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Tree-ring $\delta^{13}C$ of archeological charcoals as indicator of past climatic seasonality. A case study from the Neolithic settlements of Lake Chalain (Jura, France)

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ABSTRACT

Charcoal fragments from the Neolithic settlements of Lake Chalain (Jura Mountains, France) were characterized by dendro-anthracology (charcoal-pith distance, tree-ring width, earlywood/latewood proportion) and ring-scale isotope geochemistry (^{13}C) to assess the relevance of this combined approach for paleoclimate reconstructions. Two differing climatic periods were investigated: (i) a climatic deterioration period characterized by cool and moist conditions and (ii) a climatic improvement period characterized by slightly less precipitation and warmer temperature. Latewood proportion in charcoal tree-rings was similar for the two studied climatic periods. However, the charcoal tree-rings exhibited width and ^{13}C-content significantly different between the two studied periods, in agreement with previously inferred climatic difference. Monitoring ring-to-ring ^{13}C variation within each charcoal fragment revealed no noticeable climatic trend, for none of the studied periods. However, calculation of the difference in ^{13}C-content between earlywood and latewood of a given tree-ring suggested that the cool and moist climatic period also corresponded to higher seasonal contrast than the dryer climatic period. Although this exploratory study needs further confirmation, it opens promising developments for paleoclimatic reconstructions based on the stable carbon isotope composition of archeological charcoals: the potential for recording subtle paleoclimatic variations and seasonal contrasts.

1. Introduction

The stable carbon isotope composition ($\delta^{13}C$) of plant tissues depends on: (i) the inorganic carbon source used by the plants for their photosynthesis (*i.e.* atmospheric CO_2), (ii) the photosynthetic pathway used by plants (*i.e.* C_3, C_4 or CAM), and (iii) environmental conditions (Farquhar et al., 1980; O'Leary, 1981; Leavitt and Long, 1983; Tieszen, 1991; McCarroll and Loader, 2004). A number of environmental parameters (*e.g.* irradiance, nutrient supply, temperature, water availability, etc.) may influence plant $\delta^{13}C$ values, water availability probably being one of the most important, in both arid and temperate climates (Farquhar et al., 1982; Dawson et al., 2002; Kress et al., 2010; Saurer et al., 2014). Applied to ancient plants, stable carbon isotope studies allowed reconstructions of past photosynthetic pathways (e.g. Bocherens et al., 1993; Cotton et al., 2012), of isotope composition of past atmospheric CO_2 (e.g. Gröcke, 1997), or of the water-stress experienced by plants in the past (Nguyen Tu et al., 2002). Stable isotope characterization of tree-ring series from recent woods was established as an efficient approach to document detailed variations in temperature and rainfall over the last centuries (Leavitt and Long, 1991; Feng and Epstein, 1995; Treydte et al., 2001; Danis et al., 2006; Young et al., 2012). Owing to their sensibility to temperature and/or precipitation, dendrometric patterns of woods, such as ring width or earlywood/latewood proportions (i.e. springwood/summerwood

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proportions) of a given growth ring, also constitute helpful paleoclimatic proxies (Nola, 1996; Zhang, 1997; Briffa et al., 2002; Dittmar et al., 2003; Büntgen et al., 2006). Combining ring width and stable isotope composition further provides better constrained paleoclimatic estimations, as they record complementary climatic signals (Ballantyne et al., 2006; Weigl et al., 2007). Indeed, ring-width characteristics are often considered as more sensitive to local factors than $\delta^{13}C$ which may give access to larger scale climatic signals (Andreu et al., 2008). Stable isotope measurements are generally achieved on latewood/summerwood in dendroclimatology. Indeed, contrary to earlywood that is synthesized before bud break (Essiamah and Eschrich, 1985), latewood is expected to be little influenced by remobilization of the carbon stored the preceding years (Borella et al., 1998; Barbaroux and Bréda, 2002).

Charcoals are rather frequent in the sedimentological and archeological records as charcoalification confers wood a crystalized structure with higher chemical stability and resistance to degradation processes, when compared with uncharred woods (Figueiral, 1999; Bird and Ascough, 2012). Charcoalification generally preserves wood anatomy allowing taxonomic identification and dendrological studies (Couvert, 1970; Marguerie and Hunot, 2007). Archeological sites commonly yield numerous charcoal fragments produced either by fire events or domestic fires that are associated with heating, lighting and cooking activities. Dendrological characterization of charcoals (*i.e.* dendro-anthracology) from domestic firewood allows reconstructing variations in past woodland structure as well as firewood and woodland management (*e.g.* Lundström-Baudais, 1986; Ludemann and Nelle, 2002; Dufraisse, 2005, 2006; Marguerie and Hunot, 2007; Deforce and Haneca, 2015). As far as it has not been significantly affected by combustion and post-depositional processes, isotope composition of archeological charcoals potentially constitutes an efficient paleoenvironmental proxy. Selectively working on charcoals from a single type of fire (*i.e.* domestic fire), isotope composition was proven useful in archeological context to reconstruct paleoenvironmental parameters, particularly those related to water availability (February and Van der Merwe, 1992; Vernet et al., 1996; Ferrio et al., 2006; Vernet, 2006; Hall et al., 2008; Aguilera et al., 2009; Drake et al., 2012; Masi et al., 2013; Fiorentino et al., 2014). For example, systematic isotope characterization of charcoals dated from Bronze to Iron Ages allowed spatial paleoclimate reconstruction for the Iberian Peninsula, showing that precipitation was significantly higher during the so-called Iron Age Cold Epoch than present-day values (Aguilera et al., 2009).

