# RADIOCARBON ANALYSIS OF A NOVEL BONE SAMPLE TYPE: SNAPPER AND BARRACOUTA BONE FROM NEW ZEALAND ARCHAEOLOGICAL SITES

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## ABSTRACT

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

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

Convergence). In addition, inbuilt age is often cited as reasons for anomalous $^{14}C$ determinations. This also appears to be of nominal influence, due in part to the precision of the radiocarbon technique, but also because of the relatively rapid replacement of collagen.

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

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

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

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

resulted in bones of poorer preservation. This, in combination with inadequate pretreatment (typically an acid wash, or acid/alkali/acid pretreatment) has resulted in some erroneous determinations.

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

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# CHAPTER 1

# INTRODUCTION

New Zealand has a short prehistoric chronology with Polynesian colonisation believed to have occurred less than 1000 years ago (Anderson 1991; Higham and Hogg 1997). Consequently, the reliability of different samples for radiocarbon dating has become a key issue in New Zealand archaeology (Anderson 1991, 1996, 1998a, 1998b; Higham 1994; Schmidt 1996; Anderson, Smith and Higham 1996; Sparks, Beavan and Redvers-Newton 1997; Sparks 1998; Higham *et al.* in prep).

## WHICH SAMPLE TYPE ?

According to Higham (1993:80) the ideal choice of sample type;

-must relate precisely to the event being dated,
-must be found regularly in archaeological sites, and
-must be as resistant as possible to post-depositional contamination.

Charcoal and marine shell are the two main sample types routinely used to date archaeological sites in New Zealand. Neither of these materials are, however, ideal as both shell and charcoal are prone to sample specific problems. Charcoal radiocarbon determinations, for example, may be affected by inbuilt age (either storage age or growth age) which can result in errors of hundreds of years unless short-lived species (McFadgen 1982:384) or twigs are selected (Anderson 1991:781; Schmidt 1996:57) and even then a non-systematic error may occur. Modern contamination by humic acids may also be a problem, but in the New Zealand environment Higham (1993:155) concluded that they will have a negligible affect on the true age of the charcoal. Similarly, estuarine shells may be prone to a hardwater effect where old carbon becomes incorporated via dissolved bicarbonate from marine and terrestrial sources (*e.g.* limestone) (Anderson 1991:777; Higham 1993:129; Schmidt 1996:63-64). Deposit feeding (Higham 1993; Higham and Hogg 1995:409; Anderson, Smith and Higham 1996) or ingestion of terrestrial organic carbon may also result in problematic determinations (Higham 1993:145-146; Schell 1983; Schmidt 1996:65-66). Anomalous results have been recorded for marine shell $^{14}C$ estimations near upwelling zones (Kalish 1993:551), but the influence of $\Delta^{14}C$ depleted deep ocean water appears to be minor in the New Zealand situation (Higham 1993:137). This has not, however, been extensively investigated. It is also possible that sub-fossil shell may become incorporated in the lowest deposits of sites (Schmidt 1996:178). Recently, the use of

eggshell for dating has met with success (Higham 1994). Unfortunately, eggshell has a somewhat limited distribution even within Moa hunting sites. Clearly, there is no one ideal sample type, therefore ideally the selection of a suitable $^{14}C$ material should depend on the specific question asked with any potential sample specific problem kept in mind.

Until recently moa bone was the preferred sample type when dating sites containing moa remains. Its principal advantage was that it dated the archaeological event in question, that is the death of a moa (Trotter 1968; Law 1971; McCulloch and Trotter 1975a; Trotter and McCulloch 1984; Caughley 1988). Discrepancies in bone determinations have, however, resulted in considerable uncertainty as to their accuracy. Explanations for anomalous bone ages include carbon fractionation due to dietary preferences, inadequate sample pretreatment, varied radiocarbon standards, diagenetic effects and/or contamination (Rafter 1978:138; Grant-Taylor 1974:160; Jansen 1984:17; Caughley 1988:247; Anderson and McGovern-Wilson 1990:44-45; Anderson 1991:777, 779). Consequently, bone "collagen" has been considered to be of low priority as a datable material by the New Zealand archaeological community (Anderson 1991:779; Higham 1993:97; Schmidt 1996:9; Anderson, Smith and Higham 1996). Recent debate over the accuracy of *Rattus exulans* bone gelatin results (Anderson 1996, 1998a, 1998b; Holdaway 1996; Beavan and Sparks 1997; Ladefoged, Matisoo-Smith and Allen 1997; Smith and Anderson 1998; Sparks 1998) has, however, highlighted the importance of bone as a radiocarbon medium as well as the need for further analysis.

## A CHANGING CHRONOLOGY: THE ROLE OF "BONE" RADIOCARBON ANALYSES IN NEW ZEALAND.

The first review of different sample types for dating in New Zealand was undertaken by Rafter *et al.* (1972). McCulloch and Trotter (1975a) published an extended review of radiocarbon determinations on different materials, including moa bone, for early ("Moa hunter") sites in the South Island. The collagen ages displayed a "remarkably constant" geographical distribution, with a tendency to become younger going to the south (*i.e.* 735 - 421 years ago)(McCulloch and Trotter 1975a:5). Shell results were considered to be less reliable due to uncertainties with the shell standard, despite reflecting the same general pattern as bone (McCulloch and Trotter 1975a:7). Charcoal was the least consistent of the sample types (McCulloch and Trotter 1975a:11, 13), a factor attributed to humic contamination and inbuilt age (McCulloch and Trotter 1975a:9; Trotter and McCulloch 1984:718)(Figure 1.1).

McCulloch and Trotter (1975a:13) used the shell and bone collagen chronology to suggest a main early cultural era between 800 - 400 BP[1], a little later than expected. The moa results also indicated a build up of population in the north between 600 and 700 BP, which moved southward over the next 200 - 300 years, expanding inland and along the West Coast later than initial settlement in eastern coastal regions (see also Trotter and McCulloch 1984). Moore and Tiller (1975) criticised this picture of rapid southward spread. They noted a reliance on charcoal determinations in the North Island compared to the use of bone and shell results in the South. Given that a possible difference of up to 200 years between these materials could exist (*i.e.* Rafter *et al.* 1972:643; McCulloch and Trotter 1975a) Moore and Tiller (1975) doubted if North and South Island dates were directly comparable, and therefore whether the apparent chronological trends were a true reflection of events (Moore and Tiller 1975:99-100).

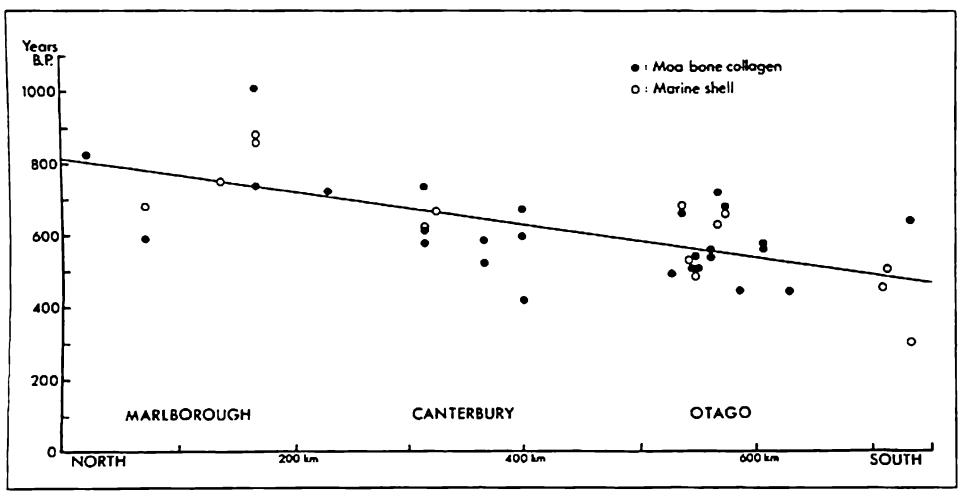


Figure 1.1: Comparison of moa bone and marine shell radiocarbon determinations for Moa-hunter sites on the east coast of the South Island (from Trotter and McCulloch 1984:721, figure 32.7)

By 1984 a number of discrepancies between shell and bone determinations had occurred which Trotter and McCulloch (1984:720) could not account for. Consequently, they could not form any definite conclusions about the spread of moa hunting, though the evidence suggested a "brevity of co-existence" between moa and humans in any one region, with extinction taking around 300 years (Trotter and McCulloch 1984:720). Trotter and McCulloch (1984:722-725), therefore sought to demonstrate the magnitude of human impact on moa and the environment using radiocarbon estimates obtained from natural moa bone deposits, sub-fossil logs, pollen analysis and buried charcoal indicative of forest destruction.

[1] Radiocarbon years before present (*i.e.* 1950).

Caughley (1988:247, 250) would later note that the choice of most reliable radiocarbon sample type was open to debate. Caughley (1988:249-250) was, however, of the opinion that moa bone results had an advantage, as they were more consistent than determinations on marine shell, had less within-site variation and dated the death of the moa. He went on to use regression analysis to demonstrate that the tendency of collagen determinations to become younger down the east coast of the South Island was statistically sound. While this supported Trotter and McCulloch's (1984) model, Caughley (1988:245) adapted the model by suggesting a point of first landfall at Kaikoura (Figure 1.2) with a spread both north and south at an accelerating rate (Trotter and McCulloch (1984:720) had suggested an entry point at D'Urville Island). Caughley (1988:260-261) conceded, however, that an absolute chronology could not be developed due to the limited number of measurements. In particular, early results in the North Island could falsify the model. Indeed, orthodox theory at this time (Bellwood 1978:386; Green 1975:609; Davidson 1984:223) advocated rapid colonisation with no imprint on the radiocarbon results (Caughley 1988:254).

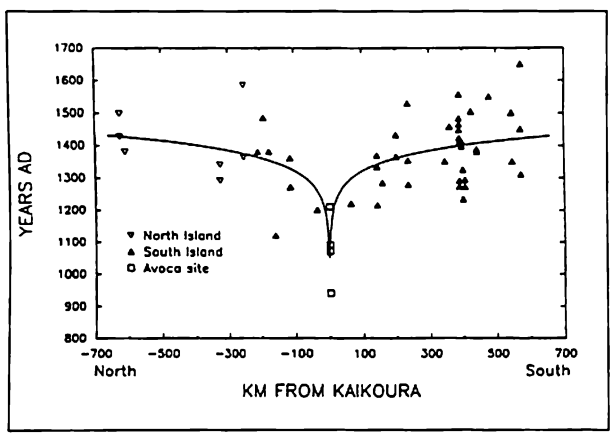


Figure 1.2. Exponential regression of dates on distance from the Kaikoura Peninsula (from Caughley 1988:257, figure 4).

Consequently, Anderson (1982a:47) concluded that the "...chronology of the southern Archaic is at present in a state of confusion...", making assessment of the transition between the Archaic and Maori culture difficult (Anderson 1982b:112). Anderson (1982a:47) challenged previous opinions on the most suitable sample type (see also Coutts 1972:524) because the discrepancy between charcoal and shell or moa bone collagen results (*i.e.* 200 - 300 years) was not uniform (Figure 1.3). He also believed that the longer chronology could not be rejected on the basis of inbuilt age because some charcoal determinations, of short lived species, had given acceptable values of 800 - 900 years ago.

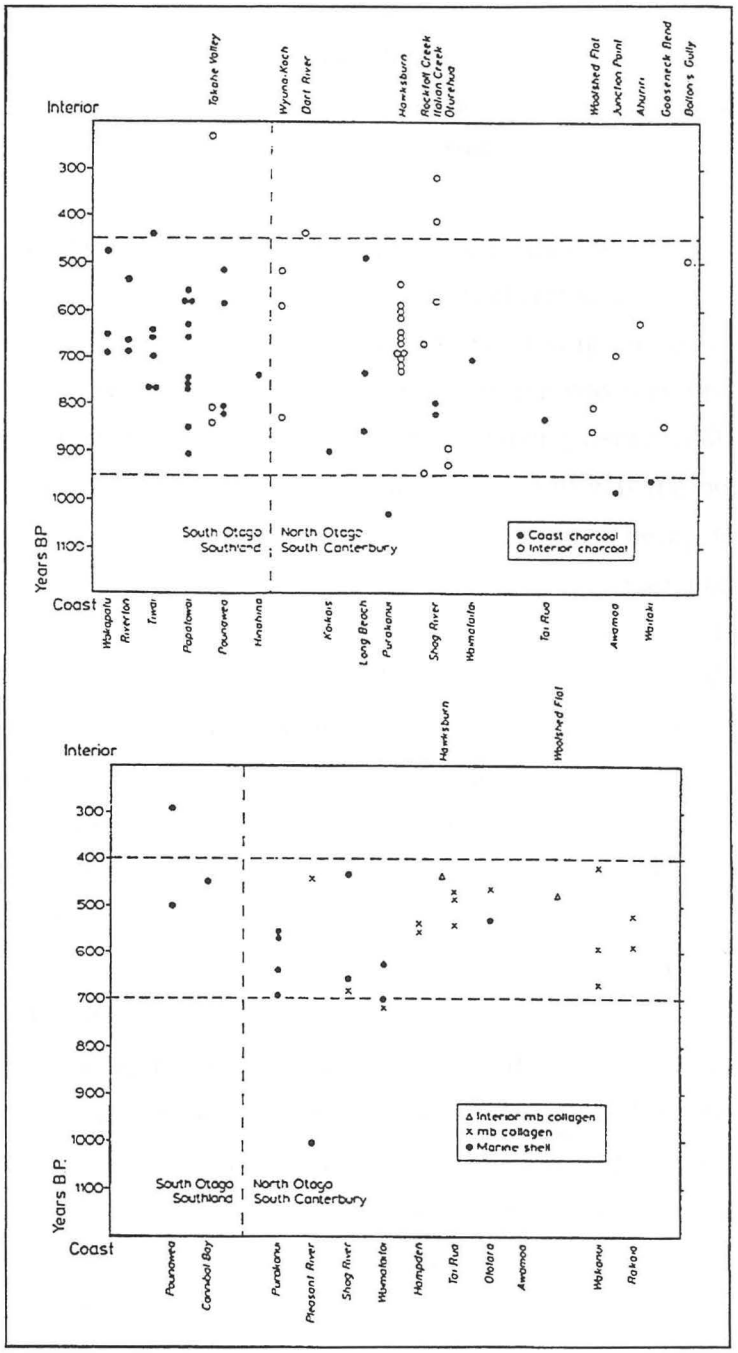


Figure 1.3: Comparison of sample types used to date New Zealand southern Archaic archaeological sites by Anderson (1982a:48, figure 2).

By 1984 Anderson (1984:733) had adopted the charcoal chronology ostensively because it was the most comparable to radiocarbon determinations used for reconstructing vegetational changes. Anderson (1984:733, see also 1991:779) also believed that McCulloch and Trotter's (1975a) and Trotter and McCulloch's (1984) objections to charcoal ages were no longer valid as recent samples had been treated for soil contamination and screened for species and lifespan composition. Application of this charcoal chronology resulted in the date of moa hunting being pushed back to around 1000 years ago, with intensive subsistence activity occurring between 900 and

600 years ago depending on regional variation. Opportunistic hunting continued along the coast until about 500 years ago and in the western interior until 300 - 200 years ago, with the possible survival of moa in the remote districts until European arrival (*i.e.* 600 - 700 years of moa hunting) (Anderson 1984:734).

To resolve the question of most suitable sample type, Anderson (1989) compared the overall pattern of reservoir corrected marine shell, charcoal and moa bone collagen radiocarbon determinations from Moa hunter sites. Using cumulative probability curves Anderson (1989:175) suggested that moa hunting was well underway by 900 BP with a phase of relatively intensive hunting occurring between 400 and 800 BP (Figure 1.4). The results also suggested that marine shell was the odd sample type out, with the charcoal and moa bone collagen curves both being leptokurtic and slightly positively skewed (Anderson 1989:175). This was at variance not only with previous radiocarbon sample comparisons, which tended to indicate a closer relationship between shell and moa bone collagen (*i.e.* Trotter and McCulloch (1975a) and Caughley (1988)), but also with subsequent assessment by Anderson and McGovern-Wilson (1990). Anderson and McGovern-Wilson (1990:48-49) had instead suggested that neither the shell nor charcoal measurements demonstrated the correlation between age and distance evident in Caughley's (1988) or McCulloch and Trotter's (1984) analyses of the collagen results.

Anderson and McGovern-Wilson (1990:49) thought a fairer method of comparison would be to assess mean results for each site rather than individual determinations. Using charcoal, as well as bone and shell ages, they concluded that a better match was given by a model of chaotic colonisation in combination with "explosive coastwise colonisation", no direction of dispersal and a longer period of co-existence between moa and people. This was supported by sites that had evidence of an early extensive hunting period that subsequently tapered off, with a possible survival of moa until the 16$^{th}$ century as suggested by young results obtained from Tautuku and Pleasant River (Anderson and McGovern-Wilson 1990:52). This was in effect a restatement of the Green, Bellwood and Davidson model (Anderson and McGovern-Wilson 1990:55).

Kirch's (1986) re-analysis of the prehistoric sequence of East Polynesia suggested colonisation of New Zealand before the more orthodox estimate of 1200 years ago. Consequently, Sutton (1987) suggested that New Zealand had been colonised earlier than hitherto anticipated (*i.e.* 1400 - 1900 years ago), and used palynological and palaeo-environmental indicators from natural sites to argue for human presence at such an early date (Anderson 1991:767-768). This air of general uncertainty prompted Anderson (1991) to take a renewed look at the chronology. He culled radiocarbon

determinations on the basis of inbuilt age, contamination and reproducibility (1991:779). Moa bone and shell results were excluded as it could not be determined "...which dates exhibit significant errors, or to what extent..." (Anderson 1991:781-782). This decision appears to have been largely based on inconsistent results obtained on collagen from Shag River Mouth (Figure 4.2), as well as large standard errors associated with some bone and shell determinations (*i.e.* Avoca Point and Titirangi) (Anderson 1991:782; Anderson, Smith and Higham 1996:67). Using the charcoal date list, Anderson (1991:792) concluded that exploration appeared to have been rapid, and that no reasonably acceptable $^{14}C$ estimate extended two standard deviations earlier than the 12$^{th}$ century AD.

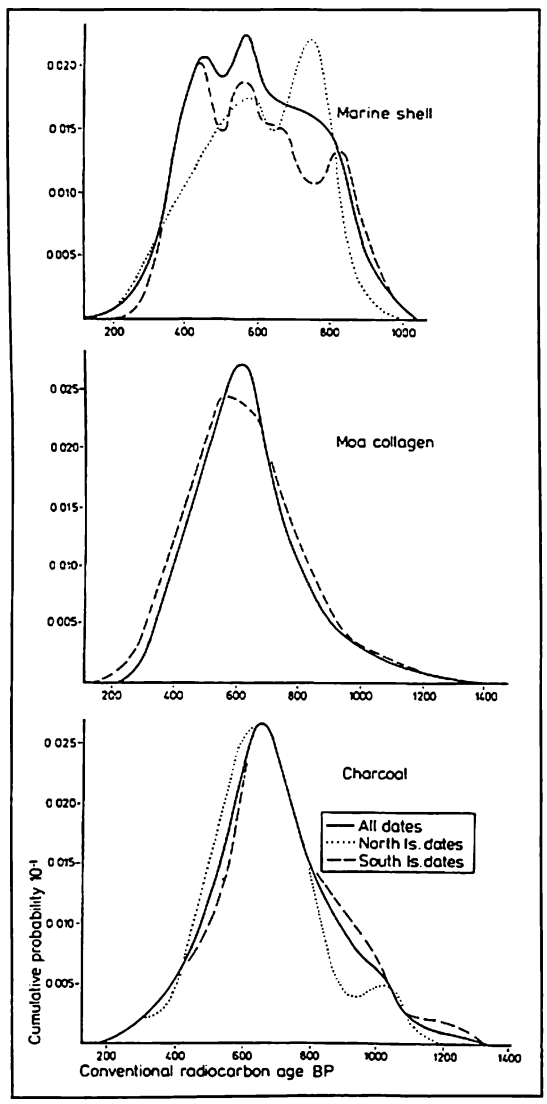


Figure 1.4: Cumulative probability curves from Anderson (1989:175, figure 13.3).

McGlone, Anderson and Holdaway (1994) reconsidered the more orthodox view of New Zealand's prehistory as outlined by Davidson (1984) and Anderson (1991). Given this short chronology and growing evidence for the brevity of occupation at many sites (*e.g.* Houhora (Anderson and Wallace 1993), Papatowai (Anderson and Smith 1992) and Shag River Mouth (Anderson 1991; Anderson, Smith and Higham 1996)), McGlone, Anderson and Holdaway proposed a "southern" view of New Zealand settlement. This perspective emphasised wild food and the total landscape utilisation associated with hunting and gathering. In addition, they concluded that settlement was late, by a large population and that agriculture was of less importance than wild food (McGlone, Anderson and Holdaway 1994:138). The short chronology continued, however, to be challenged (*e.g.* Sutton 1994; Elliot *et al.* 1995).

In order to substantiate the date of initial human colonisation of New Zealand, Anderson and Holdaway (*in* Anderson 1996:178) undertook a dating program using the Polynesian rat (*Rattus exulans*). Mitochondrial DNA from *Rattus exulans*, a human commensal, had already been used to trace the exploration and colonisation of early Polynesian voyagers (Matisoo-Smith 1994; Allen *et al.* 1996). A series of old *Rattus exulans* gelatin results, including a 2000 year old determination from the South Island (Holdaway 1996) were, however, questioned by Anderson (1996:179, 183) who emphasised inherent problems with bone pretreatment, preservation and fractionation. Anderson's doubts were reinforced by rat gelatin results from the archaeological site at Shag River Mouth (and Pleasant River (Smith and Anderson 1998)), which were significantly older than the established chronology for the site. Conversely, Beavan and Sparks (1997:8) suggested that the Shag River Mouth rat bone samples had been badly degraded. Given the age of the rat gelatin results, the archaeological community suggested caution (McFadgen 1997:6-7; Higham and Hogg 1997:150; though see Brailsford 1997:3 and Ladefoged, Matisoo-Smith and Allen 1997).

A number of chronometric hygiene exercises, primarily on shell and charcoal, have recently been used to refine the short chronology (Schmidt 1996; Higham and Hogg 1997:152; Higham *et al.* in prep). The rat bone results have not, however, been invalidated. The possibility of contact 2000 years ago remains a hotly debated subject due, in part to the close, recognisable relationship with humans which makes rat bone a powerful dating tool. Yet when one considers the large numbers of possible uncertainties associated with dating bone, it is apparent that a thorough assessment of bone radiocarbon analysis in New Zealand is long overdue. Until such a review has occurred, it seems prudent to remain sceptical of any bone determinations that seriously challenge orthodox opinion.

## AIMS OF THIS STUDY

The aim of this research is to establish parameters associated with the dating and assessment of the reliability of radiocarbon dating of fish bone. Fish bone has a number of advantages which could make it a valuable addition to the list of potential radiocarbon sample types. First, fish bone can be related to a recognisable event, in this case fishing, and is unlikely to have been introduced from natural deposits like moa bone or shell. Fish has also been economically important throughout prehistory in New Zealand and across both the North and South Islands (Leach and Boocock 1993, 1994, 1995), unlike moa which appears to have been restricted geographically and temporally (Davidson 1984:3; McGlone, Anderson and Holdaway 1994:138). In addition, recent isotopic and archaeological studies have indicated the importance of marine food in the prehistoric New Zealand diet (*e.g.* Shawcross 1972; Taylor 1984; Smith 1985; Leach and Boocock 1993). This is supported by the location of early settlements which show a preference for coastal environs (Anderson 1991:792; Higham 1993:165). Calibrated marine measurements also have the added benefit of avoiding the multiple date ranges associated with terrestrial materials, due to a smoothing of the Suess "wiggles" in the marine calibration curve (Higham 1993:120).

The dating of fish bone is not, however, without its uncertainties. Grant-Taylor (1974:160) suggested inbuilt age may be a problem. Law (1981:234) and Grant-Taylor (1974:160) have also voiced concern over reservoir variations that may influence fish which travel outside New Zealand coastal waters, especially the likelihood of introducing old carbon from Antarctic waters or the deep ocean. Neither possibility has been adequately investigated as only two fish bone determinations have been obtained from New Zealand archaeological sites: A whole bone result on unidentified fish from False Island (NZ-142: 516 ± 73[2] BP) was measured by IGNS[3] in 1956. The calibrated age range of this sample (Cal AD 1686 - 1900 and 1927 - 1950 at 1σ) does not overlap the one secure estimate for the site (NZ-141: 789 ± 39 BP) on a sample of *Paphies australis* (Cal AD 1468 - 1528 at 1σ) (Lockerbie 1959:106). Whole bone or carbonate measurements are, however, rarely reliable (*e.g.* Rafter *et al.* 1972:643; Stafford *et al.* 1991:62; Hedges and van Klinken 1992:285). An unidentified sample of fish "collagen" (NZ-1299) from Hot Water Beach has also been dated. The CRA[4] of 647 ± 92 BP (Cal AD 1533 - 1705 at 1σ) does not overlap

[2] Recalculated by IGNS.

[3] For this thesis the abbreviation IGNS refers to the DSIR, INS, IGNS and Rafter Laboratory, Wellingon, New Zealand.

[4] Conventional Radiocarbon Age.

the only reliable result for the site, NZ-1297 (832 ± 44 BP; Cal AD 1443 - 1499 at 1σ) on a sample of *Paphies australis*. These fish bone measurements were excluded in Anderson's (1991:768) list of suitable sample types due to uncertainties with the marine reservoir effect and uptake of $\Delta^{14}C$[5]. These limited results do not, however, constitute a reliable test of material suitability.

Because fish bone is a relatively new radiocarbon sample type, a number of important considerations need to be kept in mind. In the dating of a novel sample type it is important to understand the origin and $\Delta^{14}C$ of the carbon in the sample as well as pathways of possible isotopic fractionation. Second, in order for an effective pretreatment to be chosen it is necessary to test for contamination and excessive degradation. Finally, it is necessary to compare radiocarbon determinations of bone with other stratigraphically contemporary materials in order to validate the results. Therefore, this research aims to:

1) Develop a technique which can be used routinely to identify those samples which may be prone to contamination or degradation and which cannot, therefore be accurately dated,
2) Devise a pretreatment method, or methods suitable for conventional dating techniques that will remove contamination and give an accurate, reproducible result,
3) Establish a reservoir correction for the fish species selected, and
4) Identify sources of error that may influence $^{14}C$ determinations on marine animals, as well as any abnormalities specific to those fish species selected.

This investigation will introduce a new sample type to the New Zealand archaeologist. Perhaps of greater importance to archaeologists, this research also aims to clarify problems with previous $^{14}C$ measurements of bone, and provide a base for more successful bone determinations in the future.

Chapter two introduces bone as a sample medium. This chapter focuses on fish bone, and discusses the theory concerning bone decay and contamination, including the various cultural practices and environmental influences that may affect bone survival and/or radiocarbon results. This is expanded on in Chapter three which reviews the most commonly used bone pretreatment and assessment techniques and discusses a number of problems and benefits associated with each method.

[5] The per mil (‰) depletion in $^{14}C$ normalised for isotopic fractionation ($\delta^{13}C$) and defined with reference to the absolute international standard activity of Oxalic acid HOX1 after Stuiver and Polach (1977) (Petchey and Higham in prep).

Chapter four considers the dating of archaeological bone in New Zealand, the pretreatments used, how and why these have changed over the years, what tests were run and interpretation of the results. This chapter also looks at the outcome of those interpretations.

Chapter five describes the selection of fish species as well as the setting and stratigraphy of the archaeological sites chosen for this analysis. These sites include Archaic, Classic and Transitional occupations from around New Zealand in order to evaluate the influences of time, variations in the marine environment, and the affects of differing climate and geology on bone preservation.

Chapter six outlines the pretreatment and analytical methods used to assess bone prior to radiocarbon analysis. The possibility of an accurate determination on each sample is evaluated on the basis of these assessment results. In Chapter seven the radiocarbon estimates obtained on the fish bone samples are given. These are compared to results on other materials from associated contexts.

In Chapter eight the results of this study are summarised. Bone determinations obtained from New Zealand sites over the past 30 years are re-evaluated in the light of these findings and a discard protocol applied. Finally, recommendations for dating New Zealand archaeological bone and avenues of future research are outlined.

# CHAPTER 2

# BONE: A RADIOCARBON DATING MEDIUM

*"We have had no experience with bone as such and believe that 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" (Libby 1952:44)*

## INTRODUCTION

Several researchers in New Zealand have described possible sources of error involved in dating fish, radiocarbon determinations of bone, and results of marine organisms in general. These include:

* The possiblity of inbuilt age in fish due to slow tissue turnover (M. Taylor[1], *pers. comm.* 29/1/97; Grant-Taylor 1974:160) or the accumulation of tissue that integrates changing atmospheric values over time (Beavan and Sparks 1998:603).

* The influence of diet and different carbon reservoirs on the $\Delta^{14}C$ value of bone collagen (Rafter 1978:138; Jansen 1984:17; Anderson 1991:768; Anderson 1996). In the case of fish bone this concern has specifically included the influence of coastal compared to deep ocean reservoirs and/or geographical variation in $\Delta^{14}C$ (Grant-Taylor 1974:160; Law 1981:234).

* The effects of post-depositional contamination and decay of bone collagen on $^{14}C$ results (*i.e.* Grant-Taylor 1974:160; Caughley 1988:247; Anderson and McGovern-Wilson 1990:44-45; Anderson 1991:777, 779; Beavan and Sparks 1997:8; Sparks, Beavan and Redvers-Newton 1997:207).

In this chapter, these variables are explored with reference to collagen chemistry, structure and isotopic signature, with specific reference to marine organisms. In addition, the influence of diagenesis, post-depositional contamination and cultural influences on the bone are also examined.

[1] Michael Taylor, "Archaeology North", Hokianga, New Zealand.

