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The composition and origin of Ghana medicine clays

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The mineral, organic and elemental composition of medicine clays from three shrines in the Tong Hills in northern Ghana (Gbankil, Kusanaab, and Yaane) are assessed to ascertain what additives they might contain and the implications for their recognition, for example in archaeological contexts. These are clays that are widely used for healing purposes being perceived efficacious in curing multiple ailments and which are given a divine provenance, but their collection is ascribed human agency. The Yaane clay is also supplied as part of the process of obtaining the right to operate the shrine elsewhere making it widely dispersed. Organic geochemical analyses revealed a predominance of plant-derived material with a substantial contribution of microbial origin. Based on these (supported by elemental and mineral analyses), no unnatural organic material could be detected, making an exogenous contribution to these clays unlikely. The implications are that these are wholly natural medicinal substances with no anthropogenic input into their preparation, as the traditions suggest. The very similar mineralogy of all the clays, including a non-medicine clay sampled, suggests that, unless the geology radically differed, differentiating between them analytically in an archaeological contexts would be doubtful.

Keywords: Ghana; medicine; clay; organic geochemical analysis; archaeology

1. Introduction

Organic geochemical and other analysis of medicinal substances in sub-Saharan Africa is comparatively rare, and non-existent in relation to assessing potential archaeological implications (see Insoll 2011a). Molecular analysis in combination with mineral and elemental analyses was used to evaluate the composition and origin of the (organic) materials present in three clay samples from the Gbankil, Kusanaab, and Yaane shrines in the Tong Hills, northern Ghana, to determine whether any other substances were added and thus, potentially, anthropogenic action detected. These are clays that are widely used for healing purposes being perceived efficacious in curing multiple ailments including scorpion bites, chronic headaches, joint and other bodily pains, and insanity and female infertility. The clays are given a divine provenance, as reflected in the name given the Yaane medicine clay, *Bagre Tan*, 'the God's Soil', but their collection is ascribed human agency. The Yaane clay is also supplied as part of the process of obtaining the right to operate the shrine elsewhere, making it widely

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dispersed (Insoll 2006; see also Insoll 2011a), and thus as a substance potentially amenable to being recognised in contexts outside of the Tong Hills.

2. Methods

2.1. *Study area and sampling*

The Tong Hills are located in the Upper East Region of northern Ghana (Figure 1). They are inhabited by the Talis subsection of the overall Talensi ethno-linguistic group (Allman and Parker 2005; Insoll 2006). The archaeology and ethnoarchaeology of the Talensi have been the focus of a research project co-directed by one of the authors (TI), and the clay medicine samples were collected in October–November 2008 (Kusanaab and Yaane) and July 2009 (Gbankil) as part of this research (see Insoll 2011b; Insoll, Kankpeyeng, and MacLean 2009). The three medicine clay samples were collected by the shrine custodians (Kwabena Tengdaan) or their nominated representatives (Hanson Goldaan and Kinsley Tengdaan) and immediately wrapped in aluminium foil (e.g. the clays were not ground or levigated) and stored in clean dry coffee tins for transport to the UK. For reference, a non-medicine clay was also collected from the Yikine area. This clay is one of the general clays normally used in pottery. After arrival in the UK the samples were stored cold (−20°) until analysed.

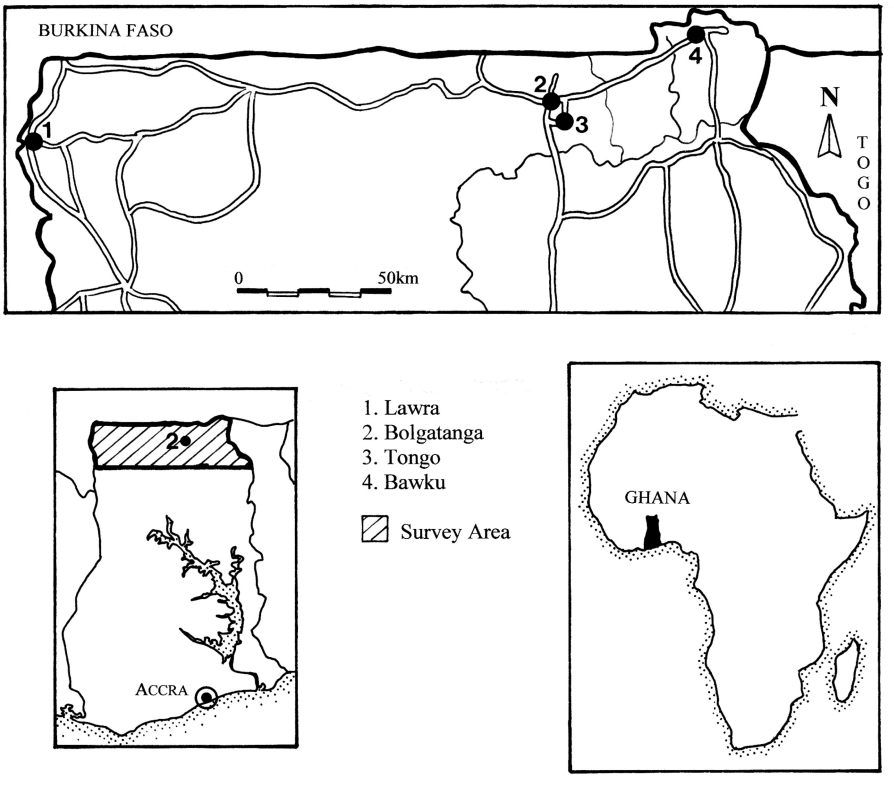

Figure 1. Map of the Upper East Region of Ghana indicating the position of the Tong Hills.

