Kerstin Lidén

COMMENTS TO *Putting the "chemistry" back into archaeological bone chemistry analysis: Modeling potential paleodietary indicators* by Joseph A. Ezzo

Joseph Ezzo has provided a review of archaeological applications of trace-element analyses on bone, published in the *Journal of Anthropological Archaeology* 13. In that paper he gives a short review of almost all papers ever published on the subject, ever since the potential of this application first became apparent in 1973; albeit omitting all east-European literature (e.g. Alexeeva 1979; Alexeeva et al. 1988; Smrcka et al. 1988; Fedosova 1991; Kozlovskaya 1993). The paper is divided into three main parts, the first provides a brief introduction to bone structure and physiology, the second discusses the principles of the strontium model, and finally the third discusses the use of eleven elements that Ezzo regards as potential palaeodietary indicators. These potential palaeodietary indicators are aluminium, barium, calcium, iron, potassium, magnesium, manganese, sodium, phosphorus, strontium, and zinc. Ezzo considers their physiological function, their nutritional significance and their relative abundance in foods. With this selection he has excluded a number of elements that also are, and have been used as, potential palaeodietary indicators, e.g. copper and selenium. He critically reviews all the former applications of the different elements as palaeodietary indicators. His main intention with his paper is, however, to "develop a general model for determining whether an element has potential as a palaeodietary indicator by maintaining that a physiological basis must be established for an element if it is to be considered such an indicator" (p. 2). He claims to have proven that the only elements that at the moment fit these criteria are strontium and barium.

In part one, Ezzo stresses the importance of using cortical bone and not trabecular bone because of the trabecular bone's higher sensitivity to diagenesis, and also the importance of analysing the same kind of bone in comparisons between individuals. He also discusses how bone is constantly remodelled throughout an individual's lifetime, and concludes that the turnover time for calcium is 2-4% per year. He does not, however, discuss the turnover time for collagen which is thought to be somewhere between seven and twenty years (Libby et al. 1964; Stenhouse & Baxter 1979; Bumsted 1985; Chisholm 1989).

Part two concludes that strontium has no demonstrable essential biochemical or physiological function, and hence should be better to use than metabolically controlled elements, since the level ingested and the level in the bone should roughly correlate. Strontium is also fractionated (depleted) up the food chain from soil to plant to herbivore to carnivore. The same arguments are put forward in favour of the use of barium as a palaeodietary discriminant. Ezzo then defines the criteria that need to be fulfilled in order for an element to be used as a palaeodietary discriminant: "for an element to be a valid paleodietary indicator it should be incorporated into the structure of bone hydroxyapatite at levels that are proportionate to levels in the diet, it should not be an essential nutrient or one subject to metabolic regulation, and it should be present in bone at levels that exceed contributions likely to occur as a result of postdepositional processes" (p. 8).

Part three re-examines the eleven different elements that are claimed to be dietary discriminants. Aluminium is soon discarded because there is no evidence that it binds to the hydroxyapatite and because Ezzo thinks it is almost certain that the detected levels of aluminum in bones reflect soil/clay inclusion. In most cases Ezzo stresses the importance of using modern bone values as comparatives to the prehistoric values. However, regarding barium and strontium he surprisingly disregards modern values as comparatives and reliable values of the biological ranges of concentrations in prehistoric human bone. He presents a study in support of the trophic-level effect of strontium from bedrock to leaf and then from leaf to herbivore, where one can detect a mean trophic effect of 4.5 times strontium and 10 times barium. Iron is disregarded because of its high concentrations in soil as compared to bone and hence the risk of contamination in sample handling and also iron's lack of incorporation into the hydroxyapatite of bone. Magnesium is not either incorporated into the hydroxyapatite and hence is unsuitable as a palaeodietary indicator. Also, magnesium's high concentration in the soil and mobility in the geochemical environment as well as it's documented leaching out of bone support this standpoint. There is no evidence that manganese is incorporated into the hydroxyapatite, although it seems as if it is associated with the organic phase of the bone. Manganese is, however, mainly discarded due to its very low concentrations in bone and its much higher concentrations in the soil. Sodium and potassium are discarded on somewhat different grounds, the main reason seems however, to be that they are common elements in the ground, that they are highly mobile, and in addition to this, that they have a very complex metabolism. No correlation between phosphorus and diet has been demonstrated so far, and there is evidence for leaching of phosphorus over time in archaeological bone. Hence phosphorus is not a palaeodietary indicator. Zinc is mainly discarded as a palaeodietary indicator on the basis of lack of information for a valid physiological model. However, there is evidence that dietary levels of zinc appear to affect the zinc concentrations in the bones of growing animals. Also, the uncertainty of whether zinc is incorporated into the apatite matrix makes Ezzo suspicious. It seems, however, clear that zinc is linked to the organic phase of bone, probably via collagen cross-linking.

