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RADIOCARBON DATING THE PREHISTORY OF NEW ZEALAND.

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CHAPTER 1

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2. ABSTRACT

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.

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CHAPTER 2

INTRODUCTION

"Everything which has come down to us from heathendom is wrapped in a thick fog; it belongs to a space of time we cannot measure. We know that it is older than Christendom, but whether by a couple of years or a couple of centuries, or even by more than a millenium, we can do no more than guess."

RASMUS NYERUP, DANISH ANTIQUARIAN, 1802 (in Trigger, 1989:71).

2.1. INTRODUCTION

Nyerup's words illustrate poignantly the critical power and importance of dating; to order time. Radiocarbon dating has been one of the most significant discoveries in 20th century science. Renfrew (1973) called it 'the radiocarbon revolution', in describing its impact upon the human sciences. Oakley (1979) suggested its development meant an almost complete re-writing of the evolution and cultural emergence of the human species. Desmond Clark (1979) wrote that were it not for radiocarbon dating, "we would still be foundering in a sea of imprecisions sometime bred of inspired guesswork but more often of imaginative speculation" (Clark, 1979:7). Writing of the European Upper Palaeolithic, Movius (1960) concluded that "time alone is the lens that can throw it into focus".

Radiocarbon dating has allowed prehistorians to develop sequences and chronologies and enabled Clark (1962) to write a prehistory of the world, made possible through cross-checked radiocarbon dates. The revolution in dating was felt first, and most importantly in Europe and the Mediterranean, where the early radiocarbon samples were dated and where the need for secular calibration was initially noted (Renfrew, 1973). By comparison, the impact of radiocarbon dating in New Zealand has been softened by the recent arrival of human communities, a well-documented proto-historic period and a short timescale.

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2.2. CHRONOLOGICAL STUDIES IN NEW ZEALAND

Prior to the application of radiocarbon dating, attempts to develop a prehistoric chronology were based principally upon artefact seriation and Maori oral traditions. Some examples of the techniques developed to obtain chronological information are described briefly below.

Chronology was a central tenet of Von Haast's (1874) investigations at the site of Shag Mouth, North Otago and his later interpretations of the antiquity of the moa and its extinction. He proposed that the 'moa hunters' were a vanished palaeolithic race who had preceded the later Maori by millennia. This he established principally through his excavations at Shag Mouth, which in some places yielded a stratigraphic distinction between a lower layer dominated by moa remains and an upper shell midden layer. Von Haast suggested that the moa remains were of considerable antiquity[^]. This view was challenged by Hutton, Curator of the Otago museum, whose views, though based largely upon the excavation reports of Booth, held that the two layers were never separated, and that they alternated in terms of upper and lower. There was no evidence, he wrote, to suggest that the moa remains were more than a century old (Hutton, 1875:107). Booth's excavation reports (in Anderson, 1989b), however, suggested that there was no uniformity in the site's stratigraphy, although moa remains were more common in the lower layers. The issue of relative chronology was resolved after other sites such as Kaikorai Mouth and Moncks's Cave yielded moa bone and shell midden remains in close association (Anderson, 1989). Thus, it became apparent that Von Haast's view was incorrect and that the span of time which separated archaeological layers comprising moa remains and those composed of shellfish and fish remains was not extensive. This finding indicated that the moa hunters were not of great antiquity.

In the late 19th century, much interest was shown in the collection of oral traditions to identify the nature of moa extinctions and then to determine the origins of the Maori people themselves. Best (1915) and Smith (1921) believed that oral traditions, passed down through the generations, could be transcribed verbatim and shed light upon the history of early settlement. These include reference to Kupe, whose date of arrival 39 generations ago would have

[^] Hutton (1875:545) at a meeting of the Otago Institute suggests Von Haast thought the moa became extinct 3000 years ago.

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occurred in 925 AD. Using the same method, Smith (1921) suggested that a migration involving a 'Great Fleet' from the Polynesian homeland of Hawaiki reached New Zealand in 1350 AD. This orthodox view was reiterated in the influential writings of Buck (1949). In terms of the prehistoric sequence, one of the most important traditions alluded to the Maruiwi. This originated on the West Coast of the North Island and described a pre-Maori occupation by the Maruiwi, a backward Melanesian culture which was conquered by the decedents of the Maori. The survivors are supposed to have fled to the Chatham Islands where they became the Moriori (Best, 1916).

This account was investigated on the basis of material culture by Skinner, who believed there was no Melanesian artefact tradition. He and Teviotdale (1932) showed through an examination of the archaeological record, that the material culture of the earliest New Zealanders and Chatham Islanders, was undoubtedly Polynesian (Skinner, 1924). The close affinities they noted between the early cultures of Murihiku and the East Polynesian culture on the one hand, and the Classic Maori phases in Otago on the other, suggested that the unifying factor was undoubtedly Polynesian, not Melanesian.

Skinner's approach involved the collection of artefacts and material remains, undertaken in association with an interpretation of 'culture areas', which were derived principally from ethnographic sources (Skinner, 1921). He was ultimately interested in the classification of artefacts, such as adzes and fish-hooks, in order to compare them with those of other Pacific contexts. By tracing their typological relationships, the pathway of cultural development could be determined. In terms of chronology, this approach was limited because it relied almost exclusively upon comparison rather than upon context and stratigraphy. There had been few excavations which heeded basic stratigraphic principles, which meant that this typological approach favoured by Skinner, and inherited by Duff, involved only the broadest and most general chronological influences. This was later termed "typological unresponsiveness" by Golson (1955:132). Nevertheless, there are important chronological conclusions which can sometimes be made on the basis of artefacts found in archaeological contexts.

The problems of constructing a relative dating method through artefactual change are much influenced by a short chronology. Where sequences are longer and ordered by artefactual and stylistic variation through time, seriation is possible before any radiocarbon dates are obtained. In New Zealand, such markers are few and their exact temporal relationships are blurred. Hjarno (1967), for example, although able to

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propose a typology of fish-hooks in Murihiku, could only divide them into early and late groups.

Studies of incremental and depositional features such as tephra, dune deposition and palaeosol formation have also provided chronological information. Adkin (1948), for example, investigated the relationships of dunes deposited in coastal Horowhenua. He was able to recognise two different dune formations differentiated on the basis of the material found within them. The dunes were formed in a seaward progression. Water-borne pumice and driftwood in one dune located some 200 metres away from another containing material culture and midden remains, suggested to Adkin a temporal difference. Pullar (1959) has outlined the significance of the Kaharoa ash layer in the central North Island for archaeological studies. This layer was dated at 900 bp¹ and provides a prehistoric marker bed of 'known' age around which cultural material may be ordered. Similarly, ash from the Rangitoto eruption of *ca.* 600 bp sealed human occupation at the Sunde site on Motutapu Island, and thereby permitted a cross-check of radiocarbon dating with the tephra layer (Law, 1975). McFadgen (1982) has investigated the water-borne Loiseles pumice (550-715 bp), which was deposited on the eastern North Island coast about the same time as the arrival of early Polynesians. The use of tephrochronological marker beds for dating may involve error if not carefully examined, however. The controversy at the site of Lake Poukawa is one example (chapter 4).

Scientific techniques for investigating prehistoric chronology include obsidian dating, most often by the hydration technique, wherein deposited obsidian builds a hydration layer through the diffusion of water into its surfaces. The hydration rim may be measured using optical spectroscopy and a date for the deposition of the obsidian calculated using two important estimates; the burial temperature and the rate constant, which refers to the rate of hydration expected for the obsidian given the depositional temperature (Aitken, 1990). Leach and Naylor (1981) and Leach, Naesar and Ward (1981) have dated obsidian using nuclear resonance and fission track analysis respectively.

Palynological analysis, in combination with radiocarbon dating, has yielded important information concerning the impact of early Polynesian groups upon the New Zealand environment (McGlone, 1983). Sutton (1987) has used evidence

¹ Now accepted to be *ca.* 700 bp (Lowe and Hogg, 1992).

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of dated charcoal horizons, which he has suggested may be due to Polynesian deforestation, to argue for an early prehistoric occupation.

Mead (1984) and Harsant (1987) have considered the temporal significance of stylistic developments in Maori art, wood carving and ornament manufacture. In the case of ornament forms, for example, early sites such as Wairau Bar contain a variety of East Polynesian type such as whale-tooth units and dentalium necklaces, whereas in later contexts single pendants are more commonly found. In addition, Bain (1985) has shown that there are stylistic differences in rock art motifs found in sites in North Otago and South Canterbury over time.

2.3. THE IMPACT OF RADIOCARBON DATING UPON NEW ZEALAND PREHISTORY

The development of radiocarbon dating in the late 1950's and its application in New Zealand coincided with Duff's (1956) excavation at the Wairau Bar site, near Blenheim. Duff, and Eyles before him, found rich burial remains amid a range of extinct fauna over a wide area of the bar. This encouraged Duff to invoke Von Haast's term 'moa hunter', when describing the occupants of the site (Anderson, 1989). The term was also used to describe their material culture, parts of which paralleled the East Polynesian assemblages found at Maupiti and Huahine on the Society Islands (Emory, 1979) and Hane in the Marquesas (Sinoto, 1979). The radiocarbon laboratory at the IGNS (Institute of Geological and Nuclear Sciences⁺) was one of the few to be built in the immediate aftermath of Libby's discovery of the radiocarbon method (Taylor, 1987) and the first dates calculated for New Zealand were from the Wairau Bar and Takahe Valley sites (Duff, 1956:XII) (Fig. 5a). The former was dated to 940 ± 110 bp (from the Yale laboratory, sample number Y-204) and 730 ± 50 bp (from the Lower Hutt laboratory, sample number NZ-50^{*}). Duff used the traditional evidence of Fleet migration to argue that the moa hunter period of Maori culture was distinct from the later Classic Maori and these dates supported his thesis that the 'moa hunters' were pre-fleet, or pre-1350 AD. Controversy surrounded the dates from Takahe Valley, however, because what was initially interpreted as being the butchery site of a *Megalapteryx* moa yielded a date of 110 ± 60 bp (Duff, 1956). This threw

⁺ Formerly the Institute of Nuclear Sciences, Lower Hutt.

^{*} Anderson (1990) gives the dates as NZ-50 (909 ± 48 bp) and Y-204 (935 ± 110 bp). These dates have been recalculated. Both are from the upper layer of the site.

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Duff's (1956) interpretation of the moa hunter culture, as defined at Wairau Bar, into controversy. He wrote that:

"...the limitations of the (radiocarbon) method for the immediate past are seen in Rafter's attribution of a sample of tussock bedding from Shelter A, Takahe Valley, to 110 ± 60 years from 1955".

ROGER DUFF.1956. The Moa Hunter Period of Maori Culture. p. XII).

Furthermore, bark from totara excavated in the same context as the tussock gave a date of 700 ± 60 bp⁺. Duff suggested this material was from an already old tree. Despite the obvious problems the more modern date dealt to his definition of moa hunter as a culture distinct from the later Classic Maori, he argued that the occupation was post-fleet[@]. The Takahe Valley dates and their interpretation, however, showed the limitations inherent in the definition of the term 'moa hunter'. Duff also pointed to limitations in the radiocarbon method, but it is likely that the errors in the dating of the site were due to archaeological, not methodological error. Golson (1959) proposed the replacement of the term 'moa hunter' because the cultural tradition associated with it was not dependent upon moa hunting *per se*; the moa hunter cultural tradition lasted after the extermination of the moa. Golson (1959) replaced moa hunter with the term "archaic", or New Zealand East Polynesian, and rejected traditional evidence to explain archaeological remains.

Lockerbie's (1959) excavations of a number of sites in South Otago including Pounaweia, Hinahina and Papatowai, showed once again that accurate dating was not straightforward. He submitted a variety of materials for dating, including charcoal and moa bone and in his date list, one can detect the problems of younging in dates of moa bone and the inbuilt age of charcoal. All charcoal dates reported by him were considerably older than moa bone dates from the same context. Lockerbie turned to dendrochronology, using trees growing on top of these sites to calculate a minimum age of occupation.

In 1959, Golson suggested that the early radiocarbon dates had contributed little to clarify the picture of prehistory due principally to imprecision. Trotter (1968) identified the problem of inbuilt age with dates of charcoal by showing that dates of wood

⁺ The Takahe valley dates are given by Anderson (1991) as NZ-51 (tussock) 289 ± 63 bp and NZ-52 (totara bark strips) 857 ± 48 bp. Again, these are recalculated.

[@] The antiquity of the Takahe Valley shelters has been considered by O'Regan (1992) who redated material from the site to ca. 600 bp (NZA-2228 dated to 611 ± 51 bp and NZA-2227 at 628 ± 39 bp).

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charcoal were older than those from other materials (chapter 7) and by the 1970's, wood was being identified prior to dating so that only short-lived species were used. Nevertheless, the problem remains to varying degrees (Anderson, 1991). The principal areas of interest in archaeological dating since the 1970's have concerned the relative benefits of each of the three main sample types, namely moa bone collagen, charcoal and shell (McCulloch and Trotter, 1975; Law, 1984; Anderson, 1991) (chapter 7) and, in particular, the use of shell as a dating material. Large discrepancies were identified between different sample chronologies, which resulted in confusion over which was 'correct'. Anderson (1973) developed a method of dating shell samples using the conchiolin, or organic fraction of the shell, but the early promise was negated by the small fractional size of the organic component in shell samples. Nevertheless, the research of Rafter *et al.* (1972), McFadgen (1982) and McFadgen and Manning (1990) in rigorously analysing the reservoir corrections necessary for accurate shell dating led to improvement. Indeed, Law (1984) has suggested that shell is probably the most useful material for radiocarbon research in New Zealand. Anderson's (1991) evaluation of the radiocarbon dates obtained from New Zealand sites since the inception of the method resulted in the rejection of a large proportion through inbuilt age, contamination and other errors and re-emphasized the crucial importance of careful sample selection for accurate dating.

Why, then, with the apparent failure of methods of relative dating has the impact of radiocarbon dating in New Zealand been limited? The lack of artefactual markers within archaeological sites should make chronologies based on radiocarbon dating more valuable to the prehistorian. Golson (1959) has suggested that poor precision is probably the principal reason. McFadgen (1982) has concluded that standard errors of radiocarbon dates become proportionately magnified within the short chronology and less useful for the archaeologist. It could, however, be argued that this is only part of the problem. There are several other reasons why the effect of radiocarbon dating on the prehistory of New Zealand has been relatively slight.

The characteristic thrust of many investigations into the prehistoric chronology in New Zealand has been to view prehistory as *ethnology*. As shown above, this approach has been influenced principally by the rich tapestry of available ethnographic data, from the period spanning the arrival of Cook, to the presence in the country of European whalers and sealers, to fullscale settlement in the early 1800's with the early ethnographers who recorded the lifestyles of the proto-historic Maori (*cf.* Best, 1916, 1927; Shortland, 1851; Boulton, in Starke, 1986). This information has clearly been a major influence

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in interpreting prehistoric cultural development and its effect has been to reduce the importance of the archaeological record and to stifle the formulation of archaeologically testable hypotheses.

This situation might help in appreciating why radiocarbon dating has neither been understood fully, nor implemented effectively by archaeologists in New Zealand, until recently. With few exceptions, the relationship between laboratory and archaeologist has been that of dater and submitter. Where archaeologists have considered the application and use of radiocarbon dating, there have been important developments, not just for New Zealand dating but for dating in other contexts (Trotter, 1968; McFadgen, 1982; Law, 1984; McFadgen and Manning, 1990; Anderson, 1991). Too often, however, archaeological radiocarbon dating has been ill-considered. For many years, the Lower Hutt laboratory provided a free dating service. Yet archaeological contexts have not been *rigorously* dated, the majority of sites being dated on the basis of only one or two determinations, too few for proper conclusions. Law (1981) urged archaeologists not to abuse the free service and argued that radiocarbon dating was not a tool that would accurately test issues of contemporaneity unless "a lot of dating is done" (Law, 1981:232). This is unfortunately true but less so is his suggestion that, "the nature of the process is such that it is not likely that any amount of dating can prove that the real time extent of occupation of a site is less than 200 years" (Law, 1981:232). He encouraged archaeologists to seek a spectrum of dates from related sites, rather than to concentrate on one. Apart from sites considered in detail in this dissertation, Foxton (10) and Hawksburn (12) have provided the largest number of acceptable dates (Anderson, 1991). Both were investigated in the past twenty years. There are also many determinations from the Wairarapa sites in addition to this (Leach and Leach, 1971, 1971b; Anderson, 1991). However, the usefulness of the radiocarbon data from these, and other sites, is restricted by uncertain sample identification in the case of charcoal. Few date lists have been published. This has resulted in a lack of use of the radiocarbon record[#]. Where date lists have been presented, there has often been a lack of critical analysis and a tendency to accept dates without due consideration of their validity (Shutler, 1980). Recently, radiocarbon dating has become a commercial operation for both New Zealand laboratories (IGNS, Lower Hutt and Radiocarbon Laboratory, University of Waikato). Costs have tended to limit the number of samples dated but have ensured more thought and planning goes into dating and sample submission.

[#] In appendix 5 of this dissertation, all University of Waikato radiocarbon dates from New Zealand archaeological sites are listed along with site names and contexts, submitter reports, dilution ratios, $\delta^{13}\text{C}$ measurements and sample type and identification. This list will be published in future (Higham and Hogg, in prep.).

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Anderson (1991:767) has suggested that there has been a broad consensus since the early 1900's on the major chronological question, that of date of discovery and settlement. Dating has therefore never been *central* to archaeological investigation and the accepted chronology has stultified thinking on other explanations (Anderson; 1991).

Finally, and perhaps most importantly, as McFadgen (1982) has suggested, the short chronology has restricted the effectiveness, importance and impact of radiometric dating. Dates with standard errors of $\pm 80 - 100$ radiocarbon years are of little use to archaeologists seeking answers to prehistoric chronological problems within a timeframe which is probably no more than eight centuries. Regional differences in geological, climatological and ecological variables, and their different adaptive responses mean that often only very general conclusions may be drawn regarding culture change and evolution in New Zealand.

The radiocarbon specialist and the archaeologist, then, inherit the problems of brief prehistory and the need for a refined timescale. In considering such issues, many areas of research and investigation remain. The radiocarbon technique as applied to short-timescale problems may be improved in terms of methodology and technology in the laboratory on the one hand and the collection of samples in the field on the other. The principal developments of radiocarbon dating in the past 10 years are the improvement in levels of precision (Liquid Scintillation counting and gas proportional) and in dating small size samples (Accelerator Mass Spectrometry - AMS). These have yet to be widely applied in New Zealand.

This is much to be regretted, because New Zealand is unique in that communities with a long involvement in tropical horticulture underwent a rapid adjustment in their novel, temperate habitat. Given the brevity of the sequence of human occupation here, what prehistoric issues may be considered and investigated with profit?

One is the date of initial settlement. Recent research has indicated that the date of first colonisation of New Zealand is later than hitherto conceded (Anderson, 1991; Irwin, 1992). Sutton (1987) had suggested that New Zealand was occupied before 800 AD. This was based on Kirch's (1986) new model of prehistory in the Hawaiian islands and its repercussions for models of Pacific colonisation. Anderson (1991) presented a detailed re-analysis of the radiocarbon evidence in New Zealand which pointed to a later date of colonisation and

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therefore a much shorter timespan within which to accommodate cultural adaptation and change.

Radiocarbon dating using the latest techniques and applied to carefully selected material from secure contexts has the potential to choose between such alternatives, as well as to consider other important issues. These include the initial exploitation of different areas of the country. Was settlement initially confined to the warmer northern districts with later penetration of the south? The prehistoric status of individual sites can be considered. Were the large early estuarine and river mouth sites of the South Island occupied by sedentary communities, or was occupation brief and seasonal? Were they re-occupied throughout the prehistoric period, or abandoned after a time? Were sites in close proximity to each other occupied contemporaneously, or were they occupied in succession? Are stratigraphically defined layers in sites separated in time, or do they represent short-term adaptation devoid of an hiatus?

2.4. OBJECTIVES AND AIMS OF THIS RESEARCH

A number of variables influence the ability of the archaeologist to obtain accurate answers to these questions. This dissertation addresses certain of the most important. The major issues and objectives are set out below within a description of each chapter. Because of the brief prehistoric period the application of *higher precision* dating to New Zealand archaeological material is long overdue. This is an underlying theme throughout this research. To achieve this, the investigation of all errors contributing to the accuracy of radiocarbon dates must be evaluated. Because radiocarbon dating possesses multiple sources of error, generated both within the laboratory and in the field, it is crucial to examine rigorously the baseline error values contributed by each.

A short background review of the technique of radiocarbon dating and the Liquid Scintillation method practised at the University of Waikato laboratory is given in chapter 3. The method of date calculation is described and the statistical tests used to compare different determinations are mentioned.

Because radiocarbon dating in itself is non-archaeological, it is important to consider the theoretical basis for dating prehistoric material. This is investigated briefly in chapter 4. Sources of error contributing to archaeological fieldwork and sample excavation and collection are discussed. The material used in

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experiments in this dissertation comes from 8 sites in New Zealand. The archaeological excavation of them and the chronological questions addressed at each site are described in chapter five.

New Zealand archaeological dates, and indeed any dates, contain errors from three major sources; those associated with counting statistics, experimental and laboratory techniques; those concerned with the sample - its collection, pretreatment and preparation; and finally, errors and uncertainty within the measurement of the half-life of ^{14}C and the variation in the concentration of ^{14}C in the atmosphere (Pearson, 1983). In chapter six, errors resulting from the first category are considered. The limits of precision in the Waikato laboratory and the requirements for dating in the short timescale of New Zealand prehistory are examined. The major sources of error which contribute to routine radiocarbon dating including benzene purity, isotopic fractionation, ^{222}Rn contamination and loss of sample benzene are investigated. A laboratory error multiplier is calculated as a measure of laboratory reproducibility. The most effective counting requirements for New Zealand archaeological samples are determined using data generated from spreadsheets. Most importantly, the critical effects of sample size and counting time upon precision for New Zealand archaeological samples and the optimal number of samples needed to solve chronological problems are presented.

The relative potential and error inherent in the three main sample types (charcoal, shell and bone) used in New Zealand archaeological dating is examined in chapter seven. Errors associated with sample types are analysed and one material not used before is investigated. Moa eggshell carbonate, hitherto dated in very small numbers from natural deposits, is examined as a material for radiocarbon dating. Analogous studies conducted overseas suggest eggshell is an excellent material, which survives well *in situ*, is mineralogically stable and dates the event closely.

In chapter eight, errors resulting from sample contamination in New Zealand archaeological material are considered. Sources of contamination and pretreatment methods are currently major issues in radiocarbon dating. It is becoming more obvious that contamination is often a serious source of error. It is crucial to obtain the indigenous sample carbon if accuracy and precision is to be maintained. The extent of contamination in New Zealand archaeological samples is an important avenue of enquiry because so little is known about it.

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Shell and charcoal material from six New Zealand sites is used in experiments to remove different sample fractions for dating to investigate specific contaminants.

The prehistoric Maori reveal a widespread preference for coastal settlement, although seasonal and regional variables also encouraged inland occupation. Many coastal sites include extensive shell middens and shell has often been used in dating prehistoric deposits. In chapter nine, its accuracy and reproducibility is investigated. Traditionally, shell dates have been viewed as being variable. Some shellfish dates are considered erroneous due to the effects of upwelling or hard water and these possibilities are investigated at two sites in North Otago using dates of modern and prehistoric shellfish. The marine reservoir effect and the ΔR correction value (McFadgen and Manning, 1990) is considered using a suite of paired sample dates from Shag Mouth and Pleasant River in North Otago and at Awaroa Inlet near Nelson. Variation in dates of different species of shellfish from the site of Pleasant River is investigated using a model of differential selectivity of carbon, and hence ^{14}C , between species within an estuarine setting. The validity of dating shell using higher precision is discussed in the light of the conclusions of these studies.

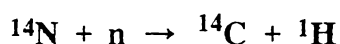
In chapter ten, the results are considered and discussed, and conclusions presented. The radiocarbon dates obtained are reviewed and considered in their archaeological contexts. The large corpus of new dates from prehistoric sites resulting from the technical tasks described above are used to elaborate upon a model of prehistoric settlement. The importance of date calibration is considered and problems are evaluated. Avenues of future archaeological dating research are described.

CHAPTER 3

RADIOCARBON DATING

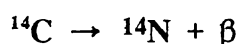
3.1. INTRODUCTION

The basis of the radiocarbon method is well known. It is based on the rate of decay of the carbon isotope ^{14}C , formed in the upper atmosphere through the effect of cosmic rays upon nitrogen 14. The reaction is:



According to Aitken (1990:262), thermal neutrons form within the atmosphere at the rate of 2/sec per cm^2 of the earth's surface, resulting in an annual production rate of 7.5 kg per annum. The ^{14}C formed is rapidly oxidised to $^{14}\text{CO}_2$ and enters the earth's plant and animal lifeways through photosynthesis and the food chain, though it varies in its rate of dispersal (Gillespie, 1982:1). Libby, Anderson and Arnold (1949) first discovered that ^{14}C decays at a constant rate. They measured the half-life ($t_{\frac{1}{2}}$), or period over which half the ^{14}C present in a sample decays, at 5568 years. This became known as the Libby half-life. Later measurements indicated this figure was *ca.* 3% too low and a more accurate half-life was 5730 years (the latter is used to calculate the "New Age" as opposed to the "Libby age" in this dissertation).

As ^{14}C decays it emits a weak beta particle (β), or electron, which possesses an energy of 160keV. The decay can be shown:

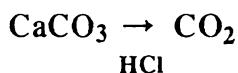
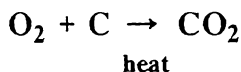


There is a quantitative relationship between the decay of ^{14}C and the production of a beta particle. The decay is *constant* but *spontaneous*. That is, the probability of decay for an atom of ^{14}C in a discrete sample is constant, thereby requiring the application of statistical methods for the analysis of counting data.

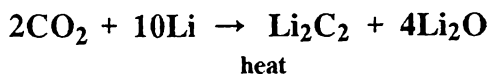
3.2. LIQUID SCINTILLATION COUNTING OF BENZENE

3.2.1 BENZENE SYNTHESIS

The method of ^{14}C counting used by Libby and his co-workers involved measuring radioactivity using modified geiger counters. The next development in counting technology was the conversion of carbon samples to CO_2 gas for measuring in gas proportional counters. In the early 1950's, Liquid Scintillation counting was developed. This method is used in radiocarbon dating investigations described in this dissertation. The sample carbon is first converted to a liquid compound, most commonly benzene (C_6H_6), because of its high carbon fraction. Benzene is formed from the original carbonaceous sample in a series of chemical conversions. The carbon is first oxidised to CO_2 gas, either by hydrolysis (for carbonates), or combustion (for organic materials):



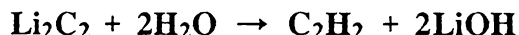
In a typical Waikato run, all organic materials were combusted in a silica tube in two oxygen streams. The gases were passed over heated CuO placed at the end of the silica tube to complete the oxidation of CO , NO , N_2O and NO_2 and also of tar substances. The CO_2 was then purified using a chain of chemical reagents; AgNO_3 and $\text{Hg}(\text{NO}_3)_2$ to precipitate halogens, and the oxidising agents KI/I_2 and $\text{K}_2\text{Cr}_2\text{O}_7$ to remove nitrogen and sulphur compounds. Silica gel and EtOH/N_2 (-80°C) traps removed any water remaining in the sample (Hogg, 1982:35). The purified CO_2 was then reacted with molten lithium in a stainless steel reaction vessel, using a furnace with temperature set at 750°C . Upon melting the temperature was reduced to 550°C * *in vacuo*:



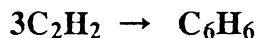
This reaction was first described by Barker (1953), who developed the reaction using lithium instead of barium, and later improved by Polach and Stipp (1967). For a 3 ml

* The temperatures given in this section are those of the furnace, not the reaction itself.

reaction, using *ca.* 7 litres of CO₂, 1.5 sticks of Li were used (weight of 1 stick=*ca.* 11 g, so *ca.* 17g of lithium was used). The CO₂ was bled through a saunders valve onto the molten Li where it was converted to Li₂C₂. The carbide was heated to *ca.* 800° C and pumped for 30 minutes to remove any unreacted gases and complete the carbide formation (Gupta and Polach, 1985). The lithium carbide was then allowed to cool and hydrolysed to C₂H₂ (acetylene):



The acetylene was purified by passing through a phosphoric acid bath to remove ammonia compounds, and two EtOH/N₂ (-80°C) traps to remove water vapour. Finally the acetylene was trimerised to benzene using a silica-alumina vanadium activated catalyst at about 5° C (cooled with water and ice):



Benzene was then driven off the catalyst at 100° C and collected under vacuum at -65±2° C. The benzene was transferred to a glass sample tube and a constant amount of air added after which the sample tube was flame sealed to await counting.

The catalyst column was regenerated by flushing with air at 600° C and then subjected to active pumping for 60 minutes.

This sequence of reactions requires a high degree of operator skill because of the complexity of the equipment and the nature of the reactions themselves. It is important that a standardised routine is followed carefully and consistently to ensure that samples are completely transferred from one operation to the next so that yields remain high and there is no cross-contamination of successive samples.

3.2.2. BETA COUNTING

Sample benzene is usually left for 3 - 4 weeks to allow any ²²²Rn (radon) within it to decay. ²²²Rn emits α and β particles, the latter with a decay energy of 5.587 meV. This decay interferes with the ¹⁴C spectrum, raising its count rate. Its short half-life of 3.82 days, however, means that it can be eliminated with time (CRC Handbook of Chemistry and Physics, 1983). ²²²Rn will significantly affect older sample count rates because of the higher ratio of non-sample counts it will contribute. Samples close to modern are less significantly affected.

The synthesized benzene is transferred into high-purity synthetic silica "Waikato" counting vials (Hogg and Noakes, 1992:394-401). The vials vary in size according to the weight of the sample benzene. The 5 ml vials are the largest and contain *ca.* 4.5 grams of benzene, 3 ml vials hold *ca.* 2.6 mls of benzene (Fig. 3.1) and 0.75 ml vials hold 0.75 grams of benzene. A space is left at the top of each vial so the liquid does not come into contact with the stainless steel stopper and O-ring, which seals each vial. 0.35 ml vials, or mini-vials (Hogg, 1992) are used for smaller sized samples. In the 0.35 ml vials, samples as small as 120-240 mg of carbon can provide dates with standard errors of *ca.* ± 120 radiocarbon years, which are useful for older material but are rather too imprecise for dating samples close to modern.

Prior to benzene loading, a proportion of scintillator is added, depending on the size of

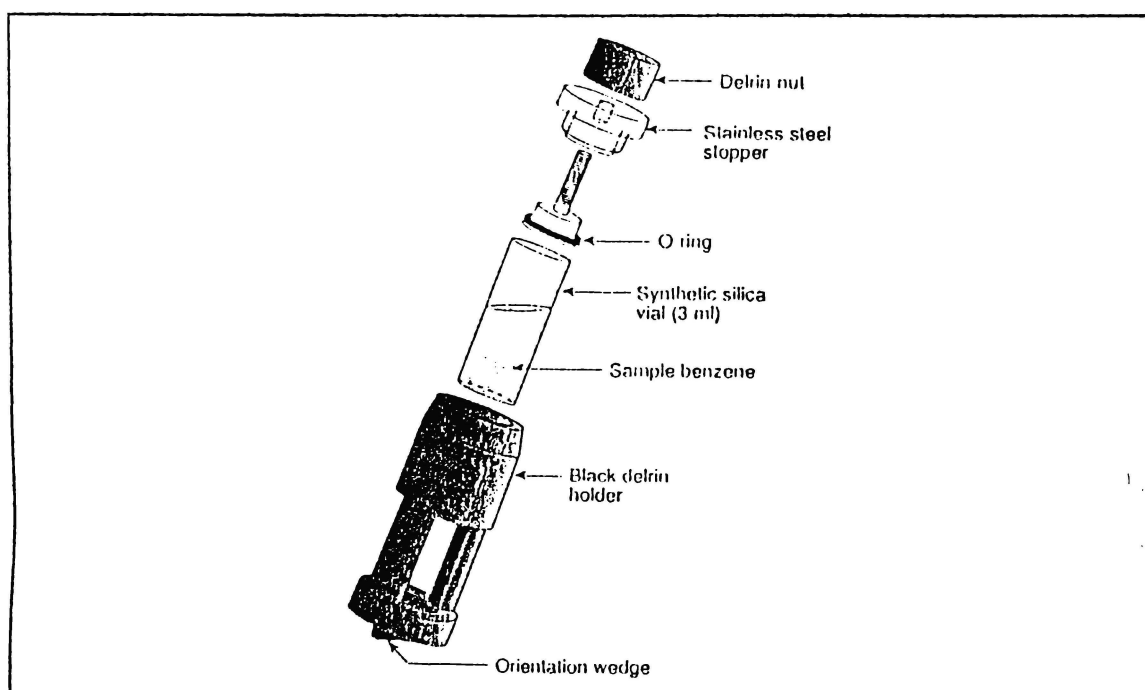


Figure 3.1. Synthetic silica Liquid Scintillation counting vial (after Hogg, 1992).

the sample (see chapter 6 for details). The scintillator used at Waikato is butyl-PBD[^] (Polach, Gower, Kojola and Heinonen, 1983). The scintillator molecules trap beta decay particles from the sample and convert their energy to light. The sealed vials are weighed accurately and then allowed to sit while the scintillator dissolves into the benzene. The vial and its counting cocktail is then transferred into one of four LKB-

[^] t-butyl-PBD is 2-(4-*tert*-butylphenyl)-5-(4-biphenyl)-1,3,4-oxadiazole. (C₂₄H₂₂N₂O).

Wallac 1220 Quantulus spectrometers and allowed to cool and dark adapt prior to counting.

The essential electronic components of the Liquid Scintillation counter, according to Gupta and Polach (1985), are multiplier phototubes (MPT's), high voltage supply, signal preamplifiers, pulse and summing amplifiers, coincidence logic, timer and scaler (Gupta and Polach, 1985:50). Put simply, the Liquid Scintillation counter electronically measures the pulses of light generated from photon emissions. The MPT's register an electronic pulse proportional to the energy of a particular beta decay when a photon or light particle is emitted within the benzene cocktail. The anode current generated from an MPT, then, is a function of the level of radioactivity (Horrocks, 1974). The Quantulus counters used in the Waikato laboratory represent the most electronically advanced and optimised instrument for the counting of low-level radioactivity.

The sample benzene vial is placed into a tray in the counter and its data (sample laboratory number, vial number, counting requirements) entered into the laboratory computers. A copper piston lifts the vial into the counting chamber. The chamber is dominated by a large lead shield which protects the sample from external radiation. Within the lead shield are housed the MPT's, which sit on either side of the sample vial (Fig. 3.2). If a beta pulse is recorded in both MPT's, within a pre-set time threshold, usually *ca.* 25 nanoseconds, it is considered a simultaneous pulse and recorded as a coincident count. Coincident and anti-counts are recorded, but only the former are used for age calculation (Gupta and Polach, 1985). In this way, pulses resulting from non-sample sources are able to be rejected. Total count time and count rates are recorded for later data recovery and date calculation.

Some of the errors which can be associated with coincidence counting include optical cross-talk, line noise, radio frequency noise, after pulse decay, chemiluminescence, static induced noise and cosmic radioactivity (Gupta and Polach, 1985). In the Quantulus spectrometer, the majority of these errors have been reduced. Optical cross-

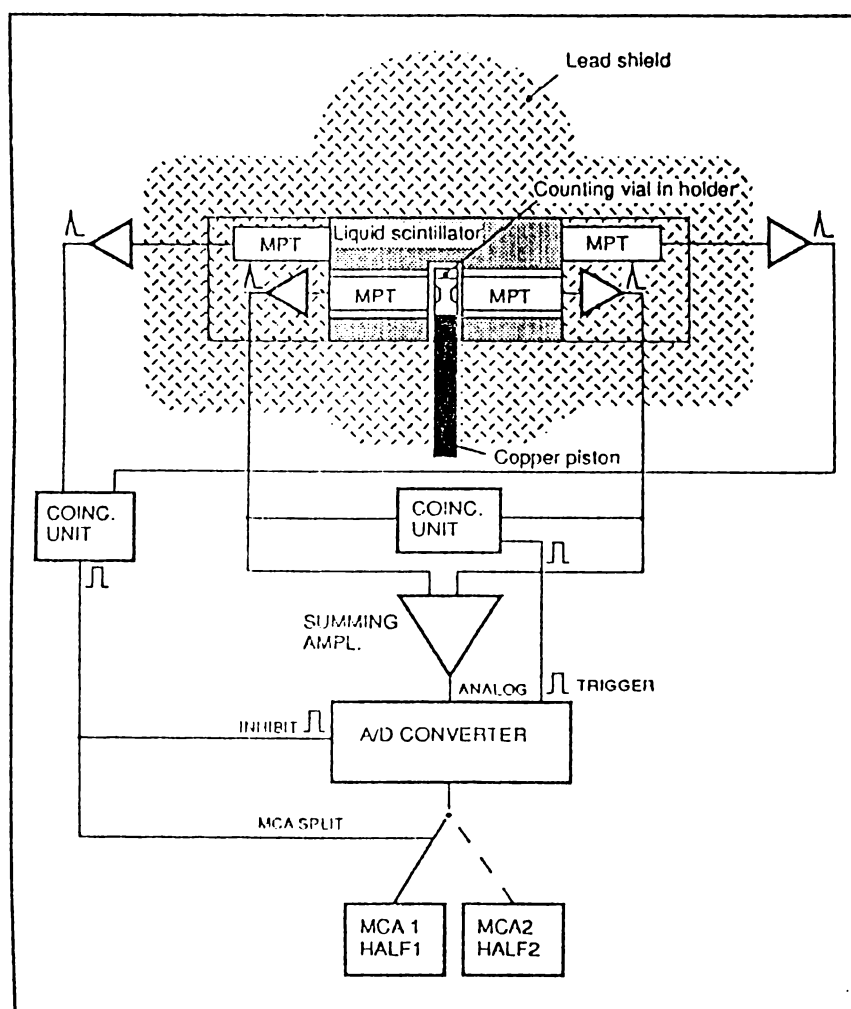


Figure 3.2: The Quantulus counter setup.

talk describes the situation when two MPT's are opposing each other and an event occurring in one initiates a pulse in the other (Noakes, 1977). Ionising radiations may occur in either MPT due to interactions between the molecules of the tube material and surrounding radiation. This may occur most obviously when there is no counting vial in the chamber, or when the vial is small enough so that the MPT's view of each other is not totally eliminated. Butterfield and Polach (1983) and Gupta and Polach (1985) have described methods used to reduce optical cross talk in Liquid Scintillation counters, both by optimising and refining electronic circuitry to enable differentiation between sample and non-sample events and by masking areas in the counting chamber to reduce reflection. Vial design is an important method of reducing cross-talk. By designing vials and holders which minimise the view of opposing MPT's to each other, cross-talk is lessened.

Line noise refers to variation in voltage feed to the counters. This can be reduced through electronic transformers and uninterruptable power supplies which ensure voltages remain stable. Stability in voltage supply is crucial because of the relationship between electronic particle detection and the energy of the decay event. At the Waikato laboratory, a UPS (uninterruptable power supply) unit ensures that counting is not affected by power cuts or surges.

Radiofrequency noise refers to interference from lights and switches in the vicinity of the counter which may be recorded within the counter circuits. Again, this can be reduced through electronic modification.

After pulse decay refers to the generation of secondary pulses caused by a buildup of positive ions near the surface of the MPT's during counting, caused by bombardment of electrons. This effect can be reduced by programming a 'dead' time after each sample pulse is recorded (Gupta and Polach, 1985:56).

Chemiluminescence describes the generation of photons as a result of chemical reaction producing excited molecular states, mimicking the properties of the scintillator. Photon emission from chemiluminescence is therefore not associated with beta decay. According to Gupta and Polach (1985), the use of appropriate scintillators is crucial to reduction of chemiluminescence in low level counting. t-butyl-PBD is one of the most useful scintillators because count rates of benzene samples containing it exhibit greater counting stability than others when impurities are contained in the cocktail (Polach *et al*, 1983). Chemiluminescence is also related to benzene purity; the fewer impurities in the sample benzene, the less is the chemiluminescence.

Static induced noise refers to the build up of static electricity through friction generated from the movement of vials throughout the counting system. Earthing of vials and holders and an ionising unit which the vials move past are used to remove static electricity prior to counting.

Finally, natural atmospheric radioactivity may affect count rates. This is reduced through shielding of the counting environment. This may be passive or active shielding. The passive shield consists of a massive 650 kg lead housing (Fig. 3.2) incorporating copper and cadmium layers to shield the counting chamber from external radiation. The term "active shielding" describes an electronic anti-coincidence guard which is situated adjacent to the immediate surrounds of the MPT's and chamber. It consists of two additional MPT's called the guard MPT's which view into a liquid

scintillator forming a cylindrical casing around the counting chamber. Ionising radiation from external sources passing through the scintillator leaves excited atoms and molecules in it which are seen by the guard tubes. If an ionising event is recorded simultaneously in the guard and sample tubes, it can be rejected as a background count, probably originating from external stimuli (1220 Quantulus Instrument Manual, 1987). All anti-coincident pulses are recorded as sample pulses, unless they are rejected for other reasons (for example, they may not be seen by both MPT's within the preset time threshold).

Coincident and anti-coincident pulses are recorded using twin multi-channel analysers, or MCA's. The MCA's are software controlled to provide complete flexibility in data acquisition. For example, under normal counting conditions, coincident pulses in both MPT's are summed and coincident pulses recorded in both guard and sample tubes rejected as background counts.

The Quantulus spectrometer thus provides multi-channel analysis of all spectra. Each pulse is converted to the MCA through a logarithmic analog to digital converter which relates each decay event to one of 1024 channels representing log energy, on a scale of 0 - 2MeV. Guard and sample detector, coincident and anti-coincident pulses and spectra can be analysed by software. The logarithmic conversion amplifies the spectra, spreading the data and enabling greater distinctions to be drawn between the different low energy isotopes. A ^{14}C spectrum is created by the total number of counts and energies recorded in each channel and software allows windows of interest to be selected using upper and lower discriminators (Fig. 3.3). This is termed 'windowless counting' and enables the user to select the window width within which the spectrum of the measured isotope is situated (see Polach *et al.*, 1983). In the Waikato laboratory, windows from channel 100 to 550 are usually selected because they embrace the majority of the ^{14}C spectrum and avoid higher energy ^{222}Rn counts and lower energy ^3H (tritium) counts. The exact choice may vary depending on counters and vial holder material (Fig. 3.3). The ^3H spectrum overlaps the ^{14}C spectrum and contributes to its overall count rate, but using Hi bias control its influence is reduced at the expense of lower energy ^{14}C events (1220 Quantulus Instrument Manual, 1987).

The Quantulus possesses an external standard (^{226}Ra) which is presented at the base of the counting vial for a set time each cycle in routine dating. The purpose of the external standard is to measure the Spectral Quench Parameter of the External Standard (SQP(E)). The SQP(E) is the end point of the external standard spectrum and its

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measurement shows the degree to which the sample is quenched (this is described in chapter 6).

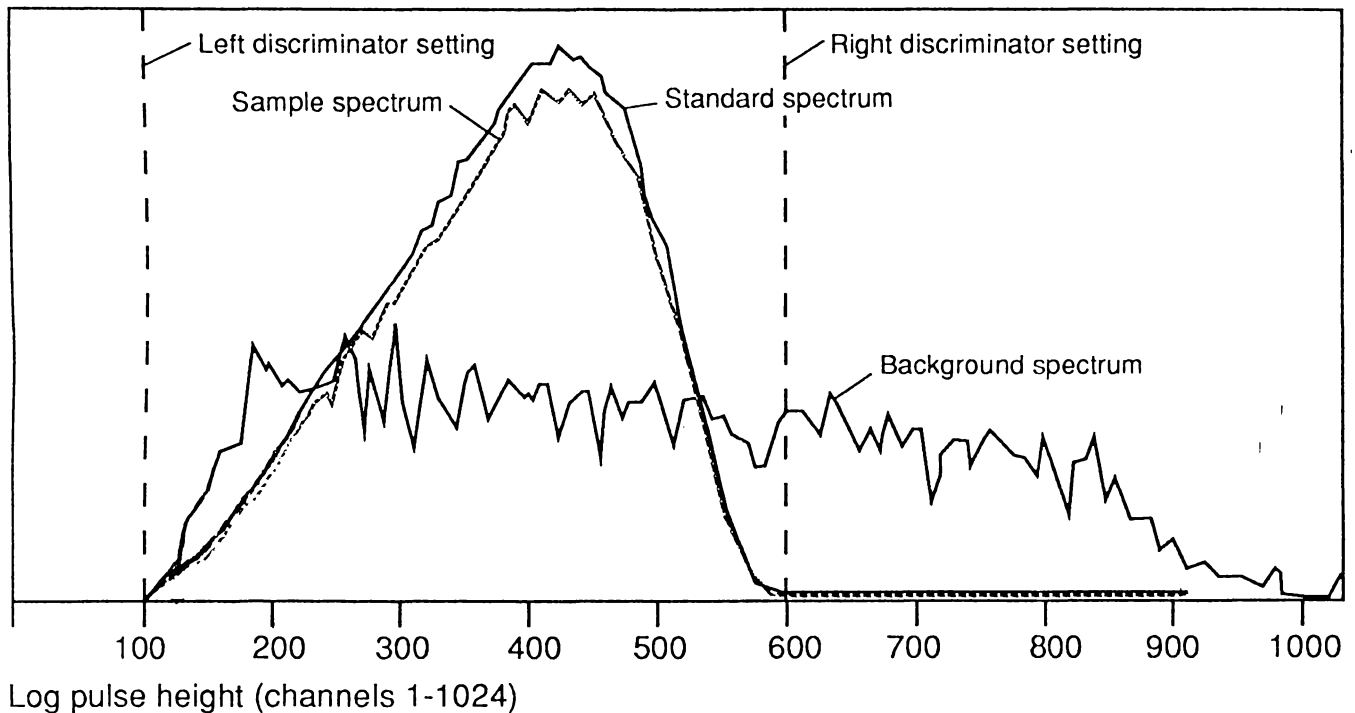


Figure 3.3: Typical set of spectra measured in a Wallac 1220 Quantulus counter. Windows 100 - 600 are selected using left and right discriminators. None of the 3 spectra possess the same scale, the standard spectra is represented by 2369 counts per channel, the sample spectra is 390 counts per channel and the background is 9 counts per channel.

3.3. DATE CALCULATION

A radiocarbon date is calculated through careful measurement of the residual activity remaining in a sample compared with modern and background count rates.

The principal standard at the Waikato laboratory is ANU sucrose. This is an internationally accepted secondary radiocarbon standard. NBS* Oxalic Acid 1 is the primary radiocarbon reference standard. Ninety-five percent of the activity of 1950 Oxalic Acid is equal to the measured activity of the absolute radiocarbon standard which is 1890 wood, growing prior to the fossil fuel effects of the industrial revolution and

* National Bureau of Standards.

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corrected for decay to 1950. Thus 1950, is year 0 BP by convention in radiocarbon dating. Total count rates obtained from modern standards, backgrounds and samples are normalised for benzene weight, dilution and isotopic fractionation (Gupta and Polach, 1985:113) and $\delta^{14}\text{C}$, which is the measurement representing the depletion in sample carbon 14 is measured by:

$$\delta^{14}\text{C} = \left(\frac{A_{\text{sn}}}{A_{\text{on}}} - 1 \right) 1000\text{‰}$$

Where A_{on} is the activity of the modern standard in counts per minute (cpm) and A_{sn} is the activity of the sample being measured (cpm). Conventional ^{14}C ages before present (in this work; bp or BP- before 1950) may be calculated using the following formula:

$$t = -8033 \ln(A_{\text{sn}}/A_{\text{on}})$$

Where -8033 represents the mean lifetime of ^{14}C (Gupta and Polach, 1985; Aitken, 1990). If the reservoir corrected age calculated is within the past 200 years, it is termed 'Modern' (Stuiver and Polach, 1977:362). If a sample age falls after 1950, it is termed greater than Modern, or >Modern. Percent modern (%M or pMC - 'percent modern carbon'), a measurement used often in this dissertation is calculated using:

$$\%M = 100 \times A_{\text{sn}}/A_{\text{on}}$$

This is simply an expression of the ratio of the net modern activity against the residual normalised activity of the sample, expressed as a percentage.

All samples measured in this dissertation are corrected for natural isotopic fractionation. Craig (1953) first identified that certain biochemical processes alter the equilibrium between the carbon isotopes. During photosynthesis for example, ^{14}C is not taken up as readily because the lighter isotopes are favoured, and so terrestrial plants possess a lower activity than the atmosphere by 3-4% (Aitken, 1990). There are two major isotopes of carbon, ^{12}C (98.89%) and ^{13}C (1.11%). If isotopic fractionation occurs in natural processes, a correction can be made by measuring the ratio of the isotope ^{13}C to the isotope ^{12}C in the sample being dated. The isotopic composition of the sample being measured is expressed as $\delta^{13}\text{C}$, which represents the parts per thousand difference (‰) between the sample carbon 13 content and the content of the international PDB®

@ PDB stands for Pee Dee Belemnite, one of the most important NBS standards. This is a belemnite from the Pee Dee formation in the eastern US.

standard carbonate (Keith *et al.*, 1964; Aitken, 1990). A $\delta^{13}\text{C}$ value, then, represents the ‰ deviation from the PDB standard.

$\delta^{13}\text{C}$ values were obtained using a VG Micromass 602C mass spectrometer¹. The standards used were W.L.S (Waikato Limestone Standard $\delta^{13}\text{C} = -4.5\text{‰}$ (Hendy, pers. comm.[^])), cross-checked using an in-lab Kapuni gas standard ($\delta^{13}\text{C} = \text{ca. } -14.5\text{‰}$). $\delta^{13}\text{C}$ values were calculated using:

$$\delta^{13}\text{C} = 1.063(\text{M45}) - 0.034(\text{M46}) - 4.50$$

All radiocarbon dates calculated are based upon the recommendations outlined by Stuiver and Polach (1977). Counting times, $\delta^{13}\text{C}$ values, $\Delta^{14}\text{C}$ values, Libby ages and 'New Ages' are given. In chapter 9, modern shell dates of *ca.* 108‰M are converted to $\Delta^{14}\text{C}$ measurements. $\Delta^{14}\text{C}$ is a value commonly used in oceanographic research (Stuiver and Polach, 1977) and is defined by:

$$\Delta = \left(\frac{A_{\text{SN}}}{A_{\text{abs}}} - 1 \right) 1000\text{‰}$$

Where A_{SN} is the normalized activity of the sample and A_{abs} is the absolute international standard activity corrected for decay between 1950 and the year of actual counting (Stuiver and Polach, 1977:355).

Some samples were diluted due to small size. Gas dilutions were carried out using 'dead' CO_2 (gas from the Kapuni natural gas field, with no residual radioactivity*). Ages are rounded off after Stuiver and Polach (1977) and Gupta and Polach (1985) with ages rounded to the nearest multiple of 10 and errors to the nearest multiple 5 up. All conventional ages, $\Delta^{14}\text{C}$, ‰Modern and $\Delta^{14}\text{C}$ values are summarized in the appendices (appendix 1).

It is often useful in radiocarbon dating to ascertain the statistical relationship between a suite of dates. Statistical tests used in this dissertation follow closely those of Ward and Wilson (1978). Radiocarbon dates are compared using either case 1 or case 2 situations. Case 1 statistics are used when the series of dates originate from material likely to be same age, or from the same piece of material. Case 2 is used when the exact

¹ M46 ($\text{C}^{12}\text{O}^{16}\text{O}^{18}$) and M45 ($\text{C}^{13}\text{O}^{16}\text{O}^{16}$).

[^] Dr. C. Hendy, Department of Chemistry, University of Waikato, Hamilton, New Zealand.

* Hogg (1992) identified a signal in the Kapuni gas used in the dilution of CO_2 samples. A correction is now applied to compensate for this residual activity.

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relationship of dates to each other is not known. In both situations, the pooled mean (A_p) is calculated:

$$A_p = \left(\sum_{i=1}^n A_i / E_i^2 \right) / \left(\sum_{i=1}^n 1 / E_i^2 \right)$$

(Equation 1).

Where A_i , $E_i \dots n$ are a series of radiocarbon determinations (A) and standard errors (E). The test statistic (T) is then applied using:

$$T = \sum_{i=1}^n (A_i - A_p)^2 / E_i^2$$

(Equation 2).

The value of T may be entered ($n-1$) in the chi-square distribution tables in order to establish its significance. In this dissertation, all statistical tests are applied at $P=0.05$, that is, the probability confidence limits are 95%. Given a case 2 situation, the corresponding value of T is termed T' . The variance ($V(A_p)$) can be calculated if the date series are shown to be statistically indistinguishable:

$$V(A_p) = \left(\sum_{i=1}^n 1 / E_i^2 \right)^{-1}$$

(Equation 3).

According to Ward and Wilson (1978:23), $V(A_p)$ is the variance of the mean of the group of observations, not the variance of the group of determinations.

An example of this statistical test and the notation used is given below.

Suppose we have four radiocarbon dates calculated from a sample of charcoal in the same layer of a site; 590 ± 40 , 600 ± 35 , 620 ± 40 and 640 ± 50 bp. We want to ascertain whether or not the results are statistically indistinguishable from one another within 95% probability limits. Our hypothesis in this instance is that the set of dates are statistically different from one another, therefore the null hypothesis is that the dates are the same. We want to disprove the null hypothesis. We calculate the pooled mean using equation 1. The A_p is 609 ± 20 bp. This is the error weighted mean of the four values.

Its validity depends upon the significance of the value of the T statistic (equation 2). In this example, T is calculated at 0.75. Entering the T value at $n-1$ (3 degrees of freedom) in the chi-square distribution tables, we find that the value for chi-square is 7.81. T is <7.81 , therefore the result is said to be *not significant*, that is, the null hypothesis is likely. The dates *are* statistically indistinguishable and may be legitimately pooled in a mean value. Were $T > 7.81$, the result would be said to be *significant* and the null hypothesis would be unlikely. The notation for this example is given in the text by:

$$A_p = 609 \pm 20 \text{ bp}$$

with,

$$(T=0.75; \chi^2_{3;0.05}=7.81)$$

The assumption inherent in the measurement of ^{14}C is that the production rates of modern carbon reservoirs are the same as those of the past, which may make calibration with known age samples necessary. This is especially relevant to studies involving the evolution and development of the human species, less important for the earth sciences. The discovery of the differences between radiocarbon time and secular time is well described by Renfrew (1973). Work on the calibration of the radiocarbon timescale which began in the 1960's and 70's has culminated in the 1993 set of curves published in the Calibration issue of *Radiocarbon* (Vol 35(1), edited by Stuiver, Long and Kra). All calibrations given in this dissertation used one of three curves given in this publication; the high-precision decadal curve (Stuiver and Becker, 1993:35-67), the high-precision bidecadal curve (Stuiver and Pearson, 1993:25-35) and the marine curve (Stuiver and Braziunas, 1993:137-91). The CALIB 3.0.3 calibration programme was used in all calibrations (Stuiver and Reimer, 1993). The choice of curve was determined by the type of sample and its estimated inbuilt age. The high-precision decadal curve was chosen when the samples approximated closest the precise characteristics of the terrestrial samples used in the calibration curve (Reimer, pers. comm. 15.6.93¹). Identified short-lived charcoal, for example, was calibrated using this curve. Material with a longer lifetime and uncertain inbuilt age was calibrated using the smoother bidecadal curve. All samples were calibrated using the recommended southern hemisphere offset of -40 years (Vogel *et al.*, (1993) measured the offset at -41 ± 5 yr.). The difference in the southern hemispheric activity was first identified by Lerman *et al.* (1970). All shell carbonate samples were calibrated using the marine

¹ P. Reimer, Department of Geological Sciences and Quaternary Research Centre, University of Washington, Seattle, Washington 98195, USA.

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curve with ΔR set at -30 ± 13 radiocarbon years (McFadgen and Manning, 1990). Calibrated data are included both in the text and listed in full in the appendices (Appendix 2-4).

CHAPTER 4

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"..in order to establish realistic relationships of radiocarbon dates to cultural events - that is, "interpret" the dates, one must identify and take into account the cultural and noncultural formation processes of the dated specimens and of the archaeological deposits that yielded them".

MICHAEL SCHIFFER, 1987. FORMATION PROCESSES OF THE ARCHAEOLOGICAL RECORD. P 309.

4.1. INTRODUCTION

This dissertation involves a combination of archaeological investigation and radiometric dating. Because the measurement of the residual ^{14}C activity of a sample and the calculation of its date is not linked to the archaeological or behavioural meaning of the material, it is important to consider the principles at the intersection of archaeology and radiocarbon dating.

In the archaeological interpretation of radiocarbon dates, three levels of explanation are required. First there is the interpretation of the archaeological record itself. This might involve, for example, the proper chronological ordering of the behaviour which led to the formation of hearths, house remains, burials and midden deposits. This is achieved principally through careful analysis of the stratigraphic relationship between different layers in a sequence of cultural deposits, an approach first advocated by Worsaae, a Danish antiquarian. *Did the building of the house post-date the construction of the drainage system? Is grave A later than, or contemporaneous to, grave B? Does the hiatus between layers 4 and 5 mean the site was abandoned for a long period?*

Second, and most important, is the question of the relationship of the dated material to the cultural remains for which dates are sought. *Does the material date the event? Are the dates of the deposition of the material analogous to the date of deposition of the structure, the midden, the adze? Is there an 'inbuilt age' that should be accounted for in the dating of the material excavated?*

Third, there is the relationship and meaning of the radiocarbon date to the site and occupation itself. Often, the radiocarbon date must be used in association with other

sources of evidence to consider chronological aspects of site or regional occupation. *Is it possible that the date is too late given a site's material culture? Can we argue that the calibrated date of 1890 - 1950 AD may be rejected because of the presence of prehistoric material? Is the date acceptable because it conforms with historical indications of the site's antiquity?*

The interpretation of radiocarbon dates from archaeological material, then, focusses on these three areas of explanation. There is a variety of errors which are worthy of consideration in the radiocarbon dating of archaeological material. Errors associated with the last two are examined below and those generated through the reporting and interpretation of radiocarbon dates are also considered.

4.2. ARCHAEOLOGICAL AND FIELD ERRORS

There is a true age between an archaeological context or artefact and the human action or behaviour which created it. A variety of factors affect the ability of the archaeologist and radiocarbon specialist to measure it. Quantifiable and non-quantifiable errors attend the relationship between the sample, and the prehistoric event and behaviour which generated it (chapter 7). Similar errors attend the actual measurement of the activity of the archaeological material (chapter 6).

The most common source of error generated in the field is the erroneous interpretation of the relationship between the sample and the context being dated. This results in a misleading interpretation of the prehistoric event. There are a number of possible ways in which this may occur:

(i) Poor excavation technique.

Poor excavation technique or interpretation may result in discrepancies between the sample and date. In some instances, material for dating may come from sites which may not actually be cultural (Spriggs and Anderson, 1993:209). Tamplin (1969), for example, has considered instances of misinterpretation of soil horizons with cultural layers and vice-versa, by archaeologists and pedologists.

(ii) Post-depositional movement.

Post-depositional movement has been identified by Kioke (1979) in her analysis of the deposition of the midden remains at the Natsumidai site in Japan, using the valve-

pairing technique. She was able to quantify natural post-depositional movement by matching the separated valves of discarded shell and measuring the difference between them. Thirty percent were greater than 30 cm apart. This may explain some instances of inverted ages with stratigraphy in dated sites.

(iii) Erosion of cultural remains through natural forces.

The displacement of a sample from its original cultural context has caused problems in New Zealand archaeological dating. One example is the dating of Lake Poukawa, Hawke's Bay (Fig. 5a). McFadgen (1979) has suggested that cultural material was redeposited beneath tephra-chronological layers through deep cracks in the sediment caused by farm cultivation. This led some to the erroneous assumption that human occupation may have predated the Taupo eruption (*ca.* 1850 bp; Lowe and Hogg, 1992).

