The Chemistry of Cosmetic and Therapeutic Clays from Isinuka Springs in Port St Johns, South Africa

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Abstract

Clay from Isinuka springs in Port St Johns area of the Eastern Cape of South Africa, are used by local people for cosmetic purposes and for treatment of an array of ailments and diseases. This study tries to relate the acclaimed cosmetic and therapeutic properties of the clay to its mineralogical composition and physico-chemical properties. It reveals that the clay from this area, though useful for therapy and cosmetics, effectively constitute a health risk. Clay samples from Insinuka were dried and subjected to pH measurement, loss on ignition (LOI), particle size distribution, sulfur content and X-ray Fluorescence (XRF) analyses leading to the detection of As, Co, Cr, Cu, Ni, Pb, Sr, U and Zn concentrations in the samples. The highest mean concentration of element recorded was strontium with a mean value of 2550 ppm. The samples were all alkaline. Based on the data analysis, dermatological properties of the clays can be ascribed to the presence of sulfur and arsenic in the samples. A microbiological analysis of the samples may further shed some light on the alleged medicinal properties of the clays.

Keywords*: Clays, therapeutic, cosmetics, chemicals, spring water, Isinuka*

1. Introduction

Clay refers to soil particles that are generally less than 2 *μm* in diameter (Heckroodt 1991; Nkoma and Ekosse 1999; Ekosse 2000; Gomes and Silva 2007) and occur widely in many parts of the world. Their use by humans and animals for various purposes dates back many centuries, evident from data traced back to 60 BC (Carretaro, 2002). In the advent of modern science there is renewed interest in clays both in rural and in urban communities and their uses encompass the making of bricks, ceramics, pottery, tiles, paint, medicine, cosmetics, filling and coating (Heckroodt 1991; Nkoma and Ekosse 1999; Mpuchane et al. 2008). While there is ongoing research into finding new applications for clays, there is also a deep rooted urge amongst researchers to explore the ancient applications of clays worldwide especially in Africa where clays in one way or the other influence the lives of most of the rural people. The use of clays by native Africans is not limited to the making of pottery and housing construction. Clays form an integral part of their cosmetic and traditional medical practice for the treatment of an array of ailments and diseases. The World Health Organization (WHO) has recognized traditional medicine as an invaluable means of satisfying the basic health care needs of about 80 % of the world's population (WHO, 1996).

In open African markets, clays of various shades and colors are sold for use in cosmetic, medicinal and dermatological applications. The Yorubas of Nigeria use clay as a cure against dysentery and cholera (Ademuwagun et al. 1979). Other uses include poultices as cure for ulcers, for cleansing purposes, detoxification, adsorption, skin emulsifiers, and cation exchange (Mpuchane et al. 2008). In Mali, the victims of smallpox are usually covered with clay poultice (Ademuwagun et al. 1979). Red ochre is used in the grasslands of Cameroon and also in Swaziland (Mpuchane et al. 2008) to culturally cement marriages, while the Maasai of Kenya smear male initiates with it from head to toe and this is believed to cleanse their skin from impurities as they progress into the next stage of life. In Namibia, the Himba tribe particularly the women use *ortijze*, a red clay to cover their entire body and this is believed to signify ideal Himba beauty and according to Namibia Direct (2006), the clay gives the body a mahogany color which provides a reddish glow under the desert sun and protects it from ultraviolet radiation. The use of clays by Africans to establish tribal uniqueness has been recorded (Ettagale 1999; Jefkins-Elnekave 2006). In Kenya, the Samburu tribe appears distinctly different from the Maasai and other surrounding tribes by their intricate and elaborate clay cosmetic decorations (Zijlma 2004).

In the Transkei region of South Africa, it is not uncommon to see women's faces covered with white, yellow or black clay, as a cosmetic, and/or protection against damaging sun rays. The same is true of male and female traditional initiates who cover their entire bodies with *ingceke*, a white clay during their annual rite of passage rituals (Ettagale, 1999). In Pondoland, children playing in courtyards are often smeared with the clay to protect them from dirt, insect bites and adverse effects of the sun (Ettagale, 1999). It is widely believed that clays originating from Isinuka valley about 20 kilometers west of Port St Johns in Eastern Cape are unique in South Africa for their efficacy as cosmetic and therapeutic agents. Stories of the healing qualities of the spring water and clays from this area abound. Reports (May, 1880) of the smell of sulfur dioxide from the spring and/or clay mine dates back hundreds of years. People come from far and wide to access treatment from this valley. While the spring water quality analysis has been reported (Faniran et al. 2001), there is little or no documentation on the chemical composition of the clays that the people mine and use from the area. It is imperative that research be carried out on Isinuka clays to relate their acclaimed cosmetic and therapeutic properties to their mineralogical composition and physic-chemical properties.

