Clays and Clay Minerals, Vol. 56, No. 6, 751–760, 2008.

MEDICINAL CLAY AND SPIRITUAL HEALING

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Abstract—The varied mineralogical composition of earthy materials and the quantity of elements extracted by simulated stomach acid substantiate the diversity of materials consumed by humans practicing geophagy. Direct consumption of 'edible earths' for medicinal and spiritual purposes occurs worldwide and is deeply rooted in 'folk medicine' and religion. The legends associated with the healing powers of the clay from Chimayo, New Mexico, provide an excellent example of the roots of geophagy. The clay mineral assemblages revealed by X-ray diffraction analysis of 22 samples from New Mexico, North America, and other parts of the world are highly variable. One might be monomineralic kaolinite or smectite, and another, a complex mixture of illite, kaolinite, smectite, and chlorite or vermiculite. The quantities of elements (Al, Si, K, Na, Ca, Mg, Fe, Mn, Ti, P, S, Ba, Sr, Pb, Zn, Cd, Co, Cu, Cr, Ni, V, Zr, Se, Mo, Be, Sb, and As) extracted by 0.12 M HCl varied from ~1.0 mg/g to the limit of detectability, 0.0001 mg/g. Potential long-term human health effects were evaluated with the Reference Dose Ratio (RDR). It divides the quantity of the element extracted from 50 g of the total sample by the recommended reference dose (RfD) reported in the Environmental Protection Agency's (EPA, USA) IRIS (Integrated Risk Information System) database. Median RDR values for Na, Cr, Sb, and As exceeded 1.0 indicating an abnormally high potential intake. Materials consumed by humans are so varied that caution should be used in comparing the results of one clay study with those of another without mineralogical and chemical data.

Key Words—Clay, Geochemistry, Healing Clay, Health, Human Geophagy, Major Elements, Medical Geology, Reference Dose Ratio, Trace Elements.

INTRODUCTION

Chimayo, a small village on State Highway 76, ~25 miles northeast of Santa Fe, New Mexico, is a location where medicinal uses of clays and spiritual healing are intimately intertwined. El Santuario, the chapel (Figure 1a) constructed in ~1816, is visited by thousands of pilgrims each year who seek the blessed clays contained in 'El Posito', a small pit (Figure 1b) in a room adjacent to the altar. According to a local historical society (http://chimayo.org/history.html), the legendary powers of the clays originated as a result of a miracle: 'Somewhere around 1810, a Chimayo friar was performing penances when he saw a light bursting from a hillside. Digging, he found a crucifix, quickly dubbed the miraculous crucifix of Our Lord of Esquipulas. A local priest brought the crucifix to Santa Cruz, but three times it disappeared and was later found back in its hole. By the third time, everyone understood that El Señor de Esquipulas wanted to remain in Chimayo, and so a small chapel was built on the site. Then, the miraculous healings began. These grew so numerous that the chapel had to be replaced by the larger, current Chimayo Shrine – an adobe mission – built in 1816.' The crucifix in the chapel depicts a Black Christ (Figure 1c) similar to that worshipped in Esquipulas, Guatemala (M. Richardson, pers. comm.).

There are many abandoned crutches and enthusiastic testimonials to the healing powers of the Chimayo clays attached to the walls of a room adjacent to the chapel. In earlier times, the clays were ingested or applied as a paste to the affected parts of the body. This practice may have been adapted from the local Indians who frequented the area to drink the mineral waters or bathe in the clays forming in springs emerging from the volcanic deposits. Now, the materials filling the pit are derived from various other sources and the local priest attributes their power to the blessing that he performs daily (Father Rocha, pers. comm.). The healing clays from Chimayo are linked to the practice in Esquipulas, Guatemala, and the widespread use of edible earths.

The deliberate consumption of earth, geophagy, is a worldwide practice associated with religious customs as in Chimayo or 'folk medicine' such as the use of 'eko' in Nigeria (Vermeer and Ferrell, 1985) for antidiarrheal purposes. As early as 1895, an anthropologist wrote in *Scientific American* that: "Among the extraordinary passions for eating uncommon things must be reckoned that which some peoples exhibit for eating earth or clay... In some places the custom has degenerated into a ceremonial, while in others the eating of this strange food still prevails as a kind of necessity to the lives of those who are addicted to it. The Mexican devotees picked up a piece of clay in the Temple of Tezcatlipoca and ate it with the greatest reverence, and also ate a piece of earth in swearing by the sun and earth. But the use of clay by the Mexicans was not merely a matter of ceremony, for the substance seems to have been an

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DOI: 10.1346/CCMN.2008.0560613

