

Determination of the Provenance of Cocoa by Soil Protolith Ages and Assessment of Anthropogenic Lead Contamination by Pb/Nd and Lead Isotope Ratios

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The Pb contents of chocolate and the products it flavors are among the highest of all commonly consumed substances. Others have shown that this Pb is acquired by cocoa beans after harvesting and is concentrated in their shells, portions of which are ground up with the cotyledons during processing. It is shown here that the shells also contain the lanthanides Nd and Sm, which they appear to take up more slowly than Pb when dried on bare soil. Consideration of Pb/Nd ratios, model Sm–Nd ages and the isotope ratios of Pb and Sr indicates that, in the absence of contamination, the relationship between Pb and Nd in shells is $y = 13.1x^{-0.383}$, where x is the Nd concentration in $\mu\text{g}/\text{kg}$ and y is the Pb/Nd ratio. For cocoa powders, the relationship is $y = 114x^{-0.988}$. Samples that plot above these curves are probably contaminated. Model ages indicate where the cocoa of cocoa powders is grown, and these same considerations point to African samples being uncontaminated but samples from Asia containing 50% anthropogenic Pb of Australian origin. No measurable Pb contamination occurs during the transport of beans and the manufacture of chocolate.

KEYWORDS: Cocoa beans; chocolate products; lanthanides; lead; lead isotopes; lead contamination; soil protolith age

INTRODUCTION

Compared to other edible substances, products containing cocoa have high concentrations of Pb (1), and, out of concern for children's health, the U.S. Food and Drug Administration has recommended that the Pb content of chocolate should not exceed 0.1 ppm, i.e., 100 $\mu\text{g}/\text{kg}$ (2,3). As yet there is no clear indication of how chocolate comes to contain Pb, whether naturally or as a result of environmental contamination, but a report (4) that all the Pb comes from the small amounts of shell permitted to be processed with the beans greatly advanced understanding of the problem. This, taken with evidence that the shell readily binds metals (5), has been claimed consistent with contamination (4), possibly from leaded gasoline, though the validity of the interpretation of the isotope ratios has been questioned (6). However, without knowing whether cocoa shells contain other nonessential metals, this interpretation is equivocal. If such metals are present in shells, it is possible they were taken up from soil when newly fermented beans were dried on patches of bare earth, as is the practice in many countries. Their presence would raise the question of how much Pb in cocoa is natural, in the sense it is Pb that was once naturally present in soil. To gauge the extent of Pb contamination, its ratio to another nonessential element could be measured and the deviation from the natural crustal ratio examined. Neodymium is a suitable choice because the crustal Pb/Nd ratio is 0.77 (7), a value conveniently close to

one. Another reason for choosing Nd is that it might be possible to obtain model Sm–Nd ages (8) on cocoa shells, which would indicate the age of the protolith of the soil with which the beans were in contact. Lead isotope ratios, corroborated by those of Sr, could then be interpreted in the light of regional geology, local sources of Pb pollution and sources of Pb pollution in the countries where chocolate was manufactured.

The methods are those of geochemistry, which have seen some application in the food and agricultural sciences. Lead isotopes, for example, have been used to study the origins of dietary Pb (9), to authenticate wine (10) and to test it for contamination (11). Lanthanide fractionation patterns have been used in authentication studies (12), but the use of model Sm–Nd ages to identify agricultural regions seems not to have been exploited. In this study, the shells (testae) and nibs (cotyledons) of 24 samples of cocoa beans, 37 cocoa powders, and 66 slabs of dark chocolate containing more than 70% cacao were analyzed. Beans came from regions differing widely in geologic age. Cocoa powders and chocolate were chosen for their country of manufacture. The concentrations of Pb, Nd, Sm and Sr and the isotope ratios, $^{208}\text{Pb}/^{207}\text{Pb}$, $^{206}\text{Pb}/^{207}\text{Pb}$, $^{143}\text{Nd}/^{144}\text{Nd}$, $^{87}\text{Sr}/^{86}\text{Sr}$, were measured in the shells and cocoa powders by thermal ionization mass spectrometry. With the exception of $^{143}\text{Nd}/^{144}\text{Nd}$, the same were measured in the nibs but in chocolate, because it is often a blend, only Pb concentrations and isotope ratios were measured.

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MATERIALS AND METHODS

Acids, Exchange Media and Spikes. All acids were prepared by distillation in vessels with quartz condensers and quartz or Teflon receivers. Lead levels were measured in each batch, and only those containing < 2 ng/L were used. Neodymium and Sm were below their detection limits of 2 ng/L, measured by evaporating 100 mL of acid. Tap water was first passed through a commercial mixed bed resin and then purified by a Millipore Milli-Q system. Exchange media were Dowex-1, X-8, 200–400 mesh anion exchange resin (Bio-Rad, Hercules, CA), Eichrom REE and Sr resins (Eichrom Technologies, Lisle, IL) and inert polystyrene beads, 200–400 mesh, coated with bis-(2-ethylhexyl) phosphoric acid (HDEHP). The last were prepared in the laboratory. Use of an enriched ^{84}Sr spike (SRM 988) and a ^{205}Pb spike allowed the concentrations and isotope ratios to be determined in a single mass spectrometric analysis. To measure Sm and Nd concentrations a mixed ^{145}Nd – ^{149}Sm spike was used. A highly enriched ^{206}Pb spike was used to measure Pb blanks.

Samples. All samples were collected over the period 2004 to 2006. Cocoa beans were obtained from health food stores or suppliers of beans to home chocolate makers. Pods from a cocoa tree (*Theobroma cacao* L.) in the conservatory of the Fort Worth Botanical Gardens, Fort Worth, Texas, provided a reference sample. Cocoa powders and chocolate were bought mostly in U.S. supermarkets or over the Internet, but a few were obtained outside the U.S.

Analytical Scheme. A 7 g sample was decomposed in nitric acid, and aliquots of the solution were spiked with the appropriate isotopes. After purification, the isotope ratios of the mixtures were measured and the concentrations calculated by the isotope dilution formula. The levels of Pb in chocolate and of Pb and Sr in the shells and cocoa powders were high enough for both concentrations and isotope ratios to be obtained from this measurement. The amounts of shell and cocoa powders that needed to be decomposed to obtain sufficient Nd for an isotopic analysis (about 3 μg) were then calculated. Quantities between 100 and 200 g were typical. As the concentrations of both Pb and the lanthanides in the nibs were low, a 33 g sample was decomposed which, after taking a small aliquot for Sr, was equally split for concentration measurement.

