# Carbon isotope composition of fossil charcoal reveals aridity changes in the NW Mediterranean Basin

**J.P. FERRIO[1], N. ALONSO[2], J.B. LÓPEZ[2], J.L. ARAUS[3] AND J. VOLTAS[1]**

[1]*Dept. Prod. Vegetal i Ciència Forestal, Univ. Lleida, Rovira Roure, 191, Lleida E-25198, Spain*
[2]*Grup d'Investigació Prehistòrica, Univ. Lleida, Víctor Siurana, 1, Lleida E-25003, Spain*
[3]*Dept. de Biologia Vegetal, Univ. Barcelona, Diagonal, 645, Barcelona E-08028, Spain*

## Introduction

Evidence of changes in aridity during the Holocene is scarce, and most is only qualitative. Thus, there is a need to concentrate efforts at the local scale in order to increase the spatial resolution of palaeoclimate records, specially regarding water availability in semi-arid zones. In this context, the use of stable isotopes in charred plant remains from archaeological sites it has been proposed as indicators of water availability (Araus and Buxó, 1993; Vernet *et al.*, 1996). Here we present a novel method to quantify changes in water availability in the past from the carbon isotope composition ($\delta^{13}C$) in fossil charcoal. We applied a model derived from present-time material to a series of archaeological samples from the Mid Ebro Depression (NE Spain) in order to reconstruct the evolution of aridity in this area during the last 4,000 years. This region is among the most arid zones in Europe, but it still remains unclear whether the present conditions are due to recent environmental changes, or to a progressive aridification which began in prehistoric times.

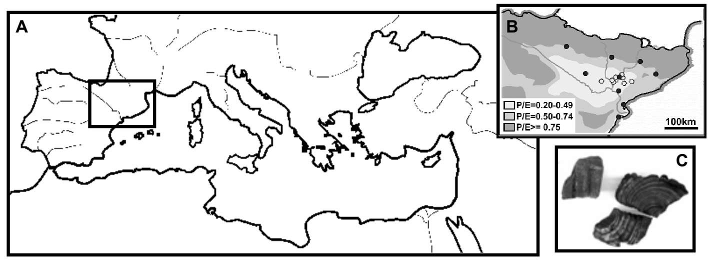


**Fig. 1.** A, B) Geographical distribution of sampling locations for reference wood cores (black circles), along with archaeological sites where fossil charcoal was collected (white circles). P/E, average ratio between precipitation and evapotranspiration. C) Examples of fossil charcoal.

### Materials and Methods

First, we studied the effect of carbonisation on the δ13C of wood. Incremental cores of Aleppo pine (*Pinus halepensis* Mill.) were collected from nine locations in NE Spain (Fig. 1) with distinct water availability (340-650 mm/year), as described in Ferrio *et al.* (2003). We distributed all samples (72) into four similar subsets: one subset was kept as control, the others were carbonised at three temperatures (300ºC, 400ºC and 500ºC) in anoxic conditions.

169 charcoal remains of *P. halepensis* were recovered from seven archaeological sites in the Segre and Cinca Valleys (Mid Ebro Depression, NE Spain, see Fig. 1) which cover the temporal range between the Bronze Age (ca. 2100 BCE) and Modern Age (XVIII c. CE).

To account for changes in $\delta^{13}C$ of atmospheric $CO_2$ ($\delta^{13}C_{air}$) during the Holocene, we calculated carbon isotope discrimination in wood ($\Delta^{13}C_w$) from $\delta^{13}C_{air}$ and wood $\delta^{13}C$ ($\delta^{13}C_w$), as described by Farquhar *et al.* (1982): $\Delta^{13}C_w=(\delta^{13}C_{air}-\delta^{13}C_w)/(1+\delta^{13}C_w/1000)$. $\delta^{13}C_{air}$ was inferred by interpolating different data from the literature, as described in Ferrio *et al.* (2005).

## Results and discussion

Changes in $\delta^{13}C$ caused by carbonization were strongly related to those in carbon concentration (%C) (Fig. 2). Nevertheless, the original climatic signal of wood $\delta^{13}C$ ($\delta^{13}C_w$) was well preserved in charcoal $\delta^{13}C$ ($\delta^{13}C_c$). Thus, we were able to estimate $\delta^{13}C_w$ from $\delta^{13}C_c$, by accounting for variation in charcoal %C ($\%C_c$): $\delta^{13}C_w=-0.706 \times \delta^{13}C_c + 0.031 \times \%C_c - 8.07$ ($r^2=0.72$, $P<0.001$). We used estimates of $\delta^{13}C_w$ to calculate $\Delta^{13}C_w$ values, which were applied to infer aridity variation across the reference locations (Fig. 3). The resulting relationships between $\Delta^{13}C_w$ and the annual ratio between precipitation and evapotranspiration (P/E) was strongly significant, and did not differ significantly (in terms of slope and intercept) from that reported in Ferrio and Voltas (2005) for intact wood.

