MANUSCRIPT

Evaluation of letsoku and related Southern African clayey soils

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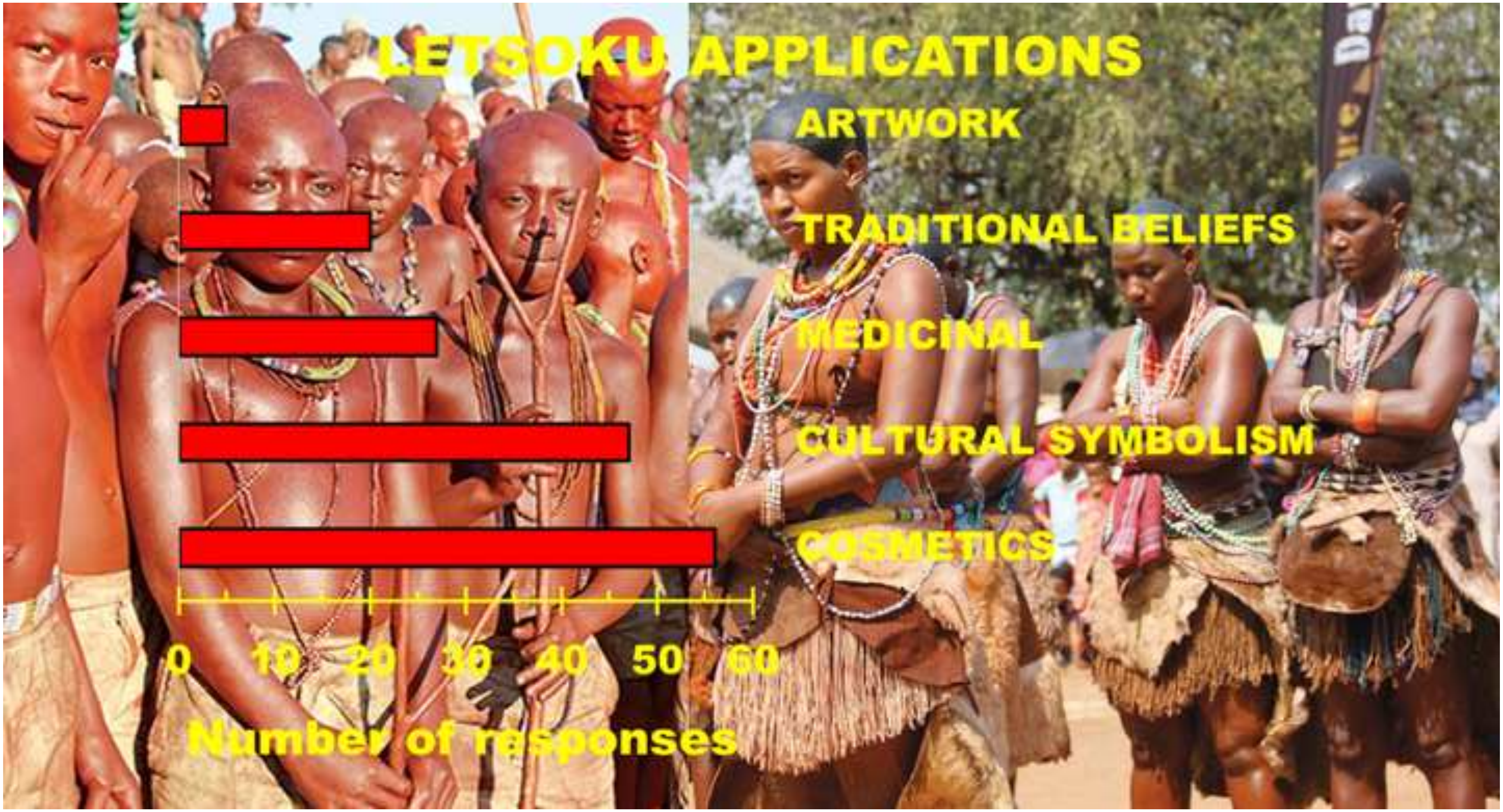
Abstract

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.

Keywords: Clayey soil; traditional knowledge; indigenes; durisol; composition

Graphical Abstract letsoku



Highlights

- Letsoku is a clayey soil used for cosmetic applications in Southern Africa
- Vast variation in color and in mineral composition
- Clays, especially kaolin feature prominently as does silica
- The black and the yellow to red pastel colors derive from iron oxides
- Gibbsite unique emergence as an ingredient in traditional topical cosmetic

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, 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 (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, 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, antiinflammatories 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; Matike et al., 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, 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^{o}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 less than 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±15Å. 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^{o}C and the P_o of 760 mm Hg.

Fig. 1. *Letsoku* sample sourcing locations on a Google Earth map. Red markers show the original sourcing sites Makurung in Limpopo and Ntoane, Maleoko hills in Mpumalanga. The rest of the markers are for commercial sites where the clayey soils where purchased from herbal shops, vendors and markets.

Table 1a: Sample codes, origin and description (za ~ South Africa; sz ~ Swaziland; zm ~ Zimbabwe; bw ~ Botswana)

Sa ID	Sourcing site	Source type	Color
za1	Arula, Asiatic Bazaar, Pretoria, SA	Commercial	orange-red *letsoku*
za2	Arula, Asiatic Bazaar, Pretoria, SA	Commercial	White *letsoku*
za3	Maleoko mountain, Ntoane, Dennilton, Mpumalanga, SA	Mouth of cave	brick red and yellow *letsoku*
za3a	Maleoko mountain, Ntoane, Dennilton, Mpumalanga, SA	Mouth of cave	brick red and yellow *letsoku*
za3b	Maleoko mountain, Ntoane, Dennilton, Mpumalanga, SA	Mouth of cave	brick red and yellow *letsoku*
za5	Engcobo,Umtata and Comfimvaba, Queenstown, SA	Commercial	yellow *imbola*
za6	Engcobo,Umtata and Comfimvaba, Queenstown, SA	Commercial	pale green *imbola*
za7	Engcobo,Umtata and Comfimvaba, Queenstown, SA	Commercial	red orange *imbola*
za9	Engcobo,Umtata and Comfimvaba, Queenstown, SA	Commercial	red orange rocks *imbola*
za8	Mbaleni,Venda,Limpopo,SA	Demolished hilltop	moist reddish stones *letsoku*
za8a	Mbaleni,Venda,Limpopo,SA	Demolished hilltop	moist reddish stones *letsoku*
za8b	Mbaleni,Venda,Limpopo,SA	Demolished hilltop	moist reddish stones *letsoku*
za8b1	Mbaleni,Venda,Limpopo,SA	Demolished hilltop	moist reddish stones *letsoku*
za8c/v1	Mbaleni,Venda,Limpopo,SA	Wetlands	wet greenish gray *vumba*
za10	Makurung, Ga-Mphahlele village, Limpopo, SA	Valley	white black granules leshaba
za11a/u1	Mtubatuba, Kwa-Zulu Natal, SA	River side	muddy gray greenish clay *ubumba*
za11b/u2	Mtubatuba, Kwa-Zulu Natal, SA	River side	muddy gray greenish clay *ubumba*
za11c/u3	Mtubatuba, Kwa-Zulu Natal, SA	River side	muddy gray greenish clay *ubumba*
za13a/w1	Nongoma, Kwa-Zulu Natal, SA	River side	muddy gray greenish clay *ubumba*
za13b/w2	Nongoma, Kwa-Zulu Natal, SA	River side	muddy gray greenish clay *ubumba*
za12	Bloemfontein market, OFS, SA	Commercial	maroon reddish powder *letsoku*
sz1	Manzini market, Swaziland	Commercial	red orange powder *libovu*
sz2	Manzini market, Swaziland	Commercial	white medium pebbles
zm1	Chiredzi, Zimbabwe	Commercial	maroon powder *chomane*
bw1	Gaborone Sun, Botswana	Commercial$^{\$}$	yellow letsoku
bw2	Gaborone Sun, Botswana	Commercial$^{\$}$	pinkish letsoku powder
bw3	Gaborone Sun, Botswana	Commercial$^{\$}$	white letsoku powder
bw4	Gaborone Sun, Botswana	Commercial$^{\$}$	bright red letsoku powder
bw5	Gaborone Sun, Botswana	Commercial$^{\$}$	maroon powder letsoku
bw6	Gaborone Sun, Botswana	Commercial$^{\$}$	purple letsoku powder
bw2a	Gaborone Sun, Botswana	Commercial$^{\$}$	pink white letsoku rocks
bw3a	Gaborone Sun, Botswana	Commercial$^{\$}$	white letsoku rocks
bw4	Gaborone Sun, Botswana	Commercial$^{\$}$	orange red letsoku rocks
bw6a	Gaborone Sun, Botswana	Commercial$^{\$}$	off white letsoku rocks
bw7	Gaborone Sun, Botswana	Commercial$^{\$}$	orange letsoku
bw8	Gaborone Sun, Botswana	Commercial$^{\$}$	whitish orange letsoku rocks
za15	Nature Life, Brooklyn Mall, Pretoria	Commercial$^{\$}$	cream powder
za19	Nature Life, Brooklyn Mall, Pretoria	Commercial$^{\$}$	green grey montmorillonite

Commercial$^{\$}$ originally from Ramatlabama

V1, u1, u2, u3, w1 and w2 is the alternative labelling used in Morekhure-Mphahlele et al. (2017) for za8c, za11a, za11b, za11c, za13a and za13b respectively.