Preparation and Decomposition. The cocoa pod obtained from the conservatory was transported intact to the laboratory where it was opened. The beans were removed in a laminar flow workstation and were dried under filtered air. They and all other beans were shelled with two pairs of stainless steel tweezers, one to tear off the shells and the other to hold the exposed nib. Nibs that broke during peeling were discarded, and every whole nib was inspected for adhering shell fragments. Small fragments of nib were tolerated in the shell samples. All samples were decomposed in Teflon PFA bottles by boiling in 70% nitric acid on hot plates modified for external temperature control. To maintain a clean environment the bottles were placed in Pyrex enclosures through which filtered air was passed. Addition of acid in small volumes was necessary to limit the ensuing strongly exothermic reaction. As a general rule, 7 g of sample, needing 60 mL of acid, could be decomposed per 100 mL of bottle capacity or, put differently, to dissolve 100 g of cocoa required three 500 mL bottles each holding 33 g. After decomposition the solution was transferred to Teflon PTFE beakers, evaporated to dryness under filtered air and charred. Sometimes the 33 g samples ignited (but the Teflon beakers were seldom damaged), causing total loss of Pb but advantageous for Nd separations by reducing organic material. If Pb was to be separated no further decomposition was necessary. For the lanthanides the soluble fraction was dissolved in dilute nitric acid (10 mL per 33 g of cocoa), centrifuged and evaporated to dryness in 15 mL Teflon PFA jars. Remaining organic material was destroyed with 2 mL of perchloric acid.

Separations and Mass Spectrometry. *Lead.* The soluble fraction of the charred residue was dissolved in 0.6 M hydrobromic acid, transferred to a clean polypropylene tube and centrifuged. Lead was separated on a column containing 0.2 mL of Dowex 1, X-8, 200–400 mesh and further purified by single bead ion exchange. The sample was loaded on a rhenium filament in a matrix of silica gel and phosphoric acid and analyzed on a Finnigan MAT 261 thermal ionization, multicollector mass spectrometer. Precision in the isotope ratios is ± 0.001 . Further details can be found in ref 13.

Strontium. The soluble fraction was dissolved in 1 mL of 3 M nitric acid and centrifuged and the supernatant loaded onto a column containing 0.2

mL of Eichrom Sr resin. After washing with 2 mL of 3 M nitric acid, Sr was stripped off with 1 mL of water. The dried sample was transferred to a Re filament with a slurry of tantalum oxide and phosphoric acid. Isotopic ratios were normalized to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$. Precision is ± 0.00002 .

Neodymium and Samarium Concentrations. The perchlorate residue was dissolved in 1 mL of 1 M nitric acid and the insoluble potassium perchlorate centrifuged out. The supernatant was loaded on a polyethylene column containing 0.2 mL of Eichrom REE resin and washed with 2 mL of 1 M nitric acid, and the Nd and Sm were stripped with 0.05 M nitric acid. As their ionization potentials are similar, they could be run simultaneously from double Re filament assemblies. To avoid isobaric interferences the ratios $^{146}\text{Nd}/^{145}\text{Nd}$ and $^{147}\text{Sm}/^{149}\text{Sm}$ were measured. Precision in the Sm/Nd ratio is about 1%.

Neodymium Isotope Ratios. Perchlorate residues from three 33 g dissolutions were each dissolved in 5 mL of 1 M nitric acid and centrifuged. Supernatants were combined, evaporated and redissolved in 5 mL of 1 M nitric acid. After centrifuging out perchlorates of low solubility, the supernatant was loaded on a column containing 0.5 mL of Eichrom REE resin and washed with 5 mL of 1 M nitric acid, and the Nd (and the other light lanthanides) were stripped with 0.05 M nitric acid. If more than 100 g of sample had been dissolved, all the Nd-bearing fractions were combined. Neodymium was separated from Sm on a calibrated column containing HDEHP-coated beads. It was run in double filament mode, and ratios were normalized to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$. Precision is ± 0.00002 .

Standards and Blanks. Spike solutions were calibrated against the Pb standards SRM 981 and SRM 982, the Sr standard SRM 987 and high purity Nd and Sm metal obtained from the Ames Laboratory, Ames, Iowa. Mass spectrometer performance was monitored by analyzing SRM 981, SRM 987 and the La Jolla Nd standard. Blanks were approximately 50 pg of Pb for the shell samples and, on account of the larger volume of acid required, 300 pg for the nibs. The Nd and Sm blanks were all less than their detection limits of 200 pg.

RESULTS

Shells and Nibs. The shells of the control sample (Con-1, **Table 1**) contained 25.4 mg/kg of Sr, undetectable Sm and Nd, and 1.1 $\mu\text{g}/\text{kg}$ of Pb. Its nibs contained 7.1 mg/kg Sr, undetectable Sm and Nd, and 0.53 $\mu\text{g}/\text{kg}$ Pb (**Table S1** in the Supporting Information). Shells of the other samples yielded rock or mineral residues on dissolution, indicating that the beans had been spread out on the ground to dry. They contained between 14 and 72 mg/kg Sr, on average 3.2 times their nibs' content, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of shell and nib closely correlated ($R = 0.999$). The similarities between the conservatory-grown control sample and the other samples indicate that the Sr in the shells is physiologically controlled and is not affected by contact with the soil. In contrast to the control sample, the other shells (**Table 1**) contained between 19 and 443 $\mu\text{g}/\text{kg}$ Nd, with Sm/Nd ratios varying from 0.174 to 0.254. Soil protolith ages ranged from 0.17 to 2.4 Gyr (1 Gyr = 10^9 years) and generally correlated with their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (range 0.7043 to 0.7271). Their Pb contents varied from 91 to 2925 $\mu\text{g}/\text{kg}$ and Pb/Nd ratios from 0.9 to 32. All nibs contained small amounts of Nd (0.05 to 0.45 $\mu\text{g}/\text{kg}$) and up to 2 $\mu\text{g}/\text{kg}$ Pb. Correlation between Nd and Pb concentrations and the shell to nib ratios for Nd and Pb indicate that, despite the precautions taken, material from the shells had contaminated the nibs. They will not be discussed further.