(iv) Disturbance of cultural remains through bioturbation.

At the Pleasant River site, (see below), rabbit burrows were found within the matrix of one of the excavated areas and the interpretation of the site occupation and deposition had to acknowledge the effect of bioturbation. Similarly, Schiffer (1987) has mentioned the effect of surface and sub-surface foragers in sites in the Arizona desert. At the Snaketown site, a Hohokam village occupied between *ca.* 500 - 1200 AD, rodent activity was responsible for the disturbance of cultural remains, making radiocarbon dating problematic and some of the results uncertain (Schiffer, 1987). Some animals may even move artefacts for nesting material over large distances (Schiffer, 1987). Similar problems have been identified in Southeast Asia. At the important site of Ban Chiang in northeast Thailand, for example, the nest building behaviour of ground-dwelling beetles living within the vicinity of the site has severely affected the prehistoric stratigraphy and relocated dateable materials from their original locations (C.F.W Higham, 1989).

(vi) Deposition of sub-fossil remains in cultural stratum.

A number of spuriously old radiocarbon dates from moa bone are likely to have come from sub-fossil remains, probably brought to sites as material for making artefacts. One example is the site of Shag Point, a sixteenth century occupation near Shag Mouth, in North Otago (Fig. 5b). Moa bone found there probably came from Shag Mouth, an older site (Trotter, 1970:477). In Northland, sub-fossil moa bone is commonly found

near, or in direct association with cultural deposits. The mobility of the dune formations in the region is likely to have influenced this redeposition (Anderson, 1989). In chapter 7, sub-fossil moa eggshell from the Mahia Peninsula in Hawkes Bay was dated under the assumption that it was prehistoric in origin. It was later suggested that it was probably deposited naturally.

4.3. INTERPRETATION OF DATES

Many archaeologists fail to understand fully the meaning of a date and its error, perceiving the date to be an absolute measure, rather than a statistically derived span of time incorporating a degree of uncertainty, based upon radioactive decay. There are also many examples of researchers neglecting to report radiocarbon dates when they fail to match their expectations. In the well-known words of Brew, for example:

"If a C-14 date supports our theories, we put it in the main text. If it does not entirely contradict them, we put it in a footnote. And if it is completely 'out of date', we just drop it."

T. Säve-Söderbergh and I.U. Olsson. ¹⁴C and Egyptian chronology. In, RADIOCARBON VARIATIONS AND ABSOLUTE CHRONOLOGY. 1970. Pp. 35-57.

This should be an outdated notion, however it continues to an extent in the practice of 'rejecting' or 'accepting' a radiocarbon date, or dates (Schiffer, 1987). This may be a subjective analysis and often based not upon a rigorous appraisal of the date itself but upon *a priori* assumptions regarding the excavators interpretation of the site, or sites.

Archaeologists must maintain a close relationship with the laboratory and anomalous results must be investigated to identify the source of the error, whatever its origin. As Waterbolk (1983) has suggested, archaeologists should become involved and educated in the method of radiocarbon dating and the two specialisations should interact more closely in order to interpret dates effectively and eliminate errors.

4.4. REPORTING OF DATES

Further errors arise in the reporting or otherwise of radiocarbon dates. Many laboratories report dates using different procedures from those accepted and outlined by Stuiver and Polach (1977). Some release dates without rounding the ages and errors. This can create a misleading sense of accuracy and precision (Story, 1990). A date of 903±34 bp, for example, unless measured using extremely high precision, cannot be

justified. In any scientific field involving analytical measurement, the quantification of the results involves a realisation of the accuracy of the values and their significant figures. By convention, New Zealand archaeological radiocarbon dates ought to be rounded up to the nearest multiple of 10 and errors to the nearest multiple of 5 up (Stuiver and Polach, 1977:362; Polach, Golson and Head, 1983). It is up to the archaeologist to make him, or herself, aware of the reporting practices of a laboratory and the responsibility of the laboratory to disseminate the appropriate information.

The publication of radiocarbon dates rests almost totally with the submitter of the material. The journal *Radiocarbon* was begun in 1958, its main function being the publication of radiocarbon date compilations produced by the world's laboratories. Today, there are many laboratories and few publish lists of results. This has resulted in a lack of use of the radiocarbon record. Where date lists have been presented, there has often been little critical analysis and a tendency to accept dates without due consideration of their validity (eg, Shutler, 1978; cf. Spriggs and Anderson, 1993). In some instances, however, date lists have been used to consider and test specific problems in archaeological radiocarbon dating. Law (1984) and McCulloch and Trotter (1975) have suggested avenues for improvement in the radiocarbon method. Caughley (1988), Anderson and McGovern-Wilson (1990), Anderson (1991) and Spriggs and Anderson (1993) have used datelists to test models of prehistoric colonisation and critical assess patterns of settlement. It is likely that the development of computer databases containing radiocarbon data will become more common and enable the rapid dissemination of information - indeed, plans for an international database have already been presented (Kra, 1989).

Anderson (1989) has suggested that archaeologists have in the past neglected to publish relevant data describing the sample, its laboratory and reference numbers, provenance and reservoir correction details:

"All too frequently radiocarbon dates for moa hunting sites have been reported without such essential details as stratigraphical provenance, sample type, secular correction or publication number."

ATHOLL ANDERSON. 1989. *Prodigious Birds. Moas and Moa hunting in prehistoric New Zealand.* P. 171.

Such practices seriously undermine the value of radiocarbon dates because they lack a meaningful context. Some of the problems associated with New Zealand dates concern variation in reporting. These may be involved with uncertain reservoir corrections,

especially for shell dates, corrections for isotopic fractionation and failure to specify whether the old or new half-life was used.

It has been common practise in New Zealand to publish secular, or calibrated dates, with no detail of the conventional age BP. Prior to the development of calibration corrections, secular dates were given by merely subtracting the conventional age from 1950 (eg, Lockerbie, 1959). To understand fully the significance of an individual radiocarbon date, the conventional age BP must be published or the enrichment or depletion of the sample activity compared with the modern standard activity, expressed in ‰, should be given (D14C). Publication of a sole secular age may invite ambiguity regarding the type of calibration curve used, the offset amount to account for the southern hemispheric difference or the question of correction for fractionation. Calibration necessarily involves further error, generated through the measurement of the curve itself, which varies depending upon the dating precision of the wood dated at different dendro-years, in addition to the standard error inherent in the original measured sample (McCormac and Baillie, 1993). Clearly, calibrating radiocarbon dates is most profitably achieved in association with the laboratory and preferably, the relative importance of obtaining calendar ages should be considered prior to the collection of samples for dating (Polach, 1983). At present, the question of the magnitude of the offset between northern and southern hemispheres remains an additional source of uncertainty and a variable which may change again. The correction was originally measured at -30 radiocarbon years (Lerman *et al*, 1970) but recent measurements suggest -41 ± 5 as a mean offset (rounded to -40) (Vogel *et al*, 1993). Barbetti *et al*. (1993), however, found little measureable difference in the offset by dating Huon pine and celery-top pine in Tasmania. Differences in this correction are an additional source of error to consider when comparing dates calibrated using different datasets when conventional ages are not reported. The offset as it applies to New Zealand is an avenue for further research. There is little doubt, however, that the calibration curves available in 1993 are the most extensive and precise yet obtained and will probably remain so for many years.

With the development of more effective international Quality Control procedures (Polach, 1992) and laboratory accountability, greater participation by laboratories in inter-calibration programmes and closer co-operation between laboratory and submitter, it is likely that many of these sources of error will be reduced. From an archaeological point of view, accurate dating begins in the field, with careful stratigraphic analysis, care in ensuring samples collected for dating are not contaminated by excavators and

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note taken of the immediate depositional environment and sources for post-depositional contamination.

CHAPTER 5

ARCHAEOLOGICAL EXCAVATIONS

5.1. INTRODUCTION

Material from 7 archaeological sites was dated in this dissertation (Figs. 5a and b). They, and their excavation will be described in detail below. Some of them have already been dated extensively before, others were undated. The chronological issues and questions which are inherent in the excavation, interpretation and dating of each site will be discussed.

5.2. SHAG MOUTH

The prehistoric site of Shag Mouth (S155/5) is located at the mouth of the Waihemo, or Shag River, near Palmerston in North Otago (Fig. 5b). It is over 2 ha in size and has a long history of archaeological investigation beginning with Von Haast (1874) in 1874. He excavated and used the site as his type for arguing a cultural dichotomy between early people who subsisted largely upon moa ("moa-hunters"), and later people with a marine focus (the "shellfish eaters"), based upon his knowledge of the mesolithic and palaeolithic divisions current in European prehistory at the time. The subsequent controversy that ensued between him and colleague Hutton is described above and in Anderson (1989b). Booth (in Anderson, 1989b) had excavated at Hutton's behest in 1875 for three months and dug a trench through the high dune at the site. The results of his excavations, although used manipulatively in the debate between Hutton and Von Haast concerning the antiquity of moa, revealed that Von Haast's (1874) conclusions of an early - late differentiation on the basis of faunal remains were simplified.

Hamilton (1890) excavated in December 1890 with a co-worker and dug a large 26-pace long trench across the high dune. He excavated 50 moa skulls but left plans and descriptions which lack detail. In contrast, Teviotdale's extensive work at Shag Mouth was outlined in a comprehensive paper, due principally to the encouragement of H.D. Skinner of the Otago Museum (Teviotdale, 1924). Teviotdale (1924) found an array of artefacts including fish-hooks dominated by a characteristic one-piece design, a large number of adzes, both complete and unfinished, chisels, drills, bone points, needles and files.

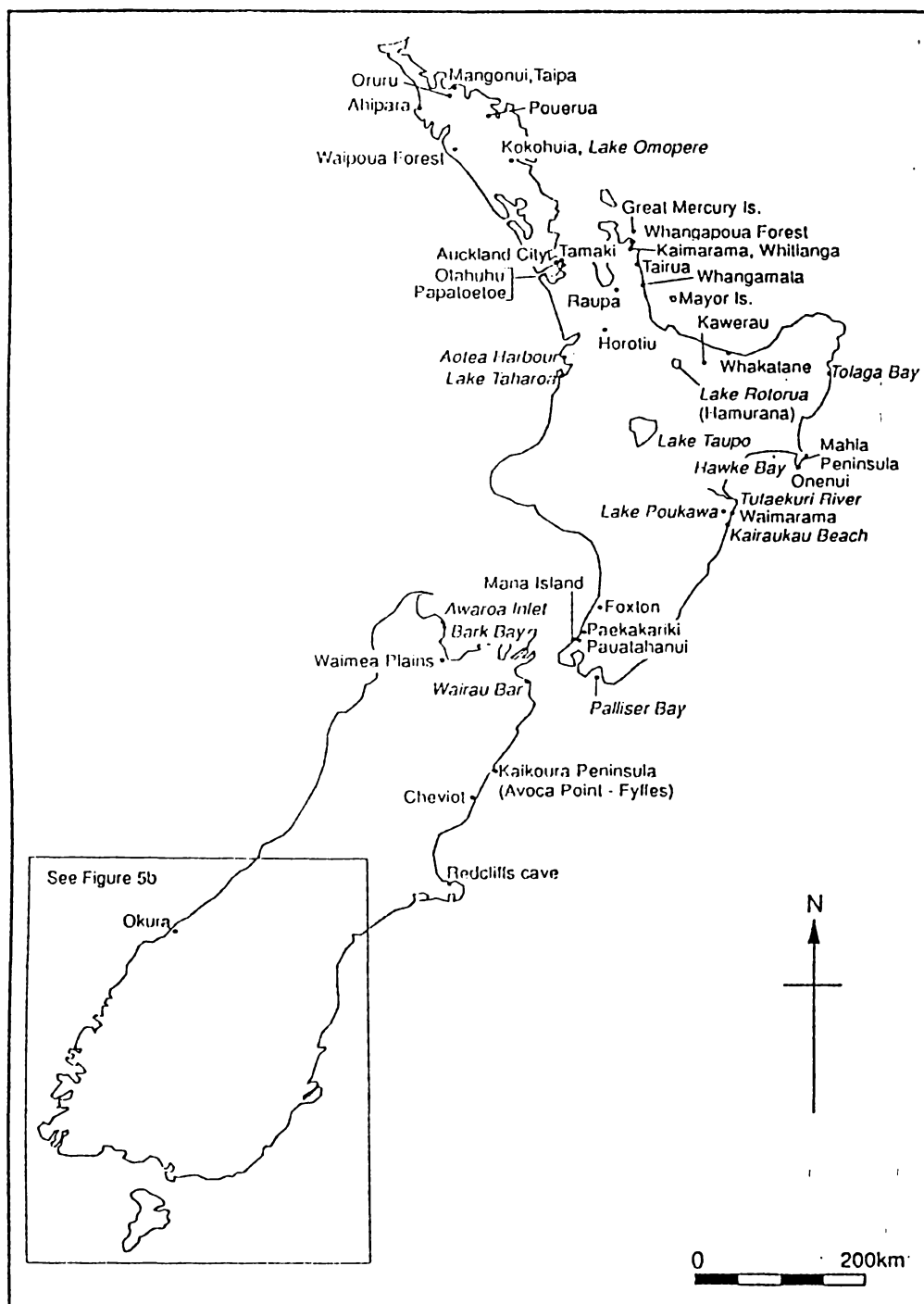


Figure 5a. New Zealand sites mentioned in the text.

He also found 36 hearths, which have been interpreted as possible dwellings at the site (Anderson, 1982; 1989)@. Skinner (1924) used the Shag Mouth assemblage to argue for a Polynesian origin for the prehistoric occupants' of the site and argued for the distinct nature of the material culture of the site which he said was unlike any other (Skinner, 1924).

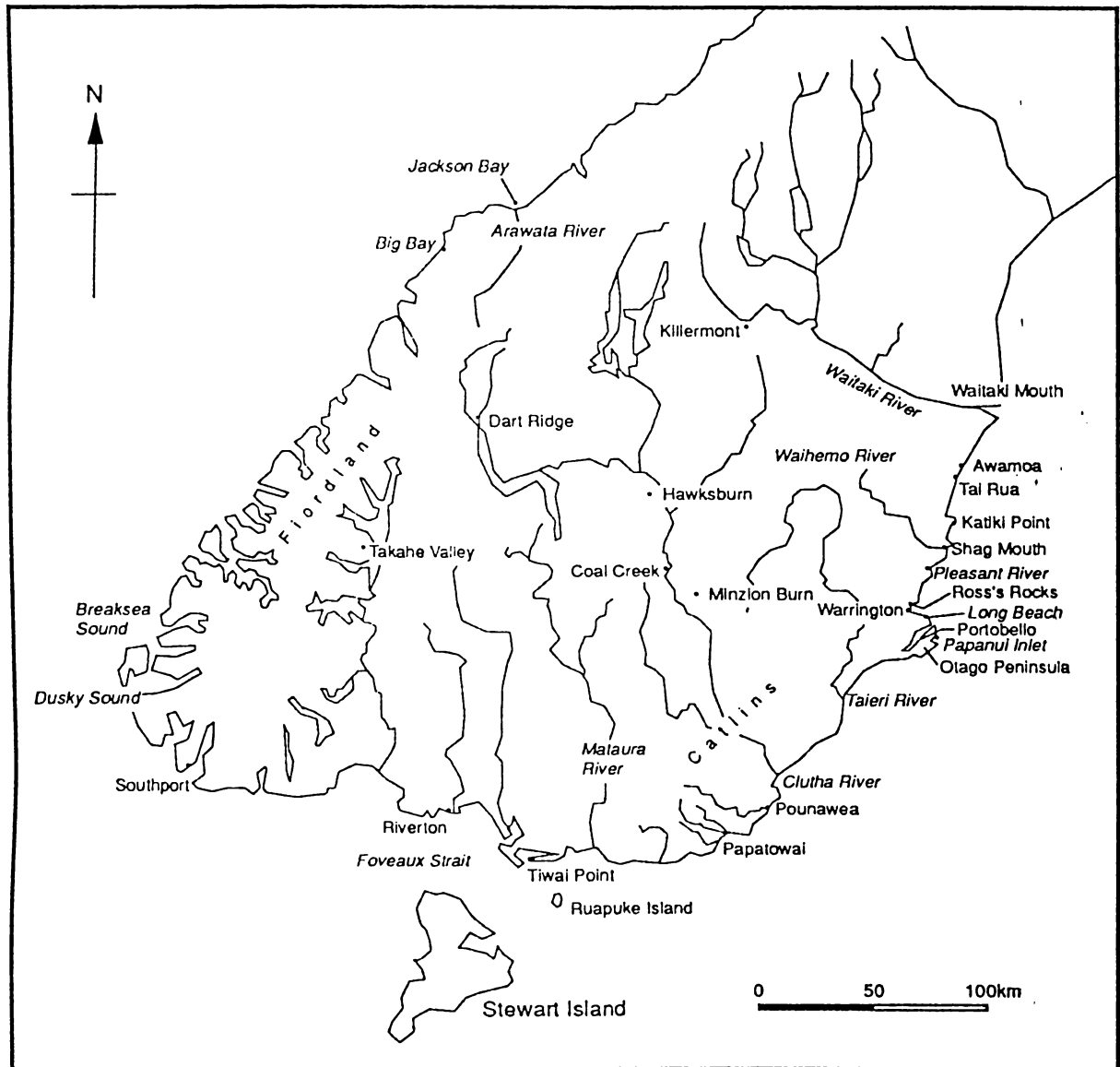


Figure 5b. Sites in Murihiku mentioned in the text.

In the 1970's, Trotter (1970) excavated at the nearby Shag Point site where he found a later occupation dated to the sixteenth and seventeenth centuries. There was no evidence

@ According to Allingham (pers.comm.) Teviotdale's diary alludes to 43 hearths in total at Shag Mouth.

for moa hunting at the site and, as mentioned above, the only faunal evidence for moa was thought to originate either from sub-fossil remains or from the older Shag Mouth site (Trotter, 1970).

In 1988, after a series of smaller test excavations, Anderson directed a large research investigation involving detailed examinations of dating and chronology, stratigraphy and taphonomy, flora and fauna, seasonality, geology and lithic technology. The material used in this dissertation comes from these excavations. The most extensive comprised one large 10 x 10 metre square on the highest part of the dune and smaller test excavations along it and down to the lower marsh land (Fig. 5.1) (Anderson, Smith and Allingham, in prep.). The high dune excavation is termed 'SM/C'. Subsequent excavations focussed upon the lower marsh and dune periphery ('SM/D').

Chronological issues concerning the occupation of Shag Mouth in prehistory have been addressed by Anderson, Smith and Higham (in prep.). The deep stratigraphy in many

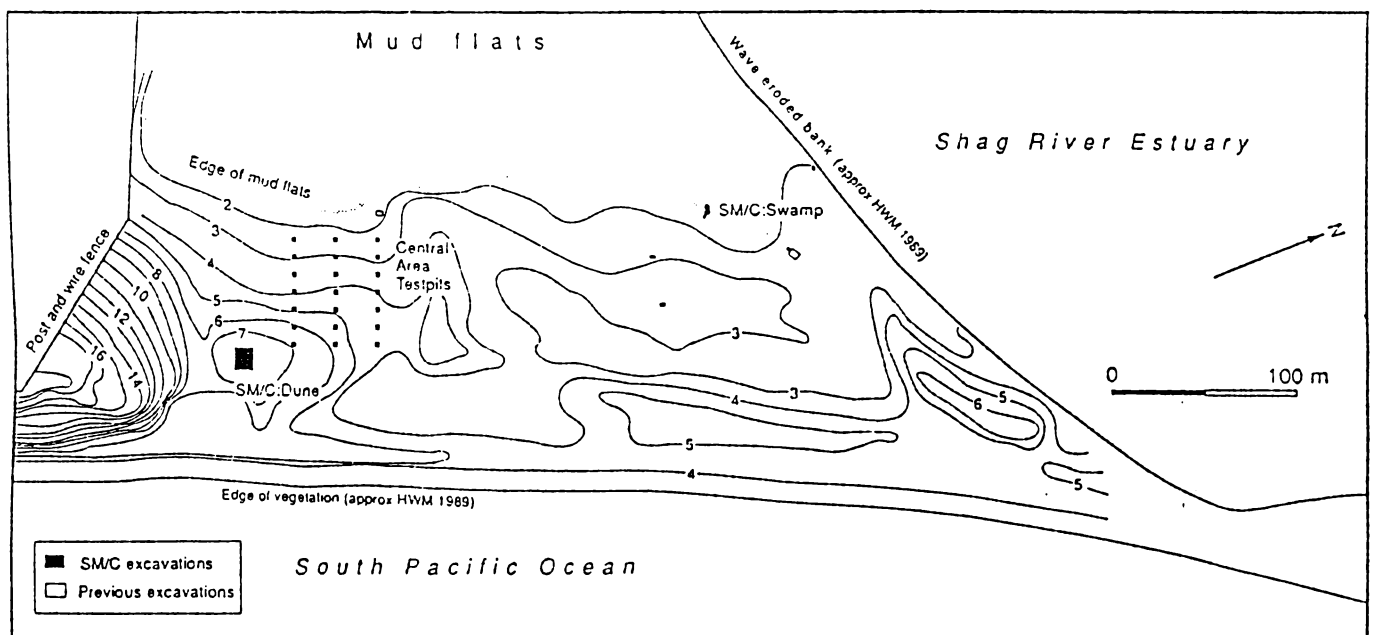


Figure 5.1: the site of Shag Mouth, showing excavated areas, 1988-1990.

parts of the site had led Skinner (1924) to the conclusion that the site was probably close to the status of a village and that occupation was likely to have been long and probably permanent, or semi-permanent. One of the major chronological objectives of the Shag Mouth project was to determine the length and type of occupation at the site, whether seasonal or permanent, and whether it was possible using radiocarbon dating

to identify any chronological distinction between layers and sequences of material culture (Anderson *et al.*, in prep.). In addition, different samples from the site were used to consider which type of material provided the most accurate dates (chapter 7) and whether or not there was any contamination present in them (chapter 8). The conclusion reached by Anderson *et al.* (in prep.) is that the site was probably occupied for a short period in prehistory (less than 50 years). This is based upon the radiocarbon evidence and the lack of any lengthy hiatus in the stratigraphy in any of the excavated areas.

5.3. PLEASANT RIVER

Like Shag Mouth, the Pleasant River site (S 155/2) was an important estuarine settlement in North Otago (Fig. 5b). An expanse of approximately 2 ha of prehistoric remains is located at the mouth of the river on low-lying *Salicornia* marshland prone to inundation by the sea - indeed, Allingham (pers. comm.*) has monitored the destruction of parts of the site by the estuary over fifteen years. Archaeological investigations were first undertaken by Gathercole between 1959 - 1969 and Teal (1975) in the 1960's. In recent years, Allingham (n.d) and Smith (1992) have conducted excavations there. Archaeological material used in this dissertation comes from a series of excavations in the 1970's by Allingham and from the excavations by Smith (1992) between 1991 - 3 (Fig. 5.2).

Allingham excavated at a site on the margins of the estuary called Pleasant River D (PRD) in 1975 and found two superimposed cultural layers which he distinguished by matrix colouration (Fig. 5.3). Cultural remains were composed of moa bone, both broken and complete and large amounts of broken and burnt moa eggshell, which in one area seemed to be from a single egg (sample PRD-2) (Allingham, pers. comm.). A variety of species of shellfish were found including *Paphies australis*, *Austrovenus stutchburyi*, *Cookia sulcata*, *Lunella smaragda* and *Paphies subtriangulatum*.

Smith (1992) test-pitted a large area of the Pleasant River site to determine the extent of occupation. One hundred and ninety-seven pits were excavated in total and although many yielded evidence of peripheral occupation, being dominated by charcoal flecks and darkened matrices, few revealed any significant cultural remains. Smith (1992)

* Mr B.J Allingham, RD1, Seacliff, Dunedin.

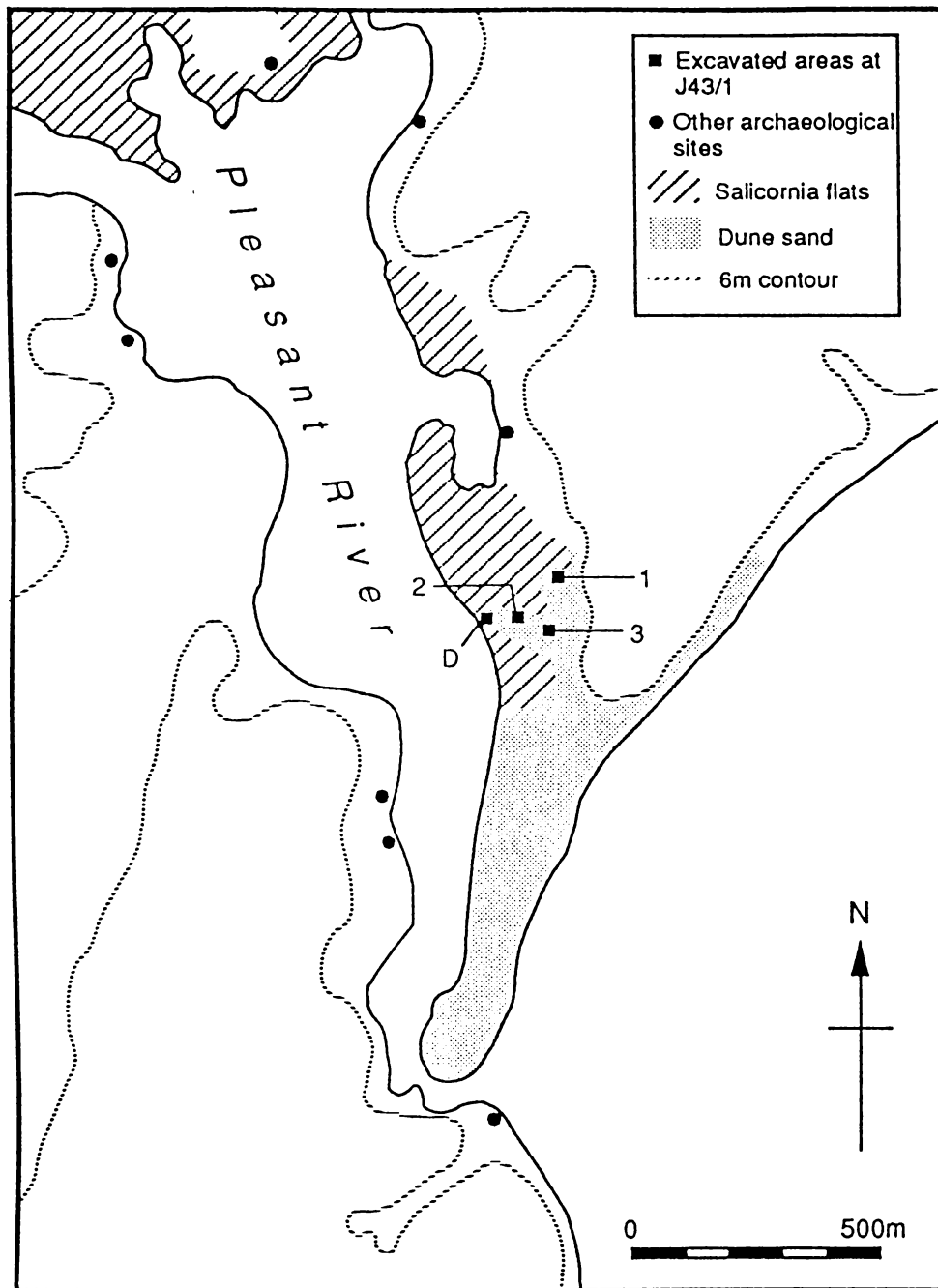


Figure 5.2: Map of the Pleasant River site, showing excavated areas D (Allingham, 1975) and 1, 2 and 3 (Smith, 1990).

has suggested many represent disturbance and spoil from previous excavations. A 5 x 5 metre square (Area 1) was excavated to investigate further the blackened deposits identified in certain test pits (Smith, 1992). One cultural layer was identified. It comprised quantities of shell midden, dominated by *Austrovenus stutchburyi* (the common cockle) and *Amphibola crenata* (mudsnail), bone remains of moa (unknown species), furseal (*Arctocephalus forsteri*), sealion (*Phocarctus hookeri*) and dog (*Canis*

familiaris). Artefacts included a nephrite adze, silcrete flakes, two polished flakes from basalt adzes, a hammerstone and a bone fishhook (Smith, 1992). Later excavations at Areas 2 and 3 were undertaken to examine further the spatial characteristics of the site and to obtain material for cross-dating.

The chronological questions asked here are similar to those asked at Shag Mouth and relate to the length of occupation (whether seasonal or permanent) and the chronological

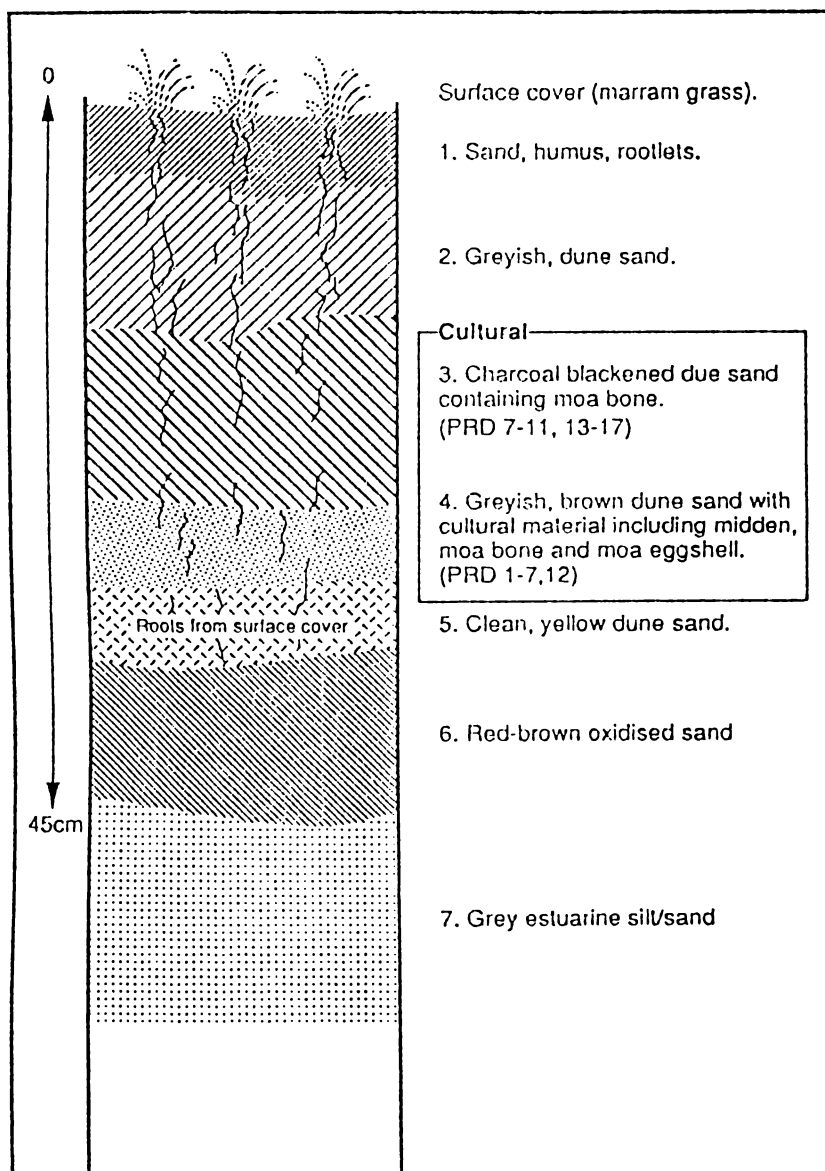


Figure 5.3: Stratigraphy of the excavation of Pleasant River, area D, 1975.

relationship of the site compared to Shag Mouth. Was it a satellite of the former, occupied contemporaneously, or was it occupied separately? The other major question concerns the relationship of parts of the site to each other, for example, is area D

contemporaneous with areas 1 and 2? Does this evidence re-occupation or merely separation of activity in a spatially distinct settlement?

The radiocarbon dating of the Pleasant River site is interesting from two perspectives. First, the dating of the site historically has been controversial. A divergence between shell and charcoal dates has been noted and a hard water effect has been mooted as the reason for some shell dates which tend to be older (Anderson, 1991). Second, the environmental situation suggests archaeological material may be affected *in situ* by the effects of inundation and flooding by water, including run off from small streams draining the valley sides and by possible dissolved bicarbonate resulting from erosion of the calcareous sand and mudstones in the area. Layer 2 at Area 1 for example, was notably damp upon excavation suggesting the site is prone to surface drainage and flooding patterns. These conditions may significantly affect the survivability and resistance of prehistoric material for dating at the site to contamination. Samples from near or below the water table are more prone to contamination from percolating ground acids and dissolved bicarbonates than those higher up. Thus, the Pleasant River site is an important one for the investigation of the range of contaminants found in recently deposited archaeological material (chapter 8) and for testing problems in the dating of shellfish (chapter 9).

5.4. KILLERMONT

The Killermont No. 2 site (S116/26) is located on the banks of the Ahuriri river in the Mackenzie Basin, near Omarama (Fig. 5.4). In 1992, the site was excavated by McGovern-Wilson, who found evidence of moa processing. Large ovens, represented by hangi stones and charcoal remains were found, with silcrete blades, moa bones and artefacts in association. Three areas of the site were identified (KLM A, B and C). According to McGovern-Wilson (pers. comm.[^]), this is the first site excavated in the Mackenzie Basin which contains evidence for moa hunting. As one of a handful of major moa butchery and processing sites excavated in the southern South Island interior it is important both archaeologically and chronologically.

The major objectives in dating this site, then, were to place it in its chronological context so that accurate comparisons could be made with other sites on the eastern Otago coast, to consider the length of occupation and the relationship of the three different living areas excavated (Fig. 5.5).

[^] Dr R. McGovern-Wilson, Department of Anthropology, University of Otago, Dunedin, New Zealand.

The charcoal obtained from the site's moa ovens suggested that the palaeoenvironment was dominated by shrub species. Wallace (pers. comm.#) has suggested on the basis of the charcoal remains that:

"The ecological picture presented in this data reveals a pure shrubland association."

Dr. R. WALLACE, (PERS. COMM. 1992).

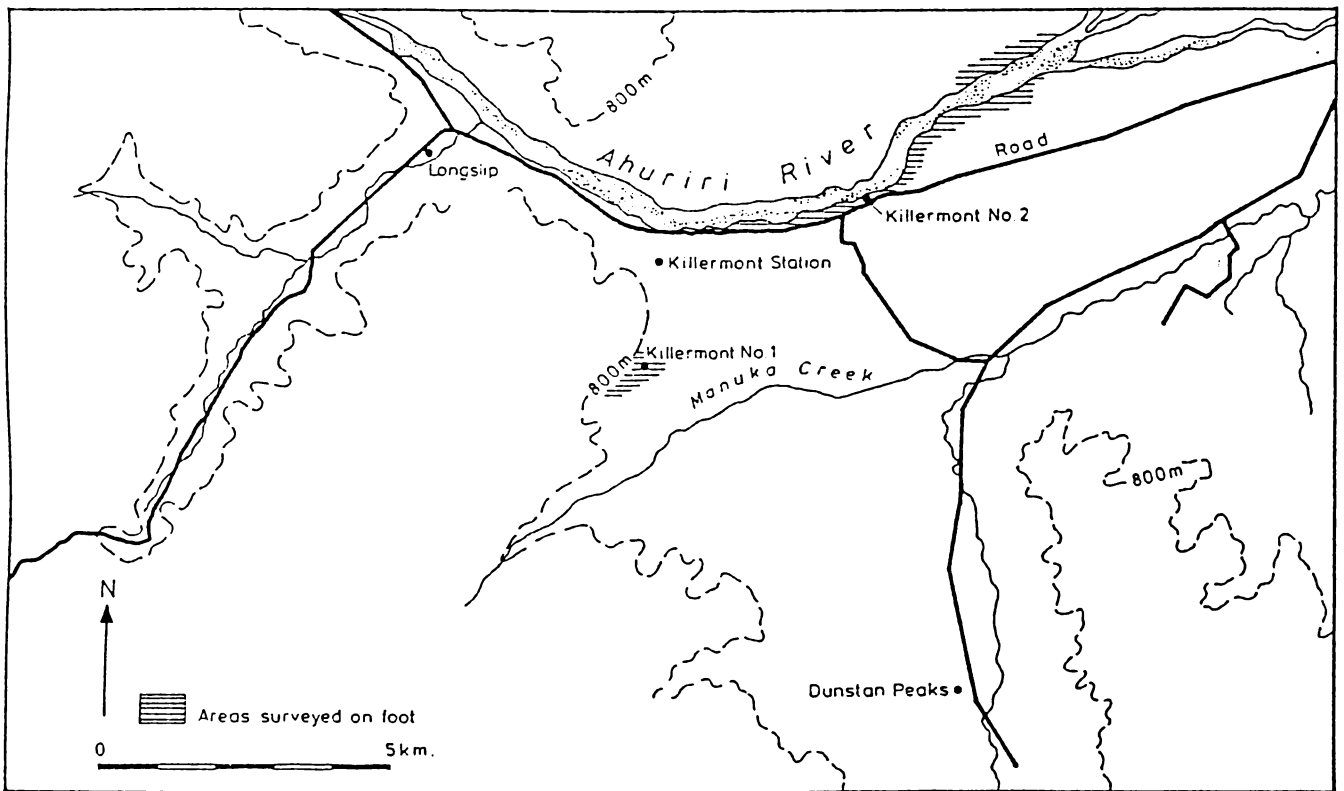


Figure 5.4: Location of the Killermont #2 site, Mackenzie basin.

Dr. R. Wallace, Department of Anthropology, University of Auckland, Auckland, New Zealand.

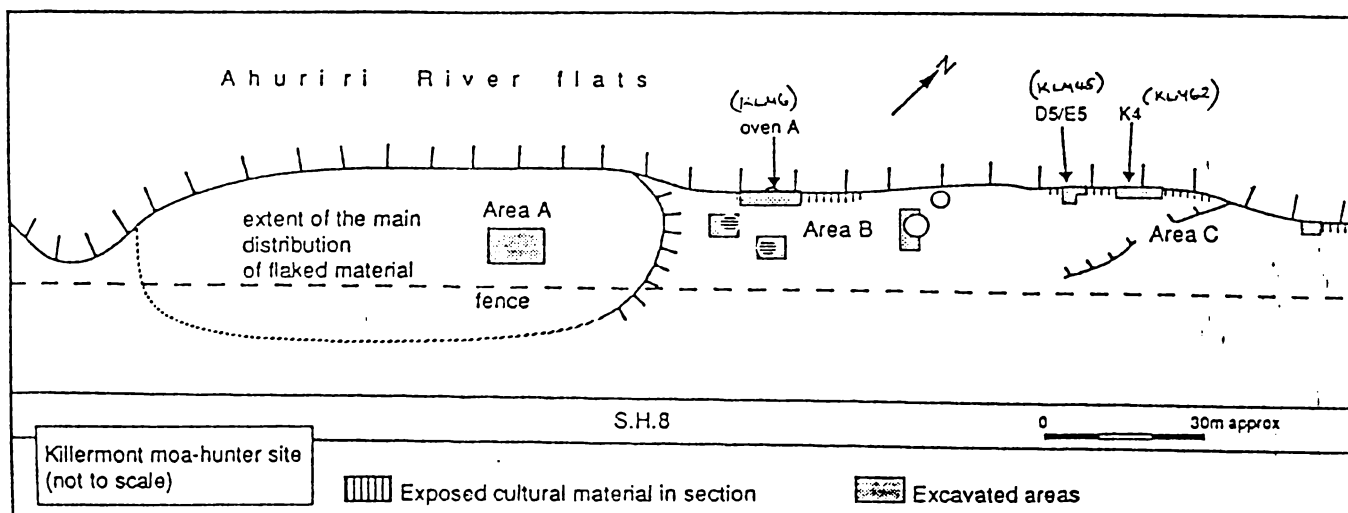


Figure 5.5: Excavated areas at the site of Killermont #2, Mackenzie basin.

Olearia sp., *Hebe* sp., *Archeria traversii*, *Coprosma* sp., *Pittosporum* sp., *Myrsine australis*, *Discaria toumatou* and one other unknown shrub species were identified. The remains are probably well-suited for dating because they are from short-lived species and thus date the prehistoric event closely. The Killermont charcoal samples presented a useful opportunity for analysing the extent of charcoal contamination in the immediate vicinity of the Killermont because large amounts of sample were available for dating. This is important given the destructive nature of certain of the chemical pretreatments undertaken in chapter 8.

5.5. AWAROA AND BARK BAY

Material excavated by Barber from sites on the northwest coast of Tasman Bay at Awaroa (N26/18) and Bark Bay (N26/16) were used in pretreatment experiments to consider contamination in shell. Shells from both sites were used to consider the extent of variation between radiocarbon dates of different species of shell. Both are located in the Abel Tasman National Park, on the "granite coast" (Fig. 5.6). Unlike the faunal assemblages found in nearby sites in this region, such as Anapai, Awamoa, Tahunanui and Rotokura (Anderson, 1989), these sites contain neither moa nor seal remains, so it is possible the Bark Bay and Awaroa assemblages bracket the regional demise of these resources. Thus, Barber (pers.comm.) has suggested an occupation around the 16th and 17th centuries.

Site N26/18 is a midden deposit located on a sandspit on the southern side of Bark Bay, a relatively small (0.45 ha) coarse sand estuary. The stratigraphy here comprises an upper and lower shell midden layer (1A and 1B) at a maximum depth of some 70 cm. The upper layer of the site is composed primarily of mollusc remains including *Paphies australis* (pipi), *Austrovenus stutchburyi* and *Mytilus* sp. (mussel). There are also finfish remains (barracouta and red cod). The lower level contains a similar range of mollusc remains with a strong ash component.

The stratigraphy at the N26/18 site at Awaroa Inlet is more complex (Fig. 5.7). The site is situated on the southwest side of Sawpit Point (Fig. 5.6) and was first recorded as a series of shell middens dominated by *Paphies australis* with a heavy charcoal matrix and a variety of argillite and quartz flake debitage. The midden deposits are generally 30-50 cm in depth but extend up to 80 cm in some areas. Spits 1-4 were excavated in a bulk sampling procedure for rigorous midden analysis. This is where the majority of the radiocarbon samples originate. The archaeological remains are dominated once more by mollusc remains including *Paphies australis*, *Amphibola crenata* and *Turbo smaragda* (catseye). Evidence was also found of stone manufacture and a variety of lithic remains including granite and greywacke were found. Structural features were identified within the lower basal matrices (a hearth and posthole) and a burial was found in the dense shell midden. This was investigated with the consent of a Ngati Rarua kaumatua and reburied on site.

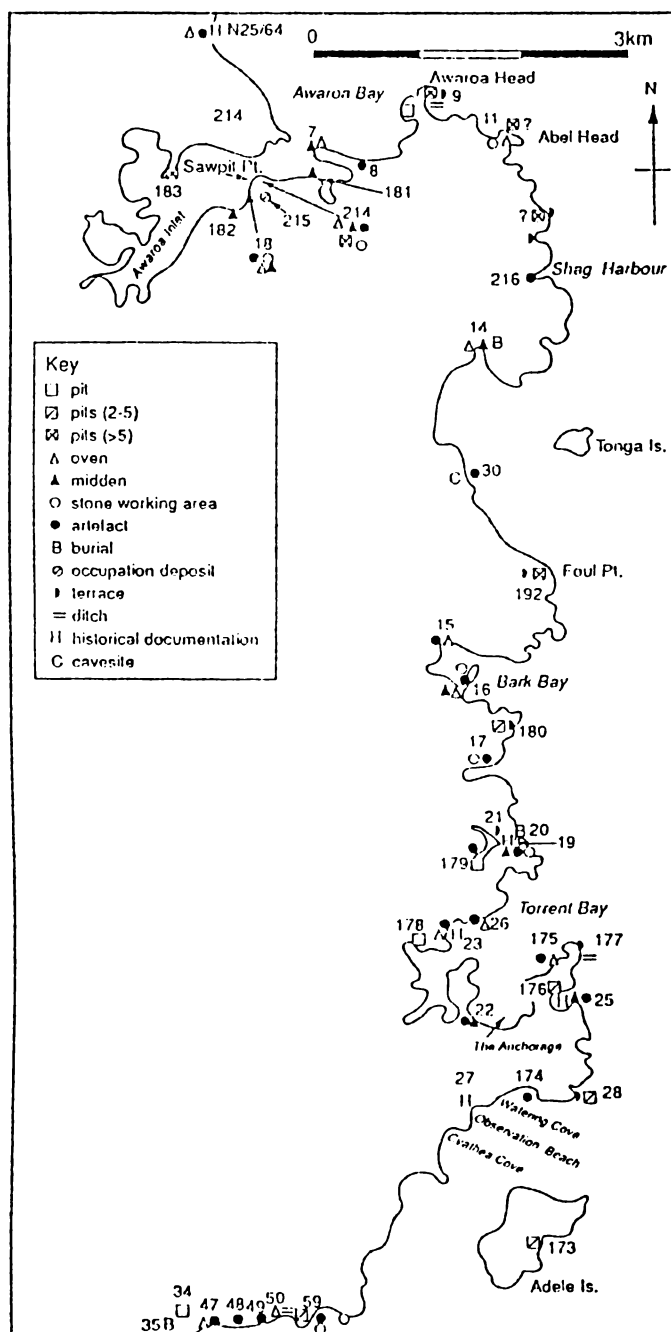


Figure 5.6: map of the Tasman Bay sites, showing excavated areas.

ARCHAEOLOGICAL EXCAVATIONS

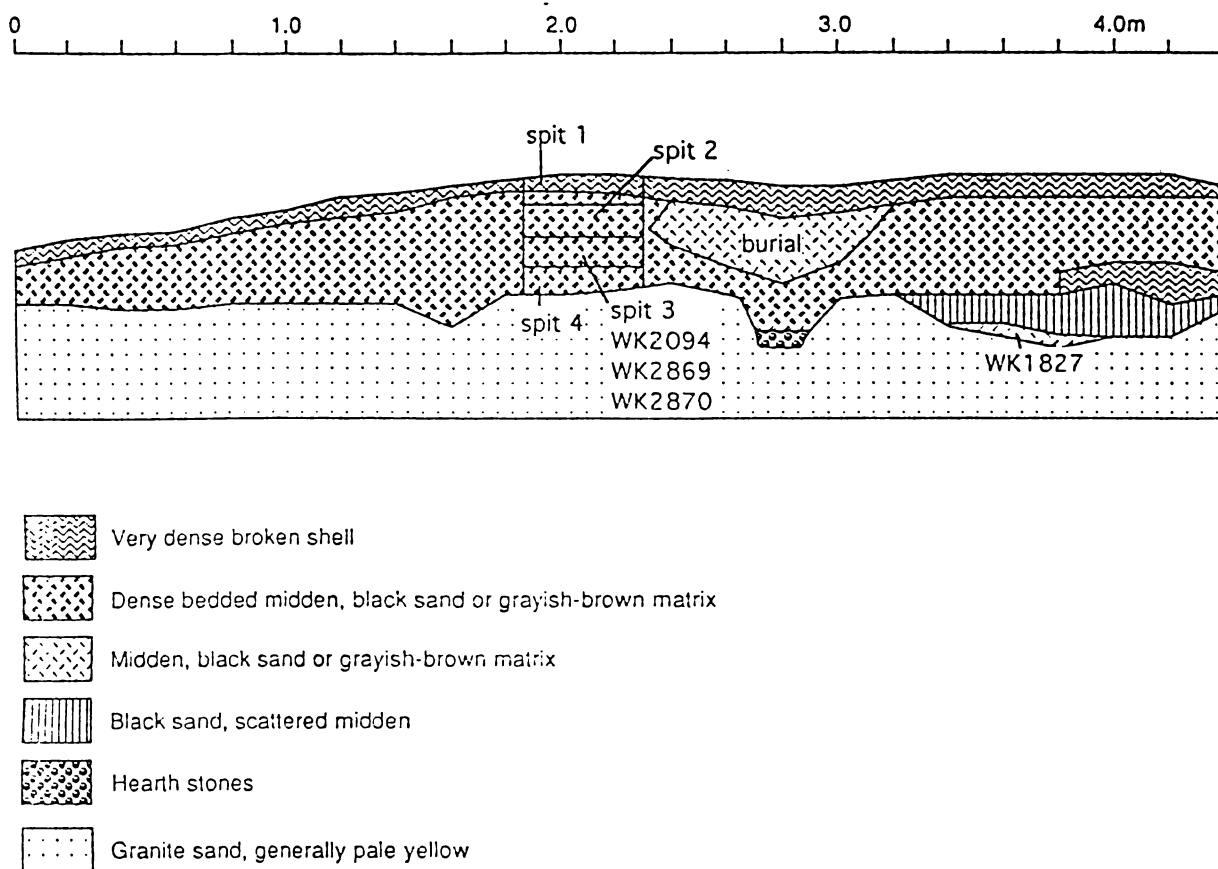


Figure 5.7: Stratigraphy at the site of Awaroa, Nelson.

5.6. LOW FLAT, RAOUL ISLAND (THE KERMADec ISLANDS)

Raoul Island, the largest of the Kermadec group, is situated some 1000 kilometres from New Zealand (Anderson, 1980). It is composed of rapidly eroding ridge and ravine land. The soils on the island are principally volcanic in composition; pumice, andesite and basalt rock being the major types. At Low Flat (K036/1), where the major prehistoric remains have been found, alluvial and colluvial soils make up the recent horizons (Johnson, 1991:3). According to Anderson (1980:131), the entire island is "densely forested, giving the appearance of fertility". Kermadec Pohutokawa (*Metrosideros kermadecensis*) is the most common forest tree. *Myrsine Kermadecensis* and *Ascarine lucida* var. *lanceolata* are also found. Karaka (*Corynocarpus laevigatus*), ti (*Cordyline terminalis*) and candlenut (*Aleurites moluccana*) tree are likely to have been introduced prehistorically (Anderson; 1980:131). The island and its archaeological landscape is shown in figure 5.8.

Anderson (1980) excavated there in 1978 and found a single 10 - 30 cm deep cultural horizon at Low Flat, composed of charcoal, basalt and obsidian fragments. At one test

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excavation (LF5), there was evidence of another cultural layer but Anderson (1980:133) suggested a short period of time had probably elapsed between the two. Radiocarbon dating, however, pointed to two separate occupations, one at *ca.* 620 bp and another at *ca.* 1030 bp (Anderson, 1980), although the earlier date (NZ-4789 at 1033 ± 58 bp) hinges on only one measurement, and may be erroneous. Anderson (1991) later rejected this date as being probably from natural charcoal and his interpretation seems to revolve now around a single occupation around *ca.* 600 bp.

Material from excavations by Johnson (1990) is used in this dissertation. He surveyed sites at the Farm Terrace (site number - K036/2), Coral Bay (K036/4, 14), Denham Bay (K036/3; 5 - 13, 16) and Low Flat (K036/1, 15) and excavated a number of test pits (Johnson, 1991:49) (Fig. 5.8). His work corroborated the archaeological findings of Anderson (1980) but not the chronological conclusions. He dated the cultural remains at the Farm Terraces and at the upper and lower layers at Low Flat (Appendix 5). The Farm Terraces yielded a consistent series of dates at 600 bp. The date for the upper layer at Low Flat was 800 ± 40 (Wk-1910) while the lower gave a date of 1070 ± 40 bp (Wk-1912). The latter mirrors the rejected date of Anderson from a similar context (1980:140). In addition, a conventional uncorrected shell date of *Patella kermadecensis* (limpet) from the upper layer gave an age of 1100 ± 45 bp (Wk-2282). The chronology of the prehistoric occupation, then, is controversial. The radiocarbon dates are variable, despite almost identical wood species (*Metrosideros kermadecensis*- Pohutokawa) being used. Part of the radiocarbon dating research described below involved resolving these chronological issues (chapter 10). Radiocarbon dates for Raoul Island are shown in figure 10.4.

The resolution of the prehistoric chronology is important in the light of research concerning the provenancing of the lithic assemblage found there. Leach *et al.* (1986) sourced some of the obsidian artefacts found on Raoul Island to Mayor Island, in New Zealand, suggesting that prehistoric people making landfall in New Zealand had made a return journey to the Kermadecs. It was suggested that Raoul was possibly a transit point for two-way voyaging between New Zealand and Polynesia. Anderson and McFadgen (1990) analysed six flakes of obsidian, four from Raoul, one from Tai Rua and one from Shag Mouth and found that XRF spectra were similar and probably from the single Raoul Island source. Accurately radiocarbon dating this site, then, assumes some importance given the crucial position of the site in models concerning the colonisation of New Zealand.

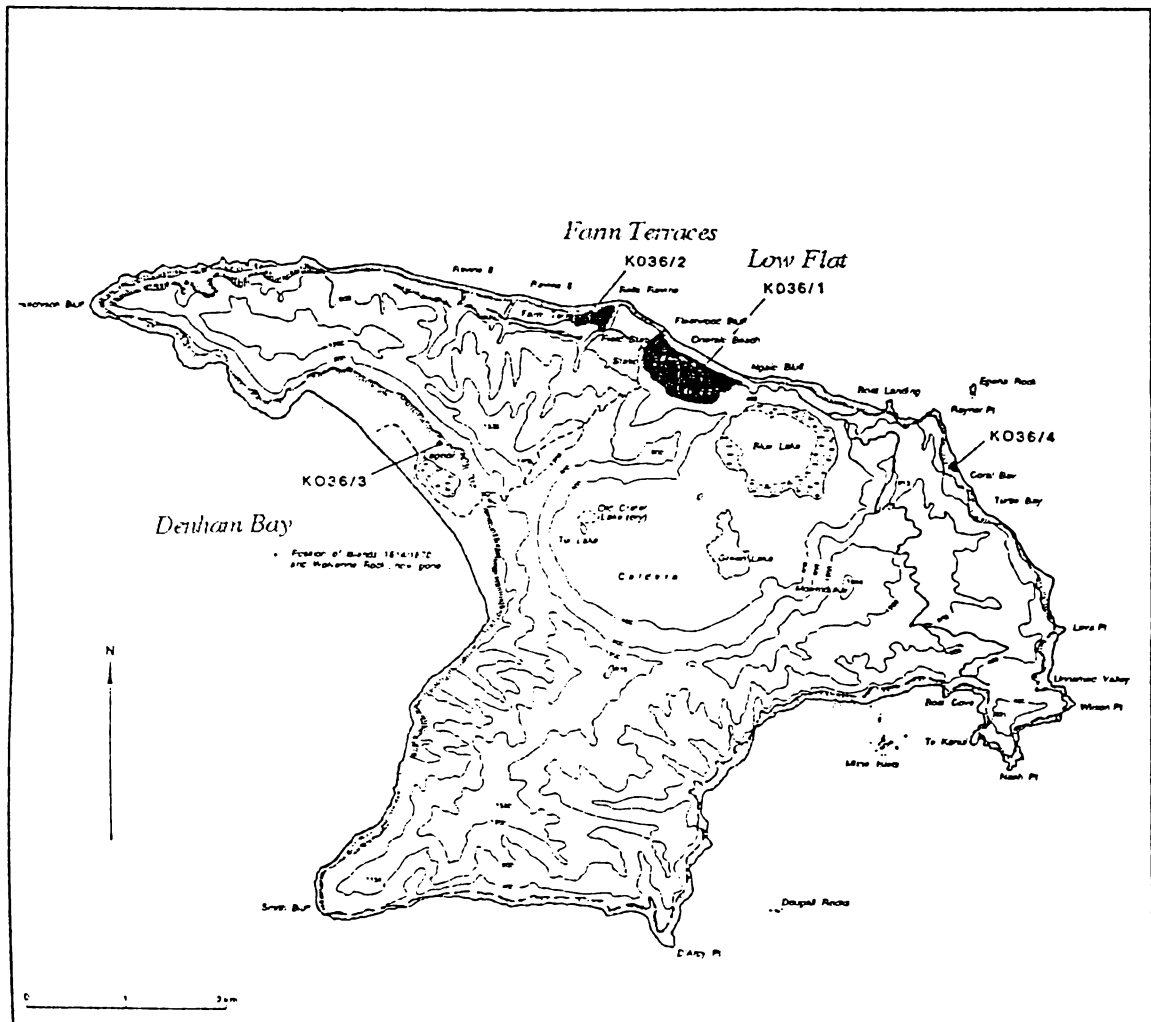


Figure 5.8: Prehistoric sites on Raoul Island, Kermadec group.

An investigation into pretreatment of prehistoric limpet shell samples (*Patella kermadecensis*) from Raoul Island using an untreated sample as a control for comparison with a treated sample was conducted. The results are discussed in chapter 8 and in chapter 10 the chronological implications of these and other radiocarbon dates are discussed.

5.7. WARRINGTON

The Warrington site (I44/177) is located on a low sand dune in front of a large tidal bay near Dunedin (Fig. 5.10). The site is approximately 2 ha in size (Allingham, 1985:2) and has a long history of excavation beginning in the late 1800's. Allingham (1985, 1986, 1988) has conducted a series of excavations, identifying 3 cultural layers. The lowest was dominated by moa remains and was probably occupied about 700 bp (Wk-1737; 1040 ± 50 bp on *Paphies subtriangulatum*). After an hiatus, the site was re-

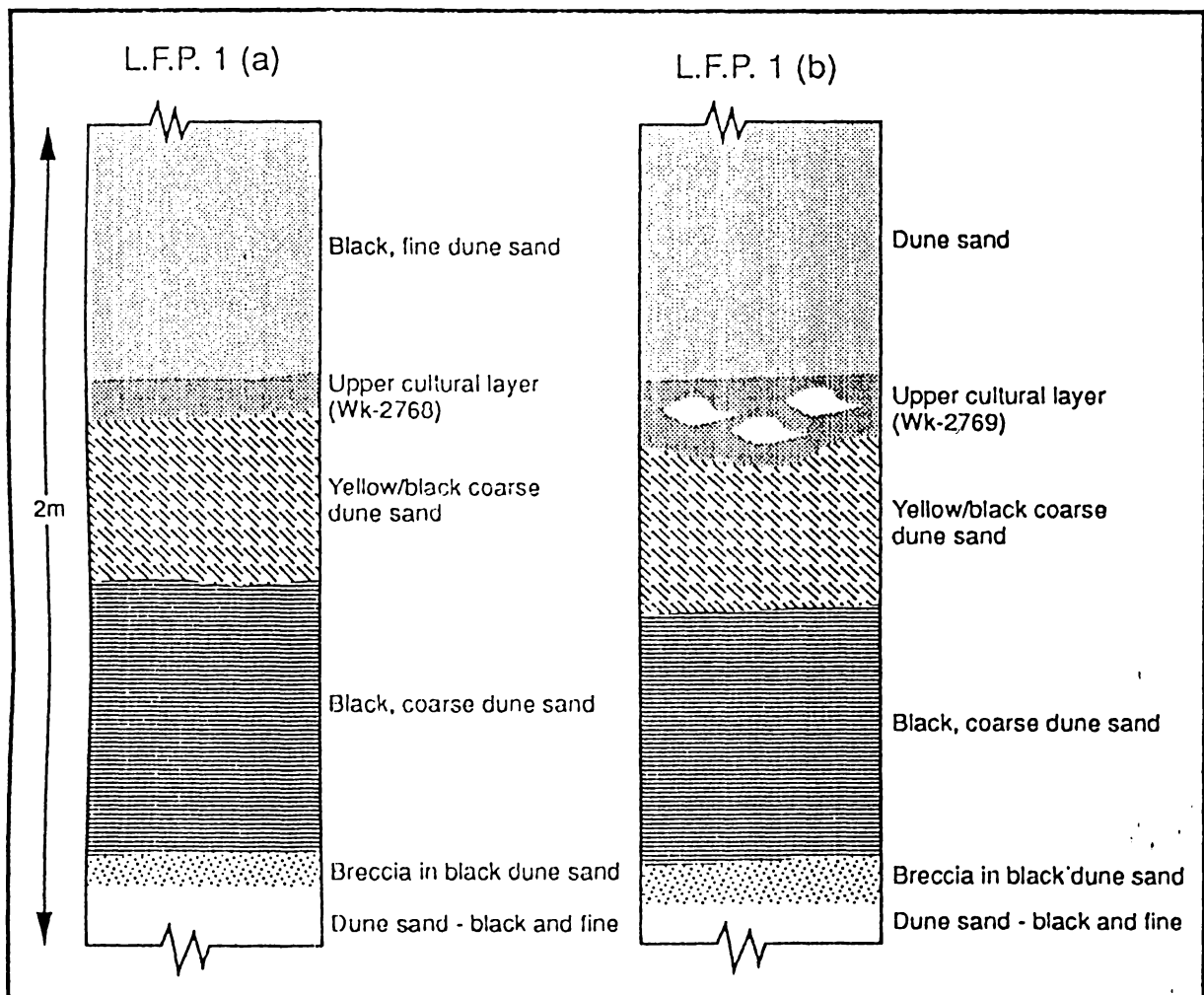


Figure 5.9: Stratigraphy at the Low Flat sites, Raoul island, Kermadec group.

occupied at a time when moa were less conspicuous some 200-300 years later (Wk-1738; 870 ± 50 bp, on *Austrovenus stutchburyi*). Finally, a third, more recent occupation layer was identified, containing "Classic Maori" type artefacts. The cultural

material at Warrington was deposited atop a natural deposit of shell (Wk-1865;1240±40 on *Paphies subtriangulatum*).

