Journal of Archaeological Science: Reports 11 (2017) 12–16

Contents lists available at ScienceDirect

Journal of Archaeological Science: Reports

journal homepage: www.elsevier.com/locate/jasrep

Hydrogen isotopes in Quaternary mammal collagen from Europe

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ARTICLE INFO

Article history:
Received 1 August 2016
Received in revised form 4 November 2016
Accepted 7 November 2016
Available online xxxx

ABSTRACT

Of the most abundant elemental constituents of organic matter, hydrogen has received the least attention due to its exchangeability with ambient water. The development of steam equilibration using two isotopically distinct waters can enable the user to calculate the proportion of exchangeable H and generate a δ^2H value of the non-exchangeable H. Three fossil faunal assemblages from Europe were selected in order to investigate collagen δ^2H with respect to body mass, diet and to compare chronological periods in the Quaternary. δ^{15}N values in each suite of fauna show trophic level enrichment, a trend which was also observed in δ^2H values. In the case of predatory species with lower δ^{15}N values than other carnivore species, the use of hydrogen isotopes could help to infer the consumption of prey with lower δ^{15}N values rather than a significant dietary contribution of plant foods. For example, a cave bear which exhibits low δ^2H values are consistent with low δ^{15}N and therefore point to an herbivorous diet and not omnivory. The combination of δ^2H, with δ^{15}N and δ^{13}C, from archaeological and ecological studies of humans and fauna could help reconstruct prey preference; which is especially important when trying to distinguish the quantity of marine versus freshwater resources in diets. Relative to dietary influences, climate variability seems to be a minor control on δ^2H in the faunal assemblages studied here.

1. Introduction

Stable isotope ratios of biologically important elements such as C, H, N, and O have widespread applications in earth sciences and biology. Of the most abundant elemental constituents of organic matter, hydrogen has received the least attention due to several factors (i.e. exchangeable hydrogen) that have, until recently, complicated the analysis and interpretation of hydrogen isotope data derived from organic materials. Recent advances in analytical techniques (Sauer et al., 2009) for organic hydrogen have facilitated the analysis of hydrogen isotope ratios (δ^2H) from organic matter to be explored.

Hydrogen in organic matter can occupy many different chemical positions, and since it is loosely bound to O and N, the hydrogen can exchange readily with ambient water. For this reason, the ^{2}H/^{1}H ratio of those hydrogen pools provides more information about the recent exposure to water vapour (e.g., laboratory air) than about primary environmental and/or biological conditions. In order to remove these affects the O- and N-bound hydrogen must either be removed or replaced. Chemical removal, nitration of cellulose is labour-intensive and requires a large initial sample. An alternative approach is to control the exchangeable hydrogen by means of exposure to a vapour or vapours of known isotopic composition(s) that has been adapted by various labs for continuous-flow IRMS approaches (Sauer et al., 2009; Meier-Augenstein et al., 2011; Wassenaar et al., 2015). A steam equilibrator enables the simultaneous analysis of 10 samples (in triplicate) of protein (Sauer et al., 2009).

Previous research on hydrogen isotope ratios in protein (Cormie et al., 1994) has revealed a strong climatic control in parallel to strong ^{2}H/^{1}H gradients in precipitation. Because many migratory bird (and some butterfly) species cross climatic gradients, ^{2}H/^{1}H ratios of non-exchangeable hydrogen of feather and insect keratin has been used to document migration patterns and regional hydrological/climatic conditions (Hobson et al., 1999; Gröcke et al., 2006, 2010; van Hardenbroek et al., 2012). Hydrogen isotope ratios in collagen from large herbivores, for example North American bison, have shown to vary through the Holocene and track changes in moisture availability and temperature (Leyden et al., 2006).

In addition to climatic influences, trophic level may also have an influence due to metabolic effects and inefficiencies in nutrient transfer up food chains; higher trophic level consumers exhibit higher δ^{15}N

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http://dx.doi.org/10.1016/j.jasrep.2016.11.020
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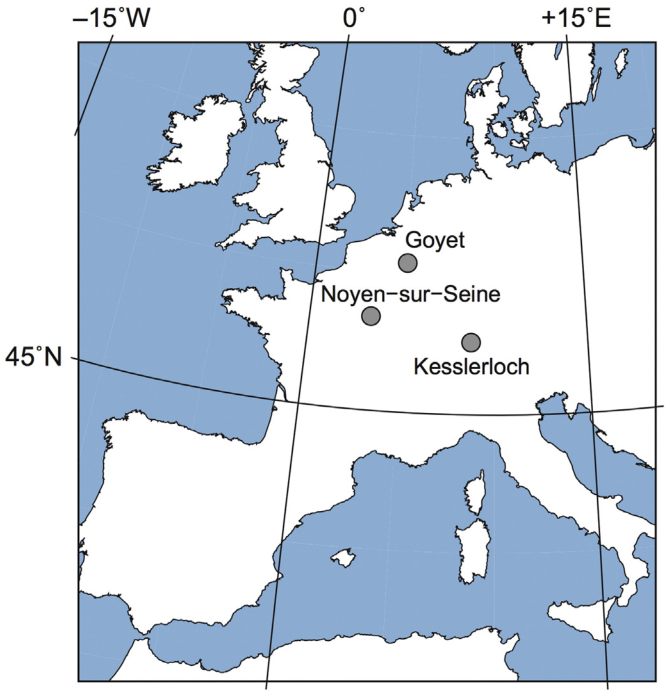

Fig. 1. Map of sample locations investigated in this study.

values than their prey (e.g., Bocherens and Drucker, 2003). A study of several European archaeological sites showed a progressive enrichment in bone collagen δ^2H from herbivores to omnivores (pigs) to carnivores (humans), with an enrichment factor of 20‰ to 50‰ (Birchall et al., 2005; Reynard and Hedges, 2008). Additionally, 12 mammalian species from a limited geographic area in Indiana, suggests that body size and respiration rates may also influence bone collagen δ^2H (Topalov et al., 2013).

