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Stable hydrogen isotopes of bone collagen in palaeodietary and palaeoenvironmental reconstruction

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Abstract

The stable hydrogen isotope ratios (δD) of bone collagen in archaeological human and animal samples demonstrate a trophic level effect, with increasing δD from herbivores to omnivores to humans, in steps of 10–30‰. In addition the archaeological sites studied (Yarnton, Eton Rowing Lake, Danebury Environs–Suddern Farm, and Windmill Hill in the UK, Balatonszárszó in Hungary, and Huari in Peru) demonstrate geographical variation in δD. The detection of manuring in prehistory by comparison of δ^{15}N to δD values in humans and a local herbivore (cattle) is also considered. This work is the first to measure δD in a large number and range of archaeological samples, with several animal species and humans. It demonstrates unequivocally that δD is different between species in ancient material, increasing from herbivores to omnivores to carnivores.

Keywords: Hydrogen; Stable isotopes; Trophic level; Palaeoclimate; Palaeodiet; Bone; Collagen

1. Introduction

In palaeodietary reconstruction by stable isotope analysis, most often carbon, nitrogen, and occasionally oxygen and sulphur isotope ratios are used. Of these, δ^{15}N values are used for estimation of the 'trophic level'. This term will be taken here to be related to the degree of carnivory of an individual (animal or human) with respect to dietary protein. For example, in the case of a human whose dietary protein is of herbivore flesh exclusively, this individual is one full trophic level above the herbivore. Any degree of omnivory decreases the trophic level to less than one. Similarly, herbivores are one full trophic level above their plant diet. DeNiro and Epstein (1981), Minagawa and Wada (1984) and Sealy et al. (1987) have found that the δ^{15}N increases from diet to consumer in a step-wise manner. This fact can be used to crudely approximate the trophic level of an animal or human. However, reliable knowledge of the diet to consumer's tissue enrichment (hereafter $\Delta^{15}N_{diet-tissue}$) is required since this underpins the assumptions used in this technique of palaeodietary analysis. The $\Delta^{15}N_{diet-tissue}$ varies according to animal, tissue, diet, and protein level, from 2‰ to 5‰ (Ambrose, 2000; DeNiro and Epstein, 1981; Hare et al., 1991; Howland, 2003; Sponheimer et al., 2003; Robbins et al., 2005; Yoshinaga et al., 1996). In theory, if one knows the $\Delta^{15}N_{diet-tissue}$ for humans, one can compare the measured human δ^{15}N and the δ^{15}N of their possible diet items to the $\Delta^{15}N_{diet-tissue}$, to determine the human dietary inputs and their trophic level. However, applying this $\Delta^{15}N_{diet-tissue}$ to palaeodietary reconstruction is problematic. Confounding factors include variability in the diet–tissue enrichment with protein level, dietary items, or between species, and difficulties with determination of the appropriate (herbivore) isotopic baseline. Another problem in nitrogen isotope analysis is that the measured values in tissue can be elevated by factors other than animal protein consumption, such as aridity (Heaton et al., 1986) and the consumption of marine (Richards and Hedges, 1999) and freshwater fish (Dufour et al., 1999; Katzenberg and Weber, 1999). See Hedges and Reynard (2007) for a more complete discussion of δ^{15}N and the trophic level of humans in archaeology.

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Finding another isotopic proxy for the trophic level in archaeological samples is therefore of significant importance. Stable hydrogen isotope ratios (δD) are a promising trophic level indicator that could resolve some of the problems with δ^{15}N. Earlier work has shown that in modern wild animals in Britain δD shows a trophic level effect, increasing from herbivores and omnivores to carnivores (Birchall, 2002; Birchall et al., 2005). This suggests that δD might make a useful trophic level indicator in archaeological contexts. Before this present work, stable hydrogen isotope ratios had not been measured in archaeological material save for limited sample numbers of two species (bison and deer (Leyden et al., 2006; Cormie, 1989, respectively)) and they had not been used to reconstruct ancient diet.

Archaeological samples are of real interest, and the animals measured in the modern study did not include the usual domestic herbivores found at archaeological sites which presumably formed the animal protein part of ancient human diet. The δD of archaeological humans had also not been measured to date. The principal aim of this work is to show that δD does indeed show a useful trophic level effect in archaeological animals and humans at a variety of sites. In addition, δD may not necessarily suffer from the limitations on δ^{15}N measurements discussed above. It therefore seems possible that stable hydrogen isotopes will be a better and less ambiguous trophic level indicator than stable nitrogen isotopes.

