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COPPER AND BARIUM AS DIETARY DISCRIMINANTS: THE EFFECTS OF DIAGENESIS

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INTRODUCTION

Trace and minor elements in excavated bone have provided new information on the ancient diet of humans (Brown 1973, Gilbert 1975, Lambert *et al.* 1979, Schoeninger 1979). Most of the early studies focused on strontium as a rough inverse correlate of meat or protein intake, since animals that are higher in the food chain tend to discriminate against this element. Diet, however, is a complex and multicomponent problem, and a single variable such as strontium cannot approach an accurate definition of the ancient diet, although it is useful in uncovering dietary differences based on sex or status. Through pattern analysis, multielement studies potentially can define various components of the ancient diet more fully. Some studies have utilized the multielement approach to achieve this end (Gilbert 1977, Lambert *et al.* 1979). In the study of any element, however, it is necessary to determine to what extent the analysed level in the bone reflects the levels at the time of death. Material from the soil environment can leach into the bone, resulting in proportions that would be meaningless for analysis of diet. In addition, elements can leach out of the bone and then give low values.

We and others (Parker and Toots 1980) have tried to establish criteria to determine whether a given element accurately reflects lifetime levels. Our research has used three different approaches. (1) Comparison of elemental levels in ribs and femurs (Lambert *et al.* 1982). The cancelous, more porous rib undergoes diagenesis more rapidly than the cortical femur, so that elements that leach in from the soil are found at higher levels in the rib, and elements that are lost to the environment are found at lower levels in the rib. (2) Electron microprobe examination of excavated femurs (Lambert *et al.* 1983). Contamination is evident as build-up on the surface. (3) Analysis of soil adjacent to burials (Lambert *et al.* 1984). Loss or gain of material from the bone results in anisotropic distributions of elements in the surrounding soil. When material is lost, levels are increased close to the bone; when material is gained, levels are decreased.

By these three methods, we established that iron (Fe), aluminum (Al), potassium (K), and manganese (Mn) move into and contaminate the bone, so that they are not useful dietary indicators. Strontium (Sr), zinc (Zn), and sometimes lead (Pb) appear not to be appreciably affected by burial and therefore should be useful in analysis of ancient diet. Calcium (Ca) and sodium (Na) leach from bone to soil, but the remaining levels may still be an accurate measure of ancient diet. Although most studies still rely on Sr, two dimensional plots of Sr *versus* Zn are beginning to find greater acceptance (Rheingold *et al.* 1983).

Both copper (Cu) and barium (Ba) are potentially important elements in the analysis of ancient diet. As a trace element, copper is necessary for blood formation and connective tissue metabolism and is a key component of metalloenzymes. Deficiencies result in anemia, depressed growth, and bone disorders (Underwood 1977). Ingested copper is readily absorbed into the body and transported in the blood plasma. Crustaceans, shellfish, and organ meats are rich in Cu content. Thus high levels of bone Cu may indicate high meat diets. Gilbert (1977) suggested that Cu would be particularly useful in diet discrimination in ancient populations. To date, the effects of bone diagenesis on Cu levels have not been studied.

Barium is a Group IIA element just below strontium in the Periodic Table. Because of its larger ionic radius, Ba may be discriminated against by carnivores to an even larger extent than is Sr, in which case Ba would be a more sensitive dietary indicator than Sr. Indeed, Wessen *et al.* (1978) found that recently killed deer had 30 times more Ba than did recently killed fur seals, whereas the average Sr content was only up to twice as high in the deer. These materials, however, were not subject to burial and to the possible effects of diagenesis. High concentrations of Ba are found in grains (20 ppm) and nuts (3000 ppm)(Underwood 1977), so that low concentrations of Ba in human bone might indicate a high meat diet. The intestinal tract absorbs about 6% of ingested Ba, which is deposited entirely in the skeleton (Bauer *et al.* 1961). Deficiencies of Ba or Sr may result in depressed growth, although there is no conclusive evidence that Ba is an essential trace element for humans.

Herein we report a detailed study of diagenetic effects on Cu and Ba in the Woodland populations that we studied earlier (Lambert *et al.* 1979, 1982, 1983, 1984). By use of the criteria of ribs *versus* femurs, by soil analysis, and by electron microprobe examination, we conclude that both Cu and Ba are subject to contaminative action by the soil and consequently are of doubtful use in diet studies for these populations.

