(*24*). However, these other maps describe an area circumscribed by our 5 and 6 ppm arsenic isopleth (soil map) and our 3 and 4 ppm isopleth (dispersion model). Thus, our maps cover a more extensive area. Further, our map (Fig. 2A) suggests long-range transport of arsenic from Commencement Bay to the Lake Sammamish Plateau. This observation may explain reports of somewhat elevated arsenic levels occasionally observed at distant monitoring stations (*24*).

There were no statistical differences for arsenic or fluoride for bees collected during July or September at similar sites. However, limited data were available so that the power of the test was low. The same result was obtained in a follow-up experiment conducted in 1983. Bees sampled weekly for 10 weeks at two sites near Commencement Bay displayed temporal coefficients of variation of about 20 percent.

Kriging errors for arsenic (Fig. 2C) show that estimated error is related to data density (that is, the number of sites sampled in a given area). Error was relatively small in the urban areas of Seattle and near Tacoma where many beekeepers obtained samples. In contrast, errors were larger in the rural areas, where sample locations were more scattered. Largest errors occurred at the perimeter of the study area and in those places where a section of the kriging grid encompassed a large mass of water. Kriging error is not synonymous with a standard deviation determined from replicate hives at a single location. Results from our studies indicate that coefficients of variation of about 20 percent with a range of 1.7 to 43 percent can be expected, depending on time of year, proximity to source, and other factors.

The predicted fluoride concentration map (Fig. 2E) suggests a different source and dispersion mechanism. On the basis of our studies in Montana (*12*), we predicted that fluoride concentrations in nearby vegetation would also be proportionately high. Data provided by the Washington State Department of Ecology show that levels in grasses near the tide flats area of Commencement Bay contained up to 100 ppm (*25*), whereas background levels for grass should be about 1 to 6 ppm (*26*). In much of the area of high concentrations of arsenic and cadmium in bees, levels are also so high in vegetables that the Pierce County Department of Health has advised against consumption (*27*).

Our results show that beekeepers can effectively use colonies of bees as a self-sustained system for environmental monitoring over large geographical areas. Honey bees provide a spatially integrated sample of all three (gas, liquid, and particulate) modes in which pollutants may be transported. Moreover, our experience indicates that this monitoring system is less expensive than, for example, high volume air samplers that only monitor particulate pollutants. To determine how bee colonies can most effectively contribute to monitoring needs, especially in terms of integrating the information obtained with decision-making and regulatory processes, will require better understanding of the extent and limitations to which colonies of bees can be used in other places and for other pollutants.