Different plant components have different isotope composition (Park and Epstein, 1961; Gleixner et al., 1993). For example, among the most abundant wood components, cellulose is systematically ^{13}C-enriched with respect to lignin (Benner et al., 1987; Ehleringer, 1991). Therefore, the isotope composition of a given plant tissue corresponds to the weighted average of the isotope composition of each of its constituents. As a consequence, the analysis of a single plant constituent is often favored in isotope dendroclimatology, so as to avoid biases due to variations in the relative proportions of different wood components (Mazany et al., 1980; Leavitt and Danzer, 1993). Although the isotope composition of lignin was shown to accurately record climate, α-cellulose has been the preferred sample material as its synthesis and deposition in wood are considered synchronous of ring formation (Robertson et al., 2004; Loader et al., 2011). Nevertheless, bulk wood $\delta^{13}C$ was proven to accurately record past climatic trends; this is notably the case for woods devoid of resin since resins are among the main components that can bias wood isotope signature (Borella et al., 1998; Loader et al., 2003; Verheyden et al., 2005). Cellulose extraction is not possible for charcoals as charcoalification mostly corresponds to carbonization, a thermal process leading to the alteration of the chemical structure of cellulose. A subsequent enrichment in aromatic moieties results from both cellulose degradation and selective preservation of lignin-derived compounds (Ishimaru et al., 2007). The effects of charcoalification on the isotope composition of wood are not well documented in domestic open fireplaces. However, muffle furnace experimentations suggested that carbonization either (i) leads to no significant isotope effect, at least at moderate temperatures (i.e. up to 300–400 °C; DeNiro and Hastorf, 1985; Turekian et al., 1998; Czimczik et al., 2002; Ascough et al., 2008) or (ii) tends to shift whole wood $\delta^{13}C$ values down to that of lignin, especially at temperatures higher than 500 °C (Czimczik et al., 2002; Turney et al., 2006; Ferrio et al., 2006; Ascough et al., 2008). Above 500 °C, carbonization thus eventually gives access to an isotope signal close to that of a single plant component (i.e. lignin) as recommended for isotope dendroclimatology on extant wood.

Isotope studies of archeological charcoals were so far achieved on bulk charcoals although a ring-scale approach may provide further paleoclimatic details. The present study thus constitutes a first approach for assessing the relevance of ring-scale isotope study, in combination with dendro-anthracology, for paleoclimatic reconstructions based on archeological charcoals. The charcoals recovered in archeological sites generally comprise less than 10 growth rings so that deriving long term climatic trends would require particularly large charcoals and/or important sample sets. Alternatively, charcoal isotope study at ring scale can provide information on short term environmental variations as well as inter-seasonal variations. Indeed, although the isotope signature of earlywood (*i.e.* springwood) is markedly influenced by previous year accumulates, comparing $\delta^{13}C$ values of earlywood and latewood of a given growth-ring may bring information on seasonal contrasts (Livingston and Spittlehouse, 1996; Helle and Schleser, 2004; Li et al., 2005). This study thus investigated inter- and intra-ring isotope composition of archeological charcoals as an attempt to document detailed inter-annual and inter-seasonal paleoclimatic/paleoenvironmental variations.

To test the response of these isotope proxies to environmental variations, charcoals from the Neolithic sites of Lake Chalain (French Jura Montains) were characterized with an integrated approach coupling dendro-anthracology and isotope geochemistry. The lake-shore settlements of “Chalain 4” offer a unique opportunity to test new paleoclimatic proxies since:

(i) The charcoal fragments come from trees located in a limited area (Dufraisse, 2008) so that variations in their isotope composition are likely mainly influenced by regional/global environmental variations, with limited influence of variations in site conditions.
(ii) The Neolithic sedimentary sequence of Lake Chalain comprises several human occupation periods. Multidisciplinary studies (i.e. malacology, palynology, sedimentology and ^{14}C geochemistry) have shown that these occupation periods follow several decades without human occupation due to unfavorable climatic conditions for Neolithic farming societies. Two main phases were thus distinguished in this study: one without human occupation corresponding to cool and wet climatic conditions, followed by a phase comprising several human occupations and corresponding to favorable climatic conditions (low lake level due to relatively warmer and drier conditions; Damon et al., 1989; Magny, 1993a; Richard, 1997; Mouthon, 1997).
(iii) “Chalain 4” settlements yielded thousands of charcoal fragments from domestic firewood. An extensive dendro-anthracological study of these charcoals showed that they all come from small woods having grown under unfavorable

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