Journal of Archaeological Science: Reports 20 (2018) 775–783

Contents lists available at ScienceDirect

Journal of Archaeological Science: Reports

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

δ^{13}C referential in three *Pinus* species for a first archaeological application to Paleolithic contexts: "Between intra- and inter-individual variation and carbonization effect"

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ARTICLE INFO

Keywords:
Stable isotopes
Carbonization
Charcoal
Pinus
Palaeoclimatology
Pleistocene

ABSTRACT

Tree-ring studies, particularly those focusing on the δ^{13}C isotopic signal, have become a reliable method to reconstruct past climatic and environmental conditions. Unfortunately, wood remains are notably absent from the very ancient archaeological record, due to degradability of plant tissue. For archaeological studies, the analysis of isotopic signals from charcoal of *Pinus* species, which is more reliably preserved over time, and continuously represented among archaeological remains, would yield more robust findings. However, methodological confirmation of this approach is required prior to the archaeological implementation of this tool. Here, we present a wood-charcoal reference set, focused on the intra-genus *Pinus* spp. Δ^{13}C data (*Pinus halepensis* L., *Pinus sylvestris* Mill., *Pinus nigra* subsp. *nigra* Arn.), which addresses both natural variability and the isotopic impact of the carbonization. Our results show the potential application of an average isotopic signal from different *Pinus* spp. either from wood and charcoal. Moreover, carbonization results offer a baseline from which to create a general correction of the δ^{13}C shift introduced during pyrolysis temperature gradients. Lastly, a primary reference set was established in the context of climatic and environmental parameters for future archaeological analyses of charcoal remains.

1. Introduction

Since Prehistory, the evolution of societies is embedded in a context of deep environmental and climatic changes modifying human/environment interactions, resources and territories accessibilities. Understanding the way ancient societies faced environmental conditions and their changes are critical issues for prehistorians. However, the complex interaction between cultural and environmental changes will notbe properly apprehended by extra-regional data only (e.g. ice cores). Most of the models are supported by proxies that show no direct connection with archaeological records (e.g. pollen, ^{18}O), providing information on the prevailing environmental conditions at wider levels. Conversely, charcoal which is usually well preserved in prehistoric occupations and provides records covering long term spans is a witness of local environment. The ecological characteristics of the taxa and the variability of their frequencies can be interpreted in palaeoecological terms. However, inferences on past climate are above all qualitative and stem mainly from the interpretation of ecological traits and the climatic meaning of the variations are sometimes difficult to decouple from the effects of human practices (i.e. wood selection). In this context, traditional charcoal analysis fails in documenting quantitative aspects of past environments, as vegetal cover density or rainfall and temperature patterns.

In recent decades, the study of isotopic signals (δ^{13}C) in tree rings has demonstrated the greatest potential to reconstruct past climates and environments (Cernusak and English, 2015; McCarroll and Loader, 2004). Indeed, the ^{13}C/^{12}C ratio of tree-ring wood reflects water availability (Farquhar and Richards, 1984; Gessler et al., 2014), soil water content (Panek and Goldstein, 2001), water-use efficiency (Battipaglia et al., 2014; Dawson et al., 2002; Farquhar et al., 1989), and xylem hydraulic properties (Panek, 1996). In Mediterranean ecosystems characterized by drought-resistant species, trees respond to

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https://doi.org/10.1016/j.jasrep.2018.06.029
Received 6 December 2017; Received in revised form 19 June 2018; Accepted 24 June 2018