The material used for dating here comes from the lowest layer at the site (Fig. 5.10).

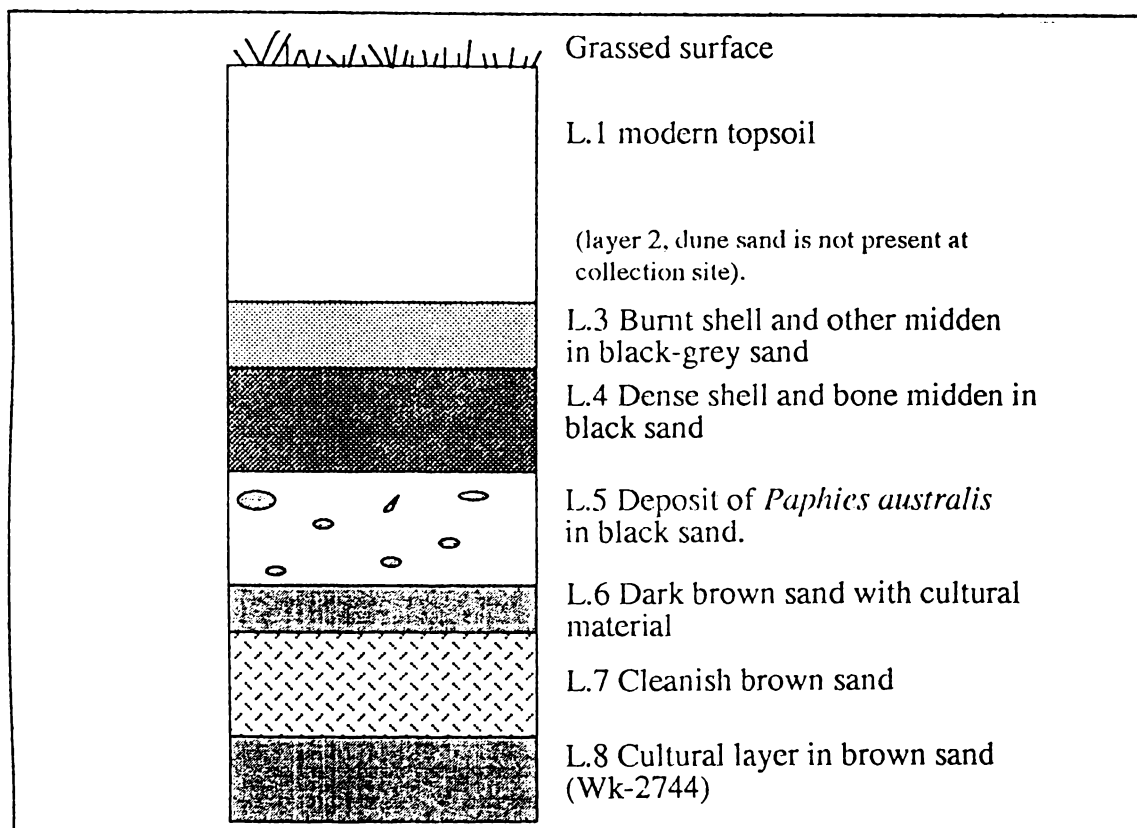


Figure 5.10: The Warrington site, near Dunedin, showing excavated section (Allingham, pers. comm.)

5.8. SUMMARY

Because of the short period of prehistoric occupation in New Zealand, errors associated with radiocarbon dating must be kept to a minimum. The application of dating at higher levels of precision will allow a more penetrating analysis of the prehistoric settlement of New Zealand sites. The principal methodological questions addressed in this dissertation are concerned with the examination of errors generated in the field and the laboratory. Throughout this dissertation, but in particular in chapter 10, the radiocarbon dates obtained are analysed within their archaeological contexts to demonstrate how precise radiocarbon dating strategies, incorporating careful sample selection and quality

assurance within the laboratory, may enable complex prehistoric problems to be resolved.

CHAPTER 6

ACCURACY, PRECISION, REPRODUCIBILITY

"Again, C14 dating is at present of limited assistance in deciding whether or not consecutive archaeological layers with overlapping dates represent continuous or intermittent occupation. Until sites can be dated with reasonable precision, portions of the systems structures, along with the changes which have taken place within them, will remain obscure".

PETER COUTTS. 1972. The 8th International Conference on Radiocarbon Dating, Wellington.

6.1. INTRODUCTION

Any improvement in dating precision reported for New Zealand archaeological dates is attractive. For valid high precision dating, all sources of error generated within the laboratory must be investigated and, if possible, quantified. In this chapter, sources of error within the radiocarbon laboratory at the University of Waikato are investigated. First, accuracy and precision is defined. Then, the results of dates measured at the Waikato laboratory as part of the 1990 Intercalibration exercise are presented, as a demonstration of laboratory accuracy. A number of important sources of error contributing to overall precision and accuracy are evaluated and the calculation of a laboratory error multiplier, a measure of laboratory consistency and reproducibility, is described. Some of the results presented are from routine laboratory procedure. The majority of research was undertaken collaboratively with Dr A.G. Hogg, the director of the laboratory.

6.2. PRECISION AND ACCURACY

It is important, initially, to define terms. Accuracy refers to a radiocarbon date being 'correct' within the statistical limits of its standard error. It is assessed most effectively through inter-laboratory comparison exercises using samples of known age, or samples assigned a mean age through consensus by a number of different laboratories (see Scott *et al.*, 1992). Precision refers to the relative size of the statistical standard error of the radiocarbon date. It follows that a date may be accurate without necessarily being highly precise. It is vital, of course, that a

highly precise date be equally accurate, otherwise the level of precision is not justified.

According to Stuiver and Pearson (1992), the majority of laboratories report the Poisson counting statistics as a laboratory standard error. This results in considerable under-reporting (Scott, Long and Kra, 1990:253-393; Stuiver and Pearson, 1992:20) because a standard error based upon counting statistics alone does not include the errors which may be incurred, for example, during sample preparation. Pearson (1979:21) has suggested:

"Those involved in radiocarbon dating should be alert to the various possible sources of error and recognize that the precision quoted on a date may be quite unrealistic if the error sources have not been investigated in detail".

GORDON PEARSON. 1979. "PRECISE ¹⁴C MEASUREMENT BY LS COUNTING". *RADIOCARBON* 21(1):1-22.

To present a date with a realistic standard error, Pearson (1980; 1983) and Pearson *et al.* (1986:929) have identified the factors which contributed significantly to errors in beta counting using Liquid Scintillation spectrometry. Ostensibly, this research was a precursor to high precision dating of Irish bog oak samples for the calibration of the radiocarbon timescale (Pearson, 1980, 1983; Pearson and Stuiver, 1993). He investigated each principal factor contributing to errors and considered their effect on overall laboratory precision and concluded that a standard error of ± 25 radiocarbon years was possible in the Belfast laboratory*. Standard errors quoted by the Belfast laboratory, then, are based upon this analysis.

Stuiver (Stuiver and Pearson, 1993) has reported that the standard errors reported in the University of Washington laboratory results are based upon a laboratory error multiplier. This approach is similar to that of Pearson in accounting for all errors associated with the radiocarbon determination, not just those obtained from counting statistics. According to Stuiver and Pearson (1993), the error multiplier (or 'K') is a measure of the laboratory reproducibility, incorporating the errors resulting from the preparation of benzene, its loading, memory effects and counting statistics. K is defined as the actual standard error divided by the quoted standard error and is usually generated through repeat dating of a standard of known age or consensus age.

* The standard errors reported in 1993 in the Belfast laboratory are now as precise as ± 21 radiocarbon years at 4000 bp (McCormac, 1993:43)

6.3. PRECISION; ANU SUCROSE AND IAEA STANDARDS

To achieve a high precision result in New Zealand archaeological dating, we really need the $\Delta^{14}\text{C}$ error to be between $\pm 2 - 3\%$ (*ca.* $\pm 16 - 24$ yrs). To consider the practicality of developing a counting system to obtain dates of this precision, or near this level of precision, we must first demonstrate laboratory accuracy, stability and reproducibility at the present level of precision. Routine archaeological samples measured in the Waikato laboratory possess standard errors of between $\pm 3.8 - 4.8\%$ (or *ca.* ± 35 and ± 45 radiocarbon years). To consider accuracy, International Atomic Energy Agency (IAEA) standards have been measured as part of the inter-calibration exercise for the radiocarbon dating community. Modern standards, (ANU sucrose (*ca.* 150‰M) and IAEA cellulose (*ca.* 130‰M)) have been dated regularly in the laboratory and their ratio and temporal relationship considered. The activity of ANU sucrose has been cross-checked with Oxalic acid 1 to consider the accuracy of the laboratory value for the ANU sucrose standard. The SQP(E) values generated using the external standard and the internal standard data have been monitored to consider the long term counting stability of the laboratory's Quantulus counters.

The IAEA co-ordinated an intercalibration exercise in 1990 (Rozanski *et al.*, 1992). Five standard samples were distributed to 300 laboratories. A summary of the samples, the "accepted consensus" IAEA values and the Waikato results are given in table 6.1. Of the 300 laboratories invited to participate, about 100 completed the analyses. The spread of results was higher than expected and the statisticians analysing the data found it necessary to reject up to half of the returned results in order to determine a precise consensus value. The number of results used when deriving the consensus values is shown in column four, with the total number of submitted samples given in brackets alongside.

The importance of inter-laboratory testing and Quality Assurance has become an important issue for the radiocarbon community after the large spread of results from the IAEA inter-calibration (Long and Kalin, 1990) and other cross-checks. A number of laboratories identified significant offsets and discrepancies in their routine results in the light of the comparison. One example is the British Museum laboratory. Over a four-year period (1980-84), lack of attention to modern laboratory standards which were slowly leaking benzene, resulted in dating errors which only became apparent through inter-calibration crosscheck participation (Bowman, Ambers and Leese, 1990). On

ACCURACY, PRECISION, REPRODUCIBILITY

average, the errors resulted in dates which were 200 - 300 years too old. The problem was solved by modifying counting procedures and increasing the regularity with which standards were analysed.

The 1990 University of Waikato determinations were statistically indistinguishable from the consensus values at the 0.95 confidence level (table 6.1).

IAEA CODE	IAEA CONSENSUS VALUES*			UNIVERSITY OF WAIKATO VALUES	
	% Modern $\pm 1\sigma$	Conventional age $\pm 1\sigma$	Number of analyses	% Modern $\pm 1\sigma$	Conventional age $\pm 1\sigma$
C1 i	0.00 $\pm$ 0.03	∞	36(73)	0.07 $\pm$ 0.04	>55,000
C2 ii	41.14 $\pm$ 0.03	7135 $\pm$ 6	64(92)	41.05 $\pm$ 0.20	7152 $\pm$ 40
C3 iii	129.41 $\pm$ 0.06	n.a.	49(84)	130.26 $\pm$ 0.49	n.a.
C4 iv	0.2 - 0.44	40-50000	67(68)	0.20 $\pm$ 0.0	50,000 $\pm$ 2000
C5 v	23.05 $\pm$ 0.02	11,788 $\pm$ 7	66(68)	23.07 $\pm$ 0.14	11,779 $\pm$ 49

Notes :

n.a : not applicable

* data from Rozanski *et al.* (1992). The IAEA ^{14}C Intercomparison Exercise 1990. *Radiocarbon* 34(3):506-19.

i: Carrara marble, prepared by IAEA, Vienna.

ii: Freshwater travertine, prepared by IAEA, Vienna.

iii: Cellulose from modern paper, prepared by W. G Mook, Groningen.

iv: Subfossil kauri, prepared by A. G Hogg & H. A Polach, University of Waikato.

(Values too spread to permit definition of consensus value).

v: Two Creeks wood, prepared by A. Long, University of Arizona.

Table 6.1: Results of the IAEA Intercomparison 1990 showing University Of Waikato determinations compared with those of other laboratories. In column 4, numbers given in brackets are the total number of laboratories which submitted results, alongside is the number of results used to generate a consensus value.

The difficulty in measuring samples close to modern and samples close to background accurately is illustrated by the number of laboratories used to derive the consensus values for samples C1 and C3.

The accuracy of the laboratory secondary standard (ANU sucrose) was tested using Oxalic acid 1. We considered the analysis of the relationship of Ox 1 to ANU sucrose important for two reasons. First, we thought the IAEA consensus value for ANU sucrose (150.61%M (Rozanski, 1991)) may be too modern because the equivalent value measured in the high precision Belfast and Groningen laboratories during the IAEA intercalibration was lower. These are high precision laboratories and their results differed significantly from the consensus value. We thought the consensus value may have been biased by results from less accurate laboratories. Second, we considered it useful for investigating the overall accuracy of the laboratory.

The ratio of the activity of sucrose with 0.95 Ox was first measured by Polach at 1.5007 ± 0.0052 (Polach, 1976b:122). Later inter-laboratory measurements put the ratio at 1.5081 (Currie and Polach, 1980). The activity of ANU sucrose was thus considered using Oxalic acid 1 as the standard. Two measurements were obtained, $150.5 \pm 0.8\%$ M and $151.1 \pm 0.8\%$ M. The pooled mean (A_p) was $150.8 \pm 0.56\%$ M ($T=0.28$; $\chi^2_{1:0.05}=3.84$). This value is indistinguishable from the accepted consensus value for ANU sucrose.

6.4. THE LIMITS OF PRECISION

The application of higher precision dating may only be validated from a laboratory viewpoint if all errors are assessed for their contribution to the overall dating error. In this section, some important variables influencing precision in routine Waikato dating, outside counting statistics, will be examined. A laboratory error multiplier (K) will then be calculated using repeat dates of IAEA standard cellulose to account for errors in reproducibility. An internal error multiplier (IEM) will also be calculated to consider the applicability of standard errors released in the laboratory.

6.4.1. ISOTOPIC FRACTIONATION

Isotopic fractionation during routine sample preparation may result in the selection of one isotope over another, affecting the measurable ratio and the resulting age. A sample may be fractionated by being burnt too rapidly, transferred with incomplete attention to vacuum pressure or through inadequate pumping. This effect should not be confused with natural isotopic fractionation, which is part of the biochemical processes of all living organisms (Craig, 1953).

A sample of CO₂ gas is obtained after hydrolysis or combustion, for $\delta^{13}\text{C}$ measurement to correct for natural fractionation.

During this research, discrepancies were noted in the $\delta^{13}\text{C}$ values of some duplicate radiocarbon samples. An investigation was therefore made into stable isotope measurement reproducibility to consider the source of the error and apply a correction. Subsequently, repeat CO₂ samples generated from Oxalic acid were measured to consider reproducibility and accuracy further.

EXPERIMENTAL

A significant error may be introduced into a radiocarbon measurement close to modern through incorrect stable isotope measurement. In figure 6.1, the error introduced into a conventional age determination (bp) by variation in $\delta^{13}\text{C}$ correction is shown. The hypothetical sample possesses a $\delta^{13}\text{C}$ of 1.0‰ and a date of 1000 ± 50 bp. Shifts of 0.5‰ in $\delta^{13}\text{C}$ will equate to an error in D14C of 1.0‰. In the example given above, this is 0.2σ shift per 0.5‰ shift in $\delta^{13}\text{C}$.

Errors were identified in some $\delta^{13}\text{C}$ measurements. Some samples affected by spectral shift (see below) were re-dated and differences were identified between the $\delta^{13}\text{C}$ values of the original samples and their duplicates. The $\delta^{13}\text{C}$ value of Wk-2369, for example, was 1.2‰. Its repeat, Wk-2507, had a measured $\delta^{13}\text{C}$ value of -1.2‰. Wk-2370, with a $\delta^{13}\text{C}$ of 1.0‰, was followed by Wk-2506 with a value of -0.3‰. The age of Wk-2506 before rounding, using -0.3‰ as a $\delta^{13}\text{C}$ value was 924 ± 32 bp; with a $\delta^{13}\text{C}$ of 1.0‰, the age was 945 ± 32 bp, so the probable error introduced in this instance was significant.

The anomalous results were considered by analysing the performance of the mass spectrometer. Standard measurements of the secondary laboratory Kapuni gas standard CO₂ were compiled over a one and a half year period. In figure 6.2 (measurements between 19.3.92 and 16.12.92) and figure 6.3 (measurements between 7.1.93 and 23.7.93) the $\delta^{13}\text{C}$ results from successive standard samples are shown. The mean δ value of the gas is -14.5‰ wrt PDB. Both graphs have the same scale. In figure 6.2, the 1992 results show significant variability

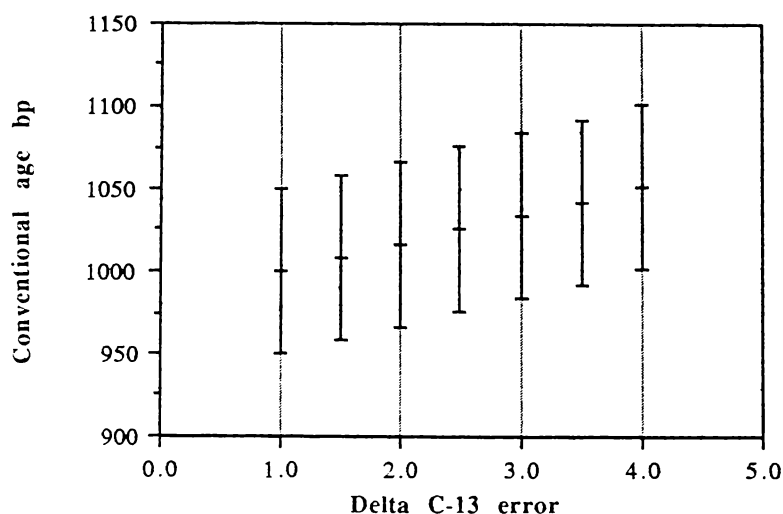


Figure 6.1: error introduced in a radiocarbon date of 1000 ± 50 bp with $\delta^{13}\text{C}$ of 1.0‰ by increasing the error in $\delta^{13}\text{C}$ measurement by 0.5‰ up to 3‰ wrt PDB.

between 10.8.92 to 18.11.92. $\delta^{13}\text{C}$ results during this period were adjusted to the mean value of -14.5‰ by correcting the formulae used in the $\delta^{13}\text{C}$ calculation (see Fig. 6.2: "DC13 results adjusted"). The variation was caused by leaking capillaries which meant unstable gas pressure in the mass spectrometer and some spurious results. Two of the duplicate samples which exhibited variation (Wk-2506 and Wk-2507) were measured on 13.8.92, immediately prior to the instrumental problem (21.8.92). No Kapuni samples were analysed with them however. Were standard results available, the disparate sample values could be corrected. In the absence of standards, samples measured at the time of the instrument problems were corrected for isotopic fractionation using either duplicated samples or, in the case of samples which were repeat dates, the $\delta^{13}\text{C}$ results of earlier samples. In some cases, the pooled mean of the $\delta^{13}\text{C}$ values measured in a series of dates from the same material was used.[#] The

[#] The corrected measurements ($\delta^{13}\text{C}$ results in brackets) were; Wk-2589 ($\delta^{13}\text{C}=-28.3$) corrected using mean of Killermont series of dates ($\delta^{13}\text{C}=-27.3$), Wk-2594 ($\delta^{13}\text{C}=-27.5$) corrected using the same mean, Wk-2508 ($\delta^{13}\text{C}=-0.2$) corrected using previously run sample value (Wk-2363; $\delta^{13}\text{C}=1.0$), Wk-2506 ($\delta^{13}\text{C}=-0.3$) using a duplicate result (Wk-2370; $\delta^{13}\text{C}=1.0$), Wk-2507 ($\delta^{13}\text{C}=-1.2$) using duplicate result (Wk-2369; $\delta^{13}\text{C}=1.2$) and Wk-2509 ($\delta^{13}\text{C}=-0.4$) using previously run Wk-2415 value ($\delta^{13}\text{C}=0.7$).

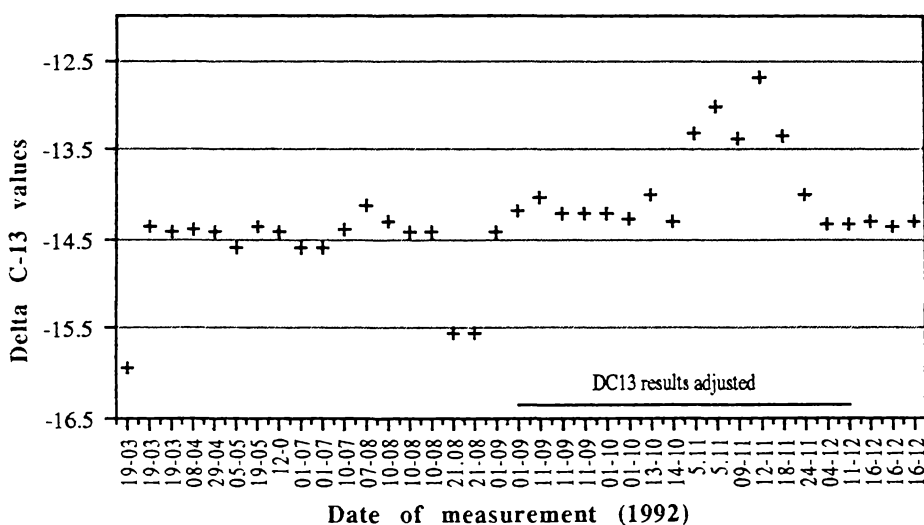


Figure 6.2: $\delta^{13}\text{C}$ measurements from Kapuni CO_2 gas 1992. The standard error for these values is $\pm 0.1\text{--}0.3\text{‰}$. The laboratory standard is W.L.S (Waikato Limestone Standard).

discrepancies identified, then, were the result of instrumental problems which could have been corrected for more accurately had standards been run with greater regularity.

In figure 6.3, the $\delta^{13}\text{C}$ results for Kapuni gas samples measured in 1993 are shown. They reveal improved reproducibility. To avoid errors associated with instrumental variation, the ratio of samples to standard $\delta^{13}\text{C}$ measurements should be increased to trace any instrument malfunction more effectively.

To consider stable isotope reproducibility further, we measured repeat samples of CO₂ gas generated from the Oxalic acid 1 standard. The results are shown in table 6.2.

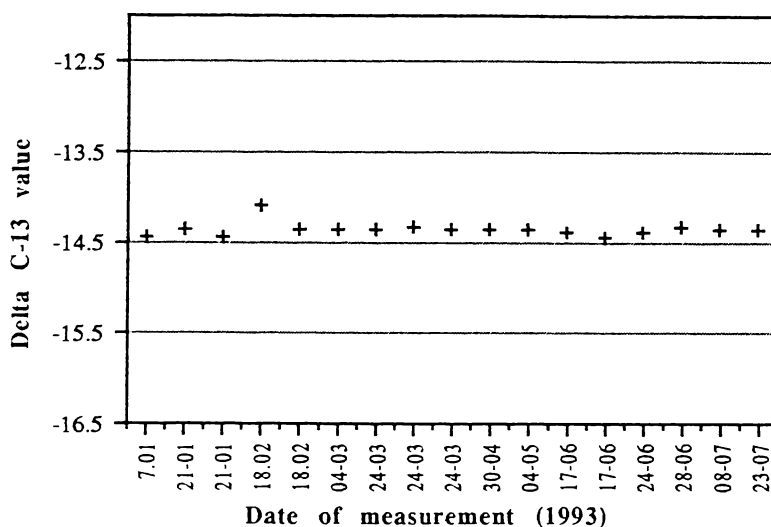


Figure 6.3: $\delta^{13}\text{C}$ measurements from Kapuni CO_2 gas between 7.1 and 23.7, 1993. The standard error for these values is $\pm 0.1\text{--}0.3\text{‰}$. The laboratory standard is W.L.S (Waikato Limestone Standard).

Laboratory Number	$\delta^{13}\text{C}$ (‰)	Pooled mean value of #1 and #2. $\delta^{13}\text{C}$ (‰)	Pooled Oxalic acid 1 $\delta^{13}\text{C}$ (‰)
Ox1B#1	-19.81	-19.72	-19.67±0.04
Ox1B#2	-19.63		
Ox1C#1	-19.50	-19.61	
Ox1C#2	-19.72		
Ox1D#1	-19.70	-19.68	
Ox1D#2	-19.66		

Table 6.2: $\delta^{13}\text{C}$ results measured using oxalic acid 1 standard. #2's are $\delta^{13}\text{C}$ values from samples which were fractionated. The standard error for the values in column 2 is $\pm 0.1\text{--}0.3\text{‰}$.

The data in table 6.2 suggest acceptable reproducibility. They also show the laboratory measures accurately the mean $\delta^{13}\text{C}$ value for Oxalic acid 1 which, according to Polach (1976b) was calculated by Craig at -19.3‰ . This is a pleasing result because of the problems associated with the combustion of Ox 1 due to the fractionation errors which

sometimes result (see Polach, 1976b for examples). To avoid these errors, Ox 1 is often wet oxidised rather than combusted.

Errors were initially identified in sample measurement, then, which introduced an error in $\delta^{14}\text{C}$ of some samples of $\pm 0.3\%$. Recent improvements in the instrument combined with more regular Kapuni sample measurement mean that this error now has been significantly reduced.

6.4.2. VARIATION OF EFFICIENCY WITH PURITY (QUENCH)

(i) INTRODUCTION

In Liquid Scintillation spectrometry, quenching describes the attenuation of the pulse height in the ^{14}C spectrum. Put simply, this means the efficiency of energy transfer from the decaying beta particle to the photon is affected, thus count rates are reduced. There are two major types of quench. Chemical quench is caused by substances incorporated into the counting solvent. Some examples of quenches include ammonia, anthracene and toluene. Oxygen, which is incorporated into the sample benzene during loading of the counting vials, is also a quench. Colour, or light quench, describes the effect on the light transmission characteristics of the sample, through solute deposited on the inside of the counting vial and by coloured substances in the vial absorbing light in the same wavelength as itself (Raaen *et al.*, 1968).

Chemical quench may be identified in the Quantulus counter through use of the MCA and the pulse height of the measured spectrum. The ^{14}C spectrum of a quenched sample may be identified by a reduction in pulse height, resulting in a shift in the spectrum to the left of an unquenched spectrum (Fig. 6.4).

(ii) IDENTIFICATION OF QUENCH

Quench is a ubiquitous problem affecting all Liquid Scintillation laboratories to varying degrees. Research into quench and its effects on accurate radiocarbon dating has been undertaken by a number of researchers, including Horrocks (1974), Pearson (1980) and McCormac (1992). Radiocarbon dating by Liquid Scintillation counting involves the careful comparative measurement of sample and standard benzene cocktails. Variation in benzene purity causes variation in counting efficiency and hence affects beta particle detection. In the radiocarbon dating of young samples and high precision samples, quenching and spectral shift have critical effects on ages. Given the emphasis

on accuracy and precision in this dissertation it is important to examine quenching and its effects.

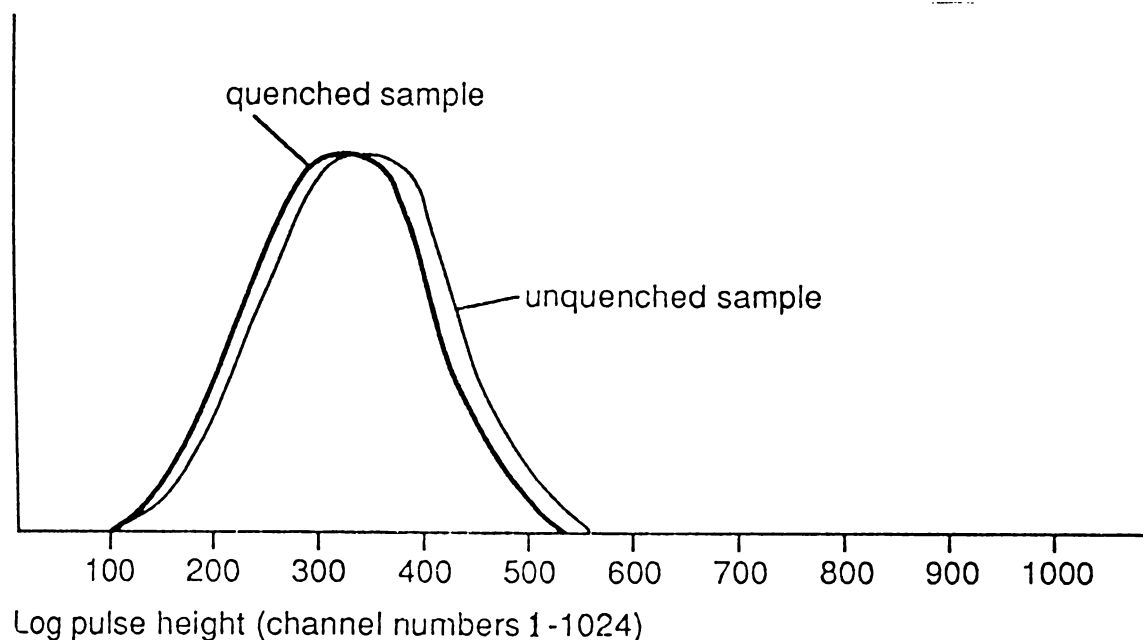


Figure 6.4: The effect of quench or spectral shift upon the pulse height of a sample ^{14}C spectrum in comparison to an unquenched standard spectrum.

Quenching was observed in some samples early in this dissertation. Initially, samples Wk-2318, 2363 and 2368 showed spectral shifts consistent with quenching. Wk-2369, a sample of *Amphibola crenata* from Pleasant River, for example, was dated initially to 1300 ± 50 bp. This date was considered too old for the site. The sample and standard spectra were misaligned (Fig. 6.4) by 4 channels (the date was later re-run and measured at 1140 ± 45 bp). In total, 6 of the first nineteen samples dated were quenched (these samples are identified in appendix 1).

The first stage in addressing the problem of quench was to consider the parameters by which it was to be most effectively observed, to enable its identification and quantification, and to estimate the error introduced. The most effective method to assess the direction of shift and the effect of quench is to measure the shift in relative pulse height. The use of an MCA in the Quantulus enables the pulse height of the ^{14}C spectrum to be analysed by end point. End point, as initially defined in this dissertation, is the channel number above which 1% of the total count rate is found. By comparing the end points of quenched and unquenched samples, we hoped to be able to accept or reject samples based on the number of channels the sample had shifted. In general, the greater the channel shift from the standard, the greater the quench, the more the

deviation from the 'true' age. Polach (pers. comm.) suggested that samples shifted from the vial modern standards by 2 channels or more, were likely to be significantly older than the true age and should either be rejected from consideration, or rerun.

This analysis failed, ostensibly because of the combined effects of ^{222}Rn influence, variation in vial material (the laboratory switched from teflon to silica vials) with associated changes in end point, and variation in end point between different vials of the same material. Only general conclusions were able to be drawn concerning quench and end point shift; the relationship between channel and end point, and sample age shift remained obscure.

The measurement of end point using 1% of the ^{14}C spectrum, rather than the total 1024 wide-window channels was implemented later. This was more accurate because it enabled the higher energy ^{222}Rn peaks to be eliminated using the upper discriminator. The upper and lower discriminators were aligned at channels 100 and 650 respectively, the lower discriminator was then moved until 1% of the spectrum was contained within the window. The end point was defined as the channel number corresponding to the lower discriminator set at 1% of the spectrum.

(iii) LITHIUM CONTAMINATION

Lithium used in the lithium carbide reaction was considered a likely source for impurities which produced chemical quenching. A batch of lithium metal rods used in the carbide reaction were coloured with a dark, crust-like surface, dissimilar to the usual soft, silvery metal. The lithium metal used in the laboratory is usually high-purity, battery grade, packed in argon within an aluminium canister. However, due to a clerical error, the lithium used at the time quenching was observed was industrial grade, stored in petroleum spirit. We thought this may be the source of the quench contaminant. One possibility was that nitrides had formed on the lithium rods because of its poor storage, resulting in nitrogen compounds in the sample benzene. We attempted to simulate the quench by leaking N_2 onto the lithium in the reactors over varying periods of time. The measured spectra resulting from this experiment, however, showed no quenching compared to a control group. XRD analyses identified the black material on the outside of the lithium rods as lithium nitride, but it was not possible to demonstrate a link with laboratory quench in these experiments.

A new batch of high grade argon-packed lithium was obtained to replace the affected material and new standards were run in the laboratory in each sample vial. An improved system of Quality Control was implemented (Polach, 1992). ANU sucrose standards were run more regularly. Spectra were analysed by end point and the results kept for reference. Laboratory sample cards were introduced to enable laboratory operators to write detailed observations regarding each reaction, at each stage of the process. This approach was designed to identify spectral shift influences generated in the laboratory more effectively.

After a year, some spectra continued to be misaligned but the problem was alleviated through the buildup of a library of standard spectra for each counting vial. A sample whose spectrum was displaced from its standard, was able to be matched with another standard run in the same vial and shifted to a similar degree. The assumption was that samples and standards with identical end point and close spectral 'fit' would give more valid radiocarbon dates than those which were distinct. Standard end points were measured and fitted with the sample having the most similar end point. This method of correction was useful as the results of re-calculated quenched samples attests. Wk-2415, for example, was initially calculated at $107.6 \pm 0.4\%M$ but was misaligned with its standard and therefore its pMC value was too low. It was re-calculated using an older standard spectra whose end point was similar, and gave a result of $108.8 \pm 0.4\%M$. Later, the sample was re-run using new material and dated to $109.7 \pm 0.5\%M$, a result indistinguishable from that recalculated using the 'best fit' spectrum.

The problem of shifted spectra, however, remained, but it became apparent gradually that spectral displacement may not be caused solely by quench. Certain modern standard spectra pulse heights were observed to be successively *increasing* in comparison to previous spectra. Furthermore, affected samples formerly thought to be quench influenced were not showing lower count rates consistent with reduced counting efficiency. In one instance, a sample with a significantly *reduced* end point in comparison to a previous modern standard in the same vial, possessed a significantly *higher* count rate. In addition, some vials showed greater stability than others. Vial 24 in Quantulus 2, for example, showed no significant shift, while others in the same counter yielded small but seemingly significant shifts with each new modern standard.

(iv) VIAL CHARACTERISTICS

Vial loading, cleaning and counting procedures were examined to attempt to identify any contribution to quench and spectral shift. Two vials (10 and 24) were selected for experimentation. The former was typical of some of the vials whose standards yielded variable standard end points. The latter was selected because it showed the most reproducible characteristics. To analyse whether the position of the vial in the counting chamber influenced variation in spectral position and count rate, a high activity benzene sample (*ca.* 900 disintegrations per minute) was counted in each vial, in four different counting positions in the Quantulus (45° apart from each other) for 500 minutes. If inconsistent vial wall characteristics were the cause of the variation, the results of each positional change would be expected to result in variable count rates and spectral shifts. No variation was noted in any position, in either vial.

More rigorous vial cleaning procedures were implemented to attempt to remove any possible solute buildup on the walls of the vials. All vials were cleaned using Decon 90 (commercial glass cleaner), chromic acid, repeat benzene, ethanol and distilled water rinses, ultrasonic bathing and vacuum pumping. These had no visible effect or improvement upon spectral position. One vial which possessed variable end point was analysed using a Scanning Electron Microscope and compared with a new vial not used for counting. No solute buildup could be identified on the walls of either.

(v) THE EXTERNAL STANDARD AND GAMMA RADIATION INFLUENCES

In the light of the investigations described above, few possible sources for spectral shift remained. We thought that perhaps the Quantulus ionising unit or the external standard may be an influence, inducing slow shift in pulse height in successive standards. The ionising unit removes any electrostatic buildup on the vial prior to counting as the vial and holder are lifted by the piston into the chamber. We have already mentioned the external standard, which is a high activity ^{226}Ra bead presented beneath the counting vial for a pre-programme time to measure SQP(E), whose variation is a function of sample benzene purity. One possibility was that the external standard was somehow artificially influencing the vials and their holders and shifting the spectra. The ^{226}Ra external standard emits primarily α and γ radiation and is considered by the manufacturer unlikely to influence sample counting.

To test this, the external standard in one Quantulus was switched off, whereupon the sample spectra in all vials, exhibited a decline in measured pulse height by up to 8 channels. This observation suggested the external standard radiation had an influence upon the position of the ^{14}C spectrum.

Dr A. Hogg coordinated an investigation into the effect of the external standard radiation and the ionising unit on count rate and counting stability using a set of 2 silica vials in delrin plastic holders, and a set of 2 low-K glass vials. The vials were loaded with high activity benzene (*ca.* 1100 cpm) and counted for 10 000 minutes with the external standard turned off. One vial in each set was then exposed to the external standard for 10% of its counting time, and the differences between it and the second group of control vials, which were not exposed, was monitored. The count rates of both sets were unaffected by the external standard radiation but the silica vials in the delrin holders showed declining end point values over the count duration. The low-K glass vials showed more variation in count rate, but they were more stable spectrally, with end points showing little shift.

The possibility that the delrin holders were influencing end point shift was considered and these were replaced with aluminium holders. Further experiments were conducted using lead and copper, with delrin as a control. It was found that spectral stability improved significantly using the aluminium and lead holders. However, no significant shift in count rate was observed in any of the holders utilised.

(vi) DISCUSSION

The analysis of quench, then, developed into a detailed analysis of the possible factors influencing spectral shift. In retrospect, samples which were initially affected by shifting spectra were probably influenced by more than one factor, which is why the accurate identification of the problem was difficult. First, there may have been a chemical quench influencing the purity of the sample benzene. This affected 6 of the samples in this dissertation and may have been caused by the lithium which had observable impurities and was not high purity grade. Second, there was an effect introduced by the external standard. This seems to have increased spectral end point over time. In some cases, this may have led to increased count rates, although this was only perceptible over a long period of counting and could not be reproduced experimentally using high activity benzene. When the source was removed, however, end points showed greater stability (see below for examples). The exact relationship

between count rate and end point, and the external standard is clearly complex and is still under investigation.

While spectra were shifting, the effects were reduced by increasing the ratio of standards to samples and decreasing the time between re-calibration of vials. Spectral shift over time was rendered less important through increasing the regularity of recalibrating standard vials. By measuring more standards, a library of spectra was able to be built up and samples literally 'fitted' with the closest matching standard as measured precisely by end point.

By late 1993, many vials used in routine dating possessed up to six standard spectra. This enabled a reassessment of the research on the relationship of spectral end point to count rate, and the quantification of the effect of spectral displacement upon the calculated radiocarbon age. The counting spectra of some prehistoric benzene samples,

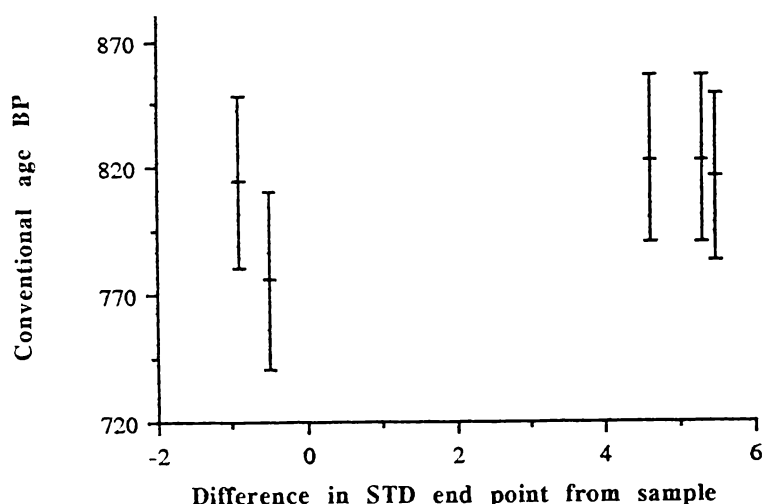


Figure 6.5: relationship between standard end point and radiocarbon age calculated for Wk-2864 in vial 24, University of Waikato Radiocarbon Dating Laboratory.

were measured against a library of standard spectra each shifted along a continuum of up to 7 channels. Were the relationship between the two close, we would expect an older radiocarbon age to be associated with increasing standard pulse height, that is, where the sample spectra is to the left of the standard. In figures 6.5 - 6.7, the results of the comparison are shown. The sample dates calculated for Wk-2864 in vial 24, using different standards with varying end points are statistically indistinguishable (Fig.

6.5). A series of standard spectra are used to calculate dates for sample Wk-2368 (Fig. 6.6). Over 5 channels in standard end point shift, the effect on the radiocarbon age is insignificant statistically, with a maximum difference of 0.5σ between the two most distant results. A >Modern sample is also analysed (Fig. 6.7). The variation in %Modern is insignificant despite a shift in end point of 4 channels.

This suggests that the effect of end point shift in the standard upon the calculated radiocarbon age is not significant at this level of precision.

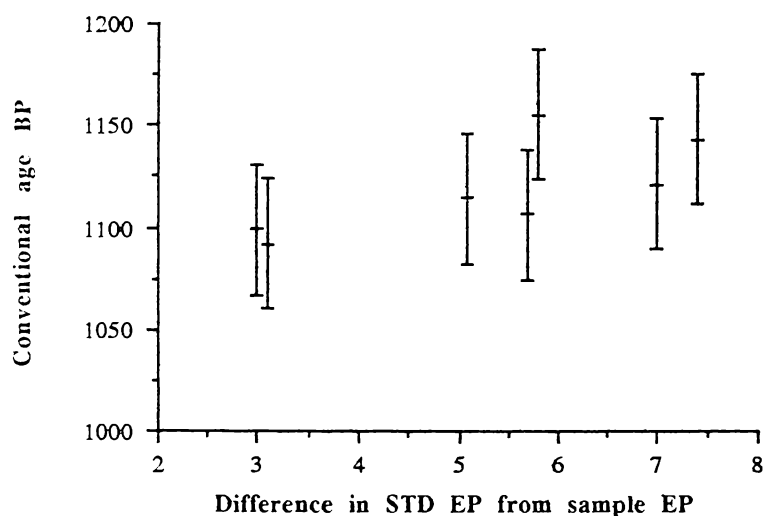


Figure 6.6: relationship between standard end point and radiocarbon age calculated for Wk-2368 in vial 23, University of Waikato Radiocarbon Dating Laboratory. Note that for this sample, a shift in standard end point of over 5 channels resulted in no significant difference in the calculated radiocarbon age, nor did calculation with a standard possessing an end point difference of >7 channels.

(vii) CONCLUSIONS

McCormac (1992) has suggested that it is crucial in high precision dating to correct for spectral shifts resulting from gain changes and from quenching. At the Belfast laboratory this is achieved principally through monitoring the deviation of the external standard spectrum (SQP(E)) from its set-up position. Corrections to affected sample measurements are made using this parameter to ensure valid high precision dates

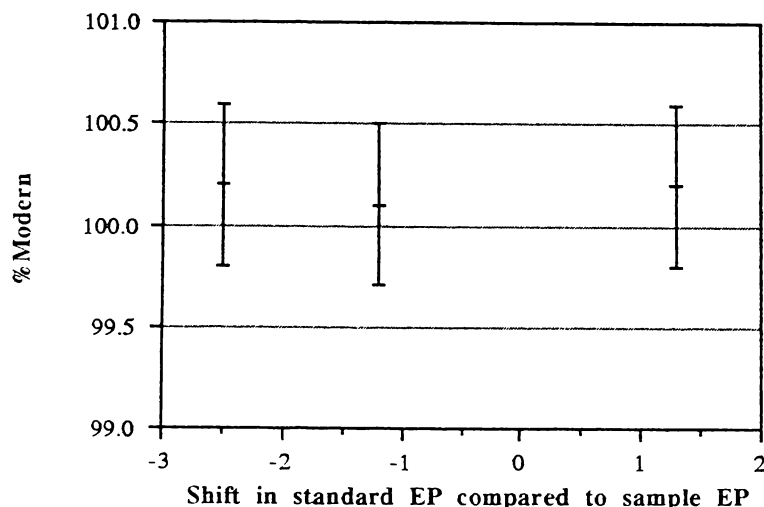


Figure 6.7: relationship between end point and radiocarbon age calculated for Wk-2969B in vial 43, University of Waikato Radiocarbon Dating Laboratory. Samples at -1 are shifted one channel to the left of the sample spectrum end point.

(McCormac, 1992). McCormac (1992) has based his quench correction programme upon the assumption that shifts in end point result in shifts in count rate. In the silica vials used at Waikato, this assumption may not be valid. Our observations show reproducible, stable count rates in some samples possessing variable end points (Figs. 6.3 - 6.7). We suggest there can be natural variability in end points over ± 2 channels, and in some cases greater, in which count rates are unaffected.

In figure 6.8, for example, the stability of recent routine standards measured in vial 43 is shown. Each counting set represents one standard generated from one benzene synthesis, so there are three separate standards in the figure, covering 6 months of counting. The first standard - M43.1, was counted for 5000 minutes and recorded a value for A_{on} (normalized cpm) of 28.489 ± 0.095 cpm. The second, M43.2 was counted for 4500 minutes and gave an A_{on} of 28.485 ± 0.099 cpm and the final, M43.3, was counted for 7000 minutes giving A_{on} of 28.474 ± 0.078 cpm. Each value for A_{on} in the three standards is indistinguishable at 0.95 probability ($A'_p = 28.481 \pm 0.051$ cpm ($T = 0.02$; $\chi^2_{2;0.05} = 5.99$). This shows excellent reproducibility, considering the high count times and low standard errors. As figure 6.9 shows, despite the high reproducibility of these

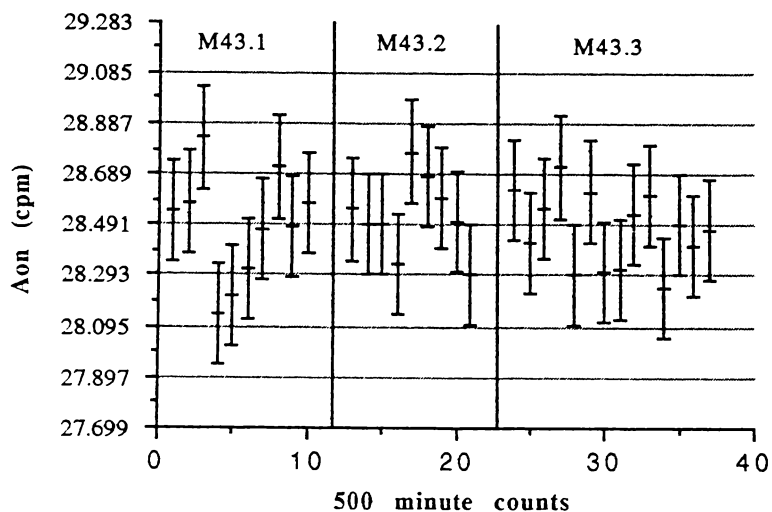


Figure 6.8: Reproducibility in silica vial 43 in aluminium holder in Quantulus 4. Each summed counting set (M43.1-3) represents one standard spectrum resulting from an ANU sucrose benzene synthesis. The normalized count rates for each are statistically indistinguishable from each other and show stability over the 6 months of time during which they were counted.

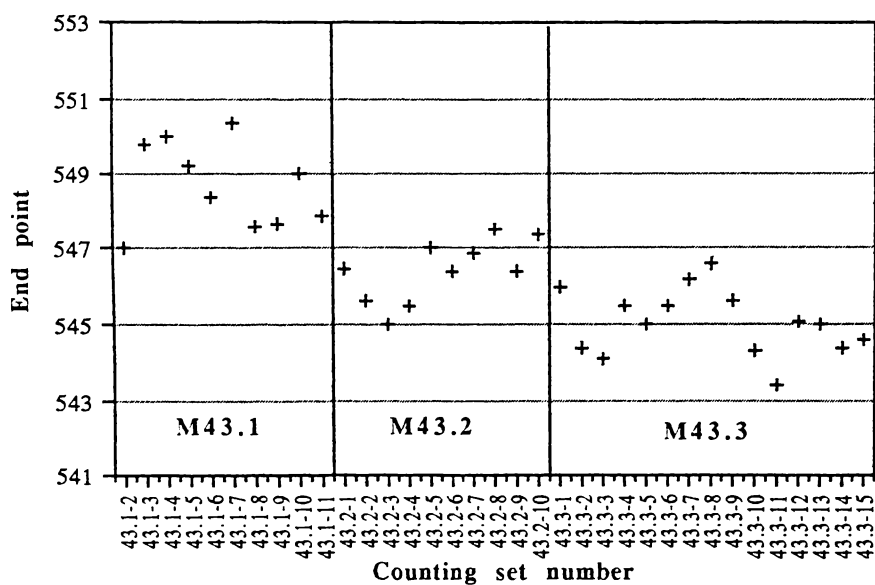


Figure 6.9: End points for 3 modern standards in silica vial 43 (in aluminium holder in Quantulus 4). Each end point is generated using one 500 minute count. The slow decline in end points referred to in the text is apparent.

results, end point variations of up to 7 channels are observed. This result is mirrored in every other laboratory vial.

The development of a high precision facility is an ongoing programme at the Waikato laboratory and the results described above constitute a part of the identification of errors which affect accuracy. A number of conclusions are apparent thus far and a variety of developments have been made:

- Stability in terms of end point shift may be related to the type of material of the vial or vial holder. Greater stability in end point was noted with aluminium and lead holders compared with delrin. Delrin is now no longer used. As a precaution, all vials within the counter are secured in place in their holders using a steel pin to prevent any rotational movement within the sample holder. All vials are kept with individual holders to ensure as much as possible, reproducibility in counting and eradication of variation in count rates due to vial rotation.

- The counters have been recalibrated and counter MPTs have been realigned using SPQ(I) values determined from high count rate (*ca.* 1000 cpm) benzene, loaded into the silica counting vials.

- The external standard is now not used during routine dating.

6.4.3. LOSS OF SAMPLE BENZENE

Loss of sample benzene may introduce significant errors in radiocarbon dating because counting efficiency varies linearly with benzene weight loss (Pearson *et al.*, 1986). Pearson *et al.* (1986:929) suggests an error of 8 years is introduced through benzene leakage of 1 mg/day if the problem is uncorrected. According to them, benzene leakage may be as much as 10 mg/day. At the Waikato laboratory, silica vials are made with stainless steel stoppers and a black chemraz O-ring which seals the benzene and restricts loss due to evaporation to <0.1mg of benzene over one week at 12° C (Hogg, and Noakes, 1992:395), thus errors due to benzene leakage are minimal.

6.4.4.VARIATION OF EFFICIENCY WITH SCINTILLATOR AND BENZENE WEIGHT

Rigorous attention is paid at Waikato to ensure as little variation as possible in the weights of scintillator and sample benzene. The development of silica vials and stainless steel stoppers which seal the cocktail have been mentioned above. The ideal weights of scintillator and sample benzene for each of the 4 vial sizes used in the Waikato laboratory are shown in table 6.3. In all cases, each vial is loaded with the weight of scintillator and sample benzene to the required precision.

Sample size (ml)	Weight butyl-PBD (g)	Sample benzene weight (g)
0.35	0.0060±0.0002	0.3500±0.0002
0.75	0.0128±0.0002	0.7500±0.0002
3.0	0.0450±0.0002	2.6370±0.0002
5.0	0.0768±0.0002	4.5000±0.0002

Table 6.3: ideal weights of sample benzene and scintillator for each of the four routine sample sizes used in the Waikato laboratory.

As mentioned above, benzene losses are reduced to <0.1 mg per week which means that over the week in which a routine sample is counted, errors due to variation in counting efficiency are considerably reduced.

6.4.5. CONTAMINATION WITH TRITIUM

^3H is introduced into benzene during the lithium carbide reaction when water containing ^3H is used in reaction. ^3H possesses a spectrum which overlaps the lower end of the ^{14}C spectrum and may introduce errors if it varies in its contribution. To reduce the error, modern Liquid Scintillation counters provide the user with a Hi bias option which automatically cuts the lower energy beta particles including part of the ^{14}C spectrum, but removing the majority of the ^3H spectrum. Part of the ^{14}C count is therefore lost. McCormac (1992) has suggested that the elimination of much of the ^3H can be achieved by setting the lower discriminator to include only the top 1% of the ^3H spectrum while excluding the remainder. This results in the loss of 8% of the total ^{14}C count but

avoids spurious counts generated from ^3H (McCormac, 1992). One possible alternative is to use water which is tritium-free, for example, from geothermal bores. The benefits of using this water in the carbide reaction are being investigated further.

6.4.6. CONTAMINATION WITH ^{222}Rn

Contamination with radon is a ubiquitous problem affecting all radiocarbon dating laboratories. Radon is one of the daughters produced from the decay series of uranium and thorium. As mentioned above, ^{222}Rn emits β particles with a decay energy of 5.587 meV, influencing the ^{14}C spectrum at the higher energy level. There is a variety of methods of reducing the influence of ^{222}Rn . The short half-life of ^{222}Rn (3.82 days) means that it can be avoided by leaving the sample benzene for 4 weeks (or about 10 half-lives) prior to dating, while it decays. Problems arise, however, when the sample needs to be dated quickly. Radon may also be removed through the rigorous heating of the lithium carbide to *ca.* 800° C under vacuum (Polach and Kaihola, 1988).

The temperature of ethanol traps used to collect benzene from the catalyst columns were raised to -65° C after Polach (pers. comm.) suggested this may reduce radon collection. Experimentation using samples close to background, showed reduced amounts of ^{222}Rn after removal at the lower temperature. Samples dated in this dissertation were left for up to 10 weeks before counting. The error introduced by ^{222}Rn may therefore be discounted.

6.5. LABORATORY ERROR MULTIPLIER (K) CALCULATION

To account for errors introduced by some of the parameters described above and to assess overall laboratory reproducibility, 11 samples of IAEA C3 standard cellulose (*ca.* 130%M) were dated. Initially, we decided to use homogenised identified charcoal from the Shag Mouth site for a demonstration of reproducibility, however, there were two advantages in opting for an IAEA standard series of measurements. First, the standard was homogeneous and of known age relative to IAEA consensus results (table 6.1). Second, a laboratory error multiplier (K) could be calculated from the results. The K value represents the factor by which each conventional radiocarbon date is multiplied to account for errors in reproducibility not included in Poisson counting statistics.

ACCURACY, PRECISION, REPRODUCIBILITY

The dates of the IAEA C3 cellulose samples are shown in table 6.4. The pooled mean result ($A(p)$) using 1 σ values was $129.91 \pm 0.15\%M$ ($T=16.30$, compared with $\chi^2_{10:0.05}=18.31$).

SAMPLE #	VIAL NUMBER	EW MEAN (%M)	STANDARD ERROR (1 σ)
C3 B	22	130.00	0.48
C3 C	23	128.39	0.48
C3 D	24	129.47	0.49
C3 E	23	130.21	0.48
C3 F	24	130.48	0.49
C3 G	22	130.54	0.48
C3 H	23	130.52	0.49
C3 I	24	130.02	0.49
C3 J	22	129.85	0.49
C3 K	24	129.63	0.49
C3 L	23	129.95	0.49

EW=error weighted mean.

Table 6.4: Repeat radiocarbon measurements of IAEA C3 standard cellulose at the University of Waikato laboratory, 1991.

Because the dates are replicates, we can assume they are the same age. In this instance, we have 11 radiocarbon dates, C3B...C3L, with corresponding errors C3B σ ...C3L σ . The true error for each date however, is not σ , but $K \times \sigma$, because K is the uncertainty introduced into each calculation. The laboratory error multiplier was calculated as follows (formulae from M. Scott, Department of Statistics, University of Glasgow). To estimate K , we first obtain the weighted average, or pooled mean of the dates using:

$$A(p) = \left(\sum_1^n C3_{B-L} / \sigma_{B-L}^2 \right) / \left(\sum_1^n 1 / \sigma_{B-L}^2 \right)$$

The error multiplier is then calculated by:

$$K = \sqrt{\sum_1^n (C3_{B-L} - A(p))^2 / \sigma_{B-L}^2}$$

The result was 1.217. The standard error for every date calculated is multiplied by this factor to account for uncertainty in reproducibility and routine errors in dating.

The purity of the benzene generated from the IAEA samples measured for the laboratory error multiplier was investigated. Analytical grade (AR) benzene and IAEA benzene were analysed by GC/MS at the University of Waikato and at the Radiocarbon Dating Laboratory, University of Arizona by Dr R. Kalin. No significant impurities were detected; spectra obtained using the benzene generated within the laboratory were indistinguishable from those of analytical grade benzene.

The reproducibility of samples dated in this dissertation was further considered using replicate dates, that is, duplicate dates generated from the same sample.

Wk#	Site	Material	Conv. Age bp/ % Modern	IEM value
2965	Pleasant River	<i>A. stutchburyi</i>	108.7±0.5	0.78
2965B	Pleasant River	<i>A. stutchburyi</i>	109.2±0.4	
2966	Papanui Inlet	<i>A. stutchburyi</i>	109.8±0.5	0.56
2966B	Papanui Inlet	<i>A. stutchburyi</i>	109.4±0.5	
2693	Portobello	<i>A. stutchburyi</i>	109.3±0.5	0.42
2694	Portobello	<i>A. stutchburyi</i>	109.0±0.5	
2711	Pleasant River.	<i>A. stutchburyi</i>	108.2±0.5	1.13
2712	Pleasant River.	<i>A. stutchburyi</i>	109.0±0.5	
2758	Pleasant River	Moa eggshell	650±45	0.99
2759	Pleasant River	Moa eggshell	590±40	
2760	Pleasant River	Moa eggshell	600±45	0.17
2967	Shag Mouth	<i>A. stutchburyi</i>	108.5±0.5	0.84
2967B	Shag Mouth	<i>A. stutchburyi</i>	109.1±0.5	
2968	Portobello	<i>A. stutchburyi</i>	108.2±0.5	0.56
2968B	Portobello	<i>A. stutchburyi</i>	107.8±0.5	
2971	Pleasant River	<i>Cellana</i> sp.	108.2±0.4	0.62
2971B	Pleasant River	<i>Cellana</i> sp.	108.0±0.5	

Table 6.5: Duplicate dissertation samples illustrating laboratory reproducibility. All errors are $\pm 1 \sigma$.

The results are shown in table 6.5. All pairs are statistically indistinguishable at 1 σ . This illustrates close reproducibility in dates measured from the same sample. The reproducibility can be further analysed against the reported standard error to estimate the internal consistency of the laboratory. The disparity between a pair of duplicate samples can be measured by the unsigned difference of the two dates divided by the square root of the sum of the squared quoted errors. If the result is less than 1, the laboratory is underestimating its internal reproducibility, that is, it is under-reporting its error (Scott *et al.*, 1990). In table 6.4, the 'internal error multiplier' is shown in column 5 as 'IEM value'. All results except one show a value less than 1. This shows the standard error in routine dating using the lab error multiplier is consistent with the reproducibility of the laboratory.