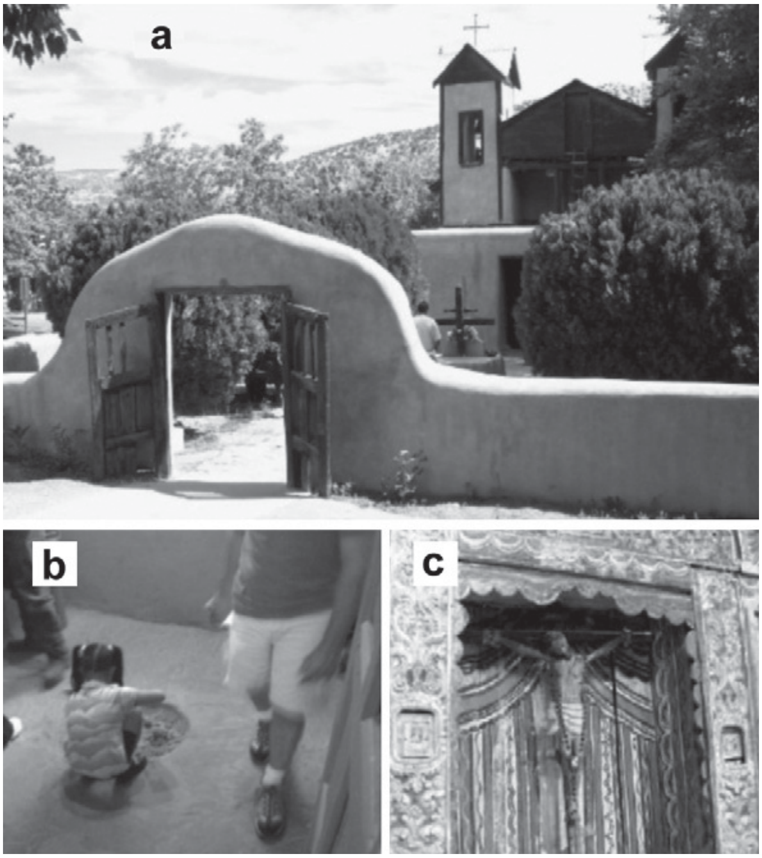


Figure 1. (a) ‘El Santuario’ is the focal point for clay healing in Chimayo, New Mexico. (b) Clay is freely available from ‘El Posito’. (c) The Black Christ in the chapel links the local practice with religious clay eating in Esquipulas, Guatemala.

esculent in common use. Edible earth was sold openly in the markets of Mexico.” Clay tablets sold in the market of Esquipulas, Guatemala, today are embossed with Indian and Christian symbols (Figure 2a,b) and distributed throughout Latin America (Hunter *et al*., 1989). Capsules containing clay may be purchased in Mexico City markets. In Nigerian markets, clay (Figure 2c) is sold in spindle-forms, as discs, and rough blocks that may be raw or smoked as in ‘eko’ (Vermeer and Ferrell, 1985). Georgia kaolin (Figure 3) is packaged by Down Home Georgia White Dirt, Inc., and distributed in grocery stores and convenience stores in many areas of the State. Several websites testify to the ‘miraculous’ powers of clays, but their claims are not supported by objective scientific studies.

Many synonyms for edible clay are known, including “akipula, beidellitic montmorillonite, chalk, clay dirt, clay tablets, colloidal minerals, fossil farina, Indian healing clay, mountain meal, panito del señor, tierra santa, *Terra sigillata*, and white mud···” (*Medicine Plus*, 2006 – www.nlm.nih.gov/medlineplus/druginfo/natural/patient-clay.html). The use of clay for medical purposes has a long history, dating back to 2500 BC when the Tablets of Nippur identified the wound healing and other properties of clays (Reinbacher, 2003). The Greeks and Romans often pressed tablets and wafers of clays, embossing their surfaces with images of gods. Some of these *Terra sigillata* tablets from the Greek Island of Lemnos were found to contain disordered or highly crystalline kaolinite, smectite (montmorillonite), or illite (Robertson, 1996). An article by Stumpf in 1906 brought new attention to the use of fine kaolin for the treatment of cholera and certain bacterial diseases. Robertson (1986) reports that Stumpf recognized the beneficial uses of clay for bacteriostatis, sterilization, membrane coating, adsorption of toxins, and the clearing of the alimentary canal, and clay (bolus alba) was listed as a remedy for many of these maladies in pharmocopeias until the middle of the last century. Robertson (1996) maintains that knowledge of the healing power of ingested clays could greatly reduce deaths due to diarrheal-like disorders that are prevalent today and becoming more immune to antibiotic drugs. The natural antibacterial properties of a French green clay in the treatment of Burundi ulcer were described by Williams *et al*. (2004, 2008). Additional geophagical functions of clays including detoxification of astringent foodstuffs and mineral supplementation were reported by Johns and

Figure 2. (a,b) Clay is marketed in Esquipulas as 5–6 cm wide embossed tablets. (c) Clay in a Nigerian market is sold in a variety of forms (photo courtesy of D. Vermeer).

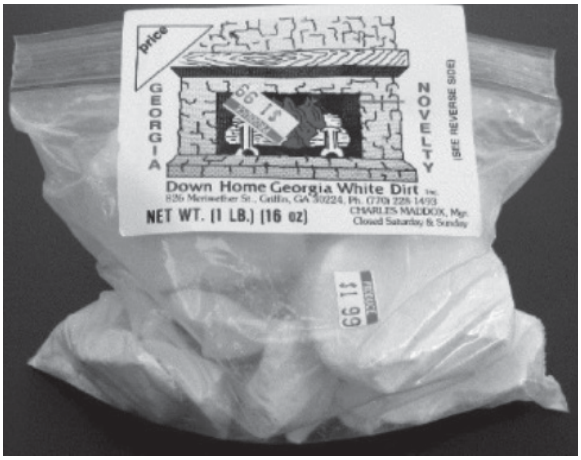


Figure 3. 'Down Home Georgia White Dirt' is found in grocery and convenience stores throughout the area near Athens, Georgia, USA.

Duquette (1991). Some of the African clays that they studied released nutritionally significant amounts of Ca, Cu, Fe, Mg, Mn, or Zn, while others did not. Three types of clay found in Italy were examined mineralogically and chemically to assess their contribution to the metals found in rat urine after clay ingestion, as a precursor to the study of human health effects (Mascolo *et al*., 1999). Considerable quantities of As and Se are present in most tests and other elements varied in relation to the composition of the ingested clays. Papers in the volume assembled by Carretero and Lagaly (2007) provide many insights into clays used for external and internal medicinal purposes.

Wilson (2003) reviewed reports of geophagy among humans and other animals in an attempt to assess the role of their mineralogical composition on their reported healing power or provision of supplemental dietary nutrients or micronutrients. Wilson concludes that "There is good evidence to support all the major hypotheses outlined; namely, detoxification, or at least enhancement of the palatability, of foodstuffs containing undesirable components; alleviation of gastrointestinal upsets such as diarrhea; mineral supplementation, particularly Fe and Ca; and as an antacid to relieve excess acidity in the digestive tract." More specific conclusions regarding the role of clay minerals in relief of specific conditions could not be reached because reports of the clay minerals present were sketchy and lacked detail. Wilson (2003) recommended the use of more specific soil mineral analyses and geochemical extractions simulating reactions in the digestive tract as essential ingredients in future studies of the causes and effects of geophagy. Further, Mahaney and Krishnamani (2003) provided strong support for the use of modern soil sampling and analysis methods in the collection of geophagic materials.