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=1.789Å). 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.

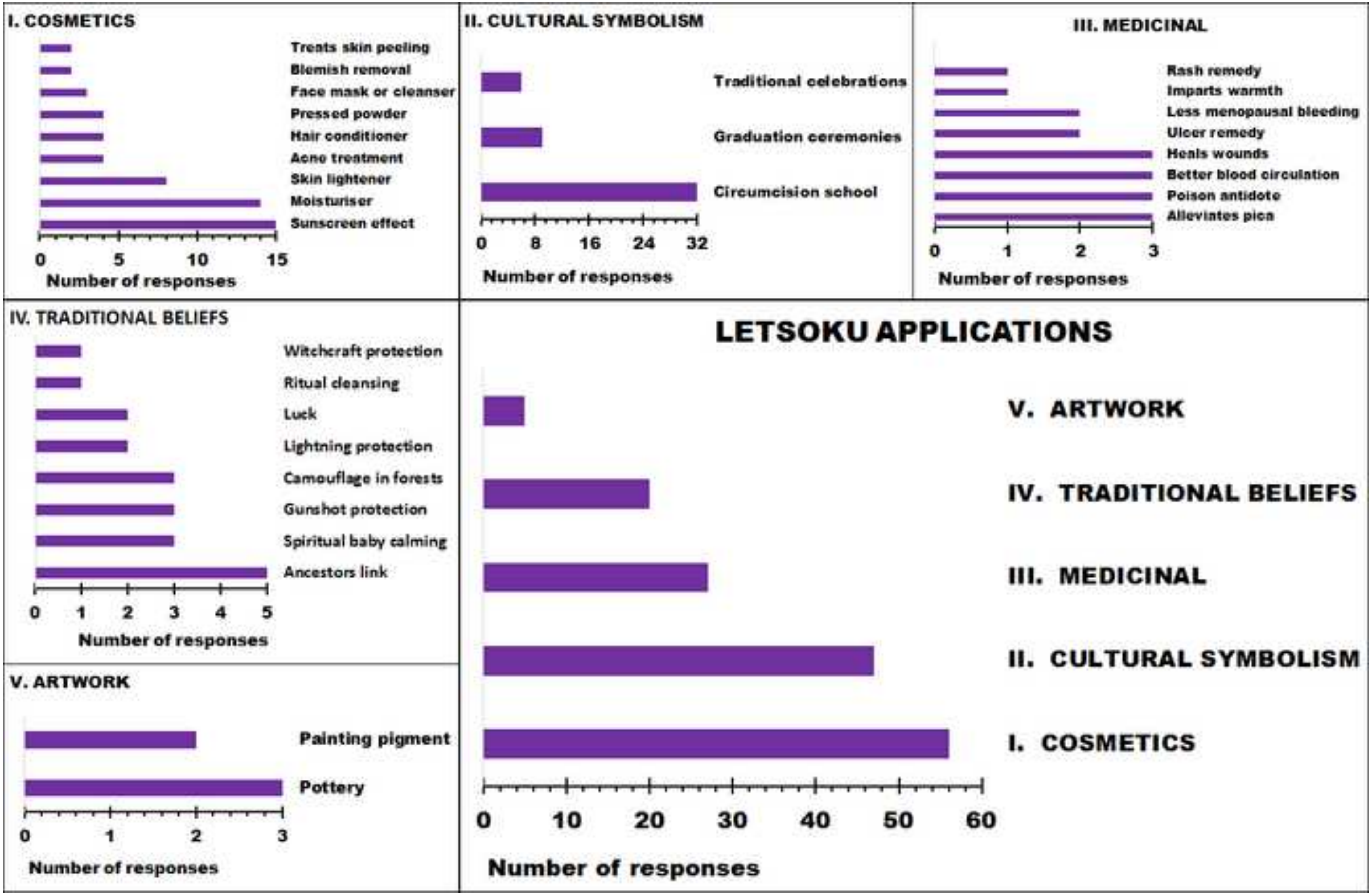
Metal oxides and trace metals content were determined using X-ray fluorescence (XRF) on the finely powdered samples of diameter <75 μm. A sample mass of 1 g was mixed with about 6 g of lithium tetra borate flux and fused at 1050°C to make stable fused glass beads for metal oxide determination. Trace 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, 1996; Jaremko, 2014) . This involved the initial saturation of the soil sample with an index cation, Ba^{2+}.

Figure 2 Letsoku thematic content analysis.



3 Results

3.1 Epistemological study

The results of the thematic content analysis are summarized in Fig. 2. In descending order of frequency, the main uses mentioned were cosmetics, cultural symbolism, medicinal, traditional beliefs and pottery. According to the respondents, *letsoku* represents a "substance that never solidifies" or it is referred to as "a soft stone".

Lobatse, Otse, Gaborone, Mmamabule and Mahalapye, Taung Notwane river, Mogobane, Moshopa, Dinokwe, Serule, Lebung area, Kweneng Laagte, Tsatsu, Kanye, Kgwakgwe, Morupule and Ramatlabama near the Botswana border were specifically mentioned as important *letsoku* source locations.

Raw *letsoku* stones are crushed with a traditional mortar and pestle or pounded on top of a grinding stone (*tshilo*) with another stone. The fine powder in common use and widely traded is then obtained by sieving. Instead, other users disintegrate dry raw *letsoku* stones into a fine powder by heating them in an empty pot. The powders are used as is or rolled into large balls before distribution.

Various colored forms of *letsoku* were mentioned. The respondents associated each color with a different function. For example, in cosmetics, yellow, orange and reddish pink are used directly as face powders. However, red is apparently first mixed with water and then used as a face wash or face mask to remove pimples and blemishes. White is recommended for eliminating bad breath or for general body cleansing and the removal of unpleasant body odors. Maroon is supposedly used to remove dark patches around the eyes. Purple was recommended as an anti-aging potion. It is mixed with petroleum jelly and applied to problem areas to eliminate wrinkles. Allegedly, excessive bleeding in menstruating women can be managed by oral ingestion of a mixture of red and lighter colored *letsoku* varieties. Some respondents also confidently asserted that there are no known *letsoku* side effects.

Tanners apparently use both *motsitsana* (an herb) and *letsoku* to impart a bright red color to leather skins, especially those to be used for clothing and shoes. Potters use *letsoku* to enhance the color of a finished clay pot. During the final stage of polishing a pot, a fine stone, *letsoku,* is added for adornment.

Field crops can supposedly be protected using letsoku. Some farmers apparently mix seeds with the red or maroon *letsoku* in a ritual called "*go gotlha dipeo*" (to rub the seed). This is meant to protect the seeds, chase away evil spirits and to prevent hail storms from damaging the plants. Farmers rub seeds thoroughly, using both hands, before planting as a form of nurturing the field in advance. Crops are treated "as infants" passing through the stages of being born, treating the umbilical cord, shaving and smearing the head for protection, etc.

Furthermore, it was mentioned that in some regions in Botswana, *letsoku* is still used to cover the bodies of youths attending initiation schools. The caretakers help to shave their heads and cover their bodies with a red or maroon *letsoku*. Some respondents claimed that *letsoku* helps to keep the initiates warm. The girls are covered with sufficient *letsoku* to ward off winter colds. Young girls used to wear *makgabe* (fringed short skirts) with *letsoku* covering the fringes. Apparently this is still practiced among the Ova Herero of Bothatogo, living in Maun, who believe it to be a symbol of innocence.