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References and Notes

1. M. K. Wallwork-Barber, R. W. Ferenbaugh, E. S. Gladney, *Am. Bee J.* **122**, 770 (1982).
2. A. S. Toshkov, M. M. Shabanov, N. I. Ibrishimov, *C.R. Acad. Bulg. Sci.* **27**, 702 (1975).
3. E. L. Atkins, E. A. Greywood, R. L. Macdonald, *Cooperative Extension Leaflet 2287* (University of California, Riverside, 1975), pp. 1–38.
4. Department of Agriculture, *Agricultural Statistics* (Government Printing Office, Washington, D.C. 1982), p. 93.
5. D. F. Mayer, *Proc. West. Apic. Soc.* **6**, 5 (1983).
6. S. C. Tong, R. A. Morse, C. A. Bache, D. J. Lisk, *Arch. Environ. Health* **30**, 332 (1975).
7. Lead in pollen samples trapped at hives near a lead smelting complex in Montana (1981).
8. S. A. Corbet, J. Deamont, D. Eisokowitch, *Plant Cell Environ.* **5**, 129 (1982).
9. G. C. White, T. E. Hakonson, K. W. Bostick, *Ecol. Model.* **18**, 241 (1983).
10. E. S. Gladney, M. K. Wallwork-Barber, R. W. Ferenbaugh, *J. Radioanal. Chem.* **78**, 209 (1983).
11. M. Debachere, *Vlaam. Imbersblad* **2**, 145 (1972).
12. J. J. Bromenshenk, in *The Bioenvironmental Impact of a Coal-Fired Power Plant*, E. M. Preston and D. W. O'Guinn, Eds. (EPA-600/3-80-052, National Technical Information Service, Springfield, Va., 1980), pp. 75–86.
13. Reports of the Ecology Committee of the Scientific Advisory Board of EPA (Environmental Protection Agency, Washington, D.C., 1980).
14. Point Source Emission Inventory (Engineering Division, Puget Sound Air Pollution Control Agency, Seattle, Wash., 1980).
15. Developed during a 1981 study of a lead smelting complex. A copy of the data processing program written in BASIC and diagrams of the pollen traps and bee aspirator can be obtained from J.J.B.
16. Although fluoride is easily lost at elevated temperatures, recoveries for fluoride added to samples before ashing ranged from 89 to 99 percent ($r^2 = 0.998$ for additions of 5, 10, 20, 50, and 100 μg).
17. W. Van Meter, "Report 55" (Montana University Joint Water Resources Research Center, Bozeman, 1974).
18. *Analytical Methods for Flame Spectroscopy* (Varian Techtron, Springvale, Australia, 1979).
19. R. F. Lazer, Ed., *Atomic Absorption Methods Manual: Flameless Operations* (Instrumentation Laboratory, Wilmington, 1976), section 4, pp. 43–48.
20. J. C. Simpson, *Publication PNL-4807* (Pacific Northwest Laboratory, Richland, Wash., 1983).
21. I. Clark, *Practical Geostatistics* (Applied Science, London, 1979).
22. A. G. Journal and Ch. J. Huijbregts, *Mining Geostatistics* (Academic Press, New York, 1978).
23. Total arsenic for forager bees sampled near a lead smelting complex in Montana in 1981.
24. Puget Sound Air Pollution Control Agency, "Final environmental impact statement for ASARCO, Inc.," Seattle, Wash. (1981), pp. V-8 and V-13.
25. F. C. Fenske, personal communication.
26. J. S. Drury *et al.*, *Reviews of the Environmental Effects of Pollutants: Fluoride* (ORNL/EIS-85, EPA-60011-78-050, Cincinnati, Ohio, 1980), vol. 9, p. 119.
27. "Cadmium and arsenic in your garden?" (Tacoma-Pierce County Health Department and Seattle–King County Department, Wash., 1982).
28. We wish to thank the beekeepers of Puget Sound for their assistance and support and R. Hinds and P. Tucker for editorial assistance. Supported by Cooperative Agreement CR-810035-01-0 for EPA's Environmental Research Laboratory in Corvallis, Ore. (to J.J.B.), and supported by EPA under a related services agreement (TD 1589) with the Department of Energy under contract DE-AC06-76RLO 1830 (with J.M.T.).

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Nigerian Geophagical Clay: A Traditional Antidiarrheal Pharmaceutical

Abstract. *The chief geophagical clay entering the West African market system comes from the village of Uzalla, Nigeria. Village inhabitants ascribe antidiarrheal properties to the clay, and they use it in traditional medicinal preparations to counteract intestinal problems. Mineralogical analyses demonstrate a striking similarity between the Uzalla village clay and the clay in the commercial pharmaceutical Kaopectate.*

Geophagy, the practice of eating earth, occurs throughout the world (*1*). In tropical West Africa, the practice appears ubiquitous among the various ethnic groups and it occurs most commonly among pregnant women. One geophagical clay that comes from the village of Uzalla, Nigeria, is widely sold in the markets of West Africa. Although considerable investigation has been devoted to nutritional questions and medical implications of geophagy (*2, 3*), we are unable to find studies of the pharmaceutical properties of geophagical clays. Our mineralogical analyses of the Uzalla clays indicate a kaolinitic composition strikingly similar to that of the clays in the pharmaceutical Kaopectate.

Geophagists in West Africa obtain edible substances either by procuring them from local sources or by purchasing them in the markets. Local sources may be as diverse as red, lateritic clays scraped from the walls of buildings, the interior of termitaria, and in some areas sand (*4*). Local clays most commonly eaten are those dug from the B soil horizon at depths of 30 to 90 cm (*5*). Local geophagical clays are used chiefly by those groups not tightly linked to the market system of the region.