In this study, we have selected three faunal assemblages including herbivores and carnivores of different sizes that lived under different climatic conditions from Europe (Fig. 1). The aim of this study was to decipher the relative role of climate, trophic level and physiology on δ^2H in archaeological large mammals to determine its application for studying ancient ecosystems.

2. Materials and methods

Three different fossil faunal assemblages from Europe, that include herbivorous and carnivorous taxa, have been sampled: Goyet Cave (Belgium; 40–27 kyrs BP), Kesslerloch (Switzerland; 14–12 kyrs BP) and Noyen-sur-Seine (France; ~8 kyrs BP) (Fig. 1). Information on each of these specific sites is provided in the Supplementary information.

Hydrogen isotope measurements were made by exposing two sets of the same collagen sample to a vapour under controlled temperature at 115 °C (Sauer et al., 2009): snow that was collected in Durham in 2010 (δ^2H = −60‰) and a ^{2}H-spiked water made at Durham (δ^2H = +1150‰). The equilibrated samples were analysed using a Thermo TC/EA coupled with a Delta V Advantage IRMS at Durham University. The δ^2H values are expressed against Vienna Standard Mean Ocean Water (VSMOW) by calibrated international standards: IAEA-CH-7 (polyethylene foil), IAEA-CH-3 (cellulose) and nC_{36} (Arndt Schimmelmann, Indiana), including an internal standard, JTNP-1 (deer collagen). Standard deviation of the standards and samples were typically <2‰ (2 SD). For more details regarding fractionation factor and calculation of exchangeable hydrogen we refer the reader to Sauer et al. (2009) whose methods were followed stringently in this study.

3. Results and discussion

The δ^2H values of terrestrial mammals exhibited a wide range of values in each site; between −40.4‰ to −99.9‰ in Goyet Cave, −38.9‰ to −111.2‰ in Kesslerloch, and −37.2‰ to −78.2‰ in Noyen-sur-Seine (see Supplementary information, Table S1, S2, S3). The single freshwater predator (otter) analysed in this study from Kesslerloch had the highest δ^2H value of +1.3‰. In all sites there was no obvious relationship between δ^2H and body size within a trophic group.

From Goyet Cave, most carnivores and herbivores were well separated, with carnivores having less negative δ^2H values than herbivores, except for the three horses (Figs. 2, 3). Wolves, which had lower δ^{15}N than other carnivores (e.g., lions and hyenas) at this site, nonetheless exhibited δ^2H as high as those carnivores. Although the mammoth, an herbivorous species, exhibited high δ^{15}N values compared to other herbivores but similar to carnivores, their δ^2H values were within the range of other herbivores at Goyet Cave, albeit in a higher part of the range (Figs. 2, 3). The adult cave bears had δ^{15}N and δ^2H values similar to those of other herbivores. One particular case was the newborn cave bear, with a very high δ^{15}N value and a very low δ^2H value.

From Kesslerloch, most terrestrial carnivores exhibited higher δ^2H values than herbivores (Figs. 2, 3). However, wolves exhibited δ^2H that overlapped those herbivores with the highest δ^2H even though their δ^{15}N are clearly suggesting carnivory. Fox and lynx, with slightly lower δ^{15}N than other carnivores had, nonetheless, high δ^2H values: a result that precludes omnivory for the fox. The differences in δ^{15}N and δ^2H between carnivore species are most likely linked to differences in

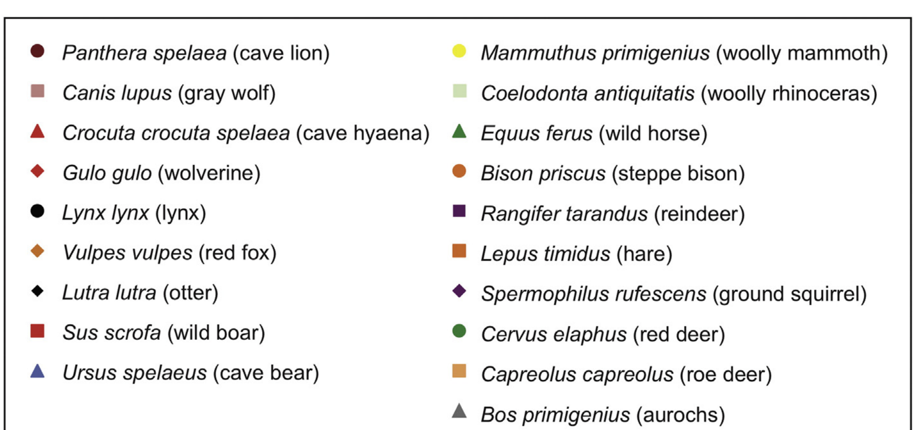

Fig. 2. Key to mammal species plotted in Fig. 3.