3.2 Characterization results

3.2.1 Physicochemical properties

Table 1b presents measured values for BET specific surface area (SSA), loss on ignition (LOI), slurry pH, Munsell color description and cation exchange capacity (CEC). The commercial controls used were bentonite (za15) and montmorillonite (za19). High SSA values correlated, as expected, with the presence of smectite clay (Fakhfakh et al., 2005). In addition high CEC values (21 up to 39 cmol kg^{-1}) were reported for very basic samples with no smectites detected: zm1 > za11b > za13a > za13b. Higher CEC values (29 up to 100 cmol kg^{-1}) were obtained for basic samples containing smectites: za19 > za15 > za11c > za10 > za8c >za11a. The pH in $CaCl_2$ appears to be slightly more acidic than the aqueous pH. This could be due to the Ca^{2+} exchange releasing the H^+ into the solution to render the solution more acidic.

The loss on ignition indicated dehydration mass loss rather than combustion of organic content. This is confirmed by the absence of any bands near 3000 cm^{-1} in the FTIR spectra shown in Fig. 4. This excludes the spectra for za19, the commercial montmorillonite control sample. The latter depicts the

Table 1b: *Letsoku* BET surface area ($m^2 g^{-1}$), slurry pH, LOI (% m/m), Munsell color description and CEC ($cmol\ kg^{-1}$); bw ~ Botswana; les ~ Lesotho; sz ~ Swaziland; za ~ South Africa: zm ~ Zimbabwe

SA	BET	pH_{H2O}	pH_{CaCl2}	LOI	HUE	Value/Chroma	Color description	CEC
za1	67.7	**5.88**	**5.74**	14.7	5 YR	6/8	pinkish white	**7**
za7	38.0	**6.22**	**6.13**	13.3	5 YR	6/8	reddish yellow	**10**
za11b	73.4	**9.12**	**8.48**	15.5	10 YR	6/4	light yellowish brown	**35**
zm1	27.9	**7.58**	**7.49**	14.5	5 YR	3/6	dark red	**39**
bw1	22.6	**7.03**	**6.87**	4.0	5 YR	8/2	pinkish white	**4**
bw1a	19.6	**7.10**	**6.97**	5.5	YR	8/6	reddish yellow	**2**
bw2	7.8	**6.21**	**6.20**	3.8	5 YR	7/3	pink	**7**
bw2a	15.1	**6.22**	**6.21**	4.6	5 YR	7/4	pink	**6**
bw3	8.2	**6.94**	**6.90**	3.4	7.5 YR	8/2	pinkish white	**6**
bw3a	21.9	**7.01**	**6.86**	4.0	5 YR	8/1	white	**6**
bw4	21.5	**6.56**	**6.51**	4.1	5 YR	4/6	red	**4**
bw5	4.7	**6.82**	**6.80**	0.1	10 YR	3/6	dark red	**3**
bw6	26.0	**6.88**	**6.79**	1.1	5 YR	7/4	pink	**5**
bw6a	19.2	**7.20**	**7.13**	4.5	5 YR	7/3	pink	**6**
bw7	14.7	**6.81**	**6.85**	3.6	5 YR	7/6	reddish yellow	**7**
bw8	22.4	**6.88**	**6.76**	3.7	5 YR	8/4	pink	**6**
les3	20.6	**6.69**	**6.63**	5.1	10 YR	5/8	red	**5**
sz1	59.1	**4.84**	**4.81**	15.7	5 YR	4/6	reddish yellow	**3**
sz2	27.0	**5.03**	**5.00**	14.0	5 YR	8/1	white	**0**
za2	45.0	**5.91**	**5.89**	12.6	7.5 YR	8/2	pinkish white	**2**
za5	48.0	**6.35**	**6.29**	8.3	7.5 YR	8/6	yellow	**15**
za6	30.5	**7.83**	**7.81**	5.7	5 YR	8/1	white (visible grey)	**18**
za8	61.0	**6.78**	**6.76**	19.6	5 YR	4/6	yellowish red	**6**
za8a	33.4	**7.43**	**7.38**	37.4	5 YR	4/6	yellowish red	**8**
za8b	8.7	**7.25**	**7.23**	18.0	5 YR	5/6	yellowish red	**6**
za8b1	44.4	**6.81**	**6.79**	19.1	5 YR	5/6	yellowish red	**6**
za8c	91.3	**6.09**	**6.05**	17.7	10 YR to 10 YR	6/4 5/4	light yellowish brown and yellowish brown	**32**
za9	26.0	**6.23**	**6.20**	6.0	7.5 YR	8/4	pink	**8**
za10	97.6	**8.35**	**8.26**	31.7	10 YR	8/2	pinkish white	**35**
za11a	75.2	**7.94**	**7.61**	14.8	2.5 Y	5/2	greyish brown	**29**
za11c	74.3	**7.96**	**7.86**	14.2	2.5 Y to 2.5 Y	7/2 6/2	light yellowish grey	**36**
za12	97.6	**7.02**	**6.97**	1.1	10 YR	4/6	red	**2**
za13a	79.2	**8.71**	**8.68**	12.0	10 YR	6/3	pale brown	**32**
za13b	45.4	**8.59**	**8.55**	4.8	2.5 YR	6/4	light yellowish brown	**21**
les1	21.5	**5.22**	**5.20**	3.6	10 YR	4/6	red	
les2	8.4	**7.32**	**7.30**	0	5 YR	8/1	very dark grey	**5**
za3	4.0	**7.02**	**7.00**	0.9	5 YR	5/4	reddish brown	**4**
za3a	19.7	**7.02**	**7.00**	2.1	5 YR	5/4	reddish brown	**3**
za3b	18.4	**7.40**	**7.10**	1.0	5 YR	7/4	pink	**3**
Za15	64.6	**8.02**	**7.99**	8.2	5 YR	8/1	white	**42**
za19	94.8	**8.73**	**7.96**	15.2	5 YR	8/2	pinkish white	**100**

potential presence of organic material with a broad band at 3000 cm^{-1}. The majority of samples had a hue of 5 YR and were reddish or yellowish red. All the muddy samples appeared to have almost the same grey-brown color but they differed with respect to the chroma values (10 YR and 2.5 Y).

3.2.2 Mineralogy from X-ray diffraction analysis

Table 2 reports XRD estimated mineralogy results. Supplementary material 1a reflects the acquired XRD patterns. Supplementary material 1b gives the detailed mineralogical results. Fig. 3a shows the XRD diffractograms categorized into groups A, B, C, D and E. Virtually **all** the groups reflect different amounts **of quartz** at 2θ of 31.0^o and other non-clay minerals such as dolomite, magnetite and calcite at higher 2θ values.

Group A, za8c, za10, za11a and za11c, reflects broadened swelling 2:1 **smectite** peaks against the sharp peaks of the commercial controls za15 and za19. **Smectite** has been indicated as having astringent and absorbent properties (Carretero and Pozo, 2010; Konta, 1995). **Kaolinite** is in only two (za8a cnd za11a) of these samples. It has high sorption capacity and opacity. **Plagioclase albite** has broad bands around 2θ of 29^o was detected in ¾ of the samples. **Epidote** is in za8c whilst **microcline** is in za10. **Goethite** is present in za11a and za11c and it is responsible for imparting color to cosmetics such as lipsticks. **Anatase** in ¾ of the samples has UV-absorbing capabilities.

Group B, za1, zm1, za7 and za11b, consists mainly of sharp 1:1 **kaolinite** peaks at around 2θ of 14^o. **Anatase** is in all of these samples except za1. Two of these (za7 and za11b) also bear the color imparting **hematite** (2θ = 38.9^o) and **goethite** respectively.

Group C is composed of za8, za8a, za8b and za8b1. The highlight of this group is the presence of **gibbsite** with a maximum of 45.1% m/m in the region of 2θ equal to 23^o. Gibbsite is associated with increased anticaking, compressibility and ease of flow in cosmetics. Only za8a and za8b1 contain **kaolinite** at less than 20 % m/m. The samples za8, za8a and za8b1 contain **muscovite** and **goethite**. The non-swelling 2:1 **chlorite** is in za8 and za8b.