2.2. *X-ray diffraction*

Small amounts of the clays were scraped into an agate mortar and ground up using an agate pestle and combined with amyl acetate to form a paste. The pastes were smeared onto glass slides, dried and the samples were analysed using a Baker D8 Advance X-ray diffraction (XRD), from 5° to 70° at 0.02° steps, with each step taking 4 seconds. The resulting spectrum was compared to the 1999 International Centre for Diffraction Data database of known minerals. Very small quantities of minerals could not be detected; therefore those determined are not an exhaustive list of the minerals that are potentially present.

2.3. *X-ray fluorescence*

X-ray fluorescence (XRF) analysis was used to determine the chemical composition of the clays. Owing to the friable nature of the samples it was not possible to analyse medicine clays in their natural form. Small fragments could break off, falling into the XRF detector and causing damage. It was therefore necessary to prepare pressed powder pellets for conventional analysis. The clays were ground in an agate ball mill for 5 minutes at 350 rpm, 12 g was weighed and added to 3 g of binding wax and mixed again in a small agate ball mill for 5 minutes at 150 rpm. The resulting mixtures were put into a steel mould and pressed to 10 tonnes to form a 37 mm diameter pellet. Concentrations of major, minor and trace elements were determined using a PANalytical Axios wavelength dispersive XRF spectrometer using the analytical programmes Omnion (major and minor elements) and Protrace (trace elements). Data are quantified using a large database of standards that have been analysed. Only those elements with a concentration above the detection limit were reported. Data quality is assessed by regularly analysing a certified reference material. The major elements were within 1%, minor within 0.1%, and trace elements of this analysis were within 10 ppm with the exception of Mn which was within 20 ppm of the certified values.

2.4. *Lipid biomarker characterisation*

2.4.1. *Extraction and fractionation*

The medicine clays were freeze-dried, crushed and extracted using a Soxhlet apparatus with dichloromethane/methanol (DCM/MeOH, 2:1, v/v) for 24 hours (Figure 2). The total lipid extracts (TLE) were concentrated using rotary evaporation, an aliquot was obtained and two standards (tetracosane-$^{2}H_{50}$ and hexadecan-2-ol) were added. Subsequently, the aliquots were separated into two fractions using Bond-Elut column chromatography (Isolute NH2; 500 mg, 6 ml; Biotage, Sweden; e.g. Kim and Salem 1990) and elution with DCM/isopropanol (2:1 v/v; 12 ml; 'neutral lipid fraction') and an acetic acid solution (a 2% solution in diethyl ether; 12 ml; 'acid fraction'). Glass Bond-Elut columns were used to avoid contamination (Russell and Werne 2007). The neutral lipid fraction was further separated into two fractions using a column packed with (100% activated) alumina by elution with hexane/DCM (9:1 v/v; 3 ml; 'hydrocarbon fraction') and DCM/MeOH (1:1 v/v; 3 ml; 'polar fraction'). The hydrocarbon, polar and acid fractions were analysed using gas chromatography/mass spectrometry (GC/MS). Prior to analyses the acid fractions

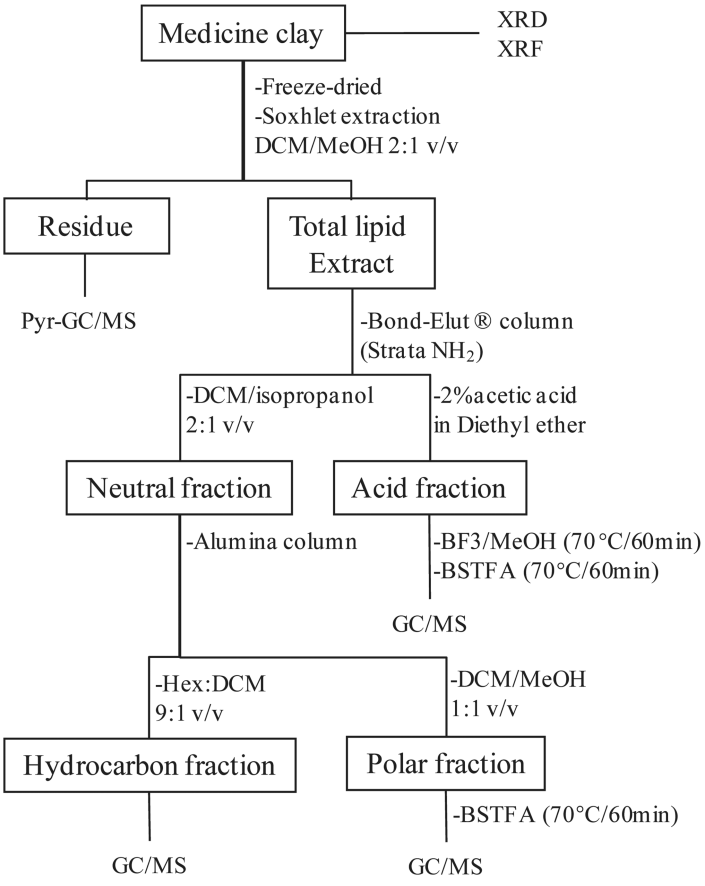

Figure 2. Extraction and isolation scheme of Ghana medicine clays.

were, after addition of a tetracosane-$^{2}H_{50}$ standard, derivatised with BF_3 in MeOH to convert acids into their corresponding methyl ester. In addition, both the polar fractions and the methylated acid fractions were dissolved in bis(trimethylsilyl)trifluroacetamide (BSTFA) and heated (70°C; 60 min) to convert alcohols into their corresponding trimethylsilyl ethers. Blanks were run to ensure that no contamination was introduced during the extraction and separation procedure and were found to be <1:100 for all target analytes. In the case of the Gbankil medicine clay, pyrolysis GC/MS (Pyr-GC/MS) was performed on the residue after extraction.

