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Murray-Darling basin freshwater shells: riverine reservoir effect

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Murray-Darling basin freshwater shells: riverine reservoir effect

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Keywords: carbon isotopes, freshwater shell, carbonate, protein

Abstract

We report carbon isotope measurements on pre-bomb museum samples of freshwater mussel shells collected alive from riverine locations in New South Wales, Australia. The calculated reservoir ages, ranging from ~60 to +112 years, are much smaller than those for Australian marine shells and not considered significant for the radiocarbon dating of Late Pleistocene freshwater shells from the Murray-Darling Basin.

Freshwater mussel shells and fish otoliths have provided the most consistent set of radiocarbon ages for the Willandra Lakes archaeological sites, but disagreements between shell and charcoal ages from the same locations have been common (e.g. Bowler et al. 1970; Barbetti and Allen, 1972; Bowler, 1998). The unexpected discovery that many black organic midden sediments contain mostly alkali-soluble material (humic acids), with little or no macroscopic charcoal, went some way toward explaining the discrepancy (Gillespie 1997), but did not address the accuracy of the shell dates. Organic, charcoal-free, residues almost always yield radiocarbon ages significantly younger than shell or fish otolith carbonate ages from the same midden.

It is possible that the shell and fish otolith carbonate ages are too young because of post-deposition infiltration by carbonate from groundwater sources, including ion exchange and recrystallisation mechanisms. This kind of field contamination is shown, for example, by the comparison of Genyornis eggshell carbonate 14C ages with OSL ages on sediments containing eggshells in Figure 1. Complementary U-series and amino acid racemisation evidence strongly supports the Genyornis OSL ages, and clearly the eggshell carbonate 14C ages are too young, which casts doubt on the oldest midden shell and fish otolith carbonate 14C ages also shown in Figure 1. Radiocarbon results are calibrated 95% confidence intervals calculated using the CalPal07r program (Weninger et al. 2007). Shell and otolith samples are from Murray-Darling Basin sites, notably the Willandra Lakes in south-western New South Wales, while Genyornis samples are from a range of locations in the Lake Eyre and Murray-Darling Basins. OSL results relevant to the Lake Mungo I and III burials might be seen as a bridge between the two datasets, and the mean burial age (gray band) also approximates the younger age limit for megafauna extinction in Australia. Data from Balme and Hope, 1990; Bowler et al. 2003; Gillespie 1997; Hope et al. 1983; Johnson and Clark, 1998; Kalish et al. 1997; Macumber 1977; Miller et al. 2005; Olley et al. 2006; Roberts et al. 2001. In addition to the possibility of appearing too young due to post-depositional groundwater contamination, the 14C age of shells and otoliths might also be too old because the water the fish and shellfish lived in was not in equilibrium with atmospheric carbon dioxide. Live-collected shells from some American hard-water lakes were found to have apparent 14C ages of up to 2000 years (Deevey et al. 1954), indicating significant incorporation of radiocarbon-depleted limestone carbonate. The possibility of a similar ‘reservoir effect’ in shells from the Willandra Lakes was raised by Bowler et al. (1970), but dismissed on the grounds that geologically old limestone is not present in the region. As shown in Figure 1, the oldest shell and otolith calibrated radiocarbon ages overlap with the 40±2 ka age for the Mungo I and III burials deduced from systematic OSL dating. Although the oldest shell and otolith results are consistent with their stratigraphic location (Bowler 1998), direct comparison of charcoal with freshwater shell ages (as Culleton 2006, for example, used on Californian lacustrine materials) is not feasible because there are few, if any, reliable charcoal 14C ages from any of the Willandra middens (Gillespie 1998).

As the first stage in a project to quantify the uncertainties in freshwater shell ages, we present new radiocarbon and stable carbon isotope data on pre-bomb live-collected shells from riverine locations in the Murray-Darling Basin.

Materials and methods

Samples of single shell valves were provided by Ian Loch from collections in the Australian Museum, Sydney:

VA-1 Velesunio ambiguous, from Castlereagh River at Gilgandra, NSW (31°43’ S. 148°40’ E), collected 1940 by Mel Ward and Frank E. Allen, C.173143.