Dissanayake (2005) identified eating clay as a worldwide practice providing a direct link between environmental geochemistry and human health. He urged research to answer several questions, including: "Why do humans and animals consume soil? Could it be that inorganic nutrients in the soil supplement our dietary intake of essential trace elements? Does the ingestion of soil cause detoxification of noxious or unpalatable compounds present in the diet? Do these soil elements alleviate gastro-intestinal ailments?"

Abrahams (2005) reviewed involuntary and voluntary consumption of earth by humans. Involuntary geophagia by children is linked to high Pb blood levels and increased intake of heavy metals. In regions associated with soils derived from the weathering of mineral deposits or mine wastes, high levels of potentially harmful elements such as Pb and radionuclides may be readily available (Barltrop *et al.*, 1974; Ljung *et al.*, 2006). Deliberate geophagy can be attributed to the use of soil as: a food supplement or detoxifier; a means to reduce a psychiatric or psychological craving; a pharmaceutical; part of a cultural practice; or a way to correct a nutritional deficiency. Mud cookies baked in the sun by Haitians in Port-au-Prince are one way that poor people reduce hunger as food prices soar (Katz, 2008).

However, geophagy by humans also has undesirable consequences. Pica, or geophagy, may produce a blockage of the bowel that must be removed surgically (Padilla and de la Torre, 2006). Other potentially harmful effects may lead to variable levels of blood K, nutritional deficiencies, parasitic diseases, metal poisoning, diseases of the mouth and gums, and a variety of gastro-intestinal problems (Carretero *et al.*, 2006; Gomes and Silva, 2007). Some have recommended stricter regulation on materials used in products intended for human consumption (Tateo and Summa, 2007).

Until more research is completed, there is no way to evaluate the risks and benefits of geophagy. Almost any element may be available in different quantities from different soils. Properties of soils that should be considered are the mineralogical controls on particle-size distribution, surface area, ion exchange capacity, and bioavailability of adsorbed and associated minor and trace elements. One should not expect the results to be the same for all soils because of their varied origins and complex mineral composition. The clay mineralogical variability of edible clays from selected worldwide locations and the quantities of elements readily extracted from them by simulated stomach acid are demonstrated here. These preliminary data call attention to the general practice of geophagy and the diversity of the materials used. The highly variable nature of the results should be considered in the design of experiments to answer the questions posed by Dissanayake. Geophagy is very important because it provides a direct connection between human health and the environment (Ferrell *et al.*, 1985).

MATERIALS AND METHODS

Present and former colleagues of the author in the Louisiana State University Department of Geography and Anthropology, Donald Vermeer, William Davidson, and Miles Richardson, supplied most of the samples studied in this investigation and a list of sample localities with a brief description of the materials is provided (Table 1). Many of the samples are actually sands or silts with small quantities of clay-sized material.

Air-dry samples were crushed gently and split into two representative fractions for chemical and mineralogical analysis. One aliquot of the first sub-sample was ground with ethanol in a McCrone Micronizer (McCrone, Chicago, Illinois) to reduce the material to a <5 μm powder. Clay minerals (<2 μm e.s.d.) were extracted from another aliquot by gravity settling. The powder was packed in a sample holder by back-loading methods to determine the mineral content of the whole-rock sample. Clay minerals were identified by scanning a smeared slide after air-drying, ethylene glycol saturation, and heat treatments at 300ºC and 550ºC for 1 h. X-ray data were collected using a Siemens (Bruker) D5000 diffractometer system operated at 40 kV and 30 mA. Mineral identification was facilitated by *MacDiff* 4.2.5 program (Petschick, 2004).

The second sub-sample of the whole powder was used for selective chemical extraction. It was dried at 105ºC overnight and then weighed to obtain 1±0.0000 g. It was extracted with 20 mL of 0.12 M HCl at 37ºC overnight to simulate reaction with stomach acid (Ferrell *et al.*, 1985). After centrifugation, 1.0 mL of the clear supernatant was withdrawn and diluted prior to elemental determination by inductively coupled plasma methods. The elements determined and their limits of detectability in the samples are listed in Table 2. Analytical results are reported as mg/g of the dry sample. Sample 4, the hydromagnesite, was not analyzed.

Table 1. Sample locations with brief descriptions, and relative amounts (wt.%) of clay-sized material.

Sample no.	Location	Description	Relative amount (wt.%) <2 μm
01	Tetteman, Ghana	Gray, silty clay, layered	42.44
02	Queretaro, Mexico	Tan, clayey silty sand	9.79
03	Paleme, Togo	Gray tablet, silty clay	19.41
04	Tela, Honduras	Hydromagnesite	Soluble
05	Jakarta, Indonesia	Gray, clayey silt	18.01
06	San Joaquin, California	Gravelly, clayey sand	18.88
07	Adidone, Arizona	Light-gray silty clay	40.66
08	Jasik Jankan, Indo.	Gray, clayey silt	14.39
09	Manilla, Phillipines	White, clayey, silty sand	12.91
10	Accura, Ghana	White, silty clay	55.92
11	Auchi, Nigeria	White, clayey, silty sand	26.28
12	Esquipulas, Guatemala	White tablet, silty clay	34.11
13	Jakarta, Indonesia	Gray, clayey silt, layered	14.80
14	Demev 6, Nigeria	Pink, clayey silt	11.29
15	Demev 7, Nigeria	Red, clayey silt	13.37
16	Demev 6a, Nigeria	Red, clayey silt	9.37
17	Demev 5, Nigeria	Brown, clayey silt	5.80
18	Auchi, Nigeria	Gray, clayey, silty sand	27.90
19	Auchi, Nigeria	Pink, clayey, silty sand	13.63
20	Chimayo01, New Mexico	Buff, tuffaceous, silty sand	3.03
21	Chimayo02, New Mexico	Buff, tuffaceous, silty sand	2.61
22	Esquipulas, Guatemala	Tan, clayey silt	4.31
23	Chiapas, Mexico	Capsule from natural-food store	5.93

RESULTS

X-ray diffraction

The XRD patterns of the ethylene glycol-saturated sample (Figure 4a–c) illustrate the highly variable nature of the clay minerals in materials used as medicinal clays and for spiritual healing. Smectite is dominant in some, while kaolinite or illite dominates others. Quartz, disordered silica, goethite, mixed-layer clays, feldspars, and clinoptilolite occur rarely.