As a secondary theme, the environmental information in δD is considered here. The variation in δD in water shows a strong geographical trend due to the underlying changes in δD in precipitation (IAEA/WMO, 2004). This signal should be incorporated into plants and animals, and should therefore be measurable in bone collagen, and more importantly in archaeological samples. This suggests that collagen δD could also be used as an indicator of geographical origins. This point highlights the fact that for trophic level estimation with δD, samples from a local area only should be compared to each other to ensure that the same environmental baseline is used. In this case the possibility of the presence of recent migrants with a different collagen δD should be borne in mind.

2. Methods

2.1. Samples

Bones of domestic herbivores and omnivores, along with humans from a variety of archaeological sites were sampled. The ages range from the Neolithic to the mid-15th century AD. The sites are listed in Table 1 and mapped in Fig. 1. Different locations were chosen to test whether the environmental variability of rainfall δD values is also preserved in ancient samples. Whenever possible we sampled 5–10 individuals from each species, including sheep, cattle, horse, deer, hare, pigs, dogs, and humans.

2.2. Analytical methodology

The analysis of stable hydrogen isotope ratios of organic material is more complex than of other isotopes which are more routinely measured for archaeological applications. Organic material including bone collagen has many oxygen- and nitrogen-bound hydrogen atoms, which are labile and exchange with hydrogen from water in the environment (generally water vapour). This introduces hydrogen atoms that are related to the environmental conditions of the laboratory where the isotope ratio measurements are made, which are not of interest. The δD of ambient water at a particular location can also change over time, introducing further variability in the measured result. The theoretical exchangeable hydrogen fraction is 21% in collagen. Correction equations to account for the contribution of ambient hydrogen to the measured isotope ratios can be used to overcome this limitation. The development of good standards is vital to ensure that the results from different analyses are comparable to each other. There is currently no common inter-laboratory collagen or other organic standard for hydrogen isotopes; VSMOW is the accepted water hydrogen isotope standard.

Two different analytical methods were used for sample preparation: (1) an offline method, in which each collagen sample was transformed to H_2 gas in a closed system by combustion with CuO and reduction by Zn and the resultant gas admitted to the mass spectrometer for isotope ratio measurement (Cormie et al., 1994; Birchall et al., 2005; Wassenaar and Hobson, 2000); (2) an online method, in which each sample was transformed to H_2 gas in a continuous-flow system, and the sample admitted to a mass spectrometer directly connected to the online preparation system (Bowen et al., 2005a; Wassenaar and Hobson, 2003). The two methods are tied together here by the use of the same bone collagen standards developed by Birchall et al. (2005), and all results are reported in permil relative to VSMOW: $\delta D_{VSMOW}(‰) = (R_{sample} - R_{VSMOW})/(R_{VSMOW}) \times 1000$. Further analytical details are in Reynard (2007).

In the offline equilibration method (1), the samples are equilibrated with water of known δD in a closed system. This replaces the exchangeable H with hydrogen atoms of known isotopic ratio. Repeating this process with at least one other equilibration water of different isotopic composition allows calculation of the non-exchangeable δD (δD_n) once the sample has been measured, as outlined below.

In the continuous-flow online method (2), also known as comparative equilibration (Bowen et al., 2005a; Wassenaar and Hobson, 2003), the equilibration of the sample with water occurs in the ambient laboratory atmosphere, and the resulting δD_n is calculated by comparison to a standard (of known δD_n) which was also subjected to the same treatment.

The stable isotope ratios of the hydrogen gas samples from the offline preparation method were measured at the NERC Isotope Geosciences Laboratory, in Keyworth, Nottingham, UK. A dual-inlet isotope ratio mass spectrometer was used. For the primary mass spectrometry standard, laboratory water standards (water from the British Antarctic Survey, BAS-HI and BAS-LO, calibrated against VSMOW and SLAP) were reduced to hydrogen gas over zinc along with the samples, and measured in the same run on the mass spectrometer.

The measurement of δD by online pyrolysis was carried out by IsoAnalytical in Cheshire, UK. For the samples reported