## RADIOCARBON

The radiocarbon method is based on the rate of decay of the carbon isotope ($^{14}C$). There are three isotopes of carbon which occur naturally - $^{12}C$, $^{13}C$ (both stable) and radioactive $^{14}C$. $^{12}C$ makes up *ca.* 99% of carbon in living material, $^{13}C$ *ca.* 1% and $^{14}C$ *ca.* $1x10^{-10}$%. $^{14}C$ is formed in the upper atmosphere through the interaction of neutrons ($^{1}n$) produced by cosmic rays with nitrogen 14:

$$^{14}N + {}^{1}n \longrightarrow {}^{14}C + {}^{1}p$$

The $^{14}C$ formed is rapidly oxidised to $^{14}CO_2$. This is taken in by plants through photosynthesis and enters the food chain. $^{14}C$ also enters the Earth's oceans in an atmospheric exchange and as dissolved carbonate. During their lifetime plants and animals exist in equilibrium with the $^{14}C$ concentration of the atmosphere or ocean reservoirs. As soon as a plant or animal dies, carbon uptake stops but $^{14}C$ decay continues (Bowman 1990:10; Higham 1995). As $^{14}C$ decays it emits a weak beta particle ($\beta$-), or electron. The decay can be shown:

$$^{14}C \longrightarrow {}^{14}N + \beta-$$

The rate of radioactive decay is called the half-life ($t\ ^{1}/_{2}$), or the time taken for half the original $^{14}C$ in the sample to decay. Because the half-life of $^{14}C$ is 5739 $\pm$ 40 years (Cambridge half-life), the technique has a limit of 50 - 60, 000 years (Taylor 1987:9). By measuring the $^{14}C$ concentration of a sample of unknown age, it is possible to calculate a $^{14}C$ estimate for the death of the organism. The production and movement of $^{14}C$ in the atmosphere has not, however, been constant and this value (the CRA) needs to be calibrated in order to derive a calender age. For marine samples the calibration curve of Stuiver and Braziunas (1993) is used, and a local correction factor ($\Delta R$) applied to account for regional variation.

## FISH BONE CHARACTERISTICS

Bone is made up of two main forms; lamellar and cancellous bone. Lamellar bone, located in the diaphysis of long bones of mammals, has a dense structure composed of concentric lamellae surrounding haversian canals which contain blood vessels and cells. Finer holes (lacuna) which permeate the hard bone contain bone cells (Pritchard 1974:3-4; Hare 1980:208; Houghton 1980:13, 15). Cancellous bone is composed of a porous mesh of bands of bone called trabeculae and is found in vertebrae, at the ends of long bones, and in many lower vertebrates including marine mammals and fish

(Ascenzi 1969:527; Pritchard 1974:5-6; Smith *et al.* 1983:447). The latter is laid down rapidly and consists of irregularly orientated collagen fibrils.

Bony fishes have a skeleton composed of collagen and hydroxyapatite which is compositionally similar to mammals (Wheeler and Jones 1989:87). Around 30% of dry mammalian bone is made up of organic proteins including 90 to 95% collagen (Figure 2.1), and minor amounts of glycoproteins, peptides, lipids, bone sialoprotein as well as non-collagenous proteins such as osteocalcin and osteonectin. The inorganic mineral, hydroxyapatite ($Ca_5(OH)(PO_4)_3$), makes up the remaining 70% of bone (Hare 1980:209; Smith *et al.* 1983:211, 446). Collagen and its derivatives (*e.g.* gelatin, tripeptides and amino acids) are the most common bone fractions isolated for isotopic analysis, although hydroxyapatite has also been used ($CO_3^{2-}$ can substitute for $PO_4^{3-}$). This is due, in part, to the stability of collagen as well as the chemical similarity between species (Hedges and Wallace 1978:379; Schoeninger and DeNiro 1984:626).

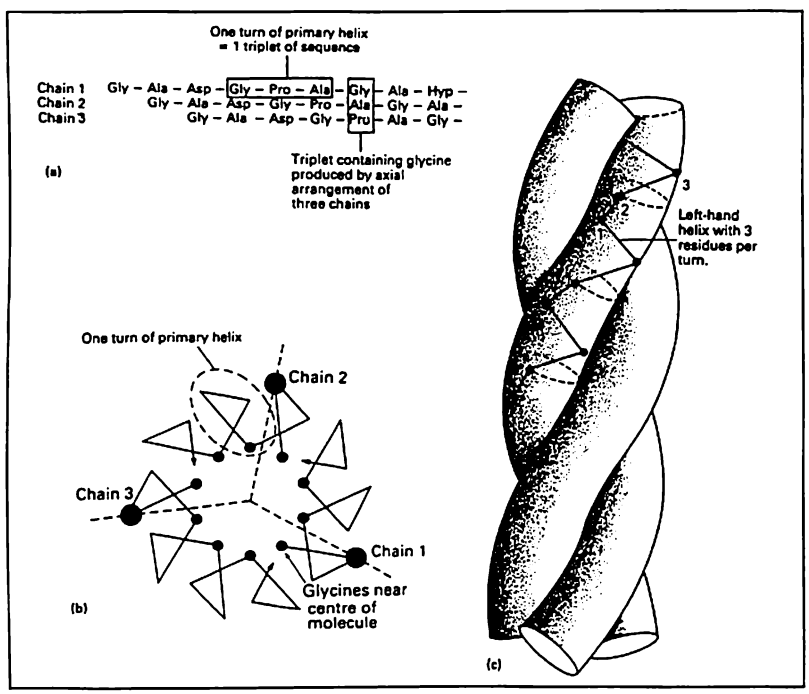


Figure 2.1: Collagen. (a) Part of the amino acid sequence. (b) End view of the triple helix. (c) The collagen triple helix (fibre) (from Woodhead-Galloway 1980: figure 3.3).

Collagen is a fibrous protein that provides the bone with strength and flexibility. Collagen molecules are formed in the osteoblasts and consist of three polypeptide chains that are wound into a left-handed helix (fibril), three of which are twisted together into a right-handed coil (fibre) (Woodhead-Galloway 1980:1-2, 23; Smith *et*

*al.* 1983:211-212) (Figure 2.1). As collagen ages, a series of cross-links and hydrogen bonds develop which stabilise the fibril structure (Smith *et al.* 1983:215-220, 447). Precipitation of hydroxyapatite around the collagen bundles increases the ratio of inorganic to organic and further enhances this stability (Love 1970:128; Hare 1980:209).

The replacement of adult mammalian collagen slows as a result of this increasing stability (Waterlow, Garlick and Millward 1978:512-514; Hare 1980:209; Smith *et al.* 1983:215, 450) with complete turn-over taking around 10 years (Chisholm 1989:20-21). Unfortunately, little is known about the turn-over rate of fish collagen, though apparently, as they age, some fish species prefer higher water temperatures, a factor consistent with greater collagen stability (Love 1970:216). Unlike mammals, however, fish have the capacity for sustained but diminishing growth throughout their lives, with new collagen forming principally at the edges of existing bone (Love 1970:126; Wheeler and Jones 1989:89, 90). In addition, fish bone is largely cancellous and, therefore turns over faster than mammalian bone (Pritchard 1974:7; Wheeler and Jones 1989:63, 87, 89; Lubinski 1996:175). Consequently, it is likely that fish bone, as with mammalian bone, includes a mixture of old and newly formed collagen, therefore averaging out any short term isotopic changes (Schell 1983:1070; Chisholm 1989:21).

### Amino acids

The collagen molecule is composed of approximately twenty naturally occurring amino acids (Table 2.1). These amino acids are linked to one another covalently between the amino ($-NH_2$) group of one residue and the carboxyl (-COOH) group of a second residue. In addition to acidic and basic properties which result from these covalent links, uncharged side-chains may also be involved in hydrophobic reactions (Woodhead-Galloway 1980:10, 23-24, 38; Smith *et al.* 1983:211-212). These properties can lead to a large number of chemical reactions following the breakdown of the helical collagen structure.

The amino acid fingerprint of mammalian collagen can be recognised by the distinctive proportions of individual amino acids. Notably, mammalian bone is characterised by a high glycine and imino acid (proline and hydroxyproline) content (Table 2.1). Fish collagen, on the other hand, tends to have a lower total imino acid content, a factor directly related to the environmental temperature of the living fish. Consequently, there is considerable variability among different fish species (Love 1970:270; Waterlow, Garlick and Millward 1978:510; Woodhead-Galloway 1980:12, 26).

Table 2.1: Typical amino acid composition of mammalian versus fish collagen (Mole %) (from Wyckoff 1972:64-65).

| Amino acid | Abbreviation | Ox collagen | Cod gelatin |
|---|---|---|---|
| Hydroxyproline | Hyp | 10.25 | 5.86 |
| Aspartic acid | Asp | 4.25 | 5.18 |
| Threonine | Thr | 1.86 | 2.38 |
| Serine | Ser | 3.48 | 6.98 |
| Glutamic acid | Glu | 6.38 | 7.2 |
| Proline | Pro | 11.81 | 9.93 |
| Glycine | Gly | 31.69 | 34.85 |
| Alanine | Ala | 10.79 | 10.66 |
| Valine | Val | 2.44 | 1.83 |
| Methionine | Met | 0.5 | 1.4 |
| Isoleucine | Ileu | 1.34 | 1.16 |
| Leucine | Leu | 3.01 | 2.30 |
| Tyrosine | Tyr | 0.72 | 0.33 |
| Phenylalanine | Phe | 1.93 | 1.14 |
| Hydroxylysine | Hyl | 0.82 | 0.82 |
| Histidine | His | 0.61 | 0.74 |
| Lysine | Lys | 3.03 | 2.33 |
| Arginine | Arg | 5.03 | 4.85 |

The collagen amino acids are ultimately obtained from the diet. A number are considered to be essential because they cannot be synthesised in the body. The specific essential amino acids vary according to species requirements. Most amino acids are, however, "non-essential" as they can be resynthesised in the body from all dietary fractions (Hibbert and James, 1987:27; Ambrose and Norr 1993:7).

## Stable isotope variation

Because each amino acid has a unique isotopic value the isotope signature of collagen is dependent on the isotopic composition of locally available dietary resources (*e.g.* $C_3$-plants versus $C_4$-plants, or $C_3$-plants versus marine pathways[2]) and on the trophic level of the animal in question (Figure 2.2) (Schoeninger and DeNiro 1984:625; Ambrose and Norr 1993). Such complexity may obscure the difference between marine and terrestrial isotopes, especially in single or bivariate isotopic analyses (Schoeninger and DeNiro 1984:635; Ambrose and Norr 1993:3; Leach, Quinn and Lyon 1996:2). In the case of marine fish, noticeable differences in $\delta^{13}C$ and $\delta^{15}N$ occur between marine and freshwater species (Table 2.2).

Isotopic analysis is further complicated by uncertainty over the "routing" of nutrients to carbonate and collagen (Ambrose and Norr 1993:1-2). Studies of rat bone have indicated that dietary protein largely influences the stable isotopic composition of collagen[3] (Chisholm 1989:36; Ambrose and Norr 1993), though where the protein intake was inadequate, energy carbon (*i.e.* carbon atoms from carbohydrates and fats)

[2] Differences in carbon fractionation occur when plants assimilate $CO_2$. $C_3$-plants include trees, flowers and grasses. $C_4$-plants include millets, maize and sugar cane. Marine plants take their carbon from dissolved $CO_2$ in the ocean (Olsson 1991:23).

[3] Collagen is generally enriched in $\delta^{13}C$ relative to the diet most likely due to catabolic activities or *de novo* synthesis (Ambrose and Norr 1993:7; Tieszen and Fagre 1993:152).

was also used for collagen synthesis and maintenance (Chisholm 1989:22; Ambrose and Norr 1993:11). On the basis of such studies into rat bone isotopes, Ambrose and Norr (1993:7-8, 29) speculated that dietary protein contributes a minimum 18% of the carbon in collagen (*i.e.* approximately 18% of the amino acids in rat collagen are "essential"), though up to 95% of the carbon in collagen could be derived from protein if dietary intake is high. Other animals may, however, differ somewhat in their protein requirements due to differences in amino acid catabolism (Crowey and Sargent 1979:4; Schoeninger and DeNiro 1984:635-636). Notably, fish do not adapt to a restriction in dietary protein (Crowey and Sargent 1979:21; Jobling 1994:35).

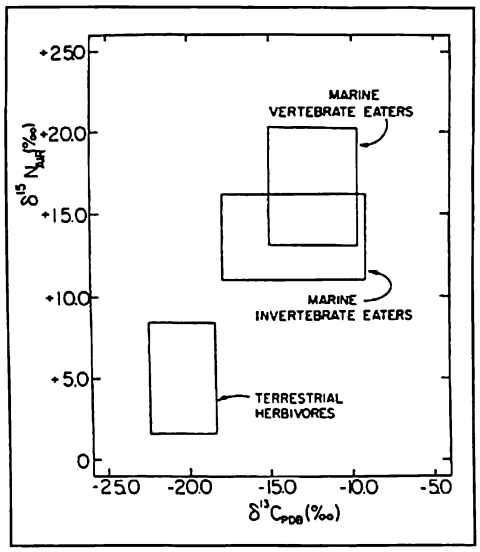


Figure 2.2: Mean (± 2 σ) of the isotope values observed for bone collagen of modern mammals belonging to the indicated feeding habits (adapted from DeNiro and Weiner 1988c:2419, figure 1).

Table 2.2: $\delta^{13}C$ and $\delta^{15}N$ values of bone collagen from marine fish (from Schoeninger and DeNiro 1984:632).

| | $\delta^{15}N$ (‰) | | $\delta^{13}C$ (‰) | |
|---|---|---|---|---|
| | mean ± sd | Range | mean ± sd | Range |
| Marine fish ($n$ = 10) | +13.8 ± 1.6 | +11.4 to +16.0 | -12.5 ± 1.4 | -14.4 to -10.0 |
| Invertebrate eaters ($n$ = 6) | +14.1 ± 0.9 | +12.5 to +14.9 | -12.2 ± 1.4 | -14.4 to -10.0 |
| Fish eaters ($n$ = 2) | +13.7 | +11.4 to +16.0 | -12.6 | -14.2 to -11.1 |
| Freshwater fish ($n$ = 5) | +8.0 ± 1.2 | +6.6 to +9.5 | -19.7 ± 4.5 | -23.7 to -12.7 |
| Anadromous fish ($n$ = 2) | +11.1 | +9.6 to +12.7 | -18.2 | -19.3 to -17.2 |
| Reef fish ($n$ = 4) | +5.5 ± 1.3 | +3.9 to +6.6 | -6.3 ± 1.9 | -8.2 to -4.5 |

It has also been suggested that the sources of dietary protein are unlikely to be nutritionally equivalent. For a well-balanced diet, meat protein may provide the main source of carbon for collagen (*i.e.* animal protein sources are around 90% protein by weight compared to legumes which are around 20% protein) (Ambrose and Norr 1993:30; Lee-Thorp, Sealy and van der Merwe 1989). For animals that feed in a

single carbon reservoir this should not incorporate variation. If both marine and terrestrial sources are sampled, however, protein rich marine resources could be expected to dominate over terrestrial resources (usually dominated by plant foods) (Ambrose and Norr 1993:31).

## MARINE CARBON

Radiocarbon determinations of marine organisms may be influenced by several factors. Fish, like shellfish, obtain their carbon from a variety of sources. Ingested organic carbon (particulate organic carbon [POC] and dissolved organic carbon [DOC]) plays a major role in determining collagen radiocarbon levels. Both POC and DOC are, however, ultimately derived from dissolved inorganic carbon (DIC) via photosynthetic fixation in the euphotic zone (0 - 100 m), though terrestrial or marine sediment derived sources of organic carbon may also contribute (Druffel *et al.* 1992:15,652; Druffel and Williams 1990:173). Consequently, it is likely that fish bone is subject to similar uncertainties in radiocarbon content as marine shell, including possible anomalies introduced by uptake of organic terrestrial carbon, upwelling, or a hardwater effect, with additional complications associated with oceanic $\Delta^{14}C$ variation and the vertical and geographical distribution of many fish species.

Surface ocean water is characterised by lower $^{14}C$ concentrations relative to atmosphere. This is the result of a delay in carbon dioxide exchange rates between atmospheric and oceanic reservoirs, a longer residence time of $^{14}C$ in the ocean compared to the atmosphere, and the dilution effect caused by the mixing of surface waters with upwelled deep water that is depleted in $^{14}C$ (Gordon and Harkness 1993:697-698; Higham 1993:123; Stuiver, Pearson and Braziunas 1986:980). Because circulation in the oceans is comparatively slow, $\Delta^{14}C$ varies geographically and with depth (Chisholm 1989:29-30; Gordon and Harkness 1993:697-698). The surface layer of the ocean is, however, homogenised by wind and thermal stresses. This well-mixed surface layer varies between about 20 and 200 m and averages around 75 m. It is at its deepest in the temperate regions (*i.e.* roughly delineated by 15 - 50°N and S) and somewhat shallower in tropical and polar regions (Lassey, Manning and O'Brien 1990:124).

The offset between oceanic and terrestrial carbon-14 (the reservoir effect) is not constant and a local correction factor ($\Delta R$) needs to be obtained to account for regional oceanic differences to determine accurately the age of a radiocarbon sample. For the relatively well-mixed Atlantic Ocean surface waters between latitudes 40°N and 40°S, the average reservoir correction for DIC proxies (*i.e.* marine shell) has been estimated

to be *ca.* 400 years (Broecker *et al.* 1960), but a wide range of values are known world wide including corrections of up to 1400 years for mammals and fish from East Antarctic waters (Gordon and Harkness 1993:698, 700-701) (Figure 2.3).

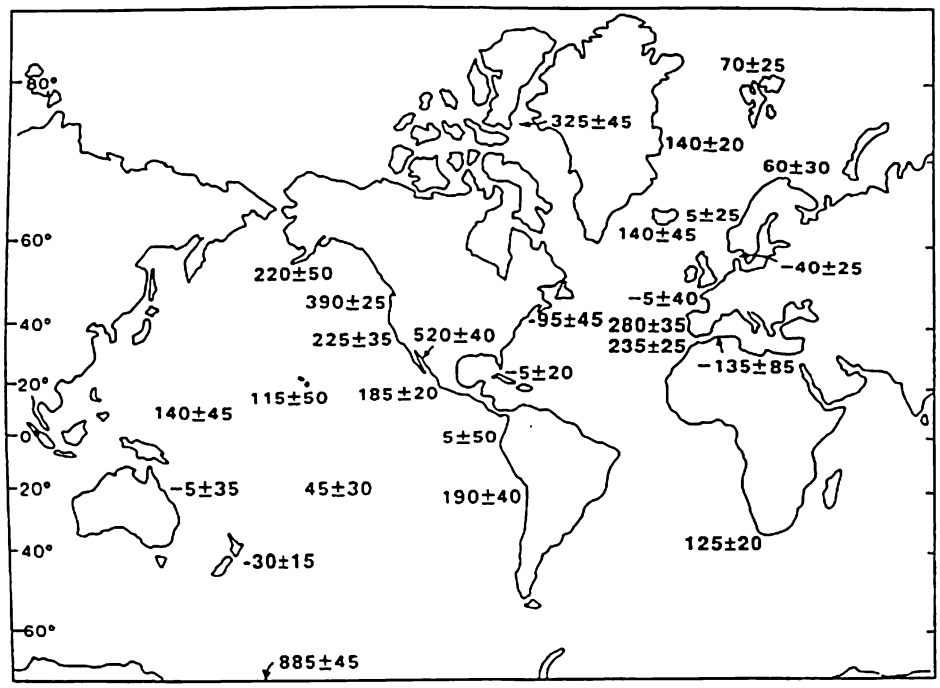


Figure 2.3: ΔR variations for oceanic regions of the world (from Stuiver and Braziunas 1993:156).

Interpretation of the distribution of marine carbon below this mixed surface layer is complicated by a $\Delta^{14}C$ gradient in the DIC formed by radioactive decay, a corresponding gradient in the DOC and suspended POC (Figure 2.4) (Stuiver, Pearson and Braziunas 1986:980; Druffel *et al.* 1989:526, 529; Druffel and Williams 1990:172-173), and from complexity in the radiocarbon uptake by marine animals depending on habitat, diet and trophic level (Gordon and Harkness 1993:698; Ambrose and Norr 1993:31; Kalish 1995:644). Dissolved organic carbon $\Delta^{14}C$ values are much lower than the $\Delta^{14}C$ in DIC, possibly a result of DOC recycling within the upper few hundred meters of the water column during photosynthesis, microbial activity, degradative process, respiration and/or mineralisation (Druffel *et al.* 1989:528-529; Druffel *et al.* 1992:15,639, 15,653; Lalli and Parsons 1993:146-147). Suspended POC $\Delta^{14}C$ values are higher than DOC, and are though to be the result of input from surface-derived material, though some recycling is also expected due to heterotrophic bacterial uptake on particles and/or physical adsorption (Druffel and Williams 1990:172-174; Druffel *et al.* 1992:15,639, 15,653). Higher $\Delta^{14}C$ values for sinking POC suggest that a larger percentage of surface derived constituents are

diatoms, protozoa, kelp, phytoplankton, humus and/or peat may be deposited by rivers (Higham 1993:145-146; Schmidt 1996:65). A removal process for much of the terrestrial DOC in offshore waters is, however, suggested by isotopic and compositional data which indicates a marine phytoplankton source for most marine organisms (Schell 1983:1068-1069; Bauer *et al.* 1997; McNichol, Ertel and Eglinton 1997), though there is the possibility of a larger contribution of terrestrial carbon to the deep-sea (Druffel *et al.* 1992:15,652).

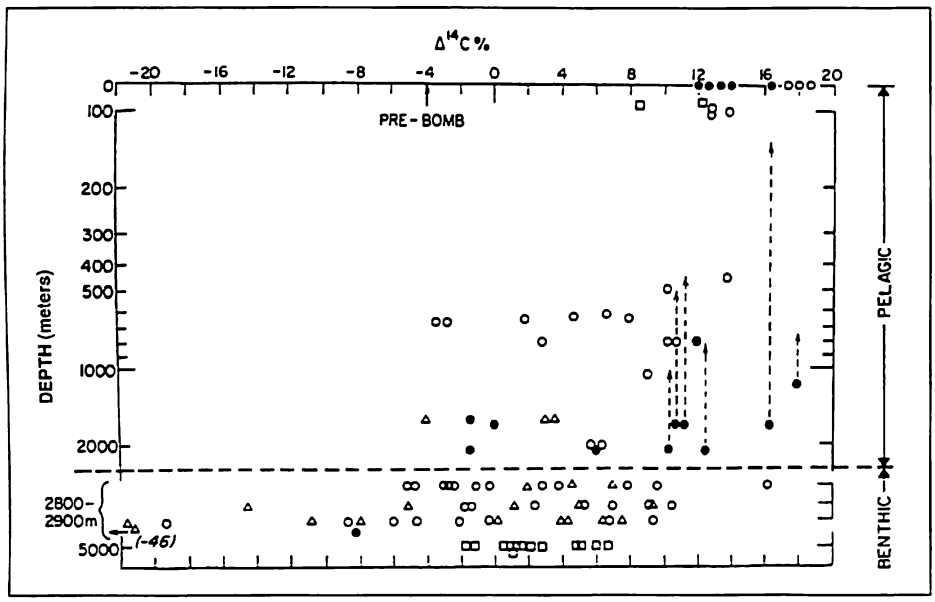


Figure 2.5: Carbon-14 values of oceanic and benthic animals vs depth. Arrows indicate suggested changes in depth of capture of vertical migrants. Carbon-14 values for benthic animals are shown below the horizontal dashed line (from Pearcy and Stuiver 1983:433, figure 1).

Marine animals living directly on terrestrially derived material are most commonly affected. Schell (1983:1069), for example noted anomalous values for *Gammarus setosus* a species of amphipod that readily metabolises $^{14}C$-labelled cellulose (see also Hogg, Higham and Dahm (1998) and Pearcy and Stuiver (1983:432)). It is, however, possible for anomalous values to be passed on to organisms that live on these animals, and Druffel and Williams (1991:294) have suggested that a diet consisting of organisms with a low $^{14}C$ activity may have been responsible for low $\Delta^{14}C$ values in anchovy and crab (*Pleuroncodes planipes*) off the Pacific Coast of Baja, California.

Introduction of old carbon into the food chain may also occur near areas of upwelling, for example the Subtropical Convergence (Sparks *et al.* 1992), or at the convergence between inshore and offshore waters (*i.e.* the upper part of the New Zealand continental slope (between 200 and 800 m)) (Ayling 1982:17). These areas are

nutrient-rich and produce more fish than either coastal or oceanic environments (Lalli and Parsons 1993:120; Kalish 1995:643) and are, therefore the most likely source of anomalous $^{14}C$ results of marine animals. Depleted $^{14}C$ values attributed to the affects of upwelling have been recorded for carbonate in corals from the Galapagos Islands (Druffel 1981) and inter-tidal mollusc shells off California (Robinson 1981).

## POST DEPOSITIONAL ALTERATION

*In vivo,* mature bone collagen is chemically very stable due to its intergrowth with hydroxyapatite, relative insolubility and its fibrous, cross-linked structure (Hedges and Wallace 1978:379; White and Hannus 1983:316; Linse 1992:330). Once the collagen structure is disturbed by denaturing or hydroxyapatite loss, this stability is reduced (Collins *et al.* 1995:178). The degraded collagen will then easily break down into smaller peptide fragments and amino acids that can be leached out and/or react with ions or micro-organisms (Garlick 1969:504; Ortner, von Endt and Robinson 1972:514; von Endt and Ortner 1984:248-249). The principle factors that affect the preservation or destruction of bone are pH, temperature, moisture content and biological activity (Ortner, von Endt and Robinson 1972:519; Linse 1992:329). Consequently, soil conditions, climate and cultural influences play a major role in the survival of bone (Henderson 1987:46), as well as bone structural characteristics.

### Micro-organisms

In most cases, the stability of collagen in the short term is dependent on the absence of micro-organisms which produce collagenase (Garlick 1969:504; Hedges and Wallace 1978:379; Child 1995:168). Collagenases are enzymes that initiate breakdown and resynthesis of collagen *in vivo* cleaving each collagen fibril in two at a position dependent on the specific collagenase (Smith *et al.* 1983:223; van Klinken, Bowles and Hedges 1994:2543). Enzymes similar to collagenase are responsible for tooth decay (Woodhead-Galloway 1980:59; Waterlow, Garlick and Millward 1978:516), and gas gangrene (*Clostridium perfringens* and *Clostridium histolyticum*). A collagenase can also be excreted by some insect larvae (Janaway 1987:130-131). The denatured collagen can then be broken down to short peptides and amino acids by more conventional enzymes and microbes (Waterlow, Garlick and Millward 1978:516-517; Child 1995:167).

Collagenases do not, however, function optimally until the hydroxyapatite is removed. Therefore, for micro-organisms to successfully decompose bone, they must ideally possess both enzymes to degrade collagen and acid to remove mineral (Waterlow,

Garlick and Millward 1978:516-517; Child 1995:167-168; Collins *et al.* 1995:182). Child (1995:172) has suggested, however, that microscopic focal destruction in bone may be caused by acid hydrolysis initiated by fungal hyphae, without enzymatic digestion.

Collagenase, and most soil organisms (except fungi which predominate in most soil conditions), are intolerant of very acidic conditions (*i.e.* pH < 4.5). Collagenase activity is greatest in a neutral or slightly alkaline medium (pH 7 - 8) and may persist, depending on the particular system, in strongly alkaline conditions (pH 9), which also favour bacteria (Garlick 1969:504, 506; Nicholson 1996a:523-524). Various agents may also inhibit collagenase activity, including ferrous iron, heavy metals (chelating agents) and some enzymes (Garlick 1969:504, 506). Dehydration by salt or drying also inhibits the growth of most proteolytic bacteria by increasing hydrophobic interactions and inter-chain ionic linkages in the collagen (Collins *et al.* 1995:181), while anoxic conditions, tend to completely arrest biological activity (Chaplin 1971:16; Henderson 1987:52; Janaway 1987:129-130).

**pH**

Native collagen is fairly resistant to weak acids and, in the absence of micro-organisms, it will undergo fairly slow hydrolysis until the polypeptide chains can be leached out (Ortner, von Endt and Robinson 1972:514). Initial protein and hydroxyapatite hydrolysis are thought to be catalysed by the action of internal water and bacteria when an organism dies (Ortner, von Endt and Robinson 1972:514; Collins *et al.* 1995:176; White and Hannus 1983:316, 321-322). Once bone is buried, however, the rate of protein degradation may be increased by acids present in the atmosphere and ground water, as well as by acid produced by micro-organisms (von Endt and Ortner 1984:249; Sillen 1989:220-221). This relatively slow breakdown of collagen can be accelerated by the loss of hydroxyapatite (Linse 1992:330; Collins *et al.* 1995:181-182). Hydroxyapatite, is poorly crystalline with a high surface-area/mass ratio. It is, therefore highly susceptible to alteration in acidic or alkaline conditions (von Endt and Ortner 1984:248-249; Waldron 1987:150; Sillen 1989:213, 218-219). Further, hydroxyapatite crystals have an affinity for anionic proteins, a property that may cause bone to attract acidic amino acids and proteins from the environment (Burky *et al.* 1998:13).

According to White and Hannus (1983) the chemical changes occurring to hydroxyapatite (dissolution, crystal maturation and new growth) are governed by an equilibrium relationship with ions such as Ca and $PO_4$ in the soil solution, and the pH

of the deposit (White and Hannus 1983:316, 322; Linse 1992:331; Sillen 1989:220-221). Although hydrogen ions from acids can replace Ca from hydroxyapatite, cessation of acidic conditions may encourage soil Ca ions to diffuse back into the bone to replace hydrogen ions in the hydroxyproline (White and Hannus 1983:321). Similarly, in alkaline conditions (up to pH 7.88) Ca ions from the soil solution replace hydrogen ions in the hydroxyapatite to stop or retard the dissolution of the bone. Hydroxyapatite solubility will, however, increase as the pH becomes increasingly alkaline, in part because collagen begins to break down exposing more surface area, but also because phosphorous leaching increases above pH 7.8 (White and Hannus 1983:316, 322; Linse 1992:338, 342). In strongly acidic soil, $PO_4$ may be precipitated as Al or Fe phosphates removing $PO_4$ ions from solution, and as a result hydroxyapatite weathering increases in order to achieve equilibrium (White and Hannus 1983:316). The introduction of new ions into the crystalline lattice (and into cavities left by collagen), or the growth of existing crystals may further undermine the protein-mineral bond (von Endt and Ortner 1984:248-249; Henderson 1987:44).

Therefore, bone is generally better preserved in soils with a neutral or slightly alkaline pH (Henderson 1987:46; Wheeler and Jones 1989:63; Millener 1981:452-4). Hedges and Millard (1995:159) calculated that bone in a closed system will take about $10^4$ years to dissolve at pH 7, but only $10^2$ years at pH 5. In practice, however, a single deposit is subject to fluctuations in temperature, moisture, ion chemistry and pH (Linse 1992:329; Nicholson 1998:395), while the importance of micro-organisms in the survival of collagen is attested to by the fact that otoliths ($CaCO_3$) out-survive bones in most acidic soils (Nicholson 1996a:526).

