

# Mineralogical and geochemical analyses of the healing elements in clayey soils from Isinuka traditional spa in Port St Johns, South Africa

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Clay from Isinuka Springs in the Port St Johns area of the Eastern Cape of South Africa is used by local people for cosmetic purposes and for the treatment of an array of ailments and diseases. This study relates the acclaimed cosmetic and therapeutic properties of the clay to its mineralogical and geochemical composition and properties. The clay samples were dried and their pH measured. They were all found to be alkaline. Particle size distribution experiments were carried out. X-ray fluorescence (XRF) analyses detected various amounts of As, Co, Cr, Cu, Ni, Pb, Sr, U and Zn in the samples. The highest mean concentration of an element recorded was for Sr, with a mean value of 2550 ppm. X-ray diffraction was used to elucidate the mineralogical composition of the samples. Results showed that the clay, though useful for therapeutic and cosmetic purposes, poses a health risk, especially on repeated exposure. The acclaimed dermatological properties of the clays may be ascribed to the presence of S, Cu, Zn, Ti and As in the samples. Microbiological analysis of the samples may shed more light on the possible medicinal properties of the clays.

**Keywords:** Clay, chemicals, mineralogy, Isinuka traditional spa, healing

## INTRODUCTION

Clay refers to soil particles that are generally less than 2  $\mu\text{m}$  in diameter (Heckroodt, 1991; Nkoma and Ekosse, 1999; Ekosse, 2000; Gomes and Silva, 2007). Clay occurs widely in many parts of the world, including Africa. The particles are composed primarily of minerals which assume a plastic nature at appropriate water content and harden when dried or fired (Guggenheim & Martin, 1995). The use of clay by humans and animals for various purposes dates back many centuries, evident from data traced back to 60 BC (Carretero, 2002). Clays form an integral part of African cultural wellbeing and are used in varied forms of traditional rituals, cosmetics and medical practices to treat an array of ailments and diseases. The concept of spa treatment (curortology), now popular in industrialized countries, is not new to Africa. Guthrie (1951) reported on the regular use of medicinal baths and mud baths by Africans, while Thompson (1965) noted that the use of vapour or steam baths to treat fevers and rheumatoid arthritis was a common feature amongst native Africans. In open African markets, clays of various shades and colours are sold for use in cosmetic, medicinal and dermatological applications. Gomes & Silva (2007) and Lopez-Galindo *et al.* (2007) claimed that clay possesses high absorption properties and is able to absorb toxins, grease and unwanted substances found beneath the skin, leaving it cleansed and refreshed. Recently, some natural clay minerals have been identified and shown to kill bacteria (Williams *et al.*, 2004; Ma'or *et al.*, 2006; Haydel *et al.*, 2008). Clay minerals such as kaolinite, talc and smectite can be used as solar protectors due to their high refractive index (Hewitt, 1992; Hoang-Minh *et al.*, 2010) and they also form a protective film over the skin, protecting it from ultraviolet radiation. As a result, clays are included in several cosmetic preparations as sunscreens (Hewitt, 1992; Carretero & Pozo, 2009).

Indigenous Africans have always used clay to protect their skin from damaging sun rays (Matike *et al.*, 2011) and other environmental hazards. For example, the Himba of Namibia apply *ortijze*, a mixture of butter and fat from head to toe (Crandall, 2000) and the Ilha women in Mozambique wear *musiro*, a special white clayey paste on their faces (Fitzpatrick, 2010) to block harmful ultraviolet rays while the Nuba of Sudan apply red ochre all over their bodies to protect themselves from insect bites (Groning, 1998; Tanne, 2000).

In the Transkei region (now part of the Eastern Cape and KwaZulu-Natal provinces) of South Africa, it is not uncommon to see women's faces covered with white, yellow or black clays as a cosmetic and/or to protect their faces from damaging sun rays. The same is true of traditional initiates, who cover their entire bodies with clays. It is believed that clays originating from Isinuka in the Port St Johns area are unique to South Africa. They are widely used for cosmetic and therapeutic purposes. Accounts of the healing qualities of the spring water and clays from this area abound. Reports of the smell of hydrogen sulphide from this spring and/or clay mine (e.g., May, 1880) date back more than one hundred years. The spa is frequented primarily by local people in search of spiritual and physical healing. However, the treatment environment differs considerably from that of high-profile luxury destination spas, day spas and hotel spas in which bathing facilities are offered. It is noteworthy that indigenous communities may not have the knowledge about the chemical properties which engender the protective properties of clay whenever it is applied to the skin; however, they do possess empirical knowledge that enables them to identify specific types of clay for the purpose of protecting their skin from external hazards (Matike *et al.*, 2011). The World Health Organization (1978) has recognized traditional medicine as an invaluable means of satisfying the basic healthcare needs of

