Role and Utility of Trace Elements in Palaeodietary Reconstruction

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Abstract: In this paper we discuss about the impotency of Trace Elements in Human and Animal Diet. Some of Trace Element such as Strontium (Sr), Barium (Ba), Calcium (Ca), Magnesium (Mg) and Zinc (Zn) played an important in the dietary reconstruction. The investigation of the chemical content of bone for reconstruction of palaeodiet, however, is a relatively recent development. Aspect of past subsistence such as the importance of Marine and Terrestrial components in the Diet, the contribution of plants versus animal and marine, can now be estimate using more rigorous, quantitative techniques involving the chemical composition of Bone.

Introduction:

Historically, faunal analysis played an important role in archaeological studies. In fact, the recognition of associations between human remains, cultural materials, and the bones of the extinct animals was the major contribution of faunal analysis provided to the nineteenth century archaeology and is in large part responsible for establishing the antiquity of humans. Even the terms Palaeolithic and Neolithic were partially founded on the co-occurrence of artifacts with particular types of fauna. In recent times, validating New World "early man" sites is often dependent upon the association of artifacts with the bones of extinct animals.

Bones have also been used to asses different aspects of behavioral activities of human and carnivores (De Niro and Epstein,1981; Binford, 1981; Klein and Cruz-Urible, 1984; Weiner et. al., 1993). The investigation of the chemical content of bone for the reconstruction of past diet, however, is a relatively recent development. Several recent reviews (Klepinger, 1984; Price et. al., 1985b; Sillen and Kavanagh, 1982) have provided an overview of bone chemistry and palaeonutrition. Aspects of past subsistence such as the importance of marine and terrestrial components in the diet; the contribution of plants versus animals, and more, can now be estimated using more rigorous, quantitative techniques involving the chemical composition of bone. Based on carbon and nitrogen isotope ratio plants and animals have been studied extensively by Schwarcz and Schoeninger (1991), Nautiyal et. al., (1995). But after the emergence of bone chemistry it is found that trace elements such as Strontium (Sr) Barium (Ba), Calcium (Ca), Magnesium (Mg) and Zinc (Zn) are significantly useful in the reconstruction of the palaeodiet and palaeo-environment.

The chemical analysis of human bone as a means to assess past dietary variability has also emerging as a major research focused mainly in bioarchaeology (Price

et.al., 1989a; Farswan et.al.,2002, 2007) and studies of the relationship between bone elemental content and past diet has been established positively by these archaeologists. Field research in modern ecosystems indicates that inter and inter-regional geological variability in elemental concentration produces variations in dietary and bone elemental values within trophic levels (Sealy and Sillen, 1988; Schoeninger, 1989). Thus animals with similar diets that are feeding in adjacent habitats may have different bone elemental concentrations.

Fortunately the investigation of the chemical composition of human bone has began to reveal new aspect of past subsistence and behaviour. Two types of analysis, 'isotopic and trace elements' are currently used for the assessment of past dietary practices. Isotopic analysis have involved two major elements to date, carbon and nitrogen, to measure the presence or importance of certain plants or marine species in the diet (Vogel and Van Der Merwe, 1977; Chisholm, et al., 1983).

It is verified from various chemical analyses that the whole cortical bone is composed of approximately 69% of inorganic, 22% organic and 9% water. However, the approximate percentage of body's Strontium, Barium and Magnesium are 99%, 93% and 65% respectively, which is located in the skeleton of an animal. Besides this composition of the elements like Fe, Mn, Zn, K, Cu etc. in the skeleton is reasonably greater. As we know that all these elements comes through various type of food intake, while, a fixed amount of these elements are utilized mostly by every animal for their different kinds of physiological activities. But a number of palaeodietary studies have proved that some trace elements (Ca, Ba, Mg, Mn, Zn, Sr etc.) are good indicator of the diet, as their values are remained stable upto many thousand of years, in well-preserved bone. It is confirmed by a lot of investigations that higher concentration of Sr, Ca, Mg and

Zn and lower value of Ba and Ba/Sr ratio observed in the bone are the remarkable indicator of marine food (Pate, 1994; Gilbert et al., 1994; Burton, 1996) and continuous intake of terrestrial food also increases the value of Ba and Ba/Sr ratio (Antoine et al., 1988; Burton and Price, 1991) in the bone of every animal. Besides this bone Zn and Mn can also be used to distinguish Carnivore from herbivore (Morgan and Schoeninger, 1989) as Zn is more concentrated in animal flesh than in most plant foods. Carnivore have higher Zn than do herbivore, while Mn is more concentrated in plants so herbivore have higher Mn than do carnivore (Francalacci, 89).