Group D consists of bw1, bw1a, bw2, bw2a, bw3, bw3a, bw4, bw5, bw6, bw6a, bw7, bw8, les3, sz1, sz2, za5, za6 and za9 at 2θ around 24^o. The non-swelling 2:1 **muscovite** is the predominant

Table 2: XRD Autoquan software estimated mineral§ content (% m/m) of *letsoku* samples

Sa ID	Ep	Mc	Pl	Kln 1:1	Ms 2:1	Tlc 2:1	Sep 2:1	Sme 2:1	Chl 2:1:1	Qz	Ant	Rt	Il	Hem	Mag	Gth	Gbs	Cal	Dol
za1	-	-	-	92.3	-	-	-	-	-	7.7	-	-	-	-	-	-	-	-	-
za7	-	-	-	76.7	-	-	-	-	-	16.5	3.5	-	-	3.3	-	-	-	-	-
za11b	-	-	-	34.4	-	-	-	-	-	47.3	5.5	-	-	-	-	12.8	-	-	-
zm1	-	-	-	90.2	-	-	-	-	-	7.3	2.6	-	-	-	-	-	-	-	-
bw1	-	3.2	-	-	43.7	-	-	-	-	53.1	-	-	-	-	-	-	-	-	-
bw1a	-	1.9	-	4.5	40.5	-	-	-	-	39.8	-	-	-	-	-	-	-	-	-
bw2	-	1.3	-	2.8	46.1	-	-	-	-	48.8	-	-	-	-	-	1.1	-	-	-
bw2a	-	1.8	-	5.1	59.0	-	-	-	-	34.1	-	-	-	-	-	-	-	-	-
bw3	-	1.4	-	-	50.6	-	-	-	-	48.0	-	-	-	-	-	-	-	-	-
bw3a	-	3.7	-	3.9	53.8	-	-	-	-	37.8	-	0.8	-	-	-	-	-	-	-
bw4	-	-	-	1.2	30.0	2.8	-	-	-	36.5	-	-	-	29.5	-	-	-	-	-
bw5	-	-	-	-	2.4	-	-	-	-	3.7	-	-	-	93.9	-	-	-	-	-
bw6	-	-	-	4.3	50.0	-	-	-	-	44.0	-	-	-	1.7	-	-	-	-	-
bw6a	-	-	-	1.4	57.7	-	-	-	-	40.9	-	-	-	-	-	-	-	-	-
bw7	-	-	-	4.7	53.4	-	-	-	-	40.1	-	-	-	1.8	-	-	-	-	-
bw8	-	-	-	5.7	35.9	-	-	-	-	57.2	-	-	-	1.3	-	-	-	-	-
les3	-	-	-	10.4	7.5	-	-	-	-	45.4	-	2.2	-	28.7	-	5.8	-	-	-
sz1	-	-	-	73.9	11.2	1.1	-	-	-	10.7	-	-	-	3.1	-	-	-	-	-
sz2	**-**	**-**	**-**	**81.2**	**3.6**	**0.4**	**-**	**-**	**-**	**12.1**	**-**	**-**	**-**	**2.7**	**-**	**-**	**-**	**-**	-
za2	-	-	-	84.1	4.0	-	-	-	-	11.7	-	-	-	-	-	-	-	0.3	-
za5	-	5.4	-	12.7	16.0	-	-	-	-	58.6	-	--	-	-	-	7.4	-	-	-
za6	-	-	-	-	41.9	-	-	-	-	58.1	-	-	-	-	-	-	-	-	-
za8	-	-	-	-	9.6	-	-	-	14.1	14.8	1.9	-	-	-	-	16.1	43.5	-	-
za8a	-	-	-	17.4	7.0	-	-	-	-	14.4	2.1	-	-	-	-	17.7	41.3	-	-
za8b	-	-	-	-	-	-	-	-	5.3	89.9	-	-	-	-	-	-	4.9	-	-
za8b1	-	-	-	18.2	4.6	-	-	-	-	11.7	2.7	-	-	-	-	17.7	45.1	-	-
za8c	6.0	-	-	7.9	-	-	-	67.3	5.6	11.0	2.2	-	-	-	-	-	-	-	-
za9	-	-	-	23.6	9.6	-	-	-	-	64.9	1.9	-	-	-	-	-	-	-	-
za10	-	8.6	12.6	-	-	-	4.5	16.0	-	4.2	-	-	-	-	-	-	-	-	54.2
za11a	-	-	5.1	4.3	-	-	-	58.0	-	26.1	1.1	-	-	-	-	5.5	-	-	-
za11c	-	-	10.7	-	-	-	-	61.2	-	23.7	1.1	-	-	-	-	3.3	-	-	-
za12	-	-	-	-	-	-	-	-	10.0	19.1	-	-	-	58.8	-	11.1	-	-	1.0
za13a	**-**	**-**	**2.7**	**35.9**	**-**	**-**	**-**	**-**	**-**	**46.9**	**5.4**	**-**	**-**	-	**-**	**9.0**	**-**	-	-
za13b	-	-	7.0	-	-	-	-	-	7.4	84.5	-	1.2	-	-	-	-	-	-	-
les1	-	-	-	-	-	-	-	-	-	1.5	-	-	-	98.5	-	-	-	-	-
les2	-	-	-	-	-	-	-	-	-	3.8	-	1.5	61.9	-	32.8	-	-	-	-
za3	-	-	-	-	-	-	-	-	-	99.2	-	-	-	0.8	-	-	-	-	-
za3a	-	-	-	-	-	-	-	-	-	93.9	-	-	-	1.5	-	4.5	-	-	-
za3b	-	-	-	-	-	-	-	-	-	99.2	-	-	-	0.8	-	-	-	-	-
za15	-	14.5	0	-	-	-	-	78.5	-	4.9	-	-	-	-	-	-	-	-	-
za19	-	--	-	-	-	-	-	96.2	-	3.8	-	-	-	-	-	-	-	-	-

§ *Clay mineral IUGS standard abbreviations used according to Whitney and Evans (2009) and Schmid (2007) - Clay mineral not detected*

Abbreviations used of the studied clays (Ep = epidote, Mc = microcline, Pl = plagioclase, Kln = kaolinite, Ms = muscovite, Tlc = talc, Sep = sepiolite, Sm = smectite, Chl = chlorite, Qz = quartz, Ant = anatase, Rt = rutile, Il = ilmenite, Hem = hematite, Mag = magnetite, Gth = goethite, Gbs = gibbsite, Cal = calcite, Dol = dolomite

Figure 3a *Letsoku* XRD representative diffractograms as categories A, B, C, D and E (Department of Geology, University of Pretoria).

