Incorporating $\delta^{18}O$ values of past waters in the calibration of radiocarbon dating

Nicolas Navarro*
UMR UB-CNRS 5561—Biogéosciences, 6 Boulevard Gabriel, 21000 Dijon, France

ABSTRACT
All scientists who study the late Quaternary are confronted by the problem of radiocarbon calibration. Since 1969, numerous high-frequency time series have been developed through the use of several stable isotopes (e.g., $\delta^{18}O$). Such time series are inefficient as dating methods because too many age possibilities are obtained for a given unique value. However, the Bayesian framework permits incorporation of these time series as a prior assumption on ages in order to improve calibrated ages obtained from a more precise absolute dating approach such as that using radiocarbon. The method is tested on data obtained from the Gigny cave (French Jura). Highly discontinuous posterior distributions are obtained with narrow highest posterior density regions. Thus, when the radiocarbon method alone gives large uncertainties, the incorporation of $\delta^{18}O$ values of meteoric waters largely diminishes these uncertainties.

Keywords: isotopes, oxygen, radiocarbon calibration, Bayesian statistic.

INTRODUCTION
Radiocarbon content of the biosphere varies with time depending on the geomagnetic field strength, solar fluctuations, and rearrangements in equilibrium between reservoirs. In order to obtain the true calendar date, radiocarbon dating needs to be calibrated in relation to a reference curve. Radiocarbon calibration is fundamental in natural sciences working on the late Quaternary. In these scientific areas, a precise temporal framework is required in order to estimate the precise time span of events, such as the onset or the duration of an extinction (Holdaway et al., 2002), or to derive an accurate depth-based age model which, for example, may permit a highly resolved palaeoclimatic record to be obtained (Cannariato and Kennett, 1999; Kennett et al., 2000).

After an initial phase in which scientists applied simple calibration methods, Bayesian statistics are now widely used to calibrate radiocarbon dating by incorporating additional available information from stratigraphy or dendrochronology as prior assumptions following different models using Markov chain Monte Carlo (MCMC) simulation (Buck et al., 1996). In the Bayesian calibration method, improvements have been developed that include alternative prior models for stratigraphic information (Nicholls and Jones, 2001), the model-choice framework (Sahu, 2004), and the modeling of the calibration curve (Gomez Portugal Aguilera et al., 2002). Moreover, improvements in calibration data sets for glacial ages and their combination in the CALPAL2000 data set (Weninger et al., 2002) permit extending these latter methodologies to ages older than the Holocene. Thus, Quaternary time possesses a potential dating framework for highly resolved analysis.

Since Dansgaard et al. (1969), Quaternary time possesses some highly resolved records (proxies) of the terrestrial climate such as the Greenland Ice Sheet Project 2 (GISP2) ice core (Grootes et al., 1993); such records may have, at least, a regional importance. One can expect that isotopic fluctuations recorded in the GISP2 core will be recorded in other areas of the Northern Hemisphere. However, $\delta^{18}O$ of biogenic apatites from mammal teeth and bones coupled with a present-day model have been widely used as proxies of the $\delta^{18}O$ of meteoric waters since Longinelli’s (1984) work. However, this isotope record proved to be an inefficient dating tool because of the flickering nature of Quaternary climate superimposed on glacial-interglacial cycles (Dansgaard et al., 1993; Grootes et al., 1993). In spite of this problem, time information is contained in measured oxygen isotope compositions when they are compared to the ice-core records, and the Bayesian framework permits one to envisage the utilization of this time information as prior knowledge in the calibration of radiocarbon dating.

