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

J.P. FERRIO¹, N. ALONSO², J.B. LÓPEZ, J.L. ARAUS and J. VOLTAS
1 Dept. Prod. Vegetal i Ciència Forestal, Univ. Lleida, Rovira Roure, 191, Lleida E-25198, Spain
2 Dept. d’Investigació Prehistòrica, Univ. Lleida, Víctor Siurana, 1, Lleida E-25003, Spain

Introduction
Evidence of changes in aridity during the Holocene is scarce, and most is 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 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 (δ¹³C) 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.

Materials and Methods
First, we studied the effect of carbonization on the δ¹³C of wood. Incremental cores of Aleppo pine (Pinus halepensis Mill.) were collected from nine locations in NE Spain (Fig. 1) with different water availability (540-650 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 carbonized at three temperatures (300°C, 400°C and 500°C) 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 δ¹³C of atmospheric CO₂ (δ¹³Cair) during the Holocene, we calculated fossil carbon isotope discrimination in wood (Δ¹³Cw) from δ¹³Cair and wood δ¹³C (Δ¹³Cc), as described by Farquhar et al. (1982): 

\[ \Delta^{13}C_w = \left( \frac{\delta^{13}C_{air}}{1000} - 1 \right) \times \delta^{13}C_{wood} = 0.706 \times \Delta^{13}C_{air} + 0.313 \times %C - 8.07 \] (r²=0.72, P<0.001)

We used estimates of Δ¹³Cw to calculate Δ¹³Cc values, which were applied to infer aridity variation across the reference locations (Fig. 3). The resulting relationships between Δ¹³Cc 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 δ¹³Cw 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 δ¹³C 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.

Results and discussion
Changes in δ¹³C caused by carbonization were strongly related to those in carbon concentration (%C) (Fig. 2). Nevertheless, the original climatic signal of wood δ¹³C (δ¹³Cc) was well preserved in charcoal δ¹³C (δ¹³Cw). Thus, we were able to estimate δ¹³Cc from δ¹³Cw by accounting for variation in charcoal %C (%Cc):

\[ \delta^{13}C_{c} = \frac{\delta^{13}C_{w}}{1+e^{-\frac{\delta^{13}C_{w}}{1000}}} \]


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 carbonization on the δ¹³C of wood. Incremental cores of Aleppo pine (Pinus halepensis Mill.) were collected from nine locations in NE Spain (Fig. 1) with different water availability (540-650 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 carbonized at three temperatures (300°C, 400°C and 500°C) 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 δ¹³C of atmospheric CO₂ (δ¹³Cair) during the Holocene, we calculated fossil carbon isotope discrimination in wood (Δ¹³Cw) from δ¹³Cair and wood δ¹³C (Δ¹³Cc), as described by Farquhar et al. (1982): 

\[ \Delta^{13}C_w = \left( \frac{\delta^{13}C_{air}}{1000} - 1 \right) \times \delta^{13}C_{wood} = 0.706 \times \Delta^{13}C_{air} + 0.313 \times %C - 8.07 \] (r²=0.72, P<0.001)

We used estimates of Δ¹³Cw to calculate Δ¹³Cc values, which were applied to infer aridity variation across the reference locations (Fig. 3). The resulting relationships between Δ¹³Cc 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 δ¹³Cw 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 δ¹³C 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.

Results and discussion
Changes in δ¹³C caused by carbonization were strongly related to those in carbon concentration (%C) (Fig. 2). Nevertheless, the original climatic signal of wood δ¹³C (δ¹³Cc) was well preserved in charcoal δ¹³C (δ¹³Cw). Thus, we were able to estimate δ¹³Cc from δ¹³Cw by accounting for variation in charcoal %C (%Cc):

\[ \delta^{13}C_{c} = \frac{\delta^{13}C_{w}}{1+e^{-\frac{\delta^{13}C_{w}}{1000}}} \]

Changes in δ¹³C caused by carbonization were strongly related to those in carbon concentration (%C) (Fig. 2). Nevertheless, the original climatic signal of wood δ¹³C (δ¹³Cc) was well preserved in charcoal δ¹³C (δ¹³Cw). Thus, we were able to estimate δ¹³Cc from δ¹³Cw by accounting for variation in charcoal %C (%Cc):

\[ \delta^{13}C_{c} = \frac{\delta^{13}C_{w}}{1+e^{-\frac{\delta^{13}C_{w}}{1000}}} \]

References
Australian Journal of Plant Physiology, 9, 121-137.
Vegetation and Arid Environments in press.
Oecologia, 137, 512-518.

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