Geophagical clays in the West African markets come principally from two production centers. One of these lies east of the Volta River among the Ewe people of Ghana (*4*); clays from this source are processed to give them a rather uniform egg shape and size, but their penetration into the market network is rather limited. A second source is located in the area occupied by the Beni-speaking peoples of Nigeria. These clays, called *eko* by the villagers who mine and process them, gain wide circulation in the well-articulated West African market system; they have been observed by one of us (D.E.V.) more than 1500 km westward in Liberia. In Ghana and Togo the *eko* clays are known as *Calabar*, a name suggesting connection with the old slave port of Calabar on the Guinea coast and with the transfer of the practice of geophagy via the slave trade to the New World (*6*).

Eko comes from the village of Uzalla in the Benin area of south-central Nigeria (Fig. 1). North of Uzalla the Aruvbi River cuts through an overburden of Pleistocene coastal sands to expose the gently southward-dipping Emo shales of Paleocene age (53 to 65 million years old). The extent and long history of shale mining in this area are manifest in the remarkable number of excavations that honeycomb the valley bottom and in the widening of the valley from human activity.

Unprocessed *eko* clays are light gray in color and massive in appearance. Bedding planes are faintly distinguished by slight color changes and occasional streaks of coarse particles and organic matter.

Women process the shales for the market by scraping away coarse and gritty materials and sun-drying the irregular blocks. Once dried, the material undergoes smoking and hardening over a smoldering fire for a 2- to 3-day period, a process that transforms the gray shales into *eko* with its characteristic rich chocolate sheen and hardness.

Eko finds outlet chiefly through women merchants who come to the Uzalla market held each fourth day. Accumulated purchases often warrant removal by a large truck to regional markets such as Lagos, Ijebu-Ode, and Ibadan for redistribution westward throughout the West African market system. Observations in Uzalla and in its market indicate that 400 to 500 tons are produced and sold each year. The widespread acceptance of *eko* among different ethnic groups many hundreds of kilometers from its source testifies to the antiquity of the trade and use of these clays.

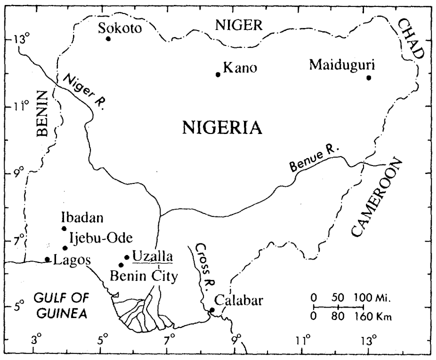

Fig. 1. Location of the village of Uzalla in south-central Nigeria.

Eko is used in several medicinal preparations in the village of Uzalla. Small chips or scrapings of it plus the liquid extracted by grinding or squeezing the leaves of selected plants are made into a potion. The village medicine man claims that eight of nineteen such preparations are for problems associated with pregnancy; the other eleven concoctions are used to ease stomach and dysenteric ailments. Salt is added to six of the preparations for stomach and dysenteric problems.

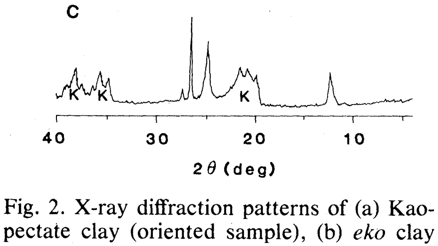

Fig. 2. X-ray diffraction patterns of (a) Kaopectate clay (oriented sample), (b) *eko* clay (oriented sample), and (c) *eko* clay (random powder). These patterns establish the mineralogical similarity of *eko* and the clay in Kaopectate. Major peaks on the oriented samples are produced by kaolinite; minor mineral peaks are labeled. Broad peaks and bands (K) in (c) are produced by poorly crystallized kaolinite of fine particle size.