2. Materials and Methods

Ten samples of clayey materials used for cosmetic and therapeutic purposes were collected from Isinuka village in the Eastern Cape Province, South Africa. Four of the samples (Samples 1, 2, 3 and 4) were collected from a cave beneath a rock outcrop where water drips constantly from the roof of the cave onto a marshy slippery white clayey sedimentary material claimed to be used for the treatment of skin diseases and skin care (Faniran et al. 2001). These samples were whitish in colour. Four other samples (Samples 5, 6, S 7, and 8) were collected from the most popular pond-like spring located on top of the rock outcrop. This spring which is where the visitors bath is about 2 m wide. The spring emits a sulfur dioxide-like odour, and the water is turbid and dark greyish in colour and used by visitors for curing acne and other skin diseases (Faniran et al. 2001). The last two samples (Samples 9 and 10) were collected from a much less frequented man-made pond about 50 m below the village hidden in the woods.

The samples were air-dried, and analysed for selected physicochemical and chemical properties at Council for Geoscience in Pretoria, South Africa. Whereas the pH of the samples was determined in a clay water suspension, the particle size distribution of the samples were determined using a Malvern Masterizer 2000 Laser Particle size analyzer fitted with a Hydro 2000G dispersion unit. The concentrations of selected trace elements were determined using a PAN Analytical Axios, sequential WDXRF spectrometer equipped with a 4 kW Rh tube. Concentrations of trace elements were determined in pressed powder pellets each comprising of a sample mixed with Hoechst wax. An amphibolite reference material was used for quality control of the data generated. Methods used for XRF analyses are described in Council for Geosciences (2011), and (Fitton 1997).

3. Results and Discussions

3.1 pH of samples

The pH of the samples ranged from 7.94 – 10.05, indicating that the samples were all alkaline. Samples 1 to 4 from the cave exhibited an average pH of 9.9 (strongly alkaline) compared to the average pH of 8.0 (moderately alkaline) for samples 5 –10 collected from the open springs. The alkaline pH values of the samples brings to question the possibility of using these clays to cure acne as has been reported to be the case with water from the spring with an average pH of 8.0 (Faniran et al. 2001). The pH of normal human skin ranges between 5.4 – 5.9 (Braun-Falco and Korting, 1986). Such high alkalinity may have an adverse effect on the skin if the clay is applied directly without any pretreatment or neutralization. The skin's pH according to (Siegenthaler, 2005) is the major factor influencing acne and other skin diseases. *Propionibacterium acnes* which causes acne thrives more on alkaline skin. Continuous application of alkaline clays on the skin may cause skin pH to increase promoting rather than preventing the development of acne. However, native Africans generally possess knowledge of clay preparations for cosmetic and/or medicinal purposes suitable for the nature of their skin.

3.2 Loss on ignition (LOI) of samples

Loss on ignition values varied between 5.87 and 40 % which indicates that these samples may have high water retaining properties. The loss on ignition was much more profound with samples 5 - 10 reaching a maximum of 40 % with sample 5 as depicted on Fig. 1. The high values for L.O.I. may also indicate that the samples minerals retain water and may therefore serve as moisturizers. A combination of high pH and high L.O I. for these samples may imply that skin dryness that is caused by alkaline pH may not be experienced upon application of these samples on the skin since they may also serve as moisturizers.

3.3 Sulfur content

Since the spring water and clays are claimed to have medicinal properties and a pungent sulfur dioxide-like smell oozing out of the springs, it was important to test for the sulfur content of the samples collected. All samples had sulfur content < 1.5 %. Samples 1 – 4 collected from inside the cave where there is no noticeable pungent gaseous smell, had lower concentrations of sulfur compared to those from the open springs. Despite lower concentrations of sulfur in samples from the cave, visitors nevertheless collect the material and use it for topical applications. Continual saturation of the whitish clay with saline water dripping from the roof of the cave might result in improving its medicinal properties. The use of bath salts for therapeutic purposes is well known. The sulfur content in samples collected from the open springs was above 0.8 %, rising to 1.3 % in sample 9 (Fig. 2). The use of sulfur in dermatological applications is well established due to its antifungal, antibacterial and keratolytic activities (Gupta and Nicol, 2004).The sulfur content in the samples may add value to the healing properties claimed.