6.6. SAMPLE SIZE, COUNTING TIME AND 'OPTIMAL DATING'

In the light of continuing investigations into the application of high precision dating, the most productive avenues for increasing sample precision towards a D14C error of $\pm 2 - 3\%$, other than the spectral shift investigations outlined above, are in analysing samples containing larger amounts of radionuclide, and in counting them for longer periods of time. Statistical errors are, of course, significantly reduced in both cases. Figure 6.9 shows the effect of increased sample size and longer counting time upon precision. The 5 ml volume consistently yields increasing precision from 500 minutes, up to 8000 minutes counting time. The optimal counting time for both 3 and 5 ml size samples is reached between 3 and 4000 minutes. Above 4000 minutes, the increase in precision is minimal when compared to the amount of extra time invested. Ten ml benzene samples are being tested for high precision dating applications.

Standard errors are also affected by the count rate of the analysed samples; a more modern ^{14}C sample may be counted for less time than an older sample with the same precision. New Zealand archaeological samples are close to modern, therefore ideal for higher precision dating.

A further, and more effective method of improving precision, is to combine two or more radiocarbon dates, generated from the same sample. The reduction in statistical errors reflects the increased certainty in the validity of the result if the

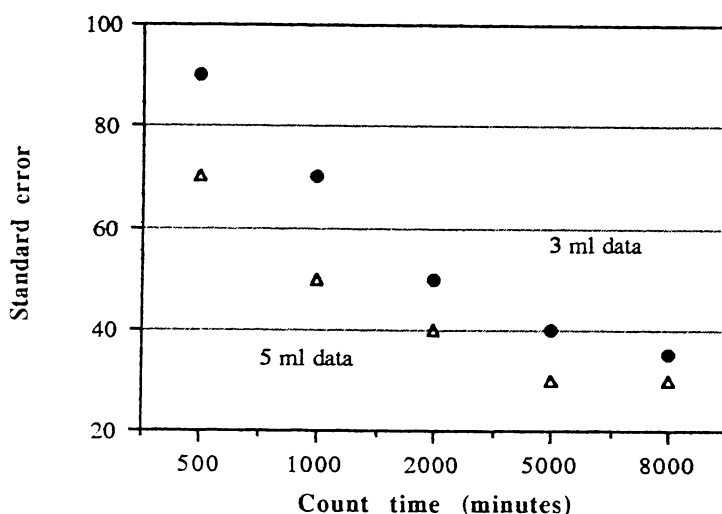


Figure 6.9: The effect on standard error in 3 and 5 ml samples through increasing counting times (includes a lab error multiplier of 1.217). 5 ml data are shown as triangles and 3 ml data as filled circles.

two determinations are able to be combined statistically. For example, two 5 ml dates on charcoal from the same discrete sample give dates of 620 ± 35 bp and 650 ± 35 bp. Statistical tests indicate the two are indistinguishable and are thus able to be combined. The pooled mean age ($A(p)$) is 640 radiocarbon years, the error calculated is ± 25 radiocarbon years. The certainty is increased with two determinations, and is reflected in the size of the standard error.

It has often been suggested that one date does not guarantee certainty. A number of dates result in increased certainty and, if statistics allow, enable a combined date to be calculated. An example of such an approach has been well illustrated by Nydal (1983, 1989) in the dating of L'Anse aux Meadows, an important Norse site, in Newfoundland, Canada. Historical references suggested the site was occupied around 1000 AD by Leif Eriksson. The large number of acceptable ^{14}C dates from the site (13) increased the dating certainty and enabled a mean age to be calculated. The spread of results and the known historical date of settlement made it possible to identify errors within dates of wood charcoal probably due to inbuilt age, and reject those dates from consideration. The calibrated mean was 1000 AD-1018 AD (at 68% confidence) (Nydal, 1989).

In New Zealand, the approach of this 'optimal dating' technique, or multi-sampling as Leach (1972) has called it, upon an archaeological context has

probably best been applied at the site of Shag Mouth (Anderson *et al.*, in prep.) where the majority of the calculated dates on charcoal, shell, moa bone and eggshell, were statistically indistinguishable and able to be combined.

6.7. CONCLUSIONS

The major factors affecting the radiocarbon dating of New Zealand archaeological samples at higher precision in the Waikato laboratory, from an instrumental and methodological stance have been:

1. *The influence of the external standard upon spectral shift.*
2. *Reproducibility in the measurement of the stable isotopes of carbon.*

Data given above concerning the reproducibility of the Kapuni gas standard has suggested the performance and reproducibility of the Micromass 602C spectrometer was affected in mid-1992. This error has been evaluated. Recent work on the mass spectrometer including its automation and computer control using Labview™ has resulted in improved reproducibility throughout 1993. This is illustrated in figure 6.3. All anomalous $\delta^{13}\text{C}$ results were corrected either by remeasurement or, in cases where the samples were part of a series generated using identical material, by substitution of $\delta^{13}\text{C}$ values from pairs or duplicates.

The most important avenue for further research is in investigating further the characteristics of spectral stability in the Quantulus Liquid Scintillation counter and its relationship with count rate. This has been the principal avenue of investigation in the laboratory during this dissertation. Initially, it was suggested that shifting spectra were influenced by quench. The most likely cause of the quench was a substandard sample of lithium metal used in the carbide reaction. After rigorous investigation, an analysis of end point showed the external standard may be artificially influencing the pulse height of successive spectra. The vial holder material was also an influence upon this. Initially, this was perceived as an avenue for potential error but subsequent analyses showed that end point variations occurred without affecting count rates, even when the samples were counted to high levels of precision.

Currently, the development of a high precision dating facility is continuing. The most profitable technique for higher precision radiocarbon work at present is 'optimal' dating, wherein a context or sample is assayed using duplicate or multi-sampled dates. The pooling of the results gives increased certainty and reduced errors and avoids the problems of validating single high precision dates.

CHAPTER 7

SAMPLE TYPE

7.1. INTRODUCTION

A number of scholars have examined errors and variation in radiocarbon dates from different samples derived from the same context in New Zealand (Law, 1984; Caughley, 1988; Anderson, 1991). In most instances, results from the three most commonly dated materials; shell, charcoal and moa bone collagen have been compared in an attempt to identify the most accurate and useful medium. This has resulted in a variety of different recommendations and consequent confusion.

In dating the prehistoric period in New Zealand, what is the ideal sample type, what are the fundamental prerequisites for accurate dating in terms of sample? In my view, they are:

- 1. The material must relate precisely to the event being dated.*
- 2. It must be as resistant as possible to post-depositional contamination.*
- 3. It must be found regularly in archaeological contexts.*

This chapter, which considers errors associated with different types of sample, will begin with a resumé of the main types of material used in radiocarbon dating in New Zealand archaeology and their suitability for dating, considered in the light of the three prerequisites listed above. An investigation into the potential of moa eggshell for archaeological dating, will follow. This will comprise a detailed analysis of the isotope chemistry of the birds' egg formation processes, consideration of sources of contamination and error, a review of research conducted into eggshell dating in other contexts and a comparison of moa eggshell radiocarbon dates with dates of other material in close stratigraphic association.

7.2. CHARCOAL

Charcoal is probably the most widely used material in radiocarbon dating in this field. Since the inception of the technique in the 1950's, charcoal has been acknowledged as a most reliable material for dating (Libby, 1955). Its major source of error has been

'inbuilt', or 'presample' age (McFadgen, 1982). This may be the result of growth age; in which the age of dead wood in the centre of the living tree is dated, or storage age; which refers to the amount of time elapsed from the death of the tree to its use by people (McFadgen, 1982). Inbuilt age may result in errors of up to hundreds of years unless only short-lived species, or twigs, are selected for dating. Even then, there remains an inbuilt age effect, albeit somewhat reduced. In the late 1950's, the issue of presample age was identified as a causal factor in the difficulties encountered in accurately cross-dating the Julian calendar with that of the Yucatan Maya of Lowland Mexico. The Mayan calendar is centred on a complex Long Count cycle which repeats every 5125.6 solar years (Fedick and Taube, 1992:404) and its decipherment in the 1950's gave archaeologists an opportunity to develop an accurate chronology for the Mayan culture (Sabloff, 1989). An attempt to correlate the Mayan Long count with secular time resulted in two different interpretations; the Goodman-Thompson-Martinez correlation and the Spinden correlation. The two differed by 260 years at the crucial Julian year of 1539, when one of the main Mayan cycles ended, and radiocarbon dating was used to try and solve which was correct. Samples of *Sapodilla* wooden beams found spanning inscribed Late Classic Mayan doorways at Tikal were dated by the University of Pennsylvania, and it was found that the Spinden correlation was correct. Shortly after the dates were released, Satterthwaite (1956; in Fedick and Taube, 1992) questioned their validity because the beams had been reduced in size and their exterior bore no resemblance to the original trees. According to him, the dates were erroneous because they failed to date the event of the building of the temple. Subsequent investigations into the dating of the Mayan Long Count focussed on dating exterior bark and samples from smaller vault beams, and it was found that the Thompson correlation was the correct interpretation when inbuilt age was negligible (Coe, 1966:29).

In the late 1960's it was suggested that New Zealand samples may be similarly affected (Trotter, 1968). Trotter (1968:86) discovered that charcoal dates from some contexts were older in comparison to those from other samples. At Tai Rua, a site in North Otago, he found charcoal dates predated those from moa bone collagen and shell by almost 300 years. This was due to inbuilt age; the dated wood came from a stake in a post hole. Similarly, at Katiki Point, a date from a wood sample predated the site occupation by over 600 years. The Redcliffs Cave dates given by Duff (1963; in Trotter, 1968:87) were also explained as being dates determined on old wood. There were 5 centuries difference between the charcoal date and the shell and collagen dates from that site.

At the 1972 Radiocarbon conference, Rafter *et al.* (1972) drew attention to the wide disparity between the dates of charcoal, shell and moa bone from the same context. In considering charcoal dates McCulloch and Trotter (1975) suggested:

"An overall survey of radiocarbon dates from South Island archaeological sites shows quite clearly that charcoal dates tend to be earlier than others on any multi-dated site, the difference ranging from up to six hundred and sixty-nine years. This is a mean difference overall of about two hundred years".

McCulloch and Trotter (1975:8-13)

They concluded that moa bone collagen was the most reliable material for New Zealand archaeological dating ostensibly because it dated the event (in this case the killing of a bird) more accurately than wood charcoal. They recommended that all charcoal material should be identified and speciated prior to radiocarbon assay to remove the possibility of dating old wood samples (McCulloch and Trotter, 1975:9).

The extent of the problem of inbuilt age eventually begged the question of which of the dates thus far determined should be rejected, and which accepted. This issue was addressed by Anderson (1991). His analysis of the radiocarbon dating record as it related to the chronology of prehistoric colonisation is most important. For the first time, the radiocarbon record was considered critically and dates were culled based on a number of variables, including inbuilt age, contamination and reproducibility.

The realisation of the error caused by inbuilt age has resulted in all charcoal samples submitted for dating being identified first, where possible. Only samples of young wood, such as twigs and small diameter wood and samples from short lived species are chosen for radiocarbon assay. According to Anderson (1991:780) and McFadgen (pers. comm.)⁺, however, even wood taxa considered adequate for dating and supposedly exhibiting small inbuilt age may produce errors. Some acceptable species, such as kanuka (*Kunzea ericoides*), manuka (*Leptospermum scoparium*) and the Coprosmas, may live up to 200 - 300 years (Anderson 1991:780). Similarly, samples such as twigs and branchwood, selected because they are small in diameter and assumed to be of restricted inbuilt age, may also give erroneous dates. In some cases, what appears to be branchwood may in fact be the eroded cores of old trunks (Anderson, 1991).

⁺ Dr B.G McFadgen, Conservation Sciences Centre, Department of Conservation, Wellington, New Zealand.

Attaching any error to charcoal dating using old wood is obviously impossible, since it is non-systematic. Any wood selected for dating incorporates an inbuilt age error but errors are significantly reduced if only short-lived species or twigs are selected for dating. In these cases, identified charcoal will always date the event more closely than older wood.

The resistance of wood and charcoal to contamination is addressed in chapter 8. From the results outlined in this dissertation, it is concluded that in the majority of sites, contamination in New Zealand charcoals <1000 years old is negligible in its effect on radiocarbon dating at routine levels of precision.

Charcoal is common in occupation sites in New Zealand and so fulfils the final prerequisite. It is considered the most reliable material for radiocarbon dating in New Zealand archaeology, despite the incorporation of varying degrees of inbuilt age, principally because it avoids reservoir correction anomalies. It is likely that charcoal chronologies are skewed in favour of antiquity. However, if the charcoal selected is identified and only short-lived species are selected for dating, the inbuilt age is probably reduced, but not altogether removed.

7.3. SHELL

The radiocarbon dating of shell is investigated in detail in chapter 9. The extent of contamination in New Zealand archaeological samples is reviewed in chapter 8. There are some areas of concern in shell dating. The reliability of dates of estuarine shell is of interest (Anderson, 1989). Many important New Zealand sites commanded estuarine locations and the majority of dated shells are estuarine. It has been suggested that limestone within some of these catchments may affect the ^{14}C label in certain species, making any radiocarbon dates too old (Anderson, 1991). Similarly, dates from marine shells in areas near upwelling zones may possess error, because deep ocean water is depleted in radiocarbon compared to surface water.

These critical issues are considered in detail in chapter 9. The usefulness of shell for accurate radiocarbon dating is considered in the light of the results.

7.4. BONE

McCulloch and Trotter (1975) suggested bone, in particular moa bone, was the most useful material for dating because it dated the event closest. In the 1950's, however, Libby (1955:44) had suggested that:

"We have had no experience with bone as such and believe it is a very poor prospect for two reasons: the carbon content of bone is extremely low, being largely in inorganic form in a very porous structure; and it is extremely likely to have suffered alteration. It is barely conceivable that measurements on bone might reveal that some reliability could be obtained. However, because the quantities required are so large, and there usually are other acceptable materials associated with a find of bone, it does not seem to be an urgent matter to pursue".

W.F LIBBY. 1955. *RADIOCARBON DATING*.

Unfortunately, Libby has been proved correct. Bone has proven to be a most problematic dating material, although recent research in biochemical applications and chemical pretreatment, allied with the development of Accelerator Mass Spectrometry has seen improvement in its acceptability.

Taylor (1987:54) has outlined that bone acquired a reputation for unreliability early on in radiocarbon dating. According to Gupta and Polach (1985), it is prone to contamination and invasion by younger carbonate ions in certain types of strata. Bone is made up of a number of organic and inorganic fractions. According to Taylor (1987:54), the inorganic fraction consists mainly of "apatite, calcium carbonate and other amorphous materials", while the organic fraction is composed principally of protein collagen. Researchers have been divided on which is the most reliable fraction for dating. Apatite[#], collagen and gelatin fractions are commonly used but are questionable in their reliability. In New Zealand, collagen has been the commonest fraction isolated for radiocarbon dating, principally because it is the largest organic fraction and has proved easiest to isolate. Taylor (1987) has suggested that the major problem in bone dating has been the difficulty in making generalizations about the precise age relationship between the inorganic and organic components. This is complex and regulated largely by environmental factors which vary from sample to sample.

[#] Apatite is formally $\text{Ca}_5(\text{PO}_4)_3\text{X}$ ($\text{X}=\text{F}_2$ OH etc): the "apatite fraction" of radiocarbon dating is carbonate-apatite, $\text{Ca}_{10}(\text{PO}_4)_6\text{CO}_3\cdot\text{H}_2\text{O}$, which is not a true apatite.

To understand the mechanics of bone contamination and the effect of chemical pretreatment, it is necessary to date various fractions and assess which fraction is least contaminated and closest to the 'true' age. An array of chemical pretreatments have been brought to bear upon bone remains. The first, and most often used, is the removal of foreign carbonates and the isolation of "apatite", the acetic acid insoluble fraction. It is this fraction that is more regularly used for dating and for further pretreatment and refinement. Collagen and gelatin, for example, are extracted from this apatite structure. Collagen is extracted using a technique first described by Longin (1971). The technique was based upon treating bone collagen with dilute acids and hot water to obtain a pure gelatin fraction from which collagen could be removed (Longin, 1971).

Recently, the emphasis in the dating of bone has moved to the blood proteins and amino acids. This is possible through AMS which is able to date microgram amounts of bone and avoids the sample-loss problem often associated with the pretreatment and isolation of collagen for radiometric dating. Gillespie (1989) has suggested that amino acid profiling reveals that the fractions most concentrated on by radiocarbon specialists are often the most poorly preserved. He suggested using biochemical techniques to isolate the total amino acid fraction and improve the purity of bone samples. Biochemists are able to identify amino acids contained in bone and select the most dependable for dating. There are 18 amino acids within bone collagen, including proline, glycine and alanine (Gupta and Polach, 1985:12). The most frequently targetted is hydroxyproline (Gillespie, 1989:245). According to Taylor (1992:383), recent investigators have considered non-collagen proteins such as phosphoproteins and especially osteocalcin. Long *et al* (1989) have suggested that these may be protected from degradation within bone because they bond strongly with apatite structures. They are also relatively abundant. Other proteins are currently the focus of further research using AMS (Taylor, 1992).

Moa bone, then, although commonly found in New Zealand archaeological contexts, especially in the southern regions, is not resistant to contamination. It does not survive well *in situ* and requires complex chemistry to isolate the original carbon.

7.5. RADIOCARBON DATING OF MOA EGGSHELL

The three main sample types, then, often possess errors which are becoming unacceptable as the technology of radiocarbon dating improves, and levels of precision increase. In considering the problems associated with certain materials, I decided that prehistoric moa eggshell carbonate may be worthy of investigation. Certainly, eggshell fulfils the first and major archaeological prerequisite, of dating the event closely. The overwhelming archaeological evidence suggests that eggs were part of a subsistence strategy based upon large-scale moa hunting. Initially, however, doubts were expressed about the reliability of the material to withstand post-depositional contamination. Certain carbonates are considered unreliable due to their ability to exchange with carbonate of differing age *in situ*. Bone carbonate, for example, is avoided for dating purposes for this reason (Rafter *et al.*, 1972; Taylor, 1987). Conversely, an analysis of marine shell carbonates from a variety of New Zealand archaeological sites has suggested that isotopic exchange in this material is rare. Shell carbonates from archaeological sites in New Zealand have been analysed using x-ray diffractometry and no evidence of any post-depositional exchange has been identified (chapter 9). In addition, a number of researchers have claimed that eggshell survives well in archaeological contexts and, again, does not readily exchange with carbon isotopes from non-contemporaneous materials (Taylor, 1987; Freundlich *et al.*, 1989).

7.5.1. PREVIOUS RESEARCH INTO DATING EGGSHELL

According to Anderson (1989:214-215), moa eggshell has been radiocarbon dated before, but only from natural deposits (table 7.1). It is unclear whether or not the samples were paired with other materials to assess the reliability of the eggshell for dating purposes. No moa eggshell dates from sites in association with human cultural remains has ever been published.

There have been previous investigations into the dating of eggshell from both extinct and extant species. Berger *et al.* (1975) have dated eggshell samples of the extinct giant elephant bird *Aepyornis* sp., from sites in the southern Malagasi Republic. They removed the exterior layer of eggshell with dilute acid as a precaution against

SAMPLE TYPE

Laboratory number (NZ)	Conventional age (BP)	Site location	Provenance and environment	$\delta^{13}\text{C}$ (‰)
1725	663±51	Redcliffe, Rakaia valley	moa nesting debris	-14.5
4611	2190±70	Northland	dune sand	-12.1
4691	2640±40	Northland	dune sand	-9.2
4835	1595±70	Northland	dune sand	-4.2
5065	3790±100	Northland	dune sand	-11.2

Table 7.1: Radiocarbon dates of moa eggshell found in natural deposits (taken from Anderson, 1989:214-215). $\delta^{13}\text{C}$ measurements from the Institute of Geological and Nuclear Sciences database (courtesy of Dr B.G McFadgen).

contamination. They suggested the material was a useful one for radiocarbon dating because the five results were similar to dates calculated from other materials in close association (Berger *et al.*, 1975:709).

Horowitz *et al.* (1978) have dated ostrich eggshell fragments excavated from the prehistoric site of Voigtspost, in Orange Free State, R.S.A. Sample Pta-1483 was dated at 1220±50 bp ($\delta^{13}\text{C}=-6.7\text{‰}$), while Pta-1520 gave a date of 6350±75 bp ($\delta^{13}\text{C}=-8.3\text{‰}$) (Horowitz *et al.*, 1978:154). Two modern samples of eggshell were also dated. After correction for isotopic fractionation, they gave an apparent age of 200 years in comparison to modern atmospheric carbon. Horowitz *et al.* (1978) concluded ostrich eggshell dates may be too old by this amount and advised caution in interpretation. There are a number of possible explanations for the old date of modern eggshell. It may have been caused by the bird drinking water from sources such as inland freshwater lake systems, which can contain dissolved bicarbonate or CO_2 , depleted in ^{14}C .

Williams (1981) has reported a date from eggshell likely to be *Genyornis newtoni*, an extinct Pleistocene ratite. This was given a minimum age of 40,680 bp (SUA-1337) by the laboratory. He also refers to SUA-885 which gave ages of 35,900±2980 and 35,900±2170 bp, concluding that the eggshell was probably from a species of duck. Williams (1981:138) also dated a modern emu eggshell which gave a date of 570±70 bp (SUA-1069). This was obviously older than expected. According to Barbetti (pers.

comm.)[^], $\delta^{13}\text{C}$ was estimated at $-5\pm 2\text{‰}$. A 1981 revision of dates from the Sydney laboratory gave a new value for the sample of 440 ± 80 bp (Barbetti, pers. comm.). Williams (1981) suggested that the reason for the discrepancy was incorporation of limestone through ingestion of gizzard stones. There may be alternative explanations, according to Head (pers. comm.)⁺. In a similar way to ostriches, emus tend to drink water from inland lakes which may contain dissolved CO_2 and bicarbonate depleted in ^{14}C which may make an emu eggshell date too old. Dates of freshwater shell in these environments may give ages up to 2500 years.

Long *et al.* (1983) dated fossil ostrich eggshell (*Dromaius novaehollandiae*) from the Sahara and elephant bird (*Aepyornis* sp.) from the southern Malagasi Republic. They considered the effect of old carbon uptake on the ^{14}C label of the eggshell by spiking the feed of two groups of domestic chickens with limestone, over 25 days. Finding no measureable difference in the ^{14}C activity between a group fed low-limestone feed and the group fed high-limestone feed, they concluded that eggshell should be reliable for dating even when carbonates depleted in ^{14}C were ingested. No dates from other samples were included for comparison.

Freundlich *et al.* (1989) used ostrich eggshell to date human occupation in the Eastern Sahara. They compared uncorrected eggshell dates with those from a variety of other materials and found an average difference of 350 ± 60 radiocarbon years. The authors' concluded that $\delta^{13}\text{C}$ measurement and normalisation to -25‰ wrt PDB should result in good agreement with other materials from identical contexts. They refer to the work of Haas and Haynes (1980), and Wendorf and Schild (1984) in the same region. Both used ostrich eggshell for dating and found no significant age differences with dates of other materials in direct association (Haas and Haynes (1980); Wendorf and Schild (1984), in Freundlich *et al.* (1989)).

7.5.2. FRACTIONATION AND PRETREATMENT

Three important issues arise in an investigation of radiocarbon dating archaeological eggshell remains. First, it is necessary to compare dates of eggshell with other materials in close stratigraphic association. This is addressed in the experimental section. Second, it is important to understand the biochemical processes of egg production in avian species and the isotopic fractionation resulting from it. There is great variability in

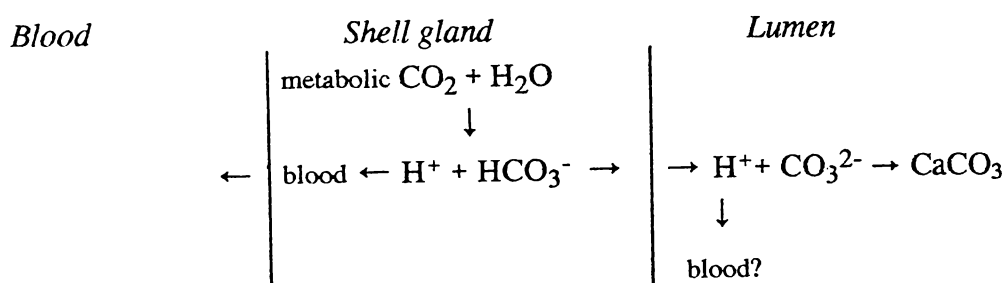
[^] Dr M. Barbetti, The NWG Macintosh Centre for Quaternary Dating, The University of Sydney, Sydney, Australia.

⁺ Mr M.J Head, Quaternary Dating Research Centre, RSPacS, Australian National University, Canberra, Australia.

the $\delta^{13}\text{C}$ results shown in table 7.1. The question is, is the range the result of natural fractionation of metabolic carbon to eggshell carbonate, or is it due to other effects, such as post-depositional contamination, variation in diet, or sample preparation? This issue is important both for the validation of radiocarbon dates and because variability in the measurement of $\delta^{13}\text{C}$ values introduces errors in the dating of samples close to modern (chapter 6). For the samples analysed here, a variation of 1‰ in $\delta^{13}\text{C}$ may result in a shift in age of *ca.* 20 radiocarbon years. Third, it is necessary to be aware of the possibility of contamination or post-depositional diagenesis within the material under examination and adequately pretreat prior to dating.

(i) FRACTIONATION

Lorcher and Hodges (1969) and Sharma and Pillai (1971) have investigated the biochemistry of eggshell production in domestic chickens. Eggshell carbonate is formed from metabolic carbon dioxide and water. Assuming the biological process of egg formation occurs under conditions of isotopic equilibrium, the simplified process can be represented thus:



Sharma and Pillai (1971) have suggested that the conversion of metabolic CO_2 to eggshell carbonate involves a total fractionation of *ca.* 10.0‰ wrt PDB. They estimated this by firstly measuring the average $\delta^{13}\text{C}$ of chicken eggshell carbonate in their samples (-9.2‰). They then suggested the fractionation from bicarbonate to carbonate was 3.8‰, while the fractionation of CO_2 to HCO_3^- was 7.0‰ (Sharma and Pillai; 1971:457). They calculated from this that the metabolic CO_2 possessed a $\delta^{13}\text{C}$ value of -20.0‰, while the bicarbonate had $\delta^{13}\text{C}$ of about -13.0‰.

Freundlich *et al.* (1989) reached a similar conclusion. According to them, metabolic CO_2 with a $\delta^{13}\text{C}$ value of -14.0‰, in equilibrium at 30°C with HCO_3^- ions with a $\delta^{13}\text{C}$ of -6.5‰, will result in carbonates yielding a $\delta^{13}\text{C}$ value around -5.0‰ (Freundlich *et al.* 1989:1034). Eggshell carbonates, then, should be *ca.* 9‰ heavier than metabolic CO_2 .

SAMPLE TYPE

In New Zealand, moa must have consumed C3 plants (Anderson, 1991) whose $\delta^{13}\text{C}$ values fall between -21 and -25‰ wrt PDB (Gupta and Polach, 1985:114). $\delta^{13}\text{C}$ values for moa bone reflect this range. According to Anderson (1991:777), 50% of moa bone $\delta^{13}\text{C}$ values measured at the IGNS, Lower Hutt averaged between -23 and -26‰. If the biological processes in moa egg production mirror those of other avian species, then, we should expect a biogenic $\delta^{13}\text{C}$ value of *ca.*-24‰ to be matched with an eggshell $\delta^{13}\text{C}$ of *ca.*-15‰.

$\delta^{13}\text{C}$ values for archaeological samples are shown in table 7.2. The results average -14‰ wrt PDB. The majority are consistent with the prediction of a fractionation of *ca.* +9‰ from biogenic CO_2 to eggshell carbonate[#].

There are a number of possible explanations for the variability in $\delta^{13}\text{C}$ values for natural samples of eggshell dated at the IGNS, Lower Hutt (table 7.1). First, both Sharma and Pillai (1971), and Long *et al.* (1983) suggest that biogenic CO_2 may be mixed with small amounts of atmospheric CO_2 ($\delta^{13}\text{C}=-7‰$) during respiration. This is probably negligible in its effect. Second, variation in $\delta^{13}\text{C}$ values have been identified in chicken eggs collected from the same bird within days of each other. Sharma and Pillai (1971), for example, identified variations of up to 2‰ in the $\delta^{13}\text{C}$ of eggs laid closely together. They suggested this was due to short-term variation in metabolic CO_2 intake. Third, it is possible that some post-depositional contamination may result in modification of the eggshell, despite Taylor's (1987) conclusion that the material is very stable *in situ*. Variation may therefore be due to the effects of contamination. Fourth, it may be that the range of $\delta^{13}\text{C}$ values reflects variation in diet. Fifth, it is possible that dissolved CO_2 and bicarbonate from inland freshwater streams and springs may have been taken in by moa and incorporated into eggshell. This should be a negligible effect given the disproportionate amounts of modern metabolic carbon ingested by birds compared with the amount of depleted ^{14}C in water HCO_3^- drunk by them each day. As mentioned above, however, modern eggshell dates from Australia and South Africa gave apparent ages, and incorporation of old carbon into eggshell is one possibility in explaining this. This is an avenue for further research.

[#] This result mirrors $\delta^{13}\text{C}$ values identified for *Aepyornis* sp., which averaged -14‰ (Long *et al.*, 1983). Ostrich eggshell from the Sahara averaged -4.5‰ (Long *et al.*, 1983). Freundlich *et al.*, (1989) found ostrich $\delta^{13}\text{C}$ values from the Sahara fell into two groups, one at *ca.* $-0.5 \pm 1.5‰$, the other at $-7.0 \pm 1.0‰$. Eggshells with $\delta^{13}\text{C}$ approaching 0‰ probably reflect a diet based around C4 plants, enriched in $\delta^{13}\text{C}$ compared with C3 plants.

SAMPLE TYPE

Dietary variation probably explains the range of $\delta^{13}\text{C}$ seen in table 7.2. Wk-2604, with a $\delta^{13}\text{C}$ value of -11.4‰ varies by *ca.* 4‰ from two other measurements from the same site, yet it gives an identical radiocarbon age. Similarly, Wk-2765 from Pleasant River is enriched in comparison to three others dated in the same layer, yet gives an age indistinguishable from them. This suggests variation in metabolic carbon intake. Variability in $\delta^{13}\text{C}$ values probably reflect the natural range of fractionation in carbonate production. The $\delta^{13}\text{C}$ measurement of NZ-4835 (-4.2‰) on natural eggshell (in table 7.1) is clearly too enriched and may be due to certain of the other factors listed above.

(ii) CONTAMINATION AND PRETREATMENT

According to Long *et al.* (1983), it is unlikely that old carbon from the uptake of gizzard material significantly affects eggshell radiocarbon determinations. The proportion of modern carbon derived from ingested food, to old carbon associated with gizzard material, is large and reduces the contribution of 'dead' carbon to the ^{14}C label in the eggshell carbonate. Furthermore, an analysis of gizzard stones found among moa remains at Shag Mouth, revealed that quartz and feldspar were the dominant types of mineral ingested by the birds. The moa favoured feldspathic quartzes presumably because they were hard and white (Anderson, pers.comm.). Because they are siliceous, the ingestion of these stones by moa would have no effect on the ^{14}C label of their eggshell carbonate.

Pretreatment was mentioned above. It has been argued by Taylor (1987) that eggshell is resistant to post-depositional exchange with non-contemporaneous carbon. All eggshell samples dated in this project were physically pretreated by cleaning in an ultrasonic bath. They were then acid washed with 2M HCl for 100 seconds, cleaned with distilled water and then dried in an oven at 90°C . The acid wash was designed to remove the outer surface layer of the eggshell where contamination is most likely to have occurred (see chapter 8 for further discussion). This was undertaken as a precaution.

In summary, moa eggshell is likely to be useful for radiocarbon dating with the following provisos. $\delta^{13}\text{C}$ values should fall within the expected natural range of values, probably between -15 and -11‰ wrt PDB. The material should be pretreated as a precaution against contamination.

7.5.3. EXPERIMENTAL

SAMPLE TYPE

Samples from 4 sites were used to date moa eggshell. The sites were Onenui, Shag Mouth, Pleasant River and Warrington (Fig. 5b). Onenui is located on the Mahia Peninsula in Hawke's Bay. The sample (Wk-2735) was collected in 1964 by T. Hosking and obtained from the University of Auckland Anthropology Department collections (Sample 2851/1, Catalogue #2; Archaeological Section). It was recovered from a disturbed site described as "a wind eroded beachfront". According to notes found with the sample, it was found along with the remains of European and prehistoric Maori material. Its exact location is unknown, but according to Jeal (pers.comm.)[#] who has surveyed many of the peninsula sites, it may be from N127/8 (Grid ref. 255 677), an open settlement site. It was dated on the assumption that it was prehistoric in origin and would give a date within the accepted boundaries of that period.

7.5.4. RESULTS

Radiocarbon dates of prehistoric moa eggshell are listed in table 7.2. Dates from three subsamples of moa eggshell (Wk-2758 - 60) likely to be from one egg at Area D of the Pleasant River site were calculated to assess the reproducibility of eggshell values and identify any bias within material from the same discrete sample. Both the $\delta^{13}\text{C}$ values and the conventional ages are statistically indistinguishable at the 0.95

Laboratory number	Conv. age (years BP)	Site	Sample identification	$\delta^{13}\text{C}$ (‰)
2735	1040±120	Onenui	Onenui 1 2851/1	-9.6
2416	600±50	Shag Mouth	SM/C E5 L7	-15.4
2417	560±40	Shag Mouth	SM/C F2/E2 L6	-15.0
2604	570±40	Shag Mouth	SM/C I3/I4 L8	-11.4
2741	650±45	Pleasant River	PRD-1	-12.1
2758	650±45	Pleasant River	PRD-2 L4 Me1	-14.0
2759	590±40	Pleasant River	PRD-2 L4 Me2	-14.1
2760	600±45	Pleasant River	PRD-2 L4 Me3	-13.9
2765	600±45	Pleasant River	PRD-8 L3 Sq D5-8	-12.1
2744	580±45	Warrington	W9	-14.7

Table 7.2: Radiocarbon dates of moa eggshell excavated from 4 archaeological sites in New Zealand.

[#] Ms M. Jeal, Archaeologist, Coromandel.

SAMPLE TYPE

confidence level (the pooled mean date ($A(p)$) for the subsamples was 611 ± 25 bp: $T=1.09$ with $\chi^2_{2;0.05}=5.99$). The pooled mean is statistically indistinguishable from the date of a second sample of eggshell (table 7.2) from a similar provenance in the same site. The Pleasant River dates indicate that moa eggshell gives acceptable reproducibility, apparently without bias. The eggshell dates from the site are compared

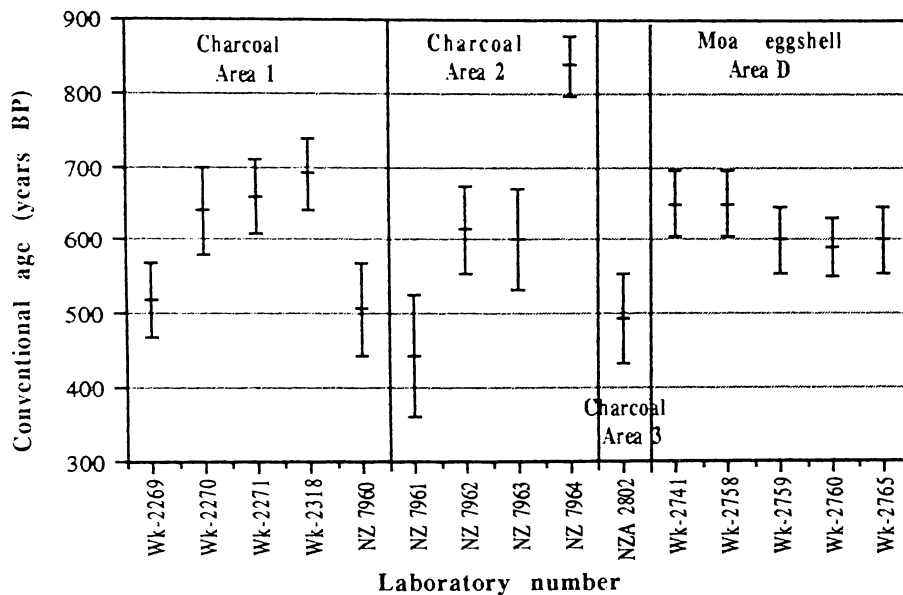


Figure 7.1: Comparison of radiocarbon dates from the site of Pleasant River, North Otago, showing charcoal dates from areas 1-3 and moa eggshell dates from area D. Dates Wk-2758-2760 are duplicate dates from the same sample. Error bars are $\pm 1\sigma$. 'NZ' is the Laboratory number for the IGNS, Lower Hutt.

in figure 7.1 with charcoal dates from different excavated areas at the same site (Areas 1, 2 and 3). The exact chronological relationship between the different excavated areas at the Pleasant River site is uncertain, but the comparison shows that the eggshell dates fall within the range of charcoal dates. Dates of two other samples of eggshell from the same Area D site are shown in figure 7.1. They are within the statistical range of the repeated eggshell dates.

Three eggshell samples were dated from Shag Mouth (table 7.2). Comparison of these results with dates from other samples of similar provenance was very favourable (Fig. 7.2). Dates from moa eggshell, moa bone collagen and charcoal compare closely. The radiocarbon dates from charcoal and shell suggest this site was probably occupied for a

SAMPLE TYPE

short period (< 50 years) in prehistory, 600 radiocarbon years BP* (Anderson *et al.*, in prep.). The moa eggshell dates corroborate this conclusion.

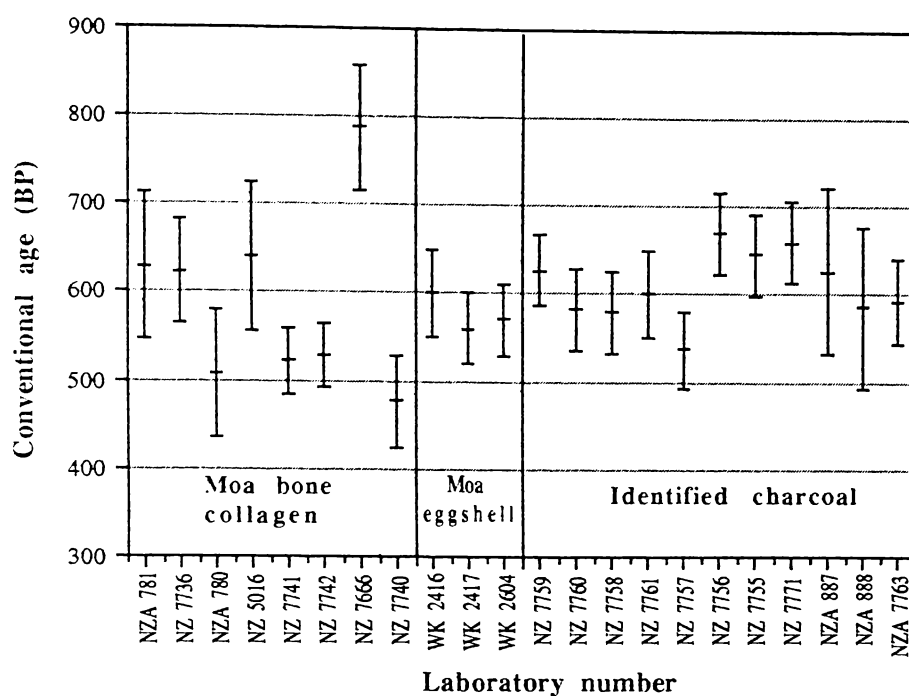


Figure 7.2: Comparison of dates of moa eggshell with those of moa bone collagen and charcoal from the site of Shag Mouth, North Otago (excavation SM/C, 1988). Error bars= $\pm 1 \sigma$. 'NZ' is the laboratory number for the Institute of Geological and Nuclear Sciences, Lower Hutt. (Shag Mouth charcoal and collagen radiocarbon dates are courtesy of Professor A.J. Anderson and Dr I.W.G. Smith).

In figure 7.3, the eggshell date from the Warrington site is shown with calibrated shell dates from a previous excavation. Although it is problematic to compare directly calibrated shell and terrestrial dates, there are no dates from any other samples available for Warrington. The eggshell sample came from a basal layer near to where the marine shell sample (Wk-1737) was excavated. It compares favourably with the date of the shell.

The date of Wk-2735 (Onenui) was 1040 ± 120 bp. It has no dateable material in stratigraphic association to check its validity. According to Jeal (pers. comm.), who has

* The pooled mean date for identified charcoal dates from Shag Mouth was 620 ± 13 bp ($T=5.31$; $\chi^2_{12;0.05}=21.03$).

SAMPLE TYPE

surveyed the area, sites around Onenui yielded small fragments of moa eggshell which she considered sub-fossil in origin.

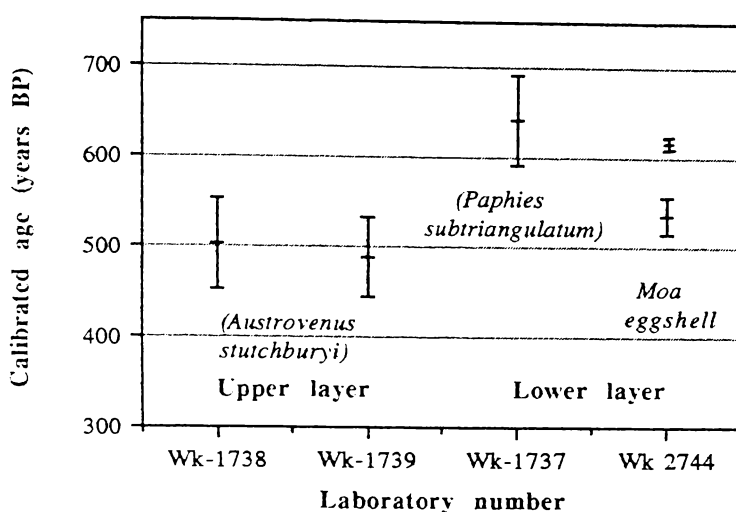


Figure 7.3: Comparison of calibrated radiocarbon dates of marine shell and moa eggshell from the upper and lower cultural layers at the Warrington site (177/144), Otago (Radiocarbon dates courtesy of B. Allingham). Error bars= $\pm 1 \sigma$. 'NZ' is the Laboratory number for the IGNS, Lower Hutt.

7.5.5. CONCLUSIONS

It may be concluded from the preliminary evidence presented above, that moa eggshell is a reliable dating material. Radiocarbon dates using moa eggshell from archaeological contexts were statistically indistinguishable from those determined using shell, moa bone and charcoal. The apparent ages for modern eggshell reported by Horowitz *et al.* (1978) and Williams (1981) are not matched in dates of prehistoric moa eggshell.

Two sources of error have been considered beginning with contamination through carbonate exchange with material of unknown age. Pretreatment with dilute HCl or exterior grinding before radiocarbon assay is suggested as a precaution against this. Second, variation in $\delta^{13}\text{C}$ values for moa eggshell. $\delta^{13}\text{C}$ results for the archaeological samples averaged -14‰, but ranged to -9.6‰ and probably reflect the natural fractionation from metabolic CO_2 to eggshell carbonate. Measurements of natural eggshell samples showed greater variation, probably due to post-depositional contamination.

In general, moa eggshell offers a number of advantages for radiocarbon dating in New Zealand archaeology. It avoids the ubiquitous inbuilt age problem which has affected the dating of other materials. It is found throughout New Zealand, but is less common in contexts in the northern North Island. Its recent age, and state of preservation *in situ* means that it may be affected less by contamination than other samples, such as moa bone - although this will, of course, vary with the type of depositional environment. Finally, much eggshell material already excavated is in storage and may be dated without further fieldwork. Thus, sites long since excavated, may be re-dated and placed in a chronological context. The eggshell excavated from burials 1 - 7 at Wairau Bar is a prime candidate (Duff, 1956:33).

7.6. DISCUSSION AND CONCLUSIONS

The sample type is an important consideration for accurate radiocarbon dating both routinely and by high precision. Moa bone is unsuitable for high precision dating using radiometric techniques unless the sample is large enough to compensate for the destructive chemistry needed to remove sources of contamination. The opportunity offered by AMS is the most profitable avenue for improvement in the radiocarbon dating of bone. Although a material which should date prehistoric hunting events with some accuracy, except in instances where sub-fossil material has been used and re-deposited in cultural strata, moa bone does not fulfil the prerequisite of resistance to contamination.

Shell is commonly found in archaeological contexts and should date the events of collection and deposition closely. However, variability in dates of certain species, both prehistoric and modern, has suggested that more research is required into aspects of shell dating, particularly of estuarine species and that high precision dating of these samples may be premature.

Preliminary results described above suggest that moa eggshell is an acceptable medium for dating. Close agreement was noted between dates of eggshell and charcoal and shell dates, from identical contexts. Dates of a sub-sample from Pleasant River yielded acceptable reproducibility with no apparent bias in the results.

Charcoal, if it is identified to young-lived species only, should give acceptable dates, although in some instances even branchwood may harbour inbuilt errors. Charcoal is

SAMPLE TYPE

commonly found and preliminary results from a number of sites suggest it avoids major contamination post-depositionally. However, pretreatments should be undertaken as a precaution.

It is recommended that materials for radiocarbon dating in New Zealand archaeology should be selected in the following order of preference:

- 1. Identified, short-lived charcoal or wood species.*
- 2. Open marine shell.*
- 3. Moa eggshell, (where found).*
- 4. Estuarine shell species, in particular - Austrovenus stutchburyi.*
- 5. Moa bone.*
- 6. Soil. Unidentified wood and charcoal. Riverine shell.*

CHAPTER 8

PRETREATMENT

"Radiocarbon dating still suffers from the fact that there are too few good chemists working with contamination problems"

REIDAR NYDAL (1982)

8.1. INTRODUCTION

From the beginnings of radiocarbon dating, both archaeologists and chemists have been confronted by the problem of sample contamination (Libby, 1955). Many methods have been developed to remove the various contaminating substances affecting samples during their post-depositional history. The removal of non-indigenous carbon material from the original carbon sample is called pretreatment.

No method, singly or in combination, can be universally applied to all types of material from archaeological or geological contexts. If pretreatments were able to be uniformly implemented, there would have to be a uniform and predictable array of post-depositional characteristics between all samples. Clearly, this is not the case. Each sample submitted for dating has its own specific post-depositional history. The variety in environment and post-depositional features is reflected in the variety and complexity of pretreatment procedures. Nevertheless, there are certain laboratory procedures which are associated with specific sample types and environments, and a number of accepted and often repeated pretreatment methods.

Contamination may be artificially or naturally caused. The former usually results from human negligence during the collection and processing of samples. Contaminants may include ash from tobacco, hair and fibres, paper from packing material and oil or grease (Hogg, 1982:21). Samples may be contaminated in the post-depositional environment by substances which alter the proper radiocarbon age, rootlet intrusion being the commonest in New Zealand. Organic samples such as wood, charcoal, soil and bone are especially prone to this. Contamination may also be caused by percolating humic acids from decayed plant material. They may exchange with, or adhere to samples that have large surface areas and alter radiocarbon results to varying degrees depending on

their activity. This surface exchange is termed 'adsorption' and is especially common in samples such as peat, charcoal and sediment.

Certain samples, especially shell, may show evidence of isotopic exchange, or recrystallisation. Recrystallisation involves the dissolution of primary aragonite, which forms the major crystalline carbonate fraction in most shells, and the subsequent reprecipitation or recrystallisation of the carbonate in a calcite structure. Often this process will alter the isotopic ratio of the carbonate and affect the true age because bicarbonates of different age may be present in the post-depositional matrix. The exchange usually occurs on the exterior shell surfaces in terrestrial environments and is common in samples found below the water table (Hogg, 1982:18). Recrystallised shells may often show a 'chalky' or powdery exterior (Taylor, 1987; Aitken, 1990). In cases where the suspected recrystallised shell is an aragonitic secrete, x-ray diffraction analysis will reveal the presence or extent of calcite and the sample may be rejected or accepted in the light of the result. Where the shell is composed mineralogically of calcite, visual observation is the only method for considering recrystallisation*.

8.2. ASSESSING THE MAGNITUDE OF CHANGE

In investigating the extent and effect of these types of sample contamination, the radiocarbon laboratory is faced with two major problems. First, it has to identify precisely the nature and extent of contamination. Second, it needs to assess its magnitude and direction of change (Gupta and Polach, 1985:129). According to Gupta and Polach (1985), the extent of contamination may only be considered if:

"i) The true age of the sample (t), ii) the age of the contaminant (t_c), and iii) the carbon fraction of the contaminant (F_c) are known or can be guesstimated."

(Gupta and Polach, 1985:129).

Olsson (1974, in Gupta and Polach, 1985), and Gupta and Polach (1985:129-134) have considered the nature of this relationship between sample, contaminant and magnitude of error. They suggested that by "guesstimating" the age difference between the 'true' sample age and that of the contaminant, and calculating the relative size of the contaminant in the sample, it was possible to determine the extent of the error caused by

* As mentioned in chapter 7, shell samples dated in this dissertation were analysed for their crystalline structure, and none found to be recrystallised. No New Zealand archaeological shells have ever been identified as contaminated by recrystallisation, so XRD analysis is not routinely implemented. Although one paua shell dated from Shag Mouth, which possessed some calcite, may have been recrystallised (Anderson *et al.*, in prep.)

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the contaminant and apply a correction. This consideration is based on the assumption that any contamination was instantaneous (Gupta and Polach, 1985:130). In general, the older the sample, the greater the effect of contamination, even if the percentage of contaminant to sample was small. Samples from the New Zealand prehistoric which are closer to modern, require larger proportions of modern contaminant to effect a significant change in radiocarbon age (table 8.1).

	% contamination by modern carbon					
	0%	1%	5%	10%	25%	50%
at 900 bp	900 (0)	890 (1)	850 (5)	810 (11)	670 (26)	440 (51)
	% contamination by old carbon					
	0%	1%	5%	10%	25%	50%
	900 (0)	980 (9)	1320 (47)	1770 (97)	3280 (264)	6630 (637)

Table 8.1: The effect of contamination by old and modern carbon upon a sample with a true age of 900 bp. Figures in brackets give the % error introduced by the contaminant (table from Caughley, 1988).

The other major issue in sample contamination concerns samples which contain *small* errors only. Dates which are clearly too old or young are easily recognised and investigated, but those that contain less significant errors are more difficult to identify. According to Olsson (1979), the danger is that these dates will often be considered to be reliable when they are not because they fall close to the expected age. This may be worth remembering in dating New Zealand samples.

There are numerous methods with which to analyse the effect of chemical and physical pretreatments. In the work reported in this dissertation, samples of charcoal and shell were pretreated and different chemical fractions removed and dated to consider the extent of contamination in them. By comparing an untreated, or "as is" sample, with treated samples, the magnitude of error may be considered. If the dates from sample and contaminant are close, the associated error will be insignificant. If there is a major difference, however, the dating error will be increased. Where different extracted fractions give statistically identical results to the "as is" date, then it may be concluded that no significant contamination has occurred. A further method of evaluation concerns the analysis of the chemical properties of successively removed fractions. This allows the types of contaminants present (based on their chemistry) and their concentration, and therefore the success of pretreatments, to be determined. The types of humic substance in the stratum may be identified by measurement of the elemental atomic ratios for each fraction. Optical density measurements may give an approximation of the

time a humic substance has been present in the sample. Solvent extraction analysis may show the range of contaminant residues (Head *et al.*, 1989). These methods, while extremely profitable, are costly and usually confined only to research programmes or to very important samples. Cross-checking dates with those of contemporaneous samples may also indicate the reliability of a treated sample. Similarly, the level of contamination within a date may be assessed using reliable cultural and stratigraphic markers as chronological reference points. For example, in Cycladic archaeology, reliable chronological markers exist in the form of pottery, which varies both stylistically and temporally through the bronze age, providing a useful reference for dates derived radiometrically (Renfrew, 1973).

8.3. TYPES OF PRETREATMENT RELEVANT TO NEW ZEALAND ARCHAEOLOGICAL SAMPLES

A variety of pretreatment methods are applicable to New Zealand archaeological materials. Physical pretreatment refers to any procedure which does not involve chemicals. There are two types of physical pretreatment routinely applied to samples; the removal of visible contaminants prior to chemical treatment, and the reduction in particle size of the sample (Gupta and Polach, 1985:13-16). The most common methods of removing contaminants include separation of sample and rootlets using tweezers under magnification, and the scraping of contaminated exteriors using a surgical scalpel, dental drill or corundum paper. The rationale behind this is that the exterior surfaces will show the effects of contamination, or isotopic exchange, first. Fragments of charcoal are scraped clean with a scalpel and shells have the 'chalky' exterior removed with dental equipment. According to Head (pers. comm.), physical pretreatment is preferable to using chemicals because it enables the worker to be selective in which parts of the sample are removed. The use of chemicals is non-selective, so pure sample may be destroyed.

A variety of methods were used to remove the rootlet contaminants from the matrices of the analysed samples. Material from the Pleasant River site was used to test the effectiveness of each. The majority of the charcoal remains from Area 1 at the site were finely divided, with few large identifiable fragments. Rootlets were observed in the matrix of feature 6 in square D2, where the sample for dating was excavated. Very small, hair-like root structures (*ca.* 2-10 mm in length) were identified and tweezers were used in an attempt to remove them after the sample was crushed. This proved unsuccessful.

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Portions of the sample were placed in a beaker of distilled water in an attempt to float off the root fraction. The majority of the sample sank because most of the roots were adhering to charcoal fragments. Only a small portion of them were able to be removed.

After ultrasonically cleaning the sample for 30 minutes, a 1000 μm sieve was used to remove rootlets. This proved more successful than flotation. The sample was eventually passed through 3 sieves; 2400 μm , 1000 μm and 355 μm . The 2400 μm sieve collected rootlets, large fragments of charcoal, pebbles, pieces of quartzite and some shell carbonate. The 1000 μm sieve collected a similar array of material. The 355 μm sieve contained sand and black flecks of charcoal. It appeared that the largest amount of charcoal had filtered through to this final sieve. To remove it, the residue was placed in a 5 litre beaker and covered with distilled water. A magnetic stirrer was used to agitate the mixture and move the charcoal into suspension. The flecks were decanted off once they were in flotation. This method was very successful.

The remaining material, composed of fine, organic charcoal and sand, was placed in a 1 litre beaker and 200 mls of distilled water was added to it. The beaker was then transferred to an oven at 90° C for 24 hours. The water gradually evaporated and the sample separated into an upper organic charcoal component and a lower sandy fraction. Using a pair of tweezers and a scalpel these two components were able to be separated.

This final method of flotation and evaporation was the most effective method used in this instance. In subsequent treatments, a combination of large rootlet removal by tweezers, flotation and then sieving was used most effectively.

After initial pretreatment, the samples are usually reduced in particle size to increase the surface area prior to further pretreatment, acid hydrolysis or combustion. Shell samples are usually crushed in a ceramic mortar and pestle. Wood is either splintered using a hammer and chisel, or ground into sawdust in a mill. Charcoal is usually ground in a petrie dish. Charcoal and wood samples should be oven dried prior to pretreatment because they may absorb water from the air, which will affect the quantitative analysis of the effects of chemical pretreatments.

Identified charcoal from two South Island sites was used in an experiment to consider the fraction-by-weight of water remaining after the samples had been air-dried and bagged in double polythene. Charcoal weighing 25.0 grams from the Killermont site in South Canterbury was dried at 105 °C in an oven for 12 hours. It weighed 20.1 grams

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after drying. This equates to 20% weight loss due to water within the sample. This result was duplicated with 50.0 grams of charcoal, which weighed 40.1 grams after the same drying time. Charcoal from the Shag Mouth site was also oven dried and disclosed 14% weight loss due to water.

Chemical pretreatments are applied to samples contaminated with material not able to be identified visually. Some samples from terrestrial environments, such as wood, charcoal and peat, contain small amounts of adsorbed carbonates from percolating groundwater. This material is usually non-contemporaneous and must be removed in order for dates to be accurate. HCl (10%) is often used in this treatment. It is added to the sample in a 1 litre beaker which is placed on a hot plate and the solution is heated slowly until boiling. After one hour it is removed and rinsed with distilled water using a buchner funnel and glass filter paper. The aim is to reduce the pH to a neutral level by continual rinsing. During this treatment, regular pH readings are taken to determine the extent of the acidity remaining. Once neutrality is achieved, two sample fractions are left; an acid insoluble fraction and an acid soluble fraction. The acid soluble fraction should contain the carbonate contaminants and is seldom used for dating purposes, except when there is a need to know the age and nature of the contamination. The acid insoluble fraction should contain the original sample, minus the carbonate contaminants, if the acid wash has had its desired effect.

Stronger acids such as HNO₃ (nitric acid) may also be used in sample pretreatment where contamination is more extensive. Methods of HNO₃ washing described below are similar to those outlined by Goh *et al.* (1978) and Hammond *et al.* (1988) to remove contaminants from peat and soil samples. At Graham's Terrace, a site in North Westland subject to soil podsolisation processes, Hammond *et al.* (1988) found contamination by younger material in peat and organic soil samples. Extensive pretreatment was required to remove it. An increase in age was associated with efficient removal of the contaminants and the greatest age improvement was found with the sample fraction treated with 70% HNO₃.

Acid washing is usually applied to samples destined for combustion. Because HCl reacts with carbonate to produce CO₂, its use in pretreatment work is restricted to non-carbonate samples. The exception is the acid washing of shells to remove surface carbonate from recrystallisation.

Sodium hydroxide (NaOH) treatment is usually associated with the removal of humic acid contaminants from soils, wood, charcoal and peat samples. There are two major

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decay contaminants present in soils; humic acids and fulvic acids. Humic acid is defined as the fraction extracted by alkaline solution which becomes insoluble after acidification (Head, 1987:144). The fulvic fraction is soluble in acid and alkaline solutions (Head, 1987). The presence of humic acids in New Zealand charcoal samples has been noted by many researchers including Bailey *et al.* (1973), Bailey *et al.* (1975), Goh and Molloy (1979) and Hammond *et al.* (1988). Goh and Molloy (1979) analysed archaeological charcoals to find the humic acid fraction within 14 samples, mainly from Canterbury. They first estimated the total oxidisable carbon fraction within each sample. They then used an alkali-pyrophosphate mixture to remove humic and fulvic acids, which comprised between 7.8 and 43% of the total oxidisable fraction. The remaining humin carbon was the principal fraction in each sample (56 to 92%). Humic acids formed the bulk of the extracted carbon (total range from 8.3 to 98% but commonly 50 to 60%). In contrast, more ancient charcoals possessed higher proportions of humic acids.

The commonest method of pretreating samples to remove humic acid contamination is with the acid-base-acid method (ABA). After being ground to reduced particle size, the sample is washed in hot 10% HCl for approximately one hour, or until any carbonate reaction has ceased. Then it is rinsed in a buchner funnel with distilled water to neutrality. After drying, the sample is boiled in a 5% NaOH solution for approximately one hour, and rinsed again. The NaOH treatment produces two fractions, base soluble and insoluble. The former (humic acid) may be kept for dating purposes by being acidified, rinsed and dried in an oven. The latter (humin) too, must be acidified because the NaOH pretreatment sometimes involves an exchange between the NaOH and atmospheric CO₂. The NaOH absorbs CO₂ from the surrounding air (Goh and Molloy, 1972:575). The final acid wash ensures that any such contamination is removed. The insoluble fraction usually contains the sample minus the contaminant and is often the most reliable dateable component except when the humic acid is a contemporaneous terrestrial component.

8.4. PRETREATMENT AND DATING OF MATERIAL FROM PLEASANT RIVER.

The environment of Pleasant River has been described above. A variety of possible contaminants in the area may affect material to be radiocarbon dated. The site is prone to waterlogging by the waters of the adjacent estuary, which is surrounded by large deposits of sandstone and mudstone. The area where the charcoal and shell used in this section was excavated, came from cultural layers below the *Salicornia* marsh, on low level flats. Material from below the water table, or in flooded areas is likely to be more exposed to contaminants than samples above it, or in dry areas. It is also possible that carbon samples in a marginal area, or an area with a fluctuating water table may be exposed to greater contamination due to the effects of the wet-dry cycle. Percolating humic acids from surface runoff and dissolved bicarbonates within the estuary and from natural or prehistoric shell deposits are two of the most likely sources of contamination here. The prehistoric material from the Pleasant River site, then, may have been modified post-depositionally and require pretreatment. In this section, charcoal excavated from Area 1 at Pleasant River is investigated for contamination.