The XRD patterns of samples generally rich in smectite (Figure 4a) are arranged from top to bottom in order of decreasing relative abundance of smectite and decreasing apparent size of the coherent scattering domain, as indicated by the decrease in the height of the S peaks (especially the major one at 5.2º2θ) and their peak breadth. Sample 23, obtained in capsule form in a Mexican market, is most like a commercial bentonite from Wyoming. In addition, it contains clinoptilolite (Cp), feldspars (Fs), quartz (Q), and disordered silica, opal-cristobalite (Oc). Small peaks due to opal-cristobalite and clinoptilolite are also present in samples 02 and 12. Their presence suggests that these samples were derived from volcanic material. Other sample XRD patterns exhibiting moderate-intensity smectite peaks are obvious in samples 07 and 03 (Figure 4c). Traces of smectite may also be seen in several of the XRD patterns (Figure 4b).

Abundant illite is recognized by high peak intensities at 8.8 and 17.8º2θ (I in Figure 4b) in XRD patterns of illite-rich samples, together with kaolinite and traces of other minerals. Illite also contributes to the QM peak at 26.7º2θ. A shoulder on the high-angle side of the 8.8º2θ peak suggests the presence of some randomly interlayered illite-rich mixed-layer materials. The MX labels indicate the presence of two regular, mixed-layer materials. Feldspars are present in sample 01 and all samples contain quartz (Q in Figure 4b). Goethite is present in a few samples (G in Figure 4b). Kaolinite peak intensities (12.4º2θ) are generally equal to or greater than the illite peaks in samples near the top of the figure and smaller than the 8.8º2θ illite peak at the bottom of the figure. Illite/kaolinite peak intensity ratios vary from 1:1 to 1:4 suggesting a similar change in the relative abundance of the two minerals. Quantitative interpretations of the changes in mineral abundances were avoided for these and other samples because of the difficulty in obtaining reference samples to calibrate the XRD determinations. Illustrating the qualitative comparisons and diversity of the clay mineral assemblages is more important.

Samples 09 and 19 (Figure 4c) are essentially pure kaolinite specimens. Three other kaolinite-dominant samples representing the Nigerian market clays shown in Figure 2c contain illite (samples 18, 11, and 15) and quartz or goethite. The XRD patterns for samples 07 and 03 are similar to mixtures of kaolinite, illite, and smectite (Figure 4a).

Selective extraction

The mean, range, standard deviation, and limits of detectability for the elements extracted by 0.12 M HCl are presented in Table 2. The distribution of the elemental extraction data is summarized in boxplots (Figures 5, 6). The maximum (■), median (▬), and minimum (□) values, as well as the size of the box enclosing values between the 1st and 3rd quartiles, exhibit considerable variability. Ca produced the greatest median value (Figure 5) and a maximum value of almost 100 mg/g. The largest Ca value is from sample 22 which contains calcite. For Al, Si, K, Na, Mg, and Fe, the median values were between 0.1 and 1.0 mg/g and the ranges varied from >0.01 to <10 mg/g. The quantities of Mn and Ti extracted were smaller and many Ti values were at or near the limit of detectability (0.0001 mg/g). The large range in quantities of major elements extracted is a result of the varied mineral composition of the samples and their solubility in simulated stomach acid.

The maximum value for a minor or trace element was 1.9 mg/g for extracted P, although most samples yielded much less (Figure 6). Extracted B, P, and Se were the most variable of the trace elements. Median values for P and Cu were the highest measured. S, Ba, Sr, Pb, and Zn median values were between 0.01 and 0.1 mg/g. The median values for the other elements were smaller and often near the limit of detectability. Minimum values for