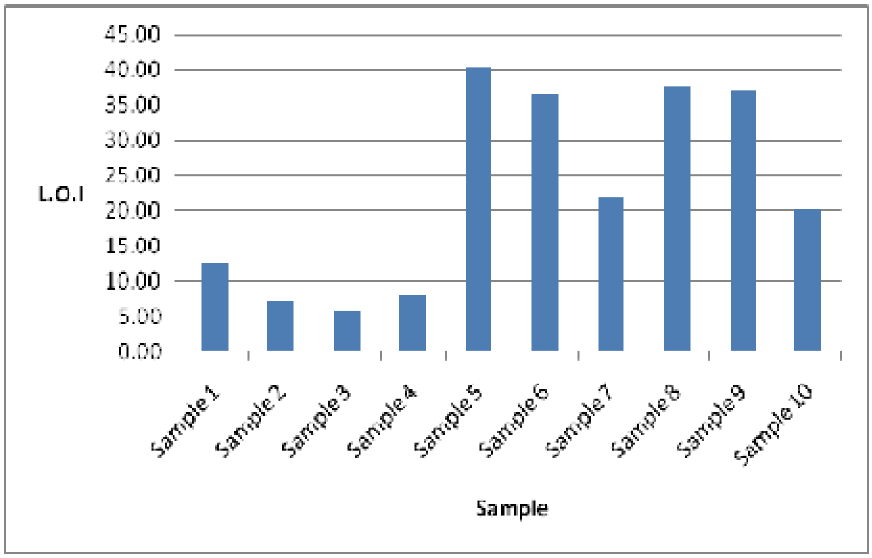

Figure1. Loss on ignition of clay samples

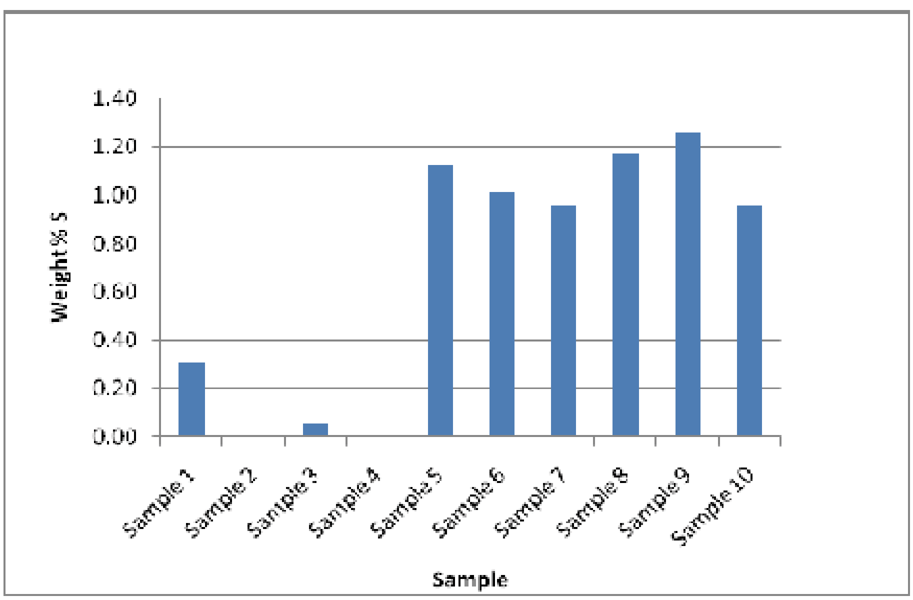

Figure 2. Weight % content of sulfur in clay samples

3.4 Particle size distribution of samples (PSD)

The samples had varied particle sizes with majority of the samples having silt as the dominant particle size. Two groups of PSD were observed (Fig 3). Samples 7, 8, 9 and 10 had finer particles than the others. The samples were therefore classified as either silt, silt loam or loam (Figure 4). Particle size plays an important role in the application of clays for cosmetic or medicinal purposes. If the material comprises of coarse particles, it may cause abrasion and damage the skin. The particle size distribution of the material may also influence its healing properties through its influence on cation exchange properties. High clay content may imply high cation exchange and adsorption properties which may play a role in the cleansing properties of the material. In addition, Particle size has been reported to play a significant role in the use of soils and clays as skin protectors because of their influence on refractive index (Hewitt, 1992; Hoang-Minh et al., 2010). The smaller the particle size, the greater the surface area of the material and the greater its potential as a cleanser.