The Pleasant River archaeological charcoal from this area was composed primarily of small particulate material, with few large wood charcoal remains. It was thought this originated from rake-out from an oven or ovens peripheral to the area. The identifiable material within the sample was young-lived *Olearia* sp, (probably *Avicenniaefolia*) and ribbonwood (probably *Plagianthus divaricatus*). The small size of the identifiable remains meant that an accurate date was not achievable. Rather, all charcoal material was homogenised for use in pretreatment experiments designed to consider the effect of various chemicals upon the radiocarbon ages of the sample. It was an unfortunate corollary that the samples be classified as unidentifiable charcoal. Other samples in close association were dated by conventional means and AMS (Fig. 8.1) as a comparison for inbuilt age.

The extraction and refinement of the dateable organic fraction from the matrix was problematic due to the small size of the material. The extraction of the rootlet fraction (Wk-2268) has already been described above. The total extracted rootlet fraction weighed only 0.6 g. The remaining sample weighed 88.7 grams. An "as is" sample (Wk-2269) was extracted from it (10.7 g). This sample was untreated. The remaining sample was acid-washed and an acid washed fraction (Wk-2270, 10.0 grams) removed for dating.

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The remaining charcoal (*ca.* 68 grams) was heated in 5% NaOH in a 1 litre beaker. The sample was reduced in particle size because of the destructive nature of the hydroxide treatment and could not be rinsed in a buchner funnel. It was centrifuged for 15 minutes and the soluble NaOH fraction was decanted off.

The soluble and insoluble fractions were acidified with 5% HCl to pH 2.4, but could not be flocculated. Flocculation in the soluble fraction was achieved at a pH of 1, using phosphoric acid which, according to Hendy (pers.comm.10.3.92) possesses better binding qualities than HCl. The soluble fraction proved difficult to dry. After two days of drying in an oven at 105° C, the remaining sample appeared pitch black and stayed soft and malleable due to the hygroscopic nature of the phosphoric acid (Head, pers. comm.).

The weights of the ABA soluble and insoluble fractions were 16.2 and 20.3 grams respectively. The radiocarbon results from this series of pretreatments are listed in table 8.2. The dates are graphed along with others from Areas 1, 2 and 3 in figure 8.1.

Wk-number	Sample fraction	Conventional age (BP)	Dilution (% sample)	$\delta^{13}\text{C}$ (‰)
2268	Rootlets	103.8±2.5 %M	31.0	-27.0
2269	"As is"	520±50	65.0	-27.7
2270	Acid washed	690±50	81.6	-26.5
2271	ABA insoluble	660±50	100.0	-26.8
2318	ABA soluble	640±50	49.9	-26.7

Table 8.2: Dates of charcoal from Pleasant River, North Otago, subjected to pretreatments.

The chemical pretreatments applied to the Pleasant River charcoal fractions had an effect on the age of the samples in comparison to the "as is" sample and indicates there was some contamination present within the original homogeneous sample (table 8.2).

The Pleasant River rootlet fraction was dated at 103.8±2.5%M. Rootlets extracted from

PRETREATMENT

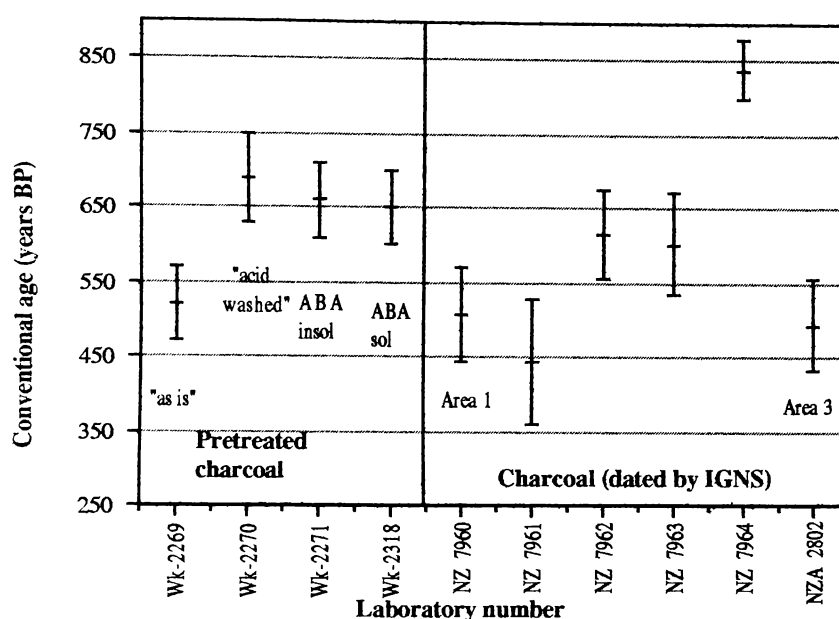


Figure 8.1: The effect of pretreatments upon the dating of a set of charcoal dates from the site of Pleasant River, North Otago, New Zealand compared with dates from other excavated areas. Unlabelled IGNS dates are excavated from Area 2. The Waikato series is from Area 1. 'NZ' is the laboratory code for the Institute of Geological and Nuclear Sciences, Lower Hutt. 'NZA' denotes an AMS measurement. 'NZ' charcoal dates are all pretreated and courtesy of Dr I.W.G Smith (Department of Anthropology, University of Otago).

the sample weighed 0.6 g, or, 0.7% of the total sample. Because the sample is so close to modern it is less affected by modern contamination than an older sample. In this instance, the error introduced is *ca.* 3.6 radiocarbon years.

The result of Wk-2269, the "as is" sample fraction (520 ± 50 bp) was significantly different from the acid washed sample Wk-2271 (690 ± 50 bp) ($T=5.78$; $\chi^2_{1:0.05}=3.84$). This may indicate that there were young percolating carbonates within the "as is" sample matrix. The base pretreatments, designed to remove mobile humic contaminants resulting from the breakdown of plant and other organic matter, gave ages statistically distinguishable from the "as is" date, but indistinguishable from the acid washed fraction date. This suggests the acid washing had the most significant effect of the chemical pretreatments. The pooled mean of the chemically pretreated dates was 663 ± 29 bp ($T=0.18$; $\chi^2_{2:0.05}=3.84$), again, significantly different from the date of the untreated sample.

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In summary, the contaminants within the material from Area 1 at Pleasant River comprise modern rootlets, adhering to, and within the sample charcoals and perhaps young carbonates within the matrix. The effect of the rootlets upon the age of the sample is negligible because of their small fractional size. The effect of acid washing the sample, however, was significant.

The pretreated charcoal dates were statistically distinguishable from the IGNS date (NZ-7960) on identified charcoal from the same Area 1 context. This suggests the Waikato material contains a degree of inbuilt age because the IGNS series were pretreated in an identical manner.

8.5. SHAG MOUTH PRETREATMENTS AND DATING.

8.5.1. CHARCOAL PRETREATMENT

Wood charcoal excavated from layer 7 in square B4 at Shag Mouth (sample # 42) was used in a series of pretreatment experiments to investigate contamination within the sample. Wood species were identified by Dr. R. Wallace as follows:

Total weight of sample:	359.5 g
< 4 mm fraction (unidentified):	133.5 g
> 4 mm fraction:	225.8 g
Species identified:	
(1) Ribbonwood (<i>Plagianthus</i> or <i>Hoheria</i> sp)	215.3 g
(2) Mapau (<i>Myrsine australis</i>)	5.7 g
(3) <i>Olearia</i> sp.	1.6 g
(4) Manuka (<i>Leptospermum scoparium</i>)	0.3 g
(5) Matai (<i>Prumnopitys taxifolia</i>)	0.2 g
	(+ 2.7 g of stone)

Ribbonwood (*Plagianthus* or *Hoheria* sp) charcoal (weighing 215.3 grams) was selected for pretreatment work. According to Wallace (pers. comm.) it is acceptable for radiocarbon dating. 146.2 grams were used in the first set of pretreatment experiments described here. The material was initially physically examined for rootlets and other contaminants and then reduced in particle size in a mortar and pestle. The sample was mixed by hand. 15.4 grams of charcoal was set aside as an "as is" fraction. Rootlets

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were removed during, and after the crushing of the samples to gauge the amount of modern contamination (Wk-2588). The charcoal was then placed in a 5 litre beaker and distilled water added to float off the rootlets in the sample. This was very successful. A physically pretreated sample was also obtained. This fraction was given a rigorous physical treatment consisting of an initial crushing, removal of root contaminants using tweezers, flotation and sieving to remove rootlets. Four sieves were used in the pretreatment; 2.36 mm, 250 μ m, 90 μ m and 63 μ m. The weight of this fraction was 9.1 grams (Wk-2594).

The remaining 121 grams of charcoal was acid washed. The sample weighed 107.9 grams after the acid treatment. An acid washed fraction (Wk-2590) was removed from the sample (9.7 grams). NaOH (5%) was then added to the 98 grams of remaining sample and the solution slowly boiled for one hour.

Pretreatment and fraction	Wk number	Weight (g)
"as is" sample extract	2589	15.4 g
sample "as is" minus rootlets	2594	9.1 g
rootlet fraction	2588	0.3*
acid washed fraction	2590	9.7 g
NaOH soluble fraction	2592	6.5 g
NaOH insoluble fraction	2591	51.4 g
HNO ₃ acid residue fraction	2593	13.4 g
Total weight at start		146.2 g

Table 8.3: weights of charcoal used in pretreatment experiments from Shag Mouth 'C', square B4, L7, 1988. *Minimum weight only, this does not represent the total rootlet fraction. This was estimated at 2 g.

The NaOH solution was filtered. Because of the destructiveness of the alkaline wash, the sample was reduced in particle size and filtration was a slow process. The insoluble fraction (Wk-2591) was rinsed and acid washed using 10% HCl, then rinsed and dried at 90° C. The soluble fraction (Wk-2592) was retained and acidified with 10% HCl. Floccing was observed after the acidification. The samples were then left overnight and later decanted. The soluble fraction was finally rinsed and dried.

The total weight of the NaOH insoluble fraction was 51.4 grams. The soluble fraction weighed 6.5 grams. Forty-two percent of the sample was lost during the treatment and the subsequent recovery of the soluble and insoluble fractions. The majority of sample

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loss occurred due to the material staying in solution and being lost during rinsing. There is also likely to have been some sample loss during the acid washing (*ca.* 10%) and physical pretreatment and preparation of the sample.

A further pretreatment on "as is" charcoal was carried out using HNO₃. More charcoal weighing 16.1 grams was boiled in 70% HNO₃ for one hour then rinsed to neutrality. The treated residue weighed 13.4 grams (17% weight loss).

The results of the pretreatment experiments are shown in table 8.4 and illustrated in figure 8.2. The radiocarbon dates were statistically indistinguishable (the pooled mean; $A(p)$ is 626 ± 23 bp ($T=3.15$; $\chi^2_{5;0.05}=11.07$)) compared with the pooled mean date on all charcoal dates for the site of 620 ± 13 bp (Anderson *et al.*, in prep.). This suggests that there is no contamination in the analysed samples.

Wk-number	Sample fraction	Conventional age (BP)	$\delta^{13}\text{C}$ (‰)
2588	Rootlets	-	-
2589	"as is"	630 ± 35	-28.3
2590	Acid washed	620 ± 35	-27.6
2591	A.B.A insoluble	660 ± 35	-27.1
2592	A.B.A soluble	580 ± 45	-27.2
2593	Nitric acid washed	600 ± 35	-27.1
2594	phys. pretreated	660 ± 45	-27.5

Table 8.4: Radiocarbon dating results from pretreatment experiments using material excavated from Shag Mouth 'C', square B4, L7, 1988. The rootlet fraction was too small to be dated. All samples were undiluted.

The only possible source of error may be the rootlet fraction. Unfortunately, it was too small to be radiometrically dated to the required precision. It would probably have given a date close to modern as the Pleasant River example showed. Clearly, root penetration must post-date the use of the material in prehistory and its subsequent deposition in the archaeological record. The small size of the sample and its close to modern date means its effect upon the 'true' age of the material is probably negligible.

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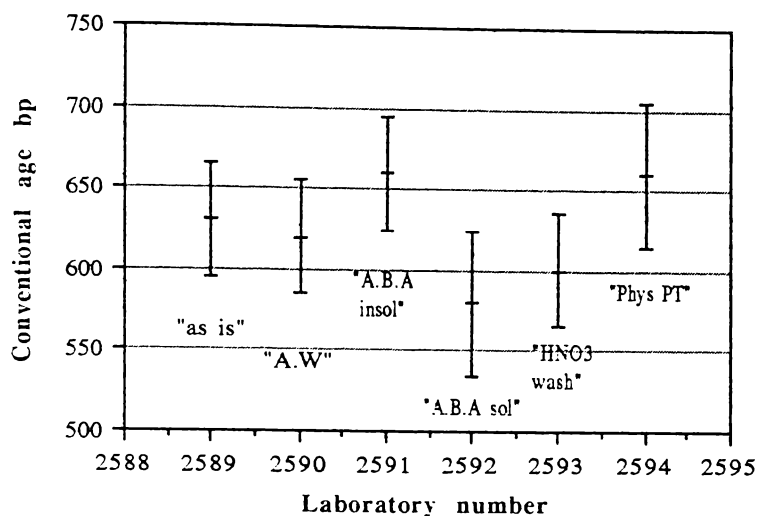


Figure 8.2: Radiocarbon Dating results from pretreatment experiments using material excavated from Shag Mouth 'C', square B4, L7, 1988.

8.5.2. SHELL PRETREATMENT

A sample of *Austrovenus stutchburyi* from Shag Mouth (square G8, spit 7) was used in an experiment to consider the extent of contamination in a deposit of archaeological shell. The sample weighing 3.8 kg was washed in 3% concentrated sodium hypochlorite for 48 hours to remove any surface accretions and weaken the structure of the shell. It was then rinsed and washed in de-ionised water and ultrasonically cleaned for 15 minutes.

The sample was divided into four fractions. The first, an "as is" sample, weighed 33 g (Wk- 2362). This sample was given only the above physical pretreatment. The second sample (33 g) was given an acid wash in 2M HCl for 100 seconds and weighed 30.2 grams after drying (Wk-2363). The outer chalky layer of the third sample (33 g) was drilled and ground with a sandblaster and drills. The grinding ceased when the pearly white, nacreous layer on each shell was reached (Wk-2364). The sample weighed 30.0 grams after pretreatment.

PRETREATMENT

Wk-number	Sample fraction	Conventional age (BP)	$\delta^{13}\text{C}$ (‰)
2362	"as is"	1010±50	1.3
2508	Acid washed	1040±45	1.0
2364	Ground fraction	1040±50	1.3
2365*	Organic fraction	1120±120	-20.0

Table 8.5: Radiocarbon dating results from pretreatment experiments using *Austrovenus stutchburyi* shell excavated from Shag Mouth 'C', 1988. All samples were undiluted 3 ml samples except for Wk-2365, an 0.35 ml sample.

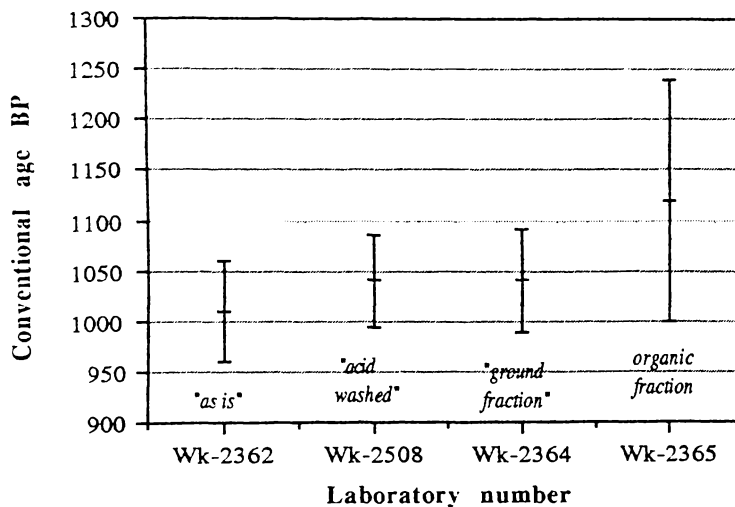


Figure 8.3: Radiocarbon dating results from pretreatment experiments using *Austrovenus stutchburyi* shell excavated from Shag Mouth 'C', 1988.

The organic fraction (Wk-2365) was also dated as a check on the dates of the inorganic carbon fractions. All material for this sample was given the above physical pretreatment and an acid wash. The carbonate fraction was evolved with 2M HCl and the organic fraction rinsed and dried using a buchner funnel. The high ratio of inorganic shell to organic fraction demanded that a large amount of shell be used. The organic carbon fraction comprises only 1% of shell carbon in modern shellfish (Aitken, 1990). In total, 3715 g of shell was used in this experiment but only 4.6 grams of organic carbon was recovered (0.123% of the sample).

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The results of these pretreatments are shown in table 8.5 and figure 8.3. All radiocarbon dates are statistically identical. None of the pretreatments resulted in any statistically meaningful variation from the "as is" sample date of Wk-2362. The date of the organic

Wk-number	Sample fraction	Conventional age (BP)	$\delta^{13}\text{C}$ (‰)
2410	"as is"	1020±50	1.5
2411	Acid washed	990±45	0.8
2412	Ground fraction	980±45	1.2

Table 8.6: Radiocarbon dating results from pretreatment experiments using *Austrovenus stutchburyi* shell excavated from square F7, Shag Mouth 'C', 1988.

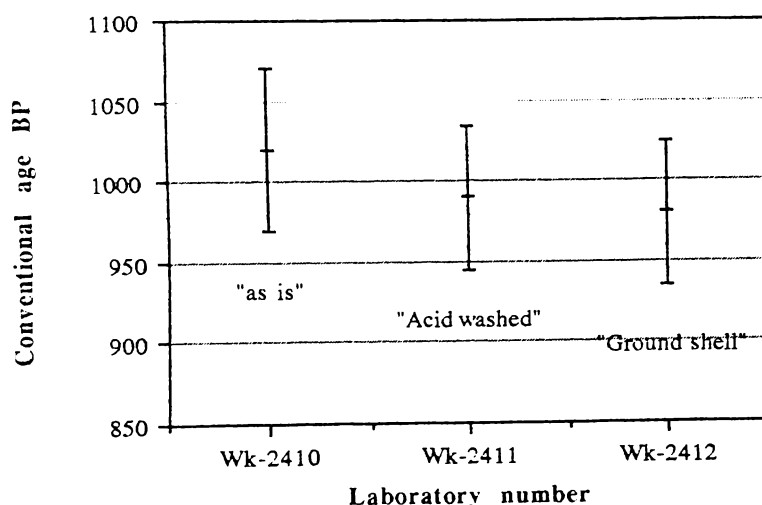


Figure 8.4: Radiocarbon dates of pretreated *Austrovenus stutchburyi* shell from the site of Shag Mouth, North Otago.

fraction was indistinguishable from the carbonate series. The standard error is high (± 120) because the sample was small. These results suggest that pretreatment might not be necessary where, as at Shag Mouth, shell material seven centuries old is sealed below a deep overburden of sand and tussock (*ca.* 1 metre deep), well above high tide. Another series of pretreatments was undertaken using *Austrovenus stutchburyi* shell from square F7, (layer 4) at Shag Mouth. They were pretreated in the same manner as the carbonate series described above. The first, an "as is" sample (Wk-2410), the second acid-washed (Wk-2411) and the third with the exterior ground (Wk-2412). The results are shown in table 8.6 and figure 8.4.

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The results of this series of pretreatment were similar to the first. The material is uncontaminated because the pretreated dates are indistinguishable from the "as is" date. Any observable differences in the dates reflects the overall variation expected in counting a suite of ^{14}C dates of the same age.

A third series of shell pretreatments from Shag Mouth was conducted using *Austrovenus stutchburyi* from square J5 (layer 4). An "as is" sample was compared with a sample given an acid wash and a ground shell sample in an identical preparation to that described above. The series was affected, however, by the loss of the "as is" sample, Wk-2855. The acid washed sample (Wk-2856) measured 980 ± 40 bp. The ground shell fraction (Wk-2857) measured 950 ± 45 bp.

8.6. PRETREATMENT OF MATERIAL FROM THE KILLERMONT SITE

The analysis of charcoal from the Killermont #2 site on the banks of the Ahuriri river in the Mackenzie country was designed to ascertain the extent of contamination. There was no apparent evidence of leaching down the profile which was composed of 10 - 15 cm of grey soil overburden, with a 4 cm deep cultural layer atop a yellow soil substrate. There was evidence however of extensive root penetration into the cultural layer and much of the charcoal excavated contained rootlets.

Pretreatment of charcoal excavated from the Killermont site initially involved physical examination of the material and crushing with a mortar and pestle, followed by oven drying at 90°C . As with the Shag Mouth and Pleasant river material, the removal and quantification of the contaminating root fraction was both problematical and time consuming. A sub-sample of charcoal was removed from the material excavated from area B, squares K9/K10 (KLM 6 - oven A). This weighed 55 grams and was sorted for root hairs under a microscope after sieving in three sieves measuring 63, 250 and $1000\mu\text{m}$. Certain portions were subjected to flotation but this proved only moderately successful. Tweezers were used to remove the majority of root hairs within the sample. Of the 55 grams analysed in this manner, 0.55 g of root hairs were removed. It was impossible to remove all rootlets since some were minute in size, so it is estimated that the rootlet contaminant comprises between 0.8 and 1.2% of this sample from the Killermont site. The remaining sample was dated as the "physically pretreated" fraction (Wk-2783).

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2781	Rootlets	370±140	64	-26.2	0.7
2782	"as is"	680±35	100	-25.5	15.0
2783	Physically pretreated	640±35	100	-25.3	45.0 (15.0 dated)
2791	Acid washed	600±40	100	-25.5	15.9
2784	ABA insoluble A	650±35	100	-25.0	15.5 (12.4 dated)
2785	ABA soluble A	590±45	100	-26.0	13.5
2786	ABA insoluble B	630±40	100	-25.5	78.0 (12.0 dated)
2787	ABA soluble B	600±60	98.5	-25.7	7.0
-	HNO ₃ acid residue fraction				20.0 (undated)
<i>Total sample used</i>					94.0g (45.1 spare)
TOTAL SAMPLE at start					5628.0 g

Table 8.7: Radiocarbon dating results from pretreatment experiments using material excavated from the Killermont #2 site, Omarama, the Mackenzie Basin. All samples are 5 ml benzene samples except Wk-2787 (3 ml) and Wk-2781 (0.35 ml).

Approximately 190 grams of the total sample was sorted and physically pretreated to remove root contaminants prior to further chemistry. Flotation methods similar to those described above were used to speed up this process. An "as is" fraction was removed, weighing 15 grams (Wk-2782).

The remaining 152 grams of sample was acid washed using 10% HCl. It was boiled for one hour, rinsed to neutral in a buchner funnel and dried in an oven. An 'acid washed' fraction weighing 15.9 grams was extracted for dating (Wk-2791). The remaining 136 grams of charcoal was split into two fractions; 20 grams for pretreatment with HNO₃ and 116 grams for sodium hydroxide pretreatment (with 5% NaOH boiled for one hour) to remove any contaminating humic acids from the sample. A total of 13.5 grams was base soluble and was kept and acidified as the 'base soluble' fraction (Wk-2785). 100.6 grams remained; 15.5 grams was removed to date the base insoluble fraction (Wk-2784). The remaining sample was washed in 5% concentrated NaOH. A base soluble B fraction weighing 7.0 grams was extracted (Wk-2787). The insoluble B fraction weighed 78 grams of which 12 grams was dated (Wk-2786).

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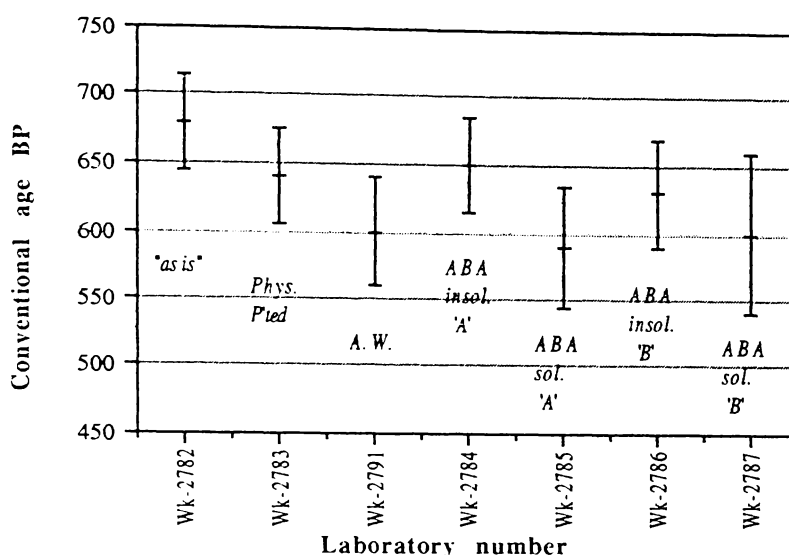


Figure 8.5: Radiocarbon dates from charcoal fractions excavated from the Killermont #2 site, Omarama, the Mackenzie country. All samples are 5 ml benzene samples except Wk-2787 (3 ml). Wk-2781 (0.35 ml) the rootlet date, is left out of the graph (370 ± 140 bp). Pretreatment details are shown in table 8.6.

The results of the pretreatment experiments are shown in table 8.7 and figure 8.5. They yielded similar results to those described above for Shag Mouth. There are no statistical grounds for considering the dates as representing anything outside a normal counting distribution. It is concluded that, with the exception of the rootlets (Wk-2781), there is no significant contamination present within the matrix at the Killermont site.

That these results are representative of a natural range of radiocarbon measurements is shown by dates from other ovens at the Killermont site, presumed to have been deposited contemporaneously; Wk-2916 gave a conventional date of 660 ± 45 bp, while Wk-2991 gave a date of 630 ± 45 bp. Both were dated "as is" (the pooled mean date for the "as is" Killermont dates is 660 ± 23 bp ($T=0.77$; $\chi^2_{2;0.05}=5.99$)).

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8.7. PRETREATMENT OF MATERIAL FROM RAOUL ISLAND

Two samples of limpet shell (*Patella kermadecensis*) excavated from prehistoric contexts at Low Flat by Johnson were obtained for pretreatment analyses. *Patella kermadecensis* is a limpet found only in the Kermadec group. The prehistoric shells were all large (up to 10 cm along the axis of maximum growth) but because of the small total size of the available samples, only two were chosen for analysis. Both came from the Low Flat sites' main upper cultural horizon.

One sample of shell was dated without treatment, this was the "as is" sample (Wk-2768). The other shell sample was acid-washed (Wk-2769).

The results again showed no statistically meaningful difference between the pretreated sample and the untreated sample. The "as is" sample gave a date of 1100 ± 45 bp. Interestingly, this is identical to an earlier shell sample submitted in 1991 (Wk-2282 dated at 1100 ± 45 bp). The acid washed sample gave a date of 1050 ± 45 bp.

These shell dates are discussed further in chapter 10, along with other dates from Raoul Island.

8.8. PRETREATMENT OF SHELL FROM NELSON-MARLBOROUGH

Shell from two Nelson sites was investigated for contamination. *Paphies australis* from Bark Bay was pretreated using acid washing and exterior grinding and the dating results compared with an "as is" sample. The results are shown in table 8.8.

Wk-number	Sample fraction	Conventional age (BP)	$\delta^{13}\text{C}$ (‰)
2863	"as is"	840 ± 45	2.0
2864	Acid washed	820 ± 45	1.9
2865	Ground fraction	880 ± 40	1.9

Table 8.8: Radiocarbon dating results from pretreatment experiments using shell excavated from Bark Bay, Nelson.

PRETREATMENT

There is no measureable, statistically significant effect on the "as is" age of the sample through pretreatment using acids and grinding. The pooled mean (A_p) is 853 ± 29 bp ($T=0.99$; $\chi^2_{2;0.05}=3.84$). This result suggests there is no significant contaminant within the Bark Bay shell, at least not at this level of dating precision.

8.9. CONCLUSIONS AND DISCUSSION

The application of higher levels of radiocarbon dating precision to chronological problems in New Zealand archaeology is valid only if sources of contamination are removed, or if it can be shown there is no significant contamination. It has been tacitly assumed that because New Zealand archaeological material is young, it is probably not contaminated. It is truer to say that New Zealand archaeological material is likely to be *less* seriously contaminated than older material because it has been deposited for a shorter time. The influence of the immediate environment upon the carbon sample, however, is a more important variable than the period of deposition in influencing the extent of contamination. The significant contamination identified by Head and Gillieson (1982), for example, in the young sites they dated in Papua New Guinea, emphasizes this.

Another more controversial example worth mentioning is the dating of prehistoric carbonized kumara from a pa pit at Pouerua in Northland. Here, a large number of dates were contaminated by material post-dating 1950, according to Yen and Head (1993). The majority gave measurements indistinguishable from the Modern Standard (ie. *ca.* 250 bp) but the authors suggested the material was contaminated by bomb carbon material because some of the results were >modern. The exact contaminants were not identified or dated, however, and it seems difficult to accept the hypothesis that post-depositional contamination *per se* is responsible for the measurements obtained for two reasons. First, the proportion of contaminant required to shift a 'true' date of 400 bp or even 150 bp to >Modern is extremely large (see Table 8.1. As an example, even a radiocarbon measurement of 150 bp requires a massive 100% contamination to give a result of 0 bp (1950 AD)). Given the extensive pretreatments applied to the kumara from the site in question (see Yen and Head, 1993 for details) it seems unlikely that such a magnitude of change could be effected without some visual identification of the contaminant itself. Second, the kumara dates are 0.35 ml samples. Experience in the Waikato laboratory has suggested that there are problems in accurately dating very old samples and samples close to modern using mini-vials and small samples. Given the difficulty in measuring samples close to modern (see

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chapter 6; page 35 for examples) it is possible that the variation shown in the modern and >modern kumara dates from the Pouerua site may be due to reasons other than contamination. It is more likely that the two prehistoric measurements from Pouerua are affected by contamination if one considers the amount of old carbon required to change a protohistoric radiocarbon date to *ca.* 900 bp. Clearly, what is required at this site is unequivocal evidence of contamination by dating extracted fractions, until then the Pouerua results cannot be viewed with confidence.

Often, smaller errors are overlooked in radiocarbon dating because their results are not questioned due to the size of the magnitude of error. The majority of the charcoal pretreatment experiments described above suggest that there may be some contamination in the material, from a variety of sources, although in most instances it is not *significantly* affecting the 'true' age of the samples. It is certain that this conclusion does not apply to all New Zealand archaeological material. Intrusion by modern rootlets is the commonest and has been identified in samples from Killermont and Pleasant River, however, their effect upon an untreated date appears insignificant because of the small size of the contaminating fraction when compared to the total sample. Humic acids isolated by base treatments were all contemporaneous. Samples treated with acids were indistinguishable from untreated samples. The exception was Pleasant River where a significant age difference was identified between treated and untreated samples. Any shifts in age between treated and untreated samples in other analysed samples are due to statistically random distribution around a mean, that is, a natural range of values.

Similarly, shell samples from the sites which were investigated showed no statistically significant shifts in age between treated and untreated fractions consistent with contamination. Variation in results represents the expected range of radiocarbon dates in a normal distribution.

Sample pretreatment will need to be addressed further if, or when, high precision dating is brought to bear upon the dateable remains of prehistoric New Zealand. At the level of precision used in the examples given above, contaminants are either negligible in their impact, or their effects are being masked by higher standard errors. Given the situation encountered at Pleasant River it is wise to err on the side of caution and pretreat all archaeological samples with simple, routine procedures.

CHAPTER 9

THE RADIOCARBON DATING OF SHELL

9.1. INTRODUCTION

Although radiocarbon dates of shell have traditionally been viewed sceptically due to variable and inconsistent results, shell does possess two important advantages for the prehistorian. First, it usually dates the event closely. Shellfish are seldom transported long distances, they are usually collected and processed in the same vicinity. The transportation of large amounts of shell across country has rarely, if ever, been documented ethnographically*. Second, the 'lag' or dilution effect of the oceanic reservoir upon the Suess 'wiggles' means that the calibration curve is smoother than for terrestrial samples. It is therefore possible to obtain more precise calendar ages at the crucial recent era (<350 radiocarbon years). Given Little's (1993) recent conclusions regarding the accuracy of the marine calibration curve, this is an important consideration for New Zealand archaeological dating.

There are several reasons why these advantages have not provided a corpus of accurate shell dates. First, there has been uncertainty over the reservoir correction as it applies to New Zealand. This has recently been addressed (McFadgen, 1978; McFadgen and Manning, 1990). Second, there are probably errors of varying magnitude introduced by dissolved bicarbonate from calcareous rock formations in estuaries around the New Zealand coast. A number of important prehistoric sites are near estuaries and old carbon is thought to have affected radiocarbon dates of shell collected in them (Anderson, 1991). Third, there is the problem of upwelling. This refers to the mixing and perturbation of ocean water. Deep ocean water which is radioactively old is brought to the surface where it dilutes the activity of shellfish living there and gives them spuriously old ages. The effects of the upwelling zone upon shellfish ^{14}C ages is particularly well documented along the coasts of California

* Anderson and Higham (in press) recently examined the possibility of transportation of shellfish in prehistory at the site of Dart Bridge, near Lake Wakatipu in Central Otago. The remains of *Ostrea lutraria* (oyster) from Foveaux strait were found at the site, in close association with prehistoric remains. Radiocarbon dating revealed the shellfish possessed a bomb carbon signal and could not be prehistoric in origin. Use of a calibration curve calculated using fish otoliths collected at a known historical date revealed collection and deposition of the material took place in the early 1970's (Anderson and Higham, in press).

and Mexico (Berger, Taylor and Libby, 1966; Druffel and Williams, 1991). In New Zealand, Anderson (1991) has invoked this effect to explain old shell dates from Avoca Point (Fyffes site) on the Kaikoura Peninsula which borders an important upwelling zone (Anderson, 1991:777). Finally, there is the problem of post-depositional contamination. Shellfish deposited *in situ* may exchange with non-contemporaneous carbonates, affecting their measureable radioactivity. The extent of this possible problem and other contamination effects is not well documented because no one has effectively investigated it. In this dissertation, questions of shell contamination have been addressed in chapter 8. Contamination in the sites investigated was found to be negligible.

It is possible, then, that the use of shell for dating at higher precision may be precluded because of certain of these factors, despite Law's (1984) assertion that standard errors on dates from marine shell are, if anything, too large. In this chapter, the first three of these problems will be analysed through radiocarbon dating shell from prehistoric and modern contexts and the efficacy of dating at high precision will be considered.

9.2. SHELL PHYSIOLOGY AND CARBON MARINE LIFEWAYS

Initially, it is important to review the characteristics of the species of shell to be examined, their physiology and metabolism and the pathways of utilised carbon.

The shell, or mantle, is deposited in the form of calcium carbonate crystals bonded in an organic matrix with a protein called conchiolin. According to Morton (1979:30), this comprises an outer layer of quinone-tanned protein (periostracum), a columnar crystalline layer usually consisting of either calcite or aragonite, and an inner, nacreous layer of thin crystalline sheets. The calcium carbonate, which is the inorganic fraction of the shell, is the most often used fraction in radiocarbon dating shell because it is largest.

Shellfish obtain carbon for shell building from two sources. Organic or metabolic carbon comes from marine or terrestrial plant material, including diatoms and protozoa, kelp and phytoplankton, or humus and peat added to estuaries and rivers (Keith, Anderson and Eichler, 1964; Tanaka, Monaghan and Rye, 1986; Little, 1993). Inorganic carbon comes from ocean water bicarbonate (which has a $\delta^{13}\text{C}$ value of close to -2‰ wrt PDB), atmospheric carbon dioxide (-7‰) and fresh water bicarbonate (usually less than -8 ‰) (Keith *et al.*, 1964). Dissolved, metabolised or

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oxidised CO₂ from terrestrial plant and humus reservoirs affect the organic sources for molluscs in food webs and the bicarbonate pool (Keith *et al.*, 1964). CO₂ from the respiration of land plants and the oxidation of humus in soil reaches the groundwater and is fed into lakes and rivers. Its effect is to lower the average $\delta^{13}\text{C}$ content of the bicarbonate that exists in continental waters (this is known as the ground water effect). The oxidation of humus within river and lake sediments also releases CO₂ for uptake by mollusc populations. The sources of carbon from terrestrial and marine systems are of variable age and $\delta^{13}\text{C}$, so an analysis of the extent of fractionation within them is vital for radiocarbon dating shell from these environments.

Keith *et al.* (1964) measured typical $\delta^{13}\text{C}$ values in shell from marine, lacustrine and riverine environments. They showed that the value of $\delta^{13}\text{C}$ is influenced primarily by the isotopic composition of the shells' immediate environment (Keith *et al.*, 1964; Head, 1991). Marine shells possess a $\delta^{13}\text{C}$ between +4.2 and -1.7‰ wrt PDB, river shells between -8.3 and -15.2‰ and shells from large clear lakes between -2.4 and 6.0‰ (Keith *et al.*, 1964).

The shells of principal interest to New Zealand archaeologists are estuarine and marine. The most important for Maori in prehistory and therefore in marine shell dating have been the bivalvia, with *Austrovenus stutchburyi* (the common cockle) and *Paphies australis* (the pipi) most commonly found in midden remains. According to Law (1984), who has reviewed shell dates from the IGNS, Lower Hutt laboratory, approximately 50% of the shell samples measured for $\delta^{13}\text{C}$ values were *Austrovenus stutchburyi* (Law, 1984: table 4). This is an estuarine species. Others commonly found and considered useful for dating include *Paphies subtriangulatum* (tuatua), *Mytilus edulis aoteanus* (blue mussel), *Protothaca crassicostra* (karoro) and *Paphies ventricosum* (toheroa).

Of the gastropoda, the mudsnail (*Amphibola crenata*) has been dated, although it is now considered unreliable (Law, 1984; Anderson, 1991) because it inhabits marginal environments. Pauas (*Haliotis* sp.), catseyes (*Lunella smaragda*), limpets (*Cellana* sp.) and chitons found on the rocky coastlines have also been used for dating.

Austrovenus stutchburyi is one of the commonest bivalves on the New Zealand coast, most visible on low tidal flats on protected beaches, sheltered bays and estuaries or wide river mouths. It occupies stable beaches where it is found in sand, submerged up to 4 cm. The pipi (*Paphies australis*) is found in similar areas. It flourishes in places

where freshwater seeps through the middle beach (Morton and Miller, 1968). Papis are usually found near the mouths of estuaries where silt has been removed by waves and currents. Though closely related to the pipi, the tuatua (*Paphies subtriangulatum*) is more common on open sand beaches with direct wave access. Its densest beds are further down the beach where it burrows 4 - 5 cm into the sand. These three bivalves obtain carbon both from filtered organic matter and dissolved inorganic carbon (DIC) in the sea or estuary (Tanaka *et al.*, 1986). The vast majority of bivalves possess paired gills or *ctenidia* within their mantle cavity, which are composed of fine cilia. They pump water into the gill, filtering the food within it (Morton and Miller, 1968).

Among the gastropoda are carnivorous, filter and deposit feeders. We are concerned principally with the Turbinidae and Haliotidae. *Haliotis iris* (the paua) live beneath stones and ledges in the clean waters of open coasts, browsing upon coralline and other algae. *Cookia sulcata*, (the Cook's Turban), is a rocky shore dweller characterized by a thick shelly operculum, marked in green and white. Cook's Turban feeds upon fronds of kelp and *Carpophyllum* (brown algae). The adult *Cookia* is restricted to low water and a few fathoms beyond, living under stones and ledges and feeding on coralline algae. Its close relative, *Lunella smaragda* (catseye) favours a similar habitat and feeds also on kelp and brown algae of the sub-littoral fringe. It favours coralline algal pools in particular. Limpets (*Cellana* sp.) and chitons favour rocky coastlines. Both feed upon the almost invisible diatom and plant particles carried in the sea.

9.3. THE RESERVOIR EFFECT

9.3.1. INTRODUCTION

One of the principal areas of concern in radiocarbon dating shell in New Zealand is the applicability of the shell reservoir correction. This is an area of particular interest for the dating of estuarine shell.

The apparent age of water in the oceans is caused both by the delay in exchange rates between atmospheric CO₂ and ocean bicarbonate, and the dilution effect caused by the mixing of surface waters with upwelled deep waters. A reservoir correction must be made to any shell dates to account for the difference in the marine reservoir. Shell dates were once corrected using the New Zealand Marine Shell Standard (Rafter *et al.*, 1972). This correction was based upon the depletion measured in a sample of *Austrovenus stutchburyi* shellfish collected live from Pounaweia, South Otago, in 1955. The net depletion in $\Delta^{14}\text{C}$ was measured at -40‰ (Rafter *et al.*, 1972). This

equated to a correction of 330 radiocarbon years, that is, shell dates were too old by that amount. This factor included a correction for the contribution of fossil fuels in the atmosphere and oceans since *ca.* 1890. Later measurements suggested the offset was -41‰, so a constant 336 years was subtracted from all shell measurements (Jansen, 1984). The problem with a constant correction, however, was that it did not account for secular variation in the amounts of ¹⁴C in the atmosphere (McFadgen and Manning, 1990). The extensive tree-ring calibration data which has been compiled in the past twenty years has shown the extent of the natural variation in atmospheric ¹⁴C first identified by de Vries (1958). The high-precision tree-ring measurements published in *Radiocarbon* 1986 (Vol. 28(2B)) and 1993 (Vol. 35(1)) enable marine dates to be calibrated and corrected for secular variation. Using a carbon box-diffusion model first developed by Oeschger *et al.* (1975), Stuiver and Braziunas (1993:137-189) model carbon exchange in oceans using the terrestrial calibration curves and the Barbadian coral curves of Bard *et al.* (1990) (dated using ²³⁴U/²³⁰Th). Global carbon exchange in the ocean is thus *simulated*. This is similar to models of pre-bomb and post-bomb carbon distributions developed by Toggweiler, Dixon and Bryan (1989). To recognise local and regional reservoir effects Stuiver, Pearson and Braziunas (1986) have calculated a further correction termed 'ΔR'. This describes the difference between the radiocarbon activity of the surface layers of the *regional* ocean and the surface layers of the average *world ocean* in AD 1950. ΔR is thus a further correction for local and regional effects and is represented by:

$$\Delta R = P - Q$$

Where P is the conventional age of an historic sample, and Q is the model calculated conventional ¹⁴C age of an historic sample.

The New Zealand ΔR value originally given by Stuiver, Pearson and Braziunas (1986) was -65±25 radiocarbon years. McFadgen and Manning (1990:229-32) recalculated this to -30±13 (see below). Conventional shell dates may be corrected either by subtracting 30 radiocarbon years prior to calibration, or -30±13 may be entered at the appropriate point in the University of Washington computer calibration programme (CALIB 3.0.3) using the marine curve. Instead of correcting a conventional shell date with a constant factor, then, the computer calibration, with ΔR set at -30±13, corrects dates on a range from about -450 to -350 radiocarbon years, depending on their age.

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The applicability of this marine shell reservoir correction for New Zealand may be analysed either by collecting more shell samples of known historical age to test the ΔR value, or by analysing the extent of variation between paired identified archaeological charcoal and shell dates.

The New Zealand ΔR value is based on only 11 shell dates because of the difficulty in obtaining shells of known age (McFadgen, 1978:312). Testing the applicability of the ΔR value using well provenanced prehistoric shell-charcoal dates is more profitable.

Similar studies have been undertaken by Law (1984) in New Zealand, and Gillespie and Temple (1977), Gillespie and Polach (1979) and Head, Jones and Allen (1983) in Australia, although they had to compare reservoir differences between conventional ages rather than ΔR displacement. Recently, Little (1993) presented paired shell-charcoal dates and ΔR offsets from the eastern seaboard of the United States. It is assumed in these comparisons that stratigraphically identical materials were simultaneously deposited and are the same age. Law (1984) has compared shell and charcoal dates from identical contexts, and suggested inbuilt age in charcoal dates for discrepancies because they were older, on average, by 83 years. The mode, or most common value of his data however was +25 years in favour of shell. Gillespie and Polach (1979) have dated shells of known historic age from Australian coastal waters and calculated a reservoir correction of 450 ± 35 radiocarbon years. They analysed shell-charcoal pairs excavated from prehistoric aboriginal middens to test the result and found age differences ranging from -25 to 775 years (Gillespie and Polach, 1979:418). They concluded that the discrepancies were due to a combination of inbuilt age and displacement of sample and event, leading to non-systematic age differences between pairs.

9.3.2. ΔR ANALYSIS

Charcoal-shell pairs have been analysed from Shag Mouth. There are thirteen identified charcoal dates from the site (Anderson *et al.*, in prep.). Nineteen shell dates from Shag Mouth have been measured for this dissertation of which 15 are applicable to this exercise (table 9.1). Instead of comparing single shell-charcoal pairs directly, shell dates below are measured against the pooled mean ($A'(p)$) of the charcoal series from Shag Mouth to calculate the ΔR value. The principal advantage in using the mean charcoal date is greater precision. The $A'(p)$ (charcoal) is 620 ± 13 bp ($T=5.31$; $\chi^2_{12:0.05}=21.03$). The surface ocean ^{14}C /atmospheric ^{14}C figures of Stuiver and Braziunas (1993:154) have been used in the calculation, with 40 radiocarbon years

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deducted for the southern hemisphere terrestrial correction. The reservoir difference ($R(t)$) between the conventional shell ages (termed P_{ma}) and terrestrial ages (P_{at}) was measured using $P_{ma} - P_{at}$ (table 9.2) (Little, 1993). The atmospheric sample date was converted to a marine date using the Stuiver and Braziunas (1993) curves to give a

Lab #	Material type	Provenance (SM/C)	Conv. date BP	$\delta^{13}C$
-	Charcoal A'(p)	SM/C	620±13	n.a
Wk-2751	<i>A. stutchburyi</i>	F7 L4	960±45	1.0
Wk-2410	<i>A. stutchburyi</i>	F7 L4	1020±50	1.5
Wk-2362	<i>A. stutchburyi</i>	G8 L4	1010±50	1.3
Wk-2368	<i>P. australis</i>	G8 L4	1080±50	1.3
Wk-2411	<i>A. stutchburyi</i>	F7 L4	990±45	0.8
Wk-2412	<i>A. stutchburyi</i>	F7 L4	980±45	1.2
Wk-2632	<i>P. australis</i>	J5 L4	980±40	1.4
Wk-2752	<i>M. edulis aoteanus</i>	J5 L4	1040±45	1.0
Wk-2508	<i>A. stutchburyi</i>	G8 spit 7	1060±45	-0.2
Wk-2364	<i>A. stutchburyi</i>	G8 spit 7	1040±50	1.3
Wk-2856	<i>A. stutchburyi</i>	J5 L4	980±40	1.0
Wk-2857	<i>A. stutchburyi</i>	J5 L4	950±45	1.0

Table 9.1: Shell dates of three species from layer 4 at the site of Shag Mouth, paired with a pooled mean charcoal date as a measure of the reservoir correction for New Zealand. Charcoal A'_p=620±13 bp ($T=5.31$; $\chi^2_{12;0.05}=21.03$).

model marine age bp (in this case 980±13). This measurement was deducted from each of the conventional shell dates to give ΔR , the reservoir correction (Stuiver and Braziunas, 1993). Each of the ΔR values may be pooled if statistically acceptable, to give the total ΔR value for the site or region. The ΔR σ was calculated by $\sqrt{\sigma_{\text{marine}}^2 + \sigma_{\text{terrestrial}}^2}$ (Little, 1993:464).

Tables 9.1 and 9.2 show all shell dates and the ΔR data for Shag Mouth.

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Lab #	Conv. date BP (P_{ma} , P_{at})	R(t) (P_{ma} - P_{at}) (reservoir age)	Cal AD or T age range $T + \sigma$ (T) $T - \sigma$	ΔR value
NZ-7805	965±26	345±29	cal BP 604 (555) 537	-15±29
NZ-7806	1022±29	402±32	cal BP 642 (626) 586	42±32
NZA-1175	974±49	354±51	cal BP 627 (561) 530	-6±50
Wk-2751	960±45	340±67	cal BP 617 (552) 525	-20±47
Wk-2410	1020±50	400±70	cal BP 650 (625) 557	40±52
Wk-2362	1010±50	390±70	cal BP 646 (619) 551	30±52
Wk-2411	990±45	370±67	cal BP 634 (592) 542	10±47
Wk-2412	980±45	360±67	cal BP 629 (570) 536	0±42
Wk-2632	980±40	360±65	cal BP 626 (570) 538	0±42
Wk-2752	1040±45	420±67	cal BP 657 (635) 600	60±47
Wk-2508	1060±45	440±67	cal BP 669 (644) 621	80±42
Wk-2364	1040±50	420±70	cal BP 659 (644) 621	60±52
Wk-2856	980±40	360±65	cal BP 626 (570) 538	0±42
Wk-2857	950±45	330±67	cal BP 606 (546) 519	-30±47
	R(t) 374±14 (EW mean) (378±33 Unweighted mean)		Pooled mean ΔR^* (Unweighted scatter =33)	16.0±11

Table 9.2: Calculation of the ΔR using shell dates from the site of Shag Mouth, North Otago. *-Pooled mean statistics are $T=8.19$; $\chi^2_{13:0.05}=22.4$. The ΔR measurements are thus statistically indistinguishable. 'NZ' is the laboratory number for the Institute of Geological and Nuclear Sciences, Lower Hutt, NZ. NZ-7805 is a date from *Austrovenus stutchburyi*, NZ-7806 and NZ-1175 are dates of *Haliotis iris*. EW mean is error weighted mean, the unweighted scatter and unweighted means are discussed in the text.

The results show that the pooled ΔR measurement of 16 ± 11 for the Shag Mouth shell series is statistically *distinguishable* from the recommended value (-30 ± 13 radiocarbon years) reported by McFadgen and Manning (1990). This is a significant result which may be explained in several ways. First, the terrestrial pooled mean date is too young in comparison to the shell dates. It may be due to contamination with younger material at the site. Second, there may be a hard water effect in the Shag estuary, making shellfish dates too old. Third, the Shag Mouth estuary, with its

complex perturbation and mixing of riverine and marine waters, may be giving shellfish apparent ages in addition to the age of the marine reservoir. Fourth, the ΔR value may be correct but does not apply to the dates from these sites at 600 bp because of prehistoric variation in local marine reservoirs around the New Zealand coast. This may be due, for example, to changes in ocean circulation patterns. Finally, the ΔR value calculated for New Zealand may be in error and does not properly correct conventional shell dates.

Although contaminants were identified in the charcoal used in pretreatment experiments, the order of magnitude of the error from them is unlikely to sustain the first possibility. The second and third explanations cannot be discounted and both are investigated further below. The fourth is impossible to prove or disprove; its investigation is dependent upon further analyses of shell-charcoal dates from sites around New Zealand. The final possibility requires some explanation. As mentioned above, the ΔR value for New Zealand was calculated using 11 shells of known historical age including *Austrovenus stutchburyi*, *Haliotis* sp., *Cellana* sp., *Protothaca crassitesta*, *Paphies* sp. and *Dosinia anus* (McFadgen, 1978; McFadgen and Manning, 1990). The samples came from open marine beaches, a river mouth and an inlet (Pauatahanui, near Wellington). The measured activities were statistically indistinguishable and were pooled using the error-weighted mean method. One depleted date (from *Amphibola crenata*) came from an estuary thought to be affected by old carbon. This was rejected from the ΔR calculation. There is no apparent reason, then, to doubt the applicability of the measured ΔR values, however, its error has been calculated differently from the way Stuiver, Pearson and Braziunas (1986) suggest. They recommend use of the larger of the errors calculated by the error-weighted mean method or the unweighted mean method for the ΔR error. The New Zealand ΔR error was calculated using the error-weighted mean value, which is less than the unweighted mean value. The error-weighted mean has been mentioned above and in chapter 3, and has been used throughout this dissertation. The unweighted mean is merely an average of a group of samples, with the standard deviation measurement based upon the scatter of the values of the ages. Thus it does not take into account the errors in individual ΔR , rather the spread of the dates themselves. Usually, the latter method results in a larger error and it is likely that Stuiver, Pearson and Braziunas (1986) recommended its use because of the few measured samples available from which to calculate ΔR and the fact that some ΔR values were not able to be pooled using error-weighted mean procedures. If Stuiver, Pearson and Braziunas' (1986) method is followed, then the scatter error in McFadgen and Manning's (1990) ΔR measurement is ± 41 years, rather than ± 13 years. If the same

method is applied to the Shag Mouth data, the scatter value is ± 33 years (table 9.2). In this situation, both ΔR results are indistinguishable. Clearly, in this instance the question of significance is affected by the chosen level of precision. Is it justifiable to use ± 13 given the spread of data in historic age shells measured by McFadgen and Manning (1990) or is it wiser to give a scatter value based on raw data standard deviation? Interestingly, Stuiver and Braziunas (1993:156) have recently rounded up the New Zealand ΔR error (± 15) slightly in order to allow for the possibility of variation. At present, one can only compare values generated using consistent methodology. Following McFadgen and Manning (1990) there is a significant difference in reservoir depletion between the New Zealand ΔR and the Shag Mouth ΔR .

9.4. THE HARD WATER EFFECT AND UPWELLING

9.4.1. INTRODUCTION

Anderson (1991) has invoked the 'hard water effect' to explain why shell dates from certain New Zealand coastal sites seem spuriously early. This involves the dilution of shell reservoirs with radioactively depleted carbon. Some lacustrine, marine and estuarine environments are known to be affected by large amounts of 'dead' CaCO_3 , which dilute the amount of radioactivity in the shellfish habitat and artificially increases the age of radiocarbon determinations. One example has recently been given from the Plitvice Lakes in the northwest of the former Yugoslav republic (Marcenko *et al.*, 1989). Here the dating of aquatic plants growing in the karstic lake environments revealed an apparent age of 4200 radiocarbon years, due to uptake by plants of bicarbonate originating from the local dissolved limestone. Another contamination effect comes from old water in areas close to upwelling zones (Anderson, 1991). Water from the middle and deep ocean is depleted in ^{14}C and shellfish living near the zone may appear too old in comparison with others of the same age but less influenced by this source of contamination. The hard water question is first addressed with reference to sites in the North Otago region, especially those at Pleasant river and Shag Mouth. Shell dating has proved contentious at the former. Upwelling will then be reviewed in the context of sites on the Kaikoura Peninsula, where this phenomenon occurs.

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9.4.2. EXPERIMENTAL

Modern samples of *Amphibola crenata* (the mudsnail) and *Austrovenus stutchburyi* (the common cockle) were collected from four sites in the North Otago and Dunedin regions between 1992 - 3 to compare the ^{14}C content of shellfish in areas with and without calcareous deposits in their wider catchments. The sites were Pleasant River, Shag Mouth, Portobello and Papanui Inlet. The environments of Pleasant River and Shag Mouth include calcareous formations and it is suggested that they are therefore prone to the hard water effect (Anderson, 1991). Both are barrier-enclosed estuaries, possessing barrier spits and narrow tidal gorges (Healy and Kirk, 1992). Pleasant River in particular possesses a narrow mouth and restricted tidal influence. Portobello and Papanui Inlet are on the Otago Peninsula, a geological region dominated by volcanic rocks - principally basalt, with little limestone (Fig. 5b). It was assumed that the hard water effect was absent. Papanui Inlet is a semi-enclosed tidal bay with wide mud flats exposed at low tide. It is a similar environment to the North Otago sites, with a large sand dune at the head almost sealing the bay from the ocean. It lacks a river and a calcareous element. Portobello is a small tidal bay within the Otago harbour. The substrate is rocky with some silt buildup within which a variety of mollusc species live. This is a marine site lacking a protective sand dune and extensive mud flats.

At Shag Mouth and Pleasant River, it must be assumed that the rates of erosion and dissolution of calcareous surrounds during the past 600 years have been constant, and any measured variation in modern shellfish ^{14}C attributed to old carbon dilution can be applied prehistorically. According to Nelson (pers. comm.)*, there should be an infinitesimal change in limestone erosion rates during the recent period (past 1000 years) and little increase in old, dissolved bicarbonate in the estuaries here. Estimates of karst solution rates have been made for some New Zealand catchments including the Riwaka basin (marble) in Nelson (Williams and Dowling, 1979) and the Mangapohue basin; (limestone) in the King Country (Gunn, 1978). None exist for the North Otago region. An erosion rate of $100 \pm 24 \text{ m}^3/\text{km}^2/\text{y}$ was estimated in northwest Nelson with average basin rainfall of 2158 mm p.a, while the sites investigated in the King Country, a rainfall of 2370 mm p.a. was estimated to result in $69^{+7}_{-18} \text{ m}^3/\text{km}^2/\text{y}$ denudation (Gunn, 1978; Williams, 1992). Coastal North Otago, which has a lower annual rainfall than either of these two sites (*ca.* 750 mm p.a.) should be less prone to erosion if, as

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Williams (1992:192) has suggested, 80% of limestone erosion results from rain falling *directly* onto outcrops.

9.4.3. RESULTS AND INTERPRETATION

It may be assumed then, that the rate of erosion in the North Otago estuarine catchments has remained constant.

The nuclear age resulted in a massive increase in radioactive atmospheric carbon. In the southern hemisphere, atmospheric bomb carbon peaked around January 1965 (Rafter and O'Brien, 1970). In the oceans, the peak was not reached until 1980 because of its dilution effect (Gupta and Polach, 1985). Since 1980, the level of bomb ^{14}C in the oceans around New Zealand has begun to decrease in response to reduced levels in the atmosphere. The dating of modern shell samples makes an understanding of the characteristics of the local flux of bomb-derived oceanic carbon important. Figure 9.1 shows a calibration curve of $\Delta^{14}\text{C}$ measurements obtained from the otoliths of New Zealand snapper (*Pagrus auratus*), corrected to date of calcification (Kalish, 1993). Individuals of this species inhabit shallow coastal waters and move less than 50 km during their lives (Kalish, 1993). They are therefore ideal for measuring the extent of ^{14}C from atom bomb effects in New Zealand coastal and estuarine waters. The otoliths were collected from the east coast of the North Island, which eliminates errors associated with upwelling. The curve shows that the level of radioactivity in the ocean in the 1990's is *decreasing*. Therefore, the relationship between age and radioactivity in present day (1993) marine organisms living since 1990 should be inverted.

To establish the applicability of the otolith curve for shellfish measurements, a series of shellfish and bryozoan samples collected in the mid-1980's by Nelson and dated at the Waikato laboratory, was analysed (Table 9.3). The $\Delta^{14}\text{C}$ results suggest the snapper otolith curve is valid in calibrating modern marine shellfish because the shell results are within, or close to, the statistical range of the curve. The results for Wk-846 and Wk-850 are within the $\pm 1\sigma$ error (Wk-846 was collected from the Aotea

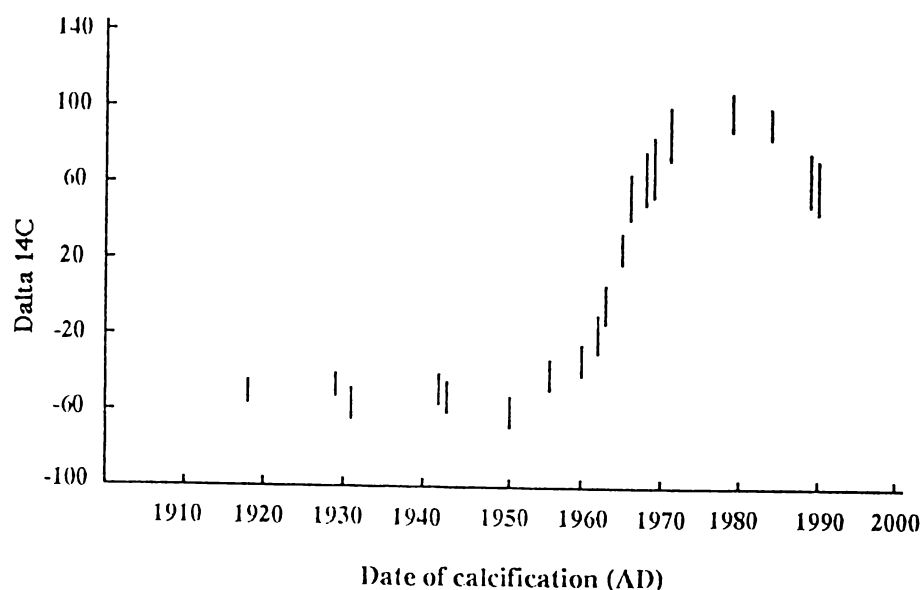


Figure 9.1: $\Delta 14\text{C}$ measurements of snapper (*Pagrus auratus*) otoliths of known age showing the increase in bomb carbon through the 1960's to 1980's and the subsequent decline in the 1990's (data from Kalish, 1993:550).

harbour, which drains a catchment notable for its large limestone deposits, yet it is indistinguishable from the otolith curve). The $\Delta 14\text{C}$ value for Wk-851 is 1σ different from the otolith value for 1985. The $\Delta 14\text{C}$ activities of historical shell reported by McFadgen and Manning (1990) are within the statistical range of the values of otoliths. Furthermore, Kalish (1993) mentions close agreement between $\Delta 14\text{C}$ measurements of surface ocean water at 39°C south latitude and otolith $\Delta 14\text{C}$ measured at the same time. These sources of evidence suggest the otolith curve should be valid for comparison with dates of modern shell.