The nature, ability and specific features of some of the trace elements used in dietary reconstruction
Strontium (Sr):

Strontium is the element most widely used for dietary reconstruction because of its biological determination or bio-purification when ascending the trophic level. Since 99% of the body's strontium is located in skeleton, analysis of bone mineral could disclose feeding habits of different animal. The first successful application of this principle was in paleontology. Toots and Voorhies (1965) reported that the mean strontium content of Pliocene vertebrates distinguished not only between carnivores and herbivores but also between browsers and grazers, the later distinction presumably reflecting higher strontium concentrations in succulent herbs than in grasses.

Later on strontium analysis was applied to the assessment of the diet of human populations. Within inland archaeological context, strontium analysis has been used to address following concerns:

(a)   Estimation of the proportion of meat and vegetables foods in the diet by comparing human and animal bone from the same site.

(b)   Comparisons of the dietary compositions of meat and vegetables between archaeological sites, with and without controls.

(c)   Estimation of dietary change at a site or region overtime.

(d)   Inference of status differentiation within a site or temporal changes in social distinctions.

(e)   Investigation of possible correlates between dietary and morphological changes.

The amount of strontium deposited in the body parts of animals depends on biological factors and on the amount of the element available to the organism. Invertebrates appear to incorporate strontium in a fashion that is different from that of vertebrates. The amount of strontium in blood is then available for incorporation into bone mineral. Virtually all of the strontium actually stored in the body is found in the skeleton system (Schroeder et al., 1972) therefore, animal flesh provides almost no strontium when it is included in a diet. An herbivore's diet provides a relatively large amount of strontium since

plant material contains about three times the amount of strontium as does animal flesh. A small percentage of herbivore's dietary strontium is deposited in its skeletal system. An omnivore from the same geographic region should have a lower bone strontium level because the meat in its diet contains virtually no strontium. A carnivore should have the least amount of bone strontium because much more of its diet in meat.

The strontium concentration in fresh bone is determined by dietary intake and metabolic process. The predominant use of strontium analysis of prehistoric bone has been the determination of the relative abundance of plants versus meat in the diet (Sillen and Kavanagh, 1982). The bones of human or other animals whose diets consist primarily of plant should contain relatively high strontium concentrations than those of species whose diets consist of either a broad mix of plants and animals or primarily animals.

The assumption that lower Sr/Ca ratio reflect relatively greater meat consumption, which in turn reflects higher status, is shaky, unless other variables are known. Not all societies regard as high status food; feudal Japan is an example. There are frequently high status meats and low status varieties. The strontium content of many non-western food items such as grubs, insects and numerous root crops is not known (Katzenberg and Schwarcz, 1984) and cannot distinguish between herbivores and omnivores on the basis of bone strontium levels at archaeological sites in Canada. There is a general tendency among the higher animals, that the Sr content in body fluids decrease, as they make evolutionary advances from a dominantly aquatic habitat to land based. This tendency reflects the increasing dependence of these groups from a seawater environment, with its originally higher Sr/Ca ratios. The measurement of strontium in human bones from archaeological sites has been proposed and applied to infer the proportional amount of meat and vegetable foods in the diet of prehistoric peoples (Brown, 1973). The techniques is based on the well documented distribution of strontium in land-based food chains. The proportion of meat and vegetable foods in palaeodiets by reference to the Sr/Ca ratios of skeletons. Because vegetable food contains higher Sr/Ca ratios than meat foods, diets heavily dependent on vegetable foods may be expected to result in relatively high Sr/Ca ratios in bone.

Barium (Ba):

Barium, like strontium, is incorporated in bones at levels that reflect its dietary abundance. Barium concentration in bone can be used as indicators of tropic position or together with strontium concentrations as indicators of the relative composition of marine versus terrestrial resources. Anomalous barium and strontium values suggest that additional dietary or environmental factors are reflected in the composition of bones from arid environments.

About 93% of the body's barium is located in bone and in the connective tissue. The intestinal epithelium discriminates against the absorption of barium even more strongly than it does against strontium. Therefore, the same arguments are applicable to the use of barium for discerning tropic levels. Barium also appears to be useful in separating from terrestrial mammal bone. Wessen and coworkers found barium levels to be dramatic discriminators between marine and terrestrial fauna of northwest coast. Barium levels in both recently modern and archaeological specimens were low for marine species and higher for terrestrial animals.

Barium, which is chemically similar to strontium, has received little attention. Elias et al., (1982) justify the use of strontium as an indicator of tropic position. Several archaeological studies have observed that barium appears to be a good palaeodietary indicator of trophic position (Francalacci and Borgognini, 1988; Francalacci, 1989). They have examined this potential of barium as a palaeodietary indicator and have found that barium not only responds at least as well as strontium to tropic position, but that by examining both strontium and barium, other aspects of diet such as the consumption of marine resources can also be estimated.

