

An analysis of the content of macro- and microelements in the teeth of an Early Neolithic population from Nemrik (Iraq)

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Introduction

For the past thirty years analyses of the macro- and microelements contained in the bone material have become a very important research tool of physical anthropology. They offer a possibility of studying the diet (Sillen & Kavanagh 1982, Klepinger 1984, Byrne & Parris 1987, Perez-Perez & Lalueza 1992, Wolfspenger 1992, Burton & Wright 1995, Ezzo et al. 1995, Głab et al. 2000, Schutkowski & Herrmann 1999, Głab & Szostek 1995), diseases (Gleń-Haduch et al. 1997), physiology, as well as the social status of individuals of modern and historical populations (Schutkowski 1994, Szostek 1992).

Studies into the chemical composition of bones, in particular teeth which are the most stable part of the skeleton, have generated anthropologists' mounting interest. They permit, among others, diet reconstruction and evaluation of the social, economic and biological status of historical populations. It is also of interest to investigate the relationship between specific pathological changes such as enamel hypoplasia, platybasia, *cribra orbitalia*, *hyperostosis frontalis interna* and the deficiencies or surpluses of certain elements (Gleń-Haduch et al. 1997).

The elements whose analysis gives a wealth of information about the biological status of the population under study are strontium, zinc, calcium, copper, iron and barium (Elias 1980, Elias et al. 1982, Burton & Price 1990, Schutkowski 1994, Szostek et al. 2003). The particularly sensitive indicators are strontium–calcium, strontium–zinc and zinc–calcium ratios: they show the relative amount of the consumed plants in relation to products of animal origin.

For a long time it has been known that the absorption and accumulation of strontium are in inverse proportion to an organism's position in the trophic pyramid. Plant organisms take up and accumulate large quantities of strontium

directly from the environment, while mammals accumulate this element secondarily, by consuming plants or other animals (Katzenberg 1992, Klepinger 1993, Radosevich 1993, Burton & Wright 1995).

The dental material used in the present study came from Pre-Ceramic Neolithic and Proto-Neolithic graves. At that time, human populations inhabiting the Near East and Anatolia were undergoing rapid changes in the structure and quality of economy, known as a Neolithic revolution. The intensification of agriculture caused sudden alterations in the quality of diet which has ever since been enriched with larger quantities of edible cereals, vegetables, milk, eggs, etc., i.e. a menu related to plant cultivation and animal husbandry.

The present study is an attempt at determining quantitative changes in the levels of trace elements accumulated in teeth which are regarded as a good indicator of qualitative changes in the modes of nutrition. A research hypothesis assumes differentiation between the levels of trace elements in Early Neolithic human populations inhabiting the area of Nemrik in Iraq for a period of c. 2000 years at the turn of the Proto-Neolithic period.

Material and methods

The study was carried out on 50 permanent and 1 deciduous teeth, derived from dead individuals in the age range from *infans I* to *maturus*, with considerable prevalence of mature individuals. Human remains were explored on a Proto-Neolithic site at Nemrik (Iraq) and were dated at c. 10000–9000 BP by radiocarbon methods. The dental material under analysis exhibited signs of fossilization upon external examination.

Prior to analyses, each tooth was carefully washed in an ultrasonic washer, being wholly immersed in water obtained from the Milipore Water Purification System. Then the teeth under study were dried at a temperature of 60°C, weighed with accuracy to 0.001 g, and subjected to wet demineralization in the 4:1 mixture of the spectrally pure nitric acid (70% Suprapur, Merck) and perchloric acid (65% Suprapur, Merck). After demineralization, samples were allocated quantitatively to calibrated flasks and were diluted with spectrally pure water.

In the thus prepared samples using an atomic absorption spectrophotometric method (AAS), levels of the following elements were determined: Ca, Ba, Mg, Sr, Zn, Cu, Fe, Pb, and Cd.

A statistical evaluation was carried out by means of the analysis of variance (ANOVA); the Bonferoni test was used as a verifying procedure at a significance level of 0.05. All the calculations were made using the statistical package Statgraf 5.0.

Results

Dental material was derived from the Proto-Neolithic and Neolithic graves explored within multi-generation huts. For interpretation purposes, six huts or grave clusters with the highest number of individuals were selected. The total number of individuals coming from the huts under study was 45.