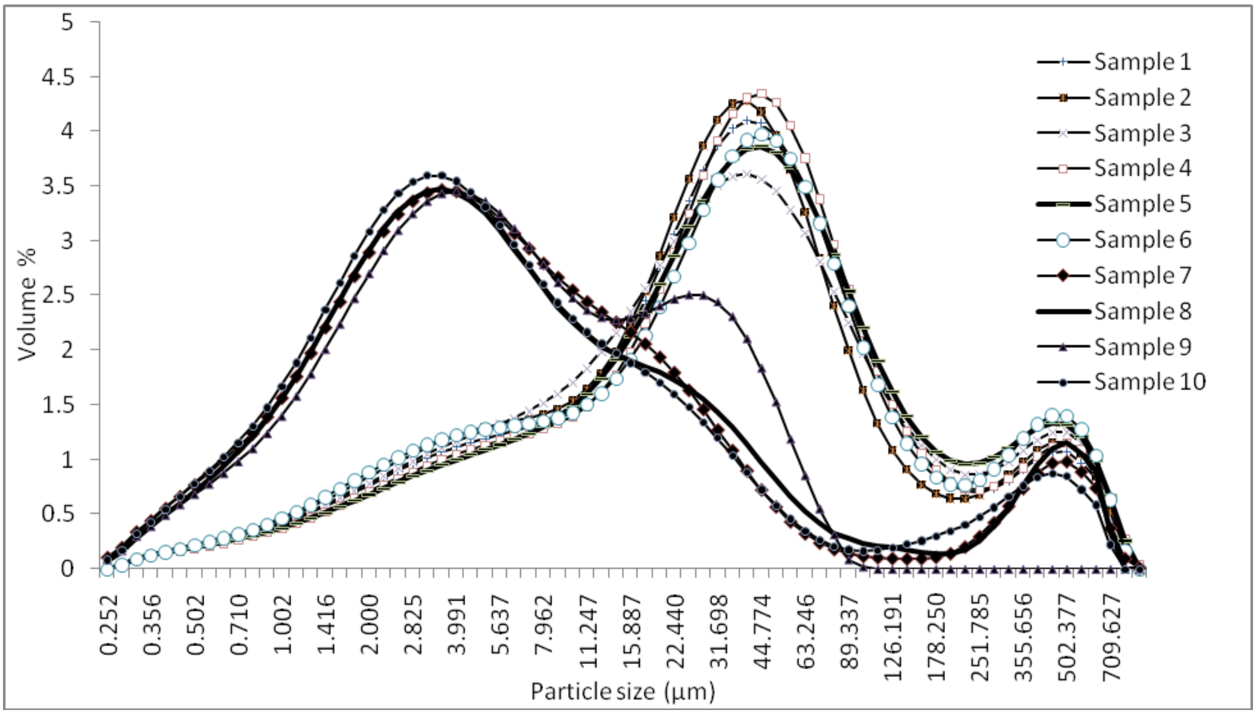

Figure 3. Particle size distribution of clay samples 1-10

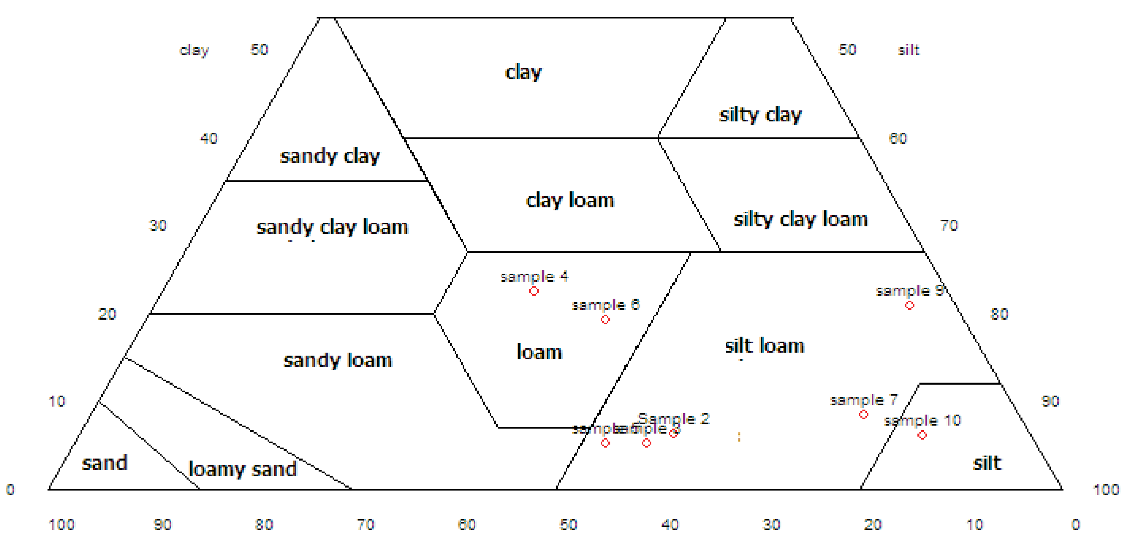

Figure 4. Texture of samples

3.5 Trace element concentration in samples

Substances applied to the skin can penetrate the skin and be able to cause local and systemic effects (Van der Bijl et al. 2000). The bromine concentration (Fig. 5) though comparatively small in samples 1- 4, ranges from about 20 - 100 ppm in samples 5-10 with a mean value of 66 ppm. This may be ascribed to the saline nature of the water in which the clay is imbedded. The concentrations of heavy metals in the samples are summarized in figures 5 to 13. Arsenic (Fig. 6) was found in all the samples tested although the concentrations are low ranging from 6-15ppm with a mean value of 9.6 ppm. Although arsenic has a history of medicinal applications (Antman, 2001, Roy and Saha, 2002), it is nevertheless an extremely toxic element and can cause severe damage to human health even at low concentrations on repeated contact exposure. The concentrations of cobalt (Fig. 7) range from 4 to about 17 ppm while chromium (Fig. 8) has concentrations that are fairly evenly distributed across all samples ranging from about 55-90 ppm with a mean value of about 70 ppm. Copper (Fig. 9) and nickel (Fig. 10) have an almost equal distribution pattern in all samples but exhibit mean concentrations 38 and 21 ppm, respectively. Higher lead concentrations are seen in white clay samples 1-4 (Fig. 11) with a mean of 30 ppm as compared to black clays samples 5-10 with a mean value of 17 ppm. The mean values of strontium (Fig. 12) in white samples 1-4 is about 225 ppm while that in black samples is 2550 ppm, a sharp difference in concentration between the white and black clays. The highest concentration of uranium (Fig. 13) in white clays is 2.8 ppm while black clays exhibit a maximum value of 8.5 ppm. Zinc (Fig 14) exhibit a similar distribution pattern across all samples with a mean concentration value of about 88 ppm.