Figure 1A shows the isotope ratios of the shells and, for reference, the semiempirical Stacey–Kramers curve (14) that describes the growth over time of Pb isotopes in the Earth's upper crust. Samples from the Ivory Coast, Peru, one from Venezuela, and all from the Caribbean and the Americas cluster close to modern Pb. One Ghanaian sample falls on the curve close to 0.25 Gyr, and the other four Venezuelan samples are arrayed along it. The two samples from Papua New Guinea lie to the right of but parallel to the curve. The three Madagascan samples lie

Table 1. Concentrations and Isotope Ratios of Trace Elements in Cocoa Shells and Model Sm–Nd Ages of the Soil Protolith

sample	Pb, $\mu\text{g}/\text{kg}$	Sr, mg/kg	Sm, $\mu\text{g}/\text{kg}$	Nd, $\mu\text{g}/\text{kg}$	Pb/Nd	Sm/Nd	$^{143}\text{Nd}/^{144}\text{Nd}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{208}\text{Pb}/^{207}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$	age, Gyr
Control Sample: Conservatory, Botanical Gardens, Fort Worth, Texas											
Con-1	1.1	25.4	nd	nd				0.70989			
Dominican Republic											
Dom-1	782	49.2	5.24	24.3	32	0.217	0.51284	0.70472	2.460	1.195	0.40
Dom-2	885	22.9	13.2	45.6	19	0.291	0.51276	0.70598	2.459	1.189	1.13
Ecuador											
Ecu-1	287	29.8	4.00	19.3	15	0.207	0.51291	0.70620	2.464	1.184	0.28
Ecu-2	2925	27.7	20.0	99.3	29	0.202	0.51259	0.70578	2.461	1.190	0.76
El Salvador											
EIS-1	1063	47.7	58.3	293	3.6	0.199	0.51287	0.70435	2.457	1.188	0.31
Ghana											
Gha-1	137	24.1	6.16	31.1	4.4	0.198	0.51196	0.71687	2.444	1.171	1.74
Gha-2	156	30.6	32.0	178	0.9	0.181	0.51140	0.72705	2.487	1.306	2.40
Ivory Coast											
IvC-1	1887	23.2	36.9	171	11	0.216	0.51177	0.72122	2.467	1.196	2.34
Madagascar											
Mad-1	305	22.8	38.7	222	1.4	0.174	0.51197	0.71302	2.459	1.158	1.51
Mad-2	388	26.5	68.0	376	1.0	0.182	0.51196	0.71322	2.482	1.163	1.59
Mad-3	849	71.5	81.7	443	1.9	0.185	0.51184	0.71034	2.450	1.155	1.79
Mexico											
Mex-1	186	14.4	13.8	72.9	2.6	0.190	0.51235	0.70722	2.465	1.191	1.07
Mex-2	2194	55.8	70.7	333	6.6	0.213	0.51274	0.70425	2.458	1.187	0.56
Panama											
Pan-1	91	30.6	6.23	27.7	3.3	0.225		0.70531	2.458	1.185	
Pan-2	339	32.4	8.56	40.0	8.4	0.214	0.51282	0.70546	2.468	1.194	0.43
Papua New Guinea											
PNG-1	368	19.7	18.5	81.3	4.5	0.229	0.51267	0.70564	2.440	1.154	0.76
PNG-2	877	14.7	8.99	35.4	25	0.254	0.51300	0.70471	2.407	1.126	0.17
Peru											
Per-1	430	42.3	39.4	206	2.1	0.193	0.51222	0.71289	2.474	1.184	1.28
Trinidad											
Tri-1	900	21.1	13.3	62.8	14	0.212	0.51193	0.70955	2.418	1.147	1.97
Venezuela											
Ven-1	98	20.8	6.29	26.8	3.7	0.235	0.51277	0.70459	2.415	1.138	0.60
Ven-2	532	25.1	4.35	217	2.5	0.201	0.51211	0.71241	2.476	1.192	1.53
Ven-3	699	19.5	27.2	136	5.1	0.200	0.51204	0.72411	2.436	1.161	1.64
Ven-4	731	20.3	31.9	160	4.6	0.213	0.51196	0.72418	2.436	1.157	1.77
Ven-5	1820	19.2	73.1	343	5.3	0.213	0.51223	0.70958	2.428	1.156	1.44

farthest to the right, and the other Ghanaian sample, with a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.306, lies too far above the curve to be incorporated in the figure.

Cocoa Powders. The results for cocoa powders are summarized in **Table 2**. The samples are assigned to types according to the age of their soil protolith. Type A consists of a single sample whose

protolith age is 2.41 Gyr. Type B contains 16 samples that have protolith ages from 2.3 Gyr to 1.7 Gyr. Type C contains 14 samples with protoliths between 1.7 and 1.1 Gyr. The remaining six were placed in type D either because their protoliths were less than 1.1 Gyr or because their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were less than 0.7110. Assignment by protolith age brings about grouping

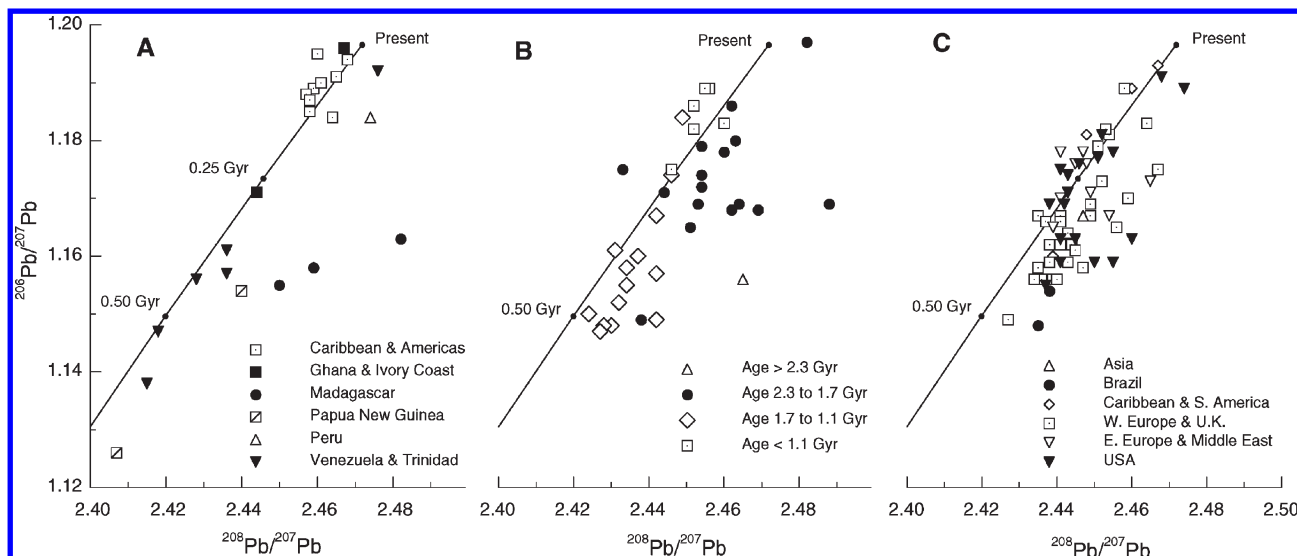


Figure 1. Plots of $^{206}\text{Pb}/^{207}\text{Pb}$ against $^{208}\text{Pb}/^{207}\text{Pb}$. (A) Cocoa shells divided as to country of origin. (B) Cocoa powders divided as to the apparent Sm–Nd age of the protolith of the soil upon which they were dried. (C) Chocolate divided as to the region of manufacture. The line shown in each panel is the Stacey–Kramers curve for the growth of Pb in the average continental crust. Labeled points along the curve indicate values of ratios at the present day and what they were at various times in the past.

