ARCHAEOLOGY IN NEW ZEALAND

RADIOCARBON DATING NEW ZEALAND ARCHAEOLOGY: ABSTRACTS FROM DISSERTATIONS AT THE RADIOCARBON DATING LABORATORY, UNIVERSITY OF WAIKATO, 1993-1999

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Abstracts of 3 PhD dissertations and one MSc dissertation produced by students at the Radiocarbon Dating Laboratory at the University of Waikato are presented below. Graduate research at Waikato has focussed upon the radiocarbon dating of New Zealand archaeological contexts, understanding the ways in which the radiocarbon technique can be improved in dating recent periods of time (<1000 yr) and investigating specific problems with dating materials from different radiocarbon reservoirs and sites in a variety of different environments. Copies of these dissertations are held in the University of Waikato Central Library in Hamilton. As usual, they may be used for private research but material within them may not be published without the direct written consent of the authors.

McKinnon, Helen, M. 1999. **Investigation of a hard water effect at Aotea Harbour, North Island, New Zealand.** MSc Dissertation, Department of Chemistry, University of Waikato. 153 pp, 33 figures, 30 tables, 3 appendices.

This dissertation investigates the hard water effect and its influence on reliably dating the New Zealand prehistoric sequence. The term 'hard water effect' results from the addition of ^{14}C-depleted bicarbonate from calcareous rock formations such as limestones, siltstones or mudstones to estuarine, lacustrine and riverine waters. This depleted water serves to dilute the affected radiocarbon reservoir, and influences radiocarbon dates of shellfish species living there by rendering them artificially old. The brevity of New Zealand's prehistory is such that a tremendous onus is placed upon accuracy and precision in radiocarbon dating. The hard water effect may be an important influence on reliable radiocarbon dating of shell from sites with a calcareous hinterland. Since ~75% of radiocarbon determinations from New Zealand archaeological sites are of marine or estuarine shell, a rigorous analysis of the hard water effect at selected sites is overdue. In this dissertation, the hard water effect is investigated at Aotea Harbour, on the west coast of the North Island, New Zealand. Aotea and its environs contain a variety of cultural site types, and the area was probably occupied from the time of first human settlement into the historic period. In addition, the rivers and streams, which enter into the Aotea Harbour, flow through a series of calcareous rock formations.

The results of a literature search on reported examples of this effect suggest that there are three critical environmental factors that predispose sites to hard water. These are; a source of ^{14}C-depleted carbon, low salinity and a long residence time of water to allow uptake of the ^{14}C-depleted carbon. An investigation of the geology, sedimentology and hydrology of Aotea Harbour was undertaken to determine if the three causal factors of hard water were present.

Two methods of investigating a hard water effect using ^{14}C were employed. ^{14}C determinations on modern (living at the time of collection) shellfish from within Aotea Harbour were compared with modern shellfish from an open beach outside the harbour.

Stratigraphically paired samples of shell and charcoal from selected archaeological sites were also dated, and the results compared to calculate a ΔR value. ΔR represents the offset between the local radiocarbon marine reservoir and the average world ocean reservoir as modelled by Stuiver, Reimer and Braziunas (1998). A ΔR value, which deviates significantly from the value of -25 ± 15 yr calculated from historic New Zealand shell samples would imply the existence of a hard water effect, although there are other variables which might be influential, such as the possible inbuilt age of charcoal samples.

^{14}C determinations of modern shellfish were found to be statistically indistinguishable. This suggests that there is a dominance of the tidal flow over river inputs in Aotea Harbour and concomitant absence of a hard water effect. ΔR comparisons did not reveal any significant differences between the ΔR values calculated at Aotea Harbour and the ΔR value for New Zealand. The exceptions were sites that yielded charcoal determinations probably affected by inbuilt age of charcoal. The conclusion from these results is that there is no hard water effect at Aotea Harbour.

A guideline for determining whether a hard water effect is likely to influence radiocarbon results from different archaeological sites is outlined along with avenues of future research.

Petchey, Fiona, J. 1998. **Radiocarbon analysis of a novel bone sample type: Snapper and Barracouta bone from New Zealand archaeological sites.** PhD dissertation, Department of Chemistry, University of Waikato, Hamilton, New Zealand. 245 pp, 69 figures, 48 tables, 6 appendices.