The iron content in one of the individuals coming from the hut labelled 'nn' by the authors was 245.2 $\mu\text{g/g}$. That result was excluded from further statistical analyses. The extremely high level of that element is difficult to explain, since iron objects were then unknown, hence its elevated level as a consequence of a diagenesis process seems most unlikely. Maybe, the individual in question had accumulated during life such an enormous quantity of that element which may have been delivered to the organism with food or water; however, precise verification of this hypothesis cannot be offered at present. The mean content and detailed characteristics of the elements under analysis are shown in **Table 1**.

The vestigial level of cadmium and a very low lead content in the teeth examined are noteworthy. These values are generally lower by an order of magnitude than those reported today. This is due to the fact that these toxic microelements were not present in prehistoric foods or in the environment of human populations of that time, hence the degree of exposure to them can practically be discarded.

In the course of an analysis of the results obtained, statistically significant differences in the content of Mg, Ba, Sr, Fe, Cd and Cu, as well as in the Sr/Zn and Sr/Ca ratios between the huts or grave clusters examined were found. Mean values of all the elements' content and the ratios estimated for particular huts are shown in **Figures 1–8**. No statistically significant differences in the Ca, Zn, Pb and Zn/Ca content were observed within different huts and grave clusters. Cadmium and lead concentrations are vestigial; moreover, in the case of the former element the obtained values are at the point of measuring error.

Statistically significant differences in the zinc content and the Zn/Ca ratio between the selected age groups were found. These differences are shown in **Figures 9 and 10**.

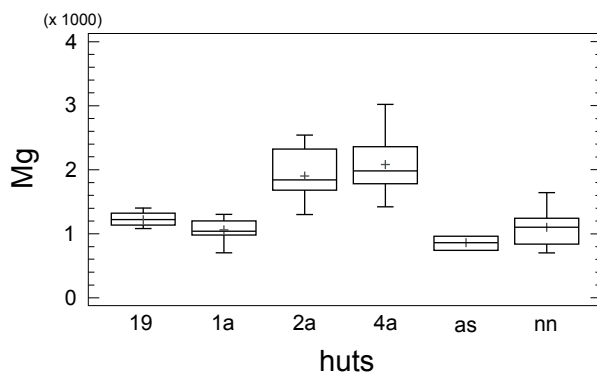


Fig. 1. Mean concentrations of Mg (ppm) in different huts ($p < 0.05$).

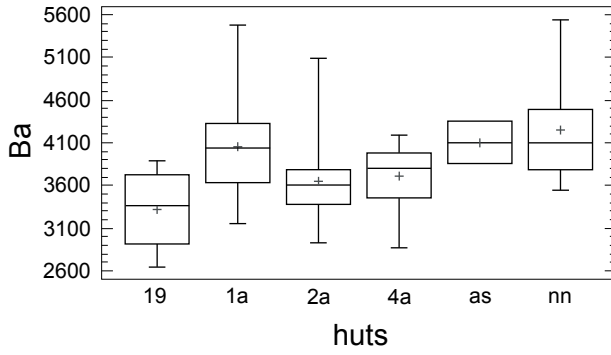


Fig. 2. Mean concentrations of Ba (ppm) in different huts (p<0.05).

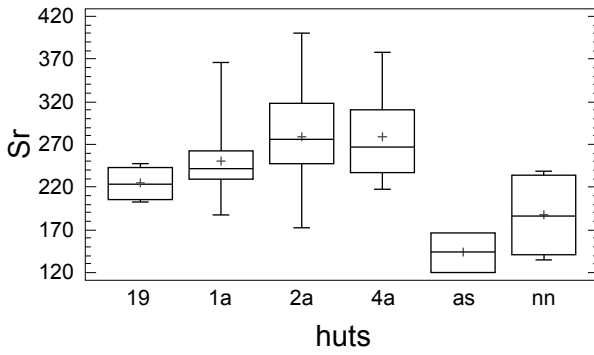


Fig. 3. Mean concentrations of Sr (ppm) in different huts (p<0.05).

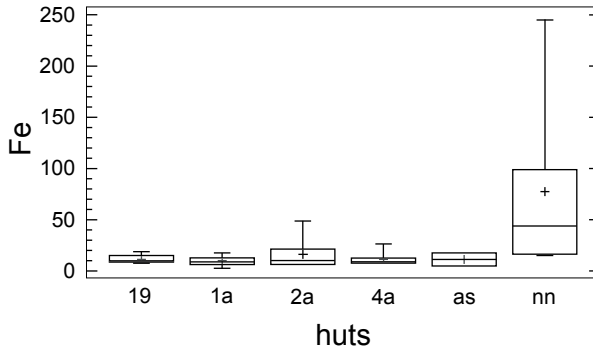


Fig. 4. Mean concentrations of Fe (ppm) in different huts (p<0.05).

