4, a UVA/UVB ratio of 1 and a critical wavelength of 389 nm. Both clays can therefore be classified as broad-spectrum protectants since their critical wavelengths are greater than 370 nm. The fact that the red clay has a higher proportion of smaller particle sizes improves its light scattering and absorbing ability. Particle dispersion is one aspect that sunscreen formulators keep foremost in mind in order to achieve good sun protection. Since the clays discussed here are formulated in the home by simple mixing with household reagents, namely, water and glycerine, particle aggregation is probably a limiting factor in achieving an improved SPF.

Discussion

This work has shown that the clays typically used in rural parts of South Africa for UV protection consist chiefly of the mineral kaolinite. Traditionally, clay soils rich in this mineral are widely used in southern Africa for a variety of medicinal purposes because they exhibit low toxicity. However, it needs to be pointed out that in some regions clays are contaminated with arsenic, therefore the toxicity of the clays needs to be assessed before widespread usage.

These traditional non-commercial sun protective measures bear some similarity to commercial physical sunblocks. They are both composed of metal/metalloid oxides. (In the case of commercial physical sunblocks the typical active agents are either titanium dioxide or zinc oxide.) They are both messy to use and can cause staining. To improve their aesthetic appeal commercial sunblocks are available in designer colours and in South Africa these are widely used and popularised by surfers and cricketers. The traditional clays discussed here have their own inherent colouring.

Although the SPF of both clays is low, they do provide some degree of UVA protection. This is an important consideration, since UVA constitutes the greater amount of incident solar radiation and has been implicated in skin cancer. Another aspect of sunscreen usage is application density. Typical commercial sunscreens are tested with an application density of 2 mg cm^{-2}, but it is well known that typical usage patterns are less than half this amount. Here, however, this is unlikely to be the case because of the 100 g of clay mixed they use 5g to cover the face which is greater than the amount advocated for suncreens.

These clays provide a cost-effective, easily available and culturally appropriate product for rural South African women. Although our study did not consider the safety profile of these clays, the indigenous women who have used these clays for decades, have not reported any cutaneous side-effects apart from a residual orange hue on the skin. Given the difficulty in finding suitable photostable and non-toxic organic sunscreen absorbers, greater consideration should be given to the potential of clays as additives for sun-protection creams.

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Figure legends

Fig. 1. Patients wearing the white and red clays.

Fig. 2. Data recorded for the characterisation of the UV-protective clays: (a) Chemical composition of the clays obtained from X-ray fluorescence, (b) energy-dispersive X-ray spectra, (c) X-ray powder diffractograms, (d) attenuated total reflectance Fourier transform infrared spectra, (e) thermogravimentric analysis curves, (f) transmission electron micrographs, (g) scanning electron micrographs, and (h) particle size distribution curves.