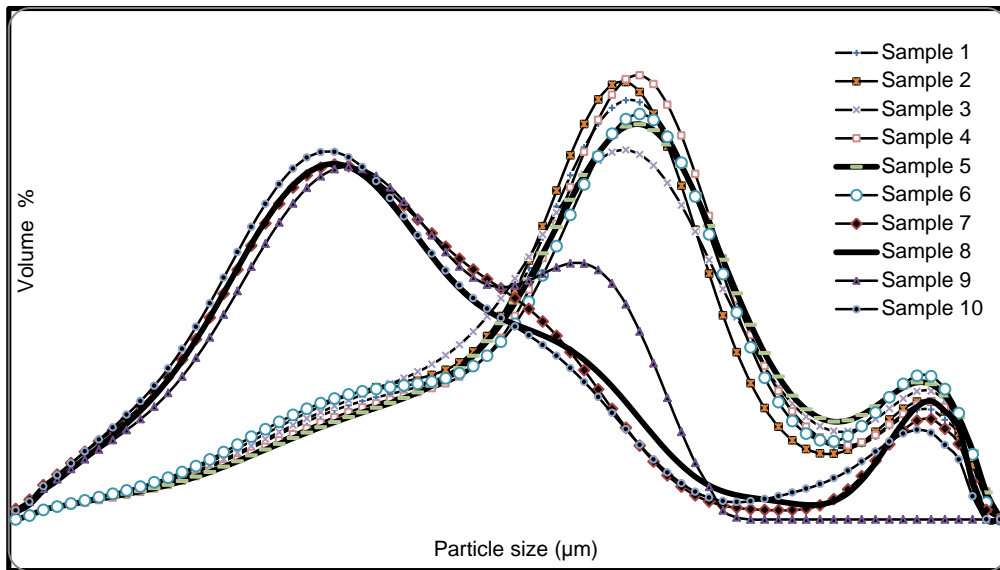


Figure 1. Particle size distribution of silty samples 1 to 10.

about 80% of the world’s population. Calls are being made for the systematic evaluation of traditional remedies by scientific methods, to ascertain their efficacies and to maintain strict observation of safety standards.

Results of partial analysis of the Isinuka healing clays have been analysed by Jumbam (2011). This work was followed by a broader study of the clays to determine their mineralogy and geochemistry, as well as to decipher which elements are responsible for the claimed healing properties. Results of these investigations are presented in this paper.

**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 (31° 35’ 0” S; 29° 28’ 0” E). 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 used for the

treatment of skin diseases and as skincare (Faniran *et al.*, 2001). These samples were whitish in colour. Four other samples (Samples 5, 6, 7 and 8) were collected from the most popular pond-like spring located above the rock outcrop. The popular bathing spring is about 3 m<sup>2</sup>. It emits a stinking hydrogen sulphide-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, and hidden in the woods.

The samples were air-dried, and analysed for selected physicochemical and geochemical properties. Mineral identification was done using X-ray diffraction techniques. The pH values of the samples was measured in a clay water suspension, and the particle size distribution was determined using a Malvern Masterizer 2000 Laser Particle Size Analyser fitted with a Hydro 2000G dispersion unit. The concentrations of selected trace elements were determined using a PAN

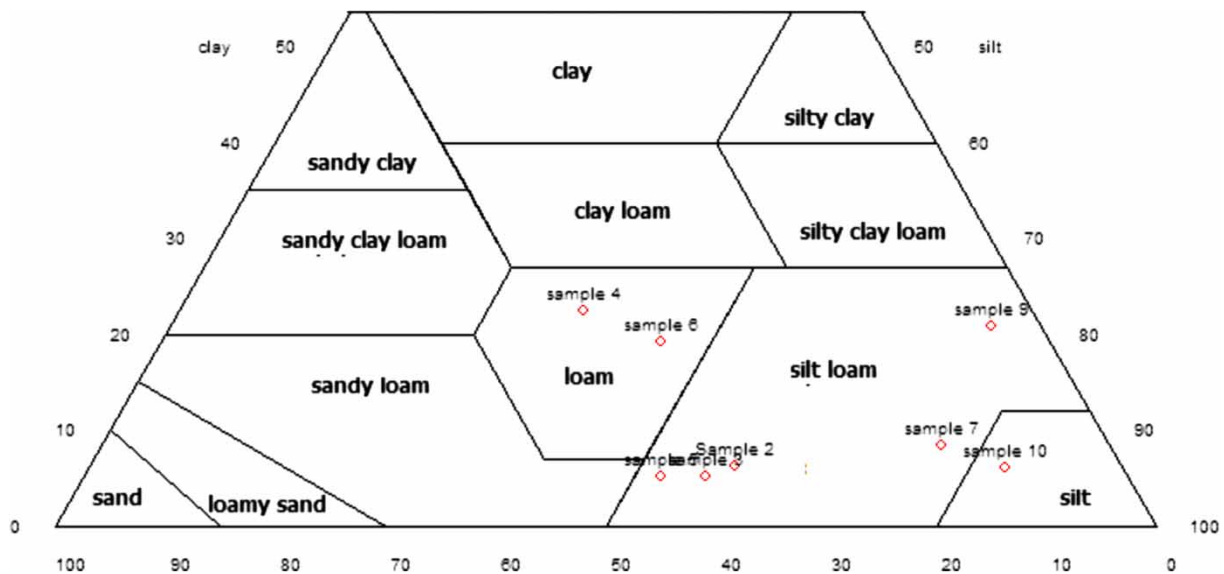


Figure 2. Particle size distribution of samples. Source: Jumbam (2011).