The other question is how the increase in bomb carbon in the oceans affects measurement of any hard water effect using modern samples in an estuarine reservoir. A recent example of radiocarbon dating at Lake Taharoa, King Country by M. Green and D. Lowe (Earth Sciences Department, University of Waikato), suggests the hard water effect is reduced through bomb carbon. Dates from the lake suggested the effect of hard water resulted in apparent ages of $ca. 450$ years ($ca. 4.5\%M$)^{*}. This was estimated using the known age of a sample near the Taupo Pumice layer (dated by consensus at 1850 ± 45 bp).

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Wk number	$\Delta 14C$	Site and species
846	86.7 ± 5.7	<i>Austrovenus stutchburyi</i> -collected alive from Aotea harbour, 1982.
850	93.5 ± 5.6	<i>Steginoporella neozelanica</i> , collected alive from Doubtless Bay, Mangonui harbour Jan, 1985.
851	70.0 ± 5.4	<i>Menipea zelandica</i> , collected alive from Princes group, 3 Kings Island, Jan, 1985.

Table 9.3: $\Delta 14C$ values of modern shell and bryozoan samples collected from Aotea harbour, Mangonui harbour and 3 Kings islands, 1982-1985. Submitted for dating at the Waikato Laboratory by Professor C. S Nelson, 1986.

However, dates of modern algae growing in the lake were compared with modern grasses growing on the lake shore to estimate the modern hard water effect, and the difference found to be only 2‰. This suggests the hard water effect may be masked by increases in the activity of certain reservoirs. Thus, a measurable hard water effect at either of the sites investigated in the South Island *may* be magnified in prehistory. While the increase in bomb carbon influences the identification of lacustrine and riverine hard water effects however, the ocean reservoir possesses greater dilution potential for bomb carbon which means it is likely that a hard water effect will still be measureable.

The shellfish for this analysis were collected alive on the 27.2.92. All were boiled, their flesh was removed, they were cleaned using scalpels, brushes and an ultrasonic bath, and finally rinsed and dried in an oven at 90 °C.

The results of the experiment into hard water effects are summarised in table 9.4.

The pooled $\Delta 14C$ *Austrovenus stutchburyi* measurements from the Pleasant River site (Wk-2413, 2711 and 2712) are depleted and less radioactive in comparison to the samples dated from Portobello. $A(p)$ (PLR- $\Delta 14C$) = $75.2 \pm 2.8\%$ ($T=1.67$, $\chi^2_{2;0.05}=5.99$), while $A(p)$ /PO- $\Delta 14C$) = $85.8 \pm 3.8\%$ ($T=0.17$, $\chi^2_{2;0.05}=5.99$). Statistical comparison between both pooled ages shows $T'=5.81$ ($\chi^2_{1;0.05}=3.84$). This shows the results are significantly different. The $\Delta 14C$ measurement for the Shag Mouth *Austrovenus* sample (Wk-2414) was $77.5 \pm 5.4\%$. This was indistinguishable statistically from the Portobello mean. Thus, Pleasant River gives a depleted $\Delta 14C$ value consistent with the hypothesis of a diluted reservoir. The measured $\Delta 14C$ of the

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Papanui Inlet sample was enriched in comparison to the other samples, but indistinguishable from the Portobello result.

There are two problems in ascribing with confidence the hard water effect as a cause of this measured variation at Pleasant River. First, there are not enough dated samples to inspire certainty. Second, Wk-2413 may be an outlier. Although it is statistically in agreement with the other two Pleasant River dates, it may be affecting the pooled dates, because there are so few determinations for consideration. As an example of the problems associated with interpretation based on such a small number of samples, the pooled mean for all three *Austrovenus* measured at Pleasant River yields a value statistically distinguishable from the mean of the Portobello dates, however, leaving out the depleted value the pooled date is statistically the same as the Portobello mean. Further dating is clearly necessary in order that firmer conclusions may be drawn. In summary, these preliminary results are interesting, but inconclusive.

Wk #	Material	Site	% Modern	$\Delta 14C$	$\Delta 14C A(p)$	$\delta^{13}C$
2413	<i>A. stutchburyi</i>	Pleasant River	107.5 $\pm$ 0.5	69.6 $\pm$ 5.2	75.2 $\pm$ 2.8	-0.2
2711	<i>A. stutchburyi</i>	Pleasant River	108.2 $\pm$ 0.4	76.3 $\pm$ 4.9		+0.5
2712	<i>A. stutchburyi</i>	Pleasant River	108.6 $\pm$ 0.4	78.2 $\pm$ 4.4		+0.7
2414	<i>A. stutchburyi</i>	Shag Mouth	108.3 $\pm$ 0.5	77.5 $\pm$ 5.4	77.5 $\pm$ 5.4	-1.4
2509	<i>A. stutchburyi</i>	Papanui Inlet	109.7 $\pm$ 0.5	91.3 $\pm$ 5.4	91.3 $\pm$ 5.4	-0.5
2693	<i>A. stutchburyi</i>	Portobello	109.3 $\pm$ 0.5	87.3 $\pm$ 5.3	85.8 $\pm$ 3.8	+0.5
2694	<i>A. stutchburyi</i>	Portobello	109.0 $\pm$ 0.5	84.2 $\pm$ 5.4		+0.6
2421	<i>A. crenata</i>	Shag Mouth ¹	109.2 $\pm$ 0.5	86.5 $\pm$ 5.4	90.5 $\pm$ 4.0	-0.2
2422	<i>A. crenata</i>	Shag Mouth ²	110.1 $\pm$ 0.6	95.2 $\pm$ 5.8		-1.4
2423	<i>A. crenata</i>	Papanui Inlet	107.6 $\pm$ 0.5	77.8 $\pm$ 5.4		-0.5

Table 9.4: % Modern and $\Delta 14C$ values obtained from *Austrovenus stutchburyi* (common cockle shell) and *Amphibola crenata* (mudsnail) from 4 sites in Otago; Pleasant river, Shag Mouth, Portobello and Papanui Inlet. All samples were collected live on the same day (27/2/92). Shag Mouth¹ originates from the estuary, Shag Mouth² from the Waihemo river.

The results from *Amphibola crenata* showed variability. *Amphibola* were collected as a comparison with the cockle dates. At Shag Mouth, samples from the estuary and the river were collected. Only three results were obtained, so again, few firm conclusions may be drawn. The $\Delta 14C$ measurements of samples from the Shag Mouth estuary and river are identical statistically. The riverine sample (Wk-2422) measured 95.2 $\pm$ 5.8‰

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while the estuarine sample (Wk-2421) measured $86.5 \pm 5.4\%$. Both *Amphibola* dates are older than the cockle date from the same site. This is consistent with prehistoric *Amphibola* results which are usually depleted in comparison to other species of shellfish such as *Austrovenus* (see below).

The variability in dates of *Amphibola crenata* compared to *Austrovenus* is due probably to their physiological adaptation and the type of environment they favour. *Amphibola* inhabit O_2 depleted areas at the very highest tidal margins, for example, near salt swamps or mangroves, where there is fine organic mud for them to process. The organic component here, and that of the tidal inflow, are their principal food sources. Experiments have shown that *Amphibola* survive for less than 6 - 7 days in freshwater and 10 - 18 days in seawater, before dying. The reason is that they are an archaic pulmonate, at a mid-point in gastropod evolution, preferring to obtain

Wk #	Material	Site	% Modern	$\Delta 14C$	$\Delta 14C A(p)$	$\delta^{13}C$
2965	<i>A. stutchburyi</i>	Pleasant River	108.7 ± 0.5	81.6 ± 5.2	83.6 ± 3.7	0.2
2965B	<i>A. stutchburyi</i>	Pleasant River	109.2 ± 0.4	85.8 ± 5.3		0.3
2966	<i>A. stutchburyi</i>	Papanui Inlet	109.8 ± 0.5	87.8 ± 5.5	89.9 ± 3.8	0.3
2966B	<i>A. stutchburyi</i>	Papanui Inlet	109.4 ± 0.5	91.9 ± 5.3		0.7
2967	<i>A. stutchburyi</i>	Shag Mouth	108.5 ± 0.5	79.7 ± 5.2	82.9 ± 3.7	-0.1
2967B	<i>A. stutchburyi</i>	Shag Mouth	109.1 ± 0.5	86.1 ± 5.2		-0.1
2968	<i>A. stutchburyi</i>	Portobello	108.2 ± 0.5	76.4 ± 5.3	74.5 ± 3.6	0.4
2968B	<i>A. stutchburyi</i>	Portobello	107.8 ± 0.5	72.8 ± 5.0		0.2

Table 9.5: Dates of *Austrovenus stutchburyi* (cockle) collected live from Otago in 1993. Pooled mean values of all $\Delta 14C$ measurements (col. 6) are statistically insignificant at 0.95 prob.

atmospheric O_2 rather than extract it from the water through gills (Morton and Miller, 1968). Variation in radiocarbon dates, then, may be caused by the gastropod processing fine organic muds, likely to be different in age from the marine reservoir, and through exchange with atmospheric CO_2 . The riverine and estuarine mudsnails at Shag Mouth are probably obtaining carbon derived from non-contemporaneous organic muds deposited in the Waihemo River giving them apparent ages in comparison to *Austrovenus* in the vicinity, who are by contrast, filter feeders.

The $\Delta 14C$ result from Papanui Inlet contradicts this. There, the *Amphibola* is less radioactive than *Austrovenus*. Variation in the ^{14}C label of the organisms' organic mud substrate may explain this anomaly.

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A further sampling strategy was undertaken to add to the corpus of dates from these sites and consider further the question of hard water effects in the North Otago estuaries. Shells were collected on 21.5.93. The $\Delta 14C$ and %Modern results obtained are shown in table 9.5. Unfortunately, they are unable to be compared statistically with the first set of data because of uncertainty concerning the scale of the decrease in bomb ^{14}C in the ocean reservoir.

The most notable results in the second series of dates come from Portobello (Wk-2968 - 2968B). The two dates are reproducible but significantly depleted in comparison to the first series. This is consistent with the expected depletion of oceanic bomb-induced ^{14}C and suggests the *Austrovenus* from this open marine site are reflecting closely the ^{14}C label of the ocean reservoir. In contrast, the other sites reveal $\Delta 14C$ measurements which are similar to the first series. None show depletion consistent with the decreasing ^{14}C content of the ocean. Dates from Papanui Inlet (Wk-2966-2966B) are enriched in ^{14}C compared with Portobello and statistically distinguishable. The date from Papanui Inlet in the first series (Wk-2509) was also the most enriched. One explanation for this is that the Papanui Inlet shellfish are occupying a reservoir distinct from the marine reservoir occupied by shellfish at Portobello and display a lag in response to declining marine carbon. Shell pooled mean dates from Portobello, Pleasant River and Shag Mouth are indistinguishable statistically. Portobello is the only open marine site here and has no hard water influence. Were hard water affecting dates from the North Otago sites, one would expect them to be depleted, or less radioactive in ^{14}C compared with Portobello. All Shag Mouth measurements are statistically indistinguishable from those at Portobello. Pleasant River measurements in the first series were significantly depleted, however in the second, they were identical statistically to the Portobello measurements.

The small number of determinations makes it difficult to refute the possibility of a hard water effect with absolute confidence. In both series, however, the dates of *Austrovenus stutchburyi* from Shag Mouth were indistinguishable from those at Portobello. In the first series, dates from Pleasant River were distinguishable from those at the Portobello site, but in the second, they were identical statistically. It is possible, given the few samples dated in the first series, that the depletion in the Pleasant River mean may have been affected by an outlier. This may only be verified by further dating. Evidence presented below will show that the range in values of modern and prehistoric shellfish $\Delta 14C$ at Pleasant River may be due to other variables in the estuary rather than a hard water effect *per se*.

Is this conclusion consistent with the geological picture in the catchments of these two estuaries? The North Otago region possesses some deposits of limestone, sandstone and siltstone. The major Goodwood formation, for example, dominates the eastern coastline of North Otago, almost to the Pleasant River mouth. Geologically, the Waihemo catchment, which empties at Shag Mouth, drains a varied assortment of quartzo-felspathic schists, Holocene glacial gravels, quartz mudstones and siltstones, with few limestones or calcareous deposits of major significance. It is not likely that there should be a large amount of dissolved inorganic carbon within the river system and estuary. Pleasant River is surrounded by sandstone and mudstone deposits, of low carbon content, which were observed to be eroding into the lower estuary reaches. The river drains a geological landscape possessing only scattered outcrops of calcareous rock, beginning atop a quartz-pebble conglomerate. Although there are calcareous formations in the catchments under study, then, these are probably not significant enough to produce a measureable hard water effect. Furthermore, low rainfall in the area probably means less erosion of calcareous sediment in the North Otago region. Jennings (1972, in Williams and Dowling, 1979), for example, has given karst solution estimates for the Cooleman Plain in the Snowy Mountains of New South Wales at $24\text{m}^3/\text{km}^2/\text{y}$. This area has a similar rainfall to North Otago but greater limestone. Thus, it can be concluded that there should be proportionately less limestone erosion influencing the estuaries of North Otago, than for areas of New Zealand possessing high rainfall and volumes of limestone, such as the King Country and northwestern Nelson (Williams, 1992).

9.4.4. THE UPWELLING FACTOR

A small study was made of the effect on modern shell dates of upwelled water presumed to be ancient. During a short stay in Kaikoura, samples of *Austrovenus stutchburyi* were collected alive off a large limestone shelf in front of the Fyffes site on the Kaikoura Peninsula. One sample was radiocarbon dated for comparison with the dates collected from sites in North Otago. The sample, Wk-2992, measured $110.6 \pm 0.5\%$ M. $\Delta 14\text{C}$ was $99.9 \pm 5.3\%$. Were the shellfish affected by old carbon due to upwelling, the $\Delta 14\text{C}$ measurement would be considerably depleted in comparison to modern values. Kalish's (1993) otolith curve gives $\Delta 14\text{C}$ measurements of $96 - 98 \pm 9\%$ in the mid-1980's. By 1993, one would expect the result to be closer to *ca.* $80 \pm 10\%$ *without depletion*, so this result is enriched in comparison and seemingly unaffected by upwelled old carbon. It is possible that seasonal influences may affect the extent of upwelling. On the Californian coast for example, upwelling is marked in

spring and early summer owing to northern wind influences, but by October is almost non-existent (Druffel and Williams, 1991:292). Similar effects may occur on the Kaikoura coast.

Clearly, the question of upwelling is an interesting avenue for research. The early dates from Avoca Point are contentious and due perhaps to admixture of natural shell material (Anderson, 1989) or to contamination of by upwelled seawater[^]. They are certainly worth investigating further. Perhaps a project involving the radiocarbon dating of water and seaweed samples from this coastal location would be useful.

9.6. VARIATION IN RADIOCARBON DATES BETWEEN DIFFERENT SHELLFISH SPECIES IN AN ESTUARY

9.6.1. INTRODUCTION

Certain species of shell are more reliable than others for radiocarbon dating. The mudsnail (*Amphibola crenata*) has already been mentioned. It has given anomalous dates in comparison to others from different materials in identical contexts. NZ-4436 from Pleasant River (Anderson, 1991), for example, gave a date of 1120 ± 26 bp which is considered too old for the site. In this research, *Amphibola* gave results adrift from the majority, for example, at Shag Mouth, the date of Wk-2367 (1160 ± 50 bp) on *Amphibola* and Wk-2368 (1080 ± 50 bp) on *Paphies australis*, showed a shift in age in comparison to terrestrial samples, with the mudsnail being older even with the slight quenching suspected in the *Paphies* date (Fig. 9.2). At Pleasant River, two dates - Wk-2507 (1140 ± 45 bp) on mudsnail and Wk-2753 (910 ± 50 bp) on *Austrovenus stutchburyi* disclosed even greater variability ($T^* = 13.06$, $\chi^2_{1:0.05} = 3.84$) (Fig. 9.3). In contrast, dates of *Austrovenus stutchburyi* and *Mytilus edulis aoteanus* (Fig. 9.6) and dates of different species from sites in Nelson (see below) showed acceptable agreement. The reasons for the problematic *Amphibola* have been mentioned. Anderson (1991) addressed the reliability of dating other types of species of shellfish briefly and considered the site at Foxton, excavated by McFadgen, where a dichotomy was noted between radiocarbon dates of *Austrovenus* and *Paphies subtriangulatum*. He suggested variation was due to differences in the reservoirs of the open beach (tuatua) and the Foxton estuary (cockle). An investigation has been made into observed variation in the measurable residual radioactivity in mollusc

[^] The two old dates from Avoca Point are NZ-2718 (1183 ± 29 bp) and NZ-2719 (1174 ± 33 bp) (Anderson, 1991:776).

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shells of different species. The impetus for addressing this problem came not only from the experience of dating *Amphibola* and finding variability in dates of open coast and estuarine species, but from the results of a prehistoric shell dating project at Pleasant river.

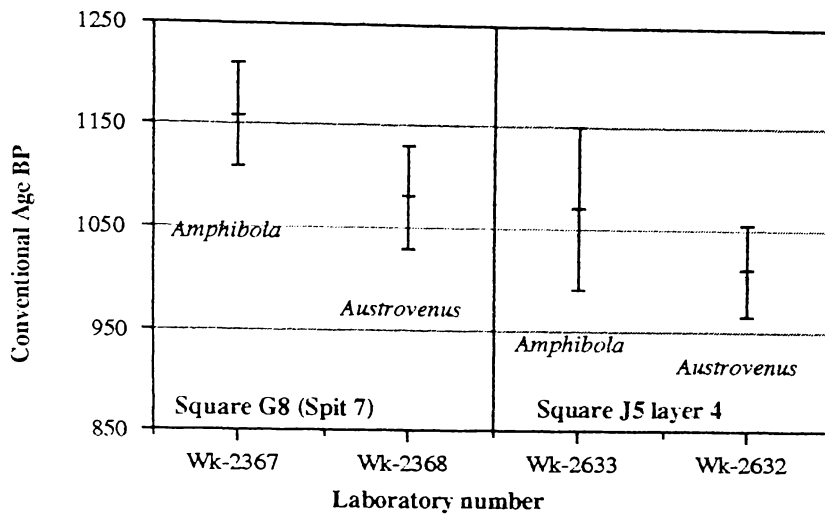


Figure 9.2: Graph showing dates of *Amphibola crenata* (the mudsnail) and *Austrovenus stutchburyi* (the common cockle) from the site of Shag Mouth, North Otago.

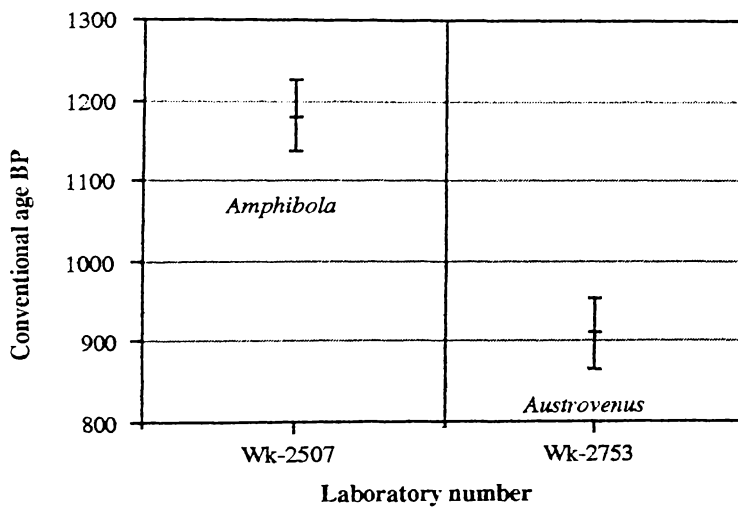


Figure 9.3: Graph showing dates of *Amphibola crenata* (the mudsnail) and *Austrovenus stutchburyi* (the common cockle) from the site of Pleasant river, North Otago. The two dates are *ca.* 5 σ apart.

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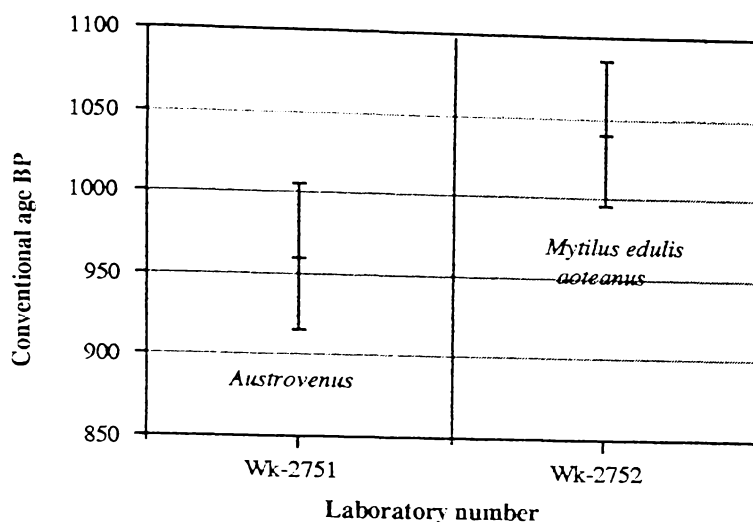


Figure 9.4: Graph showing dates of *Mytilus edulis aoteanus* (the blue mussel) and *Austrovenus stutchburyi* (the common cockle) from the site of Pleasant river, North Otago. The two dates show close agreement in comparison to dates from mudsnails.

To analyse whether different species of shell gave different radiocarbon ages, prehistoric samples from a discrete context (Area D) at the Pleasant River site were radiocarbon dated. They included *Austrovenus stutchburyi*, *Paphies australis*, *Paphies subtriangulatum* and *Cookia sulcata*. Shells from both open marine (*Paphies subtriangulatum*, *Cookia sulcata*) and estuarine environments (*Austrovenus stutchburyi*, *Paphies australis*) were chosen.

The cultural remains in this area of the Pleasant River site were probably deposited over a short period because there is no evidence of abandonment. This affords an excellent opportunity for a comparison of dates from different shell species because it is likely the shells were deposited contemporaneously (Allingham, pers. comm.).

The results are listed in table 9.6 and graphed in figure 9.5. Dates of moa eggshell and identified charcoal were used as a control for the shell dates. The terrestrial

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Wk #	Material type	Provenance	Conv. date BP	Calibrated age BP ($\pm 1\sigma$) (probability in brackets)	$\delta^{13}\text{C}$
2758*	moa eggshell	PRD-2	650 $\pm$ 45	645 - 636 (.12) 634 - 616 (.24) 612 - 579 (.44) 565 - 549 (.21)	-14.0
2759*	moa eggshell	PRD-2	570 $\pm$ 45	618 - 609 (.14) 554 - 513 (.86)	-14.1
2760*	moa eggshell	PRD-2	600 $\pm$ 45	625 - 597 (.41) 590 - 583 (.08) 562 - 527 (.50)	-13.9
2761	<i>A. stutchburyi</i>	PRD-3 L4	1070 $\pm$ 45	688 - 614	+0.8
2762	<i>P. subtriangulatum</i>	PRD-5 L4	1110 $\pm$ 45	713 - 644	+1.9
2763	<i>A. stutchburyi</i>	PRD-9 L3	920 $\pm$ 45	570 - 500	+0.2
2764	<i>P. australis</i>	PRD-10 L3	790 $\pm$ 45	492 - 415	+1.7
2765	moa eggshell	PRD-8 L3	600 $\pm$ 45	623 - 599 (.38) 586 - 585 (.01) 560 - 522 (.61)	-12.1
2771	<i>C. sulcata</i>	PRD-11	740 $\pm$ 45	451 - 347	+1.3
2772	<i>P. australis</i>	PRD-4	780 $\pm$ 45	488 - 404	+1.7
2789	charcoal	PRD-7	550 $\pm$ 90	631 - 580 (.28) 564 - 462 (.72)	-26.3
2790	charcoal	PRD-14	700 $\pm$ 90	667 - 617 (.46) 611 - 551 (.54)	-27.9
Pooled terrestrial age ($T=3.11$ compared with $\chi^2_{5;0.05}=11.07$)			607 $\pm$ 21 bp	619-605 (.44) 556-532 (.56) Summary - 619 (543) 537 Cal AD	

Table 9.6: Summary of all conventional radiocarbon dates from prehistoric samples excavated at Area D at the site of Pleasant River, North Otago. The material was excavated by Allingham in 1975. Dates marked with an asterisk are duplicates. The moa species from which the eggshell comes is not known.

(comprising identified charcoal and moa eggshell dates) pooled mean age (A'_p) was 607 $\pm$ 21 bp ($T=3.11$ compared with $\chi^2_{5;0.05}=11.07$). Calibrated dates from Wk-2761 and Wk-2763, both from *Austrovenus* shell and Wk-2762, from *Paphies subtriangulatum*, were indistinguishable from this mean. Dates of *Paphies australis* and *Cookia sulcata*, however, were ca. 6 σ distant. The archaeological implications of this for understanding the prehistoric chronology of the site are far reaching. Not only are the shell dates from *Paphies australis* and *Cookia sulcata* significantly

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different from the charcoal and eggshell values, but shell dates from *Austrovenus*

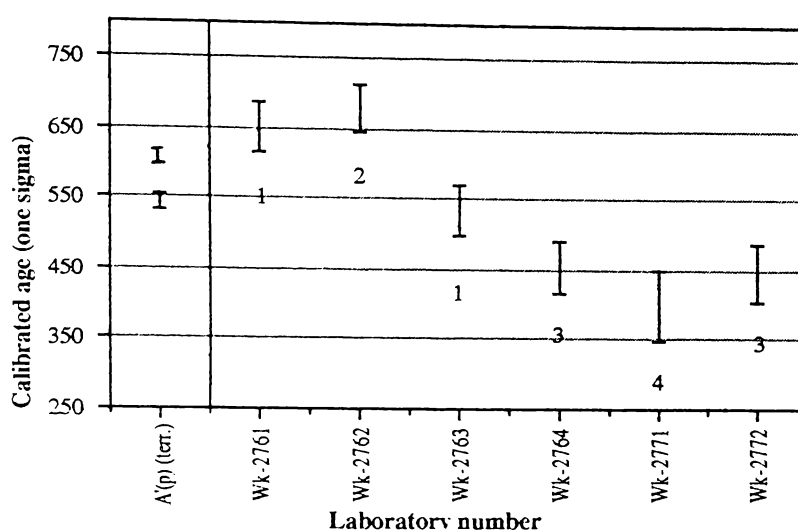


Figure 9.5: Graph showing dating series from the site of Pleasant River, North Otago. Charcoal, moa eggshell and shell dates are shown. All are calibrated using the CALIB 3.0.3 programme of Stuiver and Reimer (1993) with ΔR set at -30 ± 13 radiocarbon years for the shell dates (McFadgen and Manning, 1990). Samples marked with a '1' are *Austrovenus stutchburyi*, '2' is *Paphies subtriangulatum*, '3' are *Paphies australis* and '4' is *Cookia sulcata*. The terrestrial calibrations are based upon the pooled mean value of all eggshell and charcoal samples dated at the area D excavation, Pleasant River. The 1σ range of the pooled mean (607 ± 21 bp) is 619-605 (44%) and 556-532 (56%). Table 9.6 contains details of all data.

stutchburyi also show significant variation. Charcoal and moa eggshell dates place the date of occupation at *ca.* 600 bp, thus the dates from *Paphies australis* and *Cookia sulcata* are too young. This suggests a singular lack of a significant hard water influence. The pooled shell dates are distinguishable statistically with $T^*=61.97$ and $\chi^2_{5;0.05}=11.03$. All of the shell dates span *ca.* 350 years.

9.6.2. THE ΔR VALUE AT PLEASANT RIVER

The spread of prehistoric shell dates from the site of Pleasant River can be further evaluated by an analysis of the ΔR values (table 9.7). They ranged from -200 to +130, and were too spread to generate a consensus value ($T^*=50.2$; $\chi^2_{5;0.05}=11.07$).

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Wk #	Material type	Provenance	Conv. date BP	R(t) (P_{ma} - P_{at})	ΔR
2269	"as is" charcoal	PLR-area 1	520 $\pm$ 50		-
2753	<i>A. stutchburyi</i>	PLR-area 1	910 $\pm$ 45	390 $\pm$ 67	-60 $\pm$ 67
A'(p)	Terrestrial samples pooled date	PRD-7&14	607 $\pm$ 21		-
2761	<i>A. stutchburyi</i>	PRD-3 L4	1070 $\pm$ 45	463 $\pm$ 50	100 $\pm$ 50
2762	<i>P. subtriangulatum</i>	PRD-5 L4	1110 $\pm$ 45	503 $\pm$ 50	140 $\pm$ 50
2763	<i>A. stutchburyi</i>	PRD-9 L3	920 $\pm$ 45	313 $\pm$ 50	-50 $\pm$ 50
2764	<i>P. australis</i>	PRD-10 L3	790 $\pm$ 45	183 $\pm$ 50	-180 $\pm$ 50
2771	<i>C. sulcata</i>	PRD-11	740 $\pm$ 45	133 $\pm$ 50	-230 $\pm$ 50
2772	<i>P. australis</i>	PRD-4	780 $\pm$ 45	173 $\pm$ 50	-190 $\pm$ 50

Table 9.7: Paired shell-charcoal dates from the site of Pleasant River. Dates from areas 1 (denoted by PLR) and D (denoted by PRD) are shown. The terrestrial pooled mean date A'(p) has a value for $T=3.11$ with $\chi^2_{5;0.05}=11.07$.

Averaging the values (unweighted mean) gives -67 $\pm$ 134 but in this instance, the application of a single ΔR estimate may not be justifiable due to the range of results, especially given the close agreement in shell dates from nearby at Shag Mouth. Any ΔR value at Pleasant River would be meaningless.

Explaining the variation in the Pleasant River dates is complex. Clearly, the applicability of the ΔR value is not in question because the results measured for individual shell dates are statistically different. There are three possible explanations. First, there is post-depositional re-working and mixing of cultural remains in this part of the site. The difference in radiocarbon dates from different species are due to the mixing of material deposited during repeated occupations. Second, the cause is twofold and due to the estuarine environment and the shellfish dated; certain species exhibit variation because of differential selectivity of food resources within the complex and mixed estuarine and marine waters in which they live. Proportions of metabolic and dissolved inorganic carbon taken up by different species are highly variable and are affecting the measured ^{14}C dates. Third, certain of the shell species are affected by post-depositional contamination or recrystallisation, and are giving incorrect dates.

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The charcoal and eggshell dates suggest a single, short occupation. Cultural deposits are shallow and the lack of stratigraphical evidence for an hiatus (chapter 5) makes the first possibility unlikely. The third alternative can also be discounted because the shell samples' were all tested for recrystallisation and found to be pure aragonite. As an additional precaution, all were given routine acid wash treatments. The second explanation requires closer scrutiny.

Tanaka *et al.* (1986:520-523) have investigated the contribution of metabolic ^{14}C and DIC to the signal measured in shells from New Haven harbour, Connecticut. They were interested in predicting ancient $\delta^{13}\text{C}$ values of DIC in seawater. They found the percentage of metabolic carbon utilised in shell carbonate varied between 23 and 68% of the total shell carbonate; the remainder was obtained from the DIC in seawater. They assumed there would be a steady state relationship in ^{14}C between meat, shell carbonate and DIC sources in the harbour, but found fluctuation due to variation in the molluscs' food sources. The principal source for this was hot ^{14}C from sewage outfalls and in labelled materials thought to originate from medical facilities. They suggested there was no species-dependency exhibited in the data, despite large variations in $\Delta^{14}\text{C}$ values from different species around the harbour. At one site (Lighthouse Point, Easthaven), for example, the following results were obtained:

Shellfish species	$\Delta\text{‰}$
<i>Mytilus edulis</i>	+190±14
<i>Crassostrea virginica</i>	+145±8
<i>Balanus</i> sp.	+95±18
<i>Littorina littorea</i>	+156±11

Data from Tanaka, Monaghan and Rye (1986:520-523).

Tanaka *et al.* (1986) argue that the high Δ values are due to the incorporation of hot metabolic ^{14}C because the DIC measurements showed constant and low $\Delta^{14}\text{C}$ values in comparison. They would also seem to indicate that some species of shellfish take up carbon from different sources and may therefore yield different ^{14}C ages when measured.

Begg *et al.* (1992) measured levels of ^{14}C of shellfish and marine fauna around the outflows of the Sellafield nuclear reprocessing plant in Cumbria, UK. They found the level of radioactivity in organic material was influenced by the type of species

selected. *Mytilus edulis* gave higher measured activities than *Littorina littorea* (winkles) and local seaweeds (*Fucus* sp.) near the Sellafield plant. In their own words:

"It is immediately apparent that the level of ^{14}C present in the organic material is greatly influenced by the type of organism analyzed"

BEGG, *et al.* 1992. Anthropogenic Radiocarbon in the Eastern Irish Sea and Scottish coastal waters.

Radiocarbon 34(3):707-716.

Common activity between the different species appeared to be reached at 70 km from the nuclear plant, although this was concluded by extrapolating of the data, not by actual measurement. The reason for variation in radiocarbon measurements was the physiological adaptations of each organism. Mussels reflect the activity of the particle matter they filter in the water, winkles, the seaweed they subsist on and the particulate matter of the water they live in. Activities measured in seaweeds reflected the label of the DIC of the water (although some seaweed species may use CO_2 from the atmosphere during photosynthesis when out of water).

In both studies, bomb ^{14}C has been used to analyse the physiology of each molluscan species. Gordon and Harkness (1992:701), in an examination of radiocarbon dates from antarctic shell and seaweed samples, concluded that:

"It is uncertain to what extent, if at all, these samples have been affected by the incorporation of 'bomb ^{14}C '. The relatively wide ranges in values does suggest that there may have been some selective uptake in 'bomb ^{14}C ' particularly among the specimens with the younger age estimates."

GORDON, J.E and HARKNESS, D.D. 1992. Magnitude and geographic variation of the radiocarbon content in antarctic marine life: Implications for reservoir corrections in radiocarbon dating. *Quaternary Science Reviews* 11:697-708.

These three studies suggest organism selectivity to be an important influence on measureable $\Delta 14\text{C}$. Dietary preferences in a habitat with variable nutrients will influence resultant radiocarbon determinations. In estuarine environments, mixing and re-mixing of nutrients and food resources is continuous and probably means that a variety of material of differing ^{14}C label is available for shellfish. One explanation for the spread of conventional radiocarbon ages in table 9.6, then, is that it reflects inter-species differences in ^{14}C uptake in a variable environment.

This study concentrates on bivalvia, filter feeders that obtain their metabolic carbon primarily through food resources suspended in the water column, and gastropoda, who live predominantly upon rocks and kelp, feeding off algae and kelp formations on the rocky shore front. The sources of carbon available to these molluscs include modern vegetative detritus from surface runoff or older material derived from decayed plant materials. The most likely explanation for the young shell dates of *Paphies australis* and *Cookia sulcata* in this instance is probably that the river is carrying modern plant detritus in it, which is being taken up by molluscs in different amounts depending upon their species.

In association with variation in food selectivity by molluscs, and a mixture of marine and riverine resources within the estuary, there is also the question of the modification of feeding habits in marine molluscs with age (Keith *et al.*, 1963). Keith *et al.* (1963:1781) suggested that molluscs modified their feeding habits with age, because changes in $\delta^{13}\text{C}$ values were correlated with increased size (and age) within a local community of *Acrinonaias carinata*.

May these variables, identified in the prehistoric dating, be tested to analyse the potential sources for error when radiocarbon dating?

9.6.3. EXPERIMENTAL

To investigate differences between the radioactivity of certain molluscs living at the same time in a discrete area, modern biota from Pleasant river and other coastal Otago sites were collected. Samples of bivalves and gastropods, including *Austrovenus stutchburyi*, *Paphies australis*, *Amphibola crenata*, *Cellana* sp., *Cookia sulcata* and *Lunella smaragda* were collected alive to attempt to duplicate the prehistoric results. *Cellana* sp. was collected both on the rocky marine shore and within the estuary limits to examine any differences in age. Samples of the outer leaves of *Macrocystis pyrifera* (the bladder kelp) were collected for dating, to analyse the $\Delta^{14}\text{C}$ of the DIC in the ocean.

All samples were collected live, with the exception of *Paphies australis* and one sample of *Cookia sulcata*. No live individuals of *Paphies australis* could be found, so samples with well-preserved periostracum, assumed to be recently dead were collected for analysis. One sample of *Cookia sulcata* falls into the same category.

The location of each of the collected Pleasant river samples is shown in figure 9.6.

9.6.4. RESULTS

There is significant variation between dates of different species (table 9.8 and Fig. 9.7). The results of *Austrovenus stutchburyi* show reproducibility, unlike prehistoric

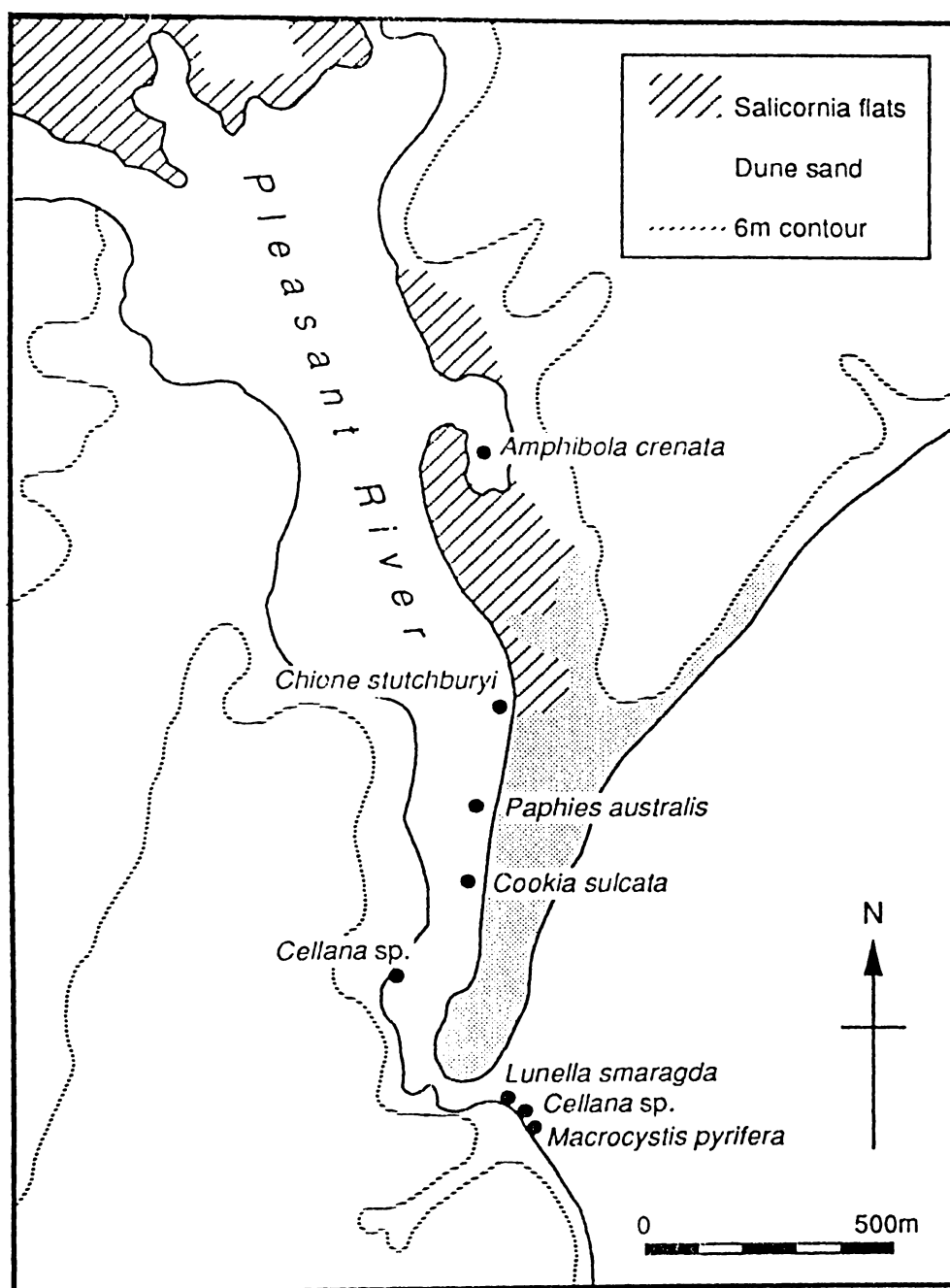


Figure 9.6: the location of modern shell species selected from the Pleasant River site for radiocarbon dating.

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cockle dates, with a pooled mean (A_p) $\Delta^{14}\text{C}$ measurement of $83.6 \pm 3.7\text{‰}$ ($T=0.32$; $\chi^2_{1:0.05}=3.84$). The results of Wk-2969B and Wk-2972 negate the assumption that dead shellfish were recently alive. These are rejected from analysis. The date of *Lunella smaragda* is similar to the values for cockles. Dates of *Cellana* sp. from the estuary were reproducible and within the statistical range of the *Austrovenus* mean. A further *Cellana* sample was dated from the open rocky shore outside the environs of the estuary. At $56.9 \pm 5.3\text{‰}$, it is statistically distinct from the other *Cellana* dates, collected within the estuary. This date suggests there may be a measureable reservoir effect between the marine and estuarine environments.

Unfortunately, no sample pair was dated to ensure reproducibility, however, the dates of paired samples of modern shellfish throughout this analysis show close agreement, so it is probably an acceptable result. In addition, Wk-2969, a date from *Cookia sulcata*, another common open marine species was statistically distinguishable from the *Austrovenus* dates at $70.4 \pm 4.9\text{‰}$. The examination of this likely reservoir difference is a most important avenue for further research.

Wk #	Material	Provenance	% Modern	$\Delta^{14}\text{C}$ (‰)	$\Delta^{14}\text{C } A(p)$	$\delta^{13}\text{C}$
2965	<i>A. stutchburyi</i>	Estuary	108.7 ± 0.5	81.6 ± 5.2	83.6 ± 3.7	0.2
2965B	<i>A. stutchburyi</i>	Estuary	109.2 ± 0.4	85.8 ± 5.3		
2969	<i>C. sulcata</i>	Rocky shores	107.6 ± 0.5	70.4 ± 4.9	70.4 ± 4.9	0.7
2969B	<i>C. sulcata</i>	Rocky shores	100.2 ± 0.5	-3.1 ± 5.2	n. a	0.4
2970	<i>A. crenata</i>	Upper estuary	108.4 ± 0.6	78.3 ± 5.7	78.3 ± 5.7	-1.2
2971	<i>Cellana</i> sp.	Estuary	108.2 ± 0.4	76.0 ± 5.4	75.2 ± 3.8	0.9
2971B	<i>Cellana</i> sp.	Estuary	108.0 ± 0.5	74.5 ± 5.4		1.0
2972	<i>P. australis</i>	River/estuary	99.7 ± 0.5	-7.8 ± 5.1	n. a	1.5
2973	<i>L. smaragda</i>	Marine coast	109.1 ± 0.5	85.3 ± 5.2	85.3 ± 5.2	-0.6
2973B	<i>Cellana</i> sp.	Marine coast	106.1 ± 0.5	56.9 ± 5.3	56.9 ± 5.3	1.0
2990	<i>Macrocystis</i>	Marine coast	104.7 ± 1.2	41.2 ± 11.6	41.2 ± 11.6	-17.5

Table 9.8: showing %M and $\Delta^{14}\text{C}$ values of living shell and seaweed (*Macrocystis*) from the site of Pleasant River. All except Wk-2972 and Wk-2969B were collected live.

The $\Delta^{14}\text{C}$ result of *Macrocystis* was $41.2 \pm 11.6\text{‰}$. This was a lower measurement than for any of the shellfish species analysed, but interestingly, it is statistically

identical with the $\Delta^{14}\text{C}$ results of the *Cellana* which were collected nearby ($A'_p=54.2\pm 4.8\text{‰}$; $T=1.51$; $\chi^2_{1:0.05}=3.84$).

What do these results reveal of ^{14}C processes in the environment of Pleasant River? The difference between certain $\Delta^{14}\text{C}$ values of the estuarine and marine samples is apparent. Kalish's (1993) marine otolith calibration curve suggests a decrease in bomb ^{14}C in the coastal New Zealand waters. Begg *et al.* (1993) have suggested that seaweed most closely reflects the $\Delta^{14}\text{C}$ of the DIC in the ocean. The $\Delta^{14}\text{C}$ measurement of *Macrocystis* was the most depleted result, suggesting values of some estuarine biota may lag in comparison to marine material. This is supported by the date of the open marine *Cellana* sp. (Wk-2973B) and by the depletion measured in the dates of *Austrovenus* from Portobello reported above. Kalish (1993) suggests the southern latitudes may show a slower decrease in bomb ^{14}C than tropical latitudes because of differences in the ocean transport of hot ^{14}C from lower to higher latitudes or greater dilution of the surface ocean by deeper, depleted water. Extrapolation of the measured data for the fish otolith's (by pooling the two 1990 values) suggests that the 1995 value should be *ca.* $64\pm 12\text{‰}$ and *ca.* $70\pm 12\text{‰}$ in 1993 if the rate of depletion is

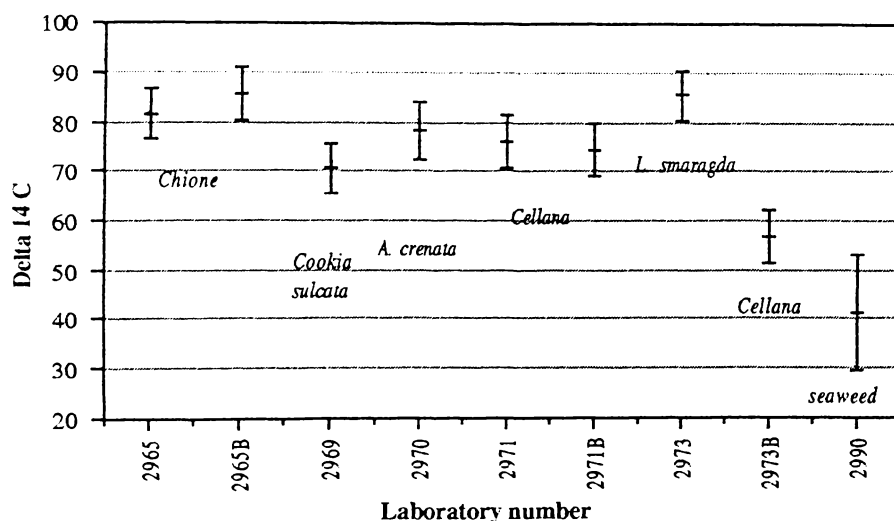


Figure 9.7: Figure illustrating $\Delta^{14}\text{C}$ values of shell species and seaweed (*Macrocystis*) from the site of Pleasant River.

constant. The results of open marine dates of seaweed and molluscs suggests the depletion of bomb carbon in the southern latitudes may mirror that identified in coral sequences from Fiji and Heron Island, Australia which show more rapid decreases (Kalish, 1993:551).

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If the conditions analysed in 1993 are similar to those at 600 bp, then , we would expect prehistoric marine and estuarine shell dates to show considerable variation. They do.

The influence of the estuary, with its complex inter-mixing of reservoirs, combined with organism selectivity means that radiocarbon dating shell from these sites will involve a degree of variability and uncertainty in results. One variable of particular importance might be the extent to which estuaries are tidally flushed. The Pleasant River estuary almost resembles a large river rather than an estuary. Its mouth is narrow and the influence of the incoming tide, like Papanui Inlet, is restricted by it (Fig. 9.6).

The environmental influence is emphasized when shell dates from the 'granite coast' sites of Nelson are considered. Dates of *Austrovenus stutchburyi* and *Paphies australis* are shown in table 9.9 and reveal close statistical agreement between the shell species from the site at Bark Bay. The environmental situation here combines granite geology with low freshwater run off and quick flushing of the estuary (Davidson, 1991). These factors appear to influence the radiocarbon dating of shellfish and ensure acceptable reproducibility between shell dates of different species. Charcoal dates from this site are presently being determined to further assess the apparent reliability of the shell series.

In table 9.10, shell-charcoal pairs are shown together with ΔR values for the site of Awaroa Inlet. This estuarine site differs principally from the southern estuaries in that it is large (290 ha) and open to the strong tidal influences of the Tasman Bay (Davidson, 1991). This ensures that the estuary is flushed and diluted regularly with ocean water.

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Wk #	Sample fraction	Conventional age (BP)	% Modern	$\delta^{13}\text{C}$ (‰)
2863	<i>P. australis</i>	840±45	90.0±0.5	2.0
2866	<i>A. stutchburyi</i>	800±50	90.5±0.5	1.0
2867	<i>A. stutchburyi</i>	770±40	90.8±0.4	1.2
2868	<i>P. australis</i>	820±45	90.3±0.5	1.9

Table 9.9: Radiocarbon dating results from shell pairs excavated from Bark Bay, Nelson.

Wk #	Sample	Conventional age (BP)	Pooled mean	Δ R value
1827	charcoal	430±60	447±38	-
2094	charcoal	460±50		
2869	<i>A. stutchburyi</i>	800±40	785±28	-40±55
2870	<i>P. australis</i>	770±40		-70±55
		Pooled mean Δ R		-55±39

Table 9.10: Radiocarbon dating results from shell-charcoal pairs excavated from Awaroa Inlet, Nelson.

ΔR values calculated from this site are statistically indistinguishable from the ΔR value of -30 ± 13 suggesting corrected shell dates give close agreement with non-marine dates and are reliable.

9.7. CONCLUSIONS

The studies presented above have shown that severe qualifications are necessary when dating shell from certain prehistoric coastal sites, and some results cannot be treated with confidence.

The marine reservoir correction has been considered through the analysis of shell-charcoal pairs and McFadgen and Manning's (1990) ΔR value has been tested. The shell samples from Shag Mouth showed increased results which were significantly different from the New Zealand ΔR value. The most likely explanation for the anomalous result is that the estuary, with its complex inter-mixing of riverine and marine reservoirs, has influenced the ages of prehistoric shellfish and made them too old. However, it is possible that the error quoted on the ΔR for New Zealand may be

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unrealistically precise. ΔR values for other regions are given the larger of the errors calculated using the unweighted and error-weighted means. The New Zealand ΔR is given the smaller error-weighted mean of ± 13 , rather than the unweighted mean standard deviation of ± 41 .

The hard water effect, has also been investigated at sites in Otago. Pleasant River, a site noted for its anomalous shell dates, was considered in the light of possible dissolved 'dead' carbon within it. Comparative dating using modern shellfish collected on the same day initially suggested there was a statistical difference between dates from this site and its calcareous surrounds, and sites near Dunedin dominated by basaltic hinterlands. Further dating revealed that the variation was probably due to the natural range of expected values rather than an inherent hard water effect. This study concluded that the effect was not significant at the sites because the results for them were indistinguishable from those of a marine site in a non-limestone area.

Prehistoric shell dates from different species were measured from the Pleasant River site and yielded considerable variation. The most notable in their divergence from the identified 'true' age were *Paphies australis* and *Cookia sulcata*. Both were significantly younger than other samples in association. A ΔR value was not applicable because of the spread of results. A number of possible explanations were considered including post-depositional contamination and reworking of cultural material, however, both were rejected as causal factors. An investigation into this variation using modern shell samples of different species suggested that species and environment rather than hard water, was a more significant variable in analysing differences in the radiocarbon dates from this site. A further study in which modern shellfish were dated to investigate this hypothesis suggested that there was a measureable reservoir difference between samples on the open marine coast and those of the lower and upper estuary at Pleasant River. It was suggested that the river, bringing resources of variable age from surface run off and decayed plant and humus material, may be influencing the radiocarbon ages of shellfish. In addition, the extent of tidal flushing of the estuary was considered important in reducing the effect of the riverine inputs.

The importance of environment upon probable species selectivity was demonstrated at sites in Nelson, where estuarine sites with open marine access and regular tidal inwash, yielded acceptable shell dates.

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The testing of these hypotheses is dependent upon further analysis of the variables described above, in particular, the environmental situation and the type of species which is selected for dating. It is apparent from the preliminary research that high precision dates of shellfish from certain marine and estuarine environments may not be justified.

CHAPTER 10

DISCUSSION AND CONCLUSIONS

10.1 RESUMÉ

Radiocarbon dating embraces multiple sources of error which affect the ability of the radiocarbon specialist and the archaeologist to date prehistoric remains accurately. Errors contributing to discrepancies and disparities between radiocarbon dates and the contexts which they are dating originate from laboratory and field situations. This dissertation has investigated a number of sources of error which must be considered if radiocarbon dating at higher levels of precision is to be undertaken.

In chapter 6, errors associated with laboratory measurement were considered. IAEA intercalibration samples measured in the laboratory between 1990 and 1991 were used to demonstrate reproducibility. All the Waikato laboratory samples were within the statistical range of the consensus values of each of the 6 IAEA standards. An analysis of certain of the significant errors contributing to laboratory precision yielded interesting results. Spectral shifts were identified in early sample results which consistent with an interpretation of chemical quenching. This error was exhaustively investigated beginning with analysis of the benzene synthesis procedures, through vial loading and counting procedures, to the influence of the external standard upon pulse heights of ^{14}C spectra. The conclusion was that the displacement of sample spectra from standards measured in the same vial was probably due to two main influences. First, there was a chemical quench, which affected 6 samples in total. This was probably caused by substandard lithium metal used in the lithium carbide reactions. Second, the external standard had an influence upon end point. When the external standard was turned off, all spectra end points decreased by up to 8 channels. We suggest that the external standard artificially increases pulse heights over time and that its effect is increased by different types of vial holder, which exhibit varying end point stability. We found that aluminium and lead holders were the most stable. The effect of drifted spectra upon calculated radiocarbon dates was investigated using samples dated with a variety of shifted standards. It was shown that the dates calculated were insignificant statistically at the level of precision used ($\pm 3.8\%$). We found that even when end point was variable, count rates remained reproducible. A typical example was given, that of vial 43, whose performance over 6 months of counting

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showed no statistical variation, despite high precision due to count times up to 7000 minutes and variation in end points in individual counting sets of up to 7 channels.

In the light of these continuing investigations, the most profitable avenue for implementing higher precision radiocarbon dating was that of 'optimal dating' wherein a date is duplicated for greater statistical certainty, or multi-dated to assess the range of values and the generation of a pooled mean date if allowable. Given that many of the sites investigated in New Zealand were probably occupied over short periods of prehistoric time, the implementation of this approach is probably overdue, despite the higher cost.

Laboratory reproducibility was further demonstrated by an analysis of duplicate radiocarbon dates from prehistoric and modern samples. The calculation of an internal error multiplier (IEM) showed the quoted standard errors of the dates were realistic. In many radiocarbon laboratories the standard error of a date is merely based upon Poisson counting statistics and therefore underestimates the sum total of errors inherent in the measurement. In order to define a more realistic standard error, a laboratory error multiplier (K) was calculated. Eleven duplicate analyses of IAEA C3 cellulose were measured and the K value was calculated at 1.217. All sample errors in this dissertation were multiplied by this value to account for routine errors incurred during the combustion, lithium carbide reaction, trimerisation to benzene, loading and counting of the samples.

The application of high precision dating to New Zealand archaeological materials involves the continued investigation of the relationship between SQP(E) and end point, quench correction and quantification of all errors.

Errors which may influence the validity of a high precision date occur also in the field. Many are associated with the type of sample which is selected for dating. In chapter 7, each of the 3 sample materials most commonly used for New Zealand archaeological dating was considered in a framework of three prerequisites for accurate dating. Does the material date the event in question? Is it resistant to post-depositional contamination? Is it found regularly in the archaeological contexts of the prehistoric people?

Charcoal fulfilled the second two prerequisites. Pretreatment experiments described in chapter 8 suggested, with one exception, that any contaminants identified in charcoal were negligible in their effect upon the 'true' age of the material. Charcoal remains are commonly found in archaeological sites. The question of the amount of inbuilt, or

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presample age, in identified charcoal in New Zealand is open to considerable speculation. Schiffer (1987:309) has suggested that a heavy reliance upon dates from wood and charcoal has probably skewed most radiocarbon dates towards an excessive antiquity. Even when identified short-lived species have been selected for dating, an inbuilt age of varying degrees will still be incorporated into the date, as Anderson (1991) has illustrated. Even the apparently ideal ecological situation at the Killermont site may involve inbuilt error because the dry climate of Central Otago and the Mackenzie Country may serve to prolong the normal lifespan of scrubland plants (McFadgen, pers. comm.). In the short New Zealand prehistoric this remains the major problem with dates of charcoal.

Moa bone collagen fulfilled the prerequisite of dating the event closely but in general, is too prone to post-depositional contamination. The organic fractions of bone exchange readily with non-sample carbon and erode rapidly in the post-depositional environment. The complex chemistry which needs to be applied to prehistoric bone means that AMS is the most profitable avenue for its dating, because it requires smaller amounts of sample. However, there are few experts in the field of extracting biochemical amino acids from prehistoric bone and the inherent variability in the type of treatment suitable for each bone sample makes obtaining an accurate date an involved task. In general, moa bone remains dominate the southern New Zealand sites, are less common in sites in the lower North Island and the Coromandel Peninsula and uncommon in the majority of far northern sites (Anderson, 1989).

The radiocarbon dating of prehistoric shell was considered in detail in chapter 9. Shell is found widely in New Zealand sites and probably dates the event of the gathering and processing of shellfish in prehistory closely. The major problems with it are associated with variation in certain shell reservoirs. The question of the reliability of dates of estuarine shells and shells near upwelling zones are the two principal areas of concern. There is also the problem of the hard water effect and the extent to which certain reservoirs are diluted by old dissolved bicarbonate eroded from calcareous rocks of variable age. Each of these problems was addressed in chapter 9.

The applicability of the marine reservoir correction, or ΔR , was also considered using shell-charcoal pairs from the site of Shag Mouth, in North Otago. Using a new method, the pooled terrestrial date for the site, based on 13 radiocarbon measurements of identified charcoal, was converted to a conventional shell date and the ΔR offset calculated. The result suggested a discrepancy between the ΔR measured at this site and the ΔR measured by McFadgen and Manning (1990) using shells of known historical

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age. The reason for the variation was given to be one of a number of possibilities including those mentioned above but mention was made that the error quoted on the ΔR value for New Zealand may have been too precise, given the spread of values in the original data.

The hard water effect was investigated by dating modern shellfish collected on the same day from sites in North Otago, where a hard water effect was blamed for several spuriously old shell dates (Anderson, 1991), and near Dunedin, which possess few calcareous surrounds. The dates from four sites in the two areas were compared. In the first series, a discrepancy was noted between $\delta^{13}C$ values from Pleasant River, which were older than corresponding dates from Dunedin sites. More samples were collected because the small number of dates made firm conclusions difficult. The results from this second series suggested the dates from North Otago were indistinguishable from those dated at Portobello. It was concluded that if there was a hard water effect, it was not distinguishable at the level of precision used and therefore negligible in its influence.