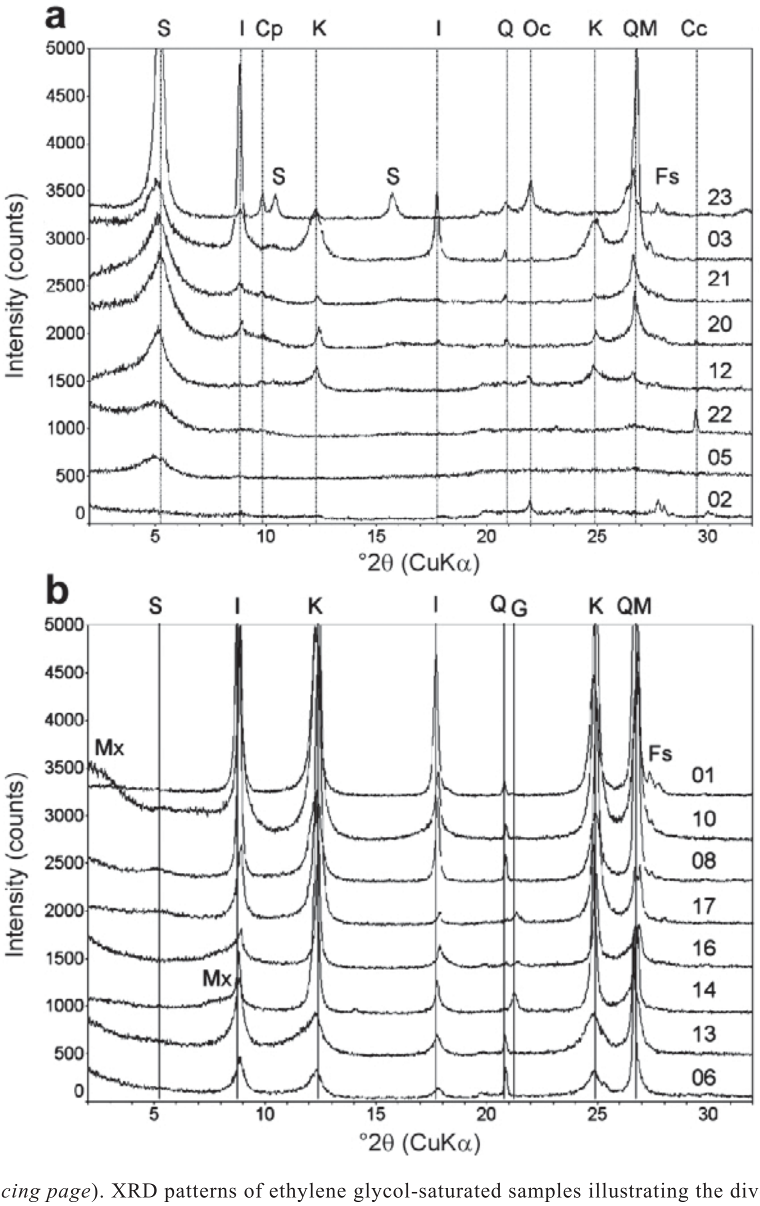
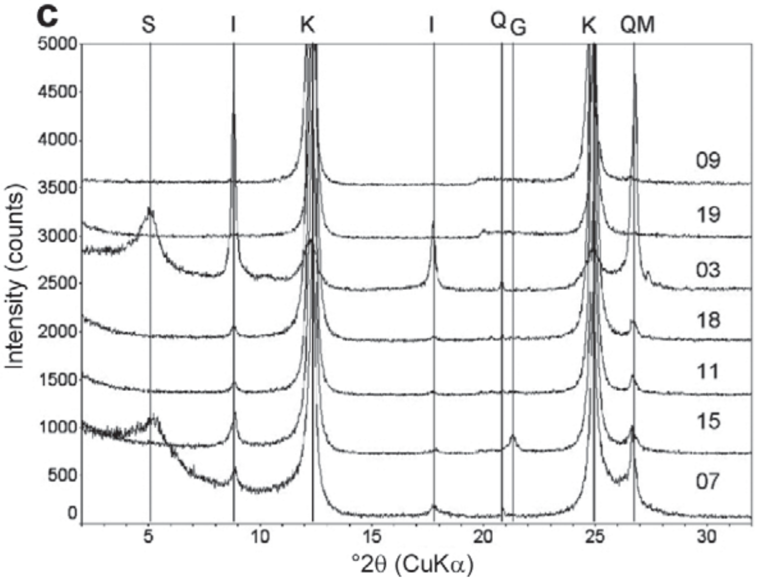


Figure 4 (*above and facing page*). XRD patterns of ethylene glycol-saturated samples illustrating the diversity of clays used for medicinal and religious purposes: (a) smectite-rich and glassy materials; (b) illite-rich clays; and (c) kaolinite-rich samples. Diagnostic peaks are labeled: S – smectite; I – illite; K – kaolinite; Q – quartz; QM – quartz, illite and smectite; Cp – clinoptilolite; Cc – calcite; Oc – disordered silica; and G – goethite. Samples are identified by the numbers on the right.

Table 2. Summary statistics and detection limits for elements leached by 0.12 M HCl at 37ºC. Analytical values are expressed in mg/g of sample.

Element	Count	Mean	St. dev.	Range	Minimum	Maximum	Det. Limit
Al	22	1.1102	0.8412	2.8118	0.1512	2.9629	0.0002
Si	22	0.8199	0.8533	2.8435	0.0527	2.8962	0.0012
K	22	0.5576	0.8476	3.9842	0.0319	4.0161	0.0008
Na	22	0.6171	0.5378	1.9458	0.0183	1.9641	0.0008
Ca	22	5.501	13.292	62.178	0.187	62.365	0.00012
Mg	22	0.7531	0.7650	2.5871	0.0199	2.6069	0.00004
Fe	22	0.28186	0.21519	0.76988	0.04141	0.81129	0.00012
Mn	22	0.09469	0.10823	0.36034	0.00067	0.36101	0.00004
Ti	22	0.00149	0.00365	0.01674	D.L.	0.01682	0.00008
P	22	0.297	0.443	1.902	0.006	1.908	0.004
S	22	0.0571	0.1192	0.5692	0.0051	0.5743	0.0012
B	22	0.0342	0.1246	0.5903	0.0010	0.5913	0.0002
Ba	22	0.0527	0.0543	0.2017	0.0016	0.2032	0.0002
Sr	22	0.03385	0.07187	0.34261	0.00105	0.34366	0.00004
Pb	22	0.054	0.040	0.157	0.013	0.170	0.002
Zn	22	0.03280	0.02162	0.07000	0.01121	0.08121	0.00032
Cd	22	0.00036	0.00042	0.00140	0.00000	0.00140	0.00016
Co	22	0.0016	0.0024	0.0084	D.L.	0.0086	0.0002
Cr	22	0.00092	0.00056	0.00178	0.00010	0.00188	0.00024
Cu	22	0.1884	0.1141	0.4315	0.0430	0.4745	0.0002
Ni	22	0.0028	0.0021	0.0082	0.0008	0.0090	0.0004
V	22	0.00301	0.00343	0.01389	0.00029	0.01418	0.00016
Zr	22	0.00049	0.00060	0.00280	0.00010	0.00290	0.00008
Se	22	0.0017	0.0049	0.0190	D.L.	0.0214	0.0024
Mo	22	0.00013	0.00035	0.0005	D.L.	0.00082	0.00032
Be	22	0.00040	0.00046	0.00112	D.L.	0.00116	0.00004
Sb	22	0.0023	0.0026	0.0095	D.L.	0.0107	0.0012
As	22	0.0017	0.0025	0.0050	D.L.	0.0082	0.0032

D.L. Minimum value equal to limit of detectability



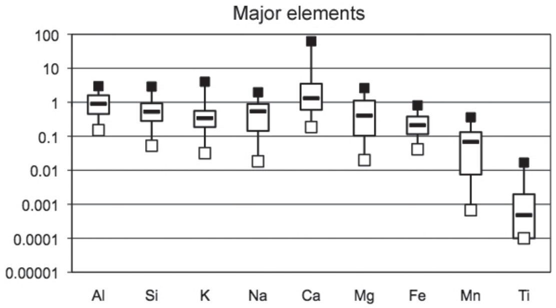


Figure 5. Boxplot of major element quantities extracted by simulated stomach acid (0.12 M HCl). The maximum (■), median (▬), and minimum (□) are shown. The box encloses values between the 1st and 3rd quartiles.