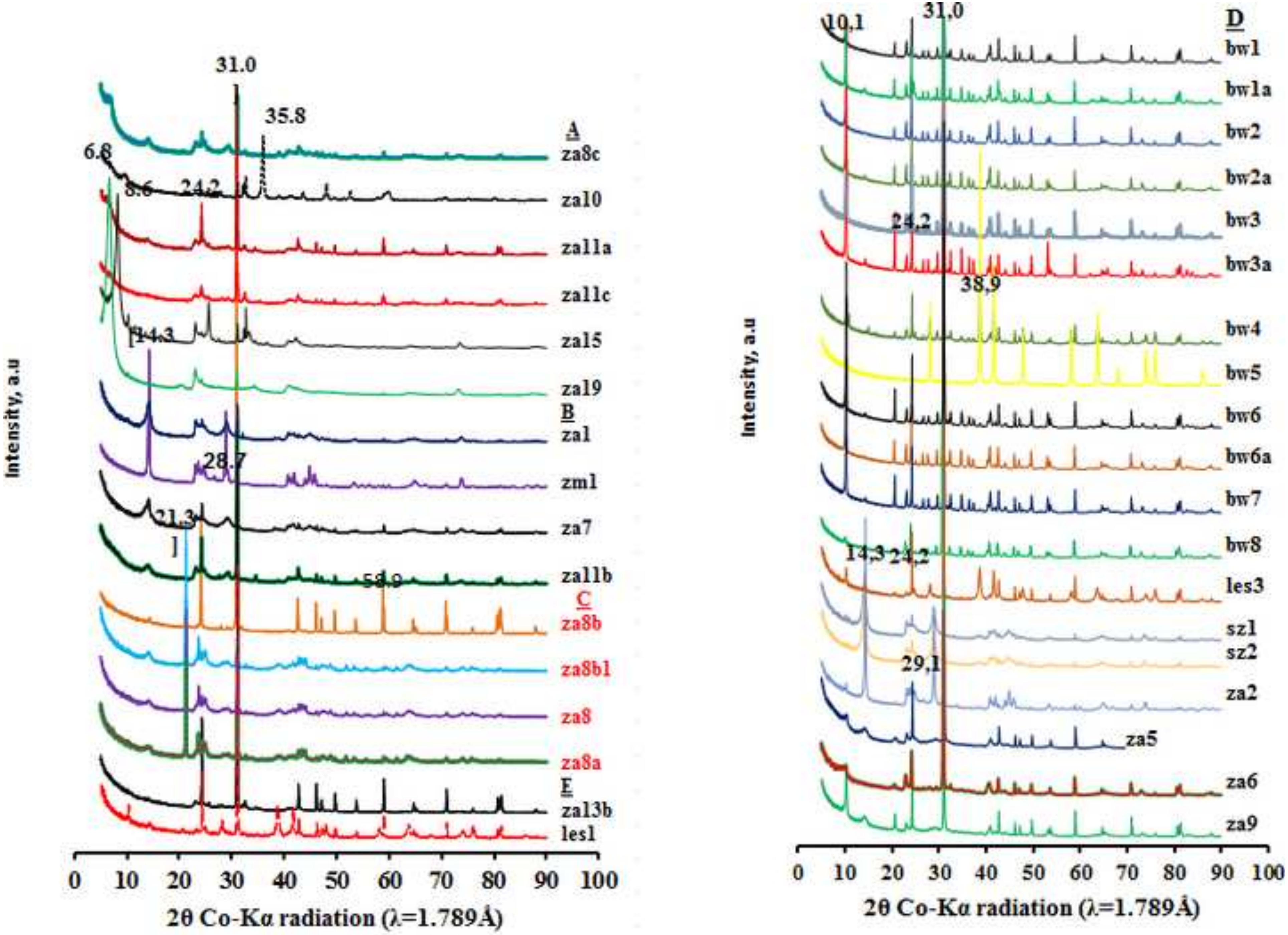
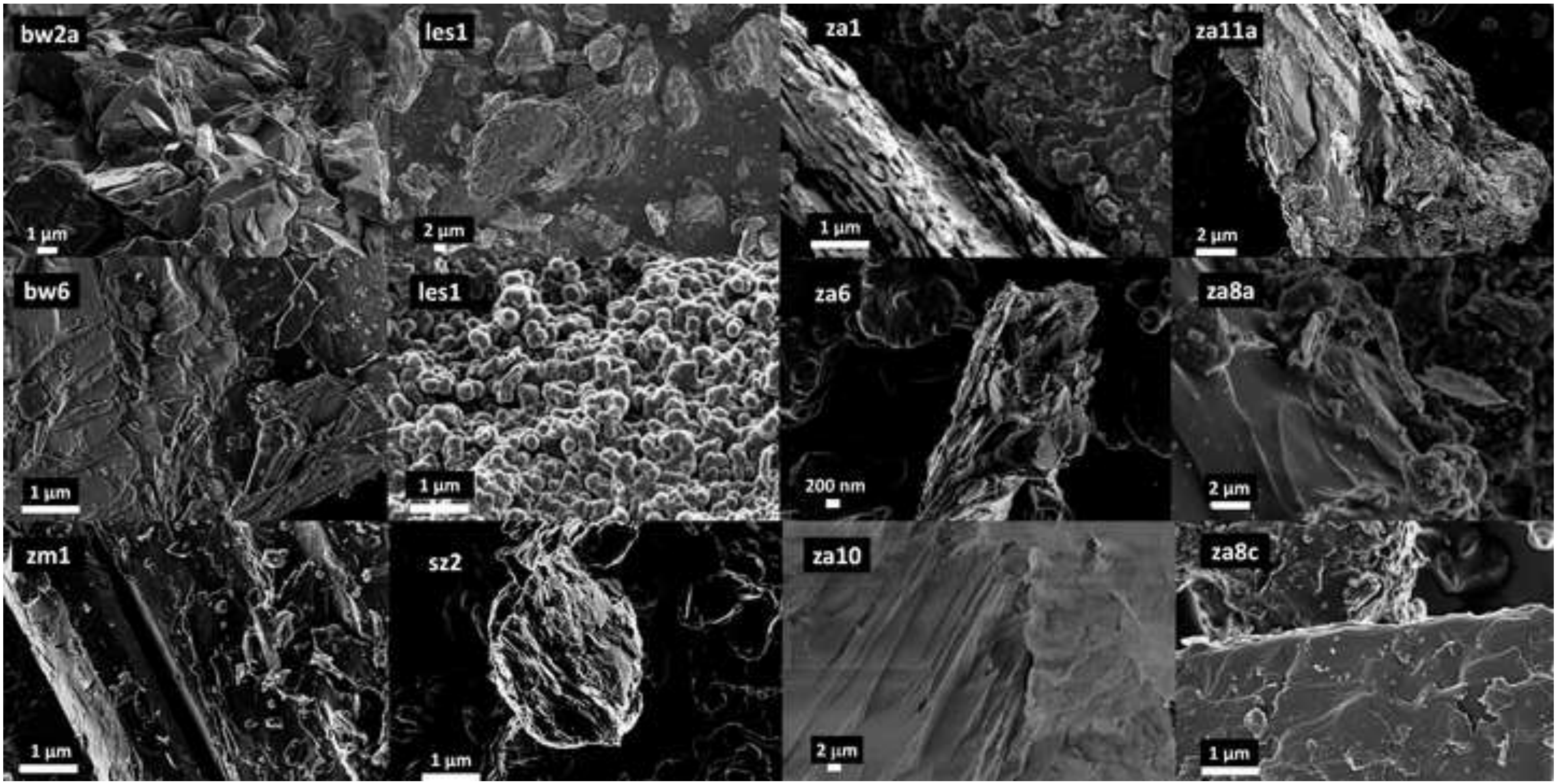


Figure 3b Micrographs of selected letsoku samples from the Zeiss Ultra 55 FESEM field emission SEM (Department of Physics, University of Pretoria).



mineral in **all** the samples and reaches up to 59.0 % m/m. Inclusion of muscovite in cosmetics imparts a luminous effect and iridescence due to its high reflectance according to Carretero and Pozo (2010). M**icrocline** was detected in six samples: bw1, bw1a, bw2, bw2a, bw3 and bw3a. The color imparting **goethite** is in les3 only**.** A trace of the solar protector **rutile** is found in bw2 and bw3a. **Talc** is in sz1 and sz2.

Group E consists of the non- swelling 2:1:1 **chlorite** in za13b and 98.5% m/m **hematite** ($2\theta = 38.9^{o}$) in les1. **Plagioclase albite, chlorite and rutile** are found in za13b. Les1 has 98.5 % m/m **hematite.**

Some local studies (Dlova et al., 2013; Jumbam, 2014; Madikizela et al., 2017; Matike et al., 2011; Morekhure-Mphahlele et al., 2017) and global ones (Carretero and Pozo, 2010; Favero et al., 2016; Mattioli et al., 2016; Silva-Valenzuela et al., 2013; Silva et al., 2011; Viseras et al., 2007) revealed the role of clay minerals and non-clay minerals in cosmetics. The above findings from the XRD mineral analysis yield potential efficacious cosmetic combinations.

A surprise finding is the conspicuous heterogeneity of the different *letsoku* varieties. All samples were complex mixtures of various minerals. They differed, not only from region to region, but even amongst some samples sourced from the same geographical area. Overall data analysis revealed varying degrees of a durisol character. Mpumalanga samples had the highest quartz content reaching 99.2 % m/m whilst those from Lesotho had the least (at most 1.5 % m/m). Kaolinite was highest in Gauteng samples with up to 92.3 % m/m and least for Botswana 1.2 % m/m. The highest muscovite content was found in a Botswana sample at 59.0 % m/m. The highest 2:1 smectite content was 67.3 % m/m found in a sample from Venda. An intensely red colored sample from Lesotho contained 98.5 % m/m hematite. A new finding was the detection of gibbsite in samples from Venda, reaching a content of 45.1 % m/m.