**Water**

Water plays a major role in the introduction of exogenous material into bone (*i.e.* cations, anions and organic compounds), as well as the dissolution of the inorganic component, and removal and breakdown of protein (Oakley 1969:37; Hedges and Millard 1995:156). The extent of change is determined by the quantity and movement of water which is dependent on humidity, mean annual precipitation, drainage and permeability (von Endt and Ortner 1984:252; Henderson 1987:46; Hedges and Millard 1995:157-158). Consequently, decay is considered to be more rapid for bones in sandy or gravelly soils which experience a high degree of ground water flow (Chaplin 1971:16; Hedges and Millard 1995:162).

Dry environments may not, however, necessarily aid in the preservation of bone as sufficient water is retained following the death of an animal for initial hydrolysis

reactions to take place (Collins *et al.* 1995:181). Under such conditions, once hydrolysis has ceased, evaporation can create a water flux from the deeper soil layers to the surface resulting in salt crystallisation which causes the bone to become brittle. The remaining collagen may, however, be protected by the re-crystallised inorganic matrix and by a dry and salty micro-environment (Grupe 1995:197-198). Salt present in marine fish may have the same effect (Prummel 1986:116).

## Temperature

Temperature (*e.g.* sunlight or cooking) affects the rate of chemical reactions, especially those involving water. Generally, temperature-induced decay takes place over a long period, though Ortner, von Endt and Robinson (1972) estimated that for every 10°C rise in temperature the decay rate of bone protein will double. Consequently collagen loss tends to be more rapid in humid conditions (*i.e.* tropical or subtropical climates) (Figure 2.6) (Protsch 1991:273). Temperature induced changes to the collagen fibre involve the dissociation of the three chains increasing the vulnerability of collagen to attack (Woodhead-Galloway 1980:24). Such practice can even denature "insoluble collagens" that remain after acid or alkaline hydrolysis and may, in extreme cases (*i.e.* roasting or heavy boiling) result in the total loss of organic matter or the preferential loss of certain amino acids (Wheeler and Jones 1989:67; Taylor, Hare and White 1995:115; Lubinski 1996:175-176).

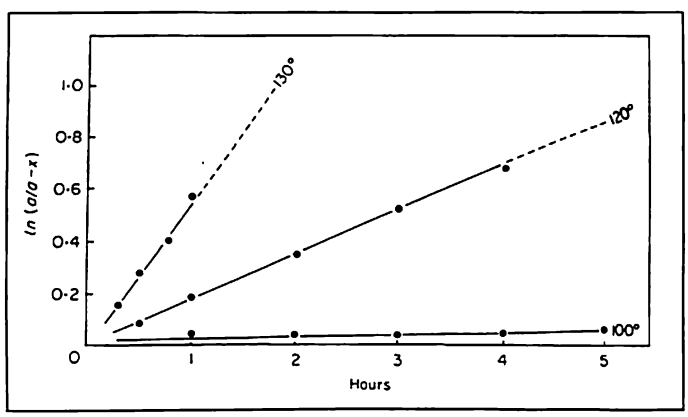


Figure 2.6: The effect of temperature on nitrogen in bone particles placed in sealed tubes filled with water at 100°C, 120°C and 130°C. The ordinate represents the amount of nitrogen remaining in bone at any given time and is expressed as the natural logarithm of the ratio between the amount of nitrogen originally present and that lost to the surrounding solution (from von Endt and Ortner 1984:250, figure 1).

The degree of temperature induced change to the fibril structure is related to the number of imino acid residues and the number of hydrogen bonds in the individual molecules (polypeptides). For mammals, denaturation of collagen fibrils occurs at

about 24°C above the body temperature, but for ectotherms (*e.g.* fish which have a low imino acid content) denaturation is directly related to the environmental temperature (Love 1970: 270; Woodhead-Galloway 1980:12, 24, 26; Brown *et al.* 1988:173). Whole bone is considered, however, to be more stable than individual fibrils, and Lees (in Collins *et al.* 1995:181) found that dry cow bone collagen will not denature until 173°C compared to 94°C following demineralisation. Collins *et al.* (1995:181) have suggested that the strength of bone collagen may be increased by calcium bridges binding collagen to the hydroxyapatite. The greater stability of restrained fibrils compared to unrestrained fibrils has also been demonstrated by Snowden and Weidemann (1978). Conversely, Richter (1986) has demonstrated that the melting of collagen fibrils from modern plaice (*Pleuronectes platessa*) bone not only occurred at a lower temperature than mammals, but possibly began as low as 12°C.

Nicholson (1996a:527, 529; 1998:401) in a recent analysis of uncooked and cooked bone (*i.e.* baked for 20 minutes at 200°C) buried in near neutral (pH of 6.5 - 7.0) or basic (pH of 7.5 - 8.0) conditions, has suggested that baked bone survives better than fresh bone. This may be the result of partial dehydration (*c.f.* Collins *et al.* 1995:181). Identification of cooked bone in an archaeological situation is, however, difficult. The main danger is that a colour change, usually indicative of protein loss, may not be visible until a temperature of 400°C is reached (Shipman, Foster and Schoeninger 1984:321). Burnt bone may also be obscured by discolouration imparted by the soil matrix (Stiner *et al.* 1995:233). The effect of boiling on bone is more extreme. Richter (1986:479-480) could not identify native collagen in bone that had been boiled for 30 minutes, and field studies by Nicholson (1996a:513; 1998:398) have demonstrated that boiled fish bone is much more likely to be destroyed than boiled mammal or bird bone.

### Bone structure

It has been noted (*i.e.* Chaplin 1971:14-15; Schiffer 1987:187; Wheeler and Jones 1989:63, 67; Nichol 1988:193; Nicholson 1996a, 1996b, 1998) that fish bone generally weathers, both chemically and physically more quickly than mammal or bird bone regardless of environmental conditions. This has been attributed to the structural characteristics of individual bones, specifically size, shape and density (von Endt and Ortner 1984:252).

Fish bone is constructed of both lamellar and cancellous forms of bone (see above). The exact ratio of compact to cancellous bone varies between fish species (Nicholson

1996a:527), but typically, fish have a light, predominantly cancellous structure (Wheeler and Jones 1989:87, 89; Bone, Marshall and Blaxter 1995:22) with a high surface area and porosity. This results in a increased susceptibility to chemical reactivity and accessibility to micro-organisms (Nicholson 1998:398; Hedges and Millard 1995:157-158). In addition, new fish bone is laid down at the edges of existing bone. This new bone has a low mineral content and is prone to rapid decay (Nicholson 1996a:513, 527). Analysis of modern buried bone by Nicholson (1996a:527) suggests that fish bone degenerates by a process of cracking and crumbling progressing from the edges. Pitting and/or channelling typically found in mammalian bone due to microbial attack was absent, though decomposition appeared to sometimes continue within the porous fish bone structure.

## CONTAMINATION

Contaminants that commonly affect collagen radiocarbon determinations include humic acids and non-humic materials such as polyphenols, polysaccharides, lignins, degraded collagen and other bone organic components (Figure 2.7) (van Klinken and Hedges 1995:264).

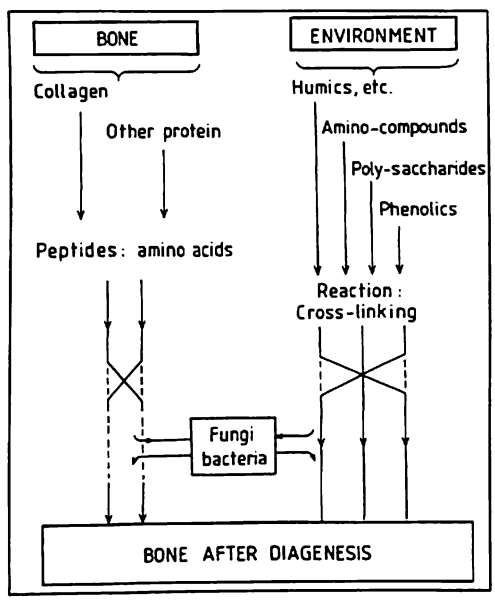


Figure 2.7: Schematic pathways by which carbon atoms may become physically and chemically mixed during diagenesis with carbon atoms indigenous to bone (from Hedges and Law 1989:250, figure 1).

## Humic acids

Humic substances (humic acid, fulvic acid and humin) arise from the chemical and biological degradation of plant and animal residues. They are amorphous, chemically complex materials with a wide molecular weight range (Stevenson and Butler 1969:534-535, 537-538; Limbrey 1975:41; van Klinken and Hedges 1995:263). Humic acids in bone are thought to originate from an influx of soil humics and/or *in situ* humification of bone organic matter by condensation of carbohydrate and protein to form relatively stable brown pigmented complexes (melanoidins). This process is termed non-enzymatic browning or the Maillard reaction (van Klinken and Hedges 1995:264). Maillard reactions also take place between exogenous humics and collagen during various pretreatments, including gelatinisation and acid hydrolysis (Hedges and van Klinken 1992:281; van Klinken and Hedges 1995:263).

Humic contamination is a major problem for bone radiocarbon analysis. Although humic acids can be extracted with an alkali wash (humin can be extracted with acid and fulvic acids with acid or alkali) (Limbrey 1975:55; Schnitzer and Kahn 1978:2), separation becomes difficult when the contamination bonds chemically to partially degraded bone material (van Klinken and Hedges 1995:268-269). Cross-links between humics or organic residuals may, however, retard dissolution of collagen by forming stable bonds between chains of molecules (Collins *et al.* 1995:180), and can hinder enzymatic digestion (van Klinken and Hedges 1995). Consequently, Nicholson (1998:401) suggested that such humic, collagen cross-links aided in the preservation of fish bones recovered from acidic damp "composting" environments.

## Non-humic contamination

Non-humic contaminants include substances such as carbohydrates, proteins, peptides, amino acids, fats, waxes, resins, and pigments. Such exogenous organic contaminants are often difficult to identify and remove from collagen. Therefore, although these contaminants tend to have a short life span in soils, or may even be collagen breakdown products, they can be a major set back to isotopic analyses (Schnitzer and Khan 1972:3; Chisholm 1989:23-24). This has been especially problematic where single amino acids have been isolated for dating as it is not known if they are collagen derived or introduced (Stafford *et al.* 1991; Hedges and van Klinken 1992:287). Bones may also be contaminated by preservatives (*e.g.* PVA, shellac, polyethylene glycol) used to consolidate samples following excavation (Law *et*

*al.* 1991; D. Johns[4], *pers. comm.* 27/2/1996). Some of these preservatives become insoluble with time by cross-linking with the collagen (Law *et al.* 1991:308).

### Contamination effects

The influence of contamination depends on the type, amount and $^{14}C$ age of the contamination in a sample (Gupta and Polach 1985:129). Major uncertainties arise, however, when dealing with the identification of small errors (Olsson 1979). The effect of modern contamination (100 % modern carbon), for example will be less significant due to the closer the age of the sample and its contaminant (Gupta and Polach 1985:132-133). Contamination by old carbon, on the other hand, has a greater impact on relatively young samples such as those from New Zealand archaeological sites (Table 2.3). In practice, however, the $^{14}C$ content of contaminants tends to be variable.

Generally speaking, 5-10% contamination in bone can be recognised analytically if the sample is reasonably well-preserved (Hedges and van Klinken 1992:284). A variety of methods exist to analyse contamination effects, including $^{14}C$ measurement of different fractions, or comparing radiocarbon results of untreated sample with treated samples, or contemporaneous materials (Gupta and Polach 1985:134; Higham 1993:100-101). A number of different pretreatments and assessment techniques may also be used to assess the ability to measure a samples $^{14}C$ activity accurately. Unfortunately, in practice such cross-checking procedures are rarely performed for routine samples (see Chapter 3).

Table 2.3: The effect of contamination by modern (*i.e.* 1950) and $^{14}C$ free carbon on the apparent age of a sample whose true age is 600 and 1000 years BP.

| | % contamination with $^{14}C$ Free Carbon | | | |
|---|---|---|---|---|
| | 1% | 5% | 10% | 15% |
| Est age: 600 BP. | 682 | 1017 | 1457 | 1922 |
| | % contamination with MODERN Carbon | | | |
| | 1% | 5% | 10% | 15% |
| Est age: 600 BP. | 595 | 574 | 547 | 521 |
| Est age: 1000 BP. | 990 | 952 | 904 | 856 |

## CONCLUSION

Aside from providing general background information to this research, this chapter has considered issues of inbuilt age, carbon source, reservoir effects and contamination. It is concluded from this discussion that collagen may be prone to a relatively small

[4] Regional Archaeological Conservator, Anthropology Department, University of Auckland, Auckland, New Zealand.

degree of inbuilt age, generally considered to be less than 10 years. This should have limited affect on the radiocarbon determinations of archaeological samples. It was also concluded that the $^{14}C$ signature of an animal is ultimately derived from the diet, specifically dietary protein. Consequently, the stable and radioactive carbon isotopes reflect both the reservoir of the animal and the reservoir of its diet. The interpretation of these isotopes may, however, be complicated by sampling from more than one reservoir. For marine animals, dietary DOC and POC are the main components influencing collagen. Unfortunately, there is some uncertainty about the uptake of POC and DOC in animals that live and feed in the deep ocean or pass through $^{14}C$ depleted waters. It is suggested, however, that fish which live and feed within the mixed surface layer should be subject to similar uncertainties in radiocarbon content as marine shell. Especially problematic, therefore is the effect of upwelling, though this will depend on the specific species habitat and dietary characteristics. The influence of hardwater and organic carbon are considered to be minor except where feeding directly on animals known to ingest non-marine $^{14}C$.

The isotopic composition of collagen may also be affected by contamination and decay. These processes are dependent on a wide range of interactions and cultural effects prior to, and following deposition, as well as biological, chemical and physical factors which vary depending upon the specific depositional environment. The influence of contamination is of particular concern to the radiocarbon dating of bone. Humic contaminants may be difficult to remove if they bond with collagen, while non-humic contaminants may also be difficult to identify and remove. Adapting the pretreatment to preservation state (the amount of remaining collagen and degree of contamination) and age are prudent steps towards obtaining accurate radiocarbon estimates of bone.

# CHAPTER 3

# THE BONE DATING METHOD

## INTRODUCTION

The aim of this chapter is to identify the most appropriate method, or methods for pretreating and selecting bone samples from New Zealand archaeological sites for radiocarbon dating. The first part reviews the wide range of radiocarbon bone pretreatments available, including routine techniques used by radiometric laboratories and the more highly specialised AMS (Accelerator Mass Spectrometry) preparations. This is followed by a discussion of some common assessment methods used to identify problem samples.

## DATING TECHNIQUES

All routine radiocarbon dating pretreatments are designed to isolate collagen, or a collagen derivative from hydroxyapatite and contaminants. Routine bone pretreatments currently used by radiocarbon laboratories include acid and alkaline washes, dialysis and gelatin pretreatments. More specialised pretreatments include ion exchange and reversed-phase chromatographic separation of total or individual amino acids, ultrafiltration, ninhydrin derivatization, or the isolation of collagen specific fractions (*i.e.* hydroxyproline and tripeptides) (Table 2.1). Most techniques take advantage of differences in chemistry, that is insolubility, ionic charge, hydrophobicity and/or molecular weight. Not all pretreatments are, however, equally successful. Ultimately, the final composition of the insoluble residue will depend on the pretreatment chosen, conditions of pretreatment, the extent of diagenesis, age of the bone and the age, type and amount of contamination (Hedges and van Klinken 1992:282; Arslanov and Svezhentsev 1993:389).

Table 3.1: Standard pretreatment techniques for radiocarbon dating bone protein.

| Pretreatment | Reference Examples |
|---|---|
| Acid wash | Rafter 1955; Berger, Horney and Libby 1964; Krueger 1965; Tamers and Pearson 1965; Sellstedt, Engstrand and Gejvall 1966; Haynes 1967; Olsson *et al.* 1974; Farid *et al.* 1978; Gurfinkel 1987. |
| Dialysis | Munnich 1957; Sinex and Faris 1959; Berger, Horney and Libby 1964; Farid *et al.* 1978; Masters 1987 |
| Acid/Alkali/Acid treatment (ABA) | Vogel and Waterbolk 1963; Berger and Libby 1966; Haynes 1967; Olsson *et al.* 1974; Gurfinkel 1987; Redvers-Newton and Coote 1994; van Klinken and Hedges 1995. |
| Untreated gelatin ("Longin" method) | Sinex and Faris 1959; Longin 1971; Gurfinkel 1987; Redvers -Newton and Coote 1994 |
| Gelatin from NaOH-washed decalcified bone | Protsch 1975; Berglund, Hakansson and Lagerlund 1976; Taylor 1987; Gurfinkel 1987; Arslanov and Svezhentsev 1993; Redvers-Newton and Coote 1994 |
| Ultrafiltration of gelatin | Brown *et al.* 1988; van Klinken and Hedges 1995 |
| Mixed amino acids: Cation exchange of collagen hydrolysate | Ho, Marcus and Berger 1969; Gillespie and Hedges 1983; Gillespie, Hedges and Wand 1984; Gillespie, Hedges and Humm 1986; Long *et al.* 1989; |
| Mixed amino acids: Reversed-phase chromatography of gelatin hydrolysate | Stafford *et al.* 1982, 1987, 1991; Stafford, Brendel, and Duhamel 1988; Redvers Newton 1995 |
| Ion exchange of purified gelatin | Hedges *et al.* 1989; Law and Hedges 1989; Law *et al.* 1991; Redvers-Newton 1995 |
| Ninhydrin | Nelson 1991; van Klinken and Hedges 1995 |
| Individual amino acids | Stafford *et al.* 1982; Gillespie, Hedges and Wand 1984; Gillespie, Hedges and Humm 1986; van Klinken and Mook 1990; Stafford *et al.* 1987, 1991; Stafford, Brendel, and Duhamel 1988; Gillespie and Hedges 1983 |
| Purified tripeptides | van Klinken and Hedges 1992; van Klinken, Bowles and Hedges 1994; van Klinken and Hedges 1995 |
| Non collagenous proteins (NCP's) | Ajie *et al.* 1990, 1992; Ascenzi *et al.* 1985; Taylor 1992; Masters 1987; Tuross, Fogel and Hare 1988 |
| Carbonate | Haynes 1968; Hassan, Termine and Haynes 1977; Sullivan and Krueger 1981; Haas and Banewicz 1980; Hassan and Ortner 1977; Lee-Thorp, Sealy and van der Merwe 1989 |

## Acid hydrolysis

The acid-insoluble fraction (commonly termed "crude collagen" or "collagen") is normally extracted by decalcifying bone in acid (*i.e.* HCl, EDTA or $H_2SO_4$). Treatment with HCl is typically carried out at low temperature (4 - 6°C) and low concentrations (around 0.5M, or higher if bone is well-preserved) as some of the collagen fibres may hydrolyse if the temperature is too high or pH too low (van Klinken and Mook 1990:159; Arslanov and Svezhentsev 1993:388-389). Acid digestion of the sample usually takes place until pH is stable (which may take several days), or until degassing stops (approximately 4 to 10 hours), though rapid stripping of carbonates can be performed under reduced pressure (*e.g.* Kruger 1965). If the bone is badly preserved, or additional purification techniques are to follow the effects of hydrolysis can be minimised by reducing demineralisation time and finely grinding the sample to less than 0.5 mm (van Klinken and Mook 1990:159; Stafford *et al.* 1991:44). Recent tests by Brown *et al.* (1988:174) demonstrated that repeated soaking

in very low acid concentrations (0.25M HCl) maximised protein yields by minimising protein degradation.

Acid treatment removes apatite and secondary carbonates, free amino acids, soluble peptides and fulvic acids. Humic acids are left as solid phases and must be rinsed out (Chisholm 1989:24). Tests by van Klinken and Hedges (1995:268) have indicated that greater than 15% contamination can remain following an acid wash, and Stafford *et al.* (1991:63, table 12) concluded that the weak-HCl-insoluble residue will, at best, give a minimum age even when using well-preserved bone (*i.e.* 2 - 3% nitrogen). Consequently, additional purification steps typically follow acid hydrolysis, though pretreatment may terminate at any step after the acid wash depending on the desired quantity and quality of extracted "collagen".

### Dialysis

Dialysis devices separate particles by a membrane that allows small molecules and ions to pass while retaining the larger particles (Hibbert and James 1987:137). This method has been used to separate degraded protein from high molecular weight contaminants and results in higher yields of protein that acid digestion alone (Hassan and Hare 1978:110; Hedges and van Klinken 1992:286).

Ethylene diamine tetra-acetate (EDTA) is commonly used if the insoluble fraction is to be analysed (Berger, Horney and Libby 1964), though HCl has also been used (Munnich 1957; Berger, Horney and Libby 1964; Hassan and Hare 1978). If EDTA is used, the sample needs to be washed carefully following pretreatment because humic acids will dissolve in the slightly basic EDTA solution (Olsson 1991:30). Dialysis pretreatment has not, however, been very successful. Stafford *et al.* (1991:63) concluded that dialysis of well-preserved bone (*i.e.* 2 - 3% nitrogen) has a very low to low probability of producing an accurate result. In addition, tests by Arslanov and Svezhentsev (1993:389) have indicated that the combined NaOH/gelatin pretreatment (see below) yielded older $^{14}C$ results than the EDTA dialysis technique, with less effort. Consequently, purification of bone protein by dialysis is relatively uncommon in radiocarbon laboratories.

### Alkali treatment (ABA)

An alkali wash, typically with NaOH, can follow the decalcification procedure (*e.g.* Vogel and Waterbolk 1963; Berger and Libby 1966; Haynes 1967; Gurfinkel 1987). Such treatment dissolves humic contaminants that may have attached to the protein

molecule. Generally the acid-insoluble fraction is treated briefly at room temperature with low NaOH concentrations (0.1M - 0.2M), though if sample stability is not a problem, longer time may apply. A harsher pretreatment is recommended for burnt bone (*e.g.* extraction with 1 M NaOH for 1 hour at 95 - 100°C) (Hedges et al. 1989:112). NaOH may, however, preferentially affect some amino acids and may, therefore affect the isotopic character of the collagen (DeNiro and Epstein 1981; Hedges and Law 1989:249). In the process NaOH may obscure diagenetic changes (Chisholm 1989:27). NaOH may also incorporate $CO_2$ from the atmosphere (J. Head[1], *pers. comm.* 15/6/95) influencing the final result. Limited exposure to NaOH, careful washing with distilled water following the alkali wash, and adjustment of the pH to 1 with acid limits this effect. Alternatively, treatment of the "crude collagen" with NaOH under a nitrogen atmosphere will prevent the absorption of $CO_2$.

Collagen solubility also increases when NaOH concentrations are greater than 0.1M (Arslanov and Svezhentsev 1993:389; Liden, Takahashi and Nelson 1995:324-325). Van Klinken and Hedges (1995:268) have suggested that treatment with a strong base (1M NaOH) will completely dissolve the collagen-humic mixtures more quickly than releasing humic acids. Recent tests on deliberately contaminated collagen have confirmed that around 10 - 15% humic contamination will remain following an ABA treatment (van Klinken and Hedges 1995:268). The NaOH step is, therefore often replaced in AMS laboratories by purification techniques such as ultrafiltration or column chromatography. Gurfinkel (1987:51), on the other hand, concluded that alkali extraction was more effective at removing humic contaminants than either the acid digestion or gelatinisation methods alone. Pending more extensive research it seems likely that the effectiveness of NaOH treatment will depend on the specific contaminant. Further, if sufficient well-preserved bone is present an alkali wash will often be used to lower contaminants prior to more extensive purification.

### Gelatinisation

Gelatinisation is the process whereby the acid-insoluble "collagen" residue is dissolved in acidic hot water. This technique denatures the collagen triple-helical structure, breaking the hydrogen bonds between the collagen molecules enabling solid impurities, insoluble collagen and degraded collagen to be removed. On cooling the helix partly re-forms into a gel (Waterlow, Garlick and Millward 1978:512; Woodhead-Galloway 1980:55; Smith *et al.* 1983:215).

[1] J. Head, formerly Quaternary Dating Research Centre, Australian National University, Australia.

In order to prevent any acid-insoluble materials from entering the solution the gelatinisation pH (typically a pH of 3) should be kept constant (Chisholm 1989:25-6; Law and Hedges 1989:250). Temperature and length of gelatinisation vary between laboratories (with temperatures in the range of 70°C to 120°C for $^1/_2$ to 20 hours) significantly influencing final yields (Figure 3.1). Initial tests undertaken for this dissertation on archaeological and modern fish bone, indicate the extent of variation depending on pretreatment specifications (Figure 3.1). The most significant differences in yield are evident when the temperature of gelatinisation is increased from 70°C to 90°C. Recent tests by Brown *et al.* (1988:173) have demonstrated, however, that yields stabilise as the denaturing temperature (Td) of an animal is reached, for mammalian collagen this is around 58°C. Gelatinisation at such low temperatures (58°C) increases the yield of the high molecular weight fraction (Brown *et al.* 1988:173) and may also prevent dissolution and bonding of exogenous compounds to the collagen fragments during subsequent procedures (Stafford *et al.* 1991:45). Gelatinisation can also be carried out in a sealed nitrogen atmosphere to prevent caramelization of carbohydrates, a process that can interfere with subsequent amino acid extraction. The supernatant is then centrifuged or filtered to remove solids, and air dried or freeze-dried.

While gelatinisation helps to remove the acid insoluble soil-derived humin and humics, fulvic acids and humic derived oligo- and polysaccharides may dissolve with the gelatin. These "free humics" can bond with the sample as the gel cools down. Alternatively, it is possible that the high temperatures and low pH will promote Amadori re-arrangement reactions (part of the Maillard complex of reactions - see page 28), resulting in stronger bonding between humic acids and collagen (Arslanov and Svezhentsev 1993:388; van Klinken and Hedges 1995:268). Gelatinisation may also result in sample losses of up to 50% depending on the extent of collagen/humic cross-linkages, gelatinisation time and temperature (Stafford *et al.* 1991:45). Consequently, the Radiocarbon Accelerator Unit at Oxford[2] only uses the gelatinisation technique for bones in "good" chemical condition (>20% original collagen remaining) (Hedges and van Klinken 1992:286).

[2] Research Laboratory for Archaeology and the History of Art, Oxford, England.

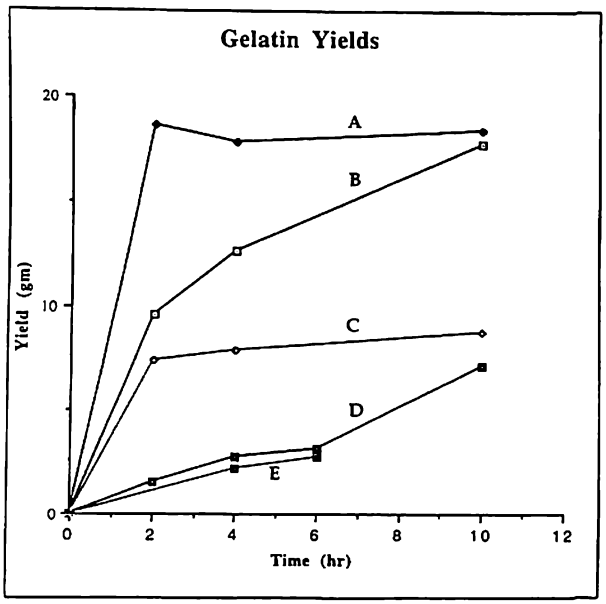


Figure 3.1: Variation in gelatin yield of test samples according to pretreatment: a) modern "acid-insoluble collagen" gelatinised at 90°C; b) modern "acid-insoluble collagen" gelatinised at 70°C; c) archaeological "acid-insoluble collagen" gelatinised at 90°C; d) archaeological "acid-insoluble collagen" gelatinised at 70°C; e) archaeological NaOH treated "acid-insoluble collagen" gelatinised at 70°C.

Recent tests by van Klinken and Hedges (1995:268) on collagen deliberately contaminated with humic acids, indicated that around 8% contamination can remain following gelatinisation. Stafford *et al.* (1991:64) similarly concluded that untreated gelatin from extremely well-preserved bone (> 3% nitrogen) would have a low to moderate possibility of an accurate radiocarbon estimate. A NaOH wash before gelatinisation could, however, improve the accuracy of the result, and the routine combination of gelatinisation with an alkali wash has been recommended by Gurfinkel (1987:51) and Arslanov and Svezhentsev (1993:389), especially when pretreating old samples.

## Ultrafiltration

Ultrafiltration devices may be used to purify the extracted gelatin (Brown *et al.* 1988; van Klinken and Hedges 1995). Such devices separate high molecular weight peptides from low molecular weight contaminants by applying suction or pressure during dialysis (Hibbert and James 1987:137, 500; Brown *et al.* 1988:171, 175). Separation of the >30,000 kD[3] fraction by ultrafiltration following low temperature gelatinisation has been shown to improve the $^{14}C$ age of well-preserved bone (2 - 3%

[3] A measure of molecular weight; 1 kDalton = 1000 amu.

nitrogen content) (Hedges and Law 1989:252; Stafford *et al.* 1991:64; Hedges and van Klinken 1992:286).

Ultrafiltration devices do not, however, eliminate contamination by high molecular weight species, or complexes of humic and degraded collagen (Hedges and van Klinken 1992:286). Consequently, while geologically-young fulvic acids with small molecular weights and greater solubility during gelatin extraction may be removed, older humic fractions that have higher molecular weights are not. Recently this technique has been used to isolate large peptide fragments prior to collagenase digestion and subsequent reversed-phase HPLC (High Performance Liquid Chromatography)[4] purification to tripeptides (van Klinken and Hedges 1992; van Klinken, Bowles and Hedges 1994).

**Ion exchange purified gelatin**

Crude gelatin may also be purified using ion exchange techniques (Law and Hedges 1989; Hedges and Law 1989:251-252; Hedges *et al.* 1989; Law *et al.* 1991). Ion exchange removes contaminants left behind following gelatinisation (*i.e.* fulvic materials and possibly oligo- and polysaccharides associated with humic acids) to below infrared detection levels (Law *et al.* 1991:312). The purified gelatin can then be hydrolysed and the total amino acids separated using ion exchange or, if necessary, the hydrolysates can be further clarified by reversed-phase methods, such as XAD resins or charcoal[5] (Hedges *et al.* 1989:101; Law and Hedges 1989:250).