Table 2. Mean Concentrations and Isotope Ratios of Trace Elements in Cocoa Powder and Model Sm–Nd Ages of the Soil Protolith^a

sample	Pb, $\mu\text{g}/\text{kg}$	Sr, mg/kg	Sm, $\mu\text{g}/\text{kg}$	Nd, $\mu\text{g}/\text{kg}$	Pb/Nd	Sm/Nd	$^{143}\text{Nd}/^{144}\text{Nd}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{208}\text{Pb}/^{207}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$	age, Gyr
Type A: Soil Protolith Age >2.3 Gyr (1 Sample)											
BrCo-1	71	21.2	3.9	23.9	3.0	0.163	0.51123	0.71774	2.465	1.156	2.41
Type B: Soil Protolith Age 2.3 to 1.8 Gyr (16 Samples)											
minimum	30	15.3	1.3	6.6	1.3	0.162	0.51155	0.71686	2.433	1.149	1.76
maximum	258	17.5	14.6	82.3	6.1	0.195	0.51185	0.72142	2.488	1.197	2.25
mean	118	16.4	8.58	49.0	2.9	0.178	0.51168	0.71958	2.458	1.173	1.97
std dev	52	0.6	4.07	24.1	1.5	0.008	0.00008	0.00121	0.014	0.011	0.12
Type C: Soil Protolith Age 1.8 to 1.1 Gyr (14 Samples)											
minimum	84	14.0	2.85	14.9	2.2	0.174	0.51185	0.71345	2.424	1.147	1.11
maximum	651	25.1	26.8	154	8.2	0.195	0.51228	0.72127	2.449	1.184	1.81
mean	276	20.0	11.9	65.2	4.7	0.185	0.51207	0.71627	2.436	1.156	1.46
std dev	162	3.8	7.47	42.4	1.6	0.005	0.00012	0.00207	0.008	0.011	0.21
Type D: Soil Protolith Age <1.1 Gyr or $^{87}\text{Sr}/^{86}\text{Sr} < 0.7110$ (6 Samples)											
minimum	46	8.4	2.17	11.1	4.1	0.188	0.51223	0.70501	2.446	1.175	0.53
maximum	175	31.6	5.91	26.3	12	0.242	0.51280	0.71070	2.460	1.189	1.23
mean	132	18.6	4.07	19.0	7.1	0.214	0.51258	0.70665	2.454	1.184	0.81
std dev	46	8.0	1.31	5.4	2.9	0.020	0.00024	0.0021	0.005	0.005	0.30

^a Geometric mean concentrations and standard deviations for Pb are as follows: type B, 107 +64/−40; type C, 232 +205/−109; type D, 122 +77/−47.

of the other variables. In type C both Pb and Nd are higher than in type B, and the Pb/Nd ratio increases from type B to type D. The Sm/Nd ratio increases from type B to type D while $^{87}\text{Sr}/^{86}\text{Sr}$ decreases. Lead isotope ratios are plotted in **Figure 1B** and cluster according to type. The single sample of type A falls far to the right of the Stacey–Kramers curve. Type B has higher ratios than type C, and both tend to lie to the right of the growth curve, while type D lies mostly on or above it. Protolith ages also divide the samples by country of manufacture. Type A is from Brazil. Twelve of 16 type B samples came from Europe and the U.K. with the remainder from the U.S. Type C is the reverse with one sample from Asia, three from Europe and the remaining 10

from the U.S. Two of the samples in type D were from Europe and four from the U.S.

Chocolate. Lead concentrations and isotope ratios are summarized in **Table 3**, with the samples grouped according to region of manufacture. Concentrations ranged from 8 to 510 $\mu\text{g}/\text{kg}$. For regions from which three or more samples were obtained, geometric means vary from 24 to 63 $\mu\text{g}/\text{kg}$. Eight samples from W. Europe and the U.K. and two from the U.S. contained more than 100 $\mu\text{g}/\text{kg}$ Pb. Isotope ratios are shown in **Figure 1C**. The samples fall into two groups: those that lie close to the growth curve, which include most of those from the Caribbean and South America, half of those from E. Europe and the Middle East, and 10 out of

Table 3. Geometric Mean Concentrations, Number >100 $\mu\text{g}/\text{kg}$, and Arithmetic Mean Isotope Ratios of Pb in Dark Chocolate

N	Pb, $\mu\text{g}/\text{kg}$				>100	$^{208}\text{Pb}/^{207}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$
	range	mean	std dev				
Region of Manufacture: Asia							
1		12			0	2.447	1.167
Region of Manufacture: Brazil							
2	19–83	40			0	2.437	1.151
Region of Manufacture: Caribbean and South America							
3	9–43	24	+33	–14	0	2.455	1.181
Region of Manufacture: E. Europe, Israel, and Turkey							
9	8–56	34	+29	–15	0	2.448	1.173
Region of Manufacture: USA							
18	12–234	54	+55	–27	2	2.449	1.171
Region of Manufacture: W. Europe and United Kingdom							
33	17–510	63	+65	–31	8	2.445	1.165

18 from the U.S.; and those that lie to the right of it, dominated by the samples from W. Europe and the U.K. but including the single sample from Asia, the two from Brazil and the remaining samples of U.S. manufacture.