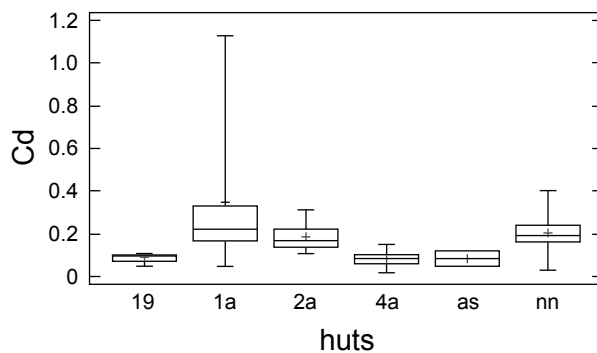


Fig. 5. Mean concentrations of Cd (ppm) in different huts ($p < 0.05$).

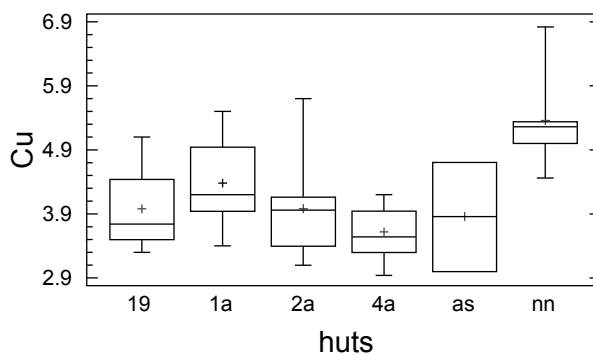


Fig. 6. Mean concentrations of Cu (ppm) in different huts ($p < 0.05$).

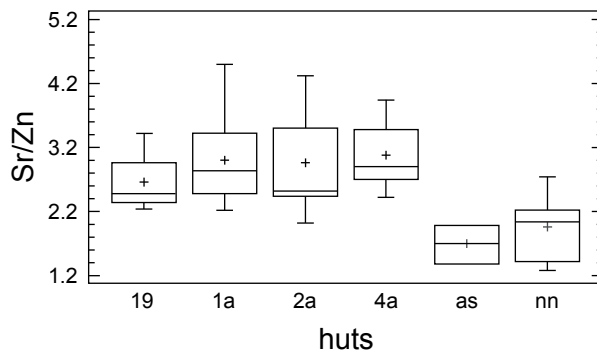


Fig. 7. Ratio of Sr/Zn in different huts ($p < 0.05$).

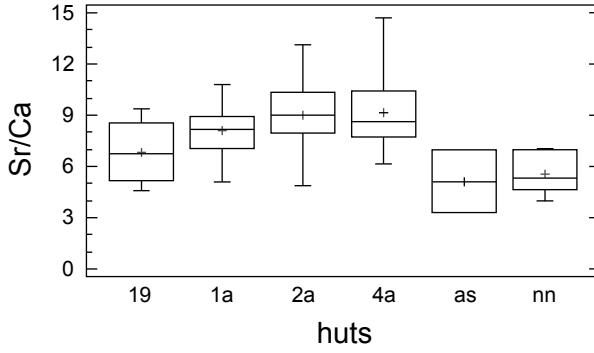


Fig. 8. Ratio of Sr/Ca in different huts (p<0.05).

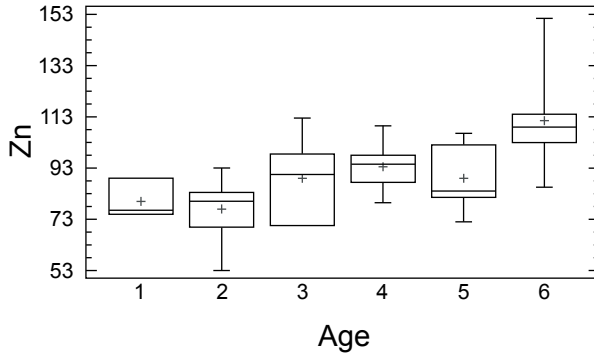


Fig. 9. Mean concentrations of Zn (ppm) in different age groups (p<0.05).