The use of ion exchange methods enables the identification and separation of collagen and its breakdown products from contaminants. In addition, sample reliability can be assessed and, therefore bone with low levels of surviving collagen (*i.e.* 2 - 5% nitrogen) may be dated (Hedges and van Klinken 1992:286). This process has been semi-automated by the Radiocarbon Accelerator Unit at Oxford in order to improve the accuracy of $^{14}C$ determinations of old and contaminated samples by reducing the effects of human error and contact with air (Law and Hedges 1989:247). Using this automated continuous flow method Law *et al.* (1991:312) were able to measure the $^{14}C$ in a sample with around 0.25% of its original collagen surviving. The automated

[4] High Performance (or pressure) Liquid Chromatography is characterised by the use of small particle sizes, narrow bore columns and high column inlet pressures to achieve separation in short periods of time. HPLC techniques may be applied to both reversed-phase and ion exchange methods (Hibbert and James 1987:232) (see below).

[5] Ion exchange chromatography separates ions via net charge (Hibbert and James, 1987:257-8). Reversed-phase chromatography is where the mobile phase is hydrophilic (solvated by water) and the stationary phase hydrophobic (not solvated by water) (Hibbert and James, 1987:289, 416).

system was not, however, successful in recent tests by van Klinken and Hedges (1995:268) who attempted to purify modern collagen that had been deliberately contaminated with humic acids. This, they suggested, was possibly the result of column overloading due to the high levels of humics present. Similar problems were encountered by Redvers-Newton (1995) (see below) suggesting column overloading may be a fairly common problem with poorly preserved bone.

**Purification of mixed amino acids**

Purification of the hydrolysed protein with reversed phase and/or ion exchange chromatography has been widely employed in AMS laboratories with varying success. The two main methods involve either the treatment of hydrolysed "collagen" (acid-insoluble residue) with activated charcoal and then absorption and elution from an ion exchange column (Gillespie, Hedges and Wand 1984, Gillespie, Hedges and Humm 1986), or alternatively passing hydrolysed gelatin through XAD resins[6] (Stafford *et al.* 1987, 1991; Stafford, Brendel and Duhamel 1988). Both methods are limited to bones with around 5% extractable protein due to large sample losses (Hedges *et al.* 1989:101; Stafford, Brendel and Duhamel 1988:2265; Law *et al.* 1991:305).

Direct hydrolysis of the acid-insoluble residue was not, however, very successful and early $^{14}C$ determinations on poorly preserved bone (*i.e.* Gillespie, Hedges and Wand 1984; Gillespie, Hedges and Humm 1986) often resulted in young ages even when the contaminants were old (Hedges and Law 1989:251-252; Law *et al.* 1991:312). Researchers at the Oxford Radiocarbon Accelerator Unit (*i.e.* Hedges *et al.* 1989:101; Law and Hedges 1989:250) concluded that hydrolysis of "crude collagen" in the presence of carbohydrates could lead to the incorporation of soil derived amino acids to the hydrolysate, while sugars released from polysaccharides during acid hydrolysis react with amino acids in the hydrolysate leading to "humin" formation and "browning" reactions. These amino acids and cross-linked collagen/humic mixtures could not always be identified and removed by XAD resins or ion exchange chromatography (Law *et al.* 1991:312).

Stafford *et al.*'s (1991:45, 64) technique was more successful as the concentration of contaminants was lowered by gelatinising the protein prior to hydrolysis. The use of XAD resin (reversed-phase chromatography) also theoretically lowered the

[6] Porous non-polar to weakly-polar absorbents used in column chromatography to isolate weakly or non-ionised aliphatic and aromatic molecules from aqueous solutions (see Stafford, Brendal and Duhamel 1988:2257-2259)

concentration of fulvic acids which were retained through hydrophobic interactions (Stafford *et al.* 1982:935; Stafford, Brendel and Duhamel 1988:2257).

Redvers-Newton (1995) recently tested both the purified amino acids following Stafford *et al.* (1987), Stafford, Brendel and Duhamel (1988) and Stafford *et al.* (1991), and the ion exchange purified gelatin method of Hedges *et al.* (1989). Radiocarbon analyses were carried out on the Pacific Region Analytical Bone Standard; a moderately well-preserved, Class III bone[7] (0.4 - 0.9% nitrogen). Despite the indication that fulvic acids were the main contaminant, Redvers-Newton (1995:107, 112-113) concluded that Stafford *et al.*'s (1991) method was no more successful than the method carried out at Oxford .

### Ninhydrin

A recent refinement to the separation of mixed amino acids involves the extraction of carboxylic carbon bonded to the amino acids (not imino acids) by reaction with ninhydrin ($H_4C_6$-COCOCOO.$H_2O$)(Nelson 1991; van Klinken and Hedges 1995). Tests by van Klinken and Hedges (1995:269) indicated that no humic carboxylic carbon is released during the ninhydrin derivatization step. This technique does not remove proteinaceous contaminants, but because such contaminants in bone are generally recycled from collagen the effect on $^{14}C$ is often negligible (van Klinken and Hedges 1998:53). While further tests are underway, Hedges, Bowles and van Klinken (1994:2544) do not believe that carbon extracted with ninhydrin will improve on the $^{14}C$ estimates of bone specific fractions. The main drawback being a lack of reliability (mainly variable yields) that make it less suitable for routine use (van Klinken and Hedges 1998:53).

### Imino acids

Early attempts to isolate and measure the $^{14}C$ in a bone specific fraction focused on imino acids (hydroxyproline and proline). Theoretically hydroxyproline, a bone specific amino acid synthesised *in vivo* by hydroxylation of proline, should have identical $^{14}C/^{12}C$, $\delta^{13}C$ and $\delta^{15}N$ values to proline. Therefore, simultaneous analysis of both hydroxyproline and proline provided a measure of sample purity (Gillespie, Hedges and Wand 1984:166; Stafford *et al.* 1982:932). Hydroxyproline and proline were initially separated from the purified total amino acids (see above) by de-amination of the primary amino acids to their alpha-hydroxy acids via nitrosylation (*i.e.* by the

[7] After Stafford, Brendel and Duhamel (1988).

addtion of nitrous acid) (see Gillespie *et al.* 2984:168). This was followed by ion exchange to remove the hydroxy acid products of the primary amino acids (Gillespie, Hedges and Wand 1984; Gillespie, Hedges and Humm 1986; Stafford *et al.* 1982, 1987; Stafford, Brendel and Duhamel 1988).

While the measurement of imino acid $^{14}C$ was met with optimism (*e.g.* Taylor 1982:469; Stafford *et al.* 1982), initial results were indistinguishable from the "less accurate" "collagen" determinations (Gillespie, Hedges and Wand 1984:169; Gillespie, Hedges and Humm 1986:454). Results on imino acids isolated from ion exchanged, XAD purified gelatin hydrolysate (Stafford *et al.* 1987; Stafford, Brendel and Duhamel 1988) were more successful (Stafford *et al.* 1991:64). This technique can not, however, adequately estimate the $^{14}C$ content of bones with less than 5% extractable collagen (~0.2% nitrogen) because a non-collagenous amino acid composition begins to predominate whereby hydroxyproline is either absent (Hedges and Law 1989:252; Stafford *et al.* 1991:44) or introduced from exogenous sources such as natural waters, animal urine, fungal cell walls, plant structural proteins and/or some micro-organisms (Waterlow, Garlick and Millward 1978:510; Woodhead-Galloway 1980:12; Hedges and van Klinken 1992:287). Derivatization techniques (nitrosylation) may also affect $\delta^{15}N$ and $\delta^{13}C$ by up to 20% and 5% respectively, therefore masking non-aminated contamination (Stafford, Brendel and Duhamel 1988:2265; van Klinken and Mook 1990:158). Further, Hedges and Law (1989:252) argue that if sufficient quantities of hydroxyproline can be isolated then alternative pretreatments may be more suitable.

### Multiple individual amino acids

Dating of multiple amino acids enables the validity of each radiocarbon estimate to be tested by comparing results of different amino acids (van Klinken and Mook 1990:162). Amino acids may also be selected for specific analytical purposes, for example glutamic acid which is the most abundant amino acid in nature and is, therefore considered to be a good test for overall contamination (van Klinken and Mook 1990:157). Stafford *et al.* (1987) and Stafford, Brendel and Duhamel (1988) ran the first $^{14}C$ determinations on multiple amino acids (aspartic and glutamic acids, glycine, serine, and threonine) specifically to test the validity of hydroxyproline results on poorly preserved and non-collagenous bones. Initial results were not successful. Further tests were carried out at Oxford where a preparative cation exchange-HPLC system was used to separate and purify multiple individual amino acids without derivatization techniques (van Klinken and Mook 1990:158). The use of HPLC also enabled better separation, direct identification of peaks, content monitoring and shorter

extraction times than the more usual chromatography techniques (van Klinken and Mook 1990:162).

Stafford *et al.* (1991) devised a similar technique at the same time to investigate the potential of non-collagenous bones. They analysed multiple fractions, including contaminants and suits of amino acids. HPLC also enabled the "non-destructive" extraction of amino acids from well-preserved samples by heating (150°C for 7 days) in a sealed tube containing water (Stafford *et al.* 1991:57). Following initial results, Stafford *et al.* (1991:35) claimed that individual amino acids could accurately estimate the $^{14}C$ content of bones with a collagenous composition (*i.e.* $\geq$ 0.1 to 0.2% nitrogen). Non-collagenous bones ($\leq$ 0.1% nitrogen) did not give reliable results as soil derived amino acids could be present. Under such circumstances, Stafford *et al.* (1991:60-61) suggested that only a minimum age could be obtained by estimating the $^{14}C$ of the humic fraction. Determinations on low collagen bones were not, however, always successful. For example, hydroxyproline $^{14}C$ measurements of a collagenous sample from Pyramid Lake gave a different result to other amino acids (Stafford *et al.* 1991:56-57). In addition, five amino acid $^{14}C$ determinations from a non-collagenous bone (the Escapule mammoth) gave concordant, but young values (Stafford *et al.* 1991:49-50, figure 4; Hedges and van Klinken 1992:288).

The use of HPLC is also costly, requires expertise, has low sample capacity, affects stable isotope measurements, and resin bleeding can introduce $^{14}C$ contaminants to samples if rigorous cleaning protocols are not followed (Burky *et al.* 1998:13). Hedges and Law (1989:252) and van Klinken, Bowles and Hedges (1994:2550) have also suggested that the reduction to single amino acids destroys valuable biological information.

### Tripeptides

The separation of tripeptides is the newest bone pretreatment (van Klinken and Hedges 1992; van Klinken, Bowles and Hedges 1994), and probably the most time consuming and expensive technique routinely available. This pretreatment method involves the separation and radiocarbon analysis of tripeptides via ultrafiltration of gelatin, followed by digestion of the >10 kD fraction with chlostridial collagenase to obtain a peptide mixture (glycine-proline-hydroxyproline [GlyProHyp] and glycine-proline-alanine [GlyProAla]), and then reversed-phase HPLC chromatography to remove hydrophobic impurities. This method has the benefit of enabling the validity of the $^{14}C$ determination to be tested by comparing results of the high molecular weight contaminants with the hydrophobic and >30 kD fractions (van Klinken,

Bowles and Hedges 1994:2544-2545). The separation of tripeptides also has an advantage over the separation of individual amino acids as collagenase reliably cleaves the collagen into specific peptides (van Klinken, Bowles and Hedges 1994:2550).

Van Klinken, Bowles and Hedges (1994:2550) suggested that the $^{14}C$ of all contaminated bone can be accurately estimated using tripeptides, provided enough "collagen" survives. Tests using stable isotope, infrared and radiocarbon data (van Klinken and Hedges 1992:293; 1995:265) indicate that collagenase treatment liberates humic acids from the tripeptides, which can then be isolated by HPLC. Severe humic contamination will, however, sterically hinder the enzymatic action of collagenase and affect yields possibly due to cross-links, or obstruction by large molecules (van Klinken, Bowles and Hedges 1994:2550; van Klinken and Hedges 1995:265, 269). Problems have also been noted when applied to bog body tissue and bone. In these samples, very little GlyProHyp could be extracted although the enzymatic digestion had produced significant quantities of this tripeptide. Following the enzymatic reaction the GlyProHyp had instantaneously complexed with the humic substances that had also been released, and the humics co-migrated with the GlyProHyp during the chromatographic separation (van Klinken and Hedges 1998:54).

The complexity of this technique also makes it particularly susceptible to laboratory introduced contamination (van Klinken and Hedges 1992), though the oldest bone determinations measured at Oxford so far are of purified tripeptides (Pestera PCR3 dated to 48,000 BP) (van Klinken, Bowles and Hedges 1994:2550).

### Non-collagenous proteins

There is increasing evidence that non-collagenous proteins (NCP's) are preferentially preserved and dominate when little collagen survives (Masters 1987:3209; Long *et al.* 1989:238; Hedges and van Klinken 1992:285). A number of non-collagenous proteins have been detected in archaeological bones, including osteocalcin (Ajie *et al.* 1992), albumin (Tuross 1989), haemoglobins (Ascenzi *et al.* 1985) and phosphoproteins (Masters 1987). Similarities in the $\delta^{13}C$ and $\delta^{15}N$ values of NCP's compared to collagen have advanced speculation that they may be useful for radiocarbon analysis. Only osteocalcin has been measured extensively (Ajie *et al.* 1990; Ajie *et al.* 1992; Taylor 1980, 1992).

Osteocalcin (or "bone Gla protein") is a non-collagen bone-matrix protein that appears to bind tightly to hydroxyapatite. Therefore, the buffering action of hydroxyapatite is thought to protect osteocalcin from biochemical degradation (Ajie *et al.* 1992:297;

Hedges and van Klinken 1992:288). In addition, Gla has not been detected in other vertebrate and plant proteins, nor in bacteria (Burky *et al.* 1998:13). Unfortunately, osteocalcin content diminishes along with bone preservation (and hydroxyproline concentration). This suggests that diagenesis may in part control the amount of intact osteocalcin (Ajie *et al.* 1992:298-299; Taylor 1992:390). In addition, $^{14}C$ values of osteocalcin and gelatin diverge as the concentration of extractable gelatin decreases, supporting this conclusion (Ajie *et al.* 1992:296; Taylor 1992:395). Recent analysis by Burky *et al.* (1998) suggests that even when bones retain significant amounts of collagen (> 25% of modern total amino acid content), Gla can yield $^{14}C$ values discordant from the expected age and from total amino-acid fractions isolated from the same sample. Hedges and van Klinken (1992:288) consider bone specific NCP's to be a low priority as they do not have a recognisable structure and therefore, cannot be adequately tested for reliability.

### Carbonate

Early tests on the carbonate fraction of bone indicated that exchange with $CO_2$ from the atmosphere was occurring (Haynes 1968:688; Rafter *et al.* 1972:643). At present no one has demonstrated that the indigenous bone carbonate will reliably give an accurate result (Stafford *et al.* 1991:62; Hedges and van Klinken 1992:285) despite the wide range of techniques used to isolate hydroxyapatite $CO_2$ (*e.g.* Haas and Banewicz 1980; Hassan and Ortner 1977; Hassan *et al.* 1977; Lee-Thorp, Sealy and van der Merwe 1989),

## ASSESSMENT TECHNIQUES

The need to detect problem samples and choose a suitable method of bone pretreatment and decontamination has seen the use of a range of quality screening procedures (Taylor 1980:972; Hedges and Law 1989:253; van Klinken and Hedges 1998:51). The most commonly adopted indices include measurement of the nitrogen content, collagen yield, isotopic composition, an atomic C/N ratio, a characteristic amino acid pattern, and the identification of a collagenous infrared spectrum. Unfortunately, many of these techniques are not sensitive enough to detect contamination and there have been few attempts to combine more than one of these techniques into a comprehensive bone assessment scheme (though see Table 3.2).

## Hand specimen identification

The measurement of physical characteristics such as density, colour and strength is the quickest method of estimating the suitability of bone for radiocarbon analysis. These methods are widely used by archaeologists interested in site taphonomy (*e.g.* McGovern-Wilson 1992) and in the selection of samples for radiocarbon dating. Such characteristics are, however, given little coverage in the $^{14}C$ literature (though see Table 3.2 above) because they are somewhat subjective, may not identify contaminants, and cannot estimate the amount of remaining collagen. The visible effects of weathering also vary depending on deposition environment, type and/or size of bone as well as species (Nicholson 1996a, 1996b, 1998).

Table 3.2: Classification of bones based on physical and chemical properties (after Stafford, Brendel and Duhamel 1988:2258 and Stafford *et al.* 1991:62-64).

| | Class I Modern | Class II Very well to well -preserved | Class III Moderately well-preserved | Class IV Poorly preserved | Class V Extremely poorly preserved |
|---|---|---|---|---|---|
| % nitrogen in whole bone | 4.5-3.5 | 3.5-0.6 | 0.9-0.4 | 0.5-0.1 | 0.1 to<0.01 |
| General amino acid description | Collagenous composition. | Collagenous composition with slight increase in alanine. | Collagenous composition with slight increase in alanine. | Collagen-derived amino acid composition. Diminished hydroxyproline and glycine. Increase in aspartic and glutamic acids. | Absence of hydroxyproline and possibly arginine. Increase in aspartic and glutamic acids, decrease in glycine and proline. |
| Physical characteristics of whole bone | Spiral and conchoidal fracturing; waxy luster; dense mineral matrix. | Chalky with loss of conchoidal fracturing: exterior still hard and waxy. Lower N%: fracturing becomes uneven. | Interior and exterior chalky. Surface hardness decreases and porosity increases with decreasing N%. Hackly fractures. | Continued decrease in hardness and increase in porosity. | Soft. Hard if inorganic replacement has occurred. |
| "Collagen" yield | ≥90wt% of collagen | >80wt% of protein | >50wt% protein | 20-50wt% protein | <10-20% of protein |
| Probability of accurate date on gelatin from NaOH-washed, decalcified bone. | Moderate to high | Very low to high | Very low to low; provides a minimum age | Zero to low | Zero to extremely low |

## Nitrogen: Total collagen content

Fresh, dry, defatted bone from large mammals contains on average between 4 and 5% organic nitrogen by weight. Protein is the only component in modern bone that contains nitrogen, and collagen makes up $^{9}/_{10}$ of the bone nitrogen (Garlick 1969:503-504). The amount of remaining collagen can, therefore be estimated by measuring the per cent nitrogen in the whole bone (*e.g.* Stafford, Brendel and Duhamel 1988:2258, table 1), or in the decalcified extract (*i.e.* protein content or amino acid content) (*e.g.* Hedges and Law 1989:250, figure 2). Such measurements do not, however, indicate if nitrogen is wholly present as collagen, nor the extent of non-nitrogenous organic contaminants (Hedges and van Klinken 1992:282).

Following burial, nitrogen quickly diminishes, with initial loss being greatest and subsequent loss decreasing with time. Consequently, there have been several attempts to use the nitrogen concentration as a relative dating technique (*e.g.* DeVries and Oakley 1959; Houghton 1977a, 1980). Early attempts were, however, unsuccessful as the rate of "collagen" decay, and therefore nitrogen loss, depends on a number of variables including temperature, pH, water flow (Ortner, von Endt and Robinson 1972; and von Endt and Ortner 1984) and the presence of micro organisms that break down collagen (*i.e.* collagenase) (Garlick 1969:506).

**Protein yield**

Measurement of the "collagen" or gelatin concentration in bone can be used to assess the preservation state. Unfortunately, the specifics of the pretreatment method and variations in the technique used to estimate the remaining "collagen" make inter-laboratory comparisons difficult (van Klinken and Hedges 1995:264). In addition, the fraction isolated needs to be carefully defined. Protein yields are generally measured as a percentage of the extractable collagen (*i.e.* as a percentage of the decalcified extract), though the concentration with respect to the amount of bone, yield following collagenase digestion (DeNiro and Weiner 1988a, 1988b) or amino acid hydrolysis (van Klinken and Hedges 1995), and $CO_2$ yield (Gurfinkel 1987:48) have been used.

Although low apparent values of surviving "collagen" indicate poor preservation (Hedges and van Klinken 1992:282), a high yield does not insure the integrity of the protein (Tuross, Fogel and Hare 1988:933). A high level (*i.e.* 5 - 10%) of contamination can, however, be recognised analytically where the bone is of good or intermediate preservation (Hedges and van Klinken 1992:284). There are a variety of markers for classifying collagen degradation. Hedges and van Klinken (1992:284) suggested that bone is of "good" preservation when >20% original collagen remains (based on a modern value of 200 mg collagen $g^{-1}$ of dry bone), "poor" preservation; <10% original collagen remaining, and "non-collagenous" preservation; <0.5% collagenous composition remaining. Alternatively, DeNiro and Weiner (1988a:2204) calculated the percentage of freeze-dried gelatin compared to bone and obtained values of 15.8 - 33.0, 1.2 - 10.7 and 0.3 - 2.1 wt% gelatin for modern, good prehistoric and bad prehistoric respectively (see also Stafford, Brendel and Duhamel 1988: 2258, table 1).

Yield measurements may also be calculated on the residue following gelatinisation, and ash following combustion. Mook and Waterbolk (1985:40-41) assessed the chemical

purification of collagen on the basis that ash left after combustion should be below 5% of the initial bone weight, while the insoluble fraction removed by centrifugation following gelatinisation should be below 10%.

### Amino acid analysis

Collagen and its breakdown products can be identified by amino-acid analysis. This has become a very popular technique in AMS laboratories using column chromatography techniques to purify the sample because amino acids may be analysed simultaneously (*e.g.* Stafford, Brendel and Duhamel 1988; 2258, table 1).

A collagenous amino acid composition predominates until around 5% of the original protein remains (*i.e.* approximately 0.2% nitrogen in whole bone). Below a 5% protein content a non-collagenous amino acid composition begins to predominate. This is exemplified by a total loss of hydroxyproline and often proline, a decrease in glycine from 33 - 20%, and a two-to-three-fold increase in the abundance of aspartic and glutamic acids (Tuross, Fogel and Hare 1988:931; Stafford *et al.* 1991:44). Some workers (*e.g.* Wyckoff 1972) suggest that the absence of the collagen amino acid signature indicates the presence of contamination. Others (*e.g.* Hare 1980) have suggested that where the organic content is extremely low (below 0.4 - 0.1% nitrogen), the amino acid pattern may reflect the indigenous NCP's rather than contamination (Taylor 1980:973). Different pretreatments and diagenesis may also selectively remove amino acids and peptides due to differences in solubility, the affect of temperature and/or susceptibility to oxidation or de-amination (Hedges and van Klinken 1992:283, 285).

The presence of contamination or a non-collagenous composition may be identified by the analysis of specific amino acid ratios, for example the ratio of glycine to aspartic acid. Glycine is abundant in collagen while aspartic acid occurs both in bone non-collagenous proteins and in most (including bacterial) protein (van Klinken and Mook 1990:157; Hedges and van Klinken 1992:282-283). Similarly, the ratio of glycine (Gly) to glutamic acid (Glu) can be used as an index of a collagen-like or non-collagen-like pattern (Taylor, Hare and White 1995:115). This is because glycine contamination is rare. Grupe (1995) hypothesised that although glycine is the most abundant collagen amino acid, it is less attractive to heterotrophic decomposers because it contains only around 17% carbon (*i.e.* two carbon atoms per molecule). Amino acids such as tyrosine, (9 carbon atoms), histidine and isoleucine (6 carbon atoms), and methionine (5 carbon atoms) are more readily altered (Grupe 1995:198-199). Several studies have also investigated the possibility of using amino acid

racemisation values as a means of characterising indigenous organics in bone samples (Taylor 1982:468; Masters 1987).

### Stable isotopes ($\delta^{13}C$ and $\delta^{15}N$)

Stable isotope analyses have been widely used in dietary studies (*e.g.* Schoeninger and DeNiro 1984; DeNiro 1985; Ambrose and Norr 1993). Diagenesis of collagen and preferential loss of amino acids may, however, alter the isotope value of the resulting organic fraction (Tuross, Fogel and Hare 1988). Humates can also have an affect on the isotopic composition of bone depending upon their concentration, $^{13}C$, $^{14}C$ and $^{15}N$ values (Stafford, Brendel and Duhamel 1988:2257). In most cases the soil $\delta^{13}C$ values rarely differ by more than 8% from protein values. This results in only a 0.5 - 0.8‰ offset in collagen for a 10% contribution from soil humics (Hedges and van Klinken 1992:283), though this does increase as the collagen content decreases (Stafford, Brendel and Duhamel 1988:2260). Contaminating materials (*e.g.* humics or amino acids) may also be formed *in situ* from collagen parts and may not, therefore be isotopically different from the original collagen fibre (van Klinken and Mook 1990:155). Interference by lipids may also influence $\delta^{13}C$ values obtained from modern bone, but should not be a problem in fossil or archaeological bone (Tuross, Fogel and Hare 1988:931). Nitrogen isotopes are more difficult to predict with only gross contamination (*i.e.* outside the range of +5 to +15‰) usually evident (Hedges and van Klinken 1992:283, 289).

In some cases, the traditional pretreatments (*i.e.* HCl, EDTA, NaOH, gelatinisation and chromatography techniques) may also change the isotopic values of bone protein (Tuross, Fogel and Hare 1988:929, 934), possibly due to incomplete removal of contamination or preferential removal of some amino acids (Taylor 1980:975; Stafford, Brendel and Duhamel 1988:2264). The change in isotopic value during sample preparation, especially in $\delta^{13}C$ can, however, be a sensitive test for the removal of contamination during pretreatment (Hedges and van Klinken 1992:289). Consequently, Stafford, Brendel and Duhamel (1988:2266) recommend the simultaneous measurement of $\delta^{14}C$, $\delta^{13}C$ and $\delta^{15}N$ isotopes when dating bone fractions.

### C/N atomic ratio

A C/N atomic ratio has been used to detect contamination in bone isotopes (DeNiro 1985; DeNiro and Weiner 1988a, 1988b). Carbon/nitrogen atomic ratios can be measured on the whole bone or extract of either the decalcified residue ("collagen") or

gelatin. Values of 2.9 - 3.6 from gelatinous extracts of bone are thought to indicate "good prehistoric" samples (DeNiro 1985; DeNiro and Weiner 1988a, 1988b). Unfortunately, C/N atomic ratios have been of little help in $^{14}C$ analysis (van Klinken and Hedges 1995). Tests by van Klinken and Hedges (1995) have shown that modern collagen, with approximately 28% humic acid contamination, had a C/N ratio of 3.9 (*i.e.* DeNiro's (1985) "bad prehistoric" collagen). Following pretreatment, a residue with C/N ratio of 3.5 ("good prehistoric" collagen) had 10% - 15% humic contamination, while a residue with a C/N of 2.9 had 8% humic contamination remaining, indicating that significant contamination may still exist in a sample with a supposedly typical collagenous C/N ratio. Further, changes to the collagen amino acid pattern that alter $\delta^{13}C$ and $\delta^{15}N$ isotopes will not necessarily cause significant shifts in the C/N value. Therefore, the use of C/N ratios limits the identification of "bad" collagens to those that have suffered a high level of alteration (DeNiro and Weiner 1988a:2204; Tuross, Fogel and Hare 1988:931; Hedges and van Klinken 1992:282-328).

## Infrared analysis

Infrared analysis measures the absorption of radiation caused by the excitation of molecular rotations or vibrations. The infrared spectrum of an organic molecule may give an indication of the functional groups it contains, while the spectrum as a whole provides a unique record of that molecule (Hibbert and James, 1987:252). Qualitative infrared spectroscopy has been used to look at protein structure and the purity of the protein under analysis (DeNiro and Weiner 1988a, 1988b; Law *et al.* 1991), screening for lipids (Liden, Takahashi and Nelson 1995:323) and/or synthetic polymers (Hedges *et al.* 1989:111; Law *et al.* 1991), organic contaminants (*i.e.* humic acids) (van Klinken and Hedges 1995) and identification of non collagenous proteins (Weiner and Bar Yosef 1990). Unfortunately, infrared assessment of bone, or pretreated bone fractions prior to radiocarbon analysis, is rare (van Klinken and Hedges 1995:263).

DeNiro and Weiner (1988a:2203, 1988b) demonstrated that well-preserved and poorly preserved bones, as identified by C/N ratios, could be differentiated by infrared analysis of acid (EDTA) soluble, acid-insoluble and "collagen" (sample pretreatment included ABA followed by gelatinisation in $10^{-3}$ M HCl at 90°C for 10 hours) fractions (Figure 3.2). A typical collagen spectrum was identified by the relative proportions of polysaccharides (a broad peak around 1050 $cm^{-1}$ (wavenumbers)) and collagen peaks (proline at 1456 $cm^{-1}$, amide I at 1650 $cm^{-1}$ and amide II at 1550 $cm^{-1}$). Bad prehistoric collagen gave neither collagen or polysaccharide peaks, and were dominated instead by a large single absorption around 1100 $cm^{-1}$ (DeNiro and Weiner

1988a:2200). Unfortunately, infrared analysis was not always successful (DeNiro and Weiner 1988a:2204).

Law *et al.* (1991) adapted infrared spectroscopy to assess the purity of various fractions (total acid-insoluble fraction, crude gelatin, and ion exchange gelatin) isolated from PVA and humic acid contaminated bone before radiocarbon assay. They found that infrared analysis was limited for severely contaminated archaeological bone samples because diagenesis and contamination could result in complex spectra (Law *et al.* 1991:308, 311). Consequently, Hedges and van Klinken (1992:283) suggest that infrared analysis cannot identify impurities less than the *ca.* 5 - 10% level. Infrared spectroscopy is, therefore commonly used to back up other data but not as a screening technique in its own right (van Klinken and Hedges 1995:263).

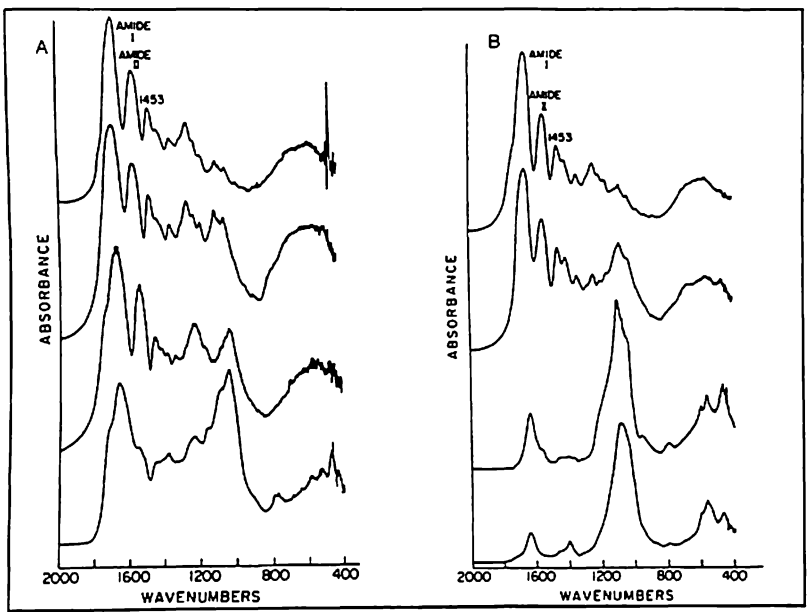


Figure 3.2: Infrared spectra of: (A) the HCl insoluble fraction extracted from modern and prehistoric bones. From top to bottom; modern, good prehistoric and bad prehistoric bones (x2); (B) "gelatin" (see text) extracted from modern and prehistoric bones. From top to bottom; modern, good prehistoric and bad prehistoric bones (x2) (from DeNiro and Weiner 1988:2203, figures 6 and 7).

