Archaeol. Oceania 44 (2009) 107–111

Murray-Darling basin freshwater shells: riverine reservoir effect

RICHARD GILLESPIE, DAVID FINK, FIONA PETCHEY and GERALDINE JACOBSEN

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 ^{14}C 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 ^{14}C ages are too young, which casts doubt on the oldest midden shell and fish otolith carbonate ^{14}C ages also shown in Figure 1. Radiocarbon results are calibrated 95% confidence intervals calculated using the $CalPal07_{Hulu}$ 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 ^{14}C 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 ^{14}C 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 ^{14}C 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 ambiguus*, 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 ambiguus*, from Darling River at Bourke,

RG: Archaeology and Natural History, Australian National University, Canberra ACT 0200, Australia and School of Earth and Environmental Sciences, University of Wollongong, NSW 2522. dizzy@better.net. DF, GJ: Institute of Environmental Research, ANSTO, PMB 1, Menai NSW 2233, Australia. FP: Radiocarbon Laboratory, University of Waikato, Private Bag 3105, Hamilton, NZ.

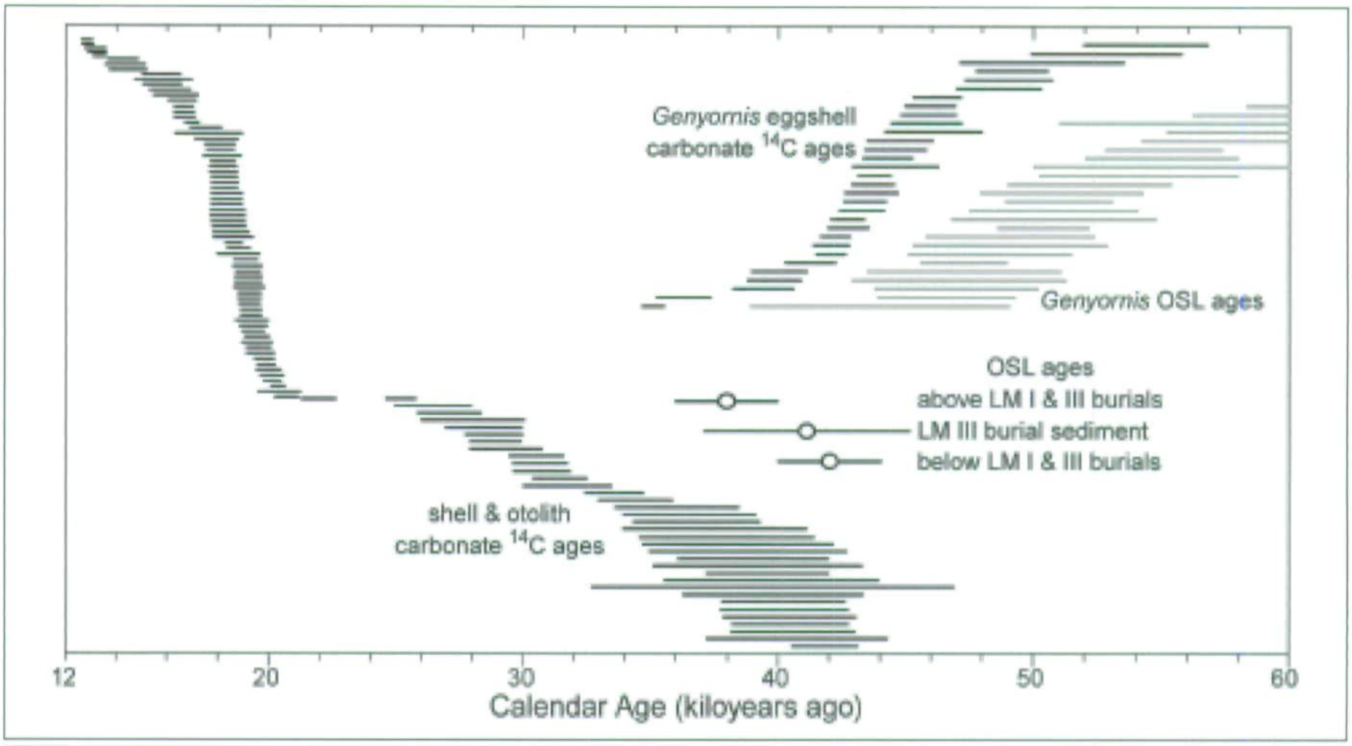