Wessen et.al., (1978) found that there are large difference in barium, but not in strontium, between marine and terrestrial archaeological bone. Consumption of either meat or marine resources lowers bone barium values, so there could be ambiguity in resolving these two components using barium data. The use of barium together with strontium has the potential for resolving both marine and tropic level effects, while leaving unchanged the pronounced differences due to marine resources. Bones from human with predominantly terrestrial diets have a biomodal distribution of Ba/Sr ratios, corresponding to desert and non-desert environments. The difference between animals in different positions in the trophic level is caused by the consumption of a monotonous diet where the ratio of strontium to calcium or barium to calcium constant. Herbivores (plant eater) have higher Sr and Ba concentration values than carnivores (meat eater) which have low values of Sr and Ba (Elias & Patterson, 1982). It is also reported that Omnivores have intermediate values between the two.

However, from the analysis of various bone samples of marine and terrestrial animals from different archaeological sites, Wessen et al., (1978), Burton and Price (1990a, 1990b), Gilbert et al., (1994) and Burton et al., (1999) have found a lower value of Ba, Ba/Sr ratio in marine animal, while higher values of the same elements in terrestrial animals. At the same time bone Ba provides a more sensitive indicator of trophic differences (Pate, 1994). Animals generally have lower Ba/Ca ratio than herbivores.

Calcium (Ca):
High levels of dietary fiber correlate with lower Ca and higher Sr and Ba in the bone. Calcium is a major constituent of bone, and belongs to alkaline earth metal group. The higher Ca content in the samples compared to the reported for modern bone (Price et al., 1985b) suggests that these bones have been well preserved and that additional post-mortem deposition of Ca has taken place during diagenesis. A similar observation was reported for the Neolithic samples from Hambledon Hill in the south of England (Antoine et al., 1988).

Animals preferentially assimilate calcium, herbivores have lower Sr/Ca ratios than the plants they eat, and carnivores have lower Sr/Ca ratio than the meat they eat. While this trophic effect appears in single-component diets, multi-component diets do not produce a simple or linear correspondence between bone Sr/Ca and the relative dietary abundance of meat and plants. Bone Sr/Ca ratios can be disproportionately dominated by idiosyncratic variation of high-calcium foods, even when present in minor amounts. Even when high-calcium foods and mineral additives can be excluded from consideration, the correspondence between bone Sr/Ca ratios and specific dietary abundances is highly equivocal.

A diet generally low in calcium (Ca), supplemented by green plants providing both higher Sr and higher Ca, would than also support the comparatively high Sr and Ba values, which are highly correlated, thus pointing the similar conditions of metabolic absorption from low-Ca food components. The general diet is likely to have been based on considerable amounts of vegetable food items. Medieval applications had at their disposal, different sources of high or low-Ca food items can be identified which may facilitate dietary reconstruction. An additional supplementation with meat is likely but cannot be detected in multi component, higher in Ca and will not show up in the trace element profile. While small amounts of strontium, because of their chemical resemblance to the calcium, can exchange for calcium in the bone crystal (Harrison et al., 1955), large amounts inhibit calcification and induce typical rickets in growing rats.

More than 99% of body calcium resides in the bone; for the average human this constitutes 1000-1200g (Avioli, 1988). The remaining calcium is primarily found circulating in plasma. Calcium absorption, like the absorption of the all-essential minerals, is a tightly controlled biological system that is influenced by the balanced between blood and extracellular fluid calcium levels. In addition, milk consumption has other consequence. Lactose may also affect absorption of calcium and strontium from cereals and the discrimination against strontium in situations of combined ingestion of milk and cereals.

Calcium is needed by plants as well for proper growth and development, although levels of calcium tremendously in plants. Generally speaking, nuts, seeds,

and some legumes contain high amounts, as do green leafy vegetables such as spinach, alfa-alfa, and beet greens. Grain such as wheat and corntend to have very little calcium in their edible portions. Because of the structural similarity of strontium to calcium, plants can not distinguish between them and therefore, do not discriminate between them; plants do, however, discriminate some what against barium uptake from the soil (Elias et al., 1982).

It has often been assumed that the amount of calcium consumed directly relates to the amount of barium and strontium consumed. For prehistoric populations taking domesticated animals that might have been used for dietary purpose, this generally holds. For the most part, the amount of barium and strontium in plants and meat reflect calcium levels.

Magnesium (Mg):
The potential utility of the magnesium in palaeonutritional assessment arises from the fact that, like strontium and manganese, magnesium is generally found in higher concentration in plant foods than in meat. About 60% to 65% of the total body magnesium is found in the skeleton, moreover, recent studies have indicated that the magnesium concentration in bone is very highly correlated to serum magnesium levels in normal patients, as well as in case of magnesium excess or depletion. Vaughan has stated that magnesium is largely intercellular, rather than a part of the bone mineral. However, Alfrey et al., (1986) have determined that 30% of bone magnesium is in a reality exchangeable, surface-limited pool; the remaining 70% was found to be an integral part of the bone crystal. They believe that this deeper magnesium pool probably reflects serum concentration at the time of deposition rather than acute fluctuations; in vitro studies have soon this pool to be nonexchangeable. The magnesium levels in trabecular bone were found to be consistently higher than in cortical bone.