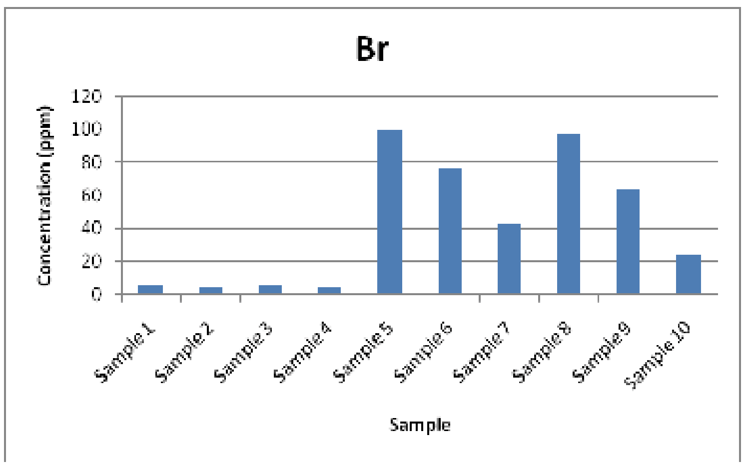

Figure 5. Bromide ion concentration in the clay samples from Isinuka

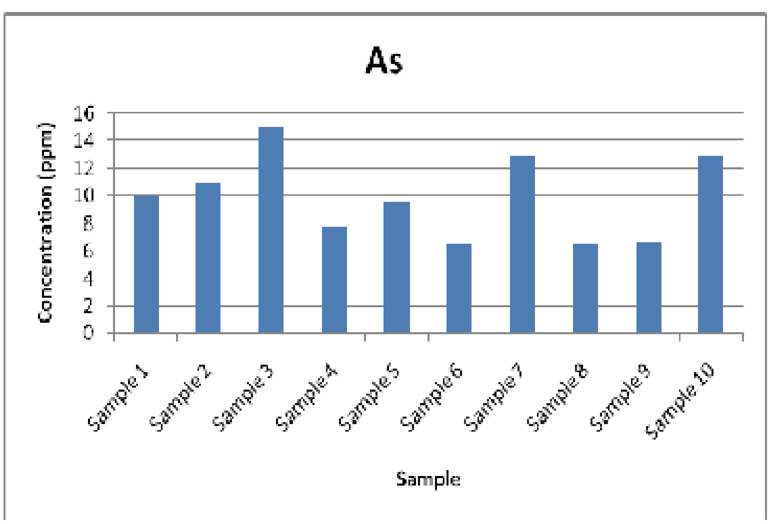

Figure 6. Arsenic concentration in the clay samples from Isinuka

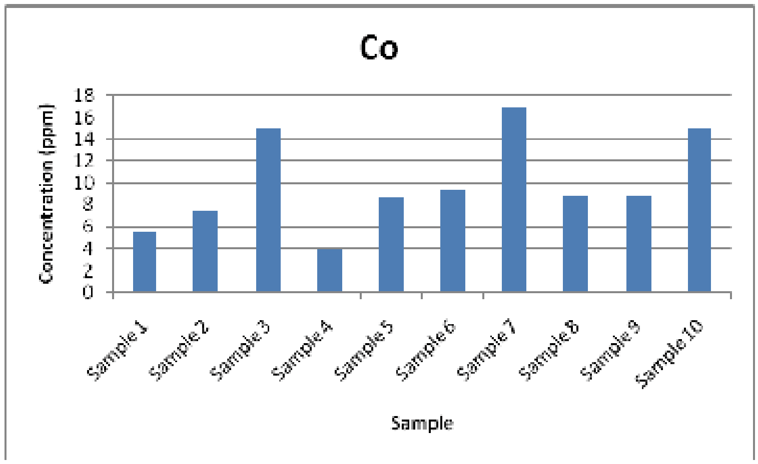

Figure 7. Cobalt concentration in the clay samples from Isinuka

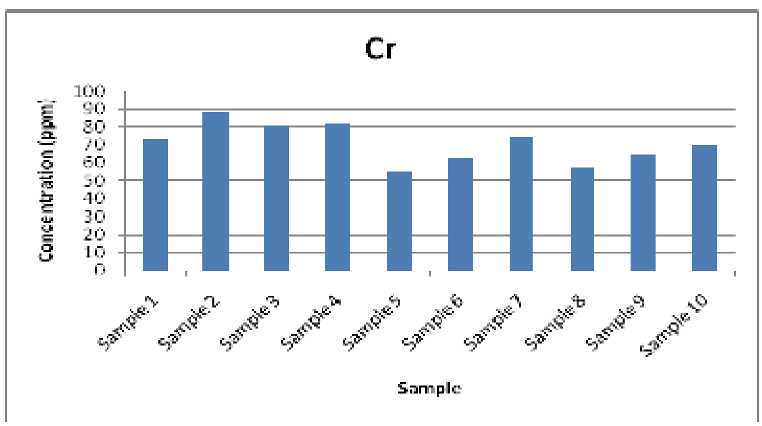

Figure 8. Cromium concentration in the clay samples from Isinuka

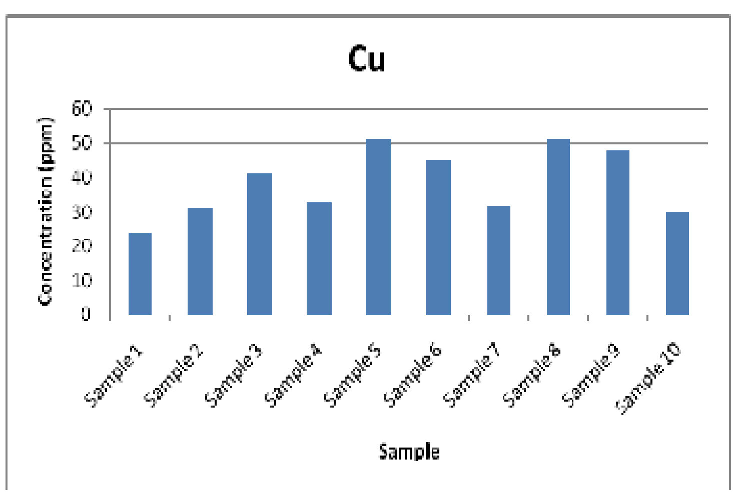

Figure 9. Copper concentration in the clay samples from Isinuka

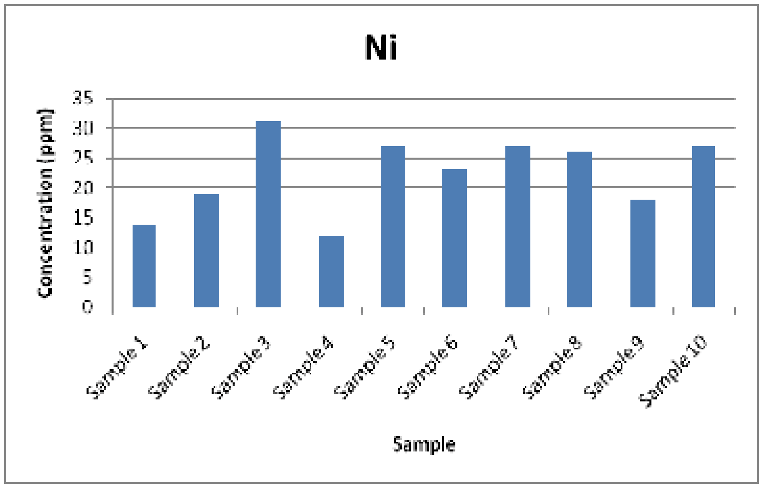

Figure 10. Nickel concentration in the clay samples from Isinuka

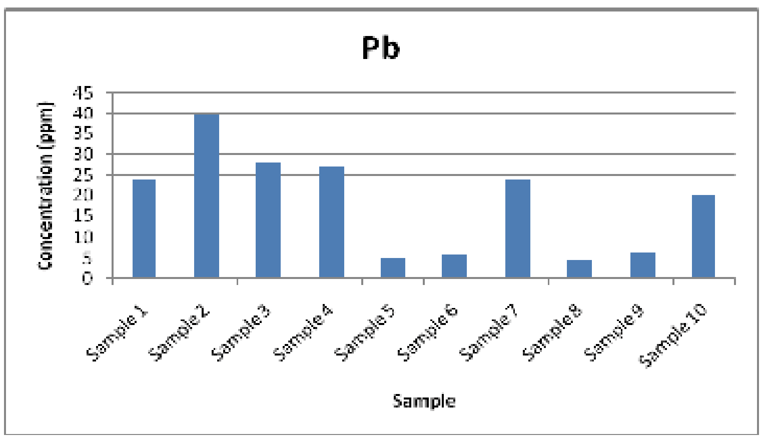

Figure 11. Lead concentration in the clay samples from Isinuka

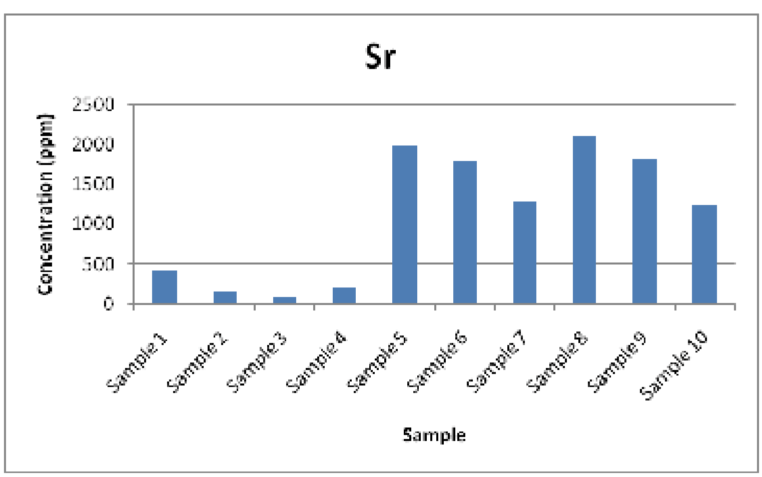

Figure12. Strontium concentration in the clay samples from Isinuka

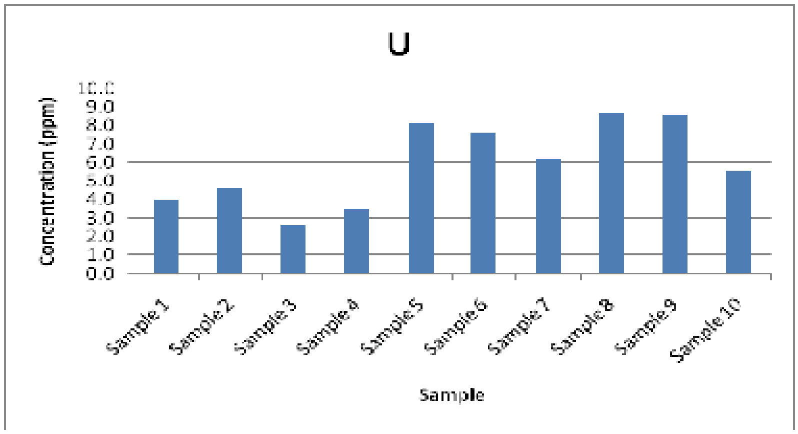

Figure 13. Uranium concentration in the clay samples from Isinuka