**Table 1.** The results (wt%) of semi quantitative X-ray diffraction (XRD) analysis of minerals identified in clayey soil samples from Isinuka spa.

Sample	Calcite	Aragonite	Gypsum	Rozenite	K-feldspar	Plagioclase	Quartz	Mica	Kaolinite	Chlorite	Halite	Pyrite	Pyrophyllite	Spinel	Smectite	Illite/ Smectite/ Interstratification
1	27	6	1	2	-	2	31	9	-	-	6	3	3	-	-	10
2	14	-	-	-	3	2	40	25	-	-	-	-	-	4	-	12
3	2	-	-	-	6	2	45	37	2	-	-	-	-	-	-	6
4	-	-	-	-	-	2	42	42	2	-	-	-	-	-	3	7
5	16	4	2	1	-	2	49	15	-	-	1	2	-	-	-	8
6	27	4	1	1	-	2	40	12	-	-	4	3	-	-	-	6
7	4	-	-	-	-	2	49	36	2	-	-	-	-	-	-	7
8	29	4	4	1	-	2	32	9	1	-	4	2	2	-	-	10
9	28	-	3	-	-	3	40	14	-	6	1	-	-	-	-	5
10	28	-	1	-	-	2	44	12	2	-	3	-	1	-	-	5

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. Amphibolite standard reference material was run on the same instrument for comparison with the sample data generated. The methods used for the X-ray diffraction (XRD) and fluorescence (XRF) analyses are described in the Council for Geosciences (2011), and Fitton (1997). All analyses were done at the Council for Geoscience, Pretoria, South Africa.

## RESULTS AND DISCUSSION

### pH of samples

The pH range of the samples was 7.94–10.05, indicating that they 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 to 10 collected from the open springs. The strong alkaline pH value range of the samples brings into question the viability of using these clays as possible cures against acne as reported by Faniran *et al.* (2001). The pH of normal human skin ranges between 5.4 and 5.9 (Braun-Falco & Korting, 1986). Such high alkalinity may have an adverse effect on the skin if the clay is applied directly without any pre-treatment 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 skin of greater alkalinity. 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. Such preparations encompass mixing the clay materials with plant and animal extracts (Matike *et al.*, 2011), while Egyptian men and women blended clay with scented oils and perfumes as early as 10 000 BC (Lambert, 2001; Erman & Tirard, 2003).

### Particle size distribution (PSD) of clayey samples

The samples had varied particle sizes with the majority of them having silt as the dominant particle size. Two groups of PSD were observed (Figure 1). Samples 7, 8, 9 and 10 had finer particles than the others. The samples were therefore classified either as silt, silt loam or loam (Figure 2). Particle size plays an important role in the application of clays for cosmetic or medicinal purposes. If the material comprises coarse particles, it may cause abrasion and damage to the skin. The particle size distribution of the material may also influence its healing qualities through cation exchange reactions. A high clay content may be indicative of cation exchange and absorption/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 the 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. Hence, the particle size distribution described may play a significant role in the healing, protection and beautification experiences encountered by the people of Isinuka and those who seek healing and wellbeing from the village.