EXPERIMENTAL METHODS

The Woodland skeletal materials have been described in our previous publications (Lambert *et al.* 1979, 1982, 1984). The procedures for electron microprobe analyses followed those of our earlier study (Lambert *et al.* 1983). The respective standards were $Ba(NO_3)_2$ and Cu metal. Analysis of both Cu and Ba in soil and bone was carried out by polarized Zeeman atomic absorption spectrophotometry on a Hitachi Model 180-70 instrument. The Zeeman effect corrects for molecular and background absorption, and use of double beam optics also corrects for interferences caused by direct spectral overlap (Koizumi *et al.* 1977, Koizumi 1978).

The bone was prepared by the method of complete dissolution (Szpunar *et al.* 1978), with about 0.700 g of bone per sample. Soil was dissolved in a similar fashion (Lambert *et al.* 1984). For Ba analysis, three 3 ml aliquots from the original 50 ml solution were diluted to 25 ml for use in the method of standard addition. One of these samples contained 0.8 ppm added Ba, another 1.6 ppm Ba, and the third no added Ba. The spectrophotometer current was 17.5 ma, the wavelength 553.5 nm, the slit 1.3 nm, the gas flow 200 ml/min, and the sample size 10 μl. The heating program was 80–120°C (dry) for 30 sec, 120–500°C (ash) for 10 sec, 2800°C (atomization) for 3 sec, and 2800°C (clean) for 3 sec. The original 50 ml solutions were used for Cu analysis. The current was 10.0 ma and the wavelength 324.7 nm. The heating program (°C) and other parameters were identical to those for Ba.

Statistical comparisons between populations were made by the *F*-test. Details have been given elsewhere (Lambert *et al.* 1979, 1982). Further information on the experimental and statistical procedures has been given by Vlasak (1983).

COPPER CONTENT

Copper levels were measured in femurs of 18 individuals from the Gibson site (10 female, 8 male) and 23 individuals from the Ledders site (11 female, 12 male). The means for the total populations and the means broken down by sex are given in table 1, together with our earlier data on ribs for the same populations (Szpunar 1978). Data for each individual may be found in the dissertations (Szpunar 1978, Vlasak 1983). In each category, the Cu level is lower in the femur than in the rib. We take this observation to indicate that the element has leached into the bone, with a higher degree of contamination for the rib (Lambert *et al.* 1982). The *F*-test showed that the means for rib and femur were different at the 99.9% level both for females and for males at either site. This same observation was made for other contaminative elements, such as Fe, Al, Mn, and K, but not for the valid dietary indicators Sr and Zn.

Table 1 *Copper analysis of rib and femur (ppm)**

	Gibson		*Ledders*	
	Rib	*Femur*	*Rib*	*Femur*
Males	9.0 ± 2.8 (23)	2.7 ± 2.3 (8)	10.3 ± 1.2 (12)	1.7 ± 1.0 (12)
Females	8.2 ± 2.5 (33)	3.2 ± 1.3 (10)	10.0 ± 2.3 (12)	2.9 ± 2.0 (11)
Total population	10.6 ± 7.5 (86)	3.0 ± 1.8 (18)	10.5 ± 2.3 (32)	2.3 ± 1.6 (23)

* Elemental means and standard deviations. Number of individuals in each group is given in parentheses.

The distribution of Cu within the femur was studied in thin sections of three specimens from the Ledders site, 1–16, 1–41, and 1–146. The amount of Cu was mapped by X-ray fluorescence on a scanning electron microscope. Figure 1 shows a dot map of Cu concentration. The outer surface of the femur is signified by a change from a higher to a lower density of dots. The dot map is 400 μm wide, and the X-ray counts were averaged over 20 sec. There are isolated areas of Cu build-up along the outer surface of the femur and 10–15 μm into the sample. Further in the sample and along the inner surface, the distribution of Cu is homogeneous. In all three specimens, similar regions of concentration were observed along the outer surface that were 3–30 times more concentrated than the homogeneous areas further in the sample. These observations give clear evidence that Cu leaches out of the soil environment and forms concentrated pockets on the bone. The pattern is the same as that for Fe, Al, K, and Mn (Lambert *et al.* 1983).

Soil samples came from burials 3–1 and 3–3A at the Elizabeth site. Each soil position was analysed four times and the means calculated. In our Cartesian convention, the y axis is vertical (positive above the burial, negative below the burial), and the femur is extended along the z axis with the feet directed toward the observer. The x axis is in the plane of the burial, with positive always indicating the direction outward from either femur (hence negative x is between both femurs). Analyses in ppm for four soil positions are given in table 2. The *F*-test indicates that the means around the right femur differ at the 90% confidence level for both burials. Higher Cu content in particular is found below and outside of the femurs. Anisotropic distribution of an element around the femur was associated with elemental flux between soil and bone (Lambert *et al.* 1984). The geometrical pattern is very similar to that of Fe, Al, or K, which were all classified as contaminative elements.