The upwelling effect has been considered briefly. Modern *Austrovenus stutchburyi* shell was collected from the Kaikoura peninsula, a site near the upwelling zone along the eastern South Island coast. The single date suggested there was no measureable depletion but clearly, this is a preliminary conclusion and more data is needed.

An analysis was made of dates of different species of prehistoric shell excavated from the site of Pleasant River. Significant variation was discovered in radiocarbon dates which came from a site thought to be occupied for a short duration, according to chronological and stratigraphical evidence. Shell dates were spread over 300 years and some were statistically distinguishable from the pooled mean date of occupation measured using terrestrial carbon samples.

Modern shell and seaweed samples were dated to test the results and try and replicate the prehistoric dating anomalies. Significant variation was found between certain samples. A dichotomy was identified between shell originating in the estuary, and shell and seaweed collected from the open marine coastline. This suggested a reservoir difference between the two environments and led to the conclusion that the reason for variable prehistoric dates was due partly to the estuarine reservoir within which there was mixing of resources from the sea and the river. Organism selectivity was suggested as being a significant variable in contributing to differences in the uptake of ^{14}C from the array of nutrient sources available within the estuarine environment. The study

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suggested that shell dates from this type of environment incorporated a degree of uncertainty and variability in the results through a *combination* of these two variables. The extent to which the estuary was flushed by tidal action was also suggested as important. Shell dates from estuaries in Tasman Bay, Nelson were considered and it was shown that at sites which were tidally flushed, with insignificant riverine inputs and non-calcareous hinterlands, shell dates would give acceptable reproducibility.

Shell from archaeological contexts in New Zealand was also investigated for contamination. None was identified. All pretreated dates were statistically indistinguishable. In addition, no recrystallised shell was identified.

In chapter 7, the radiocarbon dating of moa eggshell was investigated. Initial doubts concerning the resistance of the material to post-depositional exchange proved unfounded. The dates of eggshell from three sites showed reproducibility and close agreement with dates of charcoal, moa bone collagen and shell from identical contexts. Analogous studies conducted in sub-Saharan Africa and the Malagasy Republic suggest eggshell is resistant to contamination post-depositionally. It is also likely to date the prehistoric event closely because the archaeological evidence suggests eggs were most commonly collected for consumption. In summary, it appears a useful dating medium, particularly because material in storage from sites excavated many years ago may be dated without further excavation. Unfortunately, eggshell is not found as commonly in New Zealand archaeological sites as the other three sample types. Even in Murihiku, it is only found in significant amounts in 40% of the prehistoric sites for which quantified faunal data exists (in Anderson, 1982).

In summary, each of the sample types analysed possesses some intrinsic problem or source of error which may affect the validity of radiocarbon dates at higher levels of precision. However, identified charcoal seems the most useful type of sample for archaeological dating by virtue of its widespread occurrence and lack of reservoir correction factors.

10.2. TOWARDS A MODEL FOR ACCURATE RADIOCARBON DATING IN NEW ZEALAND

In the light of the results presented above, can we begin to identify any general patterns in radiocarbon dating in New Zealand in terms of environment, sample type and contamination influences, and develop a framework for more accurate dating?

10.2.1. SHELL

The reliability of shell dates from different species has been found to vary with the local environment. Dates of *Austrovenus stutchburyi* from the Pleasant River estuary showed variation - dates of the same species from the granite-backed and tidally flushed Bark Bay showed reproducibility. *Paphies australis*, a species usually considered acceptable for dating purposes proved anomalous for the North Otago estuaries but provided reasonable results in Nelson. It is concluded that the radiocarbon dating of shell in New Zealand should proceed only after a careful analysis of the local reservoir conditions and their likely influence upon the ages of mollusca living within it. Results of shell dates measured in this dissertation suggest that different environments may be ranked according to their likely error and variability of shell dates obtained from them. These types of shell may be listed in order of acceptability as follows:

1. Open marine species such as *Paphies subtriangulatum*.
2. Estuarine species, such as *Austrovenus stutchburyi*.
3. Riverine species.

There may be examples where an estuarine species will show closer agreement with terrestrial sample dates in comparison to an open marine species as, for example, at Pleasant River. An open marine species, however, should reflect more closely the depletion measured by ΔR . Furthermore, there are differences between estuaries which probably also affect the reliability of shell dates, so that not all estuarine shell is unreliable. Healy and Kirk (1992) give five types of estuary classified by physiography and salinity structures.

Radiocarbon dating prehistoric sites using shell remains from the following environments may be listed in decreasing order of value.

1. *Open marine sites with non-calcareous geological surrounds.*

The dating of shell from these environments should yield accurate radiocarbon dates in the absence of upwelling zones.

2. *Estuarine sites with small riverine inputs and tidal flushing.*

Radiocarbon dating at such sites in Nelson has shown that shell dates are usually reproducible and accurate.

3. *Open marine sites near upwelling zones.*

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Dating of shell from the large upwelling zone along the Californian coast (Berger, Taylor and Libby, 1966; Druffel and Williams, 1991) and the eastern US seaboard (Little, 1993) has shown that apparent ages will result. It is probable that a similar situation would occur in New Zealand although this has not been demonstrated.

4. River mouth sites with limestone hinterlands.

Shells dated from these environments would involve some uncertainty due to the variation in riverine reservoirs allied to the possibility of a hard water effect within it. Shell dating would not be advisable.

5. Estuarine sites with small river inputs.

The range of prehistoric shell from sites in the vicinity of this type of environment would dictate the efficacy of radiocarbon analysis using shell carbonate. Shells from open marine environments would be expected to provide more accurate dates than those originating from the estuary, although once again the dates at Pleasant River provide some exceptions to this.

6. Estuarine sites, with major fluvial inputs and limestone hinterlands.

Estuarine shell dating would be inadvisable from these sites as well. Marine shell or terrestrial sample types would be needed for accurate radiocarbon dating.

7. Estuarine sites, close to the upwelling zones possessing major fluvial inputs with limestone hinterlands.

Radiocarbon dating of estuarine shell excavated from sites situated in such environments should be avoided. The variability in the resources coming into the estuary from marine and fluvial sources, combined with the old carbon originating from the upwelling zone and from dissolved calcareous rock in the hinterland will result in variable and spuriously old shell results. Only prolonged investigative work could resolve the dating anomalies, even then, uncertainties would exist.

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 should vary. This may result in disagreement between dates of different species collected at the same time, whether in prehistory or today. In environments within which there is great variability in the range of available food resources, this range will be reflected in radiocarbon measurements. In environments with fewer disparate resource influences, radiocarbon measurements in different species of shellfish should yield greater reproducibility. In the case of estuaries, those which are flushed regularly with sea water and whose riverine input is low, should give reliable dating results compared to those dominated by rivers, with tidal barriers such as sand spits affecting seawater mixing.

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10.2.2. CHARCOAL

Charcoal dating seems a more profitable option as long as only short-lived material is selected for dating. Aside from the unknown errors introduced by inbuilt age, identified charcoal was found to be largely unaffected by post-depositional contamination at the sites investigated, with one exception. What initial conclusions are apparent with this material in terms of contamination?

1. At Shag Mouth, samples of charcoal from above the water table, sealed beneath a sand overburden high on a dune ridge, showed no signs of variation in any of the separated sample fractions. The samples were thus uncontaminated.
2. At the Killermont site, in the Mackenzie country, charcoal samples excavated from cultural remains 15 cm below the surface yielded no identifiable variation in any removed chemical fractions. The samples were not prone to flooding or river inundation. Again, then, no contamination.
3. At the Pleasant River site, cultural material was excavated from a site prone to inundation from the nearby estuary. Much of the site was located just above the water table. Dating of different fractions extracted from the matrix at Area 1 suggested there was significant contamination, principally young carbonates which were adsorbed onto the charcoals *in situ*.

In all cases, rootlet activity was identified. At routine levels of precision, errors due to sample contamination by rootlets are not significant. Although an error is introduced because the contaminating fraction has a different activity, the effect is small relative to σ . At higher levels of precision it may have to be taken into more serious consideration.

It is advisable that routine pretreatments be given to archaeological charcoals as a precaution against contamination. Further analysis is necessary to elucidate the range of contaminating influences in different environments. The situation in the far north of New Zealand, or in areas of high rainfall or environments prone to leaching, is sure to be different and should necessitate a more rigorous approach to pretreatment.

10.3. ARCHAEOLOGICAL INTERPRETATION

This dissertation opened by referring to Movius's (1960) observation that time, alone, will put the European Upper Palaeolithic into focus. The research summarised above has considered the chronology of several New Zealand sites and many radiocarbon dates have been obtained (appendix 1). What new light do they shed on models of prehistory at the various sites examined and the areas within their orbit?

The most extensive radiocarbon dating was conducted at the sites of Shag Mouth and Pleasant River. These, and indeed most early sites in southern New Zealand, showed a preference for an estuarine or marine location. The estuary is a rich habitat in terms of naturally replenished food resources (Odum, 1971; Healy and Kirk, 1992), and provides easy opportunities for communication and movement, both along the coast and into the interior. It must also be stressed, however, that this region lies beyond the ecological limits for horticulture, which had sustained the expansion of human settlement into the greater Pacific region (Kirch, 1984). The development of higher precision dating and the reduction in errors explored above has been undertaken to permit a more penetrating analysis of a variety of New Zealand archaeological variables. One previously mentioned concerned the initial prehistoric settlement. In the case of southern New Zealand, this required structural changes in subsistence. Several alternatives are possible. The initial settlement might have involved permanent settlement in estuarine locations, linked with seasonal movement to exploit desired resources in the hinterland. Given the skill in deep water sailing demonstrated by the very presence of human communities in New Zealand, however, it is equally possible that initial settlement involved opportunistic brief visits by small groups, perhaps including only males. This might have seen estuarine sites being occupied for a few weeks or months before abandonment. The basis for this interpretation was first proposed by Teviotdale (1932). These two alternatives represent extremes, and there are many others. It has never been intended to provide a detailed reworking of parts of the prehistoric sequence in New Zealand within this dissertation, rather to identify more precise dating strategies which would make such an objective feasible. However, the integration of precision dating and early settlement in southern New Zealand will be explored in a preliminary and tentative manner in order to provide an example of the impact of the new dating procedures and 'optimal' dating.

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This review will begin with the hypothesis that the initial settlement of southern New Zealand took place about 600 radiocarbon years ago. It can be tested by assembling acceptable dates and comparing the mean dates obtained for all available sites.

The pooled mean of charcoal dates for Shag Mouth is 620 ± 13 bp, while the Pleasant River pooled mean using all terrestrial samples is 607 ± 21 bp. The Waikato laboratory series of terrestrial dates for Shag Mouth is in close agreement with those from the IGNS laboratory in Lower Hutt (Anderson *et al.*, in prep.). Shell dates from both laboratories yielded some variation in comparison with the measured ΔR value for New Zealand (chapter 9). The IGNS dates for Areas 1, 2 and 3 at Pleasant River showed agreement with the Waikato mean ($A'(p)(\text{charcoal})$ is 602 ± 69 bp ($T=5.92$; $\chi^2_{3:0.05}=7.81$)) although they are widely spread (NZ-7964, dated at 838 ± 41 bp was rejected because it was $>2\sigma$ distant from the other samples and may be natural in origin). In addition, the dates of material from Warrington were within the statistical range of the dates from the two important North Otago sites. Moa eggshell samples probably avoid any inbuilt age and their dates are notable for their close statistical agreement (Fig. 10.1). The spread of results from the three sites is less than the charcoal dates and again, all are statistically indistinguishable ($A'_p=597 \pm 14$ bp, with $T=4.27$; $\chi^2_{8:0.05}=15.51$).

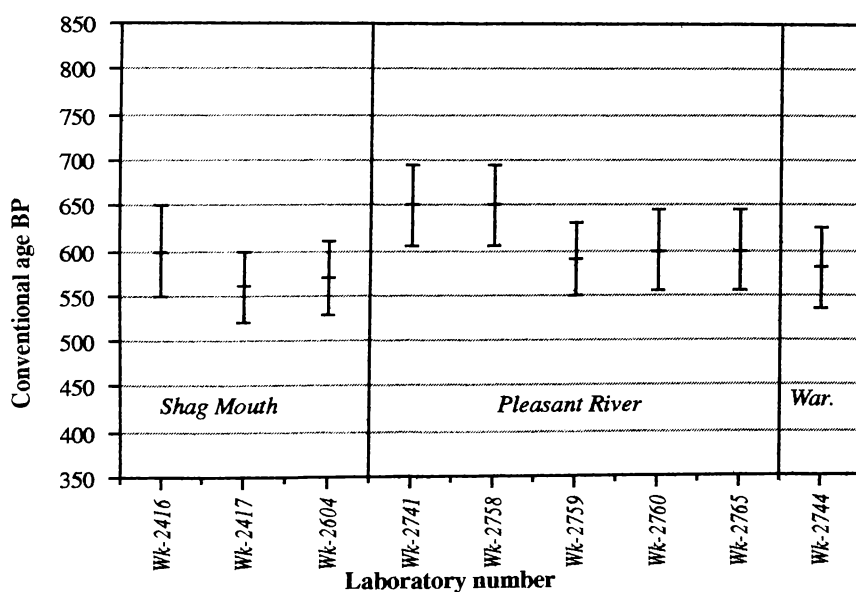


Figure 10.1. Dates of moa eggshell from three coastal Otago sites.

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The close statistical relationship between the dates from these three sites and the pooled mean data, support the hypothesis that they were occupied briefly, within a period possibly less than three decades.

In figure 10.2, dates from the lowest occupied layers of a number of coastal sites in South Canterbury and Otago are shown. It is assumed that these date the first occupation of the sites. They include Waitaki Mouth, Ross's Rocks, Long Beach, Pounawea, Papatowai, Shag Mouth and Pleasant River (Fig. 5b). All dates except NZ-Ross (Ross's Rocks) were considered acceptable by Anderson (1991), from whom the data are taken. The Ross's Rocks date is included in this analysis because it is one of the few coastal dates from the area between Dunedin and Pleasant River.

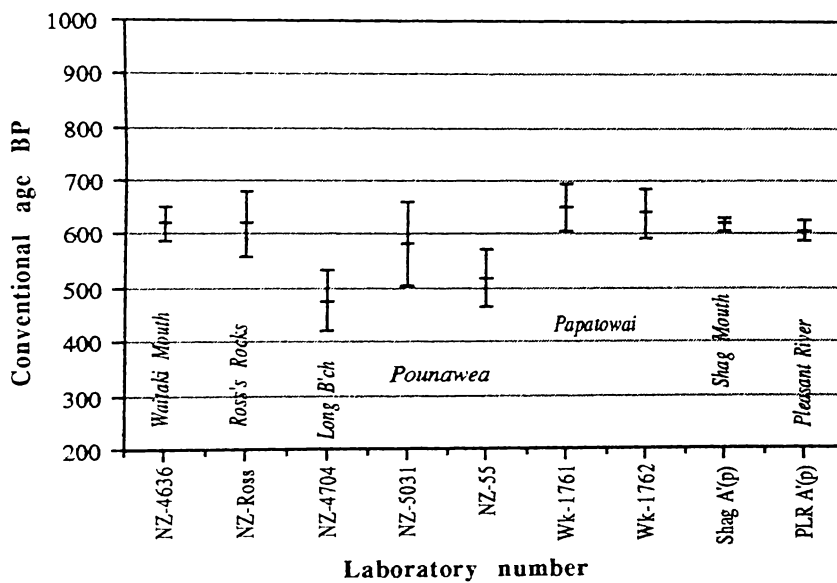


Figure 10.2. Dates of identified charcoal from sites in Murihiku, New Zealand (data from Anderson, 1991).

The spread of dates suggests these coastally oriented sites were occupied at a very similar time in prehistory, because the dates are statistically insignificant from one another ($A'_p = 611 \pm 9$ bp, with $T^* = 10.46$; $\chi^2_{8:0.05} = 15.51$).

How do the coastal dates compare with the radiocarbon record for the earliest interior sites, in Central Otago and the Mackenzie Basin? Dates from the Killermont site yielded

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a pooled mean of 660 ± 23 bp (for data - see chapter 8), again, this is statistically indistinguishable from the pooled mean for the coastal Otago sites. In figure 10.3, charcoal dates from a number of other sites in the interior are shown including Hawksburn, Coal Creek, Takahe Valley, Wyuna Koch, Minzionburn and Killermont. Only dates accepted by Anderson (1991) are considered, all those containing possible inbuilt age or uncertain context are not included.

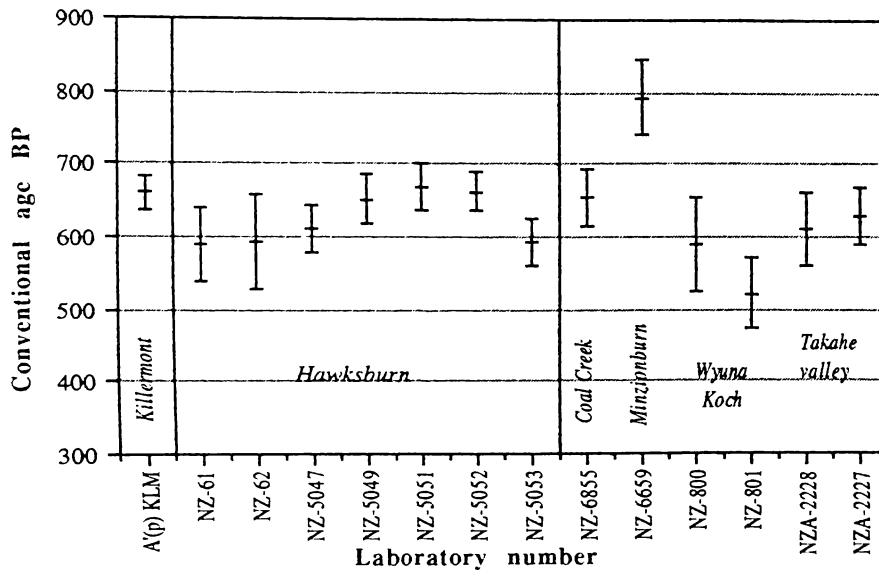


Figure 10.3. Dates of identified charcoal from sites in Central Otago and the Mackenzie Basin (dates from the Takahe valley are from O' Regan, 1992; all others except for the Killermont pooled mean are from Anderson, 1991).

With the exception of the Minzionburn result, the dates are in close agreement with those from the coastal sites. Anderson (1991) has rejected the other 3 dates from this site because they are of unknown composition and probably possess inbuilt age. This remaining date is statistically indistinguishable from the rejected dates, so may be a doubtful estimate of the true age of the site. It also appears an outlier in comparison to the other dates from central Otago (Fig. 10.2). Clearly, further radiocarbon dating should be undertaken from this site using identified and carefully selected material. In the meantime, this date is left out of consideration.

The remaining dates are indistinguishable at 1σ and may be pooled at 632 ± 10 bp ($T=13.41$; $\chi^2_{12:0.05}=21.03$). This mean is indistinguishable from the coastal site mean of 611 ± 9 bp (the pooled mean for all dates is 620.0 ± 6.6 bp with $T=2.4$;

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$\chi^2_{1:0.05}=3.84$). On the evidence of the radiocarbon determinations, the earliest dates of the occupation of these sites are statistically identical at 0.95 probability.

The radiocarbon chronology favours a single, brief period of human activity rather than one of long, permanent estuarine settlement. The analysis must, therefore, proceed on the basis of other sources of information. The nature of such sites as Shag Mouth may be considered on the basis of seasonal dating and the activities represented by archaeological remains.

Seasonality in Murihiku has been investigated by a number of researchers. The major problem with identifying precisely the type of seasonal round employed in prehistory has been that items which were seasonally abundant may have been preserved or traded and so finding their remains in archaeological sites is no guarantee of season of occupation (eg. the muttonbird (*Puffinus griseus*)). Till (1984), Till and Blattner (1986) and Higham (1990; in prep - 1994) have used the oxygen isotope method to determine seasonality using samples of *Mytilus edulis aoteanus* from Long Beach, Southport, Ross's Rocks, Pounaweia (Till and Blattner) and Shag Mouth (Higham). Winter was estimated at Shag Mouth and Long Beach, and at the upper layers of Pounaweia. At Southport, early spring was estimated, while Ross's Rocks was given a late autumn/early winter occupation. The lower levels at Pounaweia, dominated by moa remains, were estimated to have been occupied in summer (Till, 1984). The common variable in these results is that shellfishing appears an occupation undertaken in periods of local resource dearth (Higham, 1990).

At Shag Mouth, the seasonal estimate applies only to the upper shell midden layers of the site, therefore it is possible that it reflects only the winter focus of a site occupied all year round. The Long Beach and Ross's Rocks sites were probably seasonal camps, judging by the range of faunal and artefactual remains excavated from them. The Pounaweia site, once interpreted as a likely base camp or 'village' is similar to the Papatowai and Shag Mouth sites. Papatowai has been redated using only identified, short-lived charcoal samples and the results suggest a similar length of occupation to Shag Mouth (Anderson, 1991). The same situation would probably be expected at Pounaweia.

These sites may have occupied contemporaneously but, given that occupation at each appears to have been short, it seems more likely that certain of them may have been occupied in rapid succession. The conclusion of Anderson (1991:792) that all of the archaic coastal sites in this region may have been the result of rapid exploration and

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moa hunting by a small group, or groups of people, is a logical conclusion in the light of these radiocarbon dates.

It is now necessary to consider the activities represented at these sites in more detail. What, for example, are the archaeological correlates of rapid colonisation and exploration, of short site occupation and swift abandonment?

We would expect to find a dearth of evidence for permanent structures. Were permanency characteristic of the people of Murihiku at the time of their earliest presence in the archaeological record, we would expect evidence for house structures and hearths. We rarely find them. However, Anderson (1986) has argued that the house structures of the Murihiku people may have been small round huts (*whare porotaka*), almost invisible in the archaeological record save for the scattered remnants of hearths, which are often used as secondary evidence for houses (Anderson, 1986). At Shag Mouth, for example, Teviotdale described up to 43 hearths in his excavations. At the Glenaray site in Central Otago, three postulated houses have been identified on the basis of a circular pattern of stones, a central hearth, flaked debitage and moa bone. Why, in the sometimes temperate southern climes people would prefer to live in small thatched huts rather than sturdier *whare* or *wharepuni* which Prickett (1982) argues have a long history in New Zealand, may only be explained by the probable influence of the local climate upon mobile nature of hunting and gathering subsistence in the region. Alternatively, it may be that people were not inhabiting Murihiku permanently in the earliest periods and therefore did not invest time in erecting permanent houses.

We would expect to find little evidence for burial of the dead. A cemetery within an archaeological site implies permanent occupation. Wilson (1988:129) for example, has suggested that "as soon as domestication becomes the condition for living of the human species, burial becomes a condition of death". The crucial cultural repercussions which are associated with sedentism, domestication and permanence (Soffer, 1989) have been described elsewhere (Wilson, 1988; C.F.W Higham, 1989). In essence, sedentary life stimulates the accumulation of possessions and the development of ranking within communities. Both ethnographic and archaeological evidence indicates that ranked societies were widespread in Polynesia during prehistory and at historic contact (Kirch, 1984). Archaeological correlates have been described by Peebles and Kus (1977). Societal ranking, identified in the archaeological record through the differentiation in wealth between burials is one of the principal manifestations. At Wairau Bar, for example, there is variety amongst the grave goods suggesting some individuals may have possessed greater status than others. In Murihiku, however, very few documented

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burials associated with early prehistoric sites have been found. At Shag Mouth, Teviotdale records a burial in close association to two moa eggs (Anderson, 1989) and Allingham (pers. comm.) has mentioned a burial at the Pleasant River site. Teviotdale (1939:177) found no burials at the Waitaki Mouth site. There is nothing approaching the mortuary behaviour exhibited at Wairau Bar among the prehistoric sites of Murihiku. Moreover, isolated burials without supporting evidence for an established cemetery supports the notion of temporary occupation, for some people must have died while participating on opportunistic explorations.

Judging from the archaeological evidence, burial practices in New Zealand seem to have changed over the course of prehistory. The burials identified in early contexts at Wairau Bar were located near living areas (Duff, 1956; Davidson, 1984; Anderson, 1989). This situation is duplicated at Palliser Bay, near Wellington where the majority of burial remains at the Washpool site were close to domestic midden areas and in a discrete 10m² area (Leach and Leach, 1979:210). Similarly, at Opito Bay, on the Coromandel Peninsula, burial sites seem to have been located near settlements, and perhaps in small family groups (Davidson, 1984). In later periods, inter-tribal warfare and the evolution of tapu resulted in the disposal of the dead becoming more secretive. Cleft and cave burials became more common. Were sedentism, or semi-sedentism the commonest mode of settlement in the earlier occupation period of Murihiku, we would expect to find burials in, and around prehistoric settlements. We rarely do.

We would expect the earliest sites to be characterized by evidence for single occupation, with little evidence for stratigraphically defined hiatus (excluding sites with obvious signs of re-occupation at much later periods, for example at Warrington and Long Beach). This is the common situation of the majority of the earliest dated sites in Murihiku. Even the apparent repeat occupations of the Waitaki Mouth site need not necessarily have been separated in time, they could represent short-term activity related to moa hunting and processing events in different parts of the site, or seasonal occupation over 10 years.

A reasonable explanation for all the sites dated to 600 bp could be that they represent the earliest exploratory group. They might have moved their settlements frequently, or visited the area briefly from permanent bases located to the north. The traditional interpretation of sites such as Shag Mouth revolves around an early subsistence strategy based principally upon 'big game' (moa and seal) to a later strategy based upon marine resources. Equally, the dichotomy could be the manifestation of short-term, localised

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resource degeneration and subsequent site abandonment. Given such a scenario, the close agreement in the dates of sites such as Pleasant River, Shag Mouth, Warrington (lower layer), Papatowai and Killermont should hardly seem surprising.

If only a handful of male graves associated with artefacts thought to reflect male activities were found, in conjunction with evidence only for summer occupancy, it would be reasonable to conclude that Teviotdale's early views had substance. In contrast, food remains representative of all seasons and a series of well-constructed house foundations linked with a cemetery would indicate permanent and durable settlement. At present, the evidence suggests Teviotdale's interpretation falls short of explaining the prehistoric situation at Shag Mouth and Pounaweia, where seasonal evidence suggests year-round occupation. However, the second explanation cannot be sustained by the archaeological and radiocarbon record. The available evidence favours the interpretation that the majority these sites were transient rather than permanent and that occupation at some, although year round, was brief. If this was the case, where did the groups involved originate?

Anderson and McFadgen's (1990) lithic sourcing analysis of obsidian tools from Shag Mouth and Tai Rua showed that the material may have originated from the Kermadec Islands. In addition to this link, large silcrete blades and whale tooth pendants of similar form are found in certain of these contexts as well (Anderson and McFadgen, 1990). The radiocarbon data from both Raoul Island and Shag Mouth is now extensive (Fig. 10.4). The controversy concerning the dating of upper and lower layers at Low Flat has been addressed using dates of *Patella kermadecensis*. Because of the variable charcoal date chronology, due probably to varying degrees of inbuilt age, samples of *Patella* from upper and lower layers were dated to examine the temporal relationship between the two cultural deposits. Regardless of the exact reservoir correction, shell dates from both layers giving statistically indistinguishable values would suggest that a short period of time had elapsed between their deposition. If, however, the dates were distinguishable, a valid case could then be made for occupations at different times in prehistory. The two dates from the upper layer, Wk-2768 and Wk-2769 have been discussed in chapter 8. The first was untreated and gave a radiocarbon age of 1100 ± 45 bp; the second was treated by acid washing and dated to 1050 ± 45 bp. A shell sample from the lower layer of Low Flat (Wk-2770) was also pretreated and gave a date of 1040 ± 45 bp, therefore it seems likely that a short period of time has elapsed between the deposition of both cultural layers at Low Flat. Anderson's (1991) rejection of NZ-4789 as derived from natural charcoal, then, is justified in the light of this result and means that Wk-1912 from the same lower context must also be rejected for the same

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reason. Wk-1910 can be discarded because it is adrift from the other dates in the same layer by $>2\sigma$. The Raoul Island dates from both upper and lower layers from the Farm Terraces, Coral Bay and Low Flat sites, then, may be pooled at 596 ± 19 bp ($T=12.04$; $\chi^2_{7:0.05}=14.07$)[#].

The close statistical agreement between the Raoul Island radiocarbon series and those from Murihiku, in addition to the multiple examples of similarity in material culture between Raoul Island, Shag Mouth and Hawksburn provide even more compelling evidence for prehistoric links between New Zealand and island Polynesia. It is not unreasonable to suggest that initial human penetration of Murihiku involved brief exploratory visits from northern settlements. It would be unwise not to consider even the possibility of frequent movement between the area and the closer islands of tropical Polynesia.

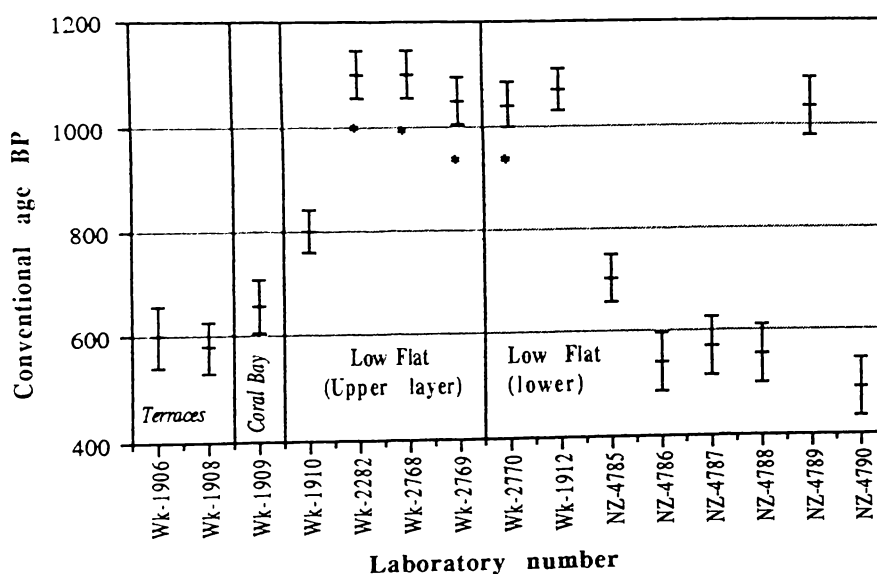


Figure 10.4. Radiocarbon dates from Raoul Island, the Kermadecs. The Wk-series, with the exception of Wk-2768, 2769 and 2770 are by Johnson from the Farm Terraces sites, the Coral Bay site and the upper and lower cultural layers at Low Flat. The NZ dates are from a series of test pits excavated by Anderson in 1978. They come from the lower cultural layer at Low Flat. Dates from shell (*Patella kermadecensis* - the Kermadec limpet) are marked with an asterisk. All other dates are from identified charcoal, predominantly Pohutokawa (see Appendix 5).

[#] It is likely that a tentative reservoir correction for the Kermadec Islands will be about 450 radiocarbon years, given the dates thus far obtained on prehistoric material.

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This model of short, rapid occupation and subsequent abandonment will require testing through further intensive radiocarbon dating. One problem, however, remains. Calibrating the dates from the Shag Mouth and Pleasant River sites, from the coast and interior sites, and from all of the assays combined, corresponds with the significant wiggle at *ca.* 600 bp in the northern hemisphere calibration. Each one of the pooled means cuts the curve at three different places, even the totalled pooled mean ($A'(p)(\text{Total})$ in table 10.1) of all dates from Otago sites hits the curve at Cal BP 616, 612 and 547 (Cal AD 1334, 1338, 1403). This means that differentiating between the most likely secular age for occupation is almost impossible based solely upon the radiocarbon evidence. In the case of Shag Mouth, for example, it is impossible to know whether the most likely occupation date is between AD 1330 - 1346, or from 1393 - 1408. Clearly it cannot have been occupied between AD 1346 - 1393 because the radioactivity measured in the samples does not correspond to the activity in the tree rings measured during that time.

Clearly, this situation requires further research. A New Zealand calibration curve for the prehistoric period may reveal the applicability not only of the southern hemisphere offset for Oceania but of the secular correction measured on northern hemisphere wood. Therefore, although the dates these sites in question are statistically indistinguishable, the secular time of occupation is still imprecise.

Dates	Pooled mean BP	Method B Cal AD range (prob.)	
SM/C $A'(p)$	580±13	1330 - 1346 (.56)	1393 - 1408 (.44)
PLR $A'(p)$	567±21	1331 - 1345 (.44)	1394 - 1413 (.56)
Coast $A'(p)$	571±9	1332 - 1342 (.47)	1396 - 1410 (.53)
Interior $A'(p)$	592±10	1328 - 1335 (.21)	1335 - 1349 (.41)
$A'(p)(\text{Total})$	579±6	1331 - 1344 (.58)	1395 - 1407 (.42)

Table 10.1: calibrated charcoal and eggshell data for the pooled mean conventional dates at Shag Mouth, Pleasant River, the Otago coast and interior. The pooled mean data includes the southern hemisphere offset of -40 years (Vogel *et al.*, 1993). $A'(p)(\text{Total})$ is the summed mean of all 4 datasets. The statistics for this are: $T=2.81$; $\chi^2_{3;0.05}=7.81$.

10.4. REPERCUSSIONS FOR RADIOCARBON DATING

The possibility that many archaeological sites in Murihiku and other parts of New Zealand were occupied for short periods of time has important repercussions for archaeological radiocarbon dating programmes. The 'optimal dating' technique described in chapter 6, when applied using carefully selected and pretreated material, has the capability to place sites in chronological perspective most accurately, with increased certainty due to larger sample size, as long as the fundamental principles identified regarding errors due to sample type are noted.

The employment of statistical techniques to determine central tendencies (the pooling of radiocarbon series), has been criticised by Schiffer (1987:309) who has suggested it is not a satisfactory method because it:

"is incapable of detecting biases in a series of dates and because it treats all dates as being equally informative about past events."

He suggests further that:

"Clearly, an approach is needed that is selective yet based on rigorous and explicit methodological principles. Moreover, one should explain why the remaining dates are anomalous".

MICHAEL SCHIFFER. 1987. Formation processes of the Archaeological Record. P. 309.

Leach (1972:116), in presenting a method for pooling dates, suggests that if used with caution, pooling is acceptable as long as archaeological context and inbuilt age is considered. In this dissertation it has been shown that some samples are more reliable than others. Only samples considered to be dependable have been used in pooling.

Anderson (1991), in his review of early dates of colonisation has described a discard protocol to accept or reject radiocarbon dates. Further refinement of specific methodological guidelines for archaeological dating has been attempted above and is reliant upon the continued analysis of a variety of further variables. Because of the critical pressure upon sample selection and identification, and accuracy in dating, New Zealand is relatively advanced in terms of its radiocarbon dating methodology and understanding of the inherent limitations and errors in archaeological dating.

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The testing of specific hypotheses regarding prehistoric settlement, colonisation and development will be depend upon multiple-dating, using carefully identified and pretreated samples and the use of a critical framework for acceptance or rejection of individual dates.

It is concluded that Movius (1960), while correct in stressing the importance of radiocarbon dating, was concerned with only part of the picture. A proper grip on chronology is essential, but it must be considered within the context of human behaviour manifested in a detailed scrutiny of the archaeological record.

10.5. CONCLUSION

After 40 years, the impact of radiocarbon dating in prehistoric contexts throughout the world is well known. At the beginning of this dissertation, some of the reasons why the effectiveness of the radiocarbon method has been relatively slight in New Zealand were examined. One of the reasons put forward was that prehistory has sometimes been addressed from an ethnological rather than an archaeological perspective. Furthermore, consensus over the date of initial colonisation seems to have stifled the use of radiocarbon dating as a research tool to answer specific questions in prehistory. Traditionally, the short prehistory has been blamed upon the reduced effectiveness of dating because standard errors are magnified within the brief context. The most important reason, however, is that radiocarbon dating has neither been understood fully, nor implemented effectively until recently. Analyses concerning the imprecision of radiocarbon dates and the difficulty in separating events accurately in time at certain levels of precision (McFadgen, 1978; Law, 1982) ignores statistical evidence enabling the comparison and pooling of radiocarbon dates (Ward and Wilson, 1978; Gupta and Polach, 1985). The growing awareness of the crucial importance of sample type and inbuilt age, combined with the technological and instrumental advances in radiocarbon dating mean that at last archaeologists are in sight of the type of precision so long desired. Nyerup's fog, which has hung over the New Zealand prehistoric period is beginning to clear. Yet there remain further avenues of improvement and research.

One of the most important concerns the accuracy of shell dating. Studies reported in this dissertation have shown that potential exists for serious errors in dating shell from within and near to estuaries, although it varies with the type of estuary and the amount of marine tidal flushing which occurs. Similar work is needed in areas near to upwelling zones. Further research is also required into examining the applicability of

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the ΔR correction for New Zealand, in the light of the comparison presented above from the Shag Mouth site.

Shell carbonate seems to avoid sample contamination, but organic samples such as charcoal warrant further examination, particularly in environments where the potential for post-depositional diagenesis is high.

One of the most profitable developments of recent years is the expansion in the variety of materials used for radiocarbon dating. AMS has enabled rice remains used in prehistoric Thai pots to be dated, cloth from centimetre-sized material cut from the Shroud of Turin to be dated, minute traces of charcoal used in Upper Paleolithic cave paintings to be dated, and so on. In this dissertation, moa eggshell remains were dated. In New Zealand sites there are probably an array of materials yet to be considered for dating which may yield profitable results. For example, feather remains, seeds and twine, mummified moa remains and charcoals used in cave art drawings. With improved precision and technological developments in radiocarbon dating, certain of these materials may be dated in the near future with some accuracy. Probably the most important avenue for research, however, is in the continued improvement of precision.

Radiocarbon dating shall remain a crucial research tool for archaeology in New Zealand. No other dating technique can be applied in this timeframe as successfully. Thermo-luminescence (TL) dating has been applied by Fankhauser (1990) in Canterbury to date earth ovens but often possesses unacceptably large standard errors. ESR has been investigated by Dennison (1989), with some promising results, but has yet to be widely applied. Other techniques, such as K-Ar and Amino acid racemization techniques are not able to be applied using samples less than 1000 years old. Obsidian hydration dating is promising, but imprecise.

The re-interpretation of the radiocarbon chronology of New Zealand (Anderson, 1991) has opened a new vista and renewed interest into the dating and re-dating of archaeological sites. Dates from many sites, once thought to be accurate, have been questioned because of the erroneous assumption that they dated the event in prehistory. There is a need now for extensive re-dating based upon careful selection of material, pretreatment and continued examination of the range of errors associated with radiocarbon dates, in association with the further development of high precision dating.

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APPENDIX 1:
Radiocarbon dates measured in this dissertation.

Wk #	Location	Sample type	Libby age BP	New Age BP	% Modern	Dil. (%)	$\delta^{13}\text{C}$	D14C
2268	Pleasant River	Charcoal	>MOD	>MOD	103.8 $\pm$ 2.5	31.0	-27.0	37.8 $\pm$ 25.0
2269	Pleasant River	Charcoal	520 $\pm$ 50	540 $\pm$ 50	93.7 $\pm$ 0.6	65.4	-27.7	-62.9 $\pm$ 5.7
2270	Pleasant River	Charcoal	690 $\pm$ 50	710 $\pm$ 50	91.75 $\pm$ 0.5	81.6	-26.5	-82.5 $\pm$ 5.2
2271	Pleasant River	Charcoal	660 $\pm$ 50	680 $\pm$ 50	92.1 $\pm$ 0.48	100	-26.8	-79.0 $\pm$ 4.8
2318*	Pleasant River	Charcoal	650 $\pm$ 60	660 $\pm$ 60	92.3 $\pm$ 0.7	49.9	-26.7	-77.2 $\pm$ 6.8
2362	Shag Mouth	<i>Austrovenus stutchburyi</i>	1010 $\pm$ 50	1040 $\pm$ 50	88.2 $\pm$ 0.5	100	+1.3	-117.9 $\pm$ 5.0
2363*	Shag Mouth	<i>Austrovenus stutchburyi</i>	1150 $\pm$ 50	1180 $\pm$ 50	86.7 $\pm$ 0.5	100	+1.0	-135.6 $\pm$ 4.52
2364	Shag Mouth	<i>Austrovenus stutchburyi</i>	1040 $\pm$ 50	1070 $\pm$ 50	87.9 $\pm$ 0.45	100	+1.3	-121.0 $\pm$ 4.55
2365	Shag Mouth	<i>Austrovenus stutchburyi</i>	1120 $\pm$ 120	1150 $\pm$ 120	87.0 $\pm$ 1.3	100	-20.0	-129.6 $\pm$ 13.0
2367	Shag Mouth	<i>Amphibola crenata</i>	1160 $\pm$ 50	1190 $\pm$ 50	86.5 $\pm$ 0.45	100	+1.4	-134.3 $\pm$ 4.5
2368*	Shag Mouth	<i>Paphies australis</i>	1080 $\pm$ 50	1110 $\pm$ 50	87.5 $\pm$ 0.5	100	+1.3	-125.4 $\pm$ 5.0
2369*	Pleasant River	<i>Amphibola crenata</i>	1260 $\pm$ 50	1290 $\pm$ 50	85.5 $\pm$ 0.5	100	+1.2	-144.9 $\pm$ 5.2
2370*	Pleasant River	<i>Austrovenus stutchburyi</i>	970 $\pm$ 50	1000 $\pm$ 50	88.6 $\pm$ 0.5	100	0.0	-114.1 $\pm$ 5.0
2410	Shag Mouth	<i>Austrovenus stutchburyi</i>	1020 $\pm$ 50	1050 $\pm$ 50	88.0 $\pm$ 0.49	100	+1.5	-119.2 $\pm$ 4.9
2411	Shag Mouth	<i>Austrovenus stutchburyi</i>	990 $\pm$ 45	1020 $\pm$ 45	88.4 $\pm$ 0.5	100	+0.8	-116.4 $\pm$ 4.6
2412	Shag Mouth	<i>Austrovenus stutchburyi</i>	980 $\pm$ 45	1010 $\pm$ 45	88.5 $\pm$ 0.4	100	1.2	-114.4 $\pm$ 4.5
2413	Pleasant River	<i>Austrovenus stutchburyi</i>	>MOD	>MOD	107.5 $\pm$ 0.5	100	+0.9	75.09 $\pm$ 5.2
2414	Shag Mouth	<i>Austrovenus stutchburyi</i>	>MOD	>MOD	108.3 $\pm$ 0.5	100	+0.9	82.99 $\pm$ 5.4
2415*	Papanui Inlet	<i>Austrovenus stutchburyi</i>	>MOD	>MOD	108.8 $\pm$ 0.6	100	+0.7	88.12 $\pm$ 5.8
2416	Shag Mouth	Moa eggshell	600 $\pm$ 50	620 $\pm$ 50	92.8 $\pm$ 0.6	52.5	-15.4	-71.8 $\pm$ 5.8
2417	Shag Mouth	Moa eggshell	560 $\pm$ 40	570 $\pm$ 45	93.32 $\pm$ 0.5	100	-15.0	-66.8 $\pm$ 4.7
2421	Shag Mouth	<i>Amphibola crenata</i>	>MOD	>MOD	109.2 $\pm$ 0.5	100	+0.2	92.0 $\pm$ 5.4
2422	Shag Mouth	<i>Amphibola crenata</i>	>MOD	>MOD	110.1 $\pm$ 0.6	91.1	-1.4	100.8 $\pm$ 5.8

APPENDIX 1

Wk #	Location	Sample type	Libby age BP	New Age BP	% Modern	Dil. (%)	$\delta^{13}\text{C}$	D14C
2423	Papanui Inlet	<i>Amphibola crenata</i>	>MOD	>MOD	107.6 $\pm$ 0.5	100	+0.9	76.3 $\pm$ 5.3
2440	Shag Mouth	<i>Austrovenus stutchburyi</i>	1050 $\pm$ 50	1080 $\pm$ 50	87.7 $\pm$ 0.5	100	+0.7	-122.5 $\pm$ 4.7
2441	Shag Mouth	<i>Austrovenus stutchburyi</i>	1070 $\pm$ 45	1105 $\pm$ 45	87.5 $\pm$ 0.4	100	+1.0	-125.1 $\pm$ 4.4
2506r 2370	Pleasant River	<i>Austrovenus stutchburyi</i>	930 $\pm$ 45	950 $\pm$ 45	89.1 $\pm$ 0.4	100	-0.3	-108.8 $\pm$ 4.5
2507 r2369	Pleasant River	<i>Amphibola crenata</i>	1180 $\pm$ 45	1210 $\pm$ 45	86.4 $\pm$ 0.5	100	1.2	-136.5 $\pm$ 4.7
2508 r2363	Shag Mouth	<i>Austrovenus stutchburyi</i>	1060 $\pm$ 45	1100 $\pm$ 45	87.6 $\pm$ 0.4	100	-0.2	-124.1 $\pm$ 4.4
2509 r2415	Papanui Inlet	<i>Austrovenus stutchburyi</i>	>MOD	>MOD	109.6 $\pm$ 0.5	100	-0.4	96.84 $\pm$ 5.4
2589	Shag Mouth	charcoal ("as is" fract'n)	630 $\pm$ 35	650 $\pm$ 40	92.5 $\pm$ 0.4	100	-28.3	-75.1 $\pm$ 3.9
2590	Shag Mouth	charcoal ("AW" fract'n)	620 $\pm$ 35	640 $\pm$ 40	92.6 $\pm$ 0.4	100	-27.6	-74.4 $\pm$ 3.9
2591	Shag Mouth	charcoal ("ABA insol" fract'n)	660 $\pm$ 35	680 $\pm$ 40	92.1 $\pm$ 0.4	100	-27.1	-78.5 $\pm$ 3.9
2592	Shag Mouth	charcoal ("ABA sol" fract'n)	580 $\pm$ 45	590 $\pm$ 50	93.1 $\pm$ 0.5	81.2	-27.2	-69.4 $\pm$ 5.1
2593	Shag Mouth	charcoal ("HNO ₃ " fraction)	600 $\pm$ 35	610 $\pm$ 40	92.8 $\pm$ 0.4	100	-27.1	-71.7 $\pm$ 3.9
2594	Shag Mouth	charcoal ("physically pretreated" fraction)	660 $\pm$ 45	670 $\pm$ 50	92.2 $\pm$ 0.5	100	-27.5	-78.4 $\pm$ 5.1
2604	Shag Mouth	Moa eggshell	570 $\pm$ 45	590 $\pm$ 45	93.2 $\pm$ 0.5	100	-11.4	-68.4 $\pm$ 4.8
2632	Shag Mouth	<i>Paphies australis</i>	1010 $\pm$ 45	1040 $\pm$ 50	88.2 $\pm$ 0.5	100	+1.4	-118.0 $\pm$ 4.8
2633	Shag Mouth	<i>Amphibola crenata</i>	1070 $\pm$ 80	1110 $\pm$ 80	87.5 $\pm$ 0.9	100	+0.7	-125.2 $\pm$ 8.7
2693	Portobello	<i>Austrovenus stutchburyi</i>	>MOD	>MOD	109.3 $\pm$ 0.5	100	0.46	92.9 $\pm$ 5.3
2694	Portobello	<i>Austrovenus stutchburyi</i>	>MOD	>MOD	109.0 $\pm$ 0.5	100	+0.6	89.7 $\pm$ 5.4
2711	Pleasant River	<i>Austrovenus stutchburyi</i>	>MOD	>MOD	108.2 $\pm$ 0.5	100	0.5	81.8 $\pm$ 4.9
2712	Pleasant River	<i>Austrovenus stutchburyi</i>	>MOD	>MOD	108.4 $\pm$ 0.4	100	0.7	83.7 $\pm$ 4.4
2735	Onenui	Moa eggshell	1040 $\pm$ 120	1070 $\pm$ 120	87.8 $\pm$ 1.3	89.0	-9.7	-121.5 $\pm$ 12.8
2741	Pleasant River	Moa eggshell	650 $\pm$ 45	670 $\pm$ 50	92.2 $\pm$ 0.5	100	-12.1	-77.7 $\pm$ 5.1

APPENDIX 1

Wk #	Location	Sample type	Libby age BP	New Age BP	% Modern	Dil. (%)	$\delta^{13}\text{C}$	D14C
2744	Warrington	Moa eggshell	580±45	590±45	93.1± 0.5	100	-14.7	-69.3±4.7
2751	Shag Mouth	<i>Austrovenus stutchburyi</i>	960±45	990±45	88.8± 0.5	100	1.0	-112.5±4.7
2752	Shag Mouth	<i>Mytilus edulis aoteanus</i>	1040±45	1070±45	87.8± 0.5	100	1.0	-121.9±4.5
2753 r2506	Pleasant River	<i>Austrovenus stutchburyi</i>	910±45	930±45	89.3± 0.5	100	0.4	-106.9±4.5
2758	Pleasant River	Moa eggshell	650±45	670±45	92.3± 0.5	100	-14.0	-77.4±4.8
2759	Pleasant River	Moa eggshell	590±40	610±45	92.8± 0.5	100	-14.2	-71.2±4.6
2760	Pleasant River	Moa eggshell	600±45	610±45	92.8± 0.5	100	-13.9	-71.7±4.7
2761	Pleasant River	<i>Austrovenus stutchburyi</i>	1120±45	1150±50	87.0± 0.5	100	0.8	-129.9±4.8
2762	Pleasant River	<i>Paphies sub-triangularum</i>	1110±45	1140±45	87.1± 0.5	100	1.9	-128.9±4.6
2763	Pleasant River	<i>Austrovenus stutchburyi</i>	920±45	950±45	89.2± 0.5	100	0.2	-108.1±4.8
2764	Pleasant River	<i>Paphies australis</i>	790±45	820±45	90.6± 0.5	100	+1.7	-93.9±4.8
2765	Pleasant River	Moa eggshell	600±45	610±45	92.8± 0.5	100	-12.2	-71.6±4.7
2768	Low Flat	<i>Patella kermadecensis</i>	1100±45	1130±50	87.2± 0.5	100	1.3	-128.2±4.7
2769	Low Flat	<i>Patella kermadecensis</i>	1050±45	1080±45	87.8± 0.5	100	1.3	-122.4±4.6
2770	Low Flat	<i>Patella kermadecensis</i>	1040±45	1070±45	87.9±0.5	100	1.3	-121.2±4.7
2771	Pleasant River	<i>Cookia sulcata</i>	740±45	760±45	91.2± 0.5	100	1.3	-88.0±4.9
2772	Pleasant River	<i>Paphies australis</i>	780±45	800±45	90.8± 0.5	100	1.7	-92.4±4.8
2781	Killermont #2	Charcoal (Rootlet fraction)	370±140	380±150	95.5± 1.7	64.1	-26.2	-44.6±16.7
2782	Killermont #2	Charcoal ("as is")	680±35	700±40	91.9± 0.4	100	-25.5	-81.3±3.9
2783	Killermont #2	Charcoal (Physically pretreated)	640±35	660±35	92.4± 0.4	100	-25.3	-76.3±3.8
2784	Killermont #2	Charcoal (ABA insol 'A')	650±35	670±40	92.3± 0.4	100	-25.0	-77.4±4.0
2785	Killermont #2	Charcoal (ABA sol 'A')	590±45	610±45	92.9± 0.5	100	-26.0	-70.9±5.0
2786	Killermont #2	Charcoal (ABA insol 'B')	630±40	650±40	92.4± 0.4	100	-25.5	-76.0±4.4

APPENDIX 1

Wk #	Location	Sample type	Libby age BP	New Age BP	% Modern	Dil. (%)	$\delta^{13}\text{C}$	D14C
2787	Killermont #2	Charcoal (ABA sol 'B')	600±60	620±60	92.8± 0.6	98.5	-25.7	-72.2±6.4
2789	Pleasant River	charcoal	550±90	570±90	93.4± 1.0	100	-26.3	-66.3±9.9
2790	Pleasant River	charcoal	700±90	720±100	91.7± 1.1	83.1	-27.9	-83.3±10.5
2791	Killermont #2	Charcoal ("AW" fraction)	600±40	620±40	92.8± 0.4	100	-25.5	-72.0±4.4
2821	Dart Bridge	<i>Ostea lutraria</i>	>MOD	>MOD	106.6±0.4	100	2.0	65.7±4.4
2851	Pleasant River	<i>Austrovenus stutchburyi</i>	970±35	1000±40	88.6± 0.4	100	+0.4	-114.0±3.8
2856	Shag Mouth	<i>Austrovenus stutchburyi</i>	980±40	1010±40	88.5± 0.4	100	+1.0	-115.0±3.9
2857	Shag Mouth	<i>Austrovenus stutchburyi</i>	950±45	970±50	88.9±0.5	100	+1.0	-111.2±4.9
2863	Bark Bay	<i>Paphies australis</i>	840±45	870±45	90.0± 0.5	100	+2.0	-99.7±4.8
2864	Bark Bay	<i>Paphies australis</i>	820±45	840±45	90.3± 0.5	100	+1.9	-96.6±4.8
2865	Bark Bay	<i>Paphies australis</i>	1050±50	1080±50	87.7±0.47	100	+0.7	-122.5±4.7
2866	Bark Bay	<i>Austrovenus stutchburyi</i>	800±50	820±50	90.5± 0.5	100	+1.0	-94.8±5.2
2867	Bark Bay	<i>Austrovenus stutchburyi</i>	770±40	790±45	90.8± 0.4	100	+1.2	-91.6±4.4
2868	Bark Bay	<i>Paphies australis</i>	820±45	840±50	90.3± 0.5	100	+1.9	-96.7±5.0
2869	Awaroa Inlet	<i>Austrovenus stutchburyi</i>	800±40	820±45	90.5± 0.4	100	+1.4	-94.9±4.4
2870	Awaroa Inlet	<i>Paphies australis</i>	770±40	790±40	90.9± 0.4	100	1.4	-90.9±4.3
2916	Killermont #2	Charcoal ("as is" fraction)	660±45	680±45	92.2± 0.5	100	-25.5	-78.4±5.0
2965	Pleasant River	<i>Austrovenus stutchburyi</i>	>MOD	>MOD	108.7±0.5	100	+0.2	87.2±5.2
2965 B	Pleasant River	<i>Austrovenus stutchburyi</i>	>MOD	>MOD	109.1±0.5	100	+0.4	91.4±3.8
2966	Papanui Inlet	<i>Austrovenus stutchburyi</i>	>MOD	>MOD	109.4±0.5	100	0.7	93.5±5.5
2966 B	Papanui Inlet	<i>Austrovenus stutchburyi</i>	>MOD	>MOD	109.8±0.5	100	0.3	97.7±5.3
2967	Shag Mouth	<i>Austrovenus stutchburyi</i>	>MOD	>MOD	108.5±0.5	100	-0.1	85.3±5.2
2967 B	Shag Mouth	<i>Austrovenus stutchburyi</i>	>MOD	>MOD	109.1±0.5	100	-0.1	90.6±5.3

APPENDIX 1

Wk #	Location	Sample type	Libby age BP	New Age BP	% Modern	Dil. (%)	$\delta^{13}\text{C}$	D14C
2968	Portobello	<i>Austrovenus stutchburyi</i>	>MOD	>MOD	108.2±0.5	100	0.4	82.0±5.0
2968 B	Portobello	<i>Austrovenus stutchburyi</i>	>MOD	>MOD	107.8±0.5	100	0.2	78.4±5.1
2969	Pleasant River	<i>Cookia sulcata</i>	>MOD	>MOD	107.6±0.5	100	0.7	76.0±4.9
2969 B	Pleasant River	<i>Cookia sulcata</i>	>MOD	>MOD	100.2±0.5	100	0.4	2.1±5.2
2970	Pleasant River	<i>Amphibola crenata</i>	>MOD	>MOD	108.4±0.6	100	-1.2	83.9±5.7
2971	Pleasant River	<i>Cellana</i> sp. (estuarine)	>MOD	>MOD	108.2±0.5	100	0.9	81.6±5.4
2971 B	Pleasant River	<i>Cellana</i> sp. (estuarine)	>MOD	>MOD	108.0±0.5	100	1.0	80.1±5.4
2972	Pleasant River	<i>Paphies australis</i>	MODERN	MODERN	99.7± 0.5	100	1.5	-2.7±5.1
2973	Pleasant River	<i>Lunella smaragda</i>	>MOD	>MOD	109.1±0.5	100	-0.6	91.0±5.2
2973 B	Pleasant River	<i>Cellana</i> sp (marine)	>MOD	>MOD	106.2±0.5	100	1.0	62.4±5.3
2990	Pleasant River	<i>Macrocytis seaweed</i>	>MOD	>MOD	104.7±1.2	93.6	-17.5	46.7±11.6
2991	Killermont #2	Charcoal ("as is")	630±45	650±45	92.5± 0.5	100	-24.8	-75.1±5.0
2992	Fyffes site, Kaikoura	<i>Austrovenus stutchburyi</i>	>MOD	>MOD	110.6±0.5	100	0.0	105.6±5.3

Notes:

• denotes a sample affected by quenching.

Sample Wk-2369 was recalculated using a spectral shift programme. Its original conventional age was 1300±50 bp.

Sample Wk-2370 was also recalculated. Previously it gave a date of 1020±50 bp.

'r' denotes a sample which was dated as a repeat of a previous affected sample (see for example Wk-2507, a repeat date of Wk-2369 which was quenched).