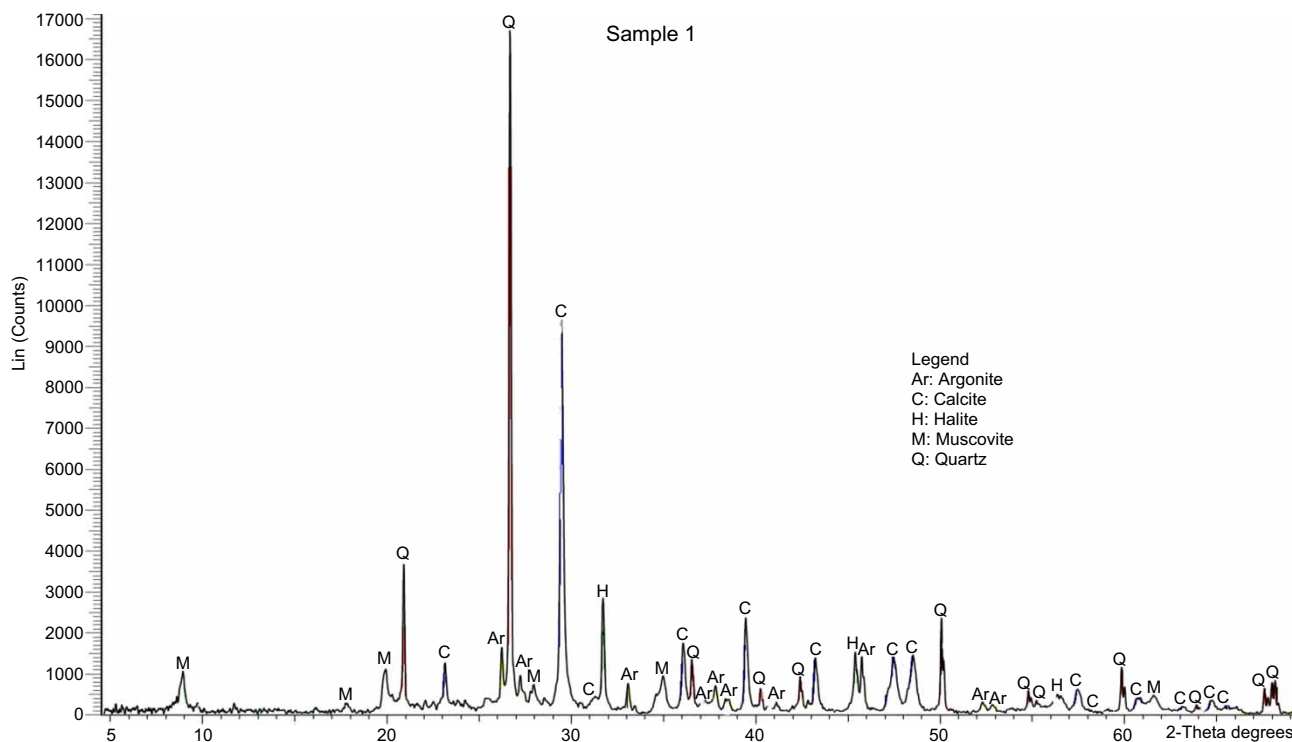


Figure 3. Diffractogram of sample 1.

#### Mineralogy of the clayey soils

Seventeen minerals were identified in the clayey samples from Isinuka spa: quartz ( $\text{SiO}_2$ ), mica, calcite ( $\text{CaCO}_3$ ), interstratified illite ( $\text{K}_{0.6}(\text{H}_2\text{O})_{0.4}\text{Al}_{1.3}\text{Mg}_{0.3}\text{Fe}_{0.1}^{2+}\text{Si}_{3.5}\text{O}_{10}(\text{OH})_2 \cdot (\text{H}_2\text{O})$ ), aragonite ( $\text{CaCO}_3$ ), gypsum  $\text{CaSO}_4 \cdot 2(\text{H}_2\text{O})$ , rozenite  $\text{Fe}^{2+}\text{SO}_4 \cdot 4(\text{H}_2\text{O})$ , K-feldspar ( $\text{KAlSi}_3\text{O}_8$ ), plagioclase ( $\text{Na, Ca}(\text{Si,Al})_4\text{O}_8$ ), kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ), chlorite ( $\text{ClO}_2$ ), halite ( $\text{NaCl}$ ), pyrite ( $\text{FeS}_2$ ), pyrophyllite ( $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ ), spinel ( $\text{MgAl}_2\text{O}_4$ ) and smectite ( $\text{Na}_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_{2 \cdot x}\text{H}_2\text{O}$ ). Table 1 gives a summary of results of the semi-quantitative analysis of identified minerals in the clayey soil samples. The results given in Table 1 are in wt%. Quartz, mica and calcite were the three dominant mineral phases in the samples, followed by interstratified illite/smectite. Figure 3 is a representative diffractogram of the analysed sample 1. The alkaline nature (pH 7.9–10) of the samples may be ascribed to the presence of calcite (limestone), neutralizing any possible acidity inherent in evolving gases. Quartz, mica and illite are very stable minerals. Based on the particle size distribution they are silty and hardly cause abrasion if the

samples are applied topically. Illite is actually applied orally and topically.

#### Geochemistry of clayey soils

##### Sulphur content

Since the spring water and clays are claimed to have medicinal properties and there was a pungent sulphur dioxide-like smell oozing out of the springs, it was important to test for the sulphur (S) content of the samples collected. All samples had S content  $< 1.5\%$ . Samples 1 to 4 collected from inside the cave, where there was no noticeable pungent gaseous smell, had lower concentrations of S compared to those from the open springs. The S content in the samples collected from the open springs was above 0.8%, rising to 1.3% in sample 9 (Figure 4). The use of S in dermatological applications is well established due to its antifungal, antibacterial and keratolytic activities (Gupta & Nicol, 2004). Pyrite ( $\text{FeS}_2$ ), an S-containing mineral, was found in the samples (Table 1), particularly those from the popular pond. Continual saturation of the whitish clay with saline water dripping from the roof of the cave might result in the improvement of its medicinal properties, similar to bath salts ( $\text{MgSO}_2$ ,  $\text{NaCl}$ ,  $\text{NaHCO}_3$ ) that are claimed to have therapeutic properties, especially in the treatment of arthritis (Sukenic *et al.*, 1990).