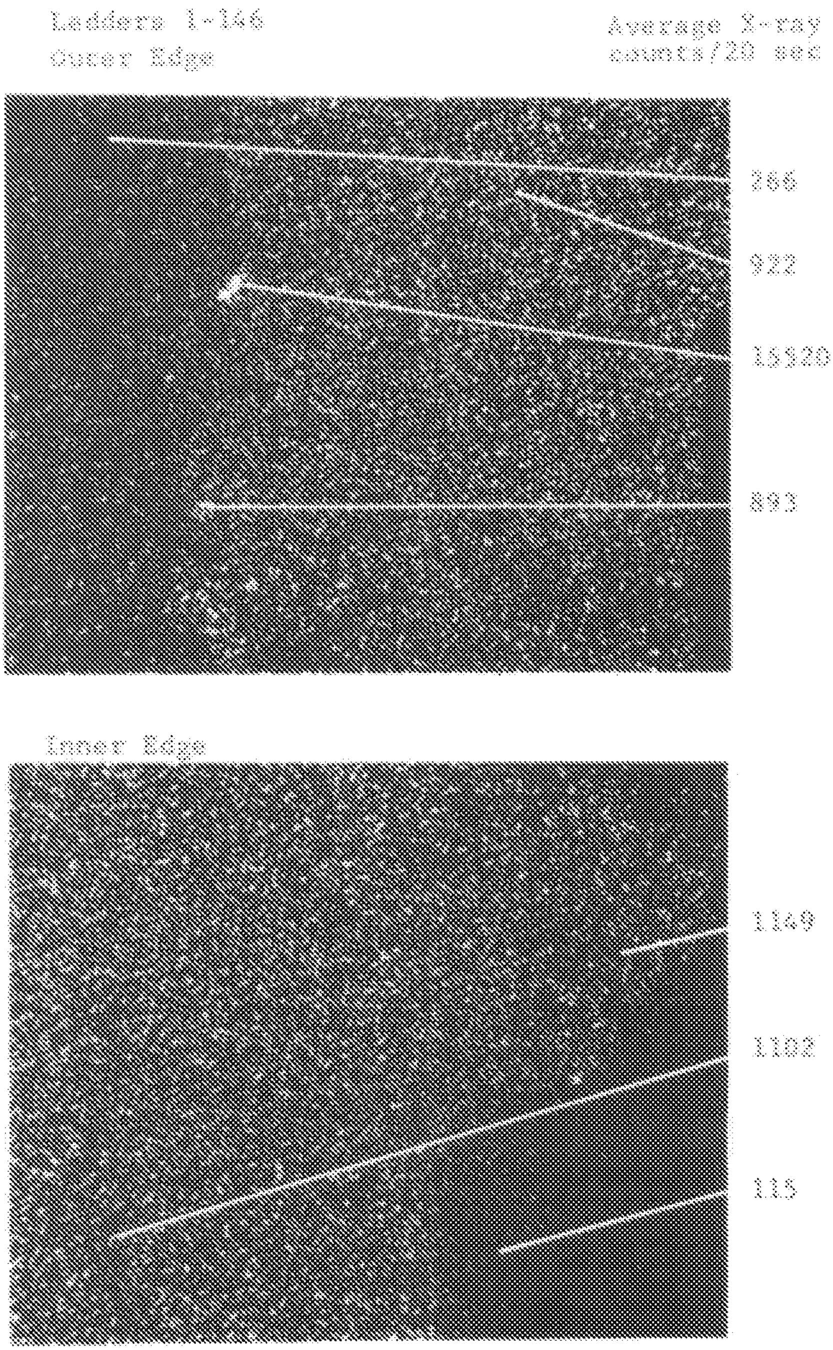

Figure 1 *Electron micrograph (× 300) showing the copper distribution in the femur of Ledders 1–146. The width of the scan is 400 μm. The figures on the right are the average number of X-ray counts in 20 sec for a volume of approximately 1 μm³ located at the left end of the white line. (Upper) Outer surface. (Lower) Inner surface.*