In an effort to assess the scientific basis for these folk practices, we compared the x-ray diffraction patterns of the edible *eko* with those of the clay in Kaopectate (Fig. 2). The three largest peaks for both samples are attributable to kaolinite; the quantities of kaolinite present and the sizes of the particles are very nearly equal, although minor and trace minerals differ. The *eko* clay contains an opaline substance and a trace of quartz, whereas Kaopectate contains the swelling clay mineral smectite, a mica, and some feldspar and quartz.

Broad bands and limited resolution of the peaks in the diffraction angle (2θ) in the range 20° to 22° from the bulk sample of *eko* (Fig. 2c) suggest a kaolinite composed of very small crystallites with a disordered crystal structure. Scanning electron microscopic analyses reveal well-formed mineral flakes ~ 1 μm in diameter. Other peaks in the diffractogram can be attributed to minor quantities (less than 10 percent by weight) of quartz and feldspar. X-ray analysis of an oriented aggregate sample of the fine clay (less than 2 μm) suggests the presence of two other trace mineral phases (less than 1 percent). The x-ray patterns of the samples after treatment with ethylene glycol exhibit broad bands centered on 14 and 4.1 Å; the former is attributable to hydroxy-interlayered vermiculite or swelling chlorite, and the latter is associated with opal-A (amorphous silica) or opal-CT (disordered cristobalite and tridymite). Limited amounts of the two minerals preclude more precise identification.

Kaolinitic clays have long been used as a base for pharmaceutical preparations designed to counteract gastric upsets and irritated intestines. Kaolinite adsorbs toxins and bacteria and has been reported to form a protective coat on the mucous membrane of the digestive tract (*7*). The absence of chemical impurities and other attributes makes kaolinite especially suitable as an ingredient in products for internal consumption. Kaolinite does not usually interfere with the absorption of zinc or iron because its cation-exchange capacity is less than 10 meq per 100 g. Minerals with higher cation-exchange capacities interfere with the absorption of iron (*8*). A small amount of the kaolinite in *eko* would yield a large number of thin plates having a relatively high surface area; this would result in an enhanced adsorptive capacity and efficacy.

The similarity of the mineral composition for *eko* and Kaopectate suggests that similar purposes are achieved by their consumption. The extent to which the many different ethnic groups in West Africa are aware of the antidiarrheal properties of *eko* is uncertain. The fact that so many medicinal preparations in the village of Uzalla use *eko*, however, supports the notion that the therapeutic qualities of the clay are recognized by those who supply it to the West African market system and possibly by those who purchase it.

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References and Notes

1. B. Laufer, *Field Mus. Nat. Hist. Publ.* **18**, 99 (1930); B. Anell and S. Lagercrantz, *Studia Ethnogr. Ups. 17* (1958).
2. D. E. Danford, *Annu. Rev. Nutr.* **2**, 303 (1982); J. A. Halsted, *Am. J. Clin. Nutr.* **21**, 1384 (1968).
3. J. R. Amerson and H. Q. Jones, *Bull. Emory Univ. Clinic* **5**, 11 (1967); M. C. Gelfand, A. Zarate, J. H. Knepshield, *J. Am. Med. Assoc.* **234**, 738 (1975).
4. D. E. Vermeer, *Ethnology* **9**, 59 (1971).
5. ———, *Ann. Assoc. Am. Geogr.* **56**, 199 (1966).
6. ——— and D. A. Frate, *Am. J. Clin. Nutr.* **32**, 2129 (1979); *Ann. Assoc. Am. Geogr.* **65**, 414 (1975).
7. E. A. Swinyard, in *The Pharmacological Basis of Therapeutics*, L. S. Goodman and A. Gilman, Eds. (Macmillan, New York, 1965), pp. 976–989.
8. V. Minnich *et al.*, *Am. J. Clin. Nutr.* **21**, 78 (1968).
9. Fieldwork support to one of us (D.E.V.) was provided by the National Geographic Society, the American Philosophical Society, and the Council on Research of the Graduate School, Louisiana State University. We thank E. Younathan, F. Hoskins, R. Freel, M. Hatch, and F. Kniffen for review and comments on the manuscript.

