



ELSEVIER

Palaeogeography, Palaeoclimatology, Palaeoecology 193 (2003) 261–267

PALAEO

www.elsevier.com/locate/palaeo

Variations in bone collagen $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of fauna from Northwest Europe over the last 40 000 years

M.P. Richards^{a,*}, R.E.M. Hedges^b

^a Department of Archaeological Sciences, University of Bradford, Bradford, West Yorkshire BD7 1DP, UK

^b Radiocarbon Accelerator Unit, Research Laboratory for Archaeology and the History of Art, 6 Keble Road, Oxford, OX1 3QJ, UK

Received 31 October 2001; accepted 31 December 2002

Abstract

We report here a signal in the temporal variation of stable isotopes in protein from surviving animal bone in Northwest Europe over the past glacial cycle. There is a change in the average $\delta^{13}\text{C}$ values of fauna in the Holocene, and there is also a significant reduction in $\delta^{15}\text{N}$ values of herbivore bone collagen towards the end of the last glaciation, with a subsequent recovery soon after the start of the Holocene. This change is observed for several species and is restricted to those regions most affected by the glacial advance. Comparison with ice core data shows that there is a strong correlation between the average $\delta^{13}\text{C}$ values of three herbivore species and ice core CO_2 concentration. The data presented here show how readily available faunal bone collagen $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ measurements provide a record of past climate and environmental change on a regional to continental scale.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: palaeoclimate; stable isotopes; $\delta^{13}\text{C}$; $\delta^{15}\text{N}$; palaeoenvironments; archaeology; Europe

1. Introduction

Human and faunal bone collagen $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values are increasingly used as palaeodietary indicators (e.g. Bocherens et al., 2001; Richards et al., 2001; Richards et al., 2000; Iacumin et al., 1996). Additionally, mammal $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values can also indirectly indicate past climatic changes, as the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values in the envi-

ronment, particularly in plants, fluctuate depending on local environmental conditions such as temperature and aridity (Leavitt and Danzer, 1992; Marino and McElroy, 1991; Stuiver and Braziunas, 1987). However, there have been only small scale studies of the effects of climate variation through time on the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of well-dated sequences of mammal bone collagen (e.g. Iacumin et al., 1997; Iacumin et al., 2000). In the course of radiocarbon dating of large numbers of faunal bone collagen samples from archaeological sites in Europe, following standard methods outlined elsewhere (Bronk Ramsey et al., 1999), we have built up a database of associated $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ measurements. We have observed that both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values vary with

* Corresponding author.

E-mail address: m.p.richards@bradford.ac.uk (M.P. Richards).

time, especially during the period of the last glaciation. We report here the main features of this observed variation.

2. The dataset

The complete database of faunal bone collagen $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values contains measurements on approximately 1800 samples. However, these comprise a wide range of species, including many unidentified bones (usually from large mammals) and cover a geographical spread from Ireland to the Ukraine, and from Northern Germany to Southern Spain. Here we have selected a sub-set of this database focusing on a smaller region and only a few species to explore variations in collagen $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values that may be attributable to changes in climate. This sub-set consists of data for horse, cattle and deer from the more northerly and westerly regions of Europe. All isotope measurements presented here were made on well-preserved collagen, as determined by collagen yield and C:N ratios (DeNiro, 1985).

Faunal bone collagen $\delta^{13}\text{C}$ values from our database are plotted in Fig. 1 (individual data) and Fig. 2 (1000-yr average values) for horses, bison/bos (bison before the Late Glacial Maximum (LGM), and bos after the LGM) and red deer, as only these animals provide data throughout the whole time range with adequate geographical spread and sufficient sampling density. The data are from the UK, Northern France, Belgium and Germany. Some regional differences between the same species in different areas may be expected – an overall trend in the $\delta^{13}\text{C}$ values across Europe, correlated with the annual July temperature, averaged over the Holocene has previously been reported (Van Klinken et al., 1994) – but these plots show that the differences are small and do not obscure the main trends in time. They also show that different time periods are not equally well represented in the different regions, but that there is no strong indication that the regional data of Northwest Europe cannot be combined.