RADIOCARBON CALIBRATION
Analysis is based on the Gigny sequence (Pleistocene, French Jura), which is a highly studied stack of karst deposits (for a synthesis, see Campy et al., 1989). Radiocarbon determinations were carried out on macrofauna for levels IV, VIII, and mixing of macrofauna and microfauna for level V (Evin, 1989; Table 1). The CALPAL2003 curve (Weninger et al., 2002) was used to calibrate these dating results. This spline curve interpolates the extended CALPAL2000 data set and provides standard error for the uncertainties on data and the precision of the spline curve (Weninger et al., 2002). This calibration curve $\mu(\theta)$ relates a $^{14}C$ measurement to a calibrated age $\theta$ according to the probabilistic model (Buck et al., 1996):

$$^{14}C|\theta \sim \mathcal{N}[\mu(\theta), \sigma^2].$$

(1)

where the $^{14}C$ dating is conditioned (the vertical bar) only on the un-

<table>
<thead>
<tr>
<th>TABLE 1. RADIOCARBON DETERMINATIONS AND OXYGEN ISOTOPE COMPOSITIONS FROM THE GIGNY CAVE (FRENCH JURA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Level</td>
</tr>
<tr>
<td>------</td>
</tr>
<tr>
<td>IV</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>V</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>VIII</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

*Oxygen isotope compositions of biogenic apatite from arvicoline teeth.
*Estimations of the oxygen isotope compositions of meteoric waters.

© 2005 Geological Society of America. For permission to copy, contact Copyright Permissions, GSA, or editing@geosociety.org.

Geology; May 2005; v. 33; no. 5; p. 369–372; doi: 10.1130/G21222.1; 1 figure; 2 tables.
The calibration curve: 8
2) converted into local values (46.45
370 GEOLOGY, May 2005
Gaussian propagation of errors of the 14 C dating and the precision of
known calibrated age \( \theta \), because \( \sigma_\theta^2 \) is known and corresponds to the
Gaussian propagation of errors of the \( ^{14} \text{C} \) dating and the precision of
the calibration curve:

\[ \sigma_\theta^2 = \sigma_{^{14} \text{C}}^2 + \sigma_{^{18} \text{O}}^2. \]  

(2)

In the Bayesian calibration, the aim is to obtain, conditional on
the observed \( ^{14} \text{C} \) dates, the distribution of the calibrated age \( \theta \) (see
e.g., Buck et al., 1996; in the context of the radiocarbon calibration or,
for more statistical books, Pawitan, 2001; Tanner, 1993). This condi-
tional density function \( \pi(\theta|^{14} \text{C}) \) of the calibrated age \( \theta \) given the ob-
served \( ^{14} \text{C} \) dates is called the posterior density. Posterior density de-
scribes updating knowledge about \( \theta \) given the data and is obtained
according to the Bayes theorem (Tanner, 1993):

\[ \pi(\theta|^{14} \text{C}) = c \, p(\theta|^{14} \text{C}) \pi(\theta), \]  

(3)

where \( c \) is the inverse of the marginal density of the data \( ^{14} \text{C} \) and is a
constant of normalization:

\[ c^{-1} = m(\theta) = \int \pi(\theta|^{14} \text{C}) \pi(\theta) \, d\theta. \]  

(4)

Thus, the posterior density relates especially to \( p(\theta|^{14} \text{C}) \) and \( \pi(\theta) \).
The first, \( p(\theta|^{14} \text{C}) \), is the probability density function of the observed
\( ^{14} \text{C} \) dating conditional on \( \theta \), and can be understood as the likelihood
\( L(\theta; ^{14} \text{C}) \) of the calibrated age \( \theta \) based on the \( ^{14} \text{C} \) dating because
the likelihood is any function proportional to this probability density (Tan-
er, 1993):

\[ L(\theta; ^{14} \text{C}) = f(\theta) \, p(\theta|^{14} \text{C}) \approx p(\theta|^{14} \text{C}). \]  

(5)

The second, \( \pi(\theta) \), is the prior distribution of \( \theta \) and corresponds to
the knowledge about \( \theta \) without knowledge of the \( ^{14} \text{C} \) dating, for example,
the stratigraphic constraints. Thus, the posterior density \( \pi(\theta|^{14} \text{C}) \) corre-
sponds to the update of the initial knowledge on \( \theta \) and is proportional
to the likelihood times the prior distribution:

\[ \pi(\theta|^{14} \text{C}) \propto L(\theta; ^{14} \text{C}) \pi(\theta). \]  

(6)

Thus, in the case of uniform prior and without any stratigraphic con-
straint, the posterior distribution of the calibrated age \( \theta \) is proportional
to the likelihood.