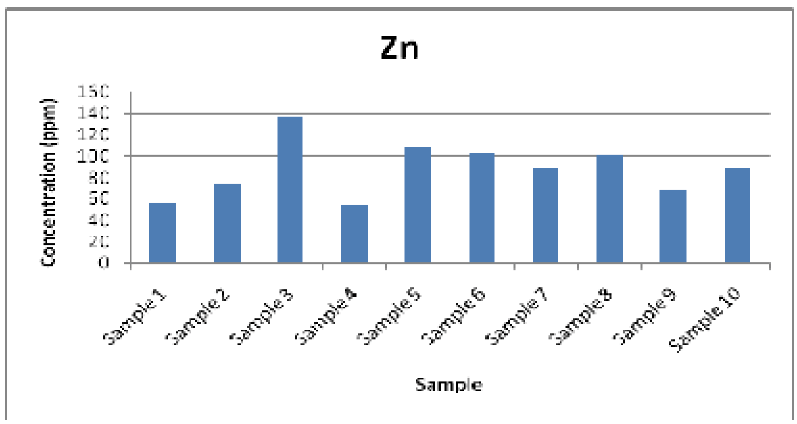

Figure 14. Zinc concentration in the clay samples from Isinuka

4. Conclusion

This paper has examined some physico-chemical properties of whitish and blackish silty material from Isinuka springs used for cosmetic and dermatological applications by the inhabitants of Isinuka, Port St Johns, the surrounding villages and towns in Pondoland of the Eastern Cape of South Africa. From the analytical data, the healing properties of the clays can be ascribed in part to the presence of sulfur known for its antibacterial and antifungal properties and the alkaline pH of the samples. Furthermore, the presence of arsenic either alone or in combination with sulfur and other elements may be responsible for the healing properties claimed. Arsenic has a history of medical applications dating back centuries prior to the arrival of penicillin as a cure against syphilis, yaws and other bacterial infections (Roy and Saha, 2002). It is a human carcinogen and extremely toxic. Although the concentrations in the Isinuka clays are considerably small with an average value of only 9.6 ppm, repeated exposure could pose a health risk and should be avoided. The presence of lead especially in the white clays is small but could be a problem on repeated topical application of the clays given the established toxicity of lead. In fact the fall of the Roman Empire was ascribed to the use of lead vessels for storing wine and water that poisoned the entire population (Gomes and Silva, 2007). Although all the elements listed in this study have some degree of negative health implications (Bensalah et al. 1998; ATSDR 2011), their low concentrations are a consoling factor inspite of the mean value of strontium being as high as 2550 ppm. Although radon was not detected in the analysis, the presence of strontium and uranium may well signal the possibility of radioactivity of the samples.