Figure 1. Late Pleistocene calibrated ^{14}C ages (95% confidence intervals, CalPal07$_{Hulu}$) for the carbonate fraction of freshwater shells, fish otoliths and *Genyornis* eggshells, with OSL ages for sediments containing *Genyornis* eggshells and for sediments pertinent to the Lake Mungo I and III 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 $\delta^{13}C$ measurements were made on graphite prepared from the carbonate fraction of shells using standard procedures at ANSTO (Fink *et al.* 2004). Separate $\delta^{13}C$ 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

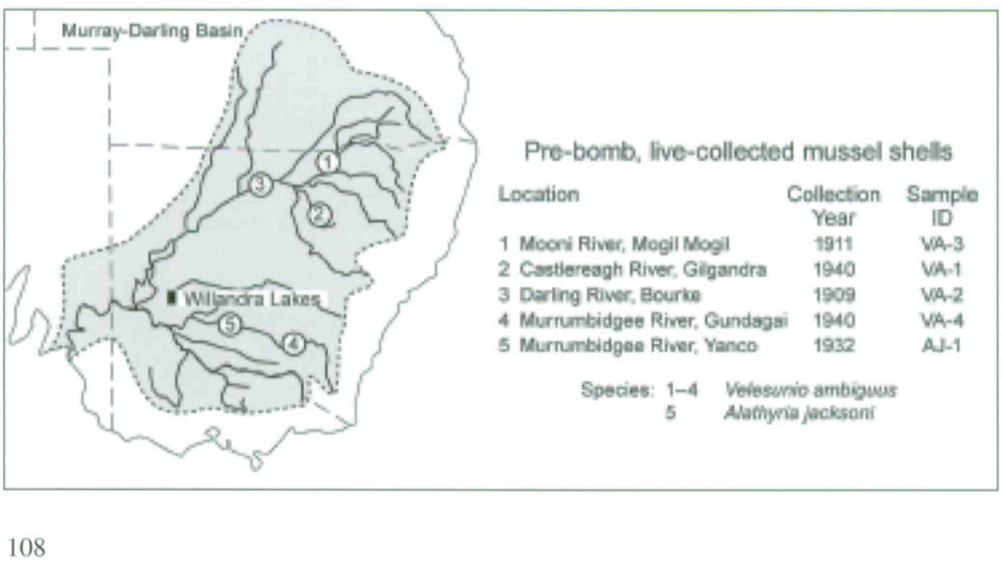

Figure 2. Map showing geographic location of live-collected riverine mussel shells from collections in the Australian Museum, Sydney, with species and year of collection.

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 (ΔR_f) was calculated from the equation:

$$\Delta R_f = Rs(t) - Rg(t)$$

where Rs(t) is the measured ^{14}C age and Rg(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 ~2‰ 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 ΔR_f = +100±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 ΔR_f = –34±27 years).

The ΔR 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 ΔR = +52±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 ΔR_f values appear similar to the ΔR marine value, they are in fact all significantly smaller than the ca. 400 year marine reservoir age. Our dataset is small and further determinations may alter this picture, but the results so far are not