Infrared spectroscopy can also be used to assess changes to the whole bone structure (both collagen and hydroxyapatite) that may have occurred as the result of diagenesis or burning and is a useful test of the breakdown of the relationship between collagen and hydroxyapatite. The splitting factor (SF), or crystallinity index (Sillen 1989; Weiner and Bar-Yosef 1990; Wright and Schwarcz 1996) and the carbonate/phosphate ratio (C/P) (Rink and Schwarcz 1995; Stiner *et al.* 1995; Wright and Schwarcz 1996) are two techniques commonly used to assess the degree of hydroxyapatite alteration in

fossil, sub-fossil, archaeological and burnt bones. This technique is, however, rarely applied to samples for radiocarbon analysis (though see Hassan, Termine and Haynes 1977).

## CONCLUSION

A wide variety of bone fractions are measured by radiocarbon laboratories. Not all fractions and pretreatment techniques have been of equal success. The isolation and measurement of $^{14}C$ in highly purified (*i.e.* ion exchange gelatin or amino acids) or bone specific fractions (*i.e.* tripeptides) appear to be the preferred techniques found in the literature. They are, however, very costly, require a high level of expertise, and are limited to AMS dating methods due to size restraints. Additionally, none of these methods have demonstrated conclusively that contamination has been removed and that the $^{14}C$ estimates are accurate, though collagenase digestion and ninhydrin derivatization show promise for estimating the $^{14}C$ content of collagenous samples (Hedges and van Klinken 1992:289; van Klinken and Hedges 1995:269). There is currently no reliable method for dating non-collagenous samples (Stafford, Brendel and Duhamel's (1988:2258) Classes IV and V). Somewhat over-shadowed are the more traditional pretreatments (*i.e.* gelatinisation and dialysis). These techniques are still used routinely world wide (B. Kromer[8], *pers. comm.* 3/5/95; G. McCormac[9], *pers. comm.* 4/5/95) and produce accurate determinations from bone considerably older than any found in New Zealand.

Following this review it is suggested that well-preserved (*i.e.* Stafford, Brendel and Duhamel's (1988:2258) Class II bone), young samples (<1000 years), with >20% collagen remaining (*i.e.* "good" preservation (Hedges and van Klinken 1992:284), should give reliable results when gelatinised following a NaOH wash. The accuracy of this method can be further improved by the use of assessment techniques to monitor sample "clean up" during pretreatment (Hedges and van Klinken 1992:289-290).

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# CHAPTER 4

# RADIOCARBON DATING BONE IN NEW ZEALAND

*" ...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" (Libby 1952:44).*

## INTRODUCTION

Debate over colonisation and settlement has dominated archaeological investigations in New Zealand. The interaction of humans with both introduced and indigenous fauna has been an important part of that debate (Duff 1950; Lockerbie 1959; Anderson 1989, 1996; Barber 1995; Holdaway 1996), with early commentary focusing on moa (*Dinornithiformes*), and more recent interest in kiore (*Rattus exulans*) remains. Consequently, the ability to date bone accurately has played an important role in the development of a radiocarbon chronology for the New Zealand prehistoric sequence, though recently bone has been considered to be less reliable than other sample types (Anderson 1991:779; Higham 1993:97; Schmidt 1996:9; Anderson, Smith and Higham 1996). This chapter examines the role of bone dating in New Zealand. The sites dated, pretreatment methods applied and the results of those dates are evaluated and a summary of the reasons for problematic dating are presented.

## BACKGROUND TO THE FIRST BONE DETERMINATIONS

Early commentators on New Zealand archaeology were interested in the cultural importance of moa, specifically the number and variety of moa encountered in prehistoric sites. The absence of absolute dating techniques had, however, precluded chronological control of the relationship between moa and humans. Excavations at the site of Wairau Bar in Marlborough enabled the first controlled investigation into the development of this relationship. Duff (1950:21), noting the "...impossibility of demonstrating its [*i.e.* Moa-hunter] greater age by direct stratigraphical methods" at Wairau Bar, used the association of moa, traditional accounts and an age area perspective, where cultural innovation is viewed as diffusing outwards from a central area, to build a chronological picture of the transition from Moa-hunter to Maori. Duff concluded "...that few members of the Fleet managed to see a live moa in the North Island" because moa were dying out naturally, and only smaller genera (*i.e. Euryapteryx*) survived on the east coast of the South Island (Duff 1950:21, 1956:280). According to Duff (1950:21, 294; 1956:20) the Moa-hunter period terminated with the

extermination of *Euryapteryx* and the overthrow of the Waitaha (a pre-Fleet tribe) in about AD 1500/1550. This interpretation was apparently confirmed by finds from South Island swamps which, in contrast to archaeological middens, contained the full range of moa species (Duff 1963:6).

Several problems were immediately apparent with Duff's (1950) hypotheses. The discovery of moa bones in a Maori fowler's shelter in the Takahe Valley, Fiordland, of "no apparent age", indicated a possible localised late survival of *Megalapteryx* (Duff 1950: 293, postscript)[1]. This was dismissed by Duff (1950:postscript; 1952:110) on the basis that *Megalapteryx* was a minor species whose wholesale slaughter did not determine the Moa-hunter period of Maori culture. He also suggested that *Megalapteryx* may have been closely related to the kiwi, and therefore incorrectly classified as a moa (1956:82). In addition, Duff (1950:276; 1952:108) dismissed the identification of six moa genera in the middens at Papatowai because he doubted the primary association of the bones and accuracy of their identification due to "...the somewhat tangled systematics of the moas...".

The first radiocarbon determinations obtained on samples from New Zealand archaeological sites compounded this controversy. Radiocarbon measurements from the Takahe Valley Shelter returned two contradictory results (NZ-51: 110 ± 60 BP[2] on tussock, and NZ-52: 700 ± 60 BP on totara bark), and Duff (1952:92, 102, 104, 1956:xii) concluded that the radiocarbon method was at fault. Therefore, when two early charcoal ages were reported for Wairau Bar (Y-204[3]: 949 ± 110 BP, and NZ-50[4]: 730 ± 50 BP), Duff (1956:xii) had to give additional support to these results, and his hypotheses, using a combination of traditional family trees and a close correlation of the Wairau Bar dates with the Polynesian $^{14}C$ record outside New Zealand. Consequently, even though Scarlett (1951:198-199) confirmed the identification of all six moa genera at Papatowai, including *Dinornis maximus*, and Lockerbie demonstrated their primary association, Duff remained sceptical. Duff (1956:280) believed that if "...genera other than *Euryapteryx* be revealed from other Otago sites, [then] our ideas regarding the role of man in the extinction of the Moas must be drastically revised", and therefore "[I]f we end by ascribing solely to man the

[1] Both Wairau Bar and Takahe Valley have been redated (see Table 8.1 and A6.1). Wairau Bar is now considered to have been occupied 750 BP (Higham, Anderson and Jacomb, in press), while recent results from the Takahe Valley shelter suggested an occupation some 600 years ago (O'Regan 1992:174-175).

[2] Radiocarbon determinations are given as specified at the time of initial publication unless otherwise noted, and may differ in the text depending on the reference cited. Recalculated values are given in Chapter 8, Table 8.1.

[3] Yale University, USA.

[4] IGNS, Wellington, New Zealand.

extinction of the moa...we must correspondingly grant him a much longer occupation than the accepted date of 950 AD", as suggested by the recent radiocarbon determinations from Wairau Bar.

This conclusion was also challenged by radiocarbon results from the Pyramid Valley swamp, where a sample of *Dinornis* gizzard material had given two different age estimates (L-129[5]: 1800 ± 150 BP and Y-129A: 670 BP). Deevy (1955) accepted the younger result and used it as evidence for the survival of this species up until first human settlement in New Zealand (Gregg 1972:153). Duff (1956:280-281) continued to doubt that *Dinornis* was contemporary with humans and had been exterminated by them, and suggested that "[I]n spite of this apparently definitive evidence...let us fall back on caution and suspend judgement" (1956:281).

## NEW ZEALAND'S FIRST BONE DETERMINATIONS

Lockerbie set out to document changes in culture over time, in particular to refute Duff's (1950:21, 1956:20) assertions that "no Moa-hunter layer has yet been shown to underlie a layer of the culture here called Maori" (Lockerbie 1959:79). Lockerbie (1959:80) was also interested in demonstrating the contemporaneity between humans and moa, especially *Dinornis*. In 1952 Lockerbie submitted, to IGNS, a sample of *Dinornis* (NZ-59) from Hawksburn, and seal bone (NZ-56) from Pounawea (Rafter 1975:46). At the time, bone was an unknown radiocarbon material, though Arnold and Libby (1951), and De Vries and Barendesen (1954) had tested naturally burned whole bone. The apparent accuracy of these early determinations had resulted in burned bone being listed, along with charcoal, at the top of Libby's hierarchy of reliable sample materials (Libby 1952:43). Libby (1952:44), however, had doubts about the potential of unburned bone as a successful dating medium because of its low organic carbon content and porous structure, which could result in putrefaction and chemical alteration.

Both the organic ("fixed carbon") and carbonate fractions from the Hawksburn and Pounawea samples were extracted and dated (see Table 4.1 for pretreatment method). Consistent ages were obtained following the development of a contemporary standard (COW),[6] and Rafter (1955:36) concluded that both the carbonate and fixed carbon

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[5] Lamont Geological Observatory, Colombia University, USA.

[6] Age wrt to COW, a sample of cow bone killed in 1955 (see Rafter 1955). Later labelled the terrestrial bone standard (IGNS no. AA3473) (Rafter *et al.* 1972:637-639). The results for Hawksburn were 290 ± 55 BP and 280 ± 55 BP for carbonate and fixed carbon respectively. Carbonate and fixed carbon determinations for Pounawea were 520 ± 55 BP and 550 ± 55 BP respectively (Rafter 1955:36).

fractions appeared to be reliable. Lockerbie also accepted the bone determinations (Lockerbie 1959:82, 106) which were apparently more consistent than associated samples, specifically a shell result from the lowest deposits at Pounawea (NZ-57: 500 ± 60 BP), which was chronologically out of place, and charcoal results (NZ-61 [590 ± 50 BP] and NZ-62 [600 ± 60 BP]) from Hawksburn. Lockerbie (1959:86) suspected that the charcoal estimates may have been subject to inbuilt age, but did not discuss the anomalous shell determination.[7]

Bone carbonate radiocarbon results were also used to prove the association of *Dinornis* at Papatowai and Tautuku (Lockerbie 1959:81). It appears, however, that the laboratory failed to inform Lockerbie of two "fixed carbon" results; NZ-137 (*R*192/1A) for Papatowai, and NZ-146 (*R*192/2A) for Tautuku (see Table 8.1). Instead the carbonate determinations (NZ-137 [*R*192/1: 460 ± 50 BP] and NZ-146 [*R*192/2: 280 ± 80 BP] respectively), reported as "moa bone" by Lockerbie (1959:106), suggested the survival of *Dinornis* into the 16th century at Papatowai, and the 17th century at Tautuku where *Dinornis* bones were in direct association with flake knives (1959:81) . Consequently, Lockerbie (1959:81) concluded that "[T]he advent of Polynesian man is the only tenable explanation" for the extinction of moa and other species.

Lockerbie was less successful at showing the progression of Moa-hunter to Maori. Although long chronologies were apparent at both Papatowai and Pounawea, neither site contained any evidence of Classic Maori material culture, nor evidence of any transition between Archaic and Classic (Lockerbie 1959:90). Therefore, Lockerbie (1959:84-85) used trees growing on the top of Pounawea and Papatowai to estimate when they had been abandoned. These data in association with the late radiocarbon estimates at Tautuku and Papatowai, enabled Lockerbie (1989:87-88) to conclude that the Moa-hunter era lasted till around AD 1700 with the continuum only being disturbed by the Ngai-Tahu invasion in AD 1650 - a date much later than Duff's (1950:21, 294; 1956:20) 16th century overthrow of the Waitaha. This compounded the terminological confusion so that the term Moa Hunter was used as a label for sites with no evidence of moa hunting (*e.g.* False Island and Cannibal Bay) (Lockerbie 1959:88).

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[7] Lockerbie redated Pounawea following recalibration of his initial results which no longer made sense, but the results have not been published. Hamel (1978a:53) obtained a series of new radiocarbon determinations on charcoal (totara)(and one anomalous shell result) following renewed excavations at Papatowai. Recently, Anderson and Smith (1992) obtained a series of reliable radiocarbon estimates for Papatowai. They suggest a shorter occupation that previously indicated (Anderson and Smith 1992:150-151). Hawksburn was also redated by Hamel (1978b:119) and Anderson (1989:224-225). See Table A6.1 for radiocarbon determinations.

Duff had to modify his previous orthodox view (*i.e.* that *Euryapteryx* was the only species found by Polynesian colonists), following the successive discoveries of a number of moa species, especially *Dinornis*, in midden sites in South Otago and the North Island (*e.g.* Makara). Duff's hypothesis was now restricted to the region on which it was founded; the east coast of Canterbury-Marlborough (Lockerbie 1959:81; Duff 1963:6-7). Consequently, when Golson (1959:67) attempted to make sense of the development of Archaic and Classic assemblages, he concluded that the early radiocarbon determinations had contributed little to clarify the picture of prehistory due to the imprecision of the method. In addition, Golson (1959:30, 36) believed Duff to be premature in his choice of terminology, and proposed the replacement of the term Moa-hunter with "Archaic" or New Zealand East Polynesian. Golson also rejected the use of traditional evidence to reconstruct the past and restricted the term "Moa-hunter" to sites where there was evidence of that activity. Duff (1963:8) would later accept primary association with moa remains as the criterion for the Moa-hunter phase.

IGNS adopted carbonate as the routine fraction of bone isolated for dating following initial tests on Lockerbie's samples, perhaps in response to Libby's (1952:44) comments (see above). Given the early success, bone carbonate determinations were often used to check on the results of other sample types. At Redcliff Flat, a bone carbonate result (NZ-460: 490 ± 90 BP) from Hine's oven was submitted to check on the reliability of an associated log charcoal sample (NZ-459: 777 ± 87 BP) following an unexpectedly old charcoal determination from an apparently contemporary excavation (Hamilton's deposit - NZ-438: 1167 ± 91 BP) (Duff to Rafter, 8/6/1962; Trotter 1968:87). Although NZ-460 and NZ-459 differed by almost 300 years the bone result was considered at the time to be closer to the date expected on the basis of cultural evidence (Duff to Rafter, 5/10/1962).

In 1962, however, a sample of *Dinornis* carbonate (NZ-480) from Makara gave a modern result (Rafter *et al.* 1972:638). Soon after, a modern radiocarbon estimate was also obtained on a sample of *Euryapteryx* carbonate (NZ-424) from Stewart Island. When a duplicate sample was measured (NZ-425), a result equivalent to that of the atmospheric $\Delta^{14}C$ at the time of collection was obtained, thus demonstrating that bone carbonate was exchanging with atmospheric carbon dioxide (Rafter 1975:47). The possibility that bone carbonate may give results younger than expected was relayed to Duff in time for his 1963 Cawthron lecture. In response, Duff (1963:9-10, 13-14) rejected all bone determinations (carbonate and "fixed carbon") measured at IGNS (*i.e.* Moa Bone Point Cave [NZ-514], Hine's oven [NZ-460], Tautuku [NZ-146; *R*192/2], Papatowai [NZ-137; *R*192/1 to NZ-140], Hawksburn [NZ-59 and NZ-60] and Pounawea [NZ-56]). Only one radiocarbon estimate remained problematic to

Duff's hypothesis; a result on *Dinornis* gizzard material from Pyramid Valley, which Duff (1963:19) considered to be "open to question" given the lack of supporting evidence.

Duff (1963:14) then, was able to "confirm" the age of the Moa-hunter phase using the early charcoal $^{14}C$ results from Wairau Bar (Duff 1963:9-10), and Hamilton's deposit (NZ-438: 1170 ± 65 BP), in combination with the glotto-chronology established by Emory (1963). Duff believed that AD 850 was a conservative result for the settlement of New Zealand, and therefore "...the problem of accepting man's extermination of a moa fauna surviving in all its genera and species becomes less formidable" (Duff 1963:14). Duff still could not, however, construct a continuous chronology for Redcliff Flat.

## THE "MOA BONE PROJECT" AND BEYOND

Following the Stewart Island bone carbonate results, IGNS began testing the collagen/carbonate method that had been used previously on Lockerbie's samples (Rafter to Trotter 9/2/1965, Rafter *et al.* 1972:638)(see Table 2.1). Despite the erroneous carbonate results, the laboratory seems to have continued to measure the carbonate fraction following overseas recommendations (*i.e.* Geyh and Guhlich 1970). It appears that they thought the carbonate and collagen fractions should agree in order to confirm the reliability of the $^{14}C$ estimate (see Rafter *et al.* 1972:641-642).

A sample from Tai Rua underwent the first routine separation of the carbonate and collagen fractions in 1965 (NZ-559 [collagen] and NZ-558 [carbonate]). The collagen determination was considered to be reliable (Rafter to Trotter 9/6/1965), but the carbonate fraction continued to give modern ages. These bone results from Tai Rua were part of a re-investigation of key moa hunting sites in Canterbury by Trotter who was concentrating on obtaining data pertinent to "...changes in Moa-hunter material culture and economy" (Trotter 1977a:361, 1982:89). For many of the sites dated, Trotter followed Lockerbie's lead and selected different sample types to test their reliability. In particular, moa bone was submitted in part to investigate the new collagen and carbonate dating method (Trotter 1967b:137). This became known as the Moa Bone Project (Rafter 1967a:28-29).

A number of archaeological bone radiocarbon determinations were initially compared with measurements of shell, charcoal and moa gizzard contents (including sites at Poukawa, Tai Rua and Hampden). Initial results indicated that the carbonate ages were almost always too young (Rafter 1966:31-32). An early radiocarbon

determination on "twig" charcoal from Woolshed Flat (NZ-798: 860 yr BP) also raised questions about the accuracy of the associated collagen determination (NZ-760: 493 yr BP) (Rafter 1967a:29). Later that year, Rafter (1967b:31) speculated that collagen results on bones found in swamp conditions (*i.e.* Pyramid Valley, Glendhu Bay and Te Akatarewa) were in close agreement with results of associated materials, whereas bone determinations from midden deposits were not. This, he suggested, was due to possible preservation differences. While investigating the sites of Ototara Glen, Woolshed Flat, Tai Rua and Hampden Beach, Trotter (1967b:139, 1968:87) formed a different opinion. He noted that cultural evidence usually supported the collagen estimates, while the age of charcoal samples was almost consistently 300 - 400 years older than the collagen or shell results from the same level, even when using samples of small diameter (*i.e.* twigs) or outer portions of larger specimens, such as at Ototara and Woolshed Flat. This Trotter (1968:86-87) suggested was due to the use of old or relic timber.

McCulloch and Trotter (1975a:5) thought that moa bone was the one material which they could be "...almost certain represented early occupation of a site...". Moa bone also had the advantage of dating directly the part humans played in the extinction of moa. In addition, both McCulloch and Trotter believed that bone was "...not readily subject to contamination from either the atmosphere or the soil..." (1975a:5), and as moa obtained its food from terrestrial sources, variation in $^{14}C$ uptake was not considered to be a problem (Trotter and McCulloch 1984:718). The ability to date bone also complemented research into extinct species (*i.e.* Tai Rua and Ototara) (Trotter 1965) and natural deposits (Trotter 1970; McCulloch and Trotter 1979). It also sparked interest in a number of relative dating methods using bone, most notably total nitrogen content (Rafter 1976:92; Houghton 1980) and fluorine analysis (Trotter and Malthus 1967).

Trotter (1968:87) concluded, therefore that "...there would appear to be little point in submitting archaeological charcoal for radiocarbon dating except as a last resort when no other materials - such as shell or bone collagen - are available". Apparently, as a result of these observations, some sites with radiocarbon estimates were redated using moa bone. One case in question being Redcliff Flat, where a discrepancy between the radiocarbon chronology and artefact interpretation placed doubt on the 8$^{th}$ century charcoal result from Hamilton's deposit (NZ-438). At Duff's request Trotter re-opened the Hamilton's deposit excavation and selected samples approximately 60 cm away from Duff's original collection point (Trotter 1975c:195, 197). The 13$^{th}$ century results obtained for collagen (NZ-1113: 735 ± 56 BP) and shell (NZ-1111: 617 ± 37 BP) were not, however, as conclusive as Trotter (1968:87) hoped, being only within

two standard deviations of each other. Due to their insecurity Duff requested more $^{14}C$ determinations (Trotter to Rafter 11/3/1969). Material was obtained from a new excavation; Sewer Trench Pit. The resulting bone collagen determinations (NZ-1162: 615 ± 40 BP and NZ-1376: 581 ± 40 BP) were only "approximately contemporaneous" with those from Hamilton's deposit (Trotter 1975c:204).

At the 1972 Radiocarbon conference held in Wellington, Rafter *et al.* (1972) summed up the research into radiocarbon dating at that point. They drew attention to the wide disparity between results of charcoal, shell and moa bone from the same contexts (Figure 4.1), and concluded that plant remains (including crop contents) usually gave radiocarbon determinations several hundred years older than reservoir corrected shell or bone collagen ages, which were in close agreement (Rafter *et al.* 1972:643).

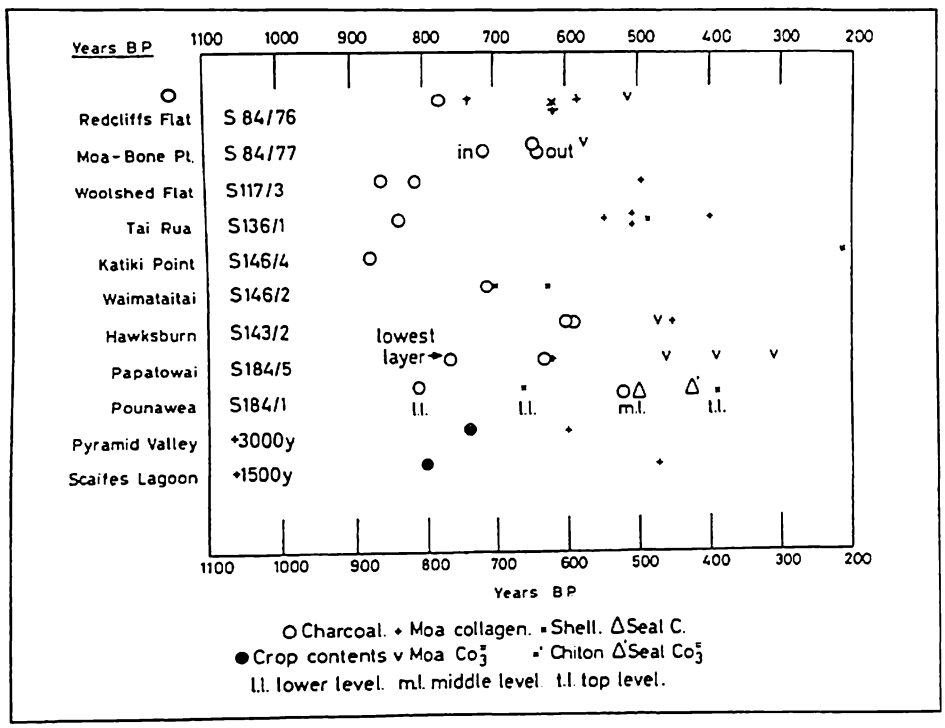



Figure 4.1: Comparison of radiocarbon ages on different sample types from New Zealand archaeological sites by Rafter *et al.* (1972:657, figure 1).

While bone collagen results were apparently successful, the bone carbonate determinations were problematic. Few carbonate radiocarbon estimates had given acceptable results since Lockerbie submitted the first burnt bone samples from Hawksburn (NZ-59b ["fixed carbon"] and NZ-59 [carbonate]). Consequently, the laboratory made requests for more burnt material (Rafter to Duff 7/4/1964). A comprehensive test of burnt bone was eventually carried out on samples of black

charred bone (NZ-927 and NZ-930), white charred bone (NZ-929) and unburnt moa bone (NZ-931 and NZ-932) from Rakaia River Mouth. The collagen results (NZ-932: 518 ± 80 BP; NZ-930: 585 ± 64 BP), while accepted, fell short of the estimate of 600 - 800 years (Trotter to Rafter 23/6/1967). The carbonate fractions (NZ-931 and NZ-927) gave modern values which were attributed to contamination by bomb carbonate. The white burnt bone, however, gave an unusually old result (956 ± 93 BP), but did not have an anomalous $\delta^{13}C$ value (see Table 8.1) normally indicative of carbonate contamination (Trotter 1972b:135). It has since been concluded that burnt moa bone carbonates (most organic material has been destroyed) give inconsistent results (Polach and Golson 1966:31; Rafter *et al.* 1972:643). A later attempt to date collagen from burnt bone recovered at Wakanui (NZ-1766 and NZ-1767) also gave an anomalous $^{14}C$ measurement (Trotter to Rafter 18/12/1973). Unfortunately, the results of tests on burnt bone have not been published in their entirety and the reliability of burnt "collagen" is unknown.

Increasing difficulties with both the carbonate and collagen determinations seems to have prompted a review of the literature by Rafter *et al.* (1972:640-643). They concluded that there was no consistent pattern in the radiocarbon measurements of bone in the literature, or method used, nor agreement over accuracy (Rafter *et al.* 1972:643). Carbonate results were, however, considered to be unreliable and were dropped soon after. Despite apparent success, collagen determinations did not always agree with results from other materials. On the basis of overseas research, Grant-Taylor (1974:160) suggested that anomalies with collagen results may be a consequence of collagen-like contamination. This remained largely unresolved due to problems with other sample types (Law 1981:234; Caughley 1988:247; Anderson and McGovern-Wilson 1990:44-45). Consequently, Caughley (1988:250) concluded that "[W]hether charcoal dates are more accurate than collagen and shell dates cannot presently be determined", but "...charcoal dates and collagen/shell dates cannot usefully be combined".

Radiocarbon determinations on different materials from Shag River Mouth including shell, charcoal, eggshell and moa bone were compared in order to assess their reliability (Figure 4.2) (Anderson 1991:791; Anderson, Smith and Higham 1996:60).[8] Radiocarbon measurements on short lived, identified charcoal, eggshell and certain species of marine shell proved to be accurate and reproducible. Moa bone determinations, on the other hand, displayed a variability inconsistent with results on

[8] A series of radiocarbon determinations (32 acceptable results on shell, charcoal and eggshell) from Shag River Mouth suggest formation of the site in the 14th or early 15th centuries AD.

other materials (see Table 8.1). Two 1200 BP estimates implied that sub-fossil bone had been used for $^{14}C$ analysis despite the selection of bones with identifiable butchery marks. Variability in the rates of "preservation" or inadequate pretreatment were also given as explanations for inconsistencies with the moa bone results[9] (Anderson, Smith and Higham 1996:60, 64, 66). Consequently, Anderson (1991:777, 779) suggested that bone "collagen" ages from archaeological deposits should be treated with caution due to pretreatment inadequacies, limited sample assessment (*i.e.* dating of multiple amino acids, and C/N ratios) and the varied pretreatments and standards used over the years (see Table 4.1). Bone was, therefore considered to be of low priority as a datable material (Higham 1993:97).

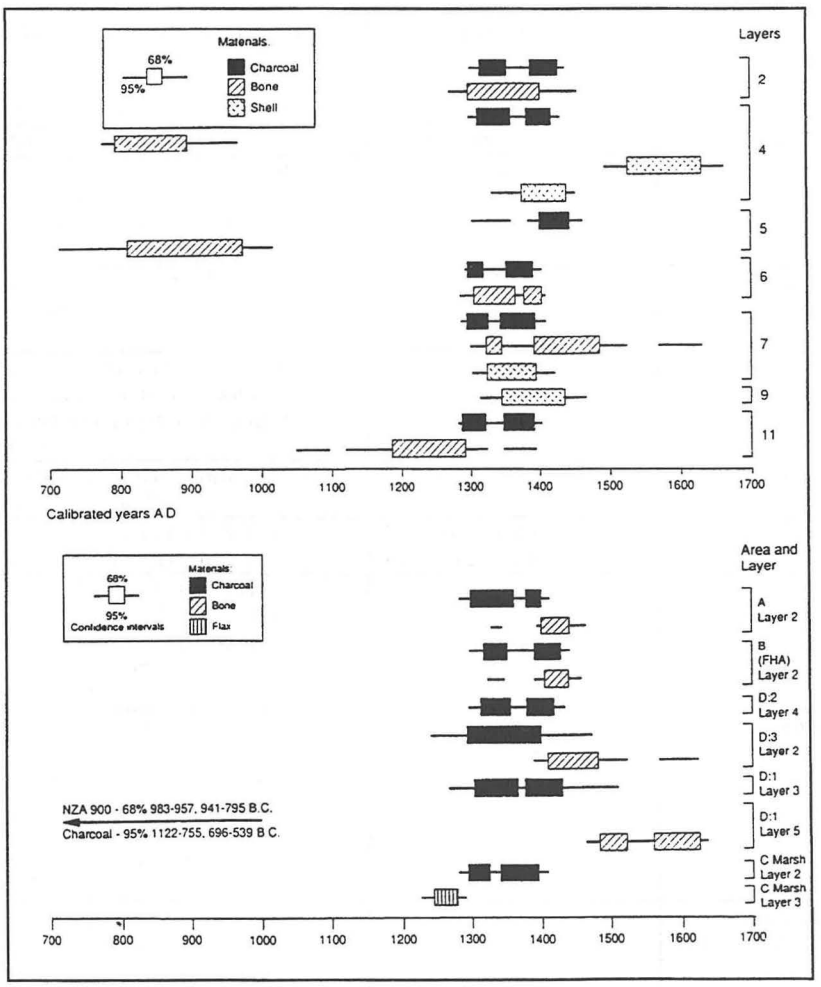



Figure 4.2: Comparison of different sample types from Anderson (1991:791, figure 12). Calibrated radiocarbon ages from excavations at Shag River Mouth, SM/C:Dune (above) and other areas (below).