DISCUSSION

Bean Processing. Descriptions of the chocolate and cocoa manufacturing process are given in Minifie (15), Wood and Lass (16) and Beckett (17). After drying, the beans are bagged and shipped to the point of processing, where they are cleaned of foreign objects and washed. Shells are broken by crushing or impact and, by virtue of their shape and density, are separated from the nibs by winnowing. The process is not perfect, and it is permissible to leave behind 1.75% of shell material, though with good technique a figure of 1% is usually achieved (15). The nibs are then ground to $< 30 \mu\text{m}$, when rupture of fat-containing cells turns the powdered material into a fluid substance called cocoa liquor. At some point, the beans, nibs or liquor are roasted, which has the 3-fold purpose of sterilization, developing flavor and reducing the moisture content of the nib from 4 to 5% to below 3%. To make cocoa powder, the liquor is pressed and the fat, amounting to about 55% of the mass, is expelled as cocoa butter. The solid cake that remains is ground to powder. However, to be legally called cocoa powder, some fat must remain and 20 to 22% is typical. Sometimes cocoa powders are treated with alkali in a process known as Dutching (17). Seven of the powders analyzed in this study were so treated, but none show aberrant concentrations or isotope ratios. In the manufacture of dark chocolate, cocoa liquor, cocoa butter and cocoa powder are blended together and their sum is the stated cacao content. The other ingredients are sugar and emulsifiers.

Soil Protolith Ages. A model Sm–Nd age is based on the decay of ^{147}Sm to ^{143}Nd and measures the time when continental crust separated from the Earth's mantle. The chemical process of separation enriches the newly formed crust in Nd, leaving behind a mantle somewhat (because mantle mass greatly exceeds continental mass) enriched in Sm. The $^{143}\text{Nd}/^{144}\text{Nd}$ ratio then

increases more slowly in the crust than in the residual mantle and, if the present day $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of each are extrapolated back, their trajectories will intersect at the time of separation, the so-called model age. Given the 106 Gyr half-life of ^{147}Sm , the crustal trajectory is a line with slope proportional to $^{147}\text{Sm}/^{144}\text{Nd}$ while that of the mantle is an empirically determined curve (8). Neither weathering nor metamorphism greatly alters rock Sm/Nd ratios so that both sediments and their metamorphosed equivalents will give model ages that reflect the age of the rock from which they were ultimately derived, i.e., the age of their crustal protolith (18). The isotope ^{87}Sr is also formed by a long-lived nuclide, in this case ^{87}Rb with a half-life of 49 Gyr, but, as natural processes readily separate parent and daughter, Rb–Sr model ages are not meaningful, although $^{87}\text{Sr}/^{86}\text{Sr}$ ratios will increase with the age of the protolith.

Central to this study is whether shells are absorbing Sm and Nd from the surface of the soil in such a way as to give a reasonable age for the protolith. The question is best answered empirically by analyzing shells from countries known to have Precambrian exposures, where dust blown from similarly aged regions of Africa (19) will not significantly change ratios. The sample from Trinidad (geologically an extension of Venezuela) and four of the Venezuelan samples have model ages between 1.44 and 1.97 Gyr. These fall in the range reported for the Guiana shield (20) which makes up the hinterland to the south and southeast of the coastal regions where cocoa is grown. All yielded quartz-rich residues on dissolution, and it is likely that they were dried on soils developed on shield-derived sediments (20). Sample Ven-1 is clearly linked to the other Venezuelan samples by its Pb isotope ratios, but its low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, young age and a residue of volcanic glass point to a possible origin in nearby Grenada where lavas have similar ratios: $^{87}\text{Sr}/^{86}\text{Sr}$ from 0.7045 to 0.7051; $^{143}\text{Nd}/^{144}\text{Nd}$ from 0.5128 to 0.5129; and Sm/Nd from 0.223 to 0.256 (21). The sample from Peru has an age of 1.28 Gyr, close to the figure of 1.40 Gyr reported for sediment from the middle and upper reaches of the Amazon (22). Ages ranging from 1.97 to 2.40 Gyr for shells from Ivory Coast and Ghana are consistent with geology, as these countries are situated on the West African craton, much of which is made up of the Birimian Group dated at 2.2 Gyr (23). The Madagascar samples provide a specific test of validity because cocoa is grown only in the northwest of the island, in the valley of the Sambirano River which drains the Sahantaha Group (24), a metamorphosed sedimentary sequence containing 1.8 Gyr detrital zircons (25). The ages obtained from the shells, which range from 1.51 to 1.79 Gyr, indicate a similar age for the protolith. Thus, uncertainties inherent in model ages notwithstanding, it appears those obtained from the shells indicate with fair accuracy the ages of their soil protoliths.

With the nibs containing none, what Nd is present in cocoa derives from the small amounts of shell ground up with the nib, so that the ages of cocoa powders ought also to indicate the age of their soil protoliths. The 2.41 Gyr age for the sample from Brazil (Table 2, type A) is reasonable given the wide extent of the Precambrian in that country. Because Brazil consumes all the cocoa it produces, type B is ascribed to West Africa's Birimian basement, i.e., to the countries of the Ivory Coast and Ghana, which together export most of the world's cocoa. Type C is as well-defined as type B and dominates the sample of U.S. manufactured cocoa. It is reasonable, therefore, to look to Indonesia which supplies about one-fourth of U.S. demand (26). Most Indonesian cocoa is grown in the southern and central regions of Sulawesi, beneath which Precambrian continental crust has been thrust and melted, producing lavas of Tertiary age that have the isotopic characteristics of much older rocks (27, 28). Their isotope ratios overlap those of type C cocoa (Figure 2).

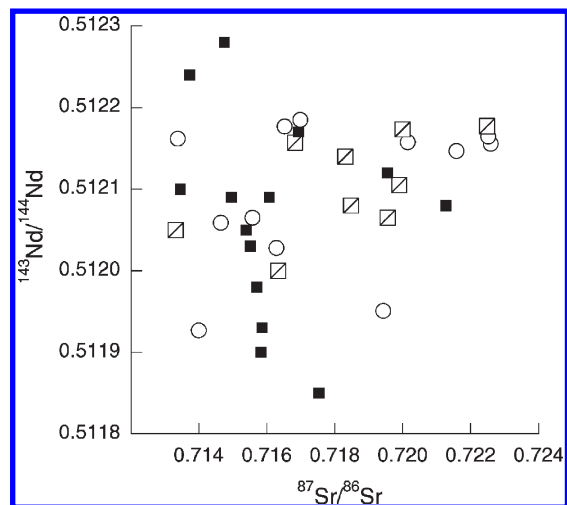


Figure 2. Plot of $^{143}\text{Nd}/^{144}\text{Nd}$ against $^{87}\text{Sr}/^{86}\text{Sr}$ for type C cocoa and volcanic rocks from central Sulawesi. Solid squares, type C cocoa; open circles, measurements of Bergman et al. (27); squares with diagonal, measurements of Marlburg and Foden (28).

Their mean model ages are similar, 1.40 Gyr vs 1.49 Gyr for type C, as are their Sm/Nd ratios, 0.190 vs 0.185 (27, 28).