After having stated this, Ezzo gives a number of erroneous applications of the use of zinc as a palaeodietary indicator, from among which I am attributed with providing one (Lidén 1990) and Birgit Arrhenius another (Arrhenius 1990). Arrhenius is criticized mainly for her interpretation of her results, rather than the use of trace elements as dietary indicators. In this case Ezzo seems to have little or no knowledge of the diet of hunter–gatherer societies. In the case of my work, Ezzo writes that I suggest in an "arbitrary manner, that the zinc and copper values for human skulls from the Neolithic site Ire (Gotland) indicate marine resources as the major dietary component" (p. 21). However, in that paper I support my assumptions not only on trace-element analysis but equally so on the analyses of stable carbon isotopes, for which there are no doubts about the origin of the main protein resources (e.g. Chisholm et al. 1981; 1982; 1983; Tauber 1981; Boutton et al. 1984; Hobson & Collier 1984; Lovell et al. 1986; Johansen et al. 1986; Walker & De Niro 1986; Sealy & van der Merwe 1988; Lidén & Nelson 1994; Tuross et al. 1994). The other main complaint, concerning the use of zinc as a palaeodietary indicator in these papers, is the exclusion of physiological references. This does not, however, satisfy Ezzo's state of mind; when referring to the next papers he is reviewing, in which physiological references are included, he discards them as having contradictory opinions. As an example of such idiosyncrasy, Ezzo refers to an analysis performed by himself in which he has studied lagomorphs (hares and rabbits) and humans in order to see if there exists a trophic effect in zinc, i.e. an accumulation of zinc up the food chain. Unfortunately for Ezzo, he has happened to choose a group of species that have a very specific physiological pathway. Not only do lagomorphs defecate, they also perform caecothropy, and above all have a special ability to sort food in their caecum (Pehrsson 1983a; 1983b). It would have been interesting to have heard some discussion on what effects this would have on the lagomorphs bone zinc values. The contradiction in his results, that the predators of the lagomorphs had the same or slightly higher values, must first be explained in terms of whether this was true for the lagomorph muscle tissue, which we assume the predators fed upon, and also whether lagomorphs were the predators main or only prey. If not, this specific analysis does not convince me that zinc can be excluded as a palaeodietary indicator regarding trophic effects. I think that Ezzo should look into the stable isotope literature before generalizing about one herbivore value in terms of all herbivores. Such would have shown him how stable isotopes tend to have an averaging effect and show a narrowing of the standard deviation up the trophic levels. Hence, it is much more fruitful to discuss averages and standard deviations, as should be done with his own examples for the strontium model and trophic-level effects. It is also interesting that copper is discarded without any other explanation than that it's metabolism is very complex. Ezzo also makes the unfounded statement that "[m]odern Western diets probably contain a higher percentage of meat than most prehistoric diets" (p. 12) – based on what? and compared with what populations?