Table 2 *Copper soil analysis (ppm)*

	+ 5y	− 5x	+ 5x	− 5y
Eliz 3−1				
Right femur	7.7 ± 1.5	7.8 ± 2.2	10.5 ± 3.2	11.7 ± 1.5
Left femur	7.6 ± 3.0	7.6 ± 0.5	9.7 ± 1.2	8.6 ± 0.9
Eliz 3−3A				
Right femur	15.5 ± 2.6	13.5 ± 3.8	14.2 ± 1.9	20.8 ± 5.3
Left femur	14.1 ± 2.2	15.3 ± 1.5	14.5 ± 1.4	15.8 ± 0.8

All three criteria indicate that Cu is a contaminative element: higher levels in the rib, build-up on the outer surface, and inhomogeneous distribution in the surrounding soil. The evidence strongly indicates that Cu in this buried bone is not a reliable measure of Cu levels at the time of death but has been altered by diagenesis. Consequently, the element is not a good indicator of ancient diet in this context.

BARIUM CONTENT

There already is some literature data on the question of barium diagenesis. Wessen *et al.* (1978) compared Ba and Sr in bones of recently killed (modern) deer and fur seals with that in archaeological samples of fur seals. Much larger standard deviations were observed in the Ba content of the archaeological samples. Ahlgren *et al.* (1981) measured the Ba content in archaeological human bones from A.D. 200–300 and found concentrations of 63–88 ppm in the rib and 37–68 ppm in the shaft of the fibula. By analogy with our study of ribs *versus* femurs (Lambert *et al.* 1982), we interpret these results as indicative of greater Ba contamination in the ribs.

Barium levels were measured in 20 femurs from the Gibson site (11 female, 9 male) and 24 from the Ledders site (12 female, 12 male). Strontium levels were measured for the same specimens. The means for these groups are given in table 3. Individual values may be found in Vlasak (1982). Significant differences (95% level) were found for comparison of Sr content between males and females at the Ledders sites. Gibson males were different from Ledders males in Sr content (99.9) but Gibson females had the same Sr levels as Ledders females. These differences have already been interpreted (Lambert *et al.* 1979, 1982). In the present study the significant result is that Ba levels were identical by the *F*-test for all subgroups (males *versus* females, Gibson *versus* Ledders). Thus Ba is a worse discriminator than Sr in the archaeological context. The major reason for the lack of discrimination is the large variance or standard deviations for Ba. Plots of Sr *versus* Ba were not linear (for example, figure 2), and the Ba ranges invariably were larger than the Sr ranges.

Distribution of Ba within the femur was studied by electron microprobe for Ledders samples 1–16, 1–41, and 1–146 and Gibson 3–1. Concentrated areas of Ba were observed along the outer surfaces in all these sections (figure 3). The regions of enhanced concentration (1.5- to 40-fold) penetrated 10–15 μm into the bone. The Ba concentration was homogeneous further in the bone and along the inner surfaces. The distribution of Sr invariably was homogeneous in all parts of the femur (Lambert *et al.* 1983).

This pattern of Ba distribution is similar to that for Fe, Mn, Al, K, and Cu (above) and is

Table 3 *Barium and strontium content in femurs (ppm)* *

	Gibson		*Ledders*	
	Ba	*Sr*	*Ba*	*Sr*
Males	288 ± 198 (9)	251 ± 60 (10)	203 ± 86 (12)	141 ± 23 (12)
Females	197 ± 91 (12)	197 ± 63 (12)	240 ± 68 (12)	168 ± 43 (13)
Total population	250 ± 141 (21)	220 ± 66 (22)	222 ± 78 (24)	155 ± 37 (25)

*Elemental means and standard deviations. Number of individuals in each group is given in parentheses.

consistent with contamination by leaching of Ba from soil to bone. Parker and Toots (1980) suggested that complex barium oxides and barite ($BaSO_4$) minerals may fill voids in the bone matrix and alter the original Ba concentrations in the bone.

The failure of Ba to discriminate between populations, the comparison of ribs and fibula, and the presence of increased levels of Ba on the surface of the bone according to SEM microprobe all indicate that Ba is subject to diagenetic effects during burial and is not a useful element here for drawing conclusions concerning ancient diet. Soil samples were not analysed for Ba.