Type D has the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and the youngest ages and, from similarities with the shells, could be from the Caribbean, Central or South America. Its low Nd content also sets it apart from the other types. Higher Sm/Nd ratios may reflect a component of young basaltic rocks whose ratios are higher than those of granites.

Pb/Nd Ratios. If, after fermentation, beans are spread out on the ground to dry, soil particles will stick to their shells and become the source of some of the Pb, Sm and Nd solubilized by the nitric acid decomposition. For example, sample Mad-2 (Table 1) yielded 16 g of silicate material per kg of shell, of which 75% was a mixture of sand-sized quartz and weathered feldspar and the remaining 25% was silt to clay-sized material. It is difficult to say which of these represents soil as such but, if the finer fraction contained 20 mg/kg of Nd, it would not contribute more than 80 $\mu\text{g}/\text{kg}$ to the 376 $\mu\text{g}/\text{kg}$ of Nd that was extracted. Similar arguments apply to Pb. On the other hand, the adsorption of metals by biomass is well documented, and wheat bran, sago waste and tea waste, in addition to cocoa shells, are reported to have Langmuir constants for Pb in excess of 30 g/kg (29). Thus, it is also possible that shells spread out on the ground to dry will adsorb metals from the surface of the soil but, if this does occur, the conditions will differ greatly from those in the laboratory. They would be scavenging metal ions bound to soil phases rather than from a solution, many more ionic species are involved, concentrations are orders of magnitude lower, and the process will continue only for the length of time that the shells are wet. The last is variable and depends on temperature, cloud cover, humidity, the hour the beans are spread out and whether rewetting by rain occurs. It was noticed that, for types B and C cocoa powders, Pb concentration tended to increase with Nd concentration but with decreasing slope, pointing to the possibility that each sample can be viewed as a batch of beans that had taken a different time to dry. The decrease in slope points to the kinetic process of adsorption with Pb ions being more rapidly adsorbed than those of Nd, as predicted by their hydration enthalpies, -1480 kJ/mol for Pb and -3400 kJ/mol for Nd (29).

As the Pb/Nd ratio is a useful means of assessing contamination, the measurements are more meaningfully presented as plots

of Pb/Nd vs Nd concentration. The shells are plotted in this manner in Figure 3A. Points lie close to the axes, suggesting that their distributions are governed by power curves, which in turn suggests adsorption as the dominant process of uptake. For the sake of discussion they have been divided into four, reasoned as follows. Shell Ecu-2, containing almost 3000 $\mu\text{g}/\text{g}$ Pb (Table 1), is placed on its own (labeled as I). Likewise the shells with the lowest Pb/Nd ratios are grouped together (curve IV). The remaining points are fitted by two curves, labeled II and III. Lead contents of the shells systematically increase along each curve as required by the adsorption model, which would not be so were they drawn any other way. Although the shells come from different countries, each curve is taken to portray adsorption from soils with similar Pb/Nd ratios.

Types A, B and C cocoas are plotted in Figure 3B. In types B and C, the samples with highest Pb concentration, labeled B1 and C1, plot apart from the others. The remaining type B samples conform to a single curve labeled B2, upon which the type A sample falls. The remaining type C samples are divided into four. Curves C2 and C3 are distinct from curve B2, but curve C5 appears identical to it. Two samples labeled C4 fall between curves C3 and C5. Five of the six samples that make type D cocoa fall on curve D1 (Figure 3C), but sample D2 plots far to the left.

Origin of Pb. The insecticide Pb arsenate or aerosols from leaded gasoline, smelters or coal-fired power plants may all contribute anthropogenic Pb to soil, which in many countries can be identified by anomalous isotope ratios. An exception is Mexico where the average anthropogenic Pb, both historic (30) and present (31–33), plots close to the Stacey–Kramers value for modern Pb and generally cannot be distinguished from the Pb that is found in young igneous rocks or older rocks with U/Pb ratios similar to the average crust. This type of anthropogenic Pb ($^{206}\text{Pb}/^{207}\text{Pb} > 1.18$) will hereafter be referred to as Mexican-type Pb. Aerosols measured in Indonesia (31, 33), on the other hand, have $^{206}\text{Pb}/^{207}\text{Pb}$ for the most part < 1.10 , similar to Australian aerosols (31, 33), and will be referred to as Australian-type. Leads with ratios that fall between these values, such as are typical of European aerosols (32), will be referred to as European-type, although the ores from which these aerosols are derived may not be mined in Europe. Ghana used this type of Pb (31), and Ecuador used both it and, more recently, a Mexican-type Pb (31, 33). There is no information for the other countries but, because shells from Venezuela and Trinidad were analyzed, isotope ratios were measured in roadside soils collected in Maracaibo (34). The $^{208}\text{Pb}/^{207}\text{Pb}$ ratios ranged from 2.365 to 2.415 (mean 2.382) and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios from 1.094 to 1.147 (mean 1.112), indicative of European-type Pb.

To turn to the origin of Pb in the shells, the content of Ecu-2 (Table 1) is so high as to unequivocally indicate contamination, even though its Mexican-type isotope ratios are ambiguous. The shells of the Papua New Guinea sample PNG-2, the Trinidad sample and the Venezuelan sample Ven-5 all have isotope ratios displaced from modern Pb in the direction of Australian or European-type Pb and lie on curve II (Figure 3A). Samples PNG-1, Ven-3 and Ven-4, which also appear mixed with the same types of Pb, lie on curve III. Curve IV, however, includes the Venezuelan sample Ven-2, which, by plotting close to modern Pb, appears not to be contaminated; the sample Gha-2, whose $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.306 cannot be anthropogenic; and the three Madagascan samples. It turns out that the rocks of northern Madagascar underwent high grade (granulite facies) metamorphism 0.51 to 0.56 Gyr ago (35). Such metamorphism brings about loss of U with respect to Th, retarding the subsequent growth of $^{206}\text{Pb}/^{207}\text{Pb}$ without changing that of $^{208}\text{Pb}/^{207}\text{Pb}$, so that the