2.4.2. *Instrumental analyses*

GC/MS was performed using a Agilent 7890A GC, equipped with an Agilent 7683B auto-sampler and programmable temperature vaporization (PTV) inlet, interfaced to an Agilent 5975C MSD mass spectrometer operated in electron ionization (EI) mode (scanning a range of m/z 50–600 at 2.7 scans s^{-1}, ionisation energy 70 eV and a solvent delay of 3 min). The heated interface temperature and PTV inlet were set at 280°C with the EI source temperature at 230°C and the MS quadruple at 150°C. Analyses were performed using an HP-5 MS column (J + W Scientific;

5% diphenyl-dimethylpolysiloxane; length 30 m, ID 250 μm, film thickness 0.25 μm) capillary column. The samples were run at constant flow (1 ml/min) with helium as the carrier gas. The oven temperature was programmed from 70°C to 130°C with 20°C min^{-1}, then to 300°C with 4°C min^{-1}, where it was kept for 25 minutes.

Residue of the Gbankil medicine clay was analysed by Pyr-GC/MS. A sample was pyrolysed using a CDS (Chemical Data Systems) 5200 series pyroprobe pyrolysis unit by heating at 750°C for 10 s to fragment macromolecular organic components. Fragments were analysed using the same Agilent GC/MS system (scanning a range of m/z 50–700 at 2.7 scans s^{-1}, ionisation energy 70 eV and a solvent delay of 10 min) and the same HP-5 fused column as described above. The pyrolysis transfer line and injector temperatures were set at 350°C, the heated interface at 280°C, the EI source at 230°C and the MS quadrupole at 150°C. Helium was used as the carrier gas and the samples were introduced in split mode (split ratio 20:1, constant flow of 1 ml/min). The oven was programmed from 40°C (hold time 6 min) to 320°C at 6°C min^{-1} and held at this temperature for 10 min. Compounds were identified by comparison of spectra with those reported in the literature.

2.4.3. *Biomarker identification and quantification*

Compounds were identified by comparison of spectra and retention times to those reported in the literature. Quantitative data were determined by comparison of individual peak areas and comparison with a known concentration of internal standard.

The long-chain ($>C_{20}$) *n*-alkane odd-over-even predominance, as well as the long-chain *n*-alkanols, *n*-alkanoic acids, *n*-dialkanoic acids and *ω*-hydroxy *n*-alkanoic acids even-over-odd predominances, are expressed in the carbon preference indexes (CPIs) using the following equation:

$$\mathrm{CPI} = \frac{1}{2}\sum(X_i + X_{i+2} + \cdots + X_n)\Big/\sum(X_{i-1} + X_{i+1} + \cdots + X_{n-1}) + \frac{1}{2}\sum(X_i + X_{i+2} + \cdots + X_n)\Big/\sum(X_{i+1} + X_{i+3} + \cdots + X_{n+1}) \quad (1)$$

where X is the compounds' abundance in the range from i to n. The average chain lengths (ACLs) of the long-chain *n*-alkanes, *n*-alkanols, *n*-alkanoic acids, *n*-dialkanoic acids and *ω*-hydroxy *n*-alkanoic acids are reported using the following equation:

$$\mathrm{ACL} = \sum(iX_i + \cdots + nX_n)\Big/\sum(X_i + \cdots + X_n) \quad (2)$$

where, similar to the CPI, X is the compounds' abundance in the range from i to n.

3. Results

3.1. *Mineralogy*

XRD analysis revealed the presence of several minerals in the medicine clays. The Gbankil medicine clay, is mainly composed of quartz SiO_2, microcline feldspar $KAlSi_3O_8$, albite $NaAlSi_3O_8$, muscovite $KAl_2Si_3AlO_{10}(OH)_2$, calcite $CaCO_3$, kaolinite $Al_2(Si_2O_5)(OH)_4$ and dravite $NaMg_3Al_6B_3Si_6O_{27}(OH)_4$, which is a variety of tourmaline (Figure 3). The other two medicine clays showed a

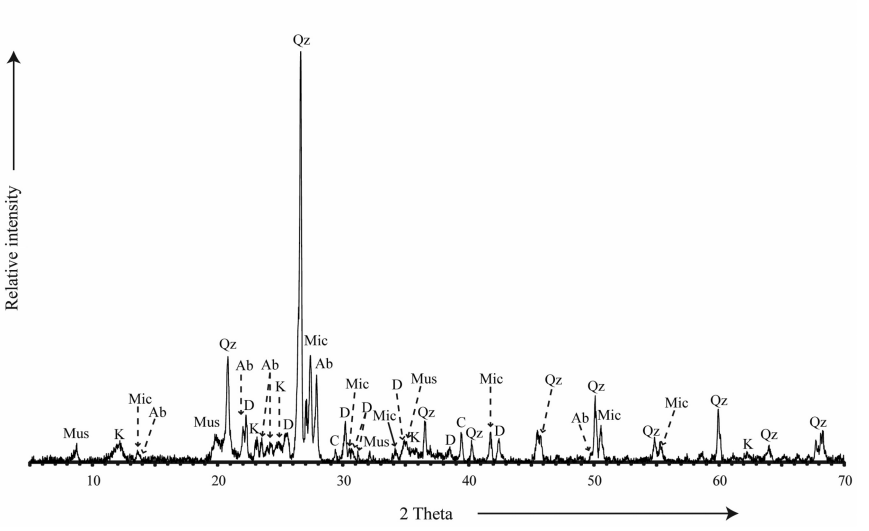

Figure 3. XRD spectrum of the Gbankil medicine clay. Qz = quartz, Ab = Albite, Mic = microcline feldspar, Mus = muscovite, D = dravite, K = Kaolinite and C = Calcite.

comparable composition with the exception of the absence of calcite in the Kusanaab medicine clay and albite in the Yaane medicine clay, but no dravite could be detected in either of these two medicine clays (not shown). The non-medicine clay from Yikine showed a composition of the same main minerals: quartz, albite, microcline feldspar and muscovite. However, no kaolinite could be detected.