The three dating levels of Gigny show relatively flat posterior
densities for their calibrated age based on the radiocarbon measure-
ments (Fig. 1; Table 2). Their highest posterior density (HPD) incor-
porates several stades and interstades of glacial chronology. For ex-
ample, the first radiocarbon determination of level IV (Fig. 1A) gives
an expected depositional period of the level between the Oldest Dryas
and the Allerød interstad. Moreover, the incorporation of stratigraphic
information using MCMC did not reduce these uncertainties in this
case because large hiatuses are present between successive dating lev-
elss (e.g., a hiatus of \( \sim 10 \) k.y. between the deposition of V and IV).
OXYGEN ISOTOPE COMPOSITIONS OF PAST WATERS

On the basis of the present-day equation, the δ18O values of past meteoric waters can be estimated from the δ18O values of biogenic apatites (Longinelli, 1984). The teeth of arvicoline rodents, analyzed here, are stratigraphically related to the 14C dating. Basically, some teeth are mixed and analyzed using wet chemistry and mass spectrometry (Navarro et al., 2004). This wet chemistry permits isolation of the PO4 component of apatite, which is more stable facing diagenetic alteration than the CO2 component (e.g., Iacumin et al., 1996; see also Zazzo et al., 2004). A fractionation equation can be established between the δ18O of ingested waters, approximated by the values of meteoric waters from the Global Network for Isotopes in Precipitation (GNIP) database (International Atomic Energy Agency—World Meteorological Organization [IAEA-WMO], 2001), and the δ18O of phosphate from present-day arvicoline rodents' teeth. Navarro et al. (2004) estimated such an equation and estimated the δ18O values of past meteoric waters (δ18Oₘₚ) for teeth of the Gigny sequence (Table 1). Derivation of the standard errors is based on parametric bootstrap simulation (Efron and Tibshirani, 1993) estimating error on regression parameters based on the analytical error of δ18O of phosphate and present-day waters.

The GISP2 record (Grootes et al., 1993) can be viewed as a time reference curve of δ18O of past meteoric waters in the Northern Hemisphere. However, in order to compare these high-latitude values with the estimation in the Gigny area, GISP2 can be translated into local values. The local value (−8.2‰) is obtained from the Oxygen Isotopes in Precipitation Calculator (http://es.ucsc.edu/~gbowen/OPC/Main.html), which is based on the updated version of the most recently published relationship (Bowen and Wilkinson, 2002; Bowen and Revenaugh, 2003) between oxygen isotope compositions and geographical variables as given in the GNIP database (IAEA-WMO, 2001). The standard error on this local value estimation is 0.38‰ (σₑ). This precise estimate of the present day is related to the location of the Gigny cave in western Europe, a particularly well sampled area for δ18O in precipitation. In poorly sampled areas, standard error can increase to 3.31‰ (Bowen and Revenaugh, 2003).

The GISP2 present-day value was estimated by the average value of the 1978–1987 annual average GISP2 data (Steig et al., 1994). The standard error of this present-day value is 0.55‰ (σₑ). The GISP2 time scale of Meese et al. (1997) based on the count of annual layers is used. The measurement error of the GISP2 data set is 0.14‰ (σₑ), considering the standard deviation reported for unique determinations (Greenland Summit Ice Cores CD-ROM, 1997). In order to convert the GISP2 data set into a calibration curve with 1 yr resolution, the δ18O values are interpolated by using a cubic function.