Faunal bone collagen $\delta^{15}\text{N}$ values from the same samples presented in Figs. 1 and 2 are plot-

ted in Fig. 3 (individual data points) and Fig. 4 (1000-yr average values). Unavoidably, some time periods are unevenly represented, primarily due to climatic changes through this period (e.g. glacial cover of much the United Kingdom at the LGM).

3. Summary of the results

All three selected species show a constant collagen $\delta^{13}\text{C}$ signal of between -19.5 and -20.5 ‰ from ca. 40 to 18 ka BP, and there is a slight trend to isotopically lighter values by about 0.6‰ over this period. Inadequate data prevent continuity through the LGM, but after 14 ka BP there is indication of depletion in ^{13}C , which becomes very apparent by 10 ka BP, with a levelling out at about 1.6‰ lighter in ^{13}C by 8.5–9 ka BP.

The $\delta^{15}\text{N}$ values appear to fluctuate more than the $\delta^{13}\text{C}$ values in the pre-glacial period, and they also exhibit a change from approximately 5–7‰ between 40 and 27 ka to values lower by about 2‰ at the LGM. Changes after the LGM are better documented, and it is clear that for horse and cattle at and before 12.5 ka BP the $\delta^{15}\text{N}$ values are much less enriched than in the recent Holocene, by about 3‰. The red deer data are especially variable, and such a trend is not recognisable. From 12.5 to 8.5 ka there is a substantial ‘rebound’ to values similar to those of the pre-glacial period between 27 and 40 ka BP, although it is not very clear how constant the values remain during the later phase of the Holocene. There is not sufficient resolution in the data to decide whether the cattle and horse $\delta^{15}\text{N}$ changes are in phase with each other and whether these changes take place at the same time throughout Northwest Europe. The data do not rule out a quite rapid change (< 2 ka), although a slower change seems more likely. Overall, the $\delta^{15}\text{N}$ values appear to be depleted between about 10 and 25 ka BP, while the $\delta^{13}\text{C}$ values are depleted only well after the LGM.

The data we have collected on other species tend to support this trend, but as few species were present in these areas over the entire last 25000 years, these other data are much less nu-

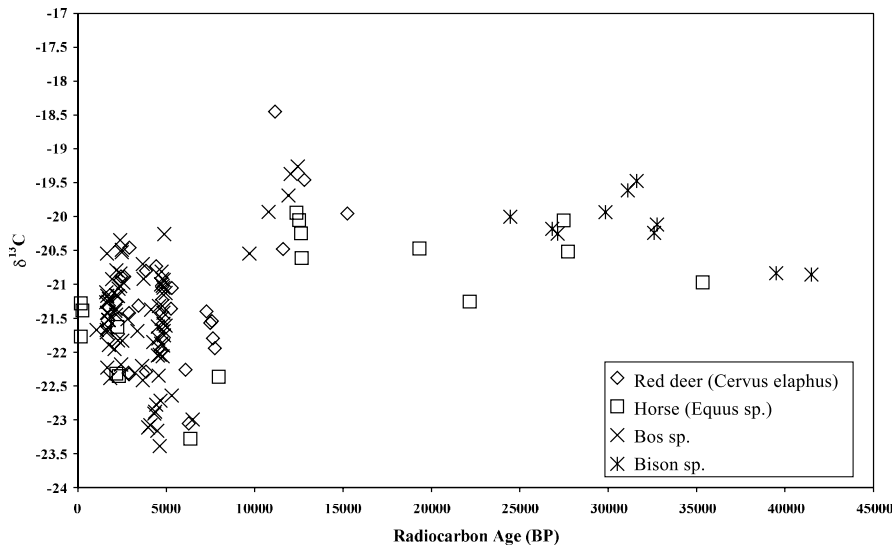


Fig. 1. $\delta^{13}\text{C}$ values of bone collagen of various faunal species from Northwest Europe (Britain, Germany, Northern France, Belgium and The Netherlands) plotted against the uncalibrated radiocarbon age (BP) of the collagen. The $\delta^{13}\text{C}$ values are measured relative to the Vienna Pee Dee Belemnite standard, and the errors (1σ) on the $\delta^{13}\text{C}$ measurements are 0.3‰ .

merous or geographically more dispersed and cannot be used to refine these observations.