3.2. *Elemental analyses*

XRF analysis of the chemical composition of all clays revealed a predominance of Al_2O_3 and SiO_2 (Table 1), consistent with the minerals determined though XRD data. A wide range of minor and trace elements were also quantified, which are comparable between the samples. There are a few exceptions, with some found at relatively high concentrations (e.g. Ba, Mn, Rb, Sr and Zr; Table 1).

3.3. *Extractable organic matter*

3.3.1. *Hydrocarbon fractions*

GC/MS analyses of the saturated hydrocarbon fractions of all three analysed medicine clays revealed predominantly C_{17}-C_{36} *n*-alkanes (Figure 4(a); Table 2) with C_{29} *n*-alkane (see Appendix, structure I) as the most abundant component ($ACL_{21–35}$ ranged from 27.8 to 30.0; Table 3) and an odd-over-even carbon-number predominance. This is well reflected in the $CPIs_{21–35}$ of the *n*-alkanes series, with values between 3.7 and 14.4 (Table 3). Besides these *n*-alkanes, substantial amounts of *n*-alkenes (predominantly C_{27} *n*-alkene, II) were present in the Gbankil medicine clay and squalene (III) in the Yaane medicine clay. In addition, diploptene (17(H),21(H)-hop-22(29)ene; IV) was present in both the Gbankil and Kusanaab medicine clay samples.

Table 1. Major, minor and trace element concentration in Ghana medicine clays and non-medicine clay for comparison (all from XRF analysis).

Compound/element	Gbankil	Kusanaab	Yaane	Yikine
Major elements (wt%)				
Na_2O	0.61 ± 0.02	0.41 ± 0.02	0.34 ± 0.02	1.29 ± 0.03
MgO	0.88 ± 0.03	0.74 ± 0.03	0.93 ± 0.03	1.13 ± 0.03
Al_2O_3	23.1 ± 0.1	24.1 ± 0.1	27.7 ± 0.1	19.0 ± 0.1
SiO_2	63.6 ± 0.1	63.2 ± 0.1	59.9 ± 0.1	66.6 ± 0.1
P_2O_5	0.21 ± 0.01	0.35 ± 0.02	0.25 ± 0.01	0.09 ± 0.01
SO_3	0.14 ± 0.01	0.21 ± 0.01	0.08 ± 0.01	0.05 ± 0.01
Cl	0.09 ± 0.01	0.08 ± 0.01	0.05 ± 0.01	0.01 ± 0.01
K_2O	4.04 ± 0.06	4.40 ± 0.06	3.80 ± 0.06	1.63 ± 0.04
CaO	1.25 ± 0.03	0.84 ± 0.03	0.62 ± 0.02	2.49 ± 0.05
Ti	0.62 ± 0.02	0.49 ± 0.02	0.57 ± 0.02	0.52 ± 0.02
Fe_2O_3	5.04 ± 0.07	4.67 ± 0.06	5.21 ± 0.07	6.66 ± 0.08
Minor and trace elements[a] (ppm)				
V	55	49	57	60
Cr	26	20	35	34
Mn	420	390	410	570
Ni	10	<10	17	14
Cu	<10	13	<10	17
Zn	50	58	61	40
Ga	25	24	30	18
Rb	140	140	150	36
Sr	440	400	310	402
Y	12	14	14	11
Zr	360	310	290	287
Nb	11	11	14	<10
Cs	10	bd	bd	<10
Ba	1100	1300	890	664
La	56	52	65	27
Ce	100	100	110	60
Nd	30	32	37	18
Pb	42	40	50	<10
Th	11	10	14	<10
U	10	<10	13	<10

[a]Concentrations above detection limits but below 10 ppm are not recorded and indicated in the table as <10.

3.3.2. *Acid fractions*

All acid fractions were dominated by a homologous series of long-chain (C_{20}-C_{35}) *n*-alkanoic acids (Figure 4(b); Table 2), with C_{28} *n*-alkanoic acid (V) being the most abundant component (the $ACL_{20\text{-}34}$ ranged from 26.0 to 27.3; Table 3) and an even-over-odd carbon number predominance. This is well reflected in the $CPI_{20\text{-}34}$ of the *n*-alkanoic acid series, with values between 5.2 and 6.1 (Table 3). Besides the long-chain *n*-alkanoic acids, substantial amounts of short chain ($< C_{20}$) *n*-alkanoic acids were present, with the C_{16} member being the most abundant component. In the Yaane medicine clay the C_{16} *n*-alkanoic acid was the most abundant compound present. Also present in all samples were homologous series of C_{20}-C_{31} ω-hydroxy alkanoic acids (Figure 4(b); Table 2), with C_{24} ω-hydroxy alkanoic acids (VI) as the most abundant component ($ACL_{20\text{-}31}$ between 24.8 and 25.0; Table 3), and C_{21}-C_{27}