This dissertation investigates the potential of fish bone, specifically barracouta (*Thyrsites atun*) and snapper (*Pagrus auratus*), for routine radiocarbon analysis. Of particular interest to this study is the perceived reliability of bone ^{14}C determinations in the New Zealand archaeological literature. Issues of bone preservation and contamination, dietary fractionation, species differences, and the reliability of different pretreatments are of key importance. Informed, critical assessment of bone determinations in New Zealand is, however, currently limited for a number of reasons. First, there have been no, or few comprehensive tests of bone pretreatment, species reliability or the influence of contamination. Second, confusion has resulted regarding the effectiveness of the varied radiocarbon pretreatments available, due in part to the complexity of some methods. This has been further hampered by the incorrect reporting of fractions isolated for ^{14}C measurement. Third, inadequate sample selection procedures have resulted in burnt bone, sub-fossil bone and severely degraded bone, each with intrinsically different chemistries, being submitted for radiocarbon assay. Fourth, insecure provenance of the sample, or associated samples to be dated, mean that few comparisons of bone reliability could have, or can be made. Fifth, publication of results and procedures have been limited. Finally, there has been limited research into the radiocarbon measurement of bone in New Zealand due to a preconception about the reliability of bone determinations. These uncertainties with bone radiocarbon measurement are addressed in this dissertation.

The sources of $\Delta^{14}C$ to fish are also critical. Bone collagen and its derivatives (*e.g.* gelatin, tripeptides, amino acids) are the most common bone fractions isolated for radiocarbon measurement. For fish, the ^{14}C in collagen is derived either directly, or indirectly via diet, from dissolved inorganic carbon in sea water. A number of uncertainties have previously been identified with the measurement of ^{14}C in marine animals, including the effects of hardwater, depleted carbon from depth, or terrestrial organic carbon. These factors are investigated, and it is determined that their impact on fish bone ^{14}C determinations depend on the immediate environment and the type of fish selected for dating. Both barracouta and snapper occupy predominantly the well-mixed surface waters around New Zealand. Studies of marine shell and snapper otolith carbon from around New Zealand, suggest that hardwater and terrestrial organic carbon are of limited influence. This requires further testing and may depend on the specific dietary preferences of each species. Of particular concern, however, is the upwelling of depleted carbon, especially at the convergence of inshore and offshore waters or at the boundary of two water masses (*i.e.* the Subtropical Convergence). In addition, inbuilt age is often cited as reasons for anomalous ^{14}C determinations. This also appears to be of nominal influence, due in part to the precision of the radiocarbon technique, but also because of the relatively rapid replacement of collagen.

A range of different bone pretreatment and assessment methods are discussed. From this review it is concluded that gelatinisation following a NaOH wash, should remove better than 8% contamination (*i.e.* a maximum error of 42 years in a well-preserved sample of 900 BP material if contaminated by modern carbon). This pretreatment method, in combination with techniques for assessing contamination and collagen preservation, will significantly improve the likelihood of a reliable radiocarbon determination. The use of an appropriate assessment methodology also provides a wealth of information about the sample and site taphonomy.

Snapper and barracouta samples from 7 archaeological sites are analysed. Fourier Transform Infrared (FTIR) spectra, stable isotope values, N% determinations and yield data, obtained prior to and during pretreatment, are presented along with ^{14}C information. Material from Pleasant River, Long Beach, Shag River Mouth, Twilight Beach, Houhora and Rotokura is identified as well-preserved. Bone removed from Tata Beach is of suspect preservation state due to low levels of remaining collagen, and contamination identified in the FTIR spectra of the acid-insoluble fraction.

Radiocarbon results from Tata Beach are, however, variable, and largely inconclusive at the level of precision used. The remaining 6 sites produced reproducible fish gelatin determinations that are statistically indistinguishable from associated marine shell determinations, and in chronological agreement with charcoal samples after calibration using the marine calibration curve of Stuiver and Braziunas (1993), corrected according to the New Zealand reservoir value (ΔR) (Higham and Hogg 1995). Determinations on purified tripeptides do not agree with these results. These are, however, not supported by archaeological evidence or associated ^{14}C determinations on reliable charcoal and shell samples.

An analysis of 46 New Zealand archaeological sites with bone determinations (human, dog, fish, seal, and moa) obtained over a 40 year period is undertaken and a discard protocol applied according to the results of this dissertation. Eleven sites with bone determinations remain after application of the discard protocol. Not all are statistically indistinguishable from associated charcoal and marine shell pairs. Using geographic and climatic information, as well as intra site data, it is apparent that sites with problematic bone radiocarbon estimates are located in high rainfall areas, which have resulted in bones of poorer preservation. This, in combination with inadequate pretreatment (typically an acid wash, or acid/alkali/acid pretreatment) has resulted in some erroneous determinations.