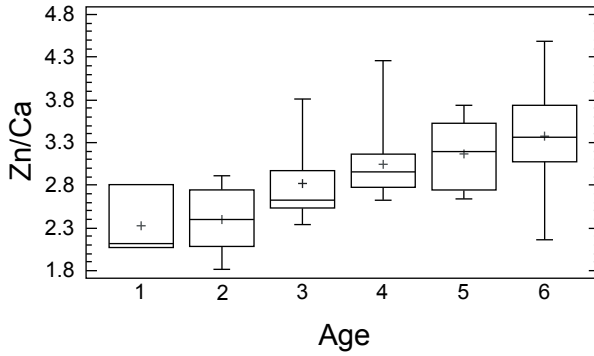


Fig. 10. Ratio of Zn/Ca in different age groups (p<0.05).

Discussion

The values of the Sr, Zn and Ca content, as well as of Sr/Ca, Zn/Ca and Sr/Zn ratios approximately show a relative share of plants and products of animal origin in the diet. The lowest values of both Sr and Sr/Ca and Sr/Zn ratios in the teeth of individuals, most probably coming from the oldest huts labelled 'as' (Assyrian) and 'nn', testify that their diet was poor in food of plant origin and diverged statistically from the remainder of the groups under study. However, in comparison with modern and medieval populations (Szostek et al. 1998), the mean value of the Sr/Zn ratio in the material examined is statistically higher, which may suggest that the share of plant products in the diet of Proto-Neolithic groups was actually greater than in the territory of Southern Poland in the Middle Ages and in the present-day population.

It should be stressed that the dental material under analysis was extremely homogeneous in respect of the content of all the elements except iron and cadmium (**Table 1**). Low variation coefficients indicate that despite the existing statistically significant differences between huts, diet and the degree of exposure to toxic trace elements such as Cd and Pb were stable throughout the whole period of settlement of that region by successive human populations.

Table 1. Concentrations of analyzed elements and ratios from proto-Neolithic site Nemrik.

| | Ca % | Mg µg/g | Ba µg/g | Sr µg/g | Fe µg/g | Zn µg/g | Cd µg/g | Pb µg/g | Cu µg/g | Sr/ Zn | Sr/ Ca | Zn/ Ca |
|-----------|---------|------------|------------|------------|------------|------------|------------|------------|------------|-----------|-----------|-----------|
| N | 51 | 51 | 51 | 51 | 50 | 51 | 51 | 51 | 51 | 51 | 51 | 51 |
| \bar{X} | 31.83 | 1451 | 3838 | 251.7 | 15.5 | 92.1 | 0.18 | 2.08 | 4.29 | 2.77 | 7.97 | 2.92 |
| SD | 3.94 | 591 | 565 | 65.4 | 16.7 | 16.6 | 0.20 | 1.27 | 0.92 | 0.74 | 2.37 | 0.56 |
| V_s | 12.4 | 40.7 | 14.7 | 26.0 | 104.5 | 18.0 | 112.3 | 61.2 | 21.6 | 26.6 | 29.7 | 19.3 |

The copper content in the teeth examined is almost identical with modern standards (Ostrowski 1988, Kabata-Pendias & Pendias 1999). Therefore it may be assumed that the homeostatically regulated concentration of this element neither significantly changes nor is prone to environmental and diagenetic influences, so its ecosensitivity can be considered to be negligible.

In the material under study, very high barium levels were observed. The information about the content of this element in bones and teeth is very sparse in the international literature. Some authors suggest that it is a better than strontium indicator of the quantity of the consumed plants. The results of our studies of this unique archeological material are exceptionally high (by ten orders of magnitude higher than the literature data) (Elias 1980, Elias et al. 1982, Schutkowski & Herrman 1999). The authors of the present report suggest that the higher barium content may be due to its intensive accumulation throughout an individual's life. It is typical of the soil of tropical and subtropical zones to contain a mineral called hollandide, barium derived from that mineral is easily accessible to plants in the form of $Ba_2Mn_8O_{10}$ (Kabata-Pendias & Pendias 1999).

On the other hand, the barium concentration and the Ba/Sr ratio values are the lowest in the case of human populations who subsist mainly on a marine

diet, while the highest values are characteristic of a typically terrestrial diet (Larsen 1997). At the same time, a decrease in barium levels can be observed for higher positions in the trophic pyramid; hence the highest concentrations of this element are characteristic of plants, lower of herbivorous animals, and the lowest of predators. Therefore the high barium concentrations and the Ba/Sr ratio values reported in the present study may testify to a typically terrestrial diet of the Proto-Neolithic population under analysis, which in view of the relatively high values of the Sr/Zn and Sr/Ca ratios indicates the prevalence of the consumption of products of plant origin.