Cd, Co, Cr, Zr, Se, Mo, Be, Sb, and As were essentially zero, the limit of detectability under the experimental conditions.

DISCUSSION

The literature contains some rather obvious conflicting reports related to the health effects of geophagy. In one case, clay consumption is reported to cause high levels of K in the blood (Gelfand *et al*., 1975). In another it is linked to low levels of K (Gonzalez *et al*., 1982). Analyses of the clays were not reported in either study, but contribution of K from an illitic material and K adsorption by smectitic clays could readily explain the difference. Even when clays are suggested to influence the results of a study, follow-up clay investigations are never undertaken (Minnich *et al*., 1968). Studies described by Wilson (2003) frequently implicated kaolinite as the active clay but the presence of kaolinite could not account for some of the observed chemical effects. Smectite is often associated with soluble Fe or Ca and a variety of macro- and micronutrients provided by clays. The XRD results of this study reveal a greater mineralogical variety of healing clays in use today than in Wilson's review. In order to understand the etiology of geophagy and human health, mineralogical analyses must become part of every study. The diversity reported in this study makes it critical to employ detailed mineralogical characterization methods as recommended by Wilson (2003) in future studies.

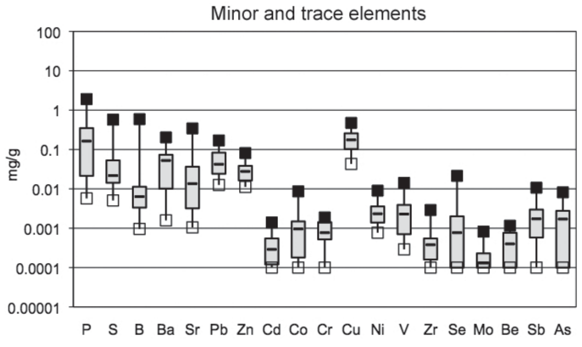


Figure 6. Boxplot of minor and trace element quantities extracted by simulated stomach acid (0.12 M HCl). The limit of detectability is 0.0001 mg/g. Boxplot symbols are the same as in Figure 5.

In the recent literature, total chemical analyses have been down-played in favor of methods that mimic the extractability of elements in the gastric tract where adsorption is assumed to take place. Total elemental analyses depict the chemical composition of the clays, but do not equate to the bio-availabilty of the elements. Abrahams (1997) used 0.1 M HCl to assess dietary Fe supplementation in Uganda and found that one of the common geophagical soils released considerable Fe, but the other did not. Abrahams and Parsons (1997) reported that acid extracts of UK soils could supply significant quantities of nutrients. Aqua regia extractions of urban soils from Uppsala, Sweden, confirmed that ingestion could provide excessive quantities of Cd, Pb, and As (Ljund *et al*., 2006). An "argillic water" technique was used by Tateo *et al.* (2006) to measure the release of Na, Si, Ca, K, MG, Fe, Al, Mn, V, Mo, Sb, and As from clays suitable for therapeutic use. They dispersed the clay in water and measured the quantity of the element in the supernatant after settling for various periods of time. The results were normalized to elemental quantities in 2 L of water and compared with drinking-water standards to determine whether intake would exceed general recommendations.

Smith *et al*. (2000) expanded the HCl acid-simulated digestion procedure to account for changes in Eh and pH of the digestive tract. He used a mixture of pepsin and organic acids in 1% HCl adjusted to pH 2 to determine that selected geophagic clays could provide a major portion of the daily recommended quantity of Fe, but not of other elements. A 0.1 M HCl extraction of edible clays consumed by women in Belize found that 26% of the total available Ca, 17% of Mg, 6.5% of K, 3% of Fe, 7% of Cu, and 14% of Zn was "bioavailable" and could account for 5−18% of the recommended daily intake of the elements (Hunter and de Kleine, 1984). The 0.12 M HCl used in this study should produce an estimate of 'bioavailability' similar to the acid-extraction techniques described above. The results will not duplicate those obtained by the 'argillic water' method because the slurry pH will vary.

The bioavailability of the elements extracted with a strong acid has been questioned by the realization that elements mobilized in simulated stomach may precipitate or be adsorbed in the higher-pH, generally reducing, environments of the intestine (Ruby *et al*., 1996; Smith *et al*., 2000; Oomen *et al*., 2002). A comparison of five *in vitro* digestion models revealed a wide range of bioaccessible As, Cd, and Pb in three contaminated soils. The available percentage was generally <50%, but values as high as 95% for As, 99% for Cd, and 91% for Pb were observed. The differences were directly attributable to: whether the extraction was simple or multiple; the pH employed; and the ratio of solid to solution (Oomen *et al*., 2002). The authors of this multinational test could not conclude which test best determined bioavailability and methods similar to those employed in this study are still in use.

Hooda *et al*. (2004) developed another procedure for the estimated potential bio-availability of Fe, Cu, Zn, Ca, Mg, and Mn by humans. They began their experiments in solutions containing 50, 80, and 100% of the daily recommended allowances of the six nutrients and then performed a sequential digestion at pH 2 (gastric phase) and pH 10 (intestinal phase). This approach allowed them to determine whether a selected soil would produce an increase or decrease in nutrient availability. The results for the micronutrients were variable, but the amounts of Fe, Cu, and Zn were always less than in the starting solution. Some soils behaved as a source of Ca, Mg, and Mn, producing final solutions in which the nutrient concentration exceeded the starting values. The specific soil reactions leading to potential nutrient deficiencies were not determined. These results and those cited above underscore the importance of method standardization and mineral analyses in future studies of bioavailability.