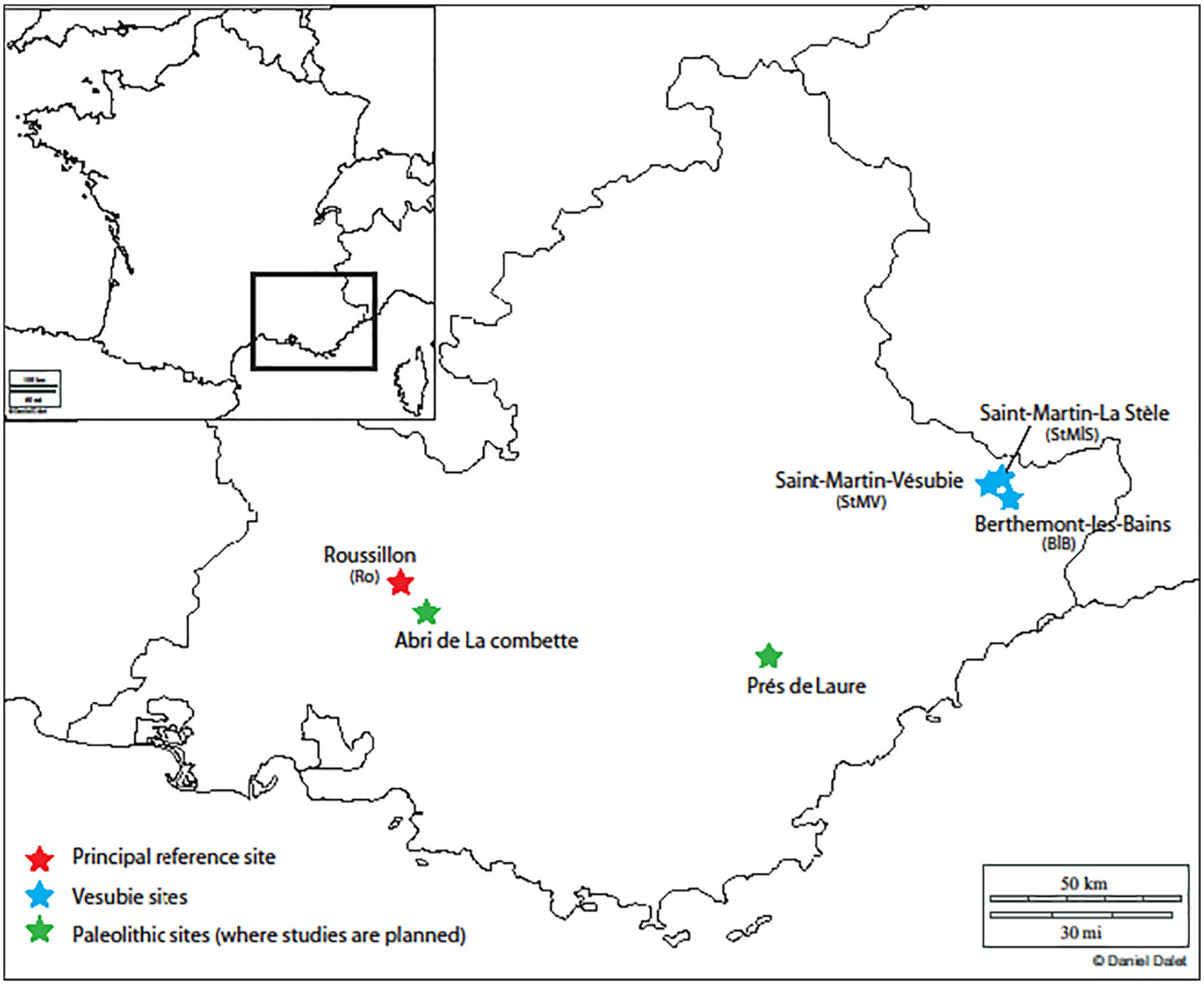

Fig. 1. Map of the reference sites. Including the principal reference site (in red), secondary reference sites (Vesubie sites in blue) and the Archaeological sites of the Paleolithic where studies are planned (in green). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

limited water resources by reducing stomatal conductance and photosynthetic rate (Ferrio et al., 2003). These phenomena induce a distribution of isotope fractionation during CO_2 uptake and fixation in leaves, and subsequently in the carbon isotope composition of organic matter (Scheidegger et al., 2000). Highlighting the environmental conditions in which tree tissues developed, $\delta^{13}C$ is a powerful proxy to study long-term climatic variations at a local scale (McCarroll and Loader, 2004; Voltas et al., 2008).

Previous analyses carried out on archaeological charcoal demonstrate that $\delta^{13}C$ variability is a useful tool to address past climate variations (Aguilera et al., 2012; Ferrio et al., 2006; Hall et al., 2008; Vernet et al., 1996; Voltas et al., 2008). However, the impact of carbonization (pyrolysis) and its specific effect on the $\delta^{13}C$ ratio has introduced a methodological bias, which has prevented the development and application of isotopic analyses from charcoal remains (Aguilera et al., 2012).

Numerous studies have focused on the chemical impact of pyrolysis on $\delta^{13}C$ values. Given the predictable augmentation of %C during the carbonization process, past studies have highlighted the response of different components. Lignin is more resistant to carbonization than cellulose, itself less oxidisable than “volatile” elements (such as waxes, esters, or oils) (Turekian et al., 1998). These compounds have different isotopic signatures: lignin is relatively depleted in ^{13}C compared to cellulose (Loader et al., 2003; Turekian et al., 1998; Turney et al., 1999; Wilson and Grinsted, 1977). Considering isotopic signals, the pyrolysis of wood at high temperatures results in reduced $\delta^{13}C$ values. A correction of burning effects, induced by carbonization temperature, was necessary to derive meaningful climatic information (Ferrio et al., 2006). Further, it has been reported that species characteristics influence the $\delta^{13}C$ of different plants (Priault et al., 2009; Rascher et al., 2010; Wegener et al., 2010), thus it is also necessary to verify the variability of $\delta^{13}C$ in contemporary samples from different taxa before any archaeological applications can be developed.

Charcoal belonging to the “Pinus” subsection of pines (including *P. sylvestris* and *P. nigra*) is abundant and well-preserved in charcoal assemblages and is a key taxon for the reconstruction of palaeoclimates from the Pleistocene (at least oxygen isotope stage 5) to the beginning of the Holocene. Previous studies have demonstrated that the physiological response of *Pinus* to water stress is pronounced and has great potential to enhance climatic records (Ehleringer and Cerling, 1995; Ferrio et al., 2003; Michelot, 2011). Thus, isotope analyses of archaeological charcoal from the *Pinus* spp. would allow the effects of environmental changes to be traced over time.

Among charcoal remains, different pines such as mountain or Mediterranean pines are generally discriminated through anatomical features. However, taphonomical alterations of the microstructure do not always insure it. Moreover, *P. sylvestris* and *P. nigra* are not anatomically discriminable. Considering the potential difficulty in taxonomical, the evaluation of the interspecific variations of $\delta^{13}C$ signals within the genus *Pinus* is a critical issue for any new archaeological