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Evaluation of letsoku and related Southern African clayey soils

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ABSTRACT

The nature of *letsoku* and related clayey soils, traditionally used by indigenous Southern African communities for a wide range of purposes, was explored. Thirty nine samples were collected from Botswana, Lesotho, Swaziland, South Africa and Zimbabwe. They were analyzed to determine their composition and physical properties. Analyses involved BET surface area determinations, pH measurements, X-ray diffraction (XRD), X-ray fluorescence spectroscopy (XRF), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). Structured interviews were used to establish the purpose of use and the location of sourcing sites. Most of the samples were in powder form and some were supplied as dry clay balls. Cosmetic applications were almost universally indicated. However, other functions, related to artwork, medicinal use, cultural symbolism and traditional beliefs were also mentioned. The *letsoku* samples covered a wide range of colors ranging from bright red to yellow but also from off-white to black with some having a light grey color. It was therefore not surprising that the mineral composition of the *letsoku* samples also varied widely. A black sample, and the yellow and reddish pastel colored samples, contained significant quantities of the corresponding, color imparting, iron oxides. As expected, clay minerals featured prominently although kaolinite was more often encountered than smectites as the dominant minerals. All samples contained silica and in some instances the content exceeded 90% m/m SiO_2. The presence of high contents (40% m/m) of gibbsite in samples from Venda represents a new finding for clayey soils in traditional usage.

1. Introduction

Cosmetics have evolved over centuries. The quest for a pale angelic white complexion was pursued using minerals and pigments with disregard for safety. One of the prominent products of the past eras was the skin whitener *ceruse* or spirits of Saturn composed of $PbCO_3$ and $Pb(OH)_2$ among the English, Greeks and Romans (Scott, 2016). The latter caused lead poisoning, skin damage, hair loss, facial tremors, muscle paralysis and death. The toxic eye paint mixtures of PbO_4, HgS, Sb and cinnabar compounded cosmetic toxicity. The PbS containing Kohl eye products and the use of arsenic increased safety risk. The current use of these trace elements in cosmetics; As, Hg and Pb, contravenes the stipulations by the International Agency for Research of Cancer (IARC), Agency for Toxic Substances and Disease Registry (ATSDR), EC Regulation1223/2009 or European laws for cosmetic products (Gomes and Silva, 2007; Mattioli et al., 2016; Roselli and Desideri, 2013; Tateo and Summa, 2007).

The above mentioned practices thrived due to the lack of regulatory control bodies. Modern regulatory functions include cosmetic composition, chemical structures, functions and ingredients toxicity. The Parliament and European Council (EC) regulate cosmetics via Regulation (EC) No. 1223/2009 (dated 30 November 2009 and the subsequent amendments thereof) of the European Parliament and of the Council on cosmetic products (Tateo and Summa, 2007). The others include the Federal Drug Agency (FDA), Occupational Safety and Health Administration (OSHA) and the Cosmetic Ingredient Review

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(CIR) which is mainly for ingredients toxicity (López-Galindo et al., 2007).

Subsequent studies revealed the important role of soils and clays in the life of mankind (Certini and Ugolini, 2013; Hartemink, 2015; Hartemink and McBratney, 2008). Ethnopedological and ethnopharmacological approaches, considered together, helped to capture spiritual, cognitive and practical aspects (Adderley et al., 2004; Barrera-Bassols and Zinck, 2003; De Smet, 1998; Krasilnikov and Tabor, 2003). The physicochemical properties of clay minerals, e.g. kaolinite, smectites and talc, are important attributes in therapeutic applications (Carretero, 2002; Carretero and Pozo, 2010; Roselli and Desideri, 2013; Schoonheydt and Johnston, 2006). Oral and topical therapeutic activity as well as the cosmetic action of clays in creams, sun screens (Madikizela et al., 2017), dermatological protectors, anti-inflammatories and gastro-intestinal medications were discussed. Matike et al. (2011) highlighted the effect of pH of cosmetics on the acid mantle of skin.

Ochre has featured in various cultural products for almost 100,000 years (Carretero, 2002; Hodgskiss and Wadley, 2017; Konta, 1993; López-Galindo et al., 2007). In essence ochre is a natural soil-based pigment that ranges in color from yellow to deep orange or brown. It is essentially a mixture of oxides of iron with varying amounts of sand and clay. Among the peoples of Southern Africa ochre, known as *letsoku* in the Sotho language, is widely used for topical administration. However, *letsoku* has also been associated with other materials, e.g. a black manganese oxide (Pahl, 1974), white clays (probably kaolin) (Bishop, 1984) and the black *sekama* or ilmenite (Ambrose et al., 2001). Previous studies (Dlova et al., 2013; Madikizela et al., 2017; Matike et al., 2011, 2014; Mpako et al., 2011) have reported on some of the properties of similar clayey soils used by the Nguni peoples of Southern Africa in the Eastern Cape and KwaZulu Natal respectively.