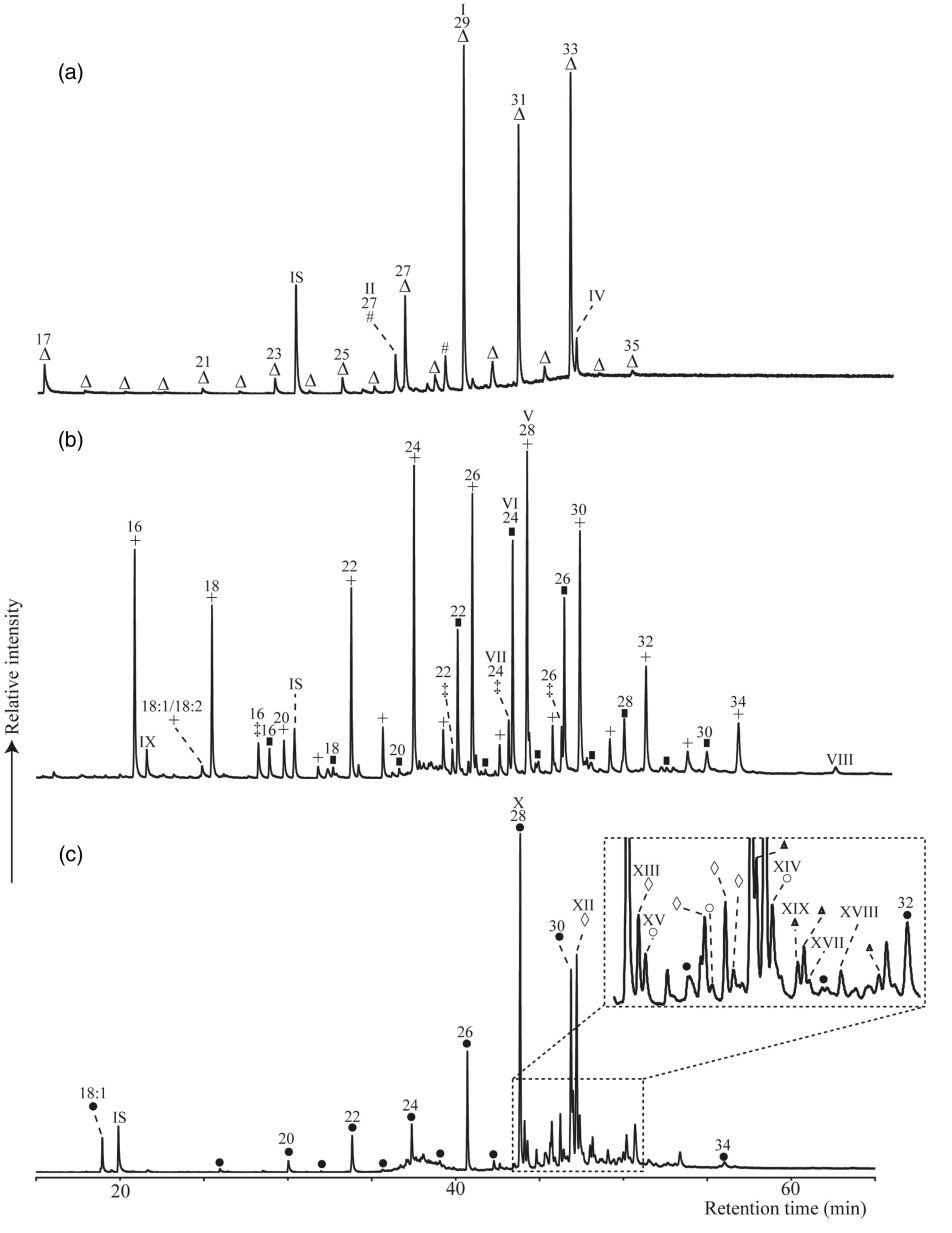

Figure 4. GC/MS total ion current chromatograms of (a) the saturated hydrocarbon fraction, (b) the acid fraction and (c) the polar fraction of the Gbankil medicine clay. (Δ) *n*-alkanes, (#) *n*-alkenes, (+) *n*-alkanoic acids, (‡) *n*-alkanoic diacids, (■) ω-hydroxy alkanoic acids, (●) *n*-alkanols, (◇) sterols, (○) stanols, (▲) triterpenols and IS = internal standard. Numbers indicate carbon chain length, numbers after the colon indicate the number of double bonds present and the roman numerals refer to the compounds shown in the Appendix.

Table 2. Concentrations of the major lipid classes in the Ghana medicine clays.

Compound (class)	Concentrations (ng g^{-1} medicine clay)		
	Gbankil	Kusanaab	Yaane
Hydrocarbon fraction			
n-alkanes[a]	1500	940	360
n-alkenes[b]	130	n.d.[m]	n.d.[m]
Squalene (III)	n.d.[m]	n.d.[m]	200
Diploptene (IV)	45	20	n.d.[m]
Acid fraction			
n-alkanoic acids short-chain ($<C_{20}$)[c]	1100	3100	3000
n-alkanoic acids long-chain ($>C_{20}$)[d]	5700	4400	1700
ω-hydroxy alkanoic acids[e]	2000	1900	500
n-alkanoic diacids[f]	410	390	84
17β(H),21β(H)bishomohopanoic acid (VIII)	37	19	11
4-methoxy-3-hydroxy-cinnamic acid (IX)	100	77	n.d.[m]
Polar fraction			
n-alkanols long-chain ($<$C20)[g]	2700	2000	680
n-alkanols short-chain ($>$C20)[d]	140	320	110
Midchain alkanols[h]	n.d.[m]	1300	n.d.[m]
Sterols[i]	1200	880	780
Stanols[j]	280	500	85
Sterones[k]	67	100	77
Triterpenoids[l]	45	700	27

[a]The sum of the concentrations of the *n*-alkanes from C_{17} till C_{37}; $\Sigma(C_{17}$-$C_{37})$;
[b]$\Sigma(II+C_{29:1})$;
[c]$\Sigma(C_{16:0}+C_{18:0}+C_{18:1}+C_{18:2})$;
[d]$\Sigma(C_{20}$-$C_{35})$;
[e]$\Sigma(C_{20}$-$C_{31})$;
[f]$\Sigma(C_{21}$-$C_{27})$;
[g]$\Sigma(C_{16:0}+C_{18:0}+C_{18:1})$;
[h]$\Sigma(C_{27}$-$C_{31})$;
[i]$\Sigma(C_{27}$-$C_{29})$;
[j]$\Sigma(C_{27:1}$-$C_{29:1}+C_{29:2})$;
[k]$\Sigma(XIV+XV+XVI)$;
[l]$\Sigma(XX+XIX)$;
[m]n.d., not detected.

n-alkanoic diacids, with the C_{24} *n*-alkanoic diacid (VII) as the most abundant component ($ACL_{21–27}$ between 24.3 and 24.6). Both the homologous series of ω-hydroxy alkanoic acids and *n*-alkanoic diacids showed an even-over-odd carbon number predominance with $CPI_{22–30}$ and $CPI_{22–26}$ between 5 and 17.4 and 3.6 and 9.9, respectively (Table 3). In addition, 17β(H),21β(H)bishomohopanoic acid (VIII) was present in all samples and 4-methoxy-3-hydroxy-cinnamicacid (IX) in both the Gbankil and Kusanaab medicine clay samples.