The potential significance of the chemical extraction results obtained in this experiment can be assessed by relating the measured quantities to the recommended reference dose (RfD) reported in the EPA's IRIS database (Integrated Risk Information System; http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?irisb.htm). RfD is "⋯an estimate of the daily exposure to the human population that is likely to be without an appreciable risk of deleterious effects during a lifetime." Values in the table were multiplied by 80 kg to convert them to the body weight of an average adult. The daily intake from clay was determined by multiplying the extracted elemental quantity in mg/g by 50 g, which is the approximate quantity of clay consumed in a typical dose (Vermeer and Frate, 1979) in Holmes Co., Mississippi, USA. In a boxplot of the results (Figure 7), the vertical axis is RDR (reference dose ratio), the ratio of the quantity of the element consumed, divided by the RfD. A value of 1 indicates that the intake and the recommended quantity are the same. Greater values indicate sample yields in excess of the recommended quantity; smaller ratios indicate that the limits have not been exceeded. Elements for which RfDs could be found in IRIS are plotted on the horizontal axis. Several potentially significant elements such as Pb, Co, and Cu are among those for which RfDs were not available.

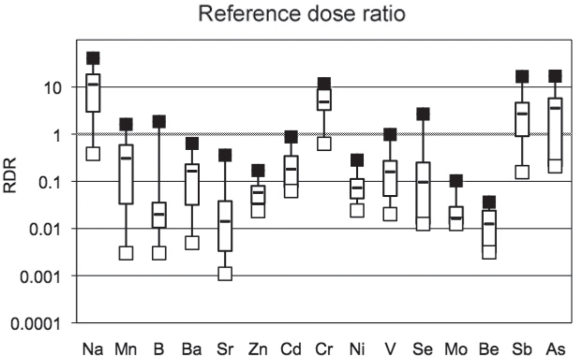


Figure 7. Reference dose ratios relating quantity extracted to the EPA Reference Dose. Boxplot symbols are the same as in Figure 5.

The RDR value for Na exceeds 1 for 22 of the 23 geophagical samples (Figure 7). The median ratio is >10. The potential contribution of Na from the kaolinite-dominant samples is smallest. It is greatest for the smectite-rich samples. Median RDR values for Cr, Sb, and As were also >1 suggesting that their potential intake should be a point of concern. Maximum values for Mn, B, Cd, V, and Se were very close to, or greater than 1. The median RDR values for Mn, Ba, Cd, and V were between 1 and 0.1. Molybdenum and Be produced the smallest median ratios.

The RDR values derived from the quantities extracted exhibit considerable variability. The range from one clay type often overlaps that for another. One advantage of the RDR is that it relates contributions of the extracted elements to a factor that has potential significance for human health, the RfD. It takes into account factors related to abundance and dietary requirements. For example, median RDR values for Na, Cr, Sb, and As all exceed 1 although their mean extracted quantities are 0.6, 0.0009, 0.0023, and 0.0017 mg/g, respectively. The extracted quantities differ by several orders of magnitude, but their potential impacts on human health are similar. The RDR values reported above should raise concern about the quantities of Na, Cr, Sb, and As that humans may ingest when they practice geophagy. However, the RfD, by definition, is not the best quantity to predict potential toxicity or harmful effects. Other measures based on doses producing short-term deleterious effects need to be developed. The RDR values or similar measures of extractable elements should be determined directly for any healing clay used in future experiments, as each clay will have a different chemical signature. The extraction process should be one that simulates *in vivo* reactions in the digestive tract.

CONCLUSIONS

Clays used in spiritual healing and for medicinal purposes are extremely variable. They may be monominerallic or polymineralic mixtures of smectite, illite, and kaolinite in a quartz sand matrix. Each of these clays is predicted to have different effects on humans because of their different physical properties and the quantities of elements extracted by reactions in the stomach and intestine. Chemical extraction with simulated stomach acid (0.12 M HCl) reveals several orders of magnitude of difference in terms of the quantities of major, minor, and trace elements in clays. The diverse origins of the materials used by geophagists preclude generalizations that are 'mineral' specific, because each smectite-rich, illite-rich, and kaolinite-rich sample is distinct.

The RDR is one way to relate soluble elements to EPA recommendations for elemental consumption. The samples tested exhibited RDRs>1 for Cr, Sb, As, and Na (with one exception). Diversity in terms of the qualitative XRD results precludes generalization that any given edible clay will have a certain mineral composition or chemical extraction result. Samples used for spiritual and medicinal healing from around the world are very different.

REFERENCES

Abrahams, P. W. (1997) Geophagy (soil consumption) and iron supplementation in Uganda. *Tropical Medicine and Institutional Health*, **2**, 617–623.

Abrahams, P.W. (2005) Geophagy and the involuntary ingestion of soil. Pp. 435-458 in: *Essentials of Medical Geology* (O. Selinus, editor-in-chief). Elsevier, Amsterdam.

Abrahams, P.W. and Parsons, J.A. (1997) Geophagy in the Tropics: an appraisal of three geophagical materials. *Environmental Geochemistry and Health*, **19**, 19–22.

Barltrop, D., Strehlow, C.D., Thornton, I., and Webb, J.S. (1974) Significance of high soil lead concentrations for childhood burdens. *Environmental Health Perspectives*, **7**, 75–82.

Carretero, M.I. and Lagaly, G., editors (2007) Clays and health: An introduction. *Applied Clay Science*, **36**, 1–3.

Carretero, M.I., Gomes, C.S.F., and Tateo, F. (2006) Clays and human health. Pp. 717–741 in: *Handbook of Clay Science* (F. Bergaya, B.K.G. Theng, and G. Lagaly, editors). Developments in Clay Science, **1**, Elsevier, Amsterdam.

Dissanayake, C. (2005) Of stones and health: Medical geology in Sri Lanka. *Science*, **309**, 883–885.