In later studies found that ionized plasma magnesium correlated very strongly with cortical bone magnesium concentration when plasma levels were below normal. There was no correlation between trabecular bone and plasma levels. All of these studies suggest that cortical bone is the more desirable for evolution of body magnesium stores. It appears that 70% 0f bone magnesium substituted for calcium in the apatite lattice in a manner and analogous to strontium, and it is the fraction that can be evaluated in archaeological context. As in the case of strontium, the possible effect of diagenetic change have yet to be clearly defined. Perhaps the determination of Mg/Ca ratios along with faunal controls may help to evaluate that variable. One analysis of three components at a single site showed that the magnesium concentration in human cortical bone increased with time since burial (as did calcium), but the rate of increase was not linear.

Magnesium is widely found in foods; it is the central atom in the chlorophyll molecule, and obviously green vegetables are a rich source. Legumes, animal products, cereal grains are also good sources. Neuman and Mulryan (1969) synthesized apatite in the presence of magnesium ions and found that the lattice rejected the ions. More recently Terpstra and Driessess (1986) synthesized apatites for magnesium inclusion and found that virtually none of the calcium positions in the lattice were occupied by magnesium ions. The fact that most bone magnesium is surface-bound, coupled with magnesium's concentration and high ionic mobility in the geochemical environment, makes it a very unlikely candidate as a palaeodietary indicator. Leaching of magnesium out of archaeological bone has been documented in several studies (Ezzo,1992; Lambert et al., 1991; Parker and Toots, 1980).

Because magnesium occurs widely in animal and plant sources of food (Shils, 1990), no tropic- level separation can be said to exist. Tight metabolic control of the mineral regulates its concentrations in bone, as indicated by a recent experiment by Klepinger (1990). Some variability related to has been found in magnesium levels in tooth enamels, with slightly higher levels correlating positively with.

Zinc (Zn):
Concentrations of zinc, in human bone can be helpful in refining the picture of prehistoric human diet. Zinc is the most abundant trace metal in the body (2-3g) and functions primarily as an metallo-enzyme co-factor. Much of the action of zinc involves its role in stabilizing cell membranes (Solomons, 1988). Zinc is found in variable amounts in foods, with meats tending to be richer sources than plant foods; much of the zinc in cereals is bound to phytates and unavailable for absorption .

Dietary levels of zinc appear to affect zinc concentrations in the bones of growing animals. Diets marginal or different in zinc have lead to reduced levels in bones and various soft tissues. It appears, however, that decreasing or increasing zinc intake in adult animals does not alter their zinc bone levels significantly (Solomons, 1988). The function and location of zinc in bon has been examined in some details, although it is still uncertain whether zinc actually becomes incorporated into the apatite matrix. Studies have shown that zinc can undergo extensive heteroionic exchange with bone calcium (Aitken, 1976).

More recently zinc is being erroneously used in conjection with strontium as a means of inferring prehistoric diets (Edward and Benfer, 1993; Williams, 1993). One of the most fundamental abuse of bone chemistry analysis has been presented by Edward et al., (1984) claims that zinc levels in bone reflected the sources of zinc in the diet. If zinc came primarily from meat, levels would be higher than if the zinc source was

primarily vegetable foods, because the latter contain phytates that inhibit zinc absorption. Lambert and Weyder-Homeyer (1993) stated that zinc levels in bone reflect protein source, with vegetable sources providing much higher zinc levels than meat sources. Klepinger (1993) claims there is strong evidence that dietary zinc levels, irrespective of their sources, directly correlated to bone zinc levels.

Carnivore bones contain greater concentrations of Zn than do those of herbivores. Additionally, Zn is also found in large concentrations in foods such as shellfish and nuts. Local values of Zn are highly variable, even more than Sr, making it difficult to generalize further (Beck, 1985. The quantity of zinc in vertebrate bone directly proportional to the quantity of food ingested.

Zinc abundance's can reflect direct contribution of zinc-rich foods to the diet in case where contamination is not considered a problem. A model proposed by Beak (1985) postulates that hunters and gatherers would have a trace-element pattern derived from eating organisms placed higher on the trophic pyramid as compared to the diet of secondary agriculturists. This difference is subsistence's pattern would be reflected in small absolute abundance for strontium with a narrow range of strontium values, whereas zinc concentration in human bone would be greater with a greater range of zinc values. The zinc concentrations in bone from the Antelope Creek sites are within the range previously observed in modern animals (Morgan and Schoeninger, 1989).

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