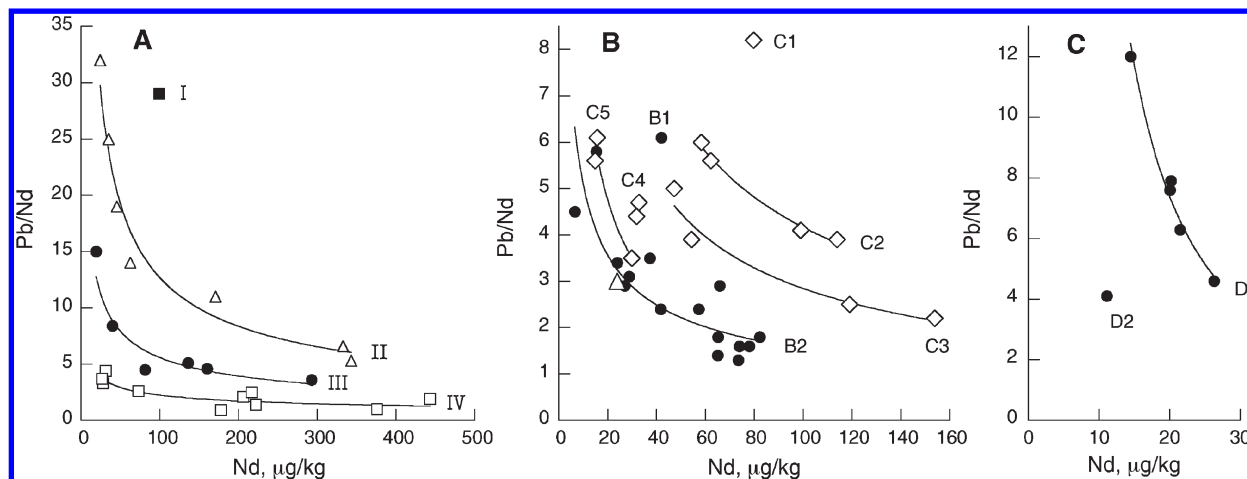


Figure 3. Plots of Pb/Nd ratio against Nd concentration. **(A)** Cocoa shells. Roman numerals designate shells in various stages of equilibrium with soil of a particular Pb/Nd ratio. **(B)** Types A (triangle), B (solid circle) and C (diamond) cocoa powders. Arabic numeral after letter designates powders derived from batches of beans in various stages of equilibrium with soil. **(C)** Type D cocoa. In all plots the points are fitted by power curves.

ratios of the affected rocks develop on a new trajectory to the right of the growth curve (**Figure 1A**). The ratios appear, therefore, to be natural. It is not clear why Ven-1 falls on this line because its isotope ratios indicate contamination, but its low Pb/Nd ratio may reflect derivation from soil developed on basaltic lavas whose ratios tend to be low. If this sample is accepted as anomalous, curve IV defines samples that have acquired Pb from uncontaminated soil and indicates that as equilibrium between shell and soil is approached Pb/Nd ratios tend to a value of one. Curves II and III, on the other hand, signify beans dried on contaminated soil.

Type B cocoa has Pb/Nd ratios that lie on a curve tending to a value of one as Nd concentration increases (curve B2; **Figure 3B**), which by analogy with the shells implies that they were derived from beans dried on uncontaminated soil. This inference is supported by the general observation that type B's isotope ratios fall in the field of old continental crust which has both lower U/Pb and Th/Pb ratios and higher Th/U ratios than today's crust, producing isotope ratios that lie to the right of the growth curve below modern Pb (36). The rocks of W. Africa appear to conform to this general rule because sediment from the mouth of the Niger, which drains terrains aged from 1.0 to 2.0 Gyr (37), plots in this part of the figure (38) and ratios reported for the preindustrial deep sea turbidite VM19-285 (36), cored in the Gulf of Guinea, span the field of type B cocoa. Furthermore, contamination can be excluded because no Pb aerosols lie in the area to the right of the growth curve between present day Pb and Pb of 0.5 Gyr ago (32). The sample labeled B1 lies off curve B2 on account of its high Pb content, but it is difficult to explain why this should be, because none of its other variables are anomalous.

Type C cocoa has higher Sr concentrations and higher Sm/Nd ratios than type B, which may result from a difference in soil type, whereas its higher Nd concentrations may result from longer drying times. Its Pb concentrations, however, are on average more than twice those of type B. Contamination can be suspected because in **Figure 3B** most of the points plot above and to the right of type B cocoa, which was argued above to be uncontaminated. It can be tested for by plotting $^{206}\text{Pb}/^{207}\text{Pb}$ against $1/\text{Pb}$. The linear trend shown by most of the samples in **Figure 4** indicates that type C cocoa is a mixture of Pb from two isotopically distinct sources that lie at unspecified points on the line. One source, however, is arguably the Pb that is naturally present in soil. To find the second, a line (**Figure 5**) is drawn from the mean isotope ratios of the Sulawesi volcanic rocks (28), through the mean ratios

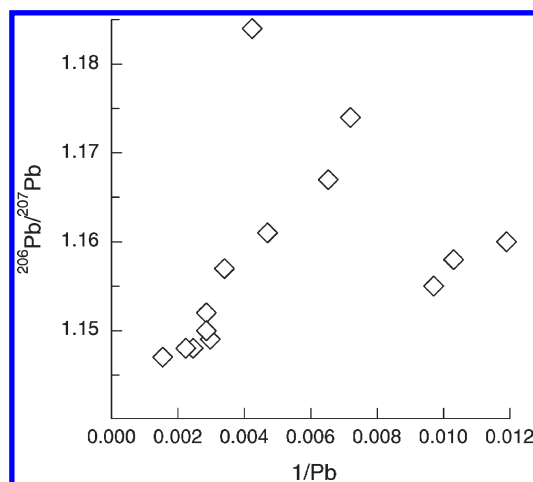


Figure 4. Plots of $^{206}\text{Pb}/^{207}\text{Pb}$ against reciprocal of Pb concentration for type C cocoa powders. Linearity indicates mixing of two sources with different isotope ratios. The three points on the right of the diagram are those that make curve C5 in **Figure 3B**.

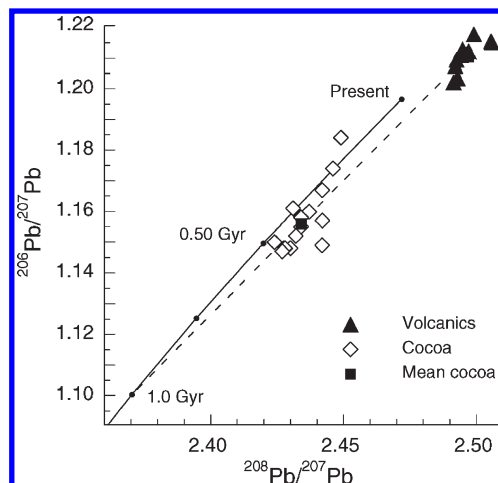


Figure 5. Plots of $^{206}\text{Pb}/^{207}\text{Pb}$ vs $^{208}\text{Pb}/^{207}\text{Pb}$ for type C cocoa and volcanic rocks from Sulawesi. The line joining the mean values of the volcanic rocks and the cocoa intersects the Stacey–Kramers growth curve at 1.0 Gyr, close to values reported for Indonesian aerosols. The isotope ratios of the rocks are from Marlburg and Foden (28).