Substances applied to the skin can penetrate the skin and produce local and systemic effects (Van der Bijl *et al.*, 2000). The bromine concentration, though comparatively low in samples 1 to 4, ranged from about 20 to 100 ppm in samples 5 to 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 major and trace elements are summarized in Table 2. Arsenic was found in all the samples tested, although the concentrations are low, ranging from 6 to 15 ppm with a mean value of 9.6 ppm. Arsenic has a history of

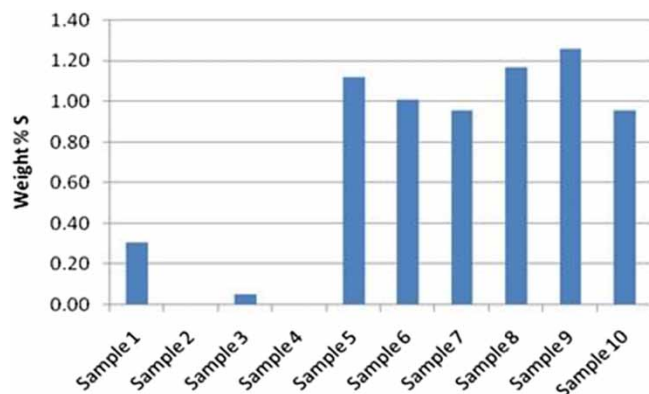


Figure 4. Sulphur content (wt%) in clayey samples.

**Table 2.** Concentrations of major elements (wt%) and trace elements as determined by X-ray fluorescence (XRF).

Sample	1	2	3	4	5	6	7	8	9	10	SARM-4	SARM-4
SiO <sub>2</sub>	48.16	58.24	58.73	57.48	25.14	30.62	41.33	26.78	33.59	41.33	52.64	50.91
TiO <sub>2</sub>	0.53	0.64	0.63	0.62	0.35	0.44	0.67	0.38	0.52	0.58	0.20	0.20
Al <sub>2</sub> O <sub>3</sub>	15.41	18.74	20.18	17.38	8.00	9.35	11.59	8.23	9.35	12.34	16.50	16.34
Fe <sub>2</sub> O <sub>3</sub> (t)	5.43	6.65	7.35	6.41	1.91	1.97	5.10	1.94	1.77	5.46	8.97	9.23
MnO	0.042	0.045	0.100	0.034	0.369	0.435	0.232	0.391	0.237	0.248	0.18	0.186
MgO	1.27	1.15	1.35	0.99	0.82	0.87	1.22	0.87	0.74	1.38	7.50	8.07
CaO	11.24	2.67	0.61	4.49	16.43	14.86	13.49	17.69	10.78	13.56	11.50	12.28
Na <sub>2</sub> O	1.10	1.01	1.12	0.95	4.41	2.99	2.57	3.99	2.64	2.09	2.46	2.56
K <sub>2</sub> O	3.58	3.94	4.14	3.83	0.97	1.34	1.68	0.97	2.10	2.17	0.25	0.31
P <sub>2</sub> O <sub>5</sub>	0.056	0.068	0.148	0.041	0.227	0.244	0.118	0.224	0.137	0.114	0.03	0.020
Cr <sub>2</sub> O <sub>3</sub>	0.010	0.014	0.013	0.013	0.008	0.010	0.013	0.008	0.010	0.011	30.000	0.007
LOI	12.58	7.01	5.87	8.08	40.13	36.30	21.91	37.57	37.21	20.33	-0.40	-0.53
Total	99.42	100.17	100.23	100.32	98.77	99.43	99.92	99.06	99.09	99.62	129.83	99.57
H <sub>2</sub> O <sup>-</sup>	1.20	1.52	1.49	1.38	4.66	4.66	1.91	4.14	4.75	1.75	259.66	0.21
As	10	11	15	7.8	9.5	6.5	13	6.5	6.7	13	33.5	39
Ba	745	761	723	751	302	359	469	322	411	484	590	609
Bi	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	1.17	<3
Br	5.6	4.3	6.4	4.4	100	77	43	98	64	24	2.9	2.1
Ce	43	48	52	38	35	35	66	37	41	51	70	67
Co	5.5	7.4	15	4.0	8.7	9.3	17	8.8	8.8	15	14.2	16
Cr	74	88	81	82	55	63	75	57	65	70	62	66
Cs	<5	<5	<5	<5	12	10	<5	8.4	<5	<5	9.0	<5
Cu	24	31	41	33	51	45	32	51	48	30	21	18
Ga	26	29	30	26	11	13	16	11	14	17	19.3	20
Ge	8.0	7.3	9.5	6.7	22	20	2.4	18	20	2.5	1.3	1.3
Hf	<3	<3	<3	<3	10	6.8	<3	9.6	12	<3	6.8	5.9
La	29	35	42	27	21	20	39	16	22	33	34	38
Mo	<2	<2	<2	<2	<2	<2	<2	<2	3.2	<2	1.4	<2
Nb	13	14	14	14	4.9	6.4	11	4.9	7.6	10	16.6	16
Nd	19	20	30	15	17	18	33	18	21	26	28	26
Ni	14	19	31	12	27	23	27	26	18	27	20.4	22
Pb	24	40	28	27	5.2	6.2	24	4.9	6.7	20	98	96
Rb	253	258	263	245	108	124	144	112	133	157	140	144
Sc	22	28	43	22	73	80	11	68	102	12	11.2	13
Se	<1	<1	<1	<1	<1	<1	<1	1.1	<1	<1	0.14	<1
Sm	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	5.2	<10
Sr	426	168	83	207	1,991	1,797	1,297	2,118	1,813	1,239	155	161
Ta	<2	2.7	<2	<2	<2	<2	<2	<2	<2	<2	1.4	<2
Th	16	18	17	17	3.3	4.6	10	3.9	5.8	12	11.6	11
Tl	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	1.0	<3
U	4.0	4.6	2.7	3.5	8.1	7.6	6.2	8.6	8.5	5.5	3.3	3.3
V	125	134	140	128	100	98	99	92	111	96	86	92
W	<3	3.2	<3	<3	<3	<3	<3	<3	<3	<3	3.1	3.4
Y	25	25	76	20	122	123	54	118	127	52	25	28
Yb	3.4	3.4	5.4	<3	13	13	5.1	12	11	4.3	2.66	<3
Zn	57	73	138	54	109	103	89	101	69	89	680	680
Zr	153	197	222	196	652	551	225	546	749	193	245	250