VA-2 Velesunio ambiguous, from Darling River at Bourke,
Figure 1. Late Pleistocene calibrated $^{14}$C ages (95% confidence intervals, CalPal07abu) for the carbonate fraction of freshwater shells, fish otoliths and *Genyornis* eggshells, with OSL ages for sediments containing *Genyornis* eggshells and for sediments pertinent to the Lake Mungo I and III burials (gray band is mean burial age). Ages are sorted in upward increasing order for extinct fauna and decreasing for extant fauna; shells and otoliths are from Murray-Darling Basin sites, eggshells are mainly from the Lake Eyre Basin, see text for data sources.

NSW (35°5’ S, 145°56’ E), collected 1909 by E.W. Powell, C.047296.

VA-3 *Velesunio ambiguus*, from Mooni River at Mogil Mogil Homestead, NSW (29°21’ S, 148°41’ E), collected 1911 by S.W. Jackson, C.061905.

VA-4 *Velesunio ambiguus*, from Murrumbidgee River at Gundagai, NSW (35°4’ S, 148°7’ E), collected 1940 by Mel Ward and Frank E. Allen, C.173155.

AJ-1 *Alathyria jacksoni*, from Murrumbidgee River near Yanco, NSW (34°38’ S, 146°22’ E), collected 1932 by Australian Museum party, C.057877.

These museum shell samples were purportedly collected alive from riverine locations in the Murray-Darling basin of NSW (Figure 2), before nuclear detonations distorted the natural atmospheric radiocarbon abundance.

Radiocarbon and δ$^{13}$C measurements were made on graphite prepared from the carbonate fraction of shells using standard procedures at ANSTO (Fink et al. 2004). Separate δ$^{18}$O measurements were made on protein fractions from the same shell valves; the outer surface protein was scraped off with a scalpel (exterior), and inner protein was collected on a glass-fibre filter after dissolution of the carbonate matrix in 1M HCl (interior). Protein samples were measured

Figure 2. Map showing geographic location of live-collected riverine mussel shells from collections in the Australian Museum, Sydney, with species and year of collection.
without further purification using standard procedures at ANU (Michael Bird, pers. comm. 2003). Carbonate $\delta^{13}C$ values were used to correct the measured carbonate $^{14}C$ activity for isotopic fractionation, and the collection year of the shell samples was converted to a $^{14}C$ age using the southern hemisphere SHCAL04 calibration dataset (McCormac et al. 2004). In a manner analogous to that used for marine shells, the reservoir effect for these freshwater shells ($\Delta R_t$) was calculated from the equation:

$$\Delta R_t = R_{s}(t) - R_{g}(t)$$

where $R_{s}(t)$ is the measured $^{14}C$ age and $R_{g}(t)$ is the atmospheric $^{14}C$ concentration in the collection year.

**Results and discussion**

Table 1 shows the isotopic measurements made on the five museum shell samples, and the freshwater reservoir effect calculated for each sample. The stable carbon isotope results, shown graphically in Figure 3A, exhibit the expected significant difference of ~20% between the carbonate and protein fractions, and also a much smaller difference of ~5%, between interior and exterior proteins which is unlikely to be important for $^{14}C$ dating. Figure 3B illustrates the difference in reservoir age between samples VA-4 and AJ-1 (mean $\Delta R_t = +100 \pm 16$ years), from the Murrumbidgee River in southern New South Wales, and those from northern New South Wales on the Darling River drainage system (mean $\Delta R_t = -34 \pm 27$ years).

The $\Delta R$ notation was introduced by Stuiver and Braziunas (1993) to formalise the observed regional variation in marine reservoir ages for calibration purposes. Ulm (2002) gave a useful summary of marine reservoir effect calculations, pointing out errors in earlier conversions of the first Australian results (Gillespie 1977); based on the latest marine model data, those six samples have mean $\Delta R = +52 \pm 51$ years (Reimer and Reimer, 2009). However, marine model ages are offset by ca. 400 years from terrestrial (atmospheric) ages, and a built-in correction is applied when marine $^{14}C$ ages are calibrated. In this study, the freshwater reservoir effect was calculated using the atmospheric model based on southern hemisphere tree-ring data with no correction, and although some of our $\Delta R_t$ values appear similar to the $\Delta R$ marine value, they are in fact all significantly smaller than the $\Delta R$ marine value, which is expected since many shell samples in this study are from a sample collected at the Willandra Lakes, which have been dry since ~18,000 calendar years ago. Since the Willandra Lakes have been dry since ~18,000 calendar years ago, no modern shells are available for measurement, but we concur with Bowler et al. (1970) that a significant reservoir correction is unlikely because there is no ancient limestone in the region to contribute $^{14}C$-free carbonate and even when full the lakes