3.3.3. *Polar fractions*

All polar fractions were dominated by a homologous series of long-chain (C_{20}-C_{35}) *n*-alkanols (Figure 4(c); Table 2), with C_{28} *n*-alkanol (X; Gbankil and Kusanaab medicine clay) or C_{30} *n*-alkanol (Yaane medicine clay) being the most abundant

Table 3. Relative distributions of the high molecular *n*-alkanes, *n*-alkanols, *n*-alkanoic acids, *n*-dialkanoic acids and ω-hydroxy *n*-alkanoic acids in Ghana medicine clay samples.

Distributions	Gbankil	Kusanaab	Yaane
n-alkanes			
$ACL_{27\text{-}35}$[a]	30.0	29.2	27.8
$CPI_{21\text{-}35}$[a]	10.1	14.4	3.7
n-alkanoic acids			
$ACL_{20\text{-}34}$[a]	5.9	6.1	5.2
$CPI_{20\text{-}34}$[a]	27.3	26.0	26.6
long-chain/short-chain[b]	4.6	1.1	0.5
ω-hydroxy alkanoic acids			
$ACL_{20\text{-}31}$[a]	25.0	24.8	24.9
$CPI_{22\text{-}30}$[a]	12.7	17.4	5.0
n-alkanoic diacids			
$ACL_{21\text{-}27}$[a]	24.3	24.6	24.3
$CPI_{22\text{-}26}$[a]	5.9	9.9	3.6
n-alkanols			
$ACL_{20\text{-}34}$[a]	28.0	27.4	27.1
$CPI_{20\text{-}34}$[a]	17.8	15.8	12.1
long-chain/short-chain[b]	19.4	6.1	6.3

[a]As determined in paragraph 2.4.3 [b]Ratio of the sum of the long-chain *n*-alkanoic acids or *n*-alkanols to the sum of the short-chain *n*-alkanoic acids or *n*-alkanols (see Table 2).

component ($ACL_{20\text{-}34}$ between 27.1 and 28.0; Table 3) and an even-over-odd carbon number predominance. This is well reflected in the $CPI_{20\text{-}34}$ of the *n*-alkanol series, with values between 12.1 and 17.8 (Table 3). Besides the long-chain *n*-alkanols, substantial amounts of short-chain *n*-alkanols were also present, with $C_{18:1}$ *n*-alkanol (X; Gbankil and Kusanaab medicine clay) or C_{18} *n*-alkanol (Yaane medicine clay) being the most abundant component. In the Kusanaab medicine clay, substantial amounts of (C_{27}-C_{31}) midchain alkanols (Table 2), with C_{29} midchain alkanol (XI) being the most abundant component, midchain *n*-alkanols were also present. Other compounds present in the polar fractions include sterols, predominantly 24-ethylcholest-5-en-3β-ol (sitosterol; XII) in the Gbankil and Kusanaab medicine clays or cholest-5-en-3β-ol (cholesterol; XIII) in the Yaane medicine clay; stanols, predominantly ethylcholestanol (XIV) in the Gbankil and Kusanaab medicine clays or cholestanol (XV) in the Yaane medicine clay; sterones, predominantly cholest-4-en-3-one (XVI) stigmast-3,5-dien-3-one (XVII) and stigmast-4-en-3-one (XVIII); and triterpenoids, predominantly β-amyrin (XIX) in the Gbankil and Kusanaab medicine clays or taraxerol methylether (XV) in the Yaane medicine clay.

3.3. *Non-extractable organic matter*

The pyrolysate of the residue of the Gbankil medicine clay (Figure 5) is dominated by products derived from polysaccharides (peaks 1, 5, 7 and 13), N-containing compounds (peaks 2, 3, 6, 8, 9, 10 and 21) and phenols (peaks 14, 16, 18, 22, 24, 29) Also present is Guiacol (peak 19), benzene and naphthalene derivatives and a series

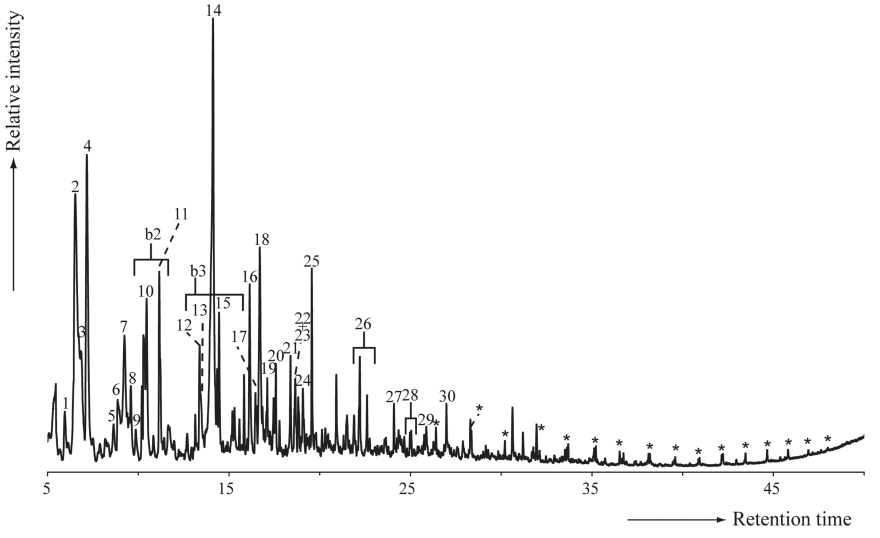

Figure 5. Pyrolysis GC trace of the Gbankil medicine clay. Closed star = *n*-alkene/*n*-alkane pair and b*x* = benzene derivative, where *x* represents the number of carbon atoms in the alkyl group. The numbers refer to the compounds listed in Table 4.

of *n*-alkenes/*n*-alkanes. A summary of the peak numbers and an assignment of the majority of the peaks is given in Table 4.