medical applications dating back centuries prior to the arrival of penicillin as a cure against syphilis, yaws and other bacterial infections (Roy & Saha, 2002). It is a human carcinogen and an extremely toxic element. It can cause severe damage to human health, even at low concentrations, especially after repeated contact exposure. Cobalt is an essential element and with a concentration range from 4 to about 17 ppm it may not pose a health risk. Chromium values were fairly evenly distributed across all samples, ranging from about 55 ppm to 90 ppm, with a mean value of about 70 ppm. While the hexavalent CrO<sub>3</sub> was not detected in the samples, it is well known as highly toxic and carcinogenic (Baker, 1997); the detected Cr<sub>2</sub>O<sub>3</sub>, on the other hand, is not so dangerous. Copper and Ni show a similar distribution pattern in all samples, but give lower mean concentration values of 38 ppm and 21 ppm, respectively. Both are useful to the human body as trace elements and Cu is well known for its antibacterial and antifouling properties (Edding *et al.*, 1995). Higher Pb

concentrations are seen in white clay samples (samples 1 to 4), with a mean of 30 ppm, as compared to black clays (samples 5 to 10) with a mean value of 17 ppm. The mean values of Sr in white samples (samples 1 to 4), is about 225 ppm, while that in black samples is 2550 ppm, which represents a sharp difference in concentration between the white and black clays. Although Sr has no specific function, it is absorbed because of its similarity to Ca. The human body contains approximately 4.6 ppm Sr. It is non-toxic when ingested at concentrations of 0.8–5 mg with food, when it only contains non-radioactive Sr. But radioactive Sr is certainly risky when taken in, based on its carcinogenic and mutagenic mechanism. Several studies have shown Sr to be associated with osteomalacia (e.g., Cohen-Solal, 2002). The highest concentration of Ur in white clays is 2.8 ppm while black clays exhibit a maximum value of 8.5 ppm. Although Sr and Ur may produce some radioactive isotopes, their presence in these samples was not investigated. Zinc exhibits a similar

distribution pattern across all samples with a mean concentration value of about 88 ppm. Zinc preparations have also been found to protect against sunburn in summer and act against windburn in winter (Emsley, 2001). Its ions have been found to be antimicrobial, even at low concentrations (McCarthy *et al.*, 1992).

The SiO<sub>2</sub> concentration in the samples ranged from 25.15 wt% to 58.73 wt% with a mean value of 42.13 wt%. The Al<sub>2</sub>O<sub>3</sub> values were 8.00 to 20.18 wt% with a mean of 13.05 wt%. The Fe<sub>2</sub>O<sub>3</sub> concentration ranged from 1.77 to 7.35 wt% with a mean value of 4.40 wt%. Its brown colour does not have a significant impact on the overall hue of the samples due to its low concentration. The presence of CaO (quicklime) is certainly a contributory factor to the recorded alkaline pH in the samples. Its concentrations range from 0.62 wt% to 17.69 wt% with a mean value of 10.57 wt%. The rest of the oxides, namely TiO<sub>2</sub>, MnO, MgO, Na<sub>2</sub>O, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub> and Cr<sub>2</sub>O<sub>3</sub> exhibit concentrations with mean values less than 4 wt%. These oxides may not pose any health risk to users of Isinuka clays, at least not in their current concentrations. In fact, titanium dioxide constitutes an important component of sunscreen formulations and its presence in the clayey soils when applied to the skin might reflect the dangerous ultraviolet rays from the sun.