3.2.3 XRF metal oxide and trace metal analysis

As expected, all samples contained significant SiO_2 and Al_2O_3 as shown in Table 3. This corroborates Table 2 mineral data. Iron oxide was present in all the samples with the highest measured content in les1 (94.0 % m/m Fe_2O_3) and the least for bw3 from Botswana (1.1 % m/m). Titanium dioxide was

Table 3: XRF composition of letsoku samples (% m/m); bw ~ Botswana; les ~ Lesotho; sz ~ Swaziland; za ~ South Africa: zm ~ Zimbabwe

Sa ID	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Cr_2O_3
za1	40.7	1.5	27.4	16.7	0.1	0.6	0.0	0.0	0.5	0.1	0.1
za7	43.6	1.6	23.3	19.8	0.1	0.1	0.0	0.0	0.2	0.1	0.1
za11b	47.6	2.1	18.2	16.8	0.1	0.8	2.6	0.9	0.1	0.0	0.0
zm1	18.0	0.2	4.7	61.9	0.1	1.7	1.0	0.0	0.3	0.1	0.0
bw1	69.5	0.8	18.3	2.6	0.0	0.4	0.0	0.1	5.1	0.1	0.0
bw1a	54.7	0.7	16.4	20.0	0.0	0.1	0.0	0.2	3.8	0.1	0.0
bw2	66.9	0.8	18.6	3.2	0.0	0.4	0.0	0.1	5.3	0.1	0.0
bw2a	60.6	1.0	22.2	4.4	0.0	0.4	0.0	0.1	6.3	0.1	0.0
bw3	69.4	0.8	18.8	1.1	0.0	0.3	0.0	0.1	5.5	0.1	0.0
bw3a	65.9	0.8	21.0	0.8	0.0	0.3	0.0	0.1	6.2	0.1	0.0
bw4	50.6	0.6	13.5	29.1	0.4	0.2	1.1	0.2	3.1	0.1	0.0
bw5	68.6	0.9	19.9	3.2	0.0	0.3	0.0	0.1	5.6	0.1	0.0
bw6	5.4	0.2	2.3	86.4	1.3	0.0	0.0	0.0	0.4	0.1	0.1
bw6a	66.0	0.9	21.0	1.2	0.0	0.3	0.0	0.1	6.3	0.1	0.0
bw7	63.2	0.9	20.0	4.4	0.0	0.4	0.0	0.1	5.8	0.1	0.0
bw8	67.9	0.7	16.5	5.3	0.0	0.3	0.0	0.1	4.2	0.1	0.0
les3	41.3	0.8	7.3	44.0	<0.01	<0.01	0.1	<0.01	0.9	0.2	0.0
sz1	44.3	0.6	26.7	16.7	0.1	0.6	0.0	0.0	0.3	0.0	0.0
sz2	46.2	3.3	34.9	0.6	0.0	0.1	0.0	0.0	0.1	0.2	0.0
za2	47.9	1.7	34.0	1.7	0.0	0.1	0.0	0.0	0.6	0.0	0.1
za5	60.6	0.8	18.8	9.4	0.0	0.5	0.0	0.0	2.5	0.1	0.0
za6	69.0	0.7	17.6	3.1	0.0	0.9	0.4	0.4	4.3	0.2	0.0
za8	78.1	0.0	0.3	1.8	0.0	0.0	0.2	0.0	0.0	0.0	0.0
za8a	24.8	2.8	33.4	32.1	0.1	0.7	0.5	0.0	0.6	0.3	0.1
za8b	72.6	0.6	6.6	4.5	0.0	1.0	0.1	0.0	0.5	0.1	0.0
za8b1	18.5	2.4	31.2	30.6	0.2	0.3	0.0	0.0	0.3	0.2	0.1
za8c	42.4	2.0	19.6	21.9	0.1	1.0	1.8	0.1	0.1	0.1	0.1
za9	62.5	0.8	18.7	6.7	0.0	0.5	0.0	0.0	3.6	0.1	0.0
za10	25.5	0.1	6.8	2.8	0.1	13.4	20.4	0.5	0.2	0.0	0.0
za11a	52.8	1.8	14.3	16.5	0.1	1.3	2.2	0.4	0.2	0.0	0.0
za11c	53.9	1.7	15.1	16.7	0.1	1.4	0.9	1.1	0.2	0.1	0.0
za12	5.9	0.1	2.2	87.3	0.8	0.0	0.0	0.0	0.2	0.1	0.1
za13a	48.8	2.2	20.4	15.8	0.1	0.7	0.8	1.1	0.1	0.01	0.0
za13b	78.2	0.8	7.8	5.3	0.1	0.5	0.8	0.7	0.8	<0.01	0.0
les1	1.3	0.3	0.3	94.0	0.0	0.0	<0.0	0.0	<0.0	<0.0	0.1
les2	44.5	0.8	7.2	46.2	<0.01	0.1	0.1	<0.01	0.9	0.0	0.0
za3	23.6	2.9	36.3	34.6	0.0	0.3	0.4	0.0	0.4	0.2	0.1
za3a	91.1	0.0	0.9	5.4	0.4	0.2	0.0	0.0	0.0	0.0	0.0
za3b	96.0	0.0	0.3	2.3	0.1	0.1	0.0	0.0	0.0	0.0	0.0
za15	0	1	20	0	18	0	8	16	149	19	0
za19	0	5	14	0	8	9	0	33	88	18	0

Table 4: XRF trace element content of *letsoku* samples (ppm)

sa ID	As	Cu	Ga	Mo	Nb	Ni	Pb	Rb	Sr	Th	U	W	Y	Zn	Zr
za1	0	8	33	0	8	19	0	50	5	0	0	1	49	85	177
za7	0	38	25	0	2	25	0	11	9	0	0	1	10	66	131
za11b	7	107	29	0	14	87	0	8	38	0	0	9	44	41	387
zm1	0	6	0	0	0	49	0	0	383	0	0	1	4	158	96
bw1	50	12	33	6	32	20	0	206	20	12	0	94	82	30	711
bw1a	355	75	34	14	22	61	0	177	25	1	0	14	83	31	607
bw2	63	10	34	6	35	21	0	216	19	18	0	47	104	34	714
bw2a	80	13	40	10	44	29	0	254	13	24	4	26	166	16	909
bw3	31	6	32	5	34	12	0	218	20	15	0	61	83	14	684
bw3a	35	5	37	7	40	12	0	247	24	20	0	26	116	9	801
bw4	9	13	20	0	13	24	0	105	75	0	0	128	44	21	434
bw5	0	0	0	0	0	30	0	0	162	0	0	1	0	0	64
bw6	66	9	35	7	35	17	0	224	20	15	0	38	97	23	755
bw6a	57	6	39	9	41	12	0	249	20	22	1	19	115	9	833
bw7	66	11	36	7	35	24	0	232	17	18	0	31	105	12	761
bw8	55	0	30	62	68	0	73	194	35	46	95	56	122	21	616
les3	0	2	15	0	2	4	0	17	23	0	0	27	3	9	255
sz1	0	61	23	0	2	133	0	9	0	0	0	30	12	71	107
sz2	13	3	37	19	75	12	104	11	64	94	4	1	60	9	1160
za 2	8	2	29	0	6	0	0	21	0	0	0	1	0	8	182
za5	20	29	24	0	14	18	0	144	32	10	0	5	33	84	173
za6	11	15	23	0	16	12	23	216	86	13	0	15	40	56	267
za8	0	386	34	3	10	285	37	6	0	0	0	1	0	40	188
za8a	0	463	36	0	2	247	0	11	20	0	0	9	1	50	193
za8b	0	102	8	0	8	62	0	19	12	4	0	151	1	41	137
za8b1	0	372	29	0	1	281	0	2	0	0	0	1	0	29	182
za8c	0	226	25	0	4	133	0	0	60	0	0	1	31	71	172
za9	1	20	24	0	16	13	14	173	22	13	0	5	32	47	218
za10	0	5	3	0	0	37	0	8	424	0	0	1	0	16	38
za11a	0	97	19	0	8	111	0	9	57	0	0	9	29	50	279
za11c	0	92	22	0	8	71	0	9	98	0	0	1	34	49	350
za12	0	0	0	0	0	22	0	0	198	0	0	1	0	0	52
za13a	0	122	27	0	11	88	0	6	30	0	0	6	41	43	351
za13b	2	38	7	0	6	31	0	34	44	0	0	88	10	29	317
les1	0	50	0	0	0	46	0	0	0	0	0	1	0	933	1
les2	0	0	26	0	779	566	0	0	0	0	0	197	0	281	532
za3	120	6	0	0	0	56	0	0	11	0	0	114	0	23	2
za3a	70	0	3	49	37	18	54	22	32	24	74	135	28	18	32
za15	0	1	20	0	18	0	8	16	149	19	0	1	17	59	166
za19	0	5	14	0	8	9	0	33	88	18	0	1	14	48	142

highest for a sample from Swaziland (3.3 % m/m TiO_2) but none was detected in some other samples e.g. those from Mpumalanga and Venda.