There are few comparable published data. A recent publication (Iacumin et al., 2000) includes pre-LGM $\delta^{15}\text{N}$ values on mammoths in Eurasia, with indications of a temporal trend in agreement with our mammoth data which is in broad agree-

ment with the overall trend reported here. Drucker et al. (2000) also observed changes in the $\delta^{15}\text{N}$ values through time in a small sample of reindeer and horse from a few sites in Southwestern France dating to approximately 30 000 to 14 000 BP. The samples were not directly dated so it was not possible to directly compare the data with

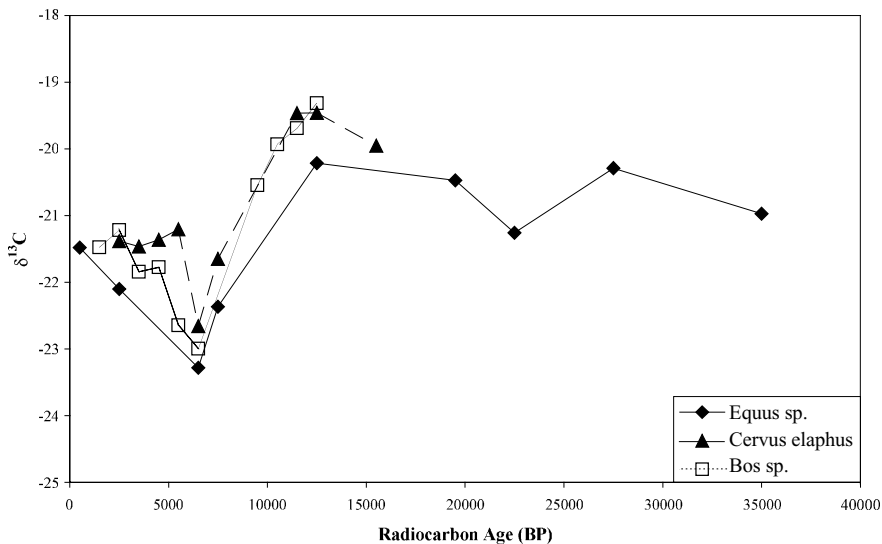


Fig. 2. Mean collagen $\delta^{13}\text{C}$ values at 1-ka-BP time intervals to show general trends, using the data plotted in Fig. 1.