[9] Bone samples were pretreated according to McFadgen and Manning (1989:4-6) (see Table 4.1). One moa bone sample required further purification through a molecular sieve to remove electronegative impurities (Anderson, Smith and Higham 1996:64).

## PRETREATMENT AND PRESERVATION

Following these results from Shag River Mouth, Redvers-Newton and Coote (1994) and Redvers-Newton (1995) undertook a number of experiments into different bone preparation methods. This included testing the new gelatinisation step which had been added in 1993. Until then the standard method of bone pretreatment at IGNS had consisted of either acid hydrolysis to separate "collagen", or "collagen" extraction followed by an alkali wash (Melhuish and Gillespie 1994). Alkali treatment was dropped from routine procedure following Redvers-Newton and Coote's (1994:273) demonstration using ion beam analysis (*i.e.* analysis of light elements (F, N, P and Na) and trace metals associated with humic materials) that alkali treatment, despite removing some humic acids, resulted in little improvement to the radiocarbon estimate.

Table 4.1: Published bone pretreatments at IGNS, 1955 -1998.

| PRETREATMENT | FRACTION | REFERENCE |
|---|---|---|
| Bone was decalcified in 1:1 HCl and heated to isolate carbonate. The insoluble residue was dried at 110°C to remove water and heated to 400°C to remove acid. | Carbonate and "fixed carbon" | Rafter (1955:23) |
| The bone was digested with cold 3 M $H_3PO_4$ to isolate carbonate. The acid insoluble residue was then dried. | Carbonate and $H_3PO_4$ insoluble residue | Rafter (1965:455) |
| Bone was digested with HCl to isolate carbonate. The acid insoluble was then treated with 1 M HCl at room temperature overnight, centrifuged and washed in distilled water. | Carbonate and HCl insoluble residue. | Rafter *et al.* (1972:639-640) |
| Bone was decalcified with phosphoric acid to isolate the organic fraction.[10] | $H_3PO_4$ insoluble residue. | Jansen (1984:29). |
| The bone was decalcified with HCl, humics removed with NaOH, washed, and dried. | NaOH purified HCl insoluble residue. | McFadgen and Manning (1989:6) |
| "Poor bone" was decalcified in 0.6 M HCl for 2 hours at room temperature, refluxed in 5 M HCl for 16-20 hours, filtered, and the filtrate evaporated.<br>"Clean bone" was decalcified in 0.6 M HCl. | Gelatin or collagen. | Melhuish and Gillespie. (1994:2) |
| Collagen A: Demineralised in 0.5 M HCl at room temperature.<br>Collagen B: Acid insoluble fraction treated with 0.1M NaOH and 0.1 M sodium pyrophosphate for 1 hour at RT.<br>Collagen A or B: Gelatinised in 0.01 M HCl under nitrogen overnight at 120°C. | HCl insoluble residue;<br>NaOH purified HCl insoluble residue;<br>Crude gelatin;<br>Gelatin | Redvers-Newton and Coote (1994:270-271) |
| Bone was demineralised in 0.5 M HCl at room temperature for 1 hour. Residue filtered and the solution gelatinised with 0.01 M HCl under nitrogen at 90°C for 16 hours. | Crude gelatin | Beavan and Sparks (1998:602) |

Redvers-Newton (1995) also compared results of XAD purified amino acids, following Stafford *et al.* (1991), against Oxford's cation exchange, purified gelatin method (Hedges *et al.* 1989). She aimed to assess whether purified amino acids from

[10] The use of HCl was dropped as the evolution of carbon dioxide would come to a halt before either carbonate or acid was exhausted. Yields were also better with phosphoric acid (Jansen 1984:29-30).

a moderately well-preserved bone (Class III: Stafford, Brendel and Duhamel 1988) produced more reliable radiocarbon determinations than purified gelatin (Redvers-Newton 1995:107). Different fractions of the Pacific Region Analytical Bone Standard were measured and fulvic acids identified as the main contaminant.[11] Although the procedure outlined by Stafford *et al.* (1991) should have preferentially removed these fulvic acids (see Chapter 3), no significant difference was identified between the two methods, and neither method was always successful (Redvers-Newton 1995:112-113). The results did, however, show "significant differences" between the ages of "collagen", gelatin and amino acid fractions (Redvers-Newton 1995:110). Further, it was concluded that gelatinisation alone could not be guaranteed to give an accurate result on Class III bone (*i.e.* 0.9 - 0.4% nitrogen) (Redvers-Newton 1995:113). Despite this result, gelatinisation remains the main bone pretreatment used at IGNS.

The bone pretreatment used at IGNS came under scrutiny when rat gelatin determinations from Shag River Mouth (Table 8.1) gave significantly older results than ion exchange purified gelatin measured at Oxford (OxA-5780: 900 ± 55 BP; OxA-6020: 930 ± 65 BP) (Anderson 1996:179, 182). Ladefoged, Matisoo-Smith and Allen (1997:106) concluded, on the basis of comparable results of contemporary charcoal and NaOH-washed rat collagen from Fiji, that differences in pretreatment (*i.e.* the presence/absence of an NaOH wash) may be responsible for the apparent discrepancies (Ladefoged, Matisoo-Smith and Allen 1997:107). Sparks, Beavan and Redvers-Newton (1997:206) dismissed this suggestion because alkali treatment could alter the collagen yield, amino acid composition and, therefore stable isotope ratio. Redvers-Newton (1995) had also demonstrated that NaOH was ineffective at removing contamination. Further, agreement between contemporaneous rat gelatin and shell (*Austrovenus stutchburyi*) determinations from middens at Pauatahanui (see Tables 8.1 and A6.1), supported Sparks, Beavan and Redvers-Newton's (1997:207) suggestions that their pretreatment technique was reliable.

Beavan and Sparks (1997:8), also concluded that anomalously old ages obtained for rat bones from natural sites (Holdaway 1996)(see Chapter 1) were not simply the result of inadequate laboratory preparation, especially as around 18 - 20% totally depleted carbon would be required to shift these ages out of line with the more orthodox views of New Zealand colonisation (in Anderson 1996:182). Instead, they questioned the preservation state of the archaeological bones and stated that "[A]

11 The Pacific Analytical Bone Standard is a mix of human bone from Namu (Leach†, *pers. comm.* 1995). Only one associated $^{14}C$ determination has been obtained; a charcoal determination (NZ-4639) (Whitehead, Devine and Leach 1986:360-361). †Dr. B.F. Leach, Archaeozoology Laboratory, Museum of New Zealand, Te Papa Tongarewa, Wellington.

feature of all these bones [*i.e.* Shag River Mouth *Rattus exulans* samples] is that they were highly degraded and contained significant quantities of contaminants that had to be removed" (Beavan and Spark 1997:8). No evidence of this was published, but the suggestion that bone at Shag River Mouth was poorly preserved has become entrenched in discussion of these results.

It appears, however, that this idea of poor preservation was based on an informal statement made to IGNS by the submitter following an interpretation of whole bone infrared spectra from associated rat remains (Anderson 1998a). These results have since been re-evaluated and Anderson (1998a:2), while recognising that contamination was still possible, concluded that there was "...nothing to indicate that the Shag River *Rattus exulans* samples are, or were, incapable of providing satisfactory radiocarbon age measurements by reason of sample degradation". A more detailed report on these bones (including crystallinity index, carbonate/phosphate ratio, collagen peak and phosphate peak values) is pending (Anderson 1998a:2).

The question of inadequate laboratory pretreatment or laboratory induced error has, however, been supported by $^{14}C$ determinations on rat from Pleasant River. Samples of rat from three areas at Pleasant River, in association with other sample types, were submitted for radiocarbon analysis to IGNS and Oxford (Smith and Anderson 1998). Two of the samples (*i.e.* OxA-6744 and NZA-6532) were considered to be from one individual (Smith and Anderson 1998:88-89). Although charcoal and shell determinations suggested a 13$^{th}$ or early 14$^{th}$ century occupation, only one of the *Rattus exulans* samples fell within this age range (OxA-6744: 515 ± 55 BP). The IGNS gelatin results, including the duplicate rat sample, were more than 500 radiocarbon years different (NZA-6536: 1591 ± 71 BP and NZA-6532: 1039 ± 69 BP) (Smith and Anderson 1998:89).

In view of these results, Smith and Anderson (1998:90) suggested that confidence in *Rattus exulans* bone radiocarbon determinations was premature, despite the apparently acceptable $^{14}C$ estimates from Pauatahanui (Sparks *et al.* 1997). They went on to suggest that, while there was a wide range of possible explanations for these results, all the evidence pointed to laboratory induced error, or variation in pretreatment between the laboratories involved (Smith and Anderson 1998:90).

Anderson (1998c) expanded on this when he presented a paper at the New Zealand Archaeological Association Conference at Picton in 1998, which claimed to detect a "production trend" in ages measured for kiore bones at IGNS between 1995-1997. Anderson's 1998 presentation focused on *Rattus exulans* radiocarbon determinations

from three archaeological sites which, on the basis of $^{14}C$ measurements on multiple sample types, were occupied between 500 and 800 BP. While $^{14}C$ determinations on *Rattus exulans* measured at the Oxford AMS laboratory fell into the expected age range (500 - 950 BP), the IGNS results on associated rat samples fell between 1500 - 2000 BP in 1995, 1600 - 900 BP in 1996 and 750 - 600 BP in 1997 (Anderson 1998b:232).

This criticism invoked concern about pretreatment procedures at IGNS, as well as the reliability of bone gelatin determinations (Sparks 1998:228). In response, Sparks (1998:229-230) suggested that this time trend was not manifest in other bone types measured by the laboratory, nor in duplicate tests run on bone standards, including the TIRI (Third International Radiocarbon Inter-comparison) whale bone, and a sample of bulk kiore bone powder. In addition, no trend had been identified in bone ages from both archaeological and natural sites that could be independently verified. Therefore, Anderson's (1998c) production trend was a true reflection of sample age and not a reflection of inadequate laboratory procedures (Sparks 1998:231).

Anderson (1998b:232-233), however, argued that Sparks (1998) had indiscriminately lumped bone determinations together, and that a similar production/age trend was not evident from results of associated samples submitted to the Oxford AMS laboratory. Anderson (1998b:233-234) also stated that the reliability of rat determinations was only in question prior to 1997, and as no comprehensive inter-laboratory test had been carried out at that time it was almost impossible to check for any sample processing problems that may have occurred, especially initial operator-variation and inter-laboratory pretreatment variation. Further, Anderson (1998b:234) criticised the limited collaboration between IGNS and archaeologists, the slow implementation of programs to investigate these problems, and the failure of IGNS to confront directly the serious contradictions created by anomalous radiocarbon results.

Tests are currently underway into the effectiveness of bone treatments and laboratory methods (Beavan and Sparks 1998:602).

## SUB-FOSSIL BONE

Uncertainty with identifying sub-fossil remains is of equal concern in the dating of bone, especially moa bone. Differences in preservation state were hoped to aid in the identification of such material. Initial tests on bone of low specific gravity (NZ-559) compared to mineralised bone (NZ-578), however, suggested that an increase in weight was a misleading means of identifying sub-fossil bone (Rafter to Trotter

9/6/1965; Trotter and Malthus 1967:151). Anderson (1989:112) argued that this was the result of limited knowledge about the effects of the diverse weathering conditions in New Zealand. Closer investigation of the expected weathering patterns (*i.e.* McGovern-Wilson 1992) has not, however, been of great benefit. It was also hoped that careful selection of bones with butchery marks would alleviate this problem, but such marks proved to be difficult to identify (Scarlett 1974:3). Although it is commonly maintained that greenstick fractures and butchery marks can be used to identify cultural damage to fresh bone (Anderson 1989:112), these methods of identification have not always been successful (*i.e.* Weka Pass (Trotter 1972a:45, 1977a:359) and Shag River Mouth (Anderson, Smith and Higham 1996)). Whether these old determinations can be attributed to a sub-fossil origin, pretreatment inadequacies or excessive contamination (Anderson, Smith and Higham 1996:60, 64) remains open to question.

As an alternative, McFadgen (1982:387, table 5) suggested that the selection of bones from articulated remains or midden refuse could minimise the effect of inbuilt age. This also proved to be unsuccessful when a CRA of 4750 ± 81 BP was obtained on bone removed from an articulated skeleton found in Whakamoenga Cave (NZA-577) (McFadgen 1989:257). Several potentially problematic regions in New Zealand for sub-fossil bone have also been identified, including dune sands, cave sites, and archaeological sites with industrial bone (Millener 1981:239-244; Anderson 1989:53, 55, 111; Anderson and McGovern-Wilson 1990:44). Despite these efforts the identification of sub-fossil material remains an arbitrary process. In some cases an anomalously old radiocarbon determination has been the only evidence used to identify a sub-fossil bone.

## SPECIES DIVERSIFICATION

In New Zealand a variety of different species including dog, seal, human, fish, and bird bone have been analysed by radiocarbon. Such a diverse selection of different species enabled the dating of sites with no moa remains. Interest in these different species also paralleled a shift in archaeological focus to the north with questions about the development of Maori culture, population movement, burial practices and warfare being asked (Houghton 1980; Brailsford 1981; Trotter 1982; Davidson 1984:2).

The first human bone determinations were obtained on samples from Cascade Cove, Fiordland, submitted in 1966. This site was thought to have been occupied late in the prehistoric sequence, possibly even up to European contact (Coutts 1982:144). The collagen results were, however, older than expected (NZ-785: 838 ± 43 BP; NZ-786:

755 ± 45 BP; NZ-787: 610 ± 56 BP (Moore and Tiller 1976:153)). Conversely, $^{14}C$ measurement on a "robust" human bone from Natush's Property, Poukawa gave results much younger than expected (NZ-2467: 347 ± 35 BP), and put an end to ideas of human presence in New Zealand at a much earlier time than previously supposed (Rafter 1969:30; 1970:60). Three new radiocarbon determinations (moa bone collagen [NZ-1838: 590 ± 60 BP], marine shell [NZ-1837: 680 ± 50 BP] and human bone collagen [NZ-1835: 780 ± 80 BP]) from Wairau Bar were later announced at the New Zealand Archaeological Association conference in 1974 (Trotter 1975b:90; McCulloch and Trotter 1975a:2). The human bone collagen determination for Wairau Bar was at the time somewhat older than expected, as was a result of 480 ± 60 BP (NZ-1834) on human bone from "Classic type burials" at Conway River (Lagoon Flat, burial 4) (McCulloch and Trotter 1975a:3, 13). Despite the differences between expectation and radiocarbon estimate, and the absence of comparable results, McCulloch and Trotter (1975a:11) believed human bone determinations fell into a "...reasonable and acceptable time-span...".

The limited success with human bone determinations, in addition to the vast amount of bone needed for radiocarbon analysis (Law (1981:229) suggests 1000 g for a full counter filling) and expense, prompted Houghton (1980:18) to experiment with nitrogen content as a relative dating technique. Houghton (1980:19, 40) believed that in New Zealand nitrogen analysis could be extended beyond the relative dating of a single site because the coastal environment over the past 1000 years had remained relatively consistent. Therefore, the rate of collagen decay was largely time dependent and not significantly affected by variation in temperature, acidity or exposure to water.

When nitrogen determinations were measured on samples of human bone from Wairau Bar (see Table 4.2), they suggested the possibility of more than one period of internment. A number of radiocarbon estimates were obtained to test this possibility and to check on Duff's original results (Fossil Record Form (FRF) associated with *R*5433/1-3). The $^{14}C$ and nitrogen results from Wairau Bar were, however, problematic (Table 4.2). Although stratigraphic evidence did not agree with either the radiocarbon measurements or nitrogen determinations (*i.e.* burials 35 and 5 were thought to have been contemporary) (Trotter to McGill 23/1/1978), Trotter concluded that the $^{14}C$ results appeared to make nonsense of the nitrogen analysis. Multiple occupation has also been suggested by Anderson (1989:123-125) on the basis of mateiral cultural evidence, but no evidence for a multiple occupation at Wairau has been forth-coming from recent radiocarbon determinations (Higham, Anderson and Jacomb, in press).

Houghton also applied nitrogen analysis to human bone samples from sites at Station Bay (Table 4.3) where radiocarbon determinations on bone collagen had given older results than supposedly contemporary late 18th century estimates on charcoal (Davidson 1978a:16, 1984:250). The bone nitrogen levels suggested that the Leahy undefended site was several centuries older than either N38/37 or N38/25, a result consistent with skeletal evidence (*i.e.* the Leahy burial had no evidence of a fern root plain) (Houghton 1977:40). There was, however, some discrepancy as the nitrogen values for the Davidson undefended site and "Pa Site" burials were inverted compared to their associated radiocarbon determinations. The radiocarbon results were also significantly older than the nitrogen age estimates. Houghton (1977:40) suggested the differences in nitrogen content at Station Bay may be due to variation in burial matrix. Despite this obvious contradiction to the hypothesis of a uniform coastal environment, Houghton (1980:20) concluded that "[W]e have yet to encounter a situation where the age of bone, as estimated by its nitrogen content, is grossly at odds with all other evidence. There are one or two situations where it disagrees with the carbon-14 date, but where other evidence suggests that the nitrogen date is more likely to be correct".

Table 4.2: Nitrogen versus $^{14}C$ determinations for Wairau Bar.

| NZ no. | Burial no. | Date Estimate | Radiocarbon Age (wrt NZ bone standard) |
|---|---|---|---|
| NZ-4444 | 35 | 800 BP | 380 ± 50 |
| NZ-4443 | 5 | 500 BP | 660 ± 60 |
| NZ-4442 | 3 | 600 BP | 630 ± 50 |

(from FRF *R*5433/1-3 and Radiocarbon Result Sheets).

Table 4.3: Nitrogen versus $^{14}C$ determinations for Station Bay sites, Motutapu Island.

| Site | | Mean Nitrogen | Date Estimate | NZ no. | Radiocarbon Age |
|---|---|---|---|---|---|
| N38/37 | Davidson undefended site | 4.00% | Late 18th century | NZ-4346 | 490 ± 50 |
| N38/30 | Leahy undefended site | 1.5% | *ca.* 1400 AD | NZ-4347 | 600 ± 50 |
| N38/25 | Pa Site - Burial one | 3.61% | Early 18th century | NZ-4348 | 410 ± 60 |
| | - Burial two | 3.46% | | | -- |

(Nitrogen measurements and estimates from Houghton 1977:37-40. Radiocarbon determinations from Davidson 1978a:15).

Houghton (1976:6, 1978:261) also obtained a series of nitrogen determinations on Burials I and II at Waihora, Chatham Islands. These nitrogen results were confirmed by toothwear analysis (Sutton 1979:80) and by a number of charcoal determinations which suggested a 16th century occupation (Sutton 1979:77). The radiocarbon estimates on the burials themselves did not apparently support this conclusion (Sutton 1979:83). The collagen radiocarbon result of human bone from Burial I was, however, wrongly reported as AD 1460 ± 310 (new $T^1/_2$ and secular corrected) (see Table 4.4). Following a closer look at previous nitrogen and $^{14}C$ estimates of human bone, Sutton calculated that radiocarbon measurements of human bone collagen were

approximately 100 years older than those on charcoal (Sutton 1979:83). Because a "...consistent correlation between the results of nitrogen, radiocarbon and other dating methods..." was not obtained, Sutton (1979:80) concluded that neither dating method could be accepted.

Table 4.4: Nitrogen assessments on burials from Area IX, Waihora.

| Burial | Mean Nitrogen | Date estimate | NZ no. | Radiocarbon Age (wrt NZ bone standard) |
|---|---|---|---|---|
| Burial II | 1.19% | 15th century | NZ-4653 | 610 ± 70 |
| Burial I | 4.26% | 19th century | NZ-4652 | carbonate 480 ± 310 |
| | | | NZ-4697 | collagen 233 ± 127 |

(Based on Sutton to Jansen 30/8/1978 and Radiocarbon Result Sheets).

Research into dog bone shed some light onto the problem with human bone "collagen' results. When two contemporary dog bone samples from Peketa pa gave distinguishable ages and $\delta^{13}C$ values[12] (NZ-4154: 570 ± 90 BP; $\delta^{13}C$ = -12.7‰, and NZ-4296: 270 ± 60 BP; $\delta^{13}C$ = -19.4‰) (Trotter to Rafter 10/12/1976), it was suggested that NZ-4154 had been affected by a marine dietary input. Research into Sr/Ca concentrations in bone was undertaken to test whether this marine dietary component could be quantified (Jansen 1984:24). Initial Sr/Ca tests were on samples of human bone from Takahanga that had failed to give satisfactory $^{14}C$ and nitrogen values (Jansen to Trotter 15/8/1978; FRF *R*5742). The results of this test remain unpublished. Rafter (1978:138) later concluded that "old Maori bones" and dog bones were problematic. Subsequent research into the relative proportions of marine and terrestrial foods in the diet has concentrated on $^{13}C/^{12}C$, $^{15}N/^{14}N$ and $^{34}S/^{32}S$ isotopes in archaeological bone collagen samples collected from the south western Pacific. Significant variations have been found, including a large marine component in the bones from the Chathams (Lyon 1988:3; Horwood 1989; Leach, Quinn and Lyon 1996). Limited work has, however, been carried out on New Zealand prehistoric population due to the complexity of identifying multiple dietary resources.

Grant-Taylor (1974) compiled a guideline of suitable materials for radiocarbon assay in response to archaeological interest. He concluded that moa bone was the best material for radiocarbon analysis because it was more likely to date moa-hunting directly, and because moa were short-lived (Grant-Taylor 1974:159-161). Grant-Taylor (1974:160) also suggested that fish species which remained close to shore (80 - 100 m depth) may be reliable, though identification of the species and measurement of the fish age needed to be determined prior to radiocarbon determination. Whale bone was not considered to be acceptable because whales could range into $^{14}C$ depleted

[12] Shell from same deposit NZ-4152 and NZ-4153 gave ages of 290 ± 50 BP and 350 ± 50 BP respectively.

Antarctic waters. Seal bone, however, appeared to be reliable. It was recommended that small bird bone should be identified to species and sea birds kept separate from land birds because of the marine component in their diets (Grant-Taylor 1974:159-161). In a revised paper, Law (1981:234-235) extended the list of unsuitable sample types to include all marine mammals and birds, especially those that obtain their food from the tropical or Antarctic seas, as well as dogs and humans because of the possibility of a high marine diet (Law 1981:235).

In the light of these results, it is surprising that dietary induced reservoir effects were not thoroughly investigated prior to the use of kiore (*Rattus exulans*) as a $^{14}C$ sample. Anderson and Holdaway (*in* Anderson 1996:178) hypothesised that rat bone collagen should be reliable for radiocarbon dating because of a limited inbuilt age and lack of marine input into the diet (Anderson 1996:178). When Holdaway (1996) published a series of rat bone gelatin ages, including the 2000 year old determination of *Rattus exulans*, the accuracy and contextual security of these results were questioned by Anderson (1996). Despite the discrepancy with orthodox opinion, these results were difficult to dismiss because of the close agreement between a rat bone gelatin determination (NZA-6636: 1775 ± 93 BP), supposedly recovered from below Taupo Tephra (1850 ± 10 BP) (see however, Anderson 1996:178-179) with radiocarbon estimates of bird (*Turnagra capensis*) bone gelatin (NZA-6190: 2995 ±72 BP) and moa eggshell (NZA-6627: 2905 ± 88 BP) from below the ash (Holdaway 1996:226). Unfortunately, little information about the context or preservation state of these samples has been formally published.

Recent $^{14}C$ determinations measured by IGNS from the archaeological site of Shag River Mouth have undermined the reliability of Holdaway's (1996) rat determinations. The gelatin results (1,500 to 2000 BP) were very different from both the established radiocarbon chronology of the site (600 BP), and ion exchange gelatin determinations pretreated and measured at Oxford (900 BP) (Anderson 1996). While the Oxford $\delta^{13}C$ results suggested a 50% marine dietary input (which would adjust their 900 year old estimate to around 750 BP), those from IGNS were interpreted as terrestrial values (Anderson 1996:181; McFadgen 1997:6). Consequently, Anderson (1996:178) speculated that a reservoir offset could have influenced the result. The range of questions surrounding these determinations led Anderson (1996:183) to concluded that "rat bone collagen cannot be regarded currently as a reliable medium for routine age measurement".

Radiocarbon determinations of rat bone from Pleasant River supported this conclusion. Stable isotope results on ion exchange gelatin measured at Oxford,

suggested a marine component to the rat diet (OxA-6743: $\delta^{13}C$ = -19.2‰ and $\delta^{15}N$ = +16.90‰) and gave a correspondingly old radiocarbon result (950 ± 60 BP). The result for OxA-6744 was closer to what was expected for the site (515 ± 55) and the $\delta^{15}N$ value implied a predominantly terrestrial diet ($\delta^{13}C$ = -20.0‰, $\delta^{15}N$ = +11.29‰)(Smith and Anderson 1998:90, table 1). Unfortunately, IGNS did not take $\delta^{15}N$ measurements of the rat bone dated by them, but the $^{14}C$ determinations were clearly erroneous (see above).

Following these results, IGNS investigated the "...possibilities for alteration of expected ages..." especially those which could give "...strongly depleted $^{14}C$ values not readily apparent in $\delta^{13}C$ and $\delta^{15}N$ diet analysis..." (Beavan and Sparks 1998:602). They gathered data from specimens linked to five specific habitats on Kapiti island (Figure 4.3). The results indicated that modern populations of *Rattus exulans* were not in equilibrium with atmospheric values of $\Delta^{14}C$, being either enriched or depleted relative to the atmospheric curve in 1996/7 (Beavan and Sparks 1998:601).

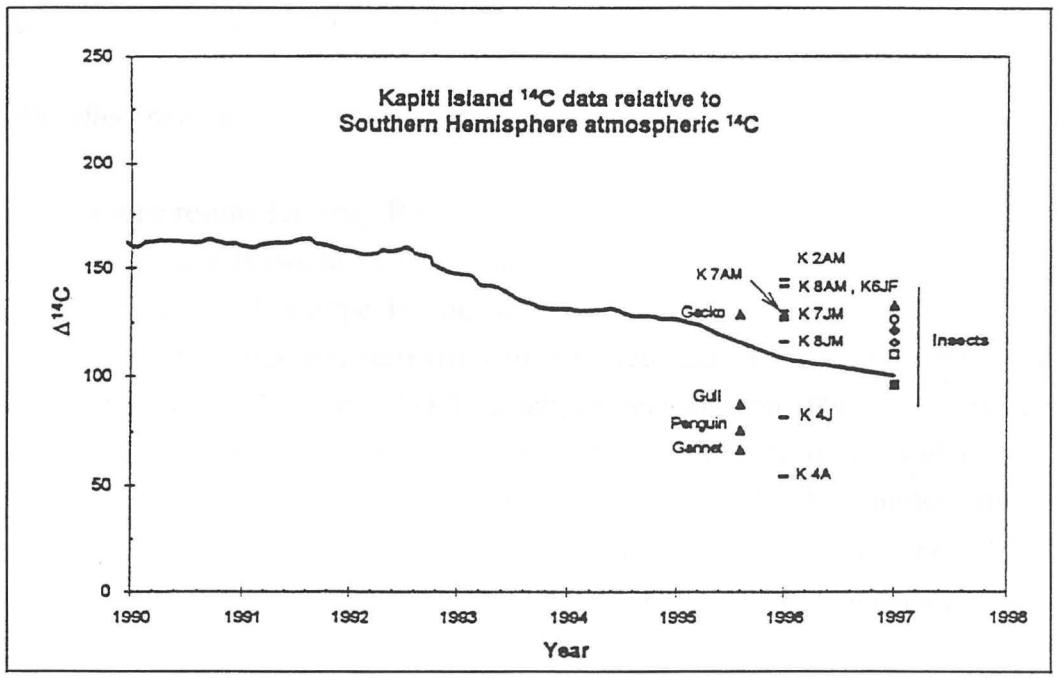



Figure 4.3: Kapiti Island rat specimens plotted against time of collection, other species, and the smoothed Southern Hemisphere atmospheric $\Delta^{14}C$ curve (from Beavan and Sparks 1998:604, figure 1).

Following the work of Ambrose and Norr (1993), Beavan and Sparks (1998:602, 608) concluded that non-essential amino acids (metabolised from energy substrates) reflected near contemporary $^{14}C$ values, while the essential amino acids (derived from protein rich foods) could carry carbon that deviated from atmospheric equilibrium. Beavan and Sparks (1998:610-611) suggested that as the essential amino acids carry around 30% of the carbon in bone gelatin, only *ca.* 30% of the carbon in bone protein

could have a dietary induced depleted carbon signature. Under such circumstances the shift in age, even if the rat's protein input was entirely from fish, was not likely to be more than about 100 years (Beavan and Sparks 1997:8, 1998:610-611). Therefore, by implication, Holdaway's (1996) rat bone determinations and those from Shag River Mouth could not be attributed solely to a marine dietary input. Still, Sparks, Beavan and Redvers-Newton (1997:208) could not be confident that the rat bone results were a true reflection of their chronological age.

Research underway at IGNS is currently attempting to make a distinction between depleted and "normal" food sources by comparing individual essential amino acids with glycine; a non-essential amino acid formed in the body from $CO_2$ and ammonia by the action of a glycine synthase. They hypothesised that glycine should have a $\Delta^{14}C$ similar to blood bicarbonate levels and, therefore be in equilibrium with atmospheric carbon during the lifetime of the individual (Beavan and Sparks 1998:611-612). There are, however, several areas that remain open to question with regards to the rat bone radiocarbon estimates:

*1. The effect of a marine versus terrestrial diet.*

Stable isotope results for Shag River Mouth were considered to represent a terrestrial diet ($\delta^{13}C$ values between -19.6‰ and -21.5‰) (Anderson 1996:179, table 1). Analysis of a single isotope is not, however, considered to be definitive in the identification of a marine, terrestrial or a mixed diet (Schoeninger and DeNiro 1984:635; Ambrose and Norr 1993:3; Leach, Quinn and Lyon 1996:2). For example, $\delta^{13}C$ values of -23.3‰ have been measured in fish from the North Central and North East Pacific (Williams, Druffel and Smith 1987:254-255, table 1). Similar values for marine protein [$\delta^{13}C$ = -20.0‰] have been noted by Higham (1993:112) for *Austrovenus stutchburyi* (Wk-2365), while Rafter *et al.* (1972:635) recorded values of -25.4‰ for penguin flesh and -24.4‰ for fish fillets.