of type C cocoa to the point where it meets the growth curve. The intersection occurs at 1 Gyr, i.e., $^{206}\text{Pb}/^{207}\text{Pb} = 1.100$; $^{208}\text{Pb}/^{207}\text{Pb} = 2.370$, which are plausible values, being close to those of Australian-type aerosols measured in Indonesia (33, 35). The position of the cocoa midway on the line indicates that it is an equal mixture of these sources but, because the concentration is twice that of type B, the amount of natural Pb is the same in both types of cocoa. The sample labeled C1 in **Figure 3B** has both the highest Pb content and the lowest $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of its type, making it the lowermost point on the linear array in **Figure 4**. Therefore, its isolated position in **Figure 3B** results from it being the most contaminated sample. The three points that make curve C5 seem from their near coincidence with curve B2 to be uncontaminated. In **Figure 4** they make the group of points lying farthest to the right and appear anomalous but their isotope ratios, protolith ages and the fact that one of them was processed in Asia tie them to that region. A possible explanation lies in the fact that the Pb/Nd ratio depends on drying time but the Nd concentration on the amount of shell ground up with the nibs. If this is smaller than average, the points will move to the left and it may be significant that these samples are the three with the lowest Pb and Nd concentrations. The sample that lies at the top of **Figure 4** forms part of curve C3 in **Figure 3A**, and its anomalous position results from its high $^{206}\text{Pb}/^{207}\text{Pb}$ ratio. There is no obvious explanation.

Type D cocoa (**Figure 2C**) with its low Nd contents and high Pb/Nd ratios seems derived from beans that dried rapidly. Curve D1 is essentially a continuation of curve B2 (**Figure 2B**), and the samples do not appear contaminated. Sample D2 may result from the shell content of the grindings being below average as explained above.

The ratios of chocolate (**Figure 1C**) share the features of cocoa. They mostly lie to the right of the growth curve and are clustered around a mean value intermediate between those of type B and type C cocoa, which is consistent with chocolate being a blend of beans from different sources. Some, including most of those from the U.S., lie on the growth curve as if derived from Caribbean sources. If contamination during processing occurred, it would be difficult to detect in chocolate from the U.K. and France because both used European-type Pb in gasoline, the net effect of which would be to shift samples down the curve to less radiogenic values. In the case of U.S. manufactured chocolate, where environmental Pb falls above the growth curve, contamination will shift the ratios upward and across the curve. If this did occur, the effects are so small that they cannot with certainty be distinguished from shifts resulting from mixing different sources. Samples containing more than 100 $\mu\text{g}/\text{kg}$ Pb are isotopically unremarkable, with the exception of the W. European sample containing 510 $\mu\text{g}/\text{kg}$, which has the lowest isotope ratios of all measured.

Rankin et al. (4) have asserted that cocoa and cocoa products have been subjected to global Pb contamination and that "most contamination occurs during shipping and/or processing of the cocoa beans and the manufacture of cocoa". Their arguments were in large part based on the observation that the isotope ratios in chocolate coincided with those of U.S. environmental Pb. By way of response, no more needs be done than remark that not one sample of chocolate measured in this study falls in the field of isotope ratios reported by them, although all their concentration measurements fall within the limits of those reported here, as do the isotope ratios they measured on cocoa.

The average concentrations of Pb in chocolate are up to one-half the averages in cocoa powders, which is to be expected. To inquire whether the concentration of Pb in the shell predicts that

of cocoa, the shell concentration is first multiplied by the fraction of shell that is usually incorporated in the liquor (about 1%) and then by a factor that accounts for the amount of fat lost during pressing (about 46%), which takes with it about 10% of the Pb (39). Moisture loss on roasting can be ignored, given the uncertainty in the above figures. The result is a conversion factor of 0.017. For Ecu-2, with 3000 $\mu\text{g}/\text{kg}$ of Pb in its shells, cocoa containing of 51 $\mu\text{g}/\text{kg}$ Pb is predicted, which is less than half the average value of 118 $\mu\text{g}/\text{kg}$ for type B powders. If only Pb concentrations had been measured, the difference between calculated and observed concentrations might well be attributed to contamination during processing, but Nd gives the same discrepancies and Nd contamination is not plausible. Sampling could be the explanation because the beans used in this study, which came largely from regions in or around the Caribbean, may not be representative of those used to produce African or Asian cocoa. If the calculation is done in reverse, shell concentrations are up to ten times higher than any observed. While these figures are much less than the Langmuir constants and so are plausible, it is reasonable to question whether it is possible for a wet shell in partial contact with dry soil to extract metals in such high concentration. Another explanation may be called for, and one worth exploring is whether the outer surfaces of the beans are abraded during winnowing, producing metal-rich dust that in some manner enters the grinding process and raises the Pb and Nd contents of the liquor to concentrations greater than those expected from the simple incorporation of shell fragments. Sampling, however, may explain why many of the beans from the Caribbean and S. America appear contaminated whereas type D cocoa powders do not, and why the reverse holds for type B powders and the sample of Ivory Coast beans. Such contradictions are not surprising as, out of the 3×10^8 kg of cocoa that are ground annually, only about 3 kg have been sampled.

In summary, this study shows that cocoa shells take up metals from contact with soil and that the amount depends on drying time. Thus a slowly drying shell may take up more Pb from uncontaminated soil than a rapidly drying shell from contaminated soil. In the absence of isotope ratios, contamination can be assessed by considering the ratio of Pb to Nd or another nonessential element. If uncontaminated, shells should fall close to curve IV of **Figure 3A**, whose equation is $y = 13.1x^{-0.383}$, where x is the Nd concentration in $\mu\text{g}/\text{kg}$ and y is the Pb/Nd ratio. For cocoa powders the corresponding equation, obtained by combining curves B2 (**Figure 3B**) and D1 (**Figure 3C**), is $y = 114x^{-0.988}$. Finally, it is noted that the isotope ratios of Pb in the U.S. diet, in contrast to those of cocoa, lie above the Stacey–Kramers curve (13), which implies that cocoa's contribution of Pb to the U.S. diet is small. Furthermore, experimental work indicates that less than 10% of this cocoa-derived Pb is bioavailable (39).

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Supporting Information Available: Tables S1, S2, and S3 containing the full data sets for the nibs, the cocoa powders and the chocolate samples. Figure S1 comparing the isotope ratios of chocolate measured in this study versus those measured by Rankin et al. (4). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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