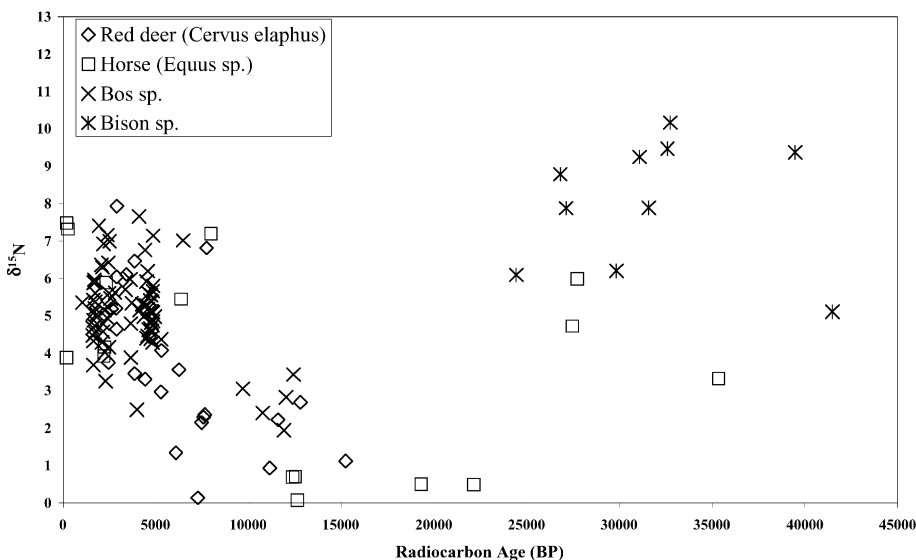


Fig. 3. Plot of bone collagen $\delta^{15}\text{N}$ values and associated radiocarbon ages of various faunal samples from Northwest Europe. $\delta^{15}\text{N}$ values are measured relative to the AIR standard. Errors (1σ) on the $\delta^{15}\text{N}$ measurements are 0.4‰ .

those presented here but there is an observable trend of slightly lower horse $\delta^{15}\text{N}$ values at the LGM. We note that no corresponding change has been observed in bone collagen $\delta^{15}\text{N}$ through similar time periods and through the LGM in Southern Italy (Iacumin et al., 1997; Iacumin et al.,

1999), and it is not observed in our database for other Mediterranean countries (however, the region is poorly represented). We conclude that the observed signals presented here are likely to be observed in regions most affected by glaciation.

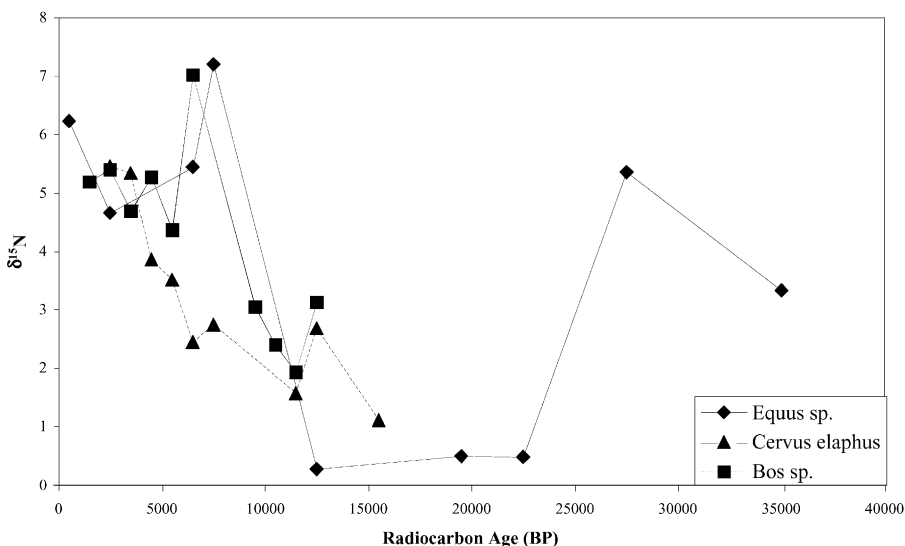


Fig. 4. Mean collagen $\delta^{15}\text{N}$ values at 1-ka-BP time intervals to show general trends, using the data plotted in Fig. 3.