Subsequent results on *Rattus exulans* have also clearly demonstrated the possibility of a marine influence (Figure 4.3). Depleted $\Delta^{14}C$ values, similar to those reported for birds with a marine based diet, were recorded for rats caught close to the shearwater nesting colony (K4A and K4J) and the black-backed gull colony (K2AF). The $\delta^{13}C$ values for K4A ($\delta^{13}C$ = -21.5‰), K4J ($\delta^{13}C$ = -20.6‰) and K2AF ($\delta^{13}C$ = -22.3‰) would not, however, have indicated the possibility of a marine dietary component without the associated high $\delta^{15}N$ values ( $\delta^{15}N$ = +11.6‰, $\delta^{15}N$ = +12.9‰ and $\delta^{15}N$ = +11.0‰ respectively)(Beavan and Sparks 1998:606) (see Table 2.2). Because $\delta^{15}N$ values are not available for the Shag River Mouth, Pleasant River, or

Holdaway's (1996) samples, the collagen in these groups of rat determinations cannot be interpreted with confidence as being entirely influenced by terrestrial carbon.

*2. Essential amino acids and diet.*

According to Ambrose and Norr (1993:7) "[E]ssential amino acids must be obtained from dietary proteins and non-essential ones can be resynthesised from all dietary fractions". They concluded that a minimum of 18% of the carbon in collagen must be obtained from dietary protein. With a protein rich diet (*i.e.* 70% protein), however, they calculated that energy sources (lipids and carbohydrates) contribute only 5 - 12% of the carbon in collagen, and that the $\delta^{13}C$ value disproportionably reflected the protein fraction (Ambrose and Norr 1993:29).

This implies that a marine correction larger than the 100 years, as suggested by Beavan and Sparks (1997:8), may be needed, possibly even greater than 95% of the standard marine correction. Interestingly, the $\Delta^{14}C$ for *Rattus exulans* sample K4AF (+54.4 ± 8.7‰) is more negative than that for marine birds (*i.e.* gull +87.5 ± 9.3‰; penguin +75.6 ± 9.2‰ and gannet +66.8 ± 8.9‰), or seawater measured at Plimmerton in 1995 (+90 ± 5.0‰)(Beavan and Sparks 1998:605). Regardless of the *Rattus exulans* $\Delta^{14}C$ result, it is immediately apparent from the $\Delta^{14}C$ value of these sea birds and of the black-backed gull (a marine and terrestrial scavenger), that marine depletions of *ca.* 100% are possible. Theoretically, this could result in large errors, even up to 1400 years if feeding on Antarctic animals (Gordon and Harkness 1993) and animals that inhabit deep-sea environs (Pearcy and Stuiver 1983; Williams, Druffel and Smith 1987). Depleted terrestrial values have also been identified (*i.e.* land snails (Rafter *et al.* 1972:650-651; Riggs 1984)).

*3. Glycine: A non diet amino acid ?*

Tieszen and Fagre (1993:149) noted that glycine and several other collagen amino acids are enriched relative to the diet (including alanine, glutamic acid, serine and threonine). They concluded that this enrichment may be a consequence of the corresponding enrichment of these amino acids in the diet. Further, they suggest that in protein-rich diets, amino acids or their keto skeletons could be incorporated directly from ingested protein (Tieszen and Fagre 1993:152). Therefore, glycine and other non-essential amino acids may not give $\Delta^{14}C$ values in equilibrium with blood bicarbonate or the atmosphere, contra to Beavan and Sparks' (1998:611-612) suggestion.

Clearly, further research is required to understand the precise reasons for the variability shown in rat gelatin ages before the results obtained by Holdaway (1996) can be accepted as reliable. The most likely cause is a combination of reservoir effect, caused by a marine diet for some of these rats, and pretreatment error.

## CONCLUSION

Bone from New Zealand's prehistoric sites has been commonly used for $^{14}C$ measurement, despite Libby's (1952:44) doubts, perhaps because of the close association between the sample type and the prehistoric event. This was certainly the impetus behind both Lockerbie's first *Dinornis* determinations, and more recent *Rattus exulans* results. On the basis of this review, it is suggested that the reputation both for and against bone dating in New Zealand has suffered from;

- a failure to report radiocarbon determinations correctly,
- limited publication of results,
- confusion between the various fractions analysed, most notably carbonate and "collagen" (or "fixed carbon") results,
- limited assessment of the preservation state of bone to be analysed,
- a failure to report specific pretreatments used on each sample,
- confusion over terminology and the accuracy of various pretreatments,
- a lack of comparisons with other reliable sample types, and
- questionable contextual security of some samples.

Consequently, the literature is somewhat confused regarding which species can be dated, what pretreatments give accurate determinations, the effects of New Zealand's environmental conditions on bone, and what errors may be introduced into the final result. It is, therefore apparent that a number of factors need to be further investigated in order to explore the reliability of future moa bone determinations and radiocarbon measurements on novel bone sample types. Specifically;

- a method for identifying sub-fossil bone needs to be developed prior to radiocarbon analysis,
- a greater understanding of the origin, fractionation, stable isotope correction and $\Delta^{14}C$ of the carbon ingested and routed to collagen is needed,
- a greater control over the selection of material and preservation state of the sample to be dated is necessary, and
- a reliable pretreatment method, or methods need to be developed.

# CHAPTER 5

# SAMPLE SELECTION

This chapter describes the seven archaeological sites selected for $^{14}C$ analysis. These are Houhora, Twilight Beach, Tata Beach, Rotokura, Pleasant River, Shag River Mouth and Long Beach. Several areas of concern, as previously outlined in Chapter 2, are also discussed about the specific fish species chosen for radiocarbon assay and the environmental conditions encountered at each site.

## INTRODUCTION

Barracouta (*Thyrsites atun*) and snapper (*Pagrus auratus*) were selected to test the reliability of $^{14}C$ determinations on fish bone. Leach and Boocock (1993:22) identified barracouta and snapper as the two dominant fish species found in New Zealand archaeological sites. Barracouta was most common in South Island middens, while snapper predominated in the North Island and northern South Island middens (Table 5.1).

Table 5.1: Percent of snapper and barracouta found in New Zealand middens according to regional divisions (from Leach and Boocock 1993:22; table 144).

| Taxon | Northern North Island | Southern North Island | Northern South Island | Southern South Island |
|---|---|---|---|---|
| *Pagrus auratus* | 65.50 | 33.33 | 22.77 | 0.10 |
| *Thyrsites atun* | 2.82 | 7.06 | 47.49 | 54.62 |

## SAMPLING

Fish bone for this dissertation was selected from sites located in each of the four regions identified by Leach and Boocock (1993:22) above (Figure 5.1). Snapper dominates the fish minimum number of individuals (MNI) at Houhora, Twilight Beach and Rotokura. Large quantities of barracouta (and red cod) were recovered from Tata Beach, while barracouta dominated the fish bone MNI's from Pleasant River, Shag River Mouth and Long Beach (see Appendix 1 for bag labels and Appendix 2 for MNI's).

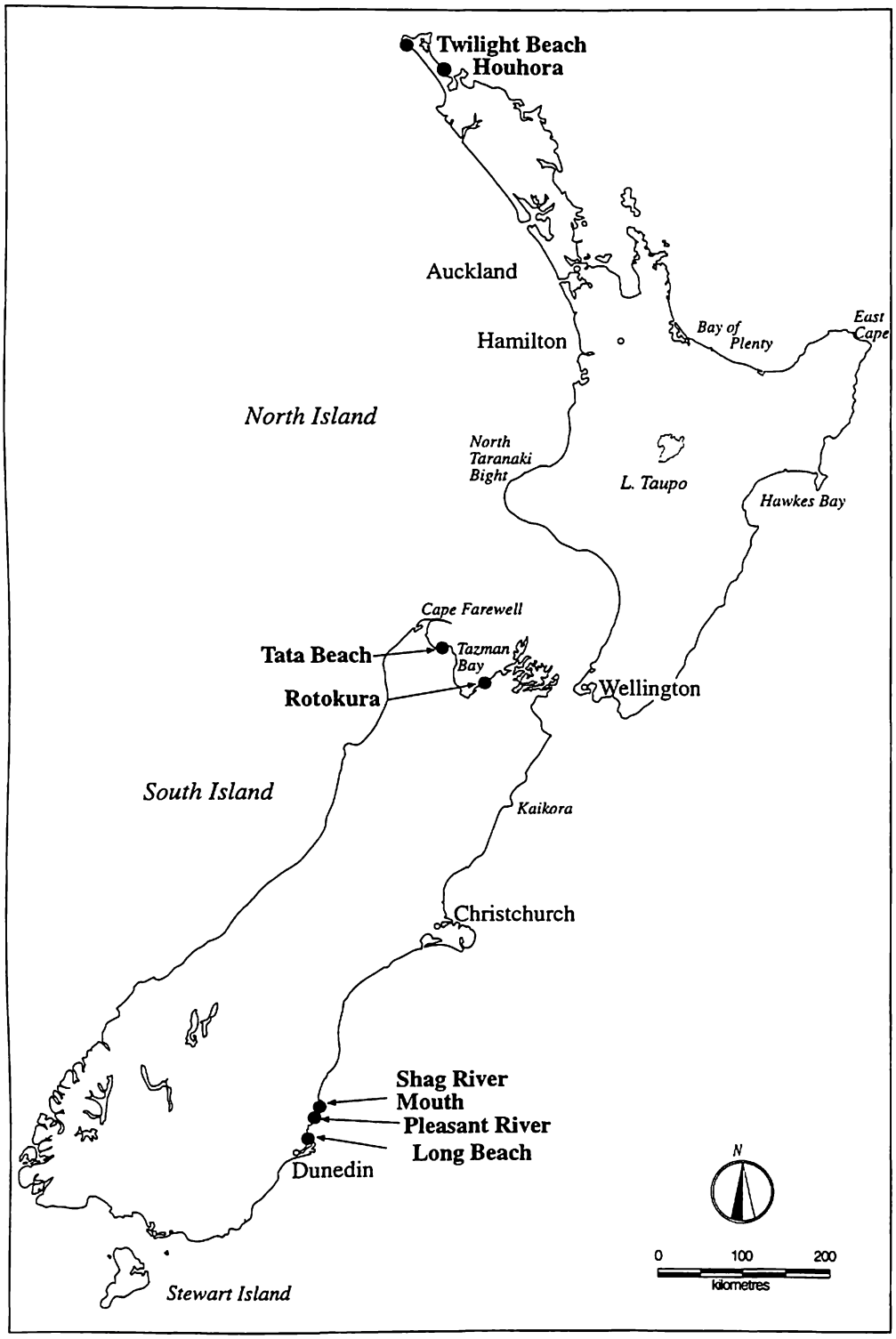



Figure 5.1: Map of New Zealand showing the location of archaeological sites sampled in this study.

## Houhora, Layer 2b/3

Houhora (NZAA[1] site number N03/59) is located at the entrance of Houhora Harbour, at the top of the North Island (Figure 5.1). The site of Houhora consists of a large coastal midden containing remains of moa and seal, fish and associated artefacts typical of early tropical East Polynesian assemblages (Anderson and Wallace 1993:5). Two major excavations were undertaken at the site. The main excavation (Figure 5.2) occurred between November 1965 and January 1966 (Shawcross and Roe 1966; Roe 1969), with squares A6, A7, half of A8 and B6 excavated in 1972 (L. Furey[2], *pers. comm.* 6/5/97). A number of reports have been compiled on these excavations. Roe (1969) discussed the 1965-1966 excavation, stratigraphy and artefact assemblage. Faunal remains were briefly discussed by Shawcross (1972), and fish remains were re-analysed by Nichol (1988). Recently, Anderson and Wallace (1993) reanalysed stratigraphy and discussed existing and new radiocarbon results.

Interpretation of the stratigraphy and layout of Houhora is subject to a number of uncertainties due, in part, to the lack of a detailed site report as well as the somewhat ambiguous and occasionally contradictory published descriptions (*i.e.* Roe 1969 and Shawcross 1972).[3] The most detailed site plan is given in Shawcross (1972). Shawcross' plan (Figure 5.2) reveals a concentration of occupation debris at the centre of the excavation. Ovens surround the perimeter with a high concentration to the south west. To the north west a high concentration of fish cranial elements was interpreted as a processing area (Shawcross 1972:606).

The only contemporary account of stratigraphy is given in Roe (1969:figure 3). Nichol (1988:201) reanalysed the stratigraphy of Houhora using bag labels on samples held in storage and identified four main layers (2a, 2b, 2c and 3). The widespread distribution of these layers generally matched Roe's (1969:figure 3) account of stratigraphy, except that Layer 2c was missing (Figure 5.3). The lower layers (Layer 2b and Layer 3a, b and c) contained remains of cooking and other general day to day activities. A later agricultural layer (Layer 2a) cut into Layer 2b (Roe 1969:14-20).

[1] New Zealand Archaeological Association.

[2] L. Furey, Auckland Institute and Museum, Auckland, New Zealand.

[3] L. Furey is currently undertaking research into the Houhora excavations.

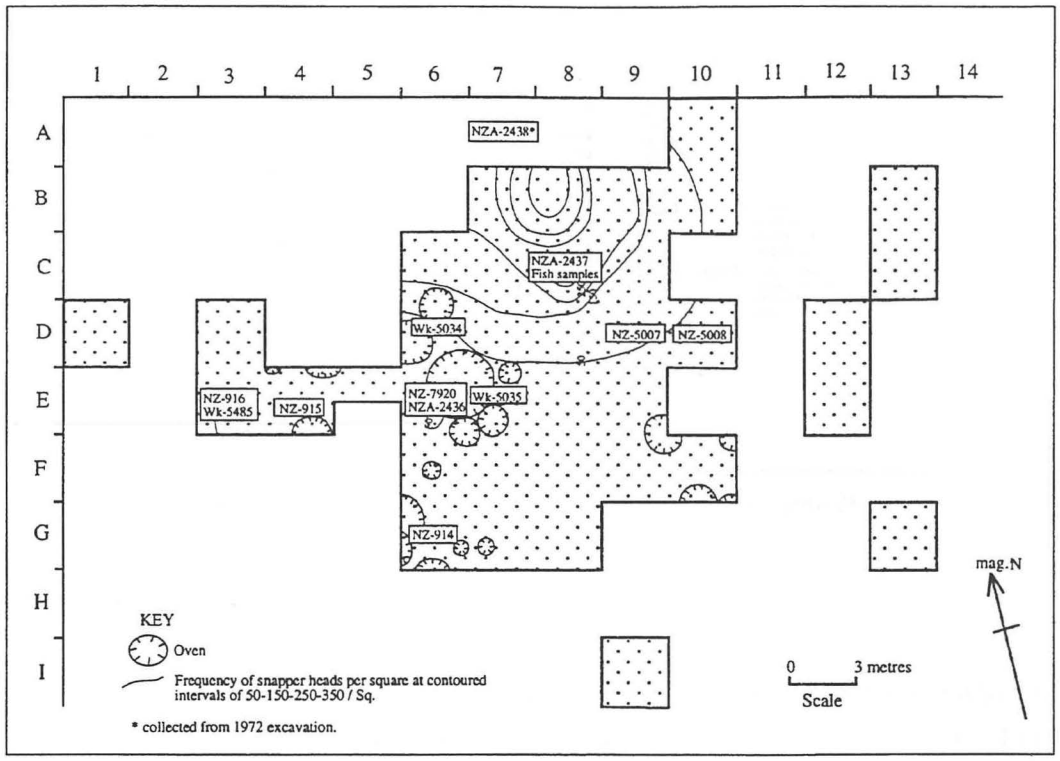



Figure 5.2: Plan of Houhora showing location of radiocarbon samples from Archaic layers (adapted from Shawcross 1972:604, figure 14.1).

Only a small portion of the site was excavated (under 2% according to Shawcross (1972:605)). The excavated area appears to have been chosen specifically because it contained large quantities of food waste. The resulting sample is, therefore considered to be biased (K. Peters, *pers. comm.* 1984, in Nichol 1988:198) and the nature of occupation at Houhora is disputed. Shawcross (1972:605) argued for intermittent occupation with short periods of abandonment on the basis of "12 superimposed floors", which were separated by thin skins of sterile sand. Roe (1969:18), however, interpreted these as oven rake-out and "working floors" confined to square C7 (Figure 5.2). Nichol (1988:206), following Roe's assessment, suggested that the site was occupied all year round and represented a series of superimposed seasonal camps. More recently, following the acquisition of nine "acceptable" radiocarbon determinations, Anderson and Wallace (1993:10, table 1) suggested that occupation began some time in the late 13th century AD. This was in keeping with a previous estimate by Roe (1969:36) based on artefact forms. Anderson and Wallace (1993:5, 14) also suggested that occupation was short lived, and that no substantial period of time had elapsed between the lowest layers (layers 2b and 3).

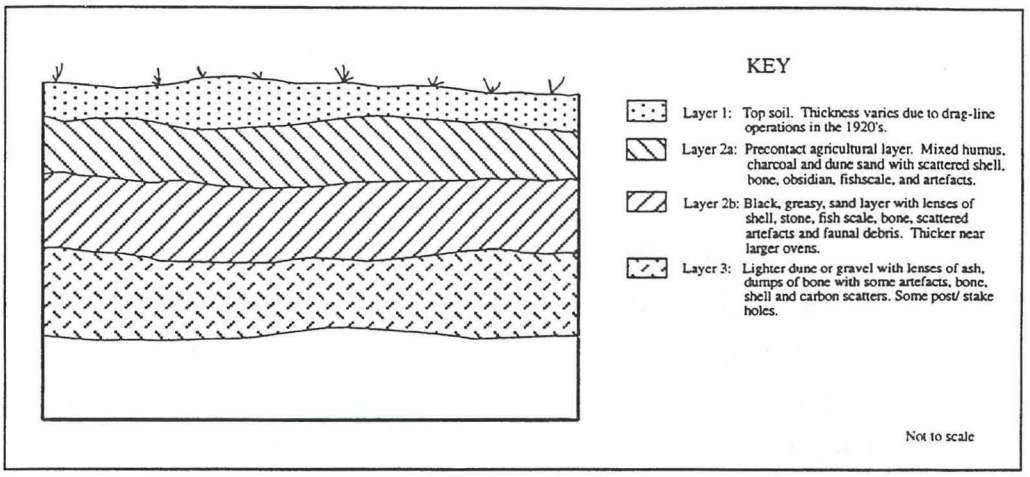



Figure 5.3: Houhora: Typical cross-section (adapted from Roe 1969: figure 3).

*Sample selection*

The Houhora fish bone sample (Wk-4920, Wk-4921, Wk-4968, Wk-4969 and OxA-7569) came from the Auckland University Anthropology Department stores. Due to selective collection at the time of excavation this stored sample consisted entirely of diagnostic snapper bones (*i.e.* maxilla, premaxilla, dentary, articular and quadrate (see Appendix 2, table A2.1 and Appendix 3, table A3.6). A number of bags labelled Houhora C8, "Fossick A", were made available for radiocarbon analysis (see Appendix 1). Unfortunately, this raises some questions about sample provenance (L. Furey, *pers. comm.* 6/5/97). It can be argued, however, that this material was associated with the two lower occupation layers (2b and 3). First, the identification of a square number (C8) strongly suggests removal from an *in situ* deposit. It is, therefore considered likely, as suggested by Nichol (1988:195-196), that this fish bone sample was removed from baulks by archaeologists following completion of the excavation. Second, the archaic layers near square C8 were rich in fish bone with a particularly high frequency of snapper head parts per square metre (Shawcross 1972:604, figure 14.1). Finally, *in situ* middens from the more recent layer (Layer 2a) did not have the bone typically associated with the older middens (Roe 1969:78).

For this dissertation, three additional samples were selected for $^{14}C$ analysis due to uncertainties with the available radiocarbon results (see Chapter 7). Archived charcoal from NZ-916, one of the original radiocarbon determinations, was obtained from IGNS, and two pieces of the short lived *Myrsine australis* removed for analysis (Wk-5485). Shell came from two bags; the first (Wk-5035), a sample of *Lunella smaragda* labelled Houhora E7, L2b, SE corner, shell; and the second (Wk-5034), a sample of *Austrovenus stutchburyi*, labelled Houhora D6, L2b, 2nd Hangi. Following Roe's

(1969) account, the second of these two samples can be provenanced to a large oven in squares C6, C7, D6 and D7 (Figure 5.2).

## Twilight Beach, Layer 3

The Twilight Beach midden (NZAA site number M02/162) (Figure 5.1) is located at the northern end of Twilight Beach, at the tip of the North Island. Bone of the New Zealand fur seal dominated the midden which was interpreted as a specialised sea mammal processing site (Leach 1989:40). Other remains included both oceanic, coastal, wetland and forest bird species, and fish (Taylor 1984:103-104; Leach 1989:37-38). An excavation at Twilight Beach was carried out in 1981 and discussed by M. Taylor (Taylor 1984). Taylor's research was primarily concerned with the outcome of taphonomic influences on mammalian bone assemblages.

Taylor (1984) identified three distinct cultural layers (Figures 5.4 and 5.5), with Layer 3 forming the bulk of the deposit. The composition of Layer 3 varied between North and South ends of the excavation. In the south the layer consisted of grey to black sand with abundant shell and bone. This was interpreted as the product of processing activities. To the north the layer was charcoal rich with few cultural remains. Here, Taylor (1984:69-71, 198) thought layers 3a, 3b, 3c and 3d represented hangi preparation and rake-out events.

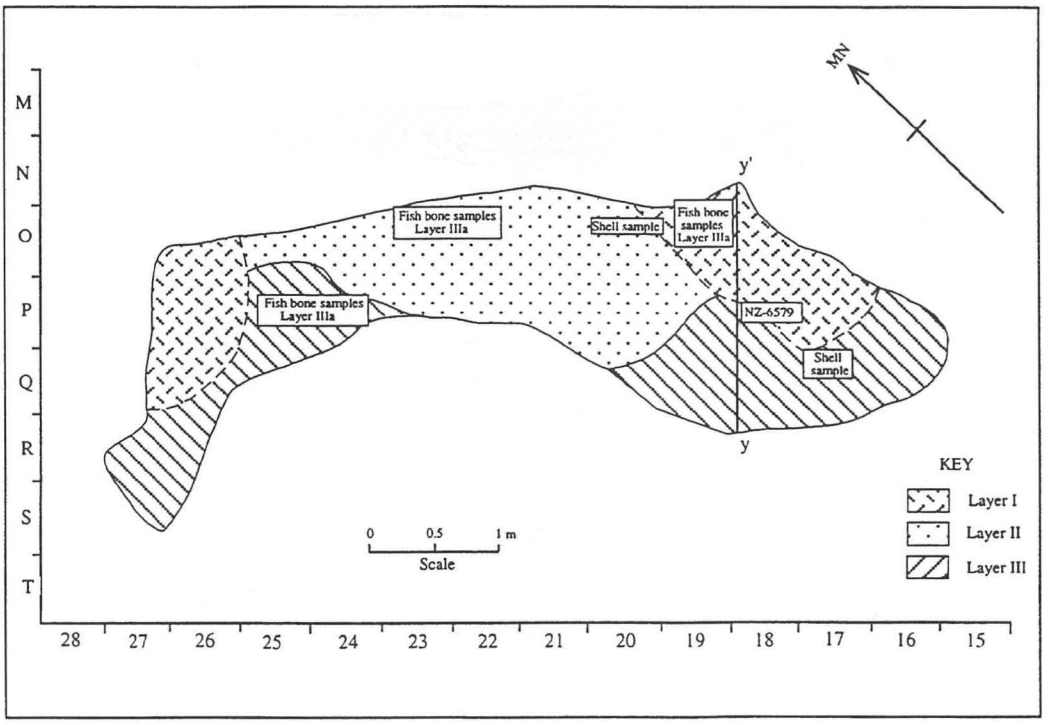



Figure 5.4: Plan of Twilight Beach showing location of radiocarbon samples from Layer 3 (adapted from Taylor 1984:58, figure 5).

On the basis of seasonal evidence, which suggested summer occupation, Taylor argued that the midden was formed over a short period (1984:199, 201). A subsequent radiocarbon measurement (NZ-6579) of toheroa (*Paphies ventricosa*), from Layer 3c (squares P18/5, 6, 14, 15) suggests that the midden was deposited in the 14th century.

*Sample selection*

Taylor's collection strategy involved the recovery of complete midden sections (Taylor 1984:65). As a consequence the Auckland Anthropology Department stores held significant quantities of non-diagnostic bone for future research. Bags of fish bone were selected from Layer 3a, squares P25, P24, O19, O22, O23 (Figure 5.4 and Appendix 1), and identified snapper bones removed for analysis (Wk-5437, Wk-5438 and Wk-5439). The MNI's for the midden as a whole suggest that 92.8% of the fish bones are snapper (Table A2.2), significantly reducing the possibility of contamination by mixed species.

Three toheroa shell samples (Wk-5032, Wk-5033 and Wk-5678) were also selected for radiocarbon assay from a concentrated shell lens at the bottom of Layer 3a (M. Taylor, *pers. comm.* 29/1/97); two from square Q17/1 and one from square O20/8 (Figure 5.5).

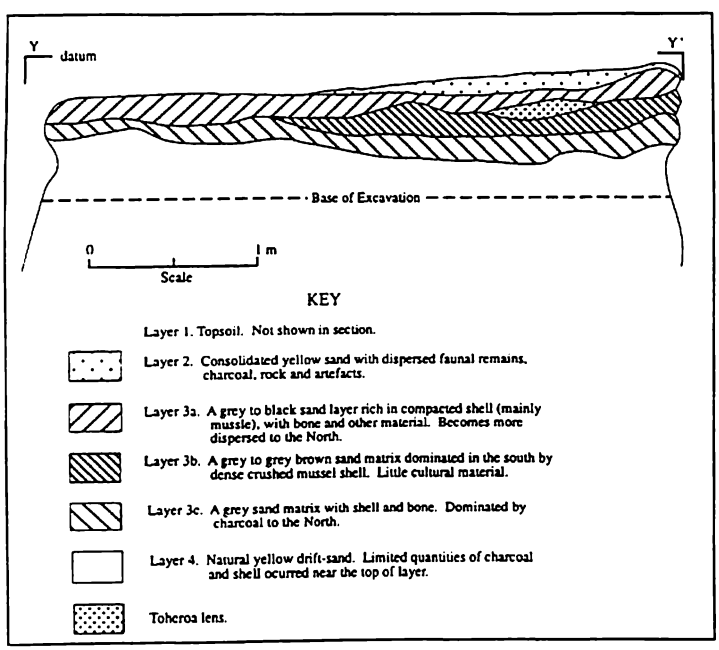



Figure 5.5: Twilight Beach: Stratigraphic profile of the East-West section (adapted from Taylor 1984:68, figure 7).

## Rotokura, Layer 4

The site of Rotokura (NZAA site number O27/1) is located next to a swampy lagoon, on the western shores of Cable Bay in Tasman Bay (Figure 5.1). An excavation took place over an extended period from November 1964 to August 1969, and a range of material was recovered including Classic, Archaic and European artefacts (Millar nd:10; Butts 1978:6). There are a number of reports on material from Rotokura, including Butts (1977) on seasonality, Smith (nd) on marine mammals, Leach and Boocock (1994) on fish remains, and Challis (1991) who looked briefly at adze and fishhook forms as part of a large body of work in the Nelson-Marlborough region.

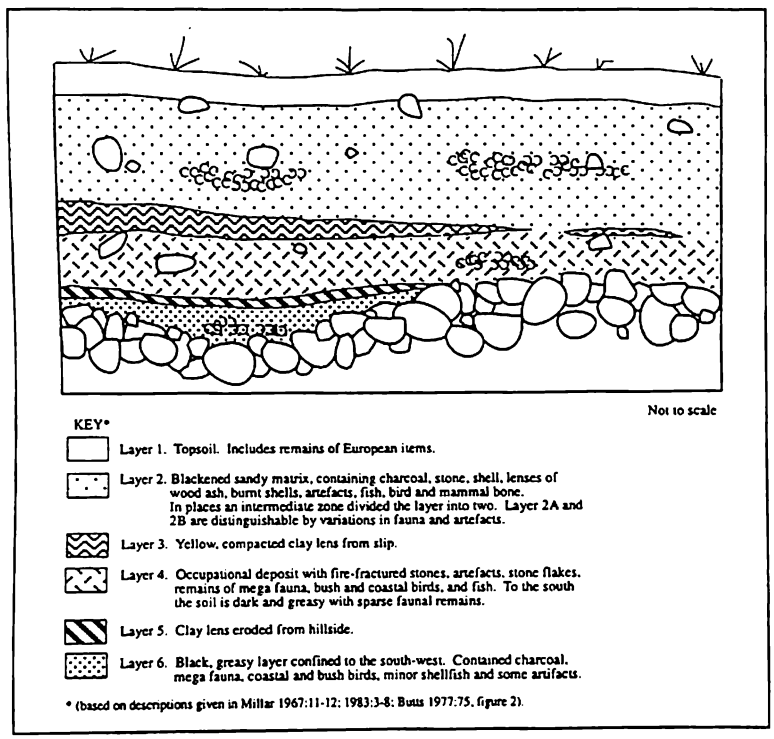



Figure 5.6: Rotokura: Typical cross-section (adapted from diagram courtesy D. Millar[4]).

Three main prehistoric occupational deposits were identified (layers 2, 4 and 6) (Figure 5.6). In places extensive fossicking obscured these layers, especially at the northern end of the site (Figure 5.7) (Millar 1967:10; nd:2). Consequently, there is some uncertainty over layer designation. Millar (nd:8), for example, suggested Layer 6 may be an internal feature of Layer 4. The identification of two divisions in Layer 2 (into Layer 2A: Classic features, and 2B: Archaic features) at the centre of the

[4] D. Millar, Taradale, Napier, New Zealand.

occupation deposit also implied greater chronological complexity (Butts 1977:22). Following reanalysis of artefact forms, Challis (1991:122-126) suggested that a progression was evident between Layer 4 and 6, and between Layer 4 and 2B, and concluded that over four centuries may separate Layer 4 and 2A.

From the analysis of faunal remains Butts (1977) suggested year round occupation of Rotokura in both the late and early phases. Using this information and artefactual evidence, Millar (1967:10-11; nd:10) concluded that the site was occupied fairly continuously by a small group of people over a long period, with initial occupation around 500 to 600 years ago. The earlier estimation was later supported by an unidentified charcoal $^{14}C$ result from Layer 4 (NZ-1105).