In the light of these results it is suggested that a bone selection protocol, using a range of chemical methods, needs to be implemented in order to identify problematic samples prior to ^{14}C analysis. Further, gelatinisation should be a minimum pretreatment. Bones <1000 years of age should be viewed with caution for radiocarbon dating when less than 40% "extractable collagen" remains, and where contamination is identified in the FTIR spectra of the acid-insoluble fraction. The adoption of complex and expensive biochemical purification techniques is not recommended.

Schmidt, Matthew, D. 1996. **Radiocarbon dating New Zealand prehistory using marine shell.** PhD dissertation, Department of Chemistry, University of Waikato, Hamilton, New Zealand. 200 pp. 73 figures, 42 tables, 2 appendices.

Testing the reliability of marine shell for radiocarbon dating New Zealand prehistory has long been overdue. Though past studies have compared marine shell and charcoal radiocarbon dates from the same context to determine the reliability of marine shell, often the charcoal samples were unidentified. These studies were therefore invalid due to the risk of inbuilt age in the charcoal samples.

This dissertation investigates the reliability of marine shell for radiocarbon dating New Zealand prehistory. Paired charcoal and marine shell radiocarbon ages from rchaeological sites excavated for this study and from already dated archaeological contexts, are compared. In this comparison, two issues are considered. First, factors which can affect the radiocarbon dating of marine shell and charcoal samples. Second, the effect of using either of two marine shell calibration methods in the comparison of marine shell and charcoal radiocarbon dates.

The upwelling and hardwater effects (causing shell ages to appear too old), and the incorporation of organic carbon (causing shell ages to appear too old or too young, depending on the source of the organics) are identified as important variables in dating shell. In the case of charcoal, it is found that although the identification of charcoal samples to twigs of short-lived species has been proposed as a solution to inbuilt age, this may still be a problem for charcoal samples. Incorrect data on the actual life span of a number of trees and shrubs identified as 'short-lived', and decay rates of various floral species after death may still influence charcoal dates.

A critique of the two methods available for calibrating marine shell radiocarbon ages is undertaken to examine the effect of each on age calibration, and in the comparison of marine shell and charcoal radiocarbon ages. The first method involves the application of a fixed reservoir correction (called R), to a marine shell radiocarbon age before calibration on an atmospheric calibration curve. The second method employs a modelled marine curve and a local reservoir value ΔR, and is based on a box diffusion model which simulates fluctuations in $R(t)$ through time. The two main differences identified between each calibration method are: a) a fixed R correction does not take into account changes in $R(t)$ through time whereas the modelled marine curve does, and b) the modelled marine curve provides more defined calibrated age ranges compared to reservoir corrected calibrated marine shell dates due to the smoothness of this curve.

Paired charcoal and marine shell radiocarbon dates from 19 archaeological deposits excavated in this study are analysed. Of these 19 deposits, 14 possess charcoal and marine shell dates which are in chronological agreement after calibration. This is not dependent on the marine shell calibration method used. However, the modelled marine curve is found to produce more defined calibrated age ranges for the post 1500 AD period of New Zealand prehistory, compared to the expanded age ranges observed when using the reservoir correction calibration method. The modelled marine curve is argued to be both precise and accurate in calibrating shell radiocarbon dates for New Zealand prehistory based on four observations. First, the marine shell radiocarbon ages calibrated using the modelled marine curve are more often in agreement with paired calibrated charcoal dates, than marine shell ages calibrated using the reservoir correction calibration method. Second, the modelled marine curve successfully simulates changes in R(t) through time. Third, ΔR values from the New Zealand archaeological sites analysed are in agreement with the current value for New Zealand. Fourth, shell dates calibrated using the modelled marine curve are in agreement with the archaeological evidence in dating the archaeological deposits.

Nine shellfish species commonly found in New Zealand archaeological sites are identified as reliable for radiocarbon dating. Though these species inhabited a variety of environments, this did not affect dating reproducibility between species. Even in locations where limestone strata is prominent, no hard water effect is detected. Charcoal ages are found to be less reproducible than marine shell for dating archaeological deposits. This is probably due to inbuilt age.

Five archaeological deposits where radiocarbon age differences are observed between charcoal and marine shell samples, are found to have been affected by post-depositional disturbance in prehistoric and modern times, and from the incorporation of sub-fossil marine shell.