## CONCLUSIONS

This paper has examined the mineralogy and geochemical properties of the clayey soil material from Isinuka springs used for cosmetic and dermatological applications by the inhabitants of Isinuka, Port St Johns, and the surrounding villages and towns in Pondoland of the Eastern Cape province of South Africa. It is not clear what may be responsible for the acclaimed healing properties of the clays. The presence of S, Cu and Zn may play a significant role given their antibacterial and antifungal properties. In a recent socioeconomic study of the activities at Isinuka springs, it was confirmed that the clayey soils were used, in part, particularly by women to protect their skin from damaging ultra violet rays (Jumbam, 2012). The presence of TiO<sub>2</sub> and Zn in the samples is most likely responsible for protecting the skin of the users from ultra violet radiation. The presence of As may also contribute to the healing properties. However, it is a human carcinogen and extremely toxic so, although the As concentrations in the Isinuka clays are rather low, with an average value of only 9.6 ppm, repeated exposure could pose a health risk and should be avoided. By the same token, Pb was detected in the white clay samples, albeit in small concentrations with a mean value of 30 ppm. The toxicity of Pb is well established such that the fall of the Roman Empire was ascribed to the use of Pb vessels for storing wine and water that poisoned the entire population (Gomes & Silva, 2007). The average concentration of Co in world soils is less than 10 ppm (Agency for Toxic Substances and Disease Registry, 2011) but this study reveals values of up to 17 ppm. It is essential in trace amounts for human health. but if too much Co is taken into the body it could affect the lungs and trigger breathing difficulties. Although the elements referred to in this study have some degree of negative health implications (Bensalah *et al.*, 1998; Agency for Toxic Substances and Disease Registry, 2011), their low concentrations are a consoling factor despite the mean value of Sr being as high as 2550 ppm. Although radon was not detected in the analysis, the presence of Sr and Ur may well signal the possibility of radioactive isotopes in the samples. Recently, some natural clay minerals have been identified, and shown

to kill bacteria (Williams *et al.*, 2004; Ma'or *et al.*, 2006; Haydel *et al.*, 2008).

This study reveals that the clay from this area, though useful for therapeutic and cosmetic purposes, may constitute a health risk on repeated exposure. However the people from Isinuka, and patients receiving treatment from this village and surroundings, are brought up to revere as holistic the healing prescription 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 to identifying appropriate beneficiation methods and technologies that make the clays safer for use.

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## REFERENCES

- AGENCY FOR TOXIC SUBSTANCES AND DISEASE REGISTRY, 2011. [www.atsdr.cdc.gov/news/index.asp](http://www.atsdr.cdc.gov/news/index.asp) (accessed 18 October 2012).
- BAKER, J.T. 1997. Material safety. <http://hazard.com/msds/mf/baker/baker/files/c4400.htm> (accessed 30 November 2012).
- BENSALAH, M., BENEST, M. & TRUC, G. 1998. Relation between emersion phase and compressive Lutetian tectonics in the southern Tellian basin (Algeria). *Comptes rendus des séances de l'Académie des sciences. Série II, Mécanique, physique, chimie, sciences de l'univers, sciences de la terre*, 13 January, Paris, pp. 124–140.
- BRAUN-FALCO, O. & KORTING, H.C. 1986. Normal pH value of human skin. *Hautarzt* 37: 126–129.
- CARRETERO, M.I. 2002. Clay minerals and their beneficial effects upon human health: a review. *Applied Clay Science* 21: 155–163.
- CARRETERO, M.I. & POZO, M. 2009. Clays and non clay minerals in the pharmaceutical industry. Part I: Excipients and medical applications. *Applied Clay Science* 46(1): 73–80.
- COHEN-SOLAL, M. 2002. Strontium overload and toxicity: impact on renal osteodystrophy. *Nephrology Dialysis Transplantation* 17(Suppl. 2): 30–34.
- COUNCIL FOR GEOSCIENCES (CGS) 2011. Guide to the services of the CGS analytical laboratory. <http://www.geoscience.org.za/index>.
- CRANDALL, D.P. 2000. *The Place of Stunted Ironwood Trees: A year in the lives of the cattle-herding Himba of Namibia*. New York, Continuum International Publishing group Inc, p. 48.
- EDDING, M.E., FLORES, H. & MIRANDA, C. 1995. Experimental usage of copper-nickel alloy mesh in mariculture. Part 1: Feasibility of usage in a temperate zone; Part 2: Demonstration of usage in a cold zone. Final report to the International Copper Association Ltd.
- EKOSSE, G. 2000. The Makoro kaoline deposit, Southeastern Botswana: its genesis and possible industrial applications. *Applied Clay Science* 16: 301–320.
- EMSLEY, J. 2001. "Zinc". *Nature's Building Blocks: An A-Z Guide to the Elements*. Oxford, Oxford University Press.
- ERMAN, A. & TIRARD, H.M. 2003. Life in ancient Egypt. <http://books.google.co.za/books?> (accessed 18 October 2012).
- FANIRAN, J.A., NGCEBA, F.S., BHAT, R.B. & OCHE, C.Y. 2001. An assessment of the water quality of the Isinuka Springs in the Transkei Region of the Eastern Cape, South Africa. *Water SA* 27(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*. Harlow, Longman, pp. 135–153.
- FITZPATRICK, M. 2010. *Mozambique*. Lonely Planet Publications, Melbourne.