This study reveals that the clay from this area, though useful for therapy and cosmetics, effectively constitute a health risk. However, the people from Isinuka and patients receiving treatment from this village are culturally brought up to revere the healing system as holistic and handed down to them by their ancestors. The socio-economic and cultural implications of advocating a stop to the use of water and clay from these springs are at present unthinkable.

Therefore, studies on the toxicological profile of these clays are necessary with a view of identifying appropriate beneficiation methods and technologies that make the clays safer for use.

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References

Ademuwagun, Z. A., J. A. A. Ayoade, et al. (1979). "African Therapeutic Systems, ." Crossroads Press, Waltham, Massachussetts: 1-273.

Antman, K. H. (2001) Introduction: the history of arsenic trioxide in cancer therapy. The Oncologist, 6(suppl 2): 1-2.

ATSDR. (2011). "Agency for toxic substances and disease registry (ATSDR)." Retrieved 03 September, 2011, from http://www.atsdr.cdc.gov/substances/toxsubstabce.asp?toxid.

Bensalah, M., M. Benest, et al. (1998). Relation between emersion phase and compressive Lutetian tectonics in the southern Tellian basin (Algeria). Comptes rendus des séances de l'Academie des sciences. Série II, Mécanique, physique, chimie, sciences de l'univers, sciences de la terre, Paris.

Braun-Falco, O. and H. C. Korting (1986). "Normal pH value of human skin." Hautarzt 37(3): 126-129.

Carretaro, M. I. (2002). "Clay minerals and their beneficial effects upon human health: A Review." Applied Clay Science 21: 155-163.

Ekosse, G. (2000). "The Makoro Kaoline Deposit, Southeastern Botswana: Its Genesis and Possible Industrial Applications." Applied Clay Science 16: 301-320.

Ettagale, B. (1999). "African Elegance." New York: Rizzoli.

Faniran, J. A., F. S. Ngceba, et al. (2001). "An assessment of the Water Quality of the Isinuka Springs in the Transkei Region of the Eastern cape, South Africa." Water SA Water SA, 27(2): 241-250(2): 241-250.

Fitton, G. (1997). "X-ray fluorescence spectrometry. In: Gill R. (Ed) Modern analytical geochemistry: an introduction to quantitative chemical analysis techniques for earth, environmental and material sciences." Addison Wesley Longman, Harlow, England.: p 135-153. Addison Wesley Longman, Harlow, England

Gomes, C. and J. Silva (2007). "Clay minerals and Human Health." Applied Clay Science 36(1-3): 4-21.

Gupta, A. K. and K. Nicol (2004). "The use of sulfur in dermatology." Journal Drugs Dermatol 3(4): 427-431.

Heckroodt, R. O. (1991). "Clay and Clay Materials in South Africa " Journal of Southern African Institute of Minerals and Metal 91(10): 343-363.

Hewitt, J. P. (1992). Titanium dioxide: A different kind of sunshield. Drug and Cosmetic Industry, 151(3): 26-32.

Hoang-Minh, T., le Kasbohm, T. and Giere, R. (2010). UV Protection characteristics of some clays. Applied Clay Science, Clay, 01828:9.

Jefkins-Elnekave. (2006). "Tribal Identity Through Body Art: Extraordinary People Living in the Remnants of Time." PSA Journal Retrieved 21 August, 2011, from www.thefreelibrary.com/Tribal identity through body art: extraordinary people living in the ...-a0148766250.

May, R. N. (1880). "Memoranda to the Chief Inspector of Public Works Department, Cape of Good Hope Minesterial Department of Crown Lands and Public Works, 1st May, 1-13."

Mpuchane, S., G. Ekosse, et al. (2008). "Mineralogy of Southern African Medicinal and Cosmetic Clays and thier Effects on the Growth of Selected Test Micro-organisms." Fresenius Environmental Bulletin 15: 547-557.

Namibia Direct. (2006). "Paint Your Body in Ochre with the Himba Tribe." Retrieved 21 August 2011
from www.namibia-direct.com/activity/himba-tribe/.

Nkoma, J. S. and G. Ekosse (1999). "X-Ray Diffraction Studey of Clays Used for Making Bricks at Lobatse: Montmorillonite, Illite, and Kaolinite." Botswana Journal of Earth Science 4: 28-33.

Roy, P. and A. Saha (2002). "Metabolism and toxicity of arsenic: a human carcinogen." Current Science 82: 38-45.

Siegenthaler, D. (2005). "Importance of Your Skin's pH." from http://ezinearticles.com/?Importance-of-Your-Skins-pH&id=55208.

Van der Bijl, P., A. D. van Eyk, et al. (2000). "Diffusion of water across human skin in the presence of two barrier creams." Skin Pharmacol Appl Skin Physiol. 13: 104-110.

WHO (1996). The magazine of the World Health Organization, 49th year, No.2, March-April.

Zijlma, A. (2004). "Tribes of Africa: The Samburu of Kenya." Retrieved 21 August, 2011, from http://goafrica.about.com/library/bl.samburu.htm.