Ferrell, R.E., Vermeer, D.E., and LeBlanc, W.S. (1985) Chemical and mineralogical composition of geophagical materials. *Trace Substances in Environmental Health XIX*, University of Missouri, pp. 47–55.

Gelfand, M.C., Zarate, A., and Knepshield, J.H. (1975) Geophagia: A cause of life-threatening hyperkalemia in patients with chronic renal failure. *Journal of the American Medical Association*, **234**, 738.

Gomes, C.S.F. and Silva, J.B.P. (2007) Minerals and clay minerals in medical geology. *Applied Clay Science*, **36**, 4–21.

Hooda, P.S., Henry, C.J.K., Seyoum, T.A., Armstrong, L.D.M., and Fowler, M.B. (2004) The potential impact of soil ingestion on human mineral nutrition. *Science of the Total Environment,*, 333, 75–87.

Hunter, J.M. and de Kleine, R. (1984) Geophagy in Central America. *The Geographical Review*, **74**, 157–168.

Hunter, J.M., Horst, O.M., and Thomas, R.N. (1989) Religious geophagy as a cottage industry: The holy clay tablet of Esquipulas, Guatemala. *National Geographic Research*, **5**, 281–295.

Gonzalez, J.J., Owens, W., Ungaro, P.C., Werk, E.E., and Wentz, P.W. (1982) Clay ingestion: a rare case of hypokalemis. *Annals of Internal Medicine*, **97**, 65–66.

Johns, T. and Duquette, M. (1991) Detoxification and mineral supplementation as functions of geophagy. *American Journal of Clinical Nutrition*, **53**, 448–456.

Katz, J.M. (2008) Hungry Haitians eat mud as cost of food soars. *The Advocate*, Wednesday, January 30, 2008, p. 3A.

Ljung, K., Selinus, O., Otabbung, E., and Berglund, M. (2006) Metal and arsenic distribution in soil particle sizes relevant to soil ingestion by children. *Applied Geochemistry*, **21**, 1613–1624.

Mahaney, W.C. and Krishnamani, R. (2003) Understanding geophagy in animals: Standard procedures for sampling soils. *Journal of Chemical Ecology*, **29**, 1503–1523.

Mascolo, N., Summa, V., and Tateo, F. (1999) Characterization of toxic elements in clays for human healing use. *Applied Clay Science*, **15**, 491–500.

Minnich, V., Orcuoglu, A., Tarcon, Y., Argosy, A., Cin, S., Yorupoglu, O., Raenda, F., and Demirag, B. (1968) Pica in Turkey II: Effect of clay upon iron absorption. *American Journal of Clinical Nutrition*, **21**, 78–86.

Oomen, A.G., Hack, A., Minekus, M., Zeijdner, E., Cornelis, C., Schoeters, G., Verstraete, W., van de Wiele, T., Wragg, J., Rompelberg., C.J.M., Sips, A.J.A.M., and van Wijnen, J.H. (2002) Comparison of five in vitro digestion methods to study the bioaccessibility of soil contaminants. *Environmental Science and Technology*, **36**, 3326–3334.

Padilla, F.V. and de la Torre, A.M. (2006) La pica: retrado de una entidad clinica poco conocida: *Nutricion Hospitalaria*, **21**, 557–566.

Petschick, R. (2004) *MacDiff* 4.2.5. Powder diffraction software. Available from: http://servermac.geologie.uni-frankfurt.de/Staff/Homepages/Petschick/RainerE.html

Reinbacher, W.R. (2003) *Healing Earths: The Third Leg of Medicine.* Published by the author, ISBN: 1-4033-5090-5, 244 pp.

Robertson, R.H.S. (1986) *Fuller's Earth: A History of Calcium Montmorillonite*: Volturna Press, Mineralogical Society, London, occasional publication.

Robertson, R.H.S. (1996) Cadavers, choleras, and clays. *Mineralogical Society Bulletin*, **113**, 3–7.

Ruby, M.V., Davis, A., Schoof, R., Eberle, S., and Sellstone, C.M. (1996) Estimation of lead and arsenic bioavailabilty using a physiologically based extraction test. *Environmental Science and Technology*, **30**, 422–430.

Smith, B., Rawlins, B.G., Cordeiro, M.J.A.R., Hutchins, M.G., Tiberindwa, J.G., Sserunjogi, L., and Tomkins, A.M. (2000) The bioaccessibility of essential and potentially toxic trace elements in tropical soils from Mukono District, Uganda. *Journal of the Geological Society of London*, **157**, 885–891.

Tateo, F. and Summa, V. (2007) Element mobility in clays for healing use. *Applied Clay Science*, **36**, 64–76.

Tateo, F., Summa, V., Gianossi, M.L., and Ferrero, G. (2006) Healing clays: Mineralogical and geochemical constraints on the preparation of clay-water suspension ('argillic water'). *Applied Clay Science*, **33**, 3–4.

Vermeer, D.E. and Ferrell, R.E. (1985) Nigerian geophagical clay: A traditional antidiarrheal. *Science*, **227**, 634–636.

Vermeer, D.E. and Frate, D.A. (1979) Geophagy in rural Mississippi: Environmental and cultural contexts and nutritional implications. *American Journal of Clinical Nutrition*, **32**, 2129–2135.

Williams, L.B., Holland, M., Eberl, D.D., Brunet, T., and Brunet de Courrsou, L. (2004) Killer Clays! Natural antibacterial clay minerals. *Mineralogical Society Bulletin*, **139**, 3–8.

Williams, L.B., Haydel, S.E., Giese, R.S., Jr., and Eberl, D.D. (2008) Chemical and mineralogical characteristics of French green clays used for healing. *Clays and Clay Minerals*, **56**, 437–452.

Wilson, M.J. (2003) Clay mineralogical and related characteristics of geophagic materials. *Journal of Chemical Ecology*, **26**, 1525–1547.

(*Received 10 June 2008; revised 12 September 2008; Ms. 170; A.E. L. Williams*)