Comment on Martínez-García et al "Heavy metals in human bones in different historical epochs"

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Abstract
Martínez-García et al. (Sci. Tot Env. *348:*51-72) have examined heavy metal exposure of humans in the Cartagena region using analysis of archaeological bones. An analysis of the lead and iron levels they report shows that they are physiologically implausible and must therefore result from diagenesis. This, and analogy with the known diagenetic origin of certain other elements, suggests that the other metal analyses they report are also unlikely to be *in vivo* concentrations. Lifetime heavy metal exposure cannot be deduced from diagenetically altered concentrations.

Keywords: Human bone; Heavy metals; Historical periods; diagenesis.

Martínez-García et al. (2005) have recently published in this journal analyses of the lead, copper, zinc, and cadmium content of human bone mineral from the Cartagena region, from which they draw conclusions about changing exposure of humans to these elements since the Neolithic. Unfortunately they neglect to undertake two essential and critical evaluations of any chemical analysis of archaeological bone:

1. Are the results physiologically plausible?
2. Could there be subtle diagenetic changes?

They also report values for teeth, treating them equally with the bone values, even though teeth are composed of two distinct tissues – dentine and enamel – with distinct properties and widely differing elemental concentrations *in vivo*, and in this brief comment I will not consider teeth further.

More than twenty years ago Waldron (Waldron, 1983) demonstrated that physiologically plausible lead concentrations could be obtained from archaeological bones, but that these values were also highly correlated with the concentrations of lead in the burial soils of the individual bones, and therefore post-mortem uptake was likely to be determining the lead concentrations in archaeological bones. Other elements are also known to be highly susceptible to diagenesis. Trickett et al. (Trickett et al., 2003) have demonstrated using isotopes that strontium in bone may be 100% diagenetically derived, even when the concentrations are within physiological limits. Pike & Richards (Pike and Richards, 2002), using theoretical considerations, have reached the conclusion that the observed levels of arsenic in archaeological bone can be diagenetically derived at levels determined solely by the partition coefficients between the soil and groundwater, and groundwater and bone. Similarly uranium concentrations are very low *in vivo*, but often high in archaeological bone due to the high partition between uranium in groundwater and bone (Millard and Hedges, 1995). Given these well established facts, all elemental concentrations measured in archaeological bone must be robustly assessed for diagenesis, on an element-by-element basis, and they should be considered suspect unless other evidence, such as isotopic ratios, or their uniform distribution in the bone plus lack of correlation with soil levels, suggests their reliability.

If one considers the physiological plausibility of the lead and iron values obtained by Martínez-García et al. (2005), it becomes apparent that diagenesis has occurred in some of their samples and may well have done in all of them.

For lead they report concentrations in adult bones up to 1035ppm and for children 269-1139ppm. Corrucini et al. (Corrucini et al., 1987), provide a preliminary equation relating blood lead and tibial lead concentrations in adults, which may be written:

$$\text{blood Pb } [\mu g/dl] = 0.531 \times (\text{dry bone Pb [ppm]} + 0.9) / (0.03 \times \text{years of exposure})$$

However a more definitive version of this equation does not seem to have been published. If we assume adults live to 50 years on average and children to 10 years, we can obtain lifetime mean blood lead levels. On this basis blood lead levels in Cartagenian adults were up to 360 μg/dl, and in children ranged 480-2000 μg/dl. Although these estimates are crude, applying a preliminary equation for adult tibial lead to other bones and to children, they are unlikely to be out by as much as an order of magnitude. The highest blood lead levels estimated here for adults and *all* those for children are extraordinarily far above the 70 μg/dl threshold which warrants emergency medical treatment in cases of acute lead poisoning, let alone the 10 μg/dl threshold which warrants medical monitoring. Above 70 μg/dl people suffer severe neurological symptoms and even death (C.D.C., 1991). Further, these estimates are lifetime averages, which if realistic for *in vivo* concentrations must represent long-term, chronic lead poisoning at a level which it is unlikely that any person could survive for a few months, let alone years. They are therefore physiologically totally implausible and likely to be diagenetic in origin.

Martínez-García et al. (2005) report iron levels ranging 36 ppm to 9600 ppm in adults and 330 ppm to 21000 ppm (i.e. 2.1%!) in children. A "standard adult human" has an Fe/Ca ratio of 0.0042 according to the data in Emsley (Emsley, 1998) and therefore if *all* the iron in the human body resided in bone mineral the iron concentration in bone mineral would be about 1680 ppm. Actually, most of the iron is in the blood and thus the true bone iron concentration will be much less than this. As Martínez-García et al. (2005) note "[i]ron absorption by the

human body is precisely regulated on the basis of existing needs", and therefore iron levels in the body rarely exceed what is necessary. Thus the observed values cannot represent true *in vivo* values of iron in bone mineral in the majority of archaeological cases here and diagenetic effects must be occurring. From the relatively high values, I suspect that the modern samples are also contaminated, this time by blood. Diagenetic addition of iron is entirely consistent with previous studies which have found iron minerals such as pyrites and vivianite in bone pores (e.g. Piepenbrink, 1989) and that iron is distributed on the outer surfaces of bone and on the walls of Haversian canals (Badone and Farquhar, 1982; Millard, 1993).

If the some of the lead and iron levels in the bones studied by Martínez-García et al. (2005) are physiologically implausible and as we have strong evidence from other studies that these elements are subject to diagenetic effects, then diagenetic alteration of these elements' concentrations seems most likely. Given this, one must suspect very strongly the possibility of diagenetic effects for copper, zinc and cadmium in these bones as well. Archaeological bone trace element concentrations are very likely to be altered from *in vivo* values by diagenesis (Millard, 2001; Reiche et al., 2003) and thus must always be handled very critically and with due caution. For the data of Martínez-García et al. (2005) it would appear that using bone element concentrations to make deductions about changing human exposure to heavy metals through the ages was a futile exercise.

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