4. Discussion

Information on the composition of Ghana medicine clays is limited. The results indicated that a combination of inorganic and biomarker analyses can be used to evaluate the composition and origin of the materials present in these clays. Although there are some differences among the medicine clays studied, all these clays generally showed a comparable composition in mineralogy, elemental composition and biomarker assemblages.

4.1. *Organic composition*

Molecular analyses suggested that the extractable organic matter (OM) of all three medicine clays is dominated by series of long-chain *n*-alkanols, *n*-alkanoic acids, ω-hydroxy alkanoic acids and *n*-alkanoic diacids (Table 2). These long-chain *n*-alkyl compounds are major components of epicuticular waxes from vascular plant leaves (Eglinton and Hamilton 1963, 1967), relatively resistant to degradation (Cranwell 1981), which makes them suitable for use as higher plant biomarkers. They have been identified in a variety of recent and ancient terrestrial and marine environments (Bird et al. 1995; Freeman and Colarusso 2001; Pancost and Boot 2004; Rieley et al. 1991; van Dongen et al. 2000, 2006) and long-chain *n*-alkanes, *n*-alkanols and *n*-alkanoic acids have been observed in fossil plant tissues (Logan, Smiley, and Eglinton 1995). The long-chain *n*-alkanes in vascular plants typically have a strong even-over-odd carbon number predominance while the long-chain *n*-alkanols and acids are

Table 4. Main identified pyrolysis products in the Gbankil medicine clay. Numbers refer to Figure 5. The compounds are related to components in the OM. Abbreviations Ps: polysaccharide; Pr; protein; Pp: polyphenol; Lg: lignin; Ar: aromatic.

No.	Compound	Origin
1	2-methylfuran	Ps
2	pyridine	Pr
3	pyrrole	Pr
4	toluene	Pp/Pr
5	3-furaldehyde	Ps
6	4-methylpyridine	Pr
7	furfural	Ps
8	2-methylpyrole	Pr
9	3-methylpyrole	Pr
10	3-methylpyridine	Pr
11	styrene	Pp/Pr
12	benzaldehyde	
13	5-methyl-2-furaldehyde	Ps
14	phenol	Pp/Pr/Lg
15	benzofuran	Ps
16	2-methylphenol	Pp/Pr/Lg
17	acetophenone	
18	3- and 4-methylphenol	Pp/Pr/Lg
19	guaiacol	Lg
20	methylbenzofuran	Ps
21	benzyl cyanide	Pr
22	C_2-phenol	Pp/Lg
23	methylindene	Ar
24	C_2-phenol	Pr
25	naphthalene	Ar
26	methylnaphthalenes	Ar
27	vinylnaphthalene	Ar
28	C_2-naphthalenes	Ar
29	phylpyridine	Pr
30	dibenzofuran	Ar

characterised by a high odd-over-even carbon number predominance, reflecting their biosynthesis from acetyl moieties (Eglinton and Hamilton 1963, 1967; Kolattukudy 1976). As a consequence, extracts from modern plants typically have very high CPIs (ranging from around 4 to 40; Collister et al. 1994), in agreement with the values observed in the medicine clays (Table 3). In addition, the ACLs are comparable for those typically observed in vascular plants, supporting a higher plant origin (Eglinton and Hamilton 1963, 1967; Kolattukudy 1976).

Other compound classes observed in the medicine clays, such as pentacyclic triterpenoids, steroids and a cinnamic acid derivative (Table 2) are also common in higher plants. β-amyrin (XIX) for instance is very abundant in angiosperms (Moldowan et al. 1994) while tarax-14-ene based structures (compound XX) are abundant in mangrove leaves (Wannigama et al. 1981) but are also commonly found in peat forming plants (Pancost et al. 2002). In addition, cinnamic acid is a known lignin moiety (Tuyet Lam, Iiyama, and Stone 1992) and sitosterol is often the most abundant sterol observed in most higher plants (Goad and Akihisa 1997).

Also present in all medicine clays are diplotene (IV) and hopanoic acid (VIII; Table 2), often observed in soils (Ries-Kautt and Albrecht 1989). These pentacyclic triterpenoids are membrane components of many bacteria, including methanotrophs, aerobic heterotrophic bacteria and cyanaobacteria (Ourisson, Rohmer, and Poralla 2003; Rohmer, Bisseret, and Neunlist 1992) indicating a contribution of microbial origin to the clays. Besides these triterpenoids, substantial amounts of short-chain *n*-alkanoic acids and *n*-alkanols are present in all three clays. Again, these are most likely of microbial origin, although these occur in the lipids of all living organisms, supporting a microbial contribution to these medicine clays.

The pyrolysate analyses of the Gbankil medicine clay residues further supports the predominantly plant derived origin of the OM present as well as a contribution of microbial origin. Polysaccharide-derived moieties were abundantly present in the pyrolysate of the Gbankil medicine clay (Figure 5 and Table 4). Considering that these biopolymers are prevalent in all plant tissues, which is in agreement with earlier observations, this may be derived from very resistant residual organic matter closely associated with the clay minerals (Schulten, Leinweber, and Sorge 1993). However, a contribution from microbes cannot be excluded (Stuczynski et al. 1997).

Also abundant were N-containing compounds such as pyrroles and pyridines (Figure 5 and Table 4). These have been frequently observed in all kind of soils/sediments and are most likely originating from amino acids, amino sugars, proteins or other polypeptides (Chiavari and Galletti 1992; Granada et al. 1991; Nierop, Pulleman, and Marinissen 2001; Tsuge and Matsubara 1985). Since N-compounds are normally more abundant in soils that are more decomposed, enriched in microbial sugars (Guggenberger, Christensen, and Zech 1994), it is likely that these are originating to a large extent from microbes, supporting a microbial contribution to these clays.