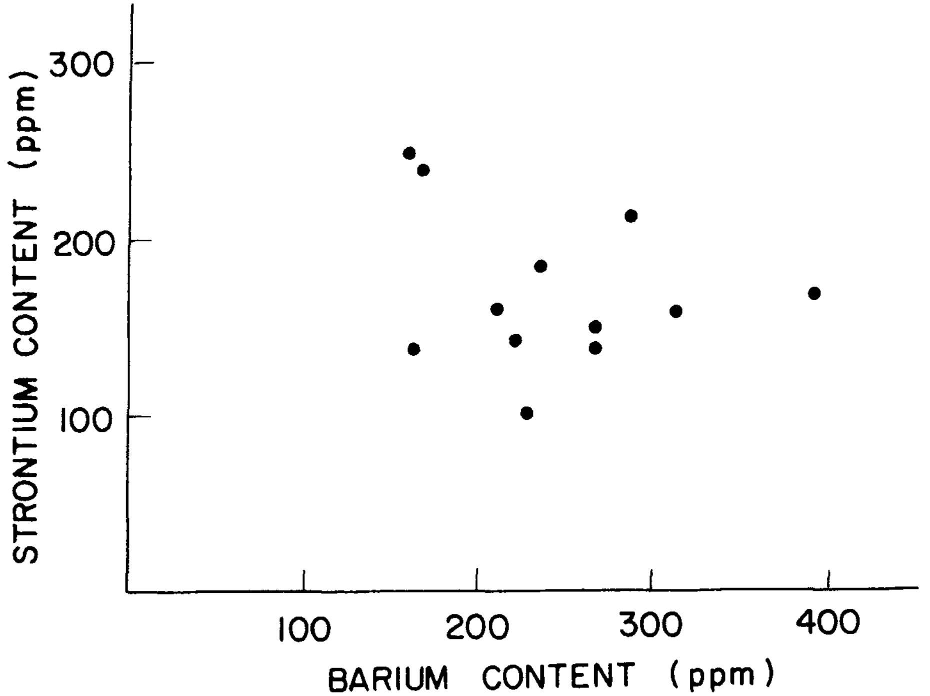

Figure 2 *Strontium content* versus *barium content for femurs from the 12 Ledders females.*

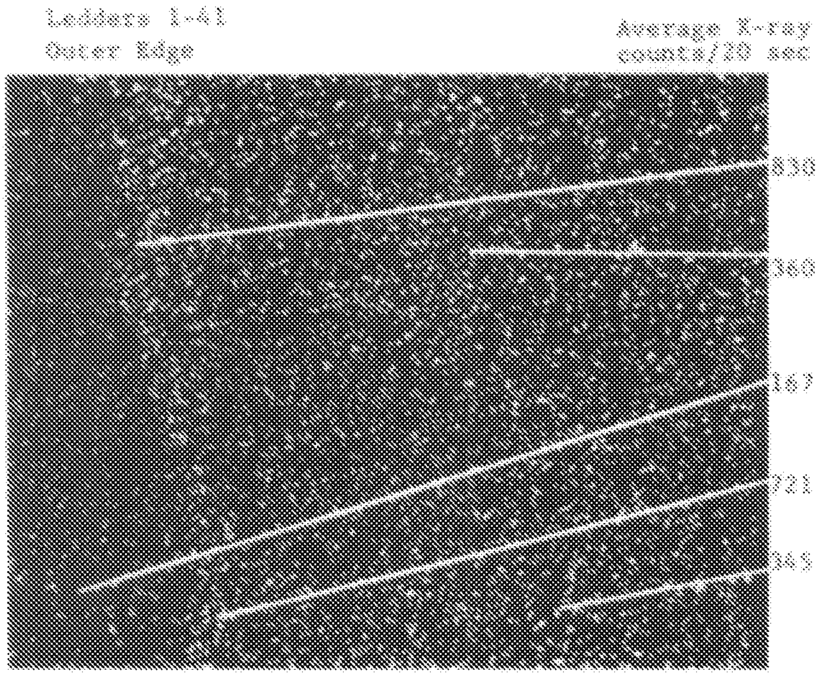

Figure 3 *Electron micrograph showing the barium distribution in the femur of Ledders 1–16. See figure 1 for details.*

CONCLUSIONS

Both copper and barium exhibit the classic profile of contaminative elements in these Woodland specimens. Concentrations are higher in ribs than in femurs for Cu (higher in ribs than fibula in another study for Ba). Both elements show build-up on the outer surface of the femurs, according to electron microprobe examination. The soil surrounding the femurs shows an inhomogeneous distribution of Cu. We cannot vouch that these results will be general for all sites. It may be possible to obtain ante-mortem concentrations for Cu or Ba by stripping off and excluding from analysis the outer portions of bone. Nonetheless, these results require that both Cu and Ba be considered suspect in any attempt to correlate elemental levels with dietary characteristics of ancient cultures.

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