I do, however, agree with Ezzo's critical approach to trace-element analyses, and his demand for a more thorough examination of the physiological background for the element's incorporation into bone. Unfortunate, though, is his choice of species, and lack of knowledge of their very specific physiology, in his argumentation about zinc. This is a drawback to his credibility in the earlier reviews. I would also like to stress even more the importance of diagenesis and the possibilitiy of detecting diagenesis (see e.g. stable isotope analyses). I would also encourage more studies of minerals bound to collagen and other proteins in the organic phase of bone, and the possibility of using them as palaeodietary indicators. For collagen there is good evidence for controlling any diagenetic changes (De Niro 1985; De Niro et al. 1985; Ambrose 1990), and we know that dietary copper is necessary for collagen synthesis (Harris et al. 1980).

As for the strontium analysis, since the geological background totally determines the outcome of strontium analyses, I think one should be very careful with inter-population comparisons and also be on the watch for prey species that are migratory or have large territories, such as many birds, large ungulates, and most of the carnivores.

Finally, it is my opinion that empirically obtained data is not necessarily wrong, although it can always be improved upon, such as in this case with more information on the physiological background using e.g. theoretically designed experiments with an empirical outcome. The use of copper as a dietary indicator has proven useful in combination with stable isotopes. In a study of prehistoric diet of two Swedish Stone Age populations (Lidén in press), high copper values were correlated with the location of the settlements close to lagoons.

References

Alexeeva, T. I. 1979. Biogeochimiya i problemy antropologii. *Tr. biogeochim. laboratorii* 17, pp. 110–120.

Alexeeva, T. I., Kozlovskaya, M. V. & Fedosova, V. N. 1988. Khanty. Opytpaleoekologicheskoi rekonstrukzii. In Alexeev, V. P. (ed.): *Paleoantropologia i arkheologia Zapadnoi i Yuzhnoi Sibiri,* pp. 83–104. Novisibirsk.

Ambrose, S. H. 1990. Preparation and characterization of bone and tooth collagen for isotopic analysis. *Journal of Archaeological Science* 17, pp. 431–451.

Arrhenius, B. 1990. Trace element analysis on skulls. *Laborativ Arkeologi* 4, pp. 15–20.

Boutton, T. W., Klein, P. D., Lynott, M. J., Price, J. E. & Tieszen, L. L. 1984. Stable carbon isotope ratios as indicators of prehistoric human diet. In Turnlund, J. R. & Johnson, P. P. (eds.): *Stable Isotopes in Nutrition.* American Chemical Society 258, pp. 191–203.

Bumsted, M. P. 1985. Past human behaviour from bone chemical analysis – respects and prospects. *Journal of Human Evolution* 14, pp. 539–551.

Chisholm, B. S. 1989. Variation in diet reconstructions based on stable carbon isotopic evidence. In Price, T. D. (ed.): *The Chemistry of Prehistoric Human Bone,* pp. 10–37. Cambridge.

Chisholm, B. S., Nelson, D. E. & Schwarcz, H. P. 1981. Dietary information from ^{13}C and ^{15}N measurements in bone collagen. *PACT* 8, pp. 392–395.

Chisholm, B. S., Nelson, D. E. & Schwarcz, H. P. 1982. Stable carbon isotope ratios as a measure of marine versus terrestrial protein in ancient diets. *Science* 216, pp. 1131–1132.

Chisholm, B. S., Nelson, D. E. & Schwarcz, H. P. 1983. Marine and terrestrial protein in prehistoric diets on the British Columbia coast. *Current Anthropology* 24, pp. 396–398.

DeNiro, M. J. 1985. Postmortem preservation and alteration of in vivo bone collagen isotope ratios in relation to palaeodietary reconstructions. *Nature* 317, pp. 806–809.

De Niro, M. J., Schoeninger, M. J. & Hastorf, C. A. 1985. Effect of heating on the stable carbon and nitrogen isotope ratios of bone collagen. *Journal of Archaeological Science* 12, pp. 1–7.