The probability that barium has been secondarily (diagenetically) transferred to an individual's tissues after his death is slight, since its levels in soils do not exceed 1000 $\mu\text{g/g}$ (Kabata-Pendias & Pendias 1999); therefore to obtain a mean value of its accumulation in teeth (ca. 3838 $\mu\text{g/g}$), the transport of this element would have to be of an active character during life. The hypothesis proposed by us may testify that barium does not undergo an intensive process of diagenesis and can be successfully used as a diagnostic element in paleodiet reconstruction.

Being indicative of the relative amount of the consumed protein of animal origin, the Zn/Ca ratio does not differentiate individuals buried in separate huts or grave clusters. It is significantly lower than its mean values for modern human populations, or for a medieval population of the townspeople of Kraków (Figures 11 and 12). On the other hand, its value does not differ from the Zn/Ca ratio for a medieval group of monks from the Cistercian abbey at Wąchock, whose diet was exceptionally poor in protein of animal origin (Szostek et al. 1998). The relationship between Zn and Ca levels indicates that the proto-Neolithic groups under study consumed small quantities of meat. Their diet was enriched with a large amount of products of plant origin. The age differentiation observed in zinc levels and the Zn/Ca ratio clearly indicates a tendency towards a growing share of protein of animal origin in older individuals, i.e. those who probably achieved a higher position in the hierarchy of early proto-Neolithic societies and whose access to qualitatively better food was undoubtedly easier.

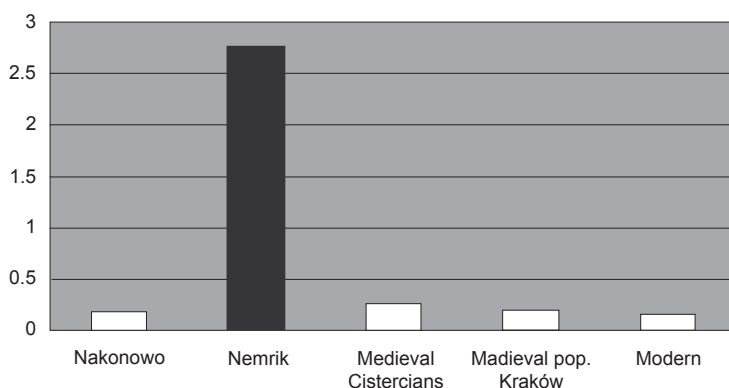


Fig. 11. Sr/Zn ratio in the course of history.

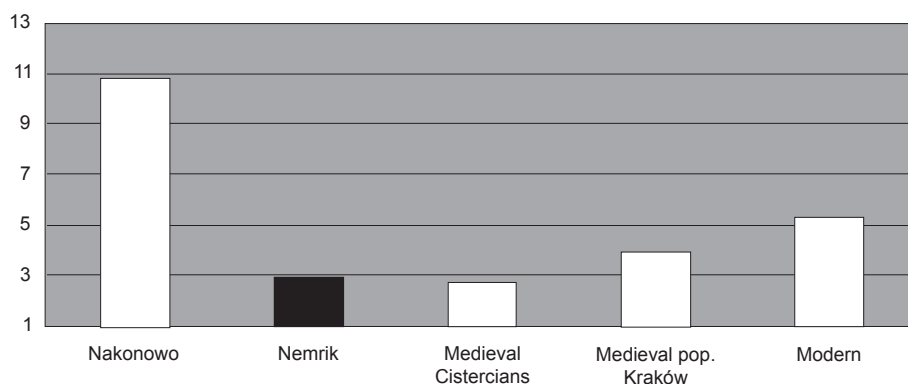


Fig. 12. Zn/Ca ratio in the course of history.

Conclusions

1. The level of the accumulated toxic trace elements (lead and cadmium) in the teeth of individuals of early Neolithic human populations from Nemrik was vestigial.
2. Statistically significant differences in the levels of Mg, Ba, Sr, Fe, Cd, Cu and in the Sr/Zn and Sr/Ca ratios were found between the huts or grave clusters under study.
3. The diet of individuals inhabiting the Nemrik area was exceptionally rich in products of plant origin. The protein of animal origin probably had a very modest share in that 'menu'.
4. The highest values of zinc content and the Zn/Ca ratio were observed in the oldest individuals, which indicates that the access to qualitatively better food (greater amounts of meat in the diet) may have been related to the social position occupied by a given individual in a group.

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