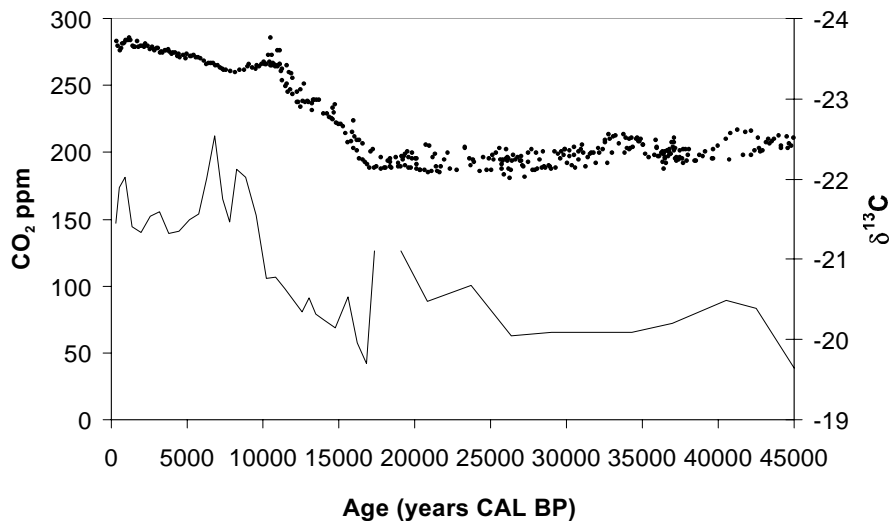


Fig. 5. The average $\delta^{13}\text{C}$ value of all three herbivore faunal species, plotted against combined CO_2 concentrations taken from Vostok (Barnola et al., 1987; Jouzel et al., 1987; Petit et al., 1990) and Antarctic (Indermuhle et al., 1999; Monnin et al., 2001) ice cores. Bone collagen radiocarbon dates were calibrated using Stuiver et al. (1998), Kitagawa and van der Plicht (2000), Voelker et al. (2000) and Beck et al. (2001).

4. Discussion

Several compilations of data from plant material (mainly tree wood cellulose) show variations in $\delta^{13}\text{C}$ over time (Leavitt and Danzer, 1992; Krishnamurthy and Epstein, 1990; Beerling, 1996; Prokopenko et al., 1999; Hatte et al., 2001) with a similar pattern to our observations on bone collagen $\delta^{13}\text{C}$. In particular, there is an approximately 2‰ depletion which appears to track the change in atmospheric CO_2 concentration at the end of the last glaciation (see especially Krishnamurthy and Epstein, 1990). This is generally explained as a change in isotopic fractionation during photosynthesis in response to changed stomatal conductance, directly due to the altered atmospheric composition and indirectly through changes in temperature, humidity and available soil water (Stuiver and Braziunas, 1987; Feng and Epstein, 1995; Hatte et al., 2001). We believe that our faunal collagen $\delta^{13}\text{C}$ values are showing the same response. A related argument has been applied to correlations between climate and both floral (charcoal) and faunal (bone collagen) in which $\delta^{13}\text{C}$ values for Holocene material from Europe as a whole is integrated over time (Van Klinken et al., 1994). In Fig. 5 we have plotted our combined herbivore bone collagen data from

our study area compared with the published CO_2 concentrations from ice-cores for the same ages. It illustrates that there is simultaneous change in both datasets.

In the case of nitrogen, the $\delta^{15}\text{N}$ values of animal bone collagen vary with trophic level, and are thought to represent dietary $\delta^{15}\text{N}$ enriched by approximately 3‰ (DeNiro and Epstein, 1981; Schoeninger and DeNiro, 1984). Herbivore bone collagen nitrogen ultimately derives from atmospheric nitrogen, but more immediately enters the animal as plant protein, which in turn can be traced to both mineralised and organic nitrogen sources in the soil. Our plots indicate a comparatively consistent set of $\delta^{15}\text{N}$ values during the later Holocene. However, quite large effects attributable to environmental influences have been recognised in some (mainly non-European) situations, for example, aridity and water stress in fauna (Heaton et al., 1986), and of temperature (and water availability) on vegetation (Handley et al., 1999).

The observed $\delta^{15}\text{N}$ depletion signal reported here could arise from a number of different, though interrelated, causes:

(1) Soil organic nitrogen isotopic composition may change, especially as, during cold periods, the loss of isotopically light volatile compo-

nents (such as ammonia) is liable to be suppressed.