Finally we applied the previous models to estimated P/E from the corrected $\delta^{13}C_w$ of fossil charcoal (Fig. 4). In general, estimated water availability in the past was higher than present values, indicating that latter-day (semi-arid) conditions are mostly due to recent climatic changes. The good agreement between our findings and other evidences (e.g. Araus and Buxó, 1993; Gutiérrez and Peña, 1998; Magny and Richard, 1992; Riera *et al.*, 2004; Vernet *et al.*, 1996), indicates that the analysis of $\delta^{13}C$ in charcoal may be useful to expand current palaeoclimatic records, specially at the local scale, as it provides a complementary (and quantitative) source of information to assess climate dynamics.

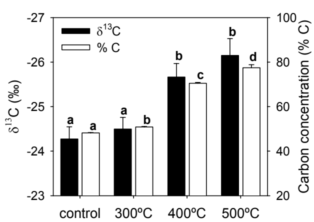


**Fig. 2.** Mean values and standard error for the $\delta^{13}C$ and %C in intact wood (control) and after carbonization at a range of temperatures. Means with the same letter did not differ significantly on the basis of a least significant difference test ($P<0.05$).

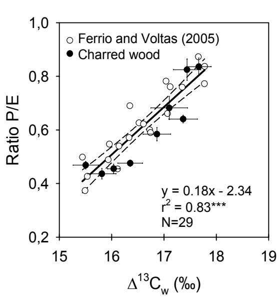


**Fig. 3.** Relationship between carbon isotope discrimination in wood ($\Delta^{13}C_w$) and the ratio precipitation/evapotranspiration (P/E). white circles, intact wood data from Ferrio and Voltas (2005); black circles, estimated $\Delta^{13}C_w$ from the analysis of experimentally carbonized wood.

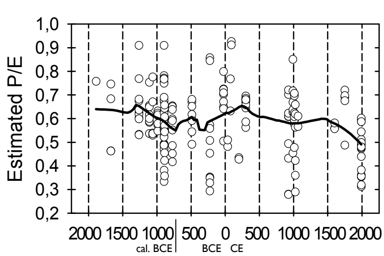


**Fig. 4.** Estimated evolution of the annual ratio between precipitation and evapotranspiration (P/E), according to the estimated $\Delta^{13}C_w$ of fossil charcoa, and using the model plotted in Fig. 3. Trend lines depict locally weighted least squares regression curves (LOESS, *span*=0.3; Cleveland, 1979) fitted to the data.

### References

Araus JL and Buxó R (1993). *Australian Journal of Plant Physiology*, **20,** 117-128.
Cleveland WS (1979). *Journal of the American Statistical Association*, **74,** 829-836.
Farquhar GD, O'Leary MH, Berry JA (1982). *Australian Journal of Plant Physiology*, **9,** 121-137.
Ferrio JP, Araus JL, Buxó R, Voltas J, Bort J (2005). *Vegetation History and Archaeobotany*. **In press**
Ferrio JP, Florit A, Vega A, Serrano L, Voltas J (2003). *Oecologia*, **137,** 512-518.
Ferrio JP and Voltas J (2005). *Tellus Series B-Chemical and Physical Meteorology*, **57B,** 164-173.
Gutiérrez-Elorza M and Peña-Monné JL (1998) Geomorphology and late Holocene climatic change in northeastern Spain. *Geomorphology*, **23,** 205-217.
Magny M and Richard H (1992). *Les nouvelles de l'archéologie*, **50,** 58-60.
Riera S, Wansard G, Julià R (2004). *Catena*, **55,** 293-324.
Vernet JL, Pachiaudi C, Bazile F *et al.* (1996). *Comptes Rendus de l'Academie des Sciences, série II a*, **323,** 319-324.

**ACKNOWLEDGEMENTS:** This work was supported by the CICYT project BTE2001-3421-C02 and the EC project MENMED (INCO-MED-ICA3-CT-2002-10022).