Trace metal analysis shown in Table 4 yielded the highest arsenic content of 355 ppm and it was found in sample bw1a from Botswana. However, none was detected in most other samples from Botswana, Eastern Cape, Gauteng, KwaZuluNatal, Makurung, Lesotho, Freestate, Swaziland, Zimbabwe and Venda. Lead was detected in six samples (bw8, sz2, za3a, za8, za6 and za9) with the highest value reaching 104 ppm Pb for a sample from Swaziland. Other maximum level of trace metals found (and their origin) were 1160 ppm zircon (Swaziland), 933 ppm zinc (Lesotho), 254 ppm rubidium (Botswana), and 95 ppm uranium (sample za3a).

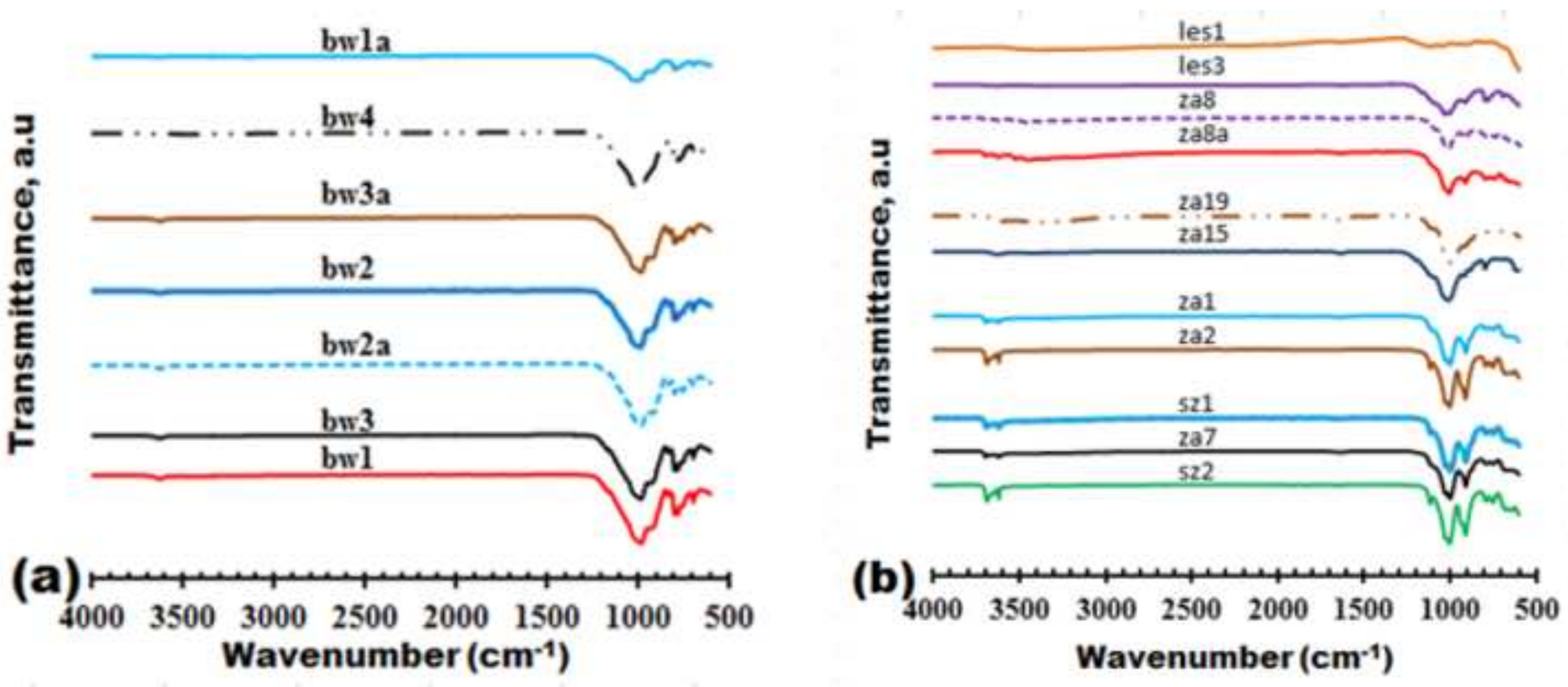
3.2.4 SEM

Fig. 3b shows micrographs of selected *letsoku* samples from the various regions in Southern Africa. The particle morphologies range from agglomerated structures comprising small globular sub-particles, to fibrous forms and platelets. Botswana sample bw2a contains muscovite, quartz and minor amounts of kaolinite. Lesotho sample les1 shows relatively darker particles which could be hematite. The second micrograph for sample les1 reveals, what appears to be, agglomerated nanoparticles. Most of the other micrographs show the presence of quartz grains. Gauteng sample za1 shows kaolinite platelets. The Mtubatuba, Kwa-Zulu Natal sample za11a features agglomerates of quartz, smectite with kaolinite platelets and plagioclase particles as impurities. Both Botswana sample bw6 and the Engcobo, Eastern Cape sample za6 contained muscovite flakes and quartz. Venda sample za8a contains mostly Gibbsite but kaolinite and quartz grains are also present. Zimbabwe sample zm1 and Swaziland sample sz2 are mainly composed of kaolinite platelets. Sample za10 is dolomite in which small crystals are embedded, together with smectite flakes. The latter are also seen in sample za8c.

3.2.5 FTIR Spectra

The FTIR spectra of virtually all the **representative samples in Fig. 4** revealed a conspicuous absence of a band at 1230–1280 cm^{-1} ((Morekhure- Mphahlele R, 2017) except for the very slight hump in les1 and za19 (the commercial montmorillonite used as a control). This also implies the absence of

Figure 4 Letsoku IR spectra from the Perkin Elmer Spectrum 100 Series ATR-FTIR (Institute of Applied Materials, Department of Chemical Engineering, University of Pretoria).



amorphous silica. In addition, there is an absence of bands near 3000 cm^{-1}. This implies that very little, if any, organic material is actually present. This negates any implication of the XRF LOI results indicating the presence of organic material. This also disadvantages these clayey soils for use as amorphous biogenic silica (Gomes and Silva, 2007) for skin rejuvenation.

4. Discussion

The expectation that *letsoku* is essentially an ochre-like earth was confirmed. Rather surprising was the wide-ranging diversity in the mineral composition. Versions containing kaolinite and muscovite occurred more frequently than those comprising smectite clays, and some samples were exceptionally rich in quartz. In fact, some amount of quartz was present in each and every sample collected. The main mineral present in the various samples was not even the same. In decreasing frequency, the main constituents were quartz (37%), muscovite (18%), kaolinite (16%), hematite, gibbsite and smectite each at 8%, and ilmenite and dolomite each at 3%. Kaolinite and muscovite were present in 61% and 56% of the samples respectively.

Discrepancies may occur between XRD and XRF results such as the TiO_2 in sz2 and za13a. The former sample has no rutile nor anatase but 3.3 % m/m TiO_2 whilst the latter has 5.4 % m/m anatase against 2.2 % m/m TiO_2. This might be due to inhomogeneous or non-representative sample in handling small amounts in preparing the discs for XRD and XRF. This is compounded by the back calculations that may be involved in expressing Ti as TiO_2. The mineral combinations indicated under 3.2.2 demonstrate that in spite of the observed heterogeneity in mineral composition, some degree of commonality may be identified. This implies that functionality may override the diversity of the regions of sampling.

Cosmetic applications were indicated as the principal *letsoku* function. In this, color is usually an important factor. This links with the realization that two thirds of the collected samples contained one or more iron mineral with strong pigmenting properties. Even those samples with a very high quartz content had a reddish color caused by the presence of iron oxide.

In addition, the gritty quartz particles, present in some of the samples, probably provided an abrasive function suitable for skin cleansing. Clay minerals were the main constituent in most of those samples that were essentially free of iron. In these materials the adsorption properties possibly provided the desired function. These two aspects are explored in more detail below.