![Figure 3](image-url) (A) Stable carbon isotope measurements on carbonate and protein fractions of riverine mussel shells. (B) Reservoir effect for riverine mussel shells, calculated using SHCal04 calibration data (McCormac et al. 2004) on carbonate fraction $^{14}C$ measurements and known collection year.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Collect.</th>
<th>Lab. No.</th>
<th>$\delta^{13}C$</th>
<th>$^{14}C$ Age BP</th>
<th>$\Delta R_t$</th>
<th>$\delta^{13}C$ ext.</th>
<th>$\delta^{13}C$ int.</th>
</tr>
</thead>
<tbody>
<tr>
<td>VA-1</td>
<td>1940</td>
<td>OZH-766</td>
<td>-6.8</td>
<td>135±30</td>
<td>-6±30</td>
<td>n/d</td>
<td>n/d</td>
</tr>
<tr>
<td>VA-2</td>
<td>1909</td>
<td>OZH-767</td>
<td>-7.1</td>
<td>65±30</td>
<td>-60±30</td>
<td>-27.1</td>
<td>-24.3</td>
</tr>
<tr>
<td>VA-3</td>
<td>1911</td>
<td>OZH-768</td>
<td>-7.0</td>
<td>90±30</td>
<td>-36±30</td>
<td>-28.4</td>
<td>-26.8</td>
</tr>
<tr>
<td>VA-4</td>
<td>1940</td>
<td>OZH-769</td>
<td>-7.4</td>
<td>230±30</td>
<td>+89±30</td>
<td>-28.3</td>
<td>-26.2</td>
</tr>
<tr>
<td>AJ-1</td>
<td>1932</td>
<td>OZH-770</td>
<td>-10.8</td>
<td>270±30</td>
<td>+112±30</td>
<td>-26.6</td>
<td>-24.2</td>
</tr>
</tbody>
</table>

Table 1. Museum shell isotopic measurements, showing $\delta^{13}C$ and $^{14}C$ age on graphite prepared from the carbonate fraction, calculated reservoir effect, and $\delta^{13}C$ of interior/exterior shell proteins; n/d = not determined.
were not deep (Bowler 1998). Our results are also relevant to the fish otoliths found in Willandra midden, because these mostly large fish (estimated from otolith growth rings as up to 50 years old at death by Kalish et al. 1997) probably spent time in both river and lake environments, and there is close agreement between Willandra fish otolith carbonate and shell carbonate ages from the same stratigraphic context.

This study does not pursue the possible effects which may accrue from the difference between riverine and lacustrine faunal habitats, nor groundwater carbonate contamination of older midden shell carbonate, as observed in Genyornis eggshell carbonate. Magee et al. (2009) report very good agreement between calibrated $^{14}$C, U-series, OSL, and AAR dating methods on an emu eggshell at 31.24±0.34 ka. Similar investigations are underway with >35,000 cal BP Genyornis eggshells and Willandra Lakes Velesanum midden shells, using isotopic measurements on carbonate-protein pairs and AAR measurements on the proteins, also on live-collected Velesanum shells from other Murray-Darling Basin lakes which still have water today.

Conclusions

We report carbon isotope measurements on five live-collected mussel shells from riverine sites in New South Wales, finding a location-dependent freshwater radiocarbon reservoir effect ranging from +100±16 to −34±27 years. Our results support the suggestion by Bowler et al. (1970) that any reservoir effect correction for Willandra Lakes Velesanum shell carbonate, and by implication fish otolith carbonate, is unlikely to be significant for Late Pleistocene $^{14}$C ages. The possibility remains that midden shells and otoliths have accumulated field contamination from groundwater sources, as some Genyornis eggshell carbonate samples have, an error which may be significant for Murray-Darling basin samples older than 30,000 cal BP.

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References