APPENDIX 2:
Marine shell calibrations (Calibration file: MARINE93.14C: Stuiver and
Braziunas, 1993) Delta R=-30.0±13.0

Wk-2362 *Chione stutchburyi*

Shag Mouth G8 L4 Radiocarbon Age BP 1010±50

Calibrated age(s) cal AD 1331 cal BP 619

(Method A):

one Sigma cal AD 1304 - 1399 (646 - 551) two Sigma cal AD 1275 - 1430 (675 - 520)

(Method B):

% area enclosed.	cal AD (cal BP).	Age ranges relative area under probability distribution.
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68.3 (1s)	cal AD 1311 - 1390 (639 - 560)	1.00
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95.4 (2s)	cal AD 1280 - 1426 (670 - 524)	1.00
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Wk-2368 *Paphies australis*

Shag Mouth G8 L4 Radiocarbon Age BP 1080±50

Calibrated age(s) cal AD 1297 cal BP 653

(Method A):

one Sigma cal AD 1263 - 1322 (687 - 628) two Sigma cal AD 1216 - 1387 (734 - 563)

(Method B):

68.3 (1s)	cal AD 1249 - 1330 (701 - 620)	1.00
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95.4 (2s)	cal AD 1213 - 1392 (737 - 558)	1.00
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Wk-2410 *Chione stutchburyi*

Shag Mouth F7 L4 Radiocarbon Age BP 1020±50

Calibrated age(s) cal AD 1325 cal BP 625

(Method A):

one Sigma cal AD 1300 - 1393 (650 - 557) two Sigma cal AD 1267 - 1424 (683 - 526)

(Method B):

68.3 (1s)	cal AD 1304 - 1385 (646 - 565)	1.00
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95.4 (2s)	cal AD 1272 - 1423 (678 - 527)	1.00
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Wk-2411 *Chione stutchburyi*

Shag Mouth F7 L4 Radiocarbon Age BP 990 ± 45

Calibrated age(s) cal AD 1358 cal BP 592

(Method A):

one Sigma cal AD 1316 - 1408 (634 - 542) two Sigma cal AD 1294 - 1435 (656 - 515)

(Method B):

68.3 (1s)	cal AD 1325 - 1398 (625 - 552)	1.00
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95.4 (2s)	cal AD 1299 - 1429 (651 - 521)	1.00
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Wk-2412 *Chione stutchburyi*

Shag Mouth F7 L4 Radiocarbon Age BP 980±45

Calibrated age(s) cal AD 1380 cal BP 570

(Method A):

one Sigma cal AD 1321 - 1414 (629 - 536) two Sigma cal AD 1299 - 1439 (651 - 511)

(Method B):

68.3 (1s)	cal AD 1330 - 1404 (620 - 546)	1.00
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95.4 (2s)	cal AD 1304 - 1433 (646 - 517)	1.00
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Wk-2632 *Paphies australis*

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Shag Mouth J5 L4 Radiocarbon Age BP 980±40
 Calibrated age(s) cal AD 1380 cal BP 570
 (Method A):
 one Sigma cal AD 1324 - 1412 (626 - 538) two Sigma cal AD 1303 - 1435 (647 - 515)
 (Method B):
 68.3 (1s) cal AD 1333 - 1402 (617 - 548) 1.00
 95.4 (2s) cal AD 1308 - 1429 (642 - 521) 1.00

Wk-2751 *Chione stutchburyi*
 Shag Mouth F7 L4 Radiocarbon Age BP 960±45
 Calibrated age(s) cal AD 1398 cal BP 552
 (Method A):
 one Sigma cal AD 1333 - 1425 (617 - 525) two Sigma cal AD 1308 - 1449 (642 - 501)
 (Method B):
 68.3 (1s) cal AD 1344 - 1419 (606 - 531) 1.00
 95.4 (2s) cal AD 1313 - 1443 (637 - 507) 1.00

Wk-2752 *Mytilus edulis*
 Shag Mouth J5 L4 Radiocarbon Age BP 1040±45
 Calibrated age(s) cal AD 1315 cal BP 635
 (Method A):
 one Sigma cal AD 1293 - 1350 (657 - 600) two Sigma cal AD 1257 - 1407 (693 - 543)
 (Method B):
 68.3 (1s) cal AD 1291 - 1369 (659 - 581) 1.00
 95.4 (2s) cal AD 1259 - 1407 (691 - 543) 1.00

Wk-2761 *Chione stutchburyi*
 Pleasant River D Radiocarbon Age BP 1070±45
 Calibrated age(s) cal AD 1301 cal BP 649 (Method A):
 one Sigma cal AD 1275 - 1324 (675 - 626) two Sigma cal AD 1233 - 1388 (717 - 562)
 (Method B):
 68.3 (1 sigma) cal AD 1262 - 1336 (688 - 614) 1.00
 95.4 (2 sigma) cal AD 1231 - 1390 (719 - 560) 1.00

Wk-2762 *Paphies subtriangulatum*
 Pleasant River D Radiocarbon Age BP 1110±45
 Calibrated age(s) cal AD 1281 cal BP 669
 (Method A):
 one Sigma cal AD 1240 - 1305 (710 - 645) two Sigma cal AD 1193 - 1328 (757 - 622)
 (Method B):
 68.3 (1 sigma) cal AD 1237 - 1306 (713 - 644) 1.00
 95.4 (2 sigma) cal AD 1182 - 1339 (768 - 611) 1.00

Wk-2763 *Chione stutchburyi*
 Pleasant River D Radiocarbon Age BP 920±45
 Calibrated age(s) cal AD 1421 cal BP 529
 (Method A):
 one Sigma cal AD 1393 - 1445 (557 - 505) two Sigma cal AD 1328 - 1471 (622 - 479)
 (Method B):
 68.3 (1 sigma) cal AD 1380 - 1450 (570 - 500) 1.00
 95.4 (2 sigma) cal AD 1330 - 1468 (620 - 482) 1.00

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Wk-2764 *Paphies australis*

Pleasant River D Radiocarbon Age BP 790±45

Calibrated age(s) cal AD 1492 cal BP 458

(Method A):

one Sigma cal AD 1463 - 1527 (487 - 423) two Sigma cal AD 1438 - 1613 (512 - 337)

(Method B):

68.3 (1 sigma) cal AD 1458 - 1535 (492 - 415) 1.00

95.4 (2 sigma) cal AD 1438 - 1613 (512 - 337) 1.00

Wk-2856 *Chione stutchburyi*

Shag Mouth J5 L4 Radiocarbon Age BP 980±40

Calibrated age(s) cal AD 1380 cal BP 570

(Method A):

one Sigma cal AD 1324 - 1412 (626 - 538) two Sigma cal AD 1303 - 1435 (647 - 515)

(Method B):

68.3 (1s) cal AD 1333 - 1402 (617 - 548) 1.00

95.4 (2s) cal AD 1308 - 1429 (642 - 521) 1.00

Wk-2771 *Cookia sulcata*

Pleasant River D Radiocarbon Age BP 740±45

Calibrated age(s) cal AD 1529 cal BP 421

(Method A):

one Sigma cal AD 1493 - 1618 (457 - 332) two Sigma cal AD 1463 - 1656 (487 - 294)

(Method B):

68.3 (1 sigma) cal AD 1499 - 1603 (451 - 347) 1.00

95.4 (2 sigma) cal AD 1473 - 1647 (477 - 303) 1.00

Wk-2772 *Paphies australis*

Pleasant River D Radiocarbon Age BP 780±45

Calibrated age(s) cal AD 1499 cal BP 451

(Method A):

one Sigma cal AD 1468 - 1535 (482 - 415) two Sigma cal AD 1443 - 1628 (507 - 322)

(Method B):

68.3 (1 sigma) cal AD 1462 - 1546 (488 - 404) 1.00

95.4 (2 sigma) cal AD 1445 - 1622 (505 - 328) 1.00

Wk-2863 *Paphies australis*

Bark Bay 3A Radiocarbon Age BP 840±45

Calibrated age(s) cal AD 1462 cal BP 488

(Method A):

one Sigma cal AD 1437 - 1490 (513 - 460) two Sigma cal AD 1411 - 1525 (539 - 425)

(Method B):

68.3 (1 sigma) cal AD 1435 - 1493 (515 - 457) 1.00

95.4 (2 sigma) cal AD 1405 - 1534 (545 - 416) 1.00

Wk-2864 *Paphies australis*

Bark Bay 3A Radiocarbon Age BP 820±45

Calibrated age(s) cal AD 1473 cal BP 477

(Method A):

one Sigma cal AD 1447 - 1505 (503 - 445) two Sigma cal AD 1422 - 1542 (528 - 408)

(Method B)

68.3 (1 sigma) cal AD 1445 - 1508 (505 - 442) 1.00

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95.4 (2 sigma)	cal AD 1414 - 1562 (536 - 388)	1.00
Wk-2865 <i>Paphies australis</i>		
Bark Bay 3A	Radiocarbon Age BP	880±40
Calibrated age(s)	cal AD 1441	cal BP 509
(Method A):		
one Sigma	cal AD 1418 - 1464 (532 - 486)	two Sigma cal AD 1394 - 1489 (556 - 461)
(Method B):		
68.3 (1 sigma)	cal AD 1416 - 1466 (534 - 484)	1.00
95.4 (2 sigma)	cal AD 1381 - 1498 (569 - 452)	1.00
Wk-2866 <i>Chione stutchburyi</i>		
Bark Bay 3A	Radiocarbon Age BP	800±50
Calibrated age(s)	cal AD 1485	cal BP 465
(Method A):		
one Sigma	cal AD 1454 - 1523 (496 - 427)	two Sigma cal AD 1428 - 1613 (522 - 337)
(Method B):		
68.3 (1 sigma)	cal AD 1450 - 1530 (500 - 420)	1.00
95.4 (2 sigma)	cal AD 1428 - 1614 (522 - 336)	1.00
Wk-2867 <i>Chione stutchburyi</i>		
Bark Bay 11/13	Radiocarbon Age BP	770±40
Calibrated age(s)	cal AD 1507	cal BP 443
(Method A):		
one Sigma	cal AD 1477 - 1540 (473 - 410)	two Sigma cal AD 1452 - 1629 (498 - 321)
(Method B):		
68.3 (1 sigma)	cal AD 1470 - 1551 (480 - 399)	1.00
95.4 (2 sigma)	cal AD 1455 - 1622 (495 - 328)	1.00
Wk-2868 <i>Paphies australis</i>		
Bark Bay 11/13	Radiocarbon Age BP	820±45
Calibrated age(s)	cal AD 1473	cal BP 477
(Method A):		
one Sigma	cal AD 1447 - 1505 (503 - 445)	two Sigma cal AD 1422 - 1542 (528 - 408)
(Method B):		
68.3 (1 sigma)	cal AD 1445 - 1508 (505 - 442)	1.00
95.4 (2 sigma)	cal AD 1414 - 1562 (536 - 388)	1.00
Wk-2869 <i>Chione stutchburyi</i>		
Awaroa Inlet spit 3	Radiocarbon Age BP	800±40
(Method B):		
68.3 (1 sigma)	cal AD 1458 - 1519 (492 - 431)	1.00
95.4 (2 sigma)	cal AD 1432 - 1581 (518 - 369)	1.00
Wk-2870 <i>Paphies australis</i>		
Awaroa Inlet Spit 3	Radiocarbon Age BP	770±40
Calibrated age(s)	cal AD 1507	cal BP 443
(Method A):		
one Sigma	cal AD 1477 - 1540 (473 - 410)	two Sigma cal AD 1452 - 1629 (498 - 321)
(Method B):		
68.3 (1 sigma)	cal AD 1470 - 1551 (480 - 399)	1.00
95.4 (2 sigma)	cal AD 1455 - 1622 (495 - 328)	1.00

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Wk-2364 <i>Chione stutchburyi</i>			
Shag Mouth	Radiocarbon Age BP	1040±50	
Calibrated age(s)	cal AD 1315	cal BP 635	
(Method A):			
one Sigma	cal AD 1291 - 1369 (659 - 581)	two Sigma	cal AD 1248 - 1413 (702 - 537)
(Method B):			
68.3 (1 sigma)	cal AD 1290 - 1373 (660 - 577)	1.00	
95.4 (2 sigma)	cal AD 1251 - 1412 (699 - 538)	1.00	
Wk-2365 <i>Chione stutchburyi</i>			
Shag Mouth	Radiocarbon Age BP	1120±120	
Calibrated age(s)	cal AD 1275	cal BP 675	
(Method A):			
one Sigma	cal AD 1158 - 1343 (792 - 607)	two Sigma	cal AD 1024 - 1442 (926 - 508)
(Method B):			
68.3 (1 sigma)	cal AD 1140 - 1364 (810 - 586)	1.00	
95.4 (2 sigma)	cal AD 1034 - 1434 (916 - 516)	1.00	
Wk-2370 <i>Chione stutchburyi</i>			
Pleasant River Area 1	Radiocarbon Age BP	970±50	
Calibrated age(s)	cal AD 1392	cal BP 558	
(Method A):			
one Sigma	cal AD 1324 - 1422 (626 - 528)	two Sigma	cal AD 1299 - 1448 (651 - 502)
(Method B):			
68.3 (1 sigma)	cal AD 1334 - 1413 (616 - 537)	1.00	
95.4 (2 sigma)	cal AD 1304 - 1443 (646 - 507)	1.00	
Wk-2440 <i>Chione stutchburyi</i>			
Shag Mouth	Radiocarbon Age BP	1050±50	
Calibrated age(s)	cal AD 1310	cal BP 640	
(Method A):			
one Sigma	cal AD 1285 - 1344 (665 - 606)	two Sigma	cal AD 1241 - 1407 (709 - 543)
(Method B):			
68.3 (1 sigma)	cal AD 1280 - 1365 (670 - 585)	1.00	
95.4 (2 sigma)	cal AD 1242 - 1407 (708 - 543)	1.00	
Wk-2441 <i>Chione stutchburyi</i>			
Shag Mouth	Radiocarbon Age BP	1070±45	
Calibrated age(s)	cal AD 1301	cal BP 649	
(Method A):			
one Sigma	cal AD 1275 - 1324 (675 - 626)	two Sigma	cal AD 1233 - 1388 (717 - 562)
(Method B):			
68.3 (1 sigma)	cal AD 1262 - 1336 (688 - 614)	1.00	
95.4 (2 sigma)	cal AD 1231 - 1390 (719 - 560)	1.00	
Wk-2507 <i>Amphibola crenata</i>			
Pleasant River	Radiocarbon Age BP	1140±45	
Calibrated age(s)	cal AD 1258	cal BP 692	
(Method A):			
one Sigma	cal AD 1214 - 1291 (736 - 659)	two Sigma	cal AD 1164 - 1313 (786 - 637)
(Method B):			
68.3 (1 sigma)	cal AD 1214 - 1291 (736 - 659)	1.00	

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95.4 (2 sigma) cal AD 1155 - 1317 (795 - 633) 1.00

Wk-2508 *Chione stutchburyi*

Shag Mouth Radiocarbon Age BP 1060±45

Calibrated age(s) cal AD 1306 cal BP 644

(Method A):

one Sigma cal AD 1281 - 1329 (669 - 621) two Sigma cal AD 1241 - 1395 (709 - 555)

(Method B):

68.3 (1 sigma) cal AD 1271 - 1347 (679 - 603) 1.00

95.4 (2 sigma) cal AD 1240 - 1396 (710 - 554) 1.00

Wk-2633 *Amphibola crenata*

Shag Mouth Radiocarbon Age BP 1070±80

Calibrated age(s) cal AD 1301 cal BP 649

(Method A):

one Sigma cal AD 1246 - 1365 (704 - 585) two Sigma cal AD 1167 - 1428 (783 - 522)

(Method B):

68.3 (1 sigma) cal AD 1240 - 1378 (710 - 572) 1.00

95.4 (2 sigma) cal AD 1156 - 1433 (794 - 517) 1.00

Wk-2753 *Chione stutchburyi*

Pleasant River Radiocarbon Age BP 910±45

Calibrated age(s) cal AD 1426 cal BP 524

(Method A):

one Sigma cal AD 1399 - 1450 (551 - 500) two Sigma cal AD 1335 - 1477 (615 - 473)

(Method B):

68.3 (1 sigma) cal AD 1391 - 1457 (559 - 493) 1.00

95.4 (2 sigma) cal AD 1336 - 1477 (614 - 473) 1.00

Wk-2768 *Patella kermadecensis*

Low Flat, Raoul Island Radiocarbon Age BP 1100±45

Calibrated age(s) cal AD 1287 cal BP 663

(Method A):

one Sigma cal AD 1248 - 1309 (702 - 641) two Sigma cal AD 1205 - 1337 (745 - 613)

(Method B):

68.3 (1 sigma) cal AD 1244 - 1312 (706 - 638) 1.00

95.4 (2 sigma) cal AD 1190 - 1353 (760 - 597) 1.00

Wk-2769 *Patella kermadecensis*

Low Flat, Raoul Island Radiocarbon Age BP 1050±45

Calibrated age(s) cal AD 1310 cal BP 640

(Method A):

one Sigma cal AD 1288 - 1339 (662 - 611) two Sigma cal AD 1248 - 1401 (702 - 549)

(Method B):

68.3 (1 sigma) cal AD 1281 - 1358 (669 - 592) 1.00

95.4 (2 sigma) cal AD 1249 - 1401 (701 - 549) 1.00

Wk-2851 *Chione stutchburyi*

Pleasant River Radiocarbon Age BP 970±35

Calibrated age(s) cal AD 1392 cal BP 558

(Method A):

one Sigma cal AD 1332 - 1415 (618 - 535) two Sigma cal AD 1312 - 1436 (638 - 514)

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(Method B):

68.3 (1 sigma)	cal AD 1343 - 1409 (607 - 541)	1.00
95.4 (2 sigma)	cal AD 1317 - 1430 (633 - 520)	1.00

Wk-2857 *Chione stutchburyi*

Shag Mouth Radiocarbon Age BP 1050±50

Calibrated age(s) cal AD 1310 cal BP 640

(Method A):

one Sigma cal AD 1285 - 1344 (665 - 606) two Sigma cal AD 1241 - 1407 (709 - 543)

(Method B):

68.3 (1 sigma)	cal AD 1280 - 1365 (670 - 585)	1.00
95.4 (2 sigma)	cal AD 1242 - 1407 (708 - 543)	1.00

APPENDIX 3:
**Calibrated dates from moa eggshell (Calibration file: UWTEN93.14C :
 Stuiver and Becker, 1993).**

Wk-2416 Shag Mouth
 Radiocarbon Age BP 560±50
 Calibrated age(s) cal AD 1408 cal BP 542
 (Method A):
 One Sigma cal AD 1328 - 1350 (622 - 600) 1390 - 1427 (560 - 523) two Sigma cal
 AD 1297 - 1441 (653 - 509)
 (Method B):
 68.3 (1s) cal AD 1326 - 1352 (624 - 598) .37
 1362 - 1366 (588 - 584) .05
 1389 - 1429 (561 - 521) .58
 95.4 (2s) cal AD 1301 - 1374 (649 - 576) .50
 1379 - 1438 (571 - 512) .50

Wk-2417 Shag Mouth
 Radiocarbon Age BP 520±40
 Calibrated age(s) cal AD 1419 cal BP 531
 (Method A):
 one Sigma cal AD 1407 - 1437 (543 - 513) two Sigma cal AD 1329 - 1348 (621 -
 602) 1391 - 1444 (559 - 506)
 (Method B):
 68.3 (1s) cal AD 1334 - 1337 (616 - 613) .05
 1403 - 1439 (547 - 511) .95
 95.4 (2s) cal AD 1323 - 1354 (627 - 596) .16
 1357 - 1368 (593 - 582) .02
 1387 - 1450 (563 - 500) .82
 1464 - 1470 (486 - 480) .01

Wk-2604 Shag Mouth
 Radiocarbon Age BP 530±40
 Calibrated age(s) cal AD 1414 cal BP 536
 (Method A):
 one Sigma cal AD 1335 - 1335 (615 - 615) 1405 - 1435 (545 - 515) two Sigma cal
 AD 1327 - 1351 (623 - 599) 1364 - 1365 (586 - 585) 1389 - 1443 (561 - 507)
 (Method B):
 68.3 (1s) cal AD 1333 - 1340 (617 - 610) .10
 1399 - 1436 (551 - 514) .90
 95.4 (2s) cal AD 1320 - 1369 (630 - 581) .24
 1386 - 1446 (564 - 504) .76

Wk-2744 Warrington
 Radiocarbon Age BP 540±45
 Calibrated age(s) cal AD 1412 cal BP 538
 (Method A):
 one Sigma cal AD 1332 - 1342 (618 - 608) 1395 - 1433 (555 - 517)
 two Sigma cal AD 1317 - 1370 (633 - 580) 1386 - 1443 (564 - 507)
 (Method B):
 68.3 (1s) cal AD 1331 - 1345 (619 - 605) .22
 1394 - 1434 (556 - 516) .78
 95.4 (2s) cal AD 1304 - 1371 (646 - 579) .36
 1385 - 1444 (565 - 506) .64

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Wk-2758 Pleasant River D
 Radiocarbon Age BP 610±45
 Calibrated age(s) cal AD 1328, 1349, 1391 cal BP 622, 601, 559
 (Method A):
 one Sigma cal AD 1300 - 1375 (650 - 575) 1375 - 1408 (575 - 542)
 two Sigma cal AD 1288 - 1425 (662 - 525)
 (Method B):
 68.3 (1s) cal AD 1305 - 1314 (645 - 636) .12
 1316 - 1334 (634 - 616) .24
 1338 - 1371 (612 - 579) .44
 1385 - 1401 (565 - 549) .21
 95.4 (2s) cal AD 1293 - 1413 (657 - 537) 1.00

Wk-2741 Pleasant River D
 Radiocarbon Age BP 610±45
 Calibrated age(s) cal AD 1328, 1349, 1391 cal BP 622, 601, 559
 (Method A):
 one Sigma cal AD 1300 - 1375 (650 - 575) 1375 - 1408 (575 - 542)
 two Sigma cal AD 1288 - 1425 (662 - 525)
 (Method B):
 68.3 (1s) cal AD 1305 - 1314 (645 - 636) .12
 1316 - 1334 (634 - 616) .24
 1338 - 1371 (612 - 579) .44
 1385 - 1401 (565 - 549) .21
 95.4 (2s) cal AD 1293 - 1413 (657 - 537) 1.00

Wk-2759 Pleasant River D
 Radiocarbon Age BP 550±45
 Calibrated age(s) cal AD 1410 cal BP 540
 (Method A):
 one Sigma cal AD 1330 - 1346 (620 - 604) 1393 - 1429 (557 - 521)
 two Sigma cal AD 1304 - 1372 (646 - 578) 1383 - 1441 (567 - 509)
 (Method B):
 68.3 (1s) cal AD 1329 - 1348 (621 - 602) .31
 1392 - 1431 (558 - 519) .69
 95.4 (2s) cal AD 1303 - 1372 (647 - 578) .43
 1383 - 1441 (567 - 509) .57

Wk-2760 Pleasant River D
 Radiocarbon Age BP 560 ± 45
 Calibrated age(s) cal AD 1408 cal BP 542
 (Method A):
 one Sigma cal AD 1329 - 1349 (621 - 601) 1391 - 1425 (559 - 525)
 two Sigma cal AD 1300 - 1375 (650 - 575) 1376 - 1439 (574 - 511)
 (Method B):
 68.3 (1s) cal AD 1327 - 1351 (623 - 599) .38
 1364 - 1365 (586 - 585) .01
 1390 - 1428 (560 - 522) .61
 95.4 (2s) cal AD 1302 - 1373 (648 - 577) .49
 1381 - 1438 (569 - 512) .51

Wk-2765 Pleasant River D
 Radiocarbon Age BP 560±45
 Calibrated age(s) cal AD 1408 cal BP 542
 (Method A):
 one Sigma cal AD 1329 - 1349 (621 - 601) 1391 - 1425 (559 - 525)
 two Sigma cal AD 1300 - 1375 (650 - 575) 1376 - 1439 (574 - 511)
 (Method B):

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68.3 (1s)	cal AD 1327 - 1351 (623 - 599)	.38
	1364 - 1365 (586 - 585)	.01
	1390 - 1428 (560 - 522)	.61
95.4 (2s)	cal AD 1302 - 1373 (648 - 577)	.49
	1381 - 1438 (569 - 512)	.51

APPENDIX 4:
**Charcoal calibrations (Calibration file: UWTEN93.14C: Stuiver and
 Becker, 1993).**

Wk-2269 Pleasant River "as is" charcoal

Radiocarbon Age BP 480±50

Calibrated age(s) cal AD 1436 cal BP 514

(Method A):

one Sigma cal AD 1413 - 1445 (537 - 505)

two Sigma cal AD 1333 - 1341 (617 - 609) 1395 - 1491 (555 - 459)

(Method B):

68.3 (1 sigma) cal AD 1409 - 1453 (541 - 497) .84

1460 - 1476 (490 - 474) .16

95.4 (2 sigma) cal AD 1327 - 1350 (623 - 600) .05

1390 - 1519 (560 - 431) .91

1595 - 1622 (355 - 328) .04

Wk-2589 Shag Mouth "as is" charcoal

Radiocarbon Age BP 590±35

Calibrated age(s) cal AD 1332, 1342, 1395 cal BP 618, 608, 555

(Method A):

one Sigma cal AD 1323 - 1354 (627 - 596) 1357 - 1368 (593 - 582) 1388 - 1411

(562 - 539) two Sigma cal AD 1295 - 1426 (655 - 524)

(Method B):

68.3 (1 sigma) cal AD 1324 - 1354 (626 - 596) .51

1357 - 1368 (593 - 582) .13

1388 - 1410 (562 - 540) .36

95.4 (2 sigma) cal AD 1300 - 1374 (650 - 576) .65

1377 - 1418 (573 - 532) .35

Wk-2782 Killermont charcoal

Radiocarbon Age BP 640±35

Calibrated age(s) cal AD 1305, 1316, 1371, 1386 cal BP 645, 634, 579, 564

(Method A):

one Sigma cal AD 1294 - 1330 (656 - 620) 1346 - 1393 (604 - 557)

two Sigma cal AD 1285 - 1409 (665 - 541)

(Method B):

68.3 (1 sigma) cal AD 1299 - 1327 (651 - 623) .43

1351 - 1364 (599 - 586) .20

1365 - 1389 (585 - 561) .37

95.4 (2 sigma) cal AD 1290 - 1334 (660 - 616) .42

1338 - 1403 (612 - 547) .58

Wk-2789 Pleasant River D charcoal

Radiocarbon Age BP 510±90

Calibrated age(s) cal AD 1425 cal BP 525

(Method A):

one Sigma cal AD 1330 - 1347 (620 - 603) 1392 - 1448 (558 - 502)

two Sigma cal AD 1291 - 1528 (659 - 422) 1558 - 1631 (392 - 319)

(Method B):

68.3 (1 sigma) cal AD 1319 - 1370 (631 - 580) .28

1386 - 1488 (564 - 462) .72

95.4 (2 sigma) cal AD 1291 - 1527 (659 - 423) .89

1558 - 1631 (392 - 319) .11

APPENDIX 4

Wk-2790 Pleasant River D charcoal

Radiocarbon Age BP 660 ± 90

Calibrated age(s) cal AD 1299 cal BP 651

(Method A):

one Sigma cal AD 1280 - 1407 (670 - 543) two Sigma cal AD 1213 - 1437 (737 - 513)

(Method B):

68.3 (1 sigma) cal AD 1283 - 1333 (667 - 617) .46

1339 - 1399 (611 - 551) .54

95.4 (2 sigma) cal AD 1216 - 1435 (734 - 515) 1.00

Wk-2916 Killermont charcoal

Radiocarbon Age BP 620 ± 45

Calibrated age(s) cal AD 1326, 1352, 1363, 1366, 1389 cal BP 624, 598, 587, 584, 561

(Method A):

one Sigma cal AD 1297 - 1406 (653 - 544) two Sigma cal AD 1286 - 1419 (664 - 531)

(Method B):

68.3 (1 sigma) cal AD 1302 - 1332 (648 - 618) .39

1342 - 1373 (608 - 577) .42

1380 - 1395 (570 - 555) .19

95.4 (2 sigma) cal AD 1292 - 1410 (658 - 540) 1.00

Wk-2991 Killermont charcoal

Radiocarbon Age BP 590 ± 45

Calibrated age(s) cal AD 1332, 1342, 1395 cal BP 618, 608, 555

(Method A):

one Sigma cal AD 1316 - 1370 (634 - 580) 1386 - 1412 (564 - 538)

two Sigma cal AD 1292 - 1433 (658 - 517)

(Method B):

68.3 (1 sigma) cal AD 1320 - 1369 (630 - 581) .66

1387 - 1411 (563 - 539) .34

95.4 (2 sigma) cal AD 1298 - 1423 (652 - 527) 1.00

APPENDIX 5:
**New Zealand archaeological dates measured in the University of Waikato
Radiocarbon Dating Laboratory 1976-1991.**

RAOUL ISLAND

Raoul island series

(Submitted 1.10.90, by L. Johnson, Dept. of Conservation, Auckland)

Raoul island, terraces.

Wk-1906 R.I.1

(charcoal)

600±60

$\delta^{13}C = -25.7\text{‰}$

N.B: species identified as; pohutokawa-(*Metrosideros kermadecensis*); mahoe-(*Melicytus ramiflorus*); kawakawa-(*Macropiper excelsium*); karo-(*Pittosporum crassifolium*); *Coprosma*; hutu-(*Corarra lucida var lanceolata*).

Comment: (LJ) The date will provide a minimum possible age for prehistoric occupation.

N.B 2: Diluted, 56.2% sample.

Wk-1907 R.I.2

(charcoal)

MODERN (D14C=-14.2)

$\delta^{13}C = -24.9\text{‰}$

Comment: (LJ) To provide a date for prehistoric settlement on the terraces.

N.B: charcoal identified as pohutokawa-(*Metrosideros kermadecensis*). Obtained from a "disturbed context".

Wk-1908 R.I.3

(charcoal)

580±50

$\delta^{13}C = -25.1\text{‰}$

N.B: charcoal identified as pohutokawa-(*Metrosideros kermadecensis*); kawakawa-(*Macropiper excelsium*); karo-(*Pittosporum crassifolium*); mahoe-(*Melicytus ramiflorus* and *Myrsine kermadecensis*).

Comment: (LJ) The date should provide a minimum possible age for construction of the archaeological feature.

N.B 2: Diluted, 85% sample.

Coral Bay.

Wk-1909 R.I.4

(charcoal)

660±50

$\delta^{13}C = -25.4\text{‰}$

Comment: (LJ) The age of the settlement at Coral Bay.

N.B: charcoal identifications; mostly pohutokawa, some mahoe-(*Melicytus ramiflorus* and *Myrsine kermadecensis*).

Raoul island, low flat.

Wk-1910 R.I.5

(charcoal)

800±40

$\delta^{13}C = -25.5\text{‰}$

Comment: (LJ) Will provide a date for the occupation of the upper cultural layer at Low Flat.

N.B: charcoal is pohutokawa (*Metrosideros kermadecensis*); all other species unidentified.

N.B 2: Diluted, 95.8% sample.

APPENDIX 5

- Wk-1911 R.I.6**
candlenut (*Aleurites mollucana*) **MODERN** (D14C=-16.18)
 $\delta^{13}C = -24.5\text{‰}$
- Comment:* (LJ) This carbon 14 date should mark the terminal point in the development of the paleosol.
- Wk-1912 R.I.7**
(charcoal) **1070±40**
 $\delta^{13}C = -25.3\text{‰}$
- N.B: charcoal is 93% Pohutokawa- (*Metrosideros kermadecensis*); 7% karo- (*Pittosporum crassifolium*).
Sample comes from a lower cultural horizon earth oven in association with obsidian blades, adze roughouts and midden remains.
- Comment:* (LJ) Age of occupation of the lower cultural horizon.
- Wk-2282 U.C.H.2 R.A.O**
shell (*Patella kermadecensis*) **1100±45**
 $\delta^{13}C = +0.8\text{‰}$
- Comment:* (LJ): Sample should provide a min age for the occupation of the upper cultural horizon.
- NORTHLAND**
- Oruru valley, Northland**
(submitted by Y. Marshall, Anthropology department, University of Auckland)
- Wk-976 7. N10/217**
shell (*Paphies australis*) **830±50**
 $\delta^{13}C = 2.19\text{‰}$
- Comment:* (YM) To date undefended storage complex in the Oruru valley.
- Wk-977 N10/238 T.P.I**
- 770±50**
 $\delta^{13}C = 2.15\text{‰}$
- Comment:* (YM) as above.
- Wk-978 N10/238b**
- 660±50**
 $\delta^{13}C = +2.2\text{‰}$
- Comment:* (YM) To date storage complex in the Oruru valley.
- Waipoua forest, Motuhuru.**
(submitted by M. Taylor, Dept. of Conservation, Waipoua forest, Dargaville)
- Wk-1083 N18/219-1**
Shell (*Turbo smaragda*) **930±45**
 $\delta^{13}C = +3.7\text{‰}$
- Comment:* (MT) Dates of deposition of midden at Motuhuru, archaeological site N18/219. Predates forest clearance.

APPENDIX 5

Wk-1084 N18/103-67
charcoal

570±105
 $\delta^{13}C = -21.3\text{‰}$

Comment: (MT) Date of occupation of pit site N18/103.

N.B: charcoal consisted of the following species; *Myrsine* sp. Rangiora, Akeake, makamaka, *Coprosma* sp, *Olearia* sp.

Wk-1085 N18/177-132
charcoal

460±50
 $\delta^{13}C = -26.4\text{‰}$

Comment: (MT) Date of occupation of house site N18/177, Waipoua forest.

N.B: charcoal consisted of the following species; twig species; rewarewa, Hinau, Matai, Puriri, kohekohe, Tarairi, Akeake, Mahoe. Short-lived species; Rangiora, Pate, fivefinger, makamaka, *Pittosporum* sp. *Coprosma* sp, *Olearia* sp.

Kokohuia, Omapere, Sth Hokianga.

Wk-1086 Koko-10
Shell (*Paphies australis*.)

880±50
 $\delta^{13}C = +1.6\text{‰}$

Comment: (MT) Date of base of midden excavated at Kokohuia, Omapere.

Waipoua forest (site N18/102)

Wk-1087 N18/102
charcoal

360±50
 $\delta^{13}C = -22.3\text{‰}$

Comment: (MT) Date of occupation of pit site N18/102, Waipoua forest.

N.B: Charcoal consisted of mainly short-lived species; makamaka, rata vine, rangiora, putaputaweta, also some punga.

Wk-1088 N18/102-12
charcoal

480±45
 $\delta^{13}C = -25.8\text{‰}$

Comment: (MT) Date of occupation of pit site N18/102.

N.B: charcoal was unidentified shrub species, all twig wood.

Mangonui (S.H 10)

(submitted by L. Johnson, Dept. of Conservation, Auckland)

Wk-1373 C.L.10 Level 5
Shell (*Austrovenus stutchburyi*)

610±50
 $\delta^{13}C = -2.18\text{‰}$

Comment: (LJ) The sample should date the latest phase of occupation of the site and offer the upper parameter for occupation of the site as a whole.

Wk-1374 C.L.2 Level 9
Shell (*Austrovenus stutchburyi*)

570±50

$\delta^{13}C = -1.99\text{‰}$

Comment: (LJ) as above.

APPENDIX 5

Taipa, Doubtless Bay

(Submitted 18.5.90, by L. Johnson, Dept. of Conservation, Auckland)

Wk-1753 M.S.4(6)

Shell (*Paphies australis*)

700±45

$\delta^{13}C = +1.6\text{‰}$

Comment: (LJ) The relationship between the midden from which this sample was taken and the wetland drainage system that we wish to date is that the two should be contemporary. However, I can not be certain about this. Apart from the drainage system itself, the midden which occurred in the swamp was the only other feature that provided dateable material.

Wk-1754 D.S.1 (N7/442)

sediment

840±55

$\delta^{13}C = -27.6\text{‰}$

Comment: (LJ) This sample should provide a minimum possible age for construction of the wetland drainage system. It appeared from the excavated profile that the fill from which the sample was taken was deposited towards the end of the use of the system or shortly after the point at which the system became redundant.

N.B: Diluted, sample was 94.1 %.

Reef Point, Ahipara

(submitted by L. Johnson, Dept. of Conservation, Auckland)

Wk-2100 N05/301.1.

wood

400±50

$\delta^{13}C = -26.1\text{‰}$

N.B: Twigs identified as *Metrosideros excelsa*, *Cassina retorta*, *Myosorum laetum*, *Myrsine australis*, *Prumnopitys taxifolia*. All shrubs.

AUCKLAND

Cryers road series, Tamaki

(Submitted by C. Fredericksen and E. Visser, NZHPT, Private Bag, Auckland)

Wk-1126 LN1

charcoal

300±50

$\delta^{13}C = -24.8\text{‰}$

Comment: (CF/EV) Dates important in establishing the phases of activity on the terrace site-able to correlate it with C14 dates from terrace and R11/1519-activities associated with occupants of Green Mount, East Tamaki.

N.B: charcoal identified as as hebe sp, fern, ngaio, broadleaf, Tawa, *Pseudopanax crassifolius*, *Nestigis* sp, *Prumuopitys taxifolia*. This sample was diluted; 67% sample.

Wk-1127 LN3

Shell (*Austrovenus stutchburyi*)

750±45

$\delta^{13}C = +1.4\text{‰}$

Comment: (CF/EV) Dates are important in establishing the length of prehistoric Maori activity in East Tamaki and the Auckland region generally.

Wk-1128 LN4Shell (*Austrovenus stutchburyi*)**700±45** $\delta^{13}C=+0.7\text{‰}$

Comment: (CF/EV) Dates will give archaeologists a time period in which this particular site was utilised. These dates can be compared to others in the Auckland area.

Wk-1129 LN5Shell (*Austrovenus stutchburyi*)**670±40** $\delta^{13}C=+0.7\text{‰}$

Comment: (CF/EV) Dates are important in establishing the length of prehistoric Maori activity in East Tamaki and the Auckland region generally.

Wk-1130 LN6Shell (*Austrovenus stutchburyi*)**590±40** $\delta^{13}C=+1.0\text{‰}$

Comment: (CF/EV) Dates are important in establishing activities of prehistoric Maori in Tamaki and comparing them to other C^{14} dates in Auckland area.

Wk-1131 LN7Shell (*Austrovenus stutchburyi*)**510±40** $\delta^{13}C=+1.0\text{‰}$

Comment: (CF/EV) Dates are important in establishing the length of prehistoric Maori activity in East Tamaki and the Auckland region generally.

Wk-1132 LN8Shell (*Austrovenus stutchburyi*)**680±45** $\delta^{13}C=+0.5\text{‰}$

Comment: (CF/EV) Dates are important in establishing the length of prehistoric Maori activity on site R11/1519, in East Tamaki and the Auckland region generally.

Wk-1133 LN9Shell (*Austrovenus stutchburyi*)**690±45** $\delta^{13}C=+1.2$

Comment: (CF/EV) Dates will give archaeologists a time period in which this particular site was utilised. Dates can be compared to others in the Auckland area. Sample taken from a low level (in terms of archaeological stratigraphy) fire scoop. This means that this could give us the earliest date for the site.

WK 1134 LN10Shell (*Austrovenus stutchburyi*)**520±45** $\delta^{13}C=-1.3\text{‰}$

Comment: (CF/EV) Sample will date the latter phase of activity on the terrace (FA41) and combined with samples LN1 and LN9, will define the time period during which the terrace was utilised.

Theatre Lane, Auckland City
(Submitted by S. Best, Dept. of Anthropology, Auckland University)

Wk-1142 R11/1559-C14/1
Shell (*Austrovenus stutchburyi*) **850±50**
 $\delta^{13}C=+1.6\text{‰}$

Comment: (SB) The first date associated with Maori occupation in the central Auckland and its relationship to forest clearance in the area.

Wk-1143 R11/1559-C14/2
leaf litter **750±50**
 $\delta^{13}C=-25.3\text{‰}$

Comment: (SB) Dates of de-afforestation in the Waihorotiu Stream watershed, and whether this occurred within the period of human occupation.

George Bourke Drive, Tamaki
(submitted by B. Sewell, Dept. of Conservation, Auckland)

Wk-1720 268
Shell (*Austrovenus stutchburyi*) **630±45**
 $\delta^{13}C=-0.4\text{‰}$

Wk-1721 269
Shell (*Austrovenus stutchburyi*) **540±45**
 $\delta^{13}C=-0.5\text{‰}$

Te Apunga o Tainui, Panama rd, Tamaki
Wk-1722 270
Shell (*Austrovenus stutchburyi*) **680±50**
 $\delta^{13}C=-0.72\text{‰}$

Tamaki river series (R11/1201-1)
(Submitted 12.90, by R. Foster, Dept. of Conservation, Auckland)

Wk-1940 ACI/R/506 F65
Shell (*Austrovenus stutchburyi*) **730±35**
 $\delta^{13}C=+0.3\text{‰}$

Comment: (RF) Dates occupation of pa site R11/1506

Wk-1941 ACI/R/506 F33
Shell (*Austrovenus stutchburyi*) **720±35**
 $\delta^{13}C=+0.4\text{‰}$

Comment: (RF) as above.

Wk-1942 ACI/R/82
Shell (*Austrovenus stutchburyi*) **670±45**
 $\delta^{13}C=+0.2\text{‰}$

Comment: (RF) as above.

Wk-1943 ACI/R/383
Shell (*Austrovenus stutchburyi*) **750±45**
 $\delta^{13}C=+0.9\text{‰}$

Comment: (RF) as above.

APPENDIX 5

Wk-1944	ACI/R/420	
	Shell (<i>Austrovenus stutchburyi</i>)	680±50
		$\delta^{13}C=+1.1\text{‰}$
<i>Comment:</i> (RF) as above.		
Wk-1945	ACI/R/421	
	Shell (<i>Austrovenus stutchburyi</i>)	690±50
		$\delta^{13}C=+0.5\text{‰}$
<i>Comment:</i> (RF) as above.		
Tamaki		
(Submitted by B. Sewell, Dept. of Conservation, Auckland)		
Wk-1946	120/-2/90	
	Shell (<i>Austrovenus stutchburyi</i>)	690±35
		$\delta^{13}C=0.0\text{‰}$
Mt Richmond, Domain, Otahuhu		
(Submitted by B. Sewell, Dept. of Conservation, Auckland)		
Wk-2013		
	Shell (<i>Austrovenus stutchburyi</i>)	600±50
		$\delta^{13}C=0.2\text{‰}$
Crater Hill, Waiokauri creek, Papatoetoe		
(Submitted by R. Foster, Dept. of Conservation, Auckland)		
Wk-2023		
	charcoal	320±45
		$\delta^{13}C=-27.4\text{‰}$
N.B: charcoal identified as 95% <i>Hebe</i> twigs.		
Wk-2024		
	charcoal	330±45
		$\delta^{13}C=-25.8\text{‰}$
N.B: charcoal identified as 95% <i>Hebe</i> twigs and 10% <i>Pseudopanax</i> sp twigs.		
Tamaki		
(Submitted by B. Sewell, Dept. of Conservation, Auckland)		
Wk-2030		
	charcoal	340±45
N.B: charcoal identified as mamaku.		
Newmarket site		
(Submitted by D. Wilson, Dept. of Anthropology, University of Auckland)		
Wk-2051		
	charcoal	MODERN
		$\delta^{13}C=-24.8\text{‰}$
<i>Comment:</i> (DW) A radiocarbon date (charcoal) excavated at site R11/1694 Auckland from prehistoric earth oven.		
N.B: charcoal identified as <i>Coprosma</i> sp and twigs-kohekohe (<i>Dysoxylum spectabile</i>).		

APPENDIX 5

WAIKATO

Horotiu

(Submitted by B.G McFadgen, NZHPT, Wellington)

Wk-502	sample 1	150±50
	charcoal (identified as <i>Coprosma/Pittosporum</i> sp)	

Comment: (BGMcF) Sample will give a minimum date for Plaggen soil on Taupo pumice river terrace at Horotiu.

Wk-503	sample 2	670±45
	shell (<i>Paphies australis</i>)	
		$\delta^{13}C=1.91\text{‰}$

Comment: (BGMcF) as above

Hamurana series, Lake Rotorua

(Submitted by D. Kahotea, Dept. of Social Anthropology, University of Waikato)

Wk-1218		MODERN
	charcoal	
		$\delta^{13}C=-27.4\text{‰}$

Wk-1219		230±125
	charcoal	
		$\delta^{13}C=-26.6\text{‰}$

Wk-1220		280±50
	charcoal	
		$\delta^{13}C=-26.5\text{‰}$

Wk-1221		MODERN
	charcoal	
		$\delta^{13}C=-32.5\text{‰}$

Wk-1222		MODERN
	charcoal	
		$\delta^{13}C=-27.1\text{‰}$

N.B; All dates on unidentified charcoal.

COROMANDEL PENINSULA/THAMES VALLEY

Te maketu, North Coralie Bay, Gt Mercury Island

(Submitted by S. Edson, Waikato Art Museum, Hamilton)

Wk-94	charcoal	410±130
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Comment: (SE) Sample derived from a large oven area associated with an extensive working floor, some 2-300 m² of which has been seriously affected by erosion and wandering stock. Site appears to be spatially substantial but probably occupied only once.

NB: sample was unidentified, below size and diluted.

APPENDIX 5

Whangapoua forest series

(submitted by L. Furey, NZFS, P.O. Box 39, Auckland)

Wk-968 T 11/644 Area 1
wood

940±45

$\delta^{13}C = -28.5\text{‰}$

Comment: (LF) Dating of prehistoric Maori occupation of inland terrace structure at Whangapoua, Coromandel.

NB: wood identified as maire branchwood (*nestigis*)

Wk-969 T 11/636
Shell (*Paphies australis*)

780±45

$\delta^{13}C = +1.8\text{‰}$

Wk-970 T 11/643-4
Shell (*Paphies australis*)

840±45

$\delta^{13}C = +3.1\text{‰}$

Comment: (LF) To date open settlement occupation at Whangapoua, Coromandel.

Wk-971 T 11/679-22 Area B
Shell (*Paphies australis*)

850±45

$\delta^{13}C = +2.4\text{‰}$

Comment: (LF) To date use of site.

Wk-972 T 11/661
Shell (*Paphies australis*)

790±45

$\delta^{13}C = +2.4\text{‰}$

Wk-973 T 11/644, trench 2, 4.5
Shell (*Paphies australis*)

720±45

$\delta^{13}C = +2.1\text{‰}$

Comment: (LF) To date open settlement (Maori) at Whangapoua, Coromandel.

Wk-974 T 11/635
Shell (*Paphies australis*)

840±45

$\delta^{13}C = +1.9\text{‰}$

Wk-975 T 11/648-18 G40 spit 9
Shell (*Paphies australis*)

770±45

$\delta^{13}C = +2.1\text{‰}$

Comment: (LF) To date open settlement occupation at Whangapoua.

Kaimarama, Whitianga
(Submitted by H. Larsen, Ferry Landing, Whitianga, R.D. 1)

Wk-1151
shell (*Paphies subtriangulatum Austrovenus*)

640±45

$\delta^{13}C = +1.0\text{‰}$

Comment: (HL) Determination of occupancy date of site.

Whangamata
(site is at Compartment 14D, Tairua block, Coromandel forest)
(Sample submitted by S. Short, Anthropology dept. University of Auckland)

APPENDIX 5

Wk-1153 T12/654 sample 1

Shell (*Austrovenus stutchburyi*)

670±50

$\delta^{13}C=+1.3\text{‰}$

Comment: (SS) Dating of second phase of terrace occupation at T12/654 Whangamata-an open settlement site.

Wk-1154 T12/654 sample 2

Shell (*Austrovenus stutchburyi*)

700±50

$\delta^{13}C=+1.8\text{‰}$

Comment: (SS) Dating of initial occupation on Terrace 1 at T12/654, an open settlement at Whangamata.

Wk-1156 T12/654 sample 6

Shell (*Austrovenus stutchburyi*)

730±50

$\delta^{13}C=+2.0\text{‰}$

Comment: (SS) To date initial occupation of terrace 3 at T12/654, an open settlement site at Whangamata.

Wk-1157 T12/654 sample 11

Shell (*Austrovenus stutchburyi*)

580±50

$\delta^{13}C=+1.4\text{‰}$

Comment: (SS) Dating of occupation at 2 adjacent terraces at T12/654, an open settlement site at Whangamata.

Onemana

(Submitted by L. Furey, NZFS, P.O. Box 39, Auckland)

Wk-1169

Shell (*Austrovenus stutchburyi*)

870±45

$\delta^{13}C=+1.0\text{‰}$

Waikorea beach (NZMS 260;R14)

(Submitted 10.9.90, by N. Ritchie, Dept. of Conservation, Hamilton)

Wk-1899 W1

(charcoal)

560±40

$\delta^{13}C=-25.7\text{‰}$

N.B: charcoal was identified; no notes attached on nature of sample.

Raupa site, Ohinemuri river, Paeroa

(Submitted by N. Prickett, Auckland Institute and Museum)

Wk-2039

shell (*Paphies australis*)

510±50

$\delta^{13}C=0\text{‰}$

Wk-2040

shell (*Paphies/Austrovenus*)

620±50

$\delta^{13}C=0.7\text{‰}$

APPENDIX 5

Wk-2041

charcoal

MODERN

$\delta^{13}C = -27.9\text{‰}$

N.B: charcoal identified but not listed on sample form.

BAY OF PLENTY

Kawerau sites

(Submitted by I.T Lawlor, Taiapa road, Waimauku)

Wk-1740 171#1 (Site N77/579)

charcoal

460±55

$\delta^{13}C = -29.0\text{‰}$

Comment: (ITL) Age estimate of occupation of site N77/579, Kawerau, Bay of Plenty.

NB: charcoal identified as mahoe *Meliccytus* sp, *ramiflorus* or *lanceolatus*)

Wk-1741 774 (adjacent to site N77/611)

charcoal

400±55

$\delta^{13}C = -27.8\text{‰}$

Comment: (ITL) Age estimate for valley gardening adjacent to site N77/611, Kawerau, Bay of Plenty.

NB: wood identified as *hebe* sp.

Wk-1742 1070 (Site N77/588-6)

charcoal

360±55

$\delta^{13}C = -26.4\text{‰}$

Comment: (ITL) Age estimate for occupation of site N77/588-6. Comparative date for adjacent shell midden age estimate.

NB: wood identified as *hebe* sp and *manuka*.

Wk-1743 1278 (Site N77/588-6)

ponga/toatoa

520±80

$\delta^{13}C = -26.4\text{‰}$

Comment: (ITL) Age estimate of occupation of site N77/588-6. Comparative date for adjacent shell midden and hangi age estimates.

NB: Wood is *Phyllocladus* sp.

Wk-1744 1514 (Site N77/587-4)

charcoal

370±55

$\delta^{13}C = -25.5\text{‰}$

Comment: (ITL) Age estimate of occupation of site N77/587-4. Post-dates use of large kumara storage pit.

NB: Wood is *kanuka* (*kunzia ericoides*).

Wk-1745 1572 (Site N77/587-4)

charcoal

350±55

$\delta^{13}C = -29.0\text{‰}$

Comment: (ITL) Age estimate of occupation of site N77/587-4. Use of large kumara storage pit.

NB: Wood is ponga.

APPENDIX 5

Tauwhare 2, Whakatane

(Submitted by K.Jones, Dept. of Conservation, Wellington)

Wk-1765 Tauwhare 2

Shell (*Paphies australis*)

670±45

$\delta^{13}C=+1.3$

Comment: (KJ) Date gives maximum age for principal surviving defensive earthworks of a major pa in the Whakatane area.

HAWKES BAY/EAST COAST

Tolaga bay

(Submitted by K. Jones, Dept. of Conservation, Wellington)

Wk-1147 TGB 4

charcoal

350±125

$\delta^{13}C=-25.2\text{‰}$

Comment: (KJ) A maximum age for defensive ditch and bank of pa N90/398, Tolaga Bay, New Zealand.

NB: Wood is *Hebe* and *Coprosma* twigs and fern stems.

Wk-1148 TGB 10

charcoal

370±70

$\delta^{13}C=-24.0\text{‰}$

Comment: (KJ) Minimum age for pa fortification on East Coast, New Zealand.

NB: Wood is *Pseudopanax*, Tawa, *Hedycarya*, *Coprosma* twigs, fern stems, Rangiora.

Heipipi Pa, Hawkes Bay

(Submitted by M. Allen, Dept. of Anthropology, UCLA)

Wk-1956

Shell (*Paphies subtriangulatum*)

730±45

$\delta^{13}C=-0.1\text{‰}$

Comment: (MA) dates a shell midden associated with an early Hawkes Bay pa.

Wk-1957

Shell (*Paphies subtriangulatum*)

680±45

$\delta^{13}C=0.4\text{‰}$

Wk-1958

Shell (*Paphies subtriangulatum*)

700±45

$\delta^{13}C=-0.2\text{‰}$

Waimarama beach, Hawkes Bay.

Wk-1959

Shell (*Paphies subtriangulatum*)

500±40

$\delta^{13}C=+1.3\text{‰}$

Wk-1960

Shell (*Paphies subtriangulatum*)

520±40

$\delta^{13}C=+1.9\text{‰}$

APPENDIX 5

Wk-1961

Shell (*Paphies subtriangulatum*)
480±40
 $\delta^{13}C=+1.9\text{‰}$

Wk-1962

charcoal
220±50
 $\delta^{13}C=-25.8\text{‰}$

Comment: (MA) The date provides a maximum age for fill and midden used to build up major defensive terraces on an inland freshwater lake pa.

N.B: charcoal species identified as; ribbonwood, hebe, *Coprosma*, mahoe, five finger, and other shrubs.

Motukumara pa, Lake Oingo

Wk-1963

charcoal
MODERN
 $\delta^{13}C=-25.4\text{‰}$

N.B: charcoal identified as lancewood twigs, 7 finger, karaka twig. Date from a hangi on rim of terraced pa.

Wk-1964

charcoal
MODERN
 $\delta^{13}C=-24.0\text{‰}$

Comment: (MA) Date for burning of bracken fern prior to pa construction.

N.B: charcoal identified as 80% bracken fern, 7 finger, *schefflera digitata*

Manawarakau Pa, Kairakau beach

Wk-1965

Shell (*Lunella smaragda*)
560±50
 $\delta^{13}C=1.9\text{‰}$

Wk-1966

Shell (*Lunella smaragda*)
590±40
 $\delta^{13}C=2.1\text{‰}$

Wk-1967

Shell (*Lunella smaragda*)
680±40
 $\delta^{13}C=2.1\text{‰}$

Ahuriri

Wk-2130 V21/9, unit 1, #10

Shell (*Austrovenus stutchburyi*)
660±55
 $\delta^{13}C=0.1\text{‰}$

Comment: (MA) Minimum age for defensive bank on headland pa above inner harbour of Hawke's Bay.

Wk-2131 V21/9, unit 1, layer D #12

Shell (*Austrovenus stutchburyi*)
790±50
 $\delta^{13}C=0.9\text{‰}$

Comment: (MA) as above.

APPENDIX 5

Koutouroa Pa, Ahuriri

Wk-2132 No. 80 (V21/26 unit 1)

Shell (*Austrovenus stutchburyi*)

750±50

$\delta^{13}C=0.9\text{‰}$

Comment: (MA) Date for shell midden on pa site along former Inner Harbour of Hawke's Bay.

Wk-2133 No. 81 (V21/26 unit 2)

Shell (*Austrovenus stutchburyi*)

840±45

$\delta^{13}C=-0.6\text{‰}$

Comment: (MA) as above.

Wk-2134 V21/26 unit 3 No. 82

Shell (*Austrovenus stutchburyi*)

710±45

$\delta^{13}C=0.1\text{‰}$

Comment: (MA) as above.

Te Mingi Pa, Tutaekuri river

Wk-2135 V21/49 unit 1, No 3

Shell (*Austrovenus stutchburyi*)

710±40

$\delta^{13}C=0.1\text{‰}$

Comment: (MA) Date for midden high on slope of large pa on the Tutaekuri river, Hawke's Bay.

Mangawharau Pa, Waimarama Beach

Wk-2136 W22/152, unit 1, No 58

Shell (*Haliotis* sp.)

640±50

$\delta^{13}C=1.3\text{‰}$

Comment: (MA) Midden on pa site at Waimarama beach, Hawke's Bay.

Wk-2137 W22/152, unit 2, No 59

Shell (*Haliotis* sp.)

710±50

$\delta^{13}C=1.6\text{‰}$

Comment: (MA) Paua cache just outside of defensive bank at pa at Waimarama beach.

Wk-2138 W22/152, unit 3, No 61

Shell (*Paphies subtriangulatum*)

570±45

$\delta^{13}C=1.7\text{‰}$

Comment: (MA) Midden on pa site at Waimarama beach, Hawke's Bay.

APPENDIX 5

WELLINGTON

Mana island (R26/141)

(Submitted 13.6.90, by M. Horwood, Wanganui Regional Museum, Wanganui)

Wk-1755 141/6

Shell (*Paphies subtriangulatum*)

820±45

$\delta^{13}C = +1.21\text{‰}$

Comment: (MH) Initial human occupation at northern end of site R26/141, Mana island, New Zealand.

Paekakariki

(Submitted by B.G. McFadgen, Dept. of Conservation, Wellington)

Wk-1756 Paek M1

Shell (*Paphies mesodesma sub.*)

680±35

$\delta^{13}C = +1.2\text{‰}$

Comment: (BGMcf) Provides maximum age for "Taupo dune" and close date for shell midden.

N.B: Diluted, sample was 62.5%.

Wk-1757 Paek M2

Shell (*Paphies mesodesma sub.*)

610±70

$\delta^{13}C = 1.4\text{‰}$

Comment: (BGMcf) Provides a minimum date for the formation of a foredune containing beds of lapilli-sized Taupo pumice and a close date for a Maori occupation.

NELSON/MARLBOROUGH

Waimea plains (Site S20/20 (Imp.), N27/122 (metric))

(Submitted by B.G. McFadgen, Dept. of Conservation, Wellington)

Wk-1776

charcoal

360±50

$\delta^{13}C = -26.1\text{‰}$

N.B: Wood identified as charcoal from matai bark (*Prumnopitys taxifolia*).

Awaroa Inlet

(Submitted by I. Barber, Department of Anthropology, University of Otago)

Wk-1827

charcoal

430±60

$\delta^{13}C = -28.4\text{‰}$

N.B: charcoal identified as Mahoe (*Melicytus ramiflorus*), five finger (*Pseudopanax arboreous*), kamahi (*Weinmannia* sp.), *Olearia* sp., Rata (*Metrosideros* sp.) and beech (*Nothofagus* sp.) fragments.

Wk-2094

charcoal

460±50

$\delta^{13}C = -26.8\text{‰}$

N.B: charcoal identified as *Melicytus ramiflorus*, *Myrsine australis*, *Coprosma* sp, *Dodonaea viscosa*, *Kunzia ericoides*, *Dracophyllum* sp, *Olearia* sp, *Pittosporum* sp, bark of unidentified species.

WESTLAND**Big Bay**

(Submitted by R. Hooker, Dept. of Conservation, Hokitika)

Wk-1167Shell (*Paphies subtriangulatum*)**960±45** $\delta^{13}C=+1.7\text{‰}$ **Wk-1168**Shell (*Paphies* and *turbo smaragda*)**900±45** $\delta^{13}C=+2.4\text{‰}$ **Arawata river mouth**

(submitted by R. Hooker, Dept. of Conservation, Hokitika)

Wk-1388 S 97/12Ashell (*Paphies subtriangulatum*)**850±50** $\delta^{13}C=+1.6\text{‰}$ **Jackson Bay****Wk-1389 S 97/4A**

charcoal

650±45 $\delta^{13}C=-28.4\text{‰}$ **Seacombe Ck, Jackson Bay.****Wk-1390 S97/15A**

charcoal

410±50 $\delta^{13}C=-29.0\text{‰}$

N.B. No species given with charcoal identification in submission forms but charcoal was identified by Rod Wallace.

Okuru, (South Westland)

(Submitted by R. Hooker, Dept. of Conservation, Hokitika)

Wk-2043shell (*Paphies subtriangulatum*)**830±40** $\delta^{13}C=1.3\text{‰}$ **Wk-2044**shell (*Paphies subtriangulatum*)**790±40** $\delta^{13}C=1.3\text{‰}$ **Wk-2045**shell (*Paphies subtriangulatum*)**920±40** $\delta^{13}C=1.2\text{‰}$ **Wk-2046**shell (*Paphies subtriangulatum*)**870±50** $\delta^{13}C=1.3\text{‰}$ **Wk-2047**shell (*Paphies subtriangulatum*)**810±50** $\delta^{13}C=1.2\text{‰}$

APPENDIX 5

CANTERBURY

Cheviot

(submitted by M.S McGlone, Botany Division, DSIR, Christchurch)

Wk-1671 x88/9
 peat

580±50

$\delta^{13}C = -28.9\text{‰}$

Comment: (MMcG) this dates the beginning of Maori burning of the surrounding vegetation.

OTAGO/SOUTHLAND

Papatowai

(Submitted by I.W.G Smith, Dept. of Anthropology, Univ. of Otago, Dunedin)

Wk-1761 THK/1
 charcoal

650±45

$\delta^{13}C = -25.9\text{‰}$

NB: Wood identified as twig from following species; manuka, ribbonwood, fivefinger, *Pseudowintera colorata*, beech, *Coprosma* sp, *pittosprum* sp, *archeria traversii*.

Wk-1762 THK/9
 charcoal

640±45

$\delta^{13}C = -25.4\text{‰}$

NB: Wood identified as manuka, raukawa, mapau, ribbonwood, *Dracophyllum* sp.

Warrington

(Submitted by B.J. Allingham, Seacliff R.D.1, Warrington)

Wk-1737 W5
 Shell (*Paphies subtriangulatum*.)

1040±50

$\delta^{13}C = +1.2\text{‰}$

Comment: (BJA) Dates base of lowest cultural layer at Warrington site 144/177.

Wk-1738
 Shell (*Austrovenus stutchburyi*)

870±50

$\delta^{13}C = +1.2\text{‰}$

Comment: (BJA) Sample dates period of moa decline in the Blueskin bay area of the Otago coast. The sample should also date the upper Maaori cultural layer of site 144/177.

Wk-1739
 Shell (*Austrovenus stutchburyi*)

840±45

$\delta^{13}C = +1.2\text{‰}$

Comment: (BJA) Sample dates an early period of occupation at site 144/177.

Wk-1865 W8
 Shell (*Paphies subtriangulatum*)

1240±40

$\delta^{13}C = +1.7\text{‰}$

Comment: (BJA) This sample is from a natural beach deposit of shells and thus predates human occupation in this area.

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