(2) Freshly developed soils, with nitrogen predominantly derived through atmospheric fixation, are also likely to be relatively depleted in $\delta^{15}\text{N}$, and this will apply especially to soil regeneration following deglaciation. Effects (1) and (2) would be registered in the local flora, and, through their diet, in the herbivores.

(3) Plants adapted to a cold (e.g. tundra) environment (see Nadelhoffer et al., 1996; Schulze et al., 1994, for studies on contemporary plants) often show very depleted $\delta^{15}\text{N}$ values, in part due to the greater competition for available nitrogen.

(4) Even when conditions are not so extreme as considered in (1), (2) and (3), there appears to be a general temperature effect on the $\delta^{15}\text{N}$ composition of plant foliage, which probably arises from the fractionation within, and metabolic losses from, the plant–soil nitrogen system (Handley et al., 1999).

(5) Herbivores may adapt to glacial or periglacial conditions by changing their diets, presumably necessitating the inclusion of plants which are more depleted in $\delta^{15}\text{N}$ – thus transmitting the effects of (3) more effectively.

(6) There may be physiological effects on the herbivores themselves – presumably through living in an environment which is both colder and perhaps less abundant in nitrogen sources, but this is unlikely.

The depletion signal we observe applies to different species with different dietary habits, although capable of a degree of adaptation. This makes effects (5) and (6), and probably (3), seem less likely to be predominant.

Although not as well documented, pre-glacial maximum $\delta^{15}\text{N}$ values seem to be much closer to the Holocene values than would be expected from considerations of temperature alone. There is not the time resolution to know if there is a sampling bias to warmer times, but the evidence does suggest that temperature alone does not account for the observed $\delta^{15}\text{N}$ variation values.

One critical issue is how fast the $\delta^{15}\text{N}$ levels ‘recover’ after the glaciation; our present results are not clear enough to give a definite answer to this, although we think that they tend to indicate

a recovery which is much slower than the temperature rise. Therefore, we think explanations (1) and (2) to be the main factors, although a geographically wider dataset is needed to confirm this.

5. Conclusions

We conclude that the $\delta^{13}\text{C}$ changes we observe are closely following changes in C_3 plant $\delta^{13}\text{C}$ values, which themselves are linked to continent-wide global climatic variation, and are explained by the change in plant physiological isotopic fractionation brought about by rising CO_2 levels. Indeed we observed a strong correlation between ice core CO_2 values and average $\delta^{13}\text{C}$ values of three herbivore species. We also conclude, although tentatively, that the observed decrease in $\delta^{15}\text{N}$ values in Northwest European herbivore collagen during the period 10–20 ka BP is due to climate-driven edaphic effects, which may still be observed today.

Our observations demonstrate the possibility of using faunal collagen $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values as sensitive indicators of climate-driven environmental changes that occurred in the past. They also show that large changes in $\delta^{15}\text{N}$ values in particular can take place comparatively rapidly. This should be considered when making inferences from the $\delta^{15}\text{N}$ values of fauna, especially in the Late Pleistocene, if their age is only approximately known.

References

- Barnola, J.M., Raynaud, D., Korotkevich, Y.S., Lorius, C., 1987. Vostok ice core provides 160,000-year record of atmospheric CO_2 . *Nature* 329, 408–414.
- Beck, J.W., Richards, D.A., Edwards, R.L., Silverman, B.W., Smart, P.L., Donahue, D.J., Herrera-Osterheld, S., Burr, G.S., Calsoyas, L., Jull, A.J.T., Biddulph, D., 2001. Extremely large variations of atmospheric C-14 concentration during the last glacial period. *Science* 292, 2453–2458.
- Berling, D.J., 1996. C-13 discrimination by fossil leaves during the late-glacial climate oscillation 12–10 ka BP: Measurements and physiological controls. *Oecologia* 108, 29–37.
- Bocherens, H., Billiou, D., Mariotti, A., Toussaint, M., Patou-Mathis, M., Bonjean, D., Otte, M., 2001. New isotopic evi-