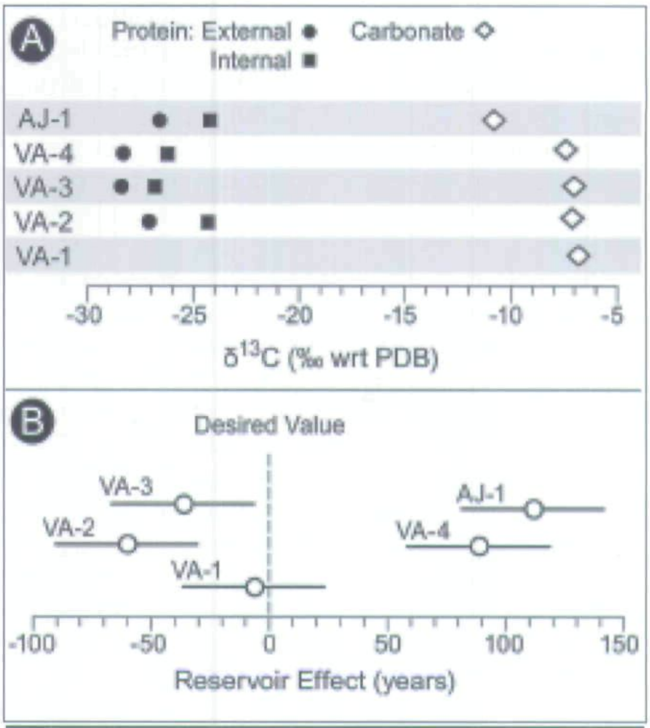

Figure 3. (A) Stable carbon isotope measurements on carbonate and protein fractions of riverine mussel shells. (B) Reservoir effect for riverine mussel shells, calculated using SHCal04 calibration data (McCormac *et al.* 2004) on carbonate fraction ^{14}C measurements and known collection year.

significant for the ^{14}C dating of Late Pleistocene samples: even +100 years is very small compared with the two standard deviations uncertainty for the calibrated shell and otolith samples >30,000 cal BP shown in Figure 1.

The shells we used are riverine samples, and not particularly close to the Willandra, so it is still possible that lacustrine shells there could have a different reservoir effect – which might change over time, as Geyh *et al.* (1998) found for lakes in Germany, Croatia and Chile. The nearest modern lacustrine shell age known to us is from a sample collected alive in the 1970s from Kow Swamp, which yielded a reasonable post-bomb result of 122.6±0.7 % Modern (Macumber 1977). 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

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

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 middens, 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 *Velesunio* midden shells, using isotopic measurements on carbonate-protein pairs and AAR measurements on the proteins, also on live-collected *Velesunio* 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 *Velesunio* 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.

Acknowledgements

We thank Ian Loch for supplying shell samples from the Australian Museum collections, and Michael Bird for $\delta^{13}C$ measurements on protein from those shells. Funding for the AMS radiocarbon dating was provided by AINSE Grant 05/065 to RG.

References

Balme, J., Hope, J. 1990. Radiocarbon dates from midden sites in the lower Darling River area of western NSW. *Archaeology in Oceania* 25, 85-101.

Barbetti, M., Allen, H. 1972. Prehistoric Man at Lake Mungo, Australia, by 32,000 years ago. *Nature* 240, 46-48.

Bowler, J.M. 1998. Willandra Lakes revisited: environmental framework for human occupation. *Archaeology in Oceania* 33(3), 120-155.

Bowler, J.M., Jones, R., Allen, H., Thorne, A.G. 1970. Pleistocene human remains from Australia: a living site and human cremation from Lake Mungo, western New South Wales. *World Archaeology* 2, 39-60.

Bowler, J.M., Johnston, H., Olley, J.M., Prescott, J.R., Roberts, R.G., Shawcross, W., Spooner, N.A. 2003. New ages for human occupation and climatic change at Lake Mungo, Australia. *Nature* 421, 837-840.

Culleton, B.J. 2006. Implications of a freshwater radiocarbon reservoir correction for the timing of late Holocene settlement of the Elk Hills, Kern County, California. *Journal of Archaeological Science* 33, 1331-1339.

Deevey, E.S., Gross, M.S., Hutchinson, G.E., Kraybill, H.L. 1954. The natural ^{14}C content of materials from hard-water lakes. *Proceedings of the National Academy of Sciences of the USA* 40, 285-288.