Color varies widely for all clayey soils. In this case, this could be due to the mineral composition, the iron oxidation state and the moisture content. The variation of color with Fe(II), Fe(II, III) and Fe(III) oxidation states is illustrated by the oxides in grey-brown ilmenite, black magnetite, red hematite and brownish-yellow goethite respectively. The highest Fe(III) content was detected in the hematite sample les1. The hydrated iron oxide goethite features as a pigment in cosmetic products such as lipstick and foundations.

The colloidal nature of the clays, with the associated high surface area of the platelets and the nature of the surfaces, the charge, cation exchange capacity and exchangeable bases influence the clay absorption properties. The BET surface area values, that were recorded for the present smectite-containing samples, accord with those reported by Fakhfakh et al. (2005) (56 - 119 $m^2\ g^{-1}$). In retrospect, the utility of kaolinite as a major ingredient in some *letsoku* samples is not that unusual as it finds application in modern cosmetics, e.g. facial masks. Here these minerals provide opacity to cover, for example, blemishes or to remove grease and toxins from the skin (Carretero and Pozo, 2010; Favero et al., 2016). A similar argument holds for the presence of non-swelling 2:1 muscovite in some of the *letsoku* samples. Modern creams include it as an ingredient to produce a luminous skin effect. Muscovite emulates the mica that is used for its high reflectance and iridescence in eye shades and lipsticks (Carretero and Pozo, 2010).

Gibbsite, also known as hydrargillite, is an ore of aluminum and makes up one of the minerals of bauxite. It is a natural version of the amphoteric aluminum hydroxide, α-$Al(OH)_3$ and hence can act as a buffer. Gibbsite is currently present in more than five hundred modern cosmetic products including eye cosmetics, suntan products, lipsticks and various skin care products (Bocca et al., 2014). Gibbsite versions of *letsoku* may offer similar advantages.

The oxides anatase and rutile have high refractive indices and therefore good light scattering properties that make them ideal for sun protection. Sample les2 contains mostly TiO_2 containing ilmenite, which is familiar to the Basotho people as the black pigment *sekama* (Ambrose et al., 2001).

The natural pH of skin is about 5.5 and skin cosmetics should approximate that value (Carretero et al., 2006). The highly basic pH values measured for samples les2, zm1, za11a and za13 could therefore be a problem for topical applications. This would especially be the case if left in contact with the skin for lengthy periods (Matike et al., 2011). The variability in pH of the iron mineral-containing slurries is remarkable. The les1 hematite slurry had a pH of 5.2 while it was 7.3 for the black sample les2 that contained Fe (II, III). Only 4/39 samples (za8c, za10, za11a and za11c) contain smectite. The values for smectite/pH are as follows: 67.3 % m/m and 6.09; 10.0 % m/m and 8.35; 58.0 % m/m and 7.94; 61.2 % m/m and 7.96 respectively

As previously mentioned, the typical supply forms for *letsoku* are rolled balls and fine powders. The latter may produce dusts under certain circumstances. The Occupational Safety and Health Administration (OSHA) prescribes limits for nuisance dusts and those generated by specific substances. The recommended limit for nuisance dusts, e.g. kaolinite, is 15 mg m^{-3} total dust and 5 mg m^{-3} respiratory exposure over an 8 hour workday. However, prolonged exposure or even inhalation of silica dust poses a high risk of developing silicosis and cancer (Fubini et al., 1995). All the samples contained quartz which, in view of this classification, implies that *letsoku* dust may have a propensity to be carcinogenic hence limits to exposure are recommended.

Trace metals may be allowed in cosmetics provided they do not pose a potential health hazard. Control may be exercised by complete exclusion or by limiting the amounts to comply with stipulated levels. The latter are recommended by regulatory bodies such as the International Cooperation on Cosmetic Regulation (ICCR) comprising FDA, Japan ministry of Health, European Directorate General for Enterprise and Industry and Health Canada. Carretero et al. (2013) warns about the dangers of dermal absorption of the trace metals which, additionally is exacerbated by high quartz levels (Khiari et al., 2014). Orisakwe and Otaraku (2013) report how topically applied cosmetics may inadvertently gain access to mucous linings of the mouth (lipstick) or eye interior (eye shadow). However, a distinction must be made between free metals and those trapped or fixed in other mineral lattices. In addition, cognizance should be taken with respect to the natural abundance of elements in soils (Shacklette and Boerngen, 1984).

The toxic heavy metals refer in particular to cadmium, mercury, lead and arsenic. They appear in the World Health Organization's list of the ten chemicals of major public concern (Andrade et al., 2017). Fortunately, cadmium and mercury were not detected in any of the *letsoku* samples. The maximum level for lead as an impurity in cosmetic products is 10 ppm (Al-Saleh et al., 2009). Only sample sz2 contained a measurable amount of lead at 115 ppm. The recommended limit for arsenic is just 3 ppm and 15 % of the present letsoku samples exceeded that level. The arsenic content of 41 % of the *letsoku* samples exceeded the Health Canada limit of 3 ppm. Only sample bw8 contained uranium (95 ppm), an element linked to cancer with the potential to damage DNA and the lungs.

Nickel can cause allergic contact dermatitis. The natural abundance in US soils is 19 ppm (Shacklette and Boerngen, 1984) and quite a number of *letsoku* samples exceeded that level by more than an order of magnitude. Copper promotes hair growth, hence its inclusion in eyelash enhancing serum. However, high copper levels cause acne and even lead to hair loss. The copper content was highest for the Venda samples za8 (372 ppm) and za8c (226 ppm). The KwaZulu-Natal samples also registered fairly high results za11a (97 ppm) and za13a (122 ppm). Unusual contrasting results were found for two sets of samples obtained from the same region: les1 (50 ppm) and les2 (0 ppm) from Lesotho and sz1 (61 ppm) and sz2 (3 ppm) from Swaziland. The natural abundance of copper in US soils is 25 ppm (Shacklette and Boerngen, 1984) and similar or lower levels were found in sample za5 (29 ppm) and Botswana samples bw4 (13 ppm), bw1 (12 ppm) and bw3 (6 ppm).

The natural abundance of strontium in US soils is 240 ppm and most of the present samples featured significantly lower concentrations. Exceptions were samples zm1 and za10. Addition of strontium salts to topical formulations can decrease the signs and symptoms of irritant skin contact dermatitis (Hahn, 1999). Zirconium compounds are generally considered to be of low toxicity and therefore the relatively high values found in the *letsoku* samples are of no concern.

Rationalizing traditional beliefs is a highly challenging problem as subjective components of indigenous knowledge are difficult, if not impossible, to justify (Barrera-Bassols and Zinck, 2003). The present study did not take into consideration the socio-cultural contexts from which the traditional beliefs and practices are derived. In order to give justice to this topic an integrated approach is required and it is necessary to consider the relevance of the cultural context and to elaborate on concepts such as the “body sick parts”, “evil spirits”, and different stages in initiation (Barrera-Bassols and Zinck, 2003; Krasilnikov and Tabor, 2003). These ideas most likely also play a role in the application of *letsoku* in the cultural context. Artwork, similarly, is a common activity which dates back to the middle stone age era (Pahl, 1974).

The thematic therapeutic categories included aspects such as chicken pox treatment, ulcer remedies and blood circulation improvement. These also raise validity challenges related to potential modes of action. Current studies in medical geology delve into the impact of clays on human health (Buck et al., 2016; Londono and Williams, 2016). For example, Fe(II) in goethite has been linked to some form of transmission mechanism (Mustafa et al., 2006). Whether *letsoku* involves any of the above-mentioned is a matter for further investigation.

5. Conclusion

Clay samples sourced via traditional healers, or purchased from traditional products outlets in Southern Africa, were analyzed. These clayey soils, some known as *letsoku* in the Sotho language, are supplied in either a wet state or as dry powders and are reportedly used as topical cosmetics with health benefits. XRD analysis revealed a surprising variability in the mineralogical composition of these soils, even in samples obtained from the same region. This implies that the actual applications must be robust with respect to clay composition. XRF analysis showed that the samples were free from radioactive elements and the toxic elements Hg and Cd. However, some samples did contain unacceptable levels of some heavy metals, e.g. As, Pb, Cu, Zn, Ni, etc. Another disconcerting discovery is the high silica content, as high as 96.0 % m/m. Even though the intended purpose relates to topical applications, these levels may pose a certain health risk to users.

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