- dence for dietary habits of Neandertals from Belgium. *J. Hum. Evol.* 40, 497–505.
- Bronk Ramsey, C., Pettitt, P., Hedges, R., Hodgins, G., Owen, D., 1999. Radiocarbon dates from the Oxford AMS system: *Archaeometry Datelist* 29. *Archaeometry* 42, 243–254.
- DeNiro, M.J., 1985. Post-mortem preservation and alteration of in vivo bone collagen isotope ratios in relation to paleodietary reconstruction. *Nature* 317, 806–809.
- DeNiro, M., Epstein, S., 1981. Influence of diet on the distribution of nitrogen isotopes in animals. *Geochim. Cosmochim. Acta* 45, 341–351.
- Drucker, D., Bocherens, H., Mariotti, A., 2000. Contribution de la biogéochimie isotopique à l'étude de la paléobiologie des grands mammifères du Pléistocène supérieur: application aux rennes et aux chevaux magdaléniens et solutréens du sud-ouest de la France. *Mém. Soc. Préh. Fr.* 28, 13–27.
- Feng, X.H., Epstein, S., 1995. Carbon isotopes of trees from arid environments and implications for reconstructing atmospheric CO₂ concentration. *Geochim. Cosmochim. Acta* 59, 2599–2608.
- Handley, L.L., Austin, A.T., Robinson, D., Scrimgeour, C.M., Raven, J.A., Heaton, T.H.E., Schmidt, S., Stewart, G.R., 1999. The N-15 natural abundance (delta N-15) of ecosystem samples reflects measures of water availability. *Aust. J. Plant. Physiol.* 26, 185–199.
- Hatte, C., Antoine, P., Fontugne, M., Lang, A., Rousseau, D.D., Zoller, L., 2001. Delta C-13 of loess organic matter as a potential proxy for paleoprecipitation. *Quat. Res.* 55, 33–38.
- Heaton, T.H.E., Vogel, J.C., von la Chevallerie, G., Collett, G., 1986. Climatic influence on the isotopic composition of bone nitrogen. *Nature* 322, 822–823.
- Iacumin, P., Bocherens, H., Delgado Huertas, A., Mariotti, A., Longinelli, A., 1997. A stable isotope study of fossil mammal remains from the Paglicci cave, Southern Italy. N and C as palaeoenvironmental indicators. *Earth Planet. Sci. Lett.* 148, 349–357.
- Iacumin, P., Bocherens, H., Mariotti, A., Longinelli, A., 1996. An isotopic palaeoenvironmental study of human skeletal remains from the Nile Valley. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 126, 15–30.
- Iacumin, P., Fattori, S., Hedges, R., Abbazzi, L., Longinelli, A., 1999. Stable isotope (O, N, C) intra-specific variations in *B. Primigenius* skeletal remains from a pleistocene cave sequence a proxy for detailed palaeoenvironmental reconstruction. *Quat. Ital. J. Quat. Sci.* 12, 63–68.
- Iacumin, P., Nikolaev, V., Ramigni, M., 2000. C and N stable isotope measurements on Eurasian fossil mammals, 40 000 to 10 000 years BP: Herbivore physiologies and palaeoenvironmental reconstruction. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 163, 33–47.
- Indermuhle, A., Stocker, T.F., Joos, F., Fischer, H., Smith, H.J., Wahlen, M., Deck, B., Mastroianni, D., Tschumi, J., Blunier, T., Meyer, R., Stauffer, B., 1999. Holocene carbon-cycle dynamics based on CO₂ trapped in ice at Taylor Dome, Antarctica. *Nature* 398, 121–126.