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Raman Microprobe Evidence for Lignin Orientation in the Cell Walls of Native Woody Tissue

Abstract. *Raman microprobe spectra from the secondary wall of earlywood tissue from* Picea mariana *(black spruce) reveal evidence of the orientation of lignin relative to the plane of the cell wall. In most instances, the aromatic rings of the phenyl propane structural units are parallel to the plane of the cell-wall surface.*

Among the structural components of plant cell walls, only cellulose has been well characterized with respect to its molecular organization within native tissue (*1, 2*). In this work we report what we believe to be the first direct evidence for the orientation of components of lignin relative to the morphological features of native woody tissue.

A central problem in studies of plant cell walls is that the methodologies for investigating morphology, namely, electron and optical microscopy, are very limited in their capacity to develop information concerning molecular structure. On the other hand, procedures traditionally used for exploring the molecular structure of cell-wall components require prior isolation of the components by extractive procedures that are frequently destructive of morphological features (*3*).

The Raman microprobe offers an opportunity to bridge this gap through spectroscopic investigation of individual morphological features in unperturbed plant tissue. The microprobe permits acquisition of Raman spectra from domains as small as 1 μm (*4, 5*). But its greatest asset in the present context is that molecular orientation within these domains can be established from analysis of the polarization of Raman scattered light (*6, 7*).

The particular question that we addressed was the possibility that lignin molecules are oriented with respect to the geometry of the cell walls in native woody tissue. Such information would be helpful for a better understanding of its function. Although some anisotropy in the structure of lignin had been postulated on the basis of measurements of ultraviolet dichroism (*8*), these measurements were later attributed to form dichroism rather than to molecular orientation (*1*). The possibility of lignin orientation is suggested by the high degree of organization of cellulose as well as by evidence for orientation of the hemicelluloses in cell walls (*9, 10*). Our experiments were specifically designed to establish whether the aromatic rings of the phenyl propane units in lignin molecules had preferential orientations with respect to the plane of the cell-wall surface. In the work reported here attention was focused on the secondary wall in earlywood tissue from *Picea mariana* (black spruce).

The microprobe system consisted of a Jobin Yvon Ramanor HG2S equipped by the manufacturer with a Nachet microscope modified for coupling to the spectrometer and designed to provide imaging on a glass screen. The microscope serves the dual functions of focusing the exciting laser beam on the domain of interest and of gathering the Raman scattered light and imaging it at the entrance slit of the monochromator. The objective used in the present study was a ×100 (numerical aperture 1.18) liquid-immersion objective corrected for water. The exciting radiation was the 5145-Å line of an argon ion laser. The system and methodology are described in detail elsewhere (*11*). Our work and that of others (*12*) indicate that the spectra arise from domains approximately 1 μm in diameter and 0.5 μm deep.

The woody tissue was sectioned both longitudinally and transversely. The sections, approximately 30 μm thick, were mounted on slides approximately 2 by 3 cm, held in place by cover slips through the centers of which small holes had been drilled. Each slide was then placed in a small flat-bottomed beaker, and D_2O was added to a depth of approximately 1 cm. After the liquid-immersion objective was brought close to the sample, the D_2O was covered with a thin layer of mineral oil to limit both evaporation and exchange with atmospheric moisture. Immersion in D_2O limited laser-induced fluorescence (*11*), and the D_2O bands provided a convenient internal reference for intensity measurements. The possibility of spectral effects arising from extractives, which constitute less than 1 percent of the secondary wall, was excluded on the basis of comparisons of spectral features from extracted and unextracted tissue.

The central point of the experiments was to compare spectra recorded with the polarization of the incident laser beam parallel and perpendicular to the plane of the cell wall. In order to avoid complications associated with the dichroism inherent in the optics of the microscope and the monochromator, a polarization scrambler was inserted in the path of the Raman-scattered light at the point of coupling of the microscope to the monochromator, and we obtained the different spectra by rotating the sample about the optical axis of the microscope. This was possible because the microscope was equipped with a rotating stage that had been precisely aligned.

We carried out the alignment of the stage by observing a micrometer slide and adjusting the stage so that it could be rotated without translation. At the higher magnifications, small amounts of residual translations could occur but these were readily compensated for by micro-