Further identified were alkylbenzenes, alkylphenols, aromatic compounds and a homologous series of *n*-alkenes and *n*-alkanes (Figure 5 and Table 4). Again, these have often been observed in clays and the origin of these compounds is diverse. Alkylbenzenes (toluene, C_2 and C_3 benzenes) and alkylphenols have, for instance, been observed on pyrolysates of tannins (Galletti and Reeves 1991), lignin (Saiz-Jimenez and de Leeuw 1986), polysaccharides (Pouwels, Eijkel, and Boon 1989) and proteins (Chiavari and Galletti 1992). The origin of the homologous series of *n*-alkenes and *n*-alkanes is still a matter of debate (Vancampenhout et al. 2010) but possible sources include microbial polymers (Lichtfouse et al. 1995, 1998), aliphatic biopolymers such as cutan and suberan (Augris et al. 1998; Tegelaar, de Leeuw, and Saiz-Jimenez 1989) or lipids that are polymerized onto clay minerals (Almendros et al. 1996). Aromatic pyrolysis products most likely originate from OM compounds derived from proteins, tannins and other (poly)phenols including black carbon (Maie et al. 2003; Saiz-Jimenez 1995; Saiz-Jimenez and de Leeuw 1986). Both *n*-alkenes and *n*-alkanes and aromatics are considered relatively recalcitrant to microbial decay (Lorenz, Preston, and Nierop 2007; Saiz-Jimenez and De Leeuw 1987) making them very likely to be observed in these type of clays. Besides a possible contribution of alkylphenols, the only lignin-derived monomer present was guaiacol (Hedges and Mann 1979), further supporting the earlier finding of the cinnamic acid derivative suggesting a (small) contribution of lignin origin to the clays.

In summary, both the molecular analyses of the extractable OM and the pyrolysate analyses of the Gbankil medicine clay indicated that the composition of

the OM in these clays is dominated by material of (higher) plant origin with a smaller contribution of microbial derived origin. Based on these analyses no unnatural organic material could be detected making an exogenous contribution to these clays less likely.

4.2. *Mineralogy and elemental composition*

Generally, the XRD and XRF analyses show that the mineralogy of all the medicine clays studied are very similar to each other (Figure 3 and Table 1). The minerals observed are all common rock-forming minerals observed in a variety of geological settings (Batty and Pring 1997; Mottana, Crespi, and Liborio 1978). Kaolinite forms mainly by the weathering of feldspars, and also from the breakdown of feldspathic rocks, e.g. granite by hydrothermal action (Batty and Pring 1997). Calcite forms by precipitation from fluids, e.g. hydrothermal or seas (Batty and Pring 1997). As granite is known to be a major rock type in the Upper East Region of Ghana, these minerals are not unusual, either from the granite itself or from the precipitation from associated hydrothermal fluids. The presence of tourmaline (Figure 3) and relative high concentration of Zr, a common accessory mineral in granites (Batty and Pring 1997), in the Gbankil medicine clay (Table 1) is also suggestive that this clay formed as a result of the weathering and re-deposition of a granitic source rock. The results of the non-medicine clay (Yikine) analyses suggests that there are no major differences between this clay and the medicine clays, with the exception of the absence of kaolinite, suggesting less weathering.

In general, the results of the XRF analyses are comparable to those of measurements for the average upper continental crust/sedimentary mud rock as described in Andrews et al. (2004); with slight exceptions for Na_2O, MgO and CaO, which are depleted and Al_2O_3 which is enriched. However, this most likely comes from the weathering of feldspars to form kaolinite, through the chemical weathering process of hydrolysis (Andrews et al. 2004). There are no significant differences between the samples in terms of their major compounds, and any slight differences can most likely be attributed to variations in the amount of weathering that has occurred. The non-medicine clay Yikine, is more pristine in nature, it has most likely not been weathered as much as the medicine samples that contain kaolinite. Therefore, the chemistry differs slightly in that there are higher concentrations of Na_2O, MgO and CaO, and a lower concentration of K_2O (Table 1). Many of the trace elements detected are comparable between the medicine clay samples (range of 10 ppm). Slightly higher variations in Rb, Ba, La and Ce were observed in the non-medicine clay if compared to the medicine clays. Any variations present at this scale will be due to variable amounts of these trace elements being incorporated into the minerals. This can result from different conditions during mineralisation, allowing greater or lesser substitution, or could be due to differences in the accessory minerals present.

To summarise, the mineralogy and elemental composition support the hypothesis that these clays are of natural, uncompromised, origin. Furthermore, the analyses indicates that if these samples were analysed as being used for unknown purposes, it would not be possible to distinguish them in terms of mineralogy, nor would it be possible to link them with a certain location or shrine.

5. Conclusions

The dispersal of the Yaane medicine clay as part of the process of obtaining the right to operate the shrine is of significant anthropological and historical, as well as potential archaeological, interest (Allman and Parker 2005; Insoll 2006). However, the very similar mineralogy of the medicine clays studied indicates that differentiating between them in archaeological contexts, unless the geology radically differed, would not be viable. Molecular analyses indicate a dominance of OM originating of (higher) plant origin with a substantial contribution of microbial origin. Based on the (pyr)-GC/MS analyses no unnatural organic material could be detected, making, supported by elemental and mineral analyses, an exogenous contribution to these clays unlikely. It would thus seem that the perceived 'power' of the medicine is derived from its shrine association rather than from any inherent or added pharmacological properties. Equally, the absence of anthropogenically-introduced elements accords with the Talensi description of the origin of the medicine clays as 'divine', if translated into 'unaltered'.

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Appendix: Structures of the most abundant compounds in the Ghana medicine clay extracts