Fink, D., Hotchkis, M., Hua, Q., Jacobsen, G., Smith, A., Zoppi, U., Child, D., Mifsud, C., van der Gaast, H., Williams, A., Williams, M. 2004. The ANTARES AMS facility at ANSTO. *Nuclear Instruments and Methods B* 223-224, 109-115.

Geyh, M.A., Schotterer, U., Grosjean, M. 1998. Temporal changes of the ^{14}C reservoir effect in lakes. *Radiocarbon* 40(2), 921-931.

Gillespie, R. 1977. Sydney University Natural Radiocarbon Measurements IV. *Radiocarbon* 19, 101-110.

Gillespie, R. 1997. Burnt and Unburnt Carbon: Dating charcoal and burnt bone from the Willandra Lakes, Australia. *Radiocarbon* 39, 239-250.

Gillespie, R. 1998. Alternative timescales: a critical review of Willandra Lakes dating. *Archaeology in Oceania* 33(3), 169-182.

Hope, J.H., Dare-Edwards, A., McIntyre, M.L. 1983. Middens and megafauna: stratigraphy and dating of Lake Tandou lunette, western New South Wales. *Archaeology in Oceania* 18, 45-53.

Johnston, H., Clark, P. 1998. Willandra Lakes archaeological investigations 1968-1998. *Archaeology in Oceania* 33(3), 105-118.

Kalish, J.M., Miller, G.H., Tuniz, C., Pritchard, J.C., Rosewater, A., Lawson, E. 1997. Otoliths as recorders of palaeo-environments: comparison of radiocarbon age and isoleucine epimerization in Pleistocene golden perch *Macquaria ambigua* otoliths from Willandra Lakes. In: Conference Handbook, Sixth Australasian Archaeometry Conference, Australian Museum, Sydney, 10-13 February 1997.

McCormac, F.G., Hogg, A.G., Blackwell, P.G., Buck, C.E., Higham, T.F.G., Reimer, P.J. 2004. SHCAL04 Southern Hemisphere calibration, 0–11.0 cal kyr BP. *Radiocarbon* 46, 1087-1092.

Macumber, P.G. 1977. The geology and palaeohydrology of the Kow Swamp fossil hominid site, Victoria, Australia. *Journal of the Geological Society of Australia* 25(6), 307-320.

Magee, J.W., Miller, G.H., Spooner, N.A., Questiaux, D.G., McCulloch, M.T., Clark, P.A. 2009. Evaluating Quaternary dating methods: radiocarbon, U-series, luminescence and amino acid racemization dates of a late Pleistocene emu eggshell. *Quaternary Geochronology* 4:84-92.

Miller, G.H., Fogel, M.L., Magee, J.W., Gagan, M.K., Clarke, S.J., Johnson, B.J. 2005. Ecosystem collapse in Pleistocene Australia and a human role in megafaunal extinction. *Science* 309, 287-290.

Olley, J.M, Roberts, R.G., Yoshida, H., Bowler, J.M. 2006. Single-grain optical dating of grave-infill associated with human burial at Lake Mungo, Australia. *Quaternary Science Reviews* 25, 2469-2474.

Reimer, P.J., Reimer, R. 2009. Marine reservoir correction data-base (online, accessed February 2009 at http://intcal.qub.ac.uk/marine/).

Roberts, R.G., Flannery, T.F., Ayliffe, L.K., Yoshida, H., Olley, J.M., Prideaux, G.J., Laslett, G.M., Baynes, A., Smith, M.A., Jones, R., Smith, B.L. 2001. New ages for the last Australian megafauna: continent-wide extinction about 46,000 years ago. *Science* 292, 1888-1892.

Ulm, S. 2002. Marine and Estuarine Reservoir Effects in Central Queensland, Australia: Determination of ΔR values. *Geoarchaeology* 17(4), 319–348.

Weninger, B., Jöris, O., Danzeglocke, U. 2007. Cologne Radiocarbon Calibration and Palaeoclimate Research Package $Calpal07_{Hulu}$ (downloadable from http://www.calpal.de).