- GOMES, C. & SILVA, J. 2007. Clay minerals and human health. *Applied Clay Science* **36**(1–3): 4–21.
- GRONING, K. 1998. *Body Decoration. A world survey of body art*. New York, Vendome Press.
- GUGGENHEIM, S. & MARTIN, R. 1995. Definition of clay and clay mineral: journal report of the AIPEA Nomenclature and CMS Nomenclature Committee. *Clay and Clay Minerals* **43**(2): 255–256.
- GUPTA, A.K. & NICOL, K. 2004. The use of sulfur in dermatology. *Journal Drugs Dermatol* **3**: 427–431.
- GUTHRIE, D. 1951. Observations on primitive medicine, with special references to native African medicine. *Proceedings of the Royal Society of Medicine* **45**: 91–94.
- HAYDEL, S.E., REMINEH, C.M. & WILLIAMS, L.B. 2008. Broad-spectrum in vitro antibacterial activities of clay minerals against antibiotic-susceptible and antibiotic-resistant bacterial pathogens. *Journal of Antimicrobial Chemotherapy* **61**: 353–361.
- HECKROODT, R.O. 1991. Clay and clay materials in South Africa. *Journal of Southern African Institute of Minerals and Metal* **91**: 343–363.
- HEWITT, J.P. 1992. Titanium dioxide: a different kind of sunshield. *Drug and Cosmetic Industry* **151**: 26–32.
- HOANG-MINH, T., LE KASBOHM, T. & GIERE, R. 2010. UV protection characteristics of some clays. *Applied Clay Science* **48**(3): 349–357.
- JUMBAM, N.D. 2011. The chemistry of cosmetic and therapeutic clays from Isinuka Springs in Port St Johns, South Africa. *1st International Conference on Clays and Clay Minerals in Africa and 2nd International Conference on Geophagia in Southern Africa*, Bloemfontein, 19–21 October.
- JUMBAM, N.D. 2012. Demographic characteristics associated with Isinuka traditional spa near Port St Johns in the Eastern Cape Province of South Africa. *Indilinga – African Journal of Indigenous Knowledge Systems* **11**(1): 20–31.
- LAMBERT, T. 2001. A brief history of cosmetics. <http://www.localhistories.org/cosmetics.html>. (accessed 18 October 2012).
- LOPEZ-GALINDO, A., VISERAS, C. & CEREZO, P. 2007. Compositional, technical and safety specifications of clays to be used as pharmaceutical and cosmetic products. *Applied Clay Science* **36**(1–3): 51–63.
- MCCARTHY, T.J., ZEELIE, J.J. & KRAUSE, D.J. 1992. The antimicrobial action of zinc ion/antioxidant combinations. *Clinical Pharmacology & Therapeutics* **17**(1): 5.
- MA'OR, Z., HENIS, Y., ALONG, Y., ORLOV, E., SORESENSEN, K.B. & OREN, A. 2006. Antibacterial properties of Dead Sea black mineral mud. *International Journal of Dermatology* **45**: 504–511.
- MATIKE, D.M.E., EKOSSE, G.I. & NGOLE, V.M. 2011. Indigenous knowledge applied to the use of clays for cosmetic purposes in Africa: an overview. *Indilinga – African Journal of Indigenous Knowledge Systems* **9**(2): 138–150.
- MAY, R.N. 1880. Memoranda to the Chief Inspector of Public Works Department, Cape of Good Hope Ministerial Department of Crown Lands and Public Works, 1 May: 1–13.
- NKOMA, J.S. & EKOSSE, G. 1999. X-Ray diffraction study of clays used for making bricks at Lobatse: montmorillonite, illite, and kaolinite. *Botswana Journal of Earth Science* **4**: 28–33.
- ROY, P. & SAHA, A. 2002. Metabolism and toxicity of arsenic: a human carcinogen. *Current Science* **82**: 38–45.
- SIEGENTHALER, D. 2005. *Importance of Your Skin's pH*. Online: <http://ezinearticles.com/?Importance-of-Your-Skins-pH&id=55208> (accessed 18 October 2012).
- SUKENIK, S., NEUMANN, L., BUSKILA, D., KLEINER-BAUMGARTEN, A., ZIMLICHMAN, S. & HOROWITZ, J. 1990. Dead Sea bath salts for the treatment of rheumatoid arthritis. *Clinical and Experimental Rheumatology* **8**(4): 353–357.
- TANNE, J.H. 2000. Body art: marks of identity. *British Medical Journal* **320**(7226): 64.
- THOMPSON, E.E. 1965. Primitive African medical lore and witchcraft. *Bulletin of the Medical Library Association* **53**: 80–94.
- VAN DER BIJL, P., VAN EYK, A.D., CILLIERS, J. & STANDER, L.A. 2000. Diffusion of water across human skin in the presence of two barrier creams. *Skin Pharmacology and Applied Skin Physiology* **13**: 104–110.
- WILLIAMS, J.M., HOLLAND, M., EBERL, D.D., BRUNET, T. & BRUNET DE COURSSOU, L. 2004. Killer clays. Natural antibacterial clay minerals. *Mineralogical Society Bulletin* **139**: 3–8.
- WORLD HEALTH ORGANIZATION 1978. The promotion and development of traditional medicine. World Health Organization Geneva. *World Health Organization Technical Report Series* **622**: 7–28.