As for radiocarbon, the δ18Oₘₚ distribution at the calibrated age is presumed to be normal and the standard deviation (σₑ) to be equal to the Gaussian propagation of errors of δ18Oₘₚ and the shifted reference record, which incorporates the error on the model, measurement error on GISP2, and error on the estimate of GISP2 present-day values:

\[ \sigma_r^2 = \sigma_{\delta^{18}O}^2 + \sigma_{\text{MODEL}}^2 + \sigma_{\text{GISP2,measures}}^2 + \sigma_{\text{GISP2,PresentDay}}^2. \]  (7)

COMBINING RADIOCARBON AND OXYGEN COMPOSITIONS

The posterior density of the calibrated age given the 14C dating and the δ18Oₘₚ values (i.e., the updated knowledge or what is known about \( \theta \) with knowledge of 14C and δ18O measurements) is proportional to the product of the likelihood of the calibrated age based on the 14C dating and the δ18Oₘₚ value, times the prior distribution of the calibrated age \( \theta \) (i.e., what is known about \( \theta \) without knowledge of 14C and δ18O measurements):

\[ p(\theta | 14C, \delta^{18}O \mid \theta) \propto \ell(14C, \delta^{18}O | \theta) \cdot p(\theta). \]  (8)

Because of the independence between δ18Oₘₚ and 14C measurements, the likelihood of calibrated age based on the measurements of δ18Oₘₚ and 14C corresponds to the product of the likelihoods (Buck et al., 1996; Pawita, 2001):

\[ \ell(14C, \delta^{18}O | \theta) = \ell(14C | \theta) \cdot \ell(\delta^{18}O | \theta). \]  (9)

Thus, the posterior distribution of the calibrated age \( \theta \) is proportional to the product of the two independent likelihoods times the prior distribution of the calibrated age \( \theta \):

\[ p(\theta | 14C, \delta^{18}O) \propto \ell(14C | \theta) \cdot \ell(\delta^{18}O | \theta) \cdot p(\theta). \]  (10)

DUAL CALIBRATION OF GIGNY SAMPLES

Because of the cyclic and flickering nature of the δ18O record (Dansgaard et al., 1993; Grootes et al., 1993), the likelihood of the calibrated ages based on δ18O values of meteoric waters shows imprecise regions of confidence. However, a uniform distribution was not obtained. Thus, δ18O values provide knowledge about the depositional period according to the climate conditions. After incorporating this prior assumption, the posterior densities obtained become radically different from those obtained previously (Fig. 1). The new posterior distributions are more discontinuous and can be extremely multimodal, as a result of the climatic mode occurring during the depositional period. In some cases, posterior distributions given the two isotopic measurements can be shifted into the tail of the posterior distributions determined for 14C alone (e.g., Figs. 1A, 1B), and the 1σ HPDs of the calibrated age considering both isotopic systems correspond to parts of the 2σ HPDs considering the 14C alone.

CONCLUSIONS

The large uncertainties in the radiocarbon calibration can be greatly reduced by taking into account the time information contained in the oxygen isotope compositions of past meteoric waters. Thus, incorporating the δ18Oₘₚ significantly improves the calibration of 14C determinations. However, in the case of large δ18O uncertainties (e.g., poor sampling area of the GNIP database), the updating of the calibration would be weak because of the weak time information provided by \( p(\theta | \delta^{18}O) \), which tends to be uniformly distributed. In such a case, the posterior density \( p(\theta | 14C, \delta^{18}O) \) will be proportional to \( p(\theta | 14C) \), and the updating will be null.

A strong initial assumption of the methodology is the use of the present-day relationship between Greenland and the study area. This constancy is relatively unlikely over a long time scale because of probable variations in atmospheric circulations between modern and glacial configurations (North Greenland Ice Core Project [NGRIP] Members, 2004). However, little is known about the variation of geographical gradients: normal (easily introduced in equation 7) or a mixture of switch states. The comparison of deep Greenland ice cores (NGRIP Members, 2004) seems to yield a gradient variation resulting from a mixture of two normal distributions. Such a case, conditional on age, would be incorporated using complex MCMC simulations. Moreover, a general...
circulation model incorporating isotopic tracers (e.g., Joussaume et al., 1984) would increase this knowledge about the range of variation and the glacial state of the gradient.

Another initial assumption is that the δ18O from averaged teeth and 14C dating of other material from the same layer represent the chronological knowledge. Quaternary record, can be used in the same way to improve the chronology: a way to monitor diagenetic alteration of bone phosphate?: Earth and Planetary Science Letters, v. 142, p. 1–6.