This study was inspired by the transition of the cosmetic industry towards more natural ingredients, and motivated by the quest to reclaim vanishing cultural practices of Southern African indigenes. Against this background, *letsoku* is being investigated to explore its nature and its viability for future commercialization. The specific aim of this study was to obtain and investigate representative *letsoku* samples from various locations in Southern Africa. Considerable efforts were made to locate the sourcing sites and structured interviews were used to uncover the purposes for which *letsoku* is used. The relevance of mineral composition to the manifold claimed traditional uses of *letsoku*, is discussed in the context of the known functions that inorganic minerals impart to modern formulations (Carretero and Pozo, 2010; López-Galindo et al., 2007; Madikizela et al., 2017; Mattioli et al., 2016; Roselli and Desideri, 2013).

2. Materials and methods

This study is a combined epistemological and empirical evaluation of thirty nine representative indigenous Southern African clayey soil samples. The red clay pastes are known as *letsoku* in Sotho culture and *libovu* among some Nguni people (Morekhure-Mphahlele et al., 2017).

2.1. Epistemological study

Traditional healers were the primary target interviewees. However, in many cases their reticence, to divulge detailed information on *letsoku*, posed challenges. In those cases, and for information pertinent to remote areas, voluntary associates were enlisted. In the end, a total of forty one respondents from various backgrounds were interviewed.

2.2. Clayey soil sample collection and processing

Every attempt was made to ensure that samples were, as far as possible, obtained in accordance with the practices employed by traditional healers. Fig. 1 is a map from the KMZ file in the Interactive plot and Table 1a provide information on the sample sourcing locations on a Google Earth map and sample codes and ID respectively.

The differences in texture and hardness of the collected samples led to a variation of sample processing. The hard rocks from Mpumalanga were ground with the jaw crusher. The muddy samples were oven dried overnight at 50 °C. A portion of each sample together with brittle samples were then milled using a tungsten carbide vessel in a swing mill. The milled samples were fine powders of particles < 75 μm. The samples were then stored at room temperature in polyethylene jars in the laboratory.

2.3. Characterization

All characterization procedures were performed on instruments at the University of Pretoria. The specific surface area was determined on a Micromeritics Tri Star II BET analyzer. The samples were degassed by vacuum drying overnight at a temperature of 100 °C to remove moisture and impurities. Thereafter the samples were reweighed before loading onto the Micromeritics Tri Star II BET analyzer. The latter is comprised of three independent ports which operate simultaneously to measure a minimum surface area of 0.01 $m^2 g^{-1}$ using nitrogen gas as an adsorbate and calibrated using the Silica-Alumina CRM P/N 004/6821/00 to read 214.8 ± 6 $m^2 g^{-1}$ at P_o = 0.990 to 0.998 and pore diameter of 115.5 ± 15 Å. It is designed to measure the saturation pressure on a continuous basis through the central port together with the sample tubes immersed in liquid nitrogen at −195 °C and the P_o of 760 mm Hg.

Color was evaluated according to the Munsell system by comparisons to the color charts. The pH was measured on supernatant liquids of both aqueous and 0.01 M $CaCl_2$ 20% m/m slurries. The Hanna pH meter was calibrated using buffers 4.00, 7.00 and 10.00.

Discs for X-ray diffractometer (XRD) analysis were prepared by compression. The XRD diffractograms were recorded on a PANalytical X'Pert Pro powder diffractometer in the 2θ configuration with an X'Celerator detector and variable divergence and fixed receiving slits with Fe filtered Co-Kα radiation (λ = 1.789 Å). The phases were identified using X'Pert High score plus software. The Rietveld method was used to estimate relative phase amounts (% m/m). The potential presence of amorphous substances and organic matter was investigated by spectroscopic analysis on the Perkin Elmer Spectrum 100 Series ATR-FTIR.

Metal oxides and trace metals content were determined using X-ray fluorescence (XRF) on the finely powdered samples of diameter < 75 μm. A sample mass of 1 g was mixed with about 6 g of lithium tetra borate flux and fused at 1050 °C to make stable fused glass beads for metal oxide determination. Trace metals were determined on samples bound with Moviol or poly(vinyl) alcohol and pressed into powder briquettes.

Scanning electron microscope (SEM) micrographs were recorded at an acceleration voltage of 1 kV. A Zeiss Ultra 55 FESEM field emission scanning electron microscope, fitted with an in-Lens detector, was used. A powdered sample was placed on a double-sided adhesive carbon tape stuck onto a steel plate. Excess powder was removed with compressed air. Carbon coating was applied using an Emitech splutter coater before viewing.

Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) spectra were recorded on an in-house Perkin Elmer Spectrum 100 Series instrument. The recording was done at 32 scans over the wavenumber range 500–4000 cm^{-1}.

CEC estimation was done by the summation of exchangeable cations Ca^{2+}, Mg^{2+}, K^+ and Na^+ (Ciesielski et al., 1996; Jaremko and Kalembasa, 2014). This involved the initial saturation of the soil sample with an index cation, Ba^{2+}