Ezzo, J. A. 1994. Putting the "chemistry" back into archaeological bone chemistry analysis: Modeling potential paleodietary indicators. *Journal of Anthropological Archaeology* 13, pp. 1–34.

Fedosova, V. N. 1991. Ecological interpretation of the temporal variations of Asian Eskimo limb bones. *Homo* 42/3, pp. 244–264.

Harris, E. D., Rayton, J, K., Balthrop, J. E., Di Silvestro, R. A. & Garcia De Quevedo, M. 1980. Copper and the synthesis of elastin and collagen. In: *Biological roles of Copper.* Ciba Foundation symposium 79. Excerpta Medica, pp.163–177. Amsterdam.

Hobson, K. A. & Collier, S. 1984. Marine and terrestrial protein in Australian aboriginals diet. *Current Anthropology* 25, pp. 238–240.

Johansen, O. S., Gulliksen, S. & Nydal, R. 1986. $\delta^{13}C$ and diet: Analysis of Norwegian human skeletons. *Radiocarbon* 28, pp. 654–761.

Kozlovskaya, M. V. 1993. Bone mineral content as an indicator of the diet and ecological situation in paleopopulations. *Homo* 44/2, pp. 134–144.

Libby, W. F., Berger, R., Mead, J. F., Alexander, G. V. & Ross, J. F. 1964. Replacement rates for human tissue from atmospheric radiocarbon. *Science* 146, pp. 1170–1172.

Lidén, K. 1990. A diet study of the MiddleNeolithic site Ire, Gotland. *Laborativ Arkeologi* 4, pp. 21–28.

Lidén, K. (in press) A dietary perspective on some Swedish hunter–gatherer and Neolithic populations: An analysis of stable isotopes and trace element. *Laborativ Arkeologi* 9.

Lidén, K. & Nelson, D. E. 1994. Stable carbon isotopes as dietary indicator, in the Baltic area. *Fornvännen* 89, pp. 13–21.

Lovell, N. C., Chisholm, B. S., Nelson, D. E. & Schwarcz, H. P. 1986. Prehistoric salmon consumption in interior British Columbia. *Canadian Journal of Archaeology* 10, pp. 51–55.

Pehrsson, Å. 1983a. Digestibility and retention of food components in caged mountain hares, Lepus timidus, during the winter. *Holarctic Ecology* 6, pp. 394–403.

Pehrsson, Å. 1983b. Caecothropy in caged mountain hares (Lepus timidus) *Journal of Zoology* 199, pp. 563–574.

Sealy, J. C. & van der Merwe, N. J. 1988. Social, spatial and chronological patterning in marine food use as determined by $\delta^{13}C$ measurements of Holocene human skeletons from south-western Cape, South Africa. *Current Anthropology* 20, pp. 87–102.

Smrcka, V., Jambor, J. & Salas, M. 1988. Diet in the 1st–2nd centuries along the northern border of the Roman Empire: A reconstruction on the basis of an analysis of chemical elements found in skeletal remains. *Anthropologie* 26/1, pp. 39–54.

Stenhouse, M. J. & Baxter, M.S. 1979. The uptake of the bomb ^{14}C in humans. In Berger, R. & Suess, H. E. (eds.): *Radiocarbon Dating.* Berkeley.

Tauber, H. 1981. ^{13}C evidence for dietary habits of prehistoric man in Denmark. *Nature* 298, pp. 332–333.

Tuross, N., Fogel, M. L., Newsom, L. & Doran, G. H. 1994. Subsistence in the Florida archaic: The stable isotope and archaeobotanical evidence from the Windover site. *American Antiquity* 59, pp. 288–303.

Walker, P. L. & De Niro, M. J. 1986. Stable nitrogen and carbon isopte ratios in bone collagen as indices of prehistoric dietary dependence on marine and terrestrial resources in Southern California. *American Journal of Physical Anthropology* 71, pp. 51–61.