- Jouzel, J., Lorius, C., Petit, J.R., Genthon, C., Barkov, N.I., Kotlyakov, V.M., Petrov, V.M., 1987. Vostok ice core: A continuous isotopic temperature record over the last climatic cycle (160,000 years). *Nature* 329, 403–408.
- Kitagawa, H., van der Plicht, J., 2000. Atmospheric radiocarbon calibration beyond 11,900 cal BP from Lake Suigetsu laminated sediments. *Radiocarbon* 42, 369–380.
- Krishnamurthy, R.V., Epstein, S., 1990. Glacial–interglacial excursion in the concentration of atmospheric CO₂-effect in the C-13/C-12 ratio in wood cellulose. *Tellus B Chem. Phys. Meteorol.* 42, 423–434.
- Leavitt, S.W., Danzer, S.R., 1992. $\delta^{13}\text{C}$ variations in C₃ plants over the past 50,000 years. *Radiocarbon* 34, 783–791.
- Marino, B.D., McElroy, M.B., 1991. Isotopic composition of atmospheric CO₂ inferred from carbon in C₄ plant cellulose. *Nature* 349, 127–131.
- Monnin, E., Indermuhle, A., Dallenbach, A., Fluckiger, J., Stauffer, B., Stocker, T.F., Raynaud, D., Barnola, J.M., 2001. Atmospheric CO₂ concentrations over the last glacial termination. *Science* 291, 112–114.
- Nadelhoffer, K., Shaver, G., Fry, B., Giblin, A., Johnson, L., McKane, R., 1996. N-15 natural abundances and N use by tundra plants. *Oecologia* 107, 386–394.
- Petit, J.R., Mounier, L., Jouzel, J., Korotkevich, Y.S., Kottlyakov, V.I., Lorius, C., 1990. Palaeoclimatological and chronological implications of the Vostok core dust record. *Nature* 343, 56–58.
- Prokopenko, A.A., Williams, D.F., Karabanov, E.B., Khursevich, G.K., 1999. Response of Lake Baikal ecosystem to climate forcing and pCO₂(2) change over the last glacial/interglacial transition. *Earth Planet. Sci. Lett.* 172, 239–253.
- Richards, M.P., Pettitt, P.B., Stiner, M.C., Trinkaus, E., 2001. Stable isotope evidence for increasing dietary breadth in the European mid-Upper Paleolithic. *Proc. Natl. Acad. Sci. USA* 98, 6528–6532.
- Richards, M.P., Pettitt, P.B., Trinkaus, E., Smith, F.H., Karavanic, I., Paunović, M., 2000. Neanderthal Diet at Vindija and Neanderthal Predation: The Evidence from Stable Isotopes. *Proc. Natl. Acad. Sci. USA* 97, 7663–7666.
- Schoeninger, M., DeNiro, M., 1984. Nitrogen and carbon isotopic composition of bone collagen from marine and terrestrial animals. *Geochim. Cosmochim. Acta* 48, 625–634.
- Schulze, E.D., Chapin, F.S., Gebauer, G., 1994. Nitrogen nutrition and isotope differences among life forms at the northern treeline of Alaska. *Oecologia* 100, 406–412.
- Stuiver, M., Braziunas, T., 1987. Tree cellulose ¹³C/¹²C isotope ratios and climatic change. *Nature* 238, 58–60.
- Stuiver, M., Reimer, P.J., Bard, E., Beck, J.W., Burr, G.S., Hughen, K.A., Kromer, B., McCormac, G., van der Plicht, J., Spurk, M., 1998. INTCAL98 Radiocarbon Age Calibration, 24,000–0 cal BP. *Radiocarbon* 40, 1041–1084.
- Van Klinken, G.J., van der Plicht, H., Hedges, R.E.M., 1994. Bone ¹³C/¹²C ratios reflect (palaeo-)climatic variations. *Geophys. Res. Lett.* 21, 445–448.
- Voelker, A.H.L., Grootes, P.M., Nadeau, M.J. et al., 2000. Radiocarbon levels in the Iceland Sea from 25–53 kyr and their link to the Earth's magnetic field intensity. *Radiocarbon* 42, 437–452.