An analysis of 40 previously dated archaeological sites with paired charcoal and marine shell radiocarbon dates is undertaken. Dubious radiocarbon ages are rejected using a discard protocol based on Anderson (1991), Spriggs and Anderson (1993) and Schmidt (1993; 1996). Eight archaeological sites remaining after application of the discard protocol, show chronological agreement between the charcoal and marine shell dates, supporting the reliability of the shellfish species identified in this study, and use of the modelled marine curve.

In light of the results of the research, the time of colonisation of New Zealand is proposed based on archaeological sites with acceptable charcoal and marine shell radiocarbon chronologies.

Higham, Thomas, F.G. 1993. **Radiocarbon Dating the prehistory of New Zealand.** PhD dissertation, Department of Chemistry, University of Waikato, Hamilton, New Zealand. 238 pp, 44 figures, 26 tables, 5 appendices.

The impact of radiocarbon dating upon chronological studies of New Zealand's prehistory has been limited for several reasons. A long standing tradition of investigating archaeology as ethnology, based on the rich sources of ethnographic data has lessened the apparent need for chronological control. Second, there has been an element of consensus regarding the date of discovery by initial human settlement due to the establishment of a chronology based on tribal traditions. There has been a failure by some archaeologists adequately to implement radiocarbon dating programmes and scientific dating effectively as a research tool. The most important reason, however, is the short span of prehistoric occupation.

This dissertation addresses a number of issues affecting accurate radiocarbon dating of New Zealand prehistoric material with particular reference to errors which restrict the application of high precision dating.

Such errors come from three principal sources - during field collection of the samples, in the measurement of the radioactivity of the sample in the laboratory and in the variation in the amounts of ^{14}C in the atmosphere and the measurement of the half-life. Field errors are common in New Zealand and often reflect post-depositional migration and erosion, and bioturbation and a failure to understand the site's stratigraphy. Errors due to the misreporting of radiocarbon dates and failure to adequately interpret them have also been common.

Accuracy, reproducibility and precision are analysed in the University of Waikato Laboratory. Close statistical agreement is shown in the results obtained from the laboratory's IAEA standard set of measurements. A laboratory error multiplier is calculated using 11 repeat dates of the IAEA C3 standard. Spectral shifts identified in certain standard and sample spectra is investigated and the external standard is found to be artificially influencing the position of the end point of successive spectra. The significance of this upon calculated radiocarbon dates is shown to be insignificant and reproducibility in count rate is maintained even with end point shifts of up to 7 channels.

The three main sample types used in New Zealand archaeological are considered for their contribution to radiocarbon errors. All possess intrinsic problems. Moa eggshell carbonate samples from sites in Otago and Hawkes Bay are investigated for accuracy. These are the first moa eggshell samples dated from cultural contexts. The material is appropriate for the radiocarbon technique, dating the prehistoric event closely and resistant to contamination. The only drawback is its irregular presence in sites.

Contamination in shell and charcoal samples is investigated. Charcoal from Shag Mouth, Pleasant River and Killermont sites is used in a series of physical and chemical pretreatments. It is largely free of contamination with the exception of the Pleasant River site, where adsorption by young carbonates has occurred. All samples possess errors due to rootlet intrusion, although these are negligible in their error.

Shell dating is investigated extensively. Hard water effects are considered at North Otago sites. Dates of modern shell limestone regions at Shag Mouth and Pleasant River are compared with those from near Dunedin. No significant differences are identified. Differences are found, however, in prehistoric dates of shell of a variety of species. The major influencing variables are the immediate environment and the type of shellfish species selected for dating. Shellfish from estuaries which are regularly flushed with tidal waters are likely to give more accurate dates than those which have larger riverine inputs and barrier spits blocking tidal encroachment. Shellfish obtain their carbon from a variety of sources. The proportion of carbon obtained from metabolic carbon and dissolved inorganic carbon utilised in their shell carbonate varies, so their radiocarbon uptake may vary. In an estuary, within which resources from a number of areas are collected, this variety may be manifested in different radiocarbon dates from different shellfish species.

Models for accurate dating using charcoal and shell in the light of different environmental situations are described. Radiocarbon dates measured in the dissertation are considered in their contexts and sites and the initial colonisation of Murihiku is reviewed. A model of rapid colonisation and the short-term occupation of coastal, estuarine sites is presented on the basis of radiocarbon and archaeological variables. Further avenues of research are then examined.