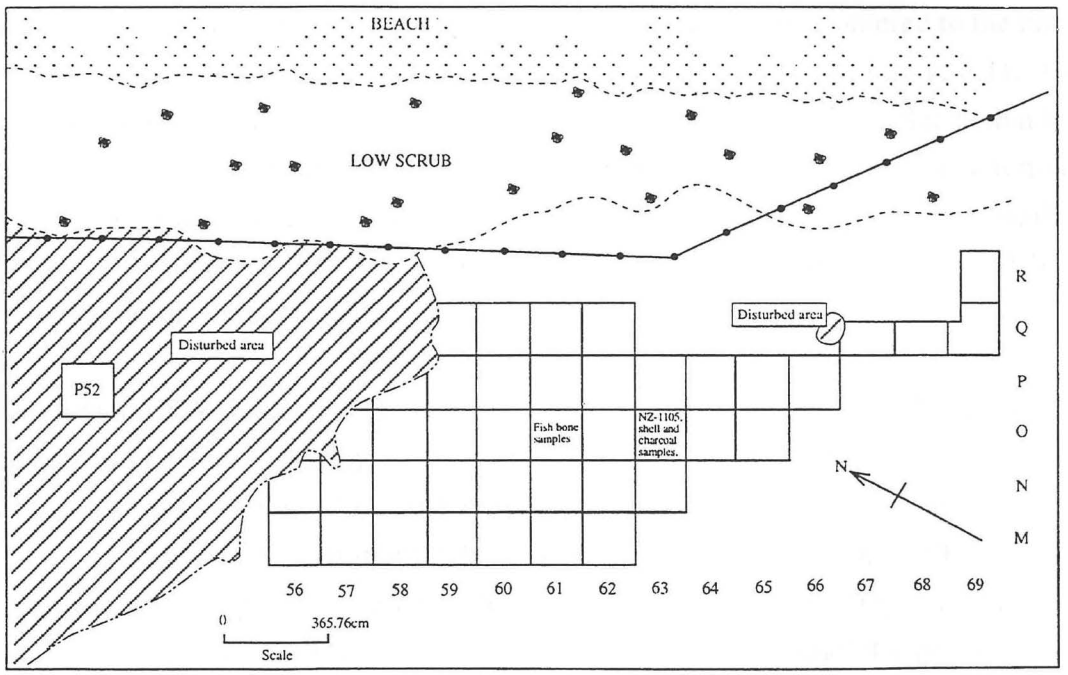



Figure 5.7: Plan of Rotokura showing location of radiocarbon samples from Layer 4 (adapted from diagram courtesy D. Millar).

*Sample selection*

Sample selection was complicated by the limited published excavation report, and uncertainties surrounding the treatment of the collection since excavation. Snapper bone from Rotokura was obtained from stored samples held at the Museum of New Zealand, Te Papa, Wellington. Non-diagnostic identified snapper bone was selected for analysis from squares O61 and N62, at the boundary of Layer 3 (sterile clay layer) and Layer 4 (Wk-4953, Wk-4954, Wk-4955 and OxA-7570)(see Table A2.3).

Shell and charcoal samples proved to be particularly difficult to locate. Two fragmentary shell samples, removed from stored material held at the Nelson museum, were selected from Layer 4 square O61 (Wk-4886; *Struthiolaria papulosa*, and Wk-4887; a mix of *Paphies australis*, *Protothaca crassicosta*, *Lunella smaragda*, and *Haliotis iris*).[5] Archived material remaining from the original unidentified charcoal sample; NZ-1105, was also located in the IGNS stores. This sample was identified by Dr. Wallace[6] and appeared to be composed entirely of short lived species (*i.e. Dodonaea viscosa, Melicytus ramiflorus,* and *Coprosma* sp.). A sample of charcoal was selected for comparison purposes (Wk-5482, Wk-5483 and Wk-5484).

**Tata Beach ESW/5, Layer 3**

Tata Beach is located on a peninsula extending into Golden Bay, bordered to the north by an open beach and to the south by an estuary (Barber 1998:2-3) (Figure 5.1). The ESW/5 midden is part of a larger archaeological landscape along Tata Beach that has revealed evidence of extensive gardening, crop storage, coastal processing, intensive animal husbandry, artefact manufacture, house construction, and burials (Barber 1998:22). A report of the salvage excavations carried out between March and June 1996 is given in Barber (1998). Full analysis is pending.

Tata Beach ESW/5, Layer 3 (Figure 5.8) was the largest midden complex along the western esplanade. This layer was divided into two lenses composed of shellfish (predominantly *Mytilus edulis* and *Paphies australis*), fish, dog, sea mammal and occasional bird bones. An intermediate zone of yellow-brown sand with scattered midden remains separated these two lenses. Barber (1998:8-9) suggested that this intermediate zone may represent a period of coastal instability and/or a period of less intense occupation activity. A change in fish species composition between the layers supported this conclusion. In the lower and intermediate units red cod dominated (*ca.* 83%) over barracouta. This trend was reversed in the upper unit (*ca.* 70% barracouta) (Barber 1998:10). A difference in charcoal was also identified between the upper and lower units, which Barber (1998:11) suggested may represent a loss of local plant diversity over time as the result of land clearance.

On the basis of radiocarbon results, obtained from different sites along the beach frontage (Wk-4911 from Cornwall Haven, ESD1, Layer 2/3, dated to AD 1450-1654, and Wk-4912 from a later horizon at the western Peninsula Road, dated to AD 1433-

[5] Species identified by Bruce Marshall, Collection Manager, Marine Invertebrates, Museum of New Zealand, Te Papa Tongarewa, Wellington, New Zealand.

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

1648), Barber (1998:11) suggested a 16th century AD upper occupation limit for the ESW/5 midden. An earlier date for the onset of Layer 3 was, however, considered likely given the 15th century occupation from a site in neighbouring Ligar Bay.

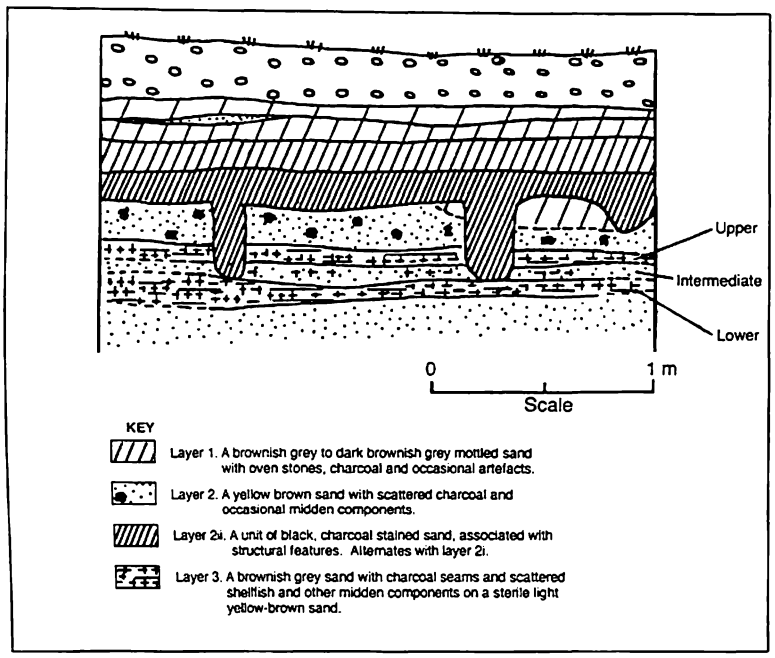



Figure 5.8: Tata Beach: Stratigraphy of the ESW/5 midden (from Barber 1998, figure 5).

*Sample selection*

Material for this research was collected at the time of the ESW/5 excavation. Four shell samples (consisting of either *Paphies australis* or *Austrovenus stutchburyi*) were selected from Layer 3, upper (Wk-4866 and Wk-4867) and Layer 3, lower (Wk-4864 and Wk-4865). Two charcoal samples from Layer 3, lower (Wk-4894) and Layer 3, upper (Wk-4893) were also measured for $^{14}C$ content.

Following the results of the shell and charcoal determinations, which indicated that no significant hiatus was present in the radiocarbon determinations (see Chapter 7), fish bone was selected from Layer 3, upper and lower lenses, as well as an undifferentiated midden sample. Non diagnostic identified barracouta bone came from the upper lens (Wk-5134 and OxA-7568), and from a bulk sample of Layer 3 midden (Wk-6032). Identified red cod bone from combined lower and intermediate lenses (Wk-5135), as well as a bulk sample (Wk-6033) from Layer 3, were also sampled. For comparison purposes a sample of scrap fish bone (assumed to be predominantly red cod (Table A2.4)) from Layer 3 was also analysed (Wk-6034).

## Shag River Mouth: SM/C:Dune, Layer 4

The Shag River Mouth site (NZAA site number J43/2) is located on sand dunes enclosing an estuary at the mouth of the Shag River (Anderson and Smith 1996a:1) on the eastern coast of the South Island (Figure 5.1). The site consists of large middens, dwelling remains, and contained a wide range of artefact types typical of the Archaic phase of New Zealand material culture, with a few artefacts characteristic of the later Classic phase. Anderson and Smith (1996b:281-282), therefore suggested that occupation could have been during the transitional period of Maori Culture.

Shag River Mouth has been extensively excavated and fossicked. The most recent excavation, on the high dunes at the southern margin of the site (SM/C:Dune), took place in 1988/9. A thick layer (around 1 m) of sand protected the occupation deposit from disturbance (Anderson and Allingham 1996:39). The excavation and analysis of material from SM/C:Dune are discussed in Shag River Mouth: The Archaeology of an Early Southern Maori Village, edited by Anderson, Allingham and Smith (1996).

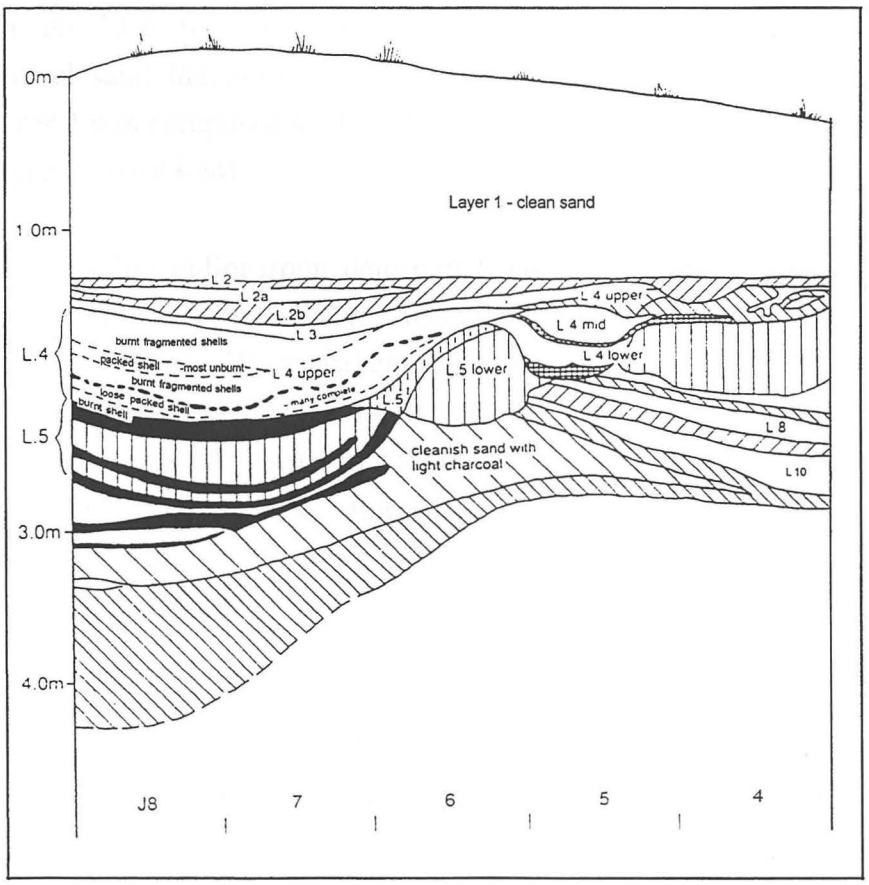



Figure 5.9: SM/C:Dune: Stratigraphic profile of east wall of squares J4-J8 (from Anderson and Allingham 1996:42, figure 5.4a).

Seven occupation layers were excavated (layers 11, 9, 7, upper 6, 5, 4, and 2) (Figure 5.9). Layers 10, 8, lower 6, and 3 are thought to represent total or partial abandonment of this area for a brief period of time (Anderson and Allingham 1996:40-47). A change in the use of the site between layers was also indicated by an increase in the number and areal extent of ovens in layers 5, 2 and 4 (Anderson and Allingham 1996:47). A similar change was noted in the artefact (*e.g.* fish hooks [Anderson and Gumbley 1996:156] and stone implements [Smith, Campbell and Bristow 1996:80, 101]) and faunal assemblages. Most notably, moa, coastal sea birds, fur seal remains and evidence of butchery dominated the lower layers (below Layer 5), but evidence of fishing and shellfish gathering were common in layers 2 to 4. Anderson and Smith (1996b:283) suggested that this did not represent a seasonal flux, but a change in subsistence patterns over time following a period of abandonment.

A large oven depression dominated the north east corner of Layer 4 (Figure 5.10). This was filled with a dense shell midden mixed with artefacts, oven stones, and bones (burnt and unburnt) of fish, dog, sea mammal, small bird and moa. Well-defined lenses of calcined shell and fish bones indicated that there had been some burning *in situ.* Elsewhere, the contents of the Layer 4 midden were sparse within a matrix of black sand, that got thinner away from the north east quadrant. The lower part of Layer 4 was composed mainly of a loose deposit of unburnt shell (Anderson and Allingham 1996:43-44).

Fourteen acceptable radiocarbon determinations (shell and charcoal) have been obtained from SM/C:Dune Layer 4. Acceptable measurements from all layers at SM/C:Dune (a total of 32 $^{14}C$ measurements) were statistically indistinguishable and suggested an occupation in the mid 14$^{th}$ century AD. In particular, there was almost no variation amongst the radiocarbon determinations from the deepest part of the site (SM/C:Dune) and top layers, indicating a brief occupation of perhaps 20 to 50 years (Anderson, Smith and Higham 1996:67; Anderson and Smith 1996b:278).

*Sample selection*

Fish bone for analysis was removed from samples of bulk unsorted midden held at Otago University. Non-diagnostic fish bone (Wk-4970, Wk-5131, Wk-5434, Wk-5435, OxA-7793 and OxA-7593) selected for analysis came from the upper part of Layer 4 (squares E7, E8, F7, F8; Layer 4 upper spit 2, square H8; and Layer 4 upper, square J8). Fish bone from the Layer 4 midden was identified as predominantly barracouta (67.95%). Significant quantities of red cod (22.50%) may, however, be included amongst the samples (Anderson and Smith 1996c:239, table 17)(see Table

A2.5). A moa sample from upper Layer 4, square G8 was also selected for $^{14}C$ measurement (Wk-5433).

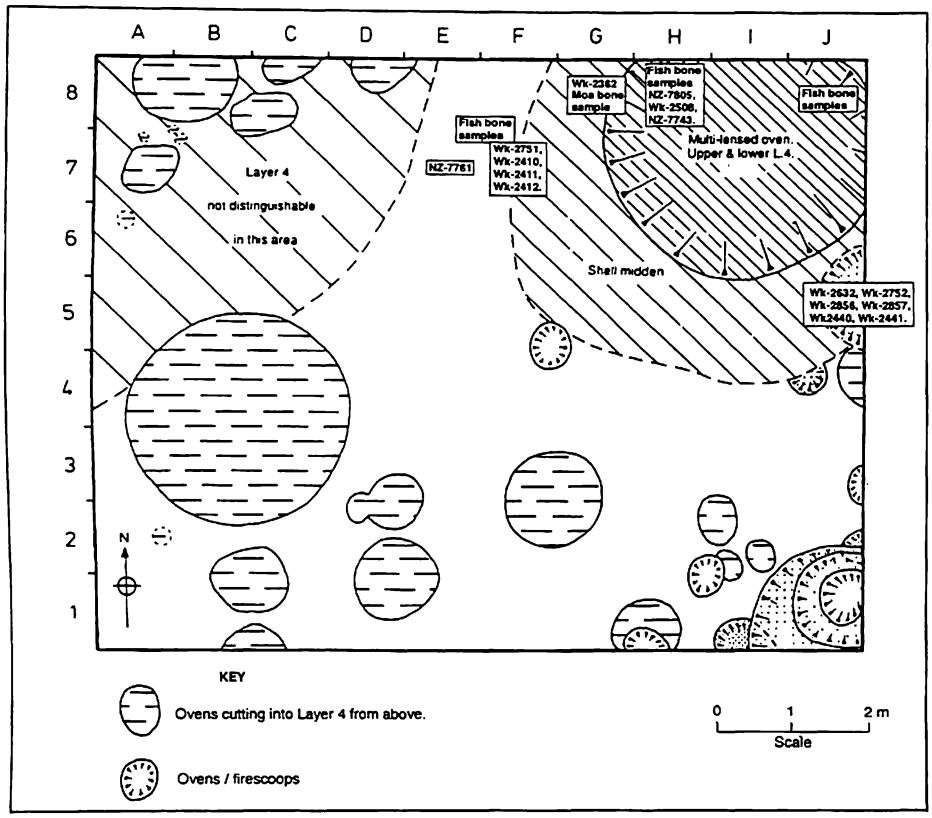



Figure 5.10: Plan of SM/C:Dune showing location of radiocarbon samples from Layer 4 (from Anderson and Allingham 1996:44, figure 5.6).

## Pleasant River: Areas 3 and 7, Layers 1 and 2a

The Pleasant River site (NZAA site number J43/1), on the east coast of the South Island, lies on the eastern bank of the Pleasant River estuary on a sand dune extending westward from the foot of the hills towards the river (Figure 5.1). The Anthropology Department, University of Otago carried out a number of excavations between 1991 and 1993 (Smith 1992). At least three phases of activity have been identified on the dunes (Samson 1995:72), but in adjacent Areas 3 and 7, evidence of only two occupational phases were found (Figure 5.11); an early period Archaic activity (Area 7, Layer 2b and Area 3, Layer 3) and a later period (Area 7, layers 1-2a and Area 3, Layer 1) of occupation predominantly characterised by fishing activities. The stratigraphic and artefactual evidence points to a series of brief seasonal encampments at Pleasant River, by small groups of people (Smith and Anderson 1998:88). The report on this excavation is pending.

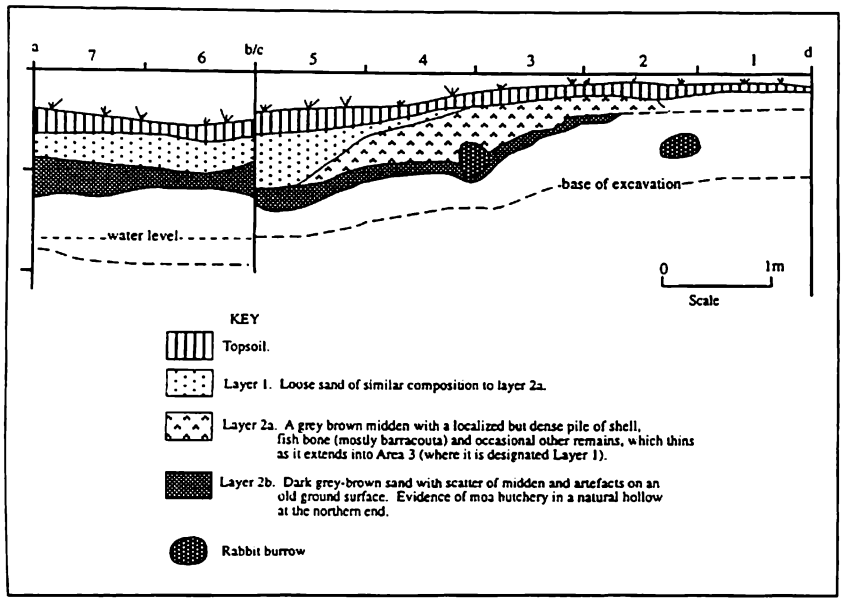



Figure 5.11: Pleasant River: Stratigraphic profile of Area 7 (courtesy Ian Smith[7]).

Two shell $^{14}C$ determinations have been obtained for Area 7, Layer 1 (Wk-3509) and Layer 2a (Wk-3510). These results support a 16th century occupation and confirm that Layer 1 was composed of disturbed material from the top of Layer 2a. This upper horizon is also dated by two charcoal determinations (NZA-2802 and NZA-3740), which despite being indistinguishable, differ by 130 years and do not overlap at two sigma with the shell ages (see page 153). This is possibly due to localised disturbance, caused by a thinning between upper and lower layers as they rose up an old dune surface, or the result of a previous excavation near NZA-3740 (Figure 5.12) (I. Smith, *pers. comm.* 23/10/96). Post-depositional re-working has also been suggested as a possible cause of anomalous radiocarbon results in other areas at Pleasant River (Higham 1993:143, 157). Smith (*pers. comm.* 23/10/96) suggests that the predominance of barracouta remains compared to moa supports an occupation of Layers 1 and 2a in the 16th century AD.

[7] Dr. I. Smith, Department of Anthropology, University of Otago, Dunedin, New Zealand.

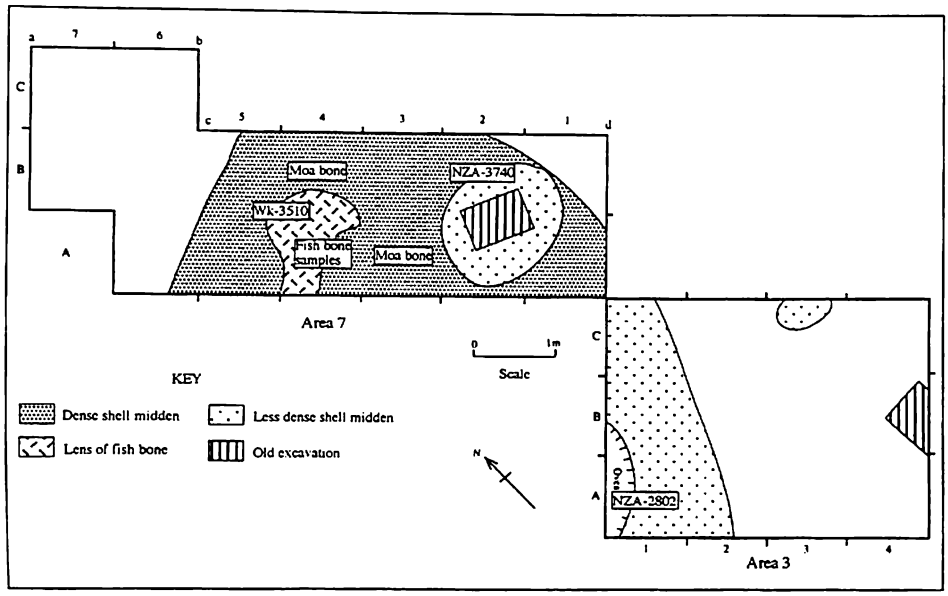



Figure 5.12: Plan of Pleasant River, Areas 3 and 7, showing location of radiocarbon samples from Layers 1 and 2a (courtesy Ian Smith).

*Sample selection*

Three samples were submitted from layers 1 and 2a, Area 7, including several fragments of moa bone (a mix of unknown species and *Euryapteryx geranoides* (PIR 1042-1, PIR 1057-1 and 2, PIR 1038-BM-1)) from Layer 2a, squares A3 and B4 (Wk-5169); one sample of barracouta pharyngobranchials (part of the gill arch) from Layer 2a, squares B4 and A4 (Wk-5036), and a sample of "fish bone residue" which included spines and other fish bone fragments from Layer 1 and 2a (Wk-4956 and Wk-5031). All fish bone samples came from a concentrated lens of fish bone (99% barracouta) (I. Smith, *pers. comm.* 23/2/1996 and 30/5/1996) (see Table A2.6). All samples were held in storage at the Otago University Anthropology department.

## Long Beach, Layer 2

The site of Long Beach (NZAA site number I44/23) is located on consolidated sand dunes, near Dunedin (Figure 5.1). Two major periods of occupation were identified (Figure 5.13); Layer 4 which contained Archaic type artefacts, and Layer 2 which contained artefacts of an Early Classic assemblage (Hamel and Leach 1979:12; Leach and Hamel 1981:109,112, 139). A salvage excavation occurred in 1977. This excavation, artefacts and faunal remains were discussed by Leach and Hamel (1981). Fyfe (1982) analysed the faunal remains, from which he inferred the existence of a

range of fishing and preparation practices. Radiocarbon results were separately presented by Hamel and Leach (1979:12).

Layer 2 included patches of dense fish bone midden, working floors, and the wall of a house (Leach and Hamel 1981:112)(Figure 5.14). This layer had been extensively disturbed by European farming activities and fossicking, especially at the western end of the site around the dwelling remains (Leach and Hamel 1981:112, 114, 122). Layer 4 consisted of three lenses of midden material (4a, 4b and 4c). The uppermost of which (Layer 4a) was only in its primary context at the southern edge of the site, the result of disturbance by wind and waves (Leach and Hamel 1981:114-119; Fyfe 1982:37-39). Leach and Hamel (1981:119-122) interpreted Layers 1 and 3 as periods of erosion, redistribution and abandonment.

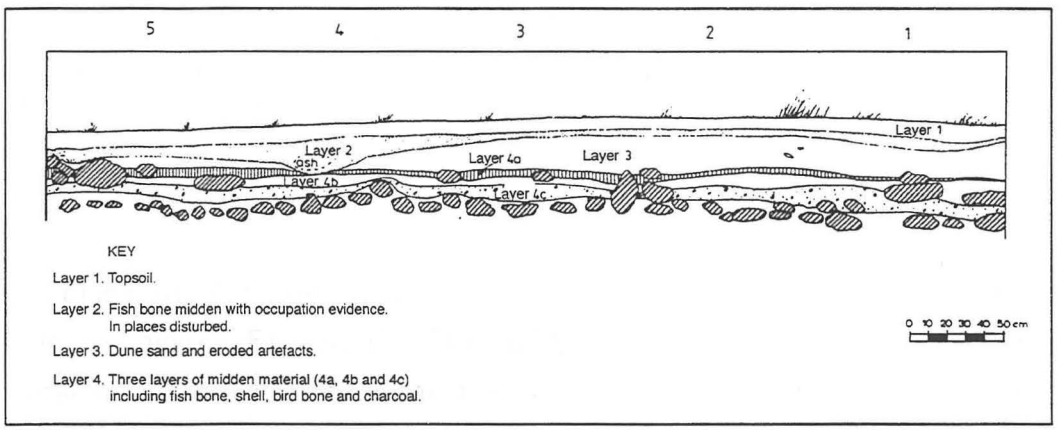



Figure 5.13: Long Beach: Stratigraphic profile (from Leach and Hamel 1981:112, figure 3).

Two radiocarbon determinations were obtained from Layer 2. One of the charcoal results (NZ-4703) consisted largely of totara (*Podocarpus totara*) and, therefore could be subject to an inbuilt error (McFadgen, Knox and Cole 1994:224). NZ-4702 was comprised of short lived species (*Leptospermum* sp., *Hebe* sp., *Coprosma* sp. and *Myrsine* sp.) and indicated an occupation in the mid-seventeenth century. This date was consistent with the Classic artefact types recovered (Leach and Hamel 1981:112). No indication of the possible length of occupation within each layer was given, though Fyfe (1982:70-72) suggested that the deposition pattern of different species indicated that the fish were processed rapidly, in a few days.

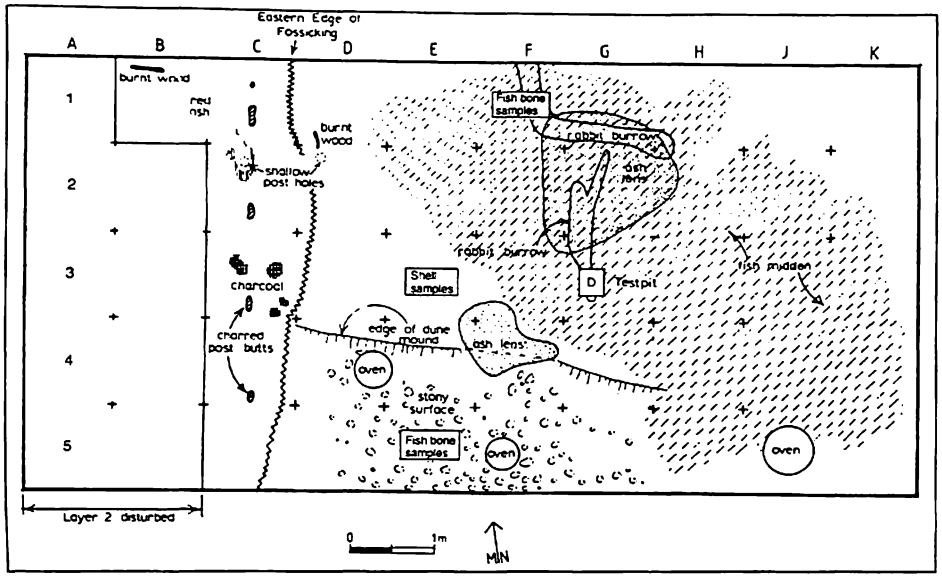



Figure 5.14: Site plan of Long Beach showing location of radiocarbon samples from Layer 2 (from Leach and Hamel 1981:111, figure 2).

*Sample selection*

Non-diagnostic fish bone scrap was selected from stored samples of bulk Layer 2 midden, squares F1 and E5 (Wk-5680, Wk-4681, Wk-5682 and Wk-5683). Barracouta dominated both squares (73.7% and 63.6% respectively), but the possibility of some red cod bones being included in the $^{14}C$ samples cannot be ruled out (15.8% and 18.2% respectively)(see Tables A2.7 and A2.8).

Three samples of *Paphies australis* from Layer 2 (square 3E) were also selected for comparison (Wk-5636, Wk-5637 and Wk-5679).

## FISH SELECTION

The discussion in Chapter 2 suggested that inbuilt age, depth of habitat, diet and migratory patterns may affect the $^{14}C$ content of marine animals. Therefore, each species selected for $^{14}C$ measurement needs to be assessed accordingly. In this dissertation, two species have been selected for analysis; snapper (*Pagrus auratus*) and barracouta (*Thyrsites atun*). Red cod (*Pseudophycis bachus*) may also be a significant "contaminating" species especially in the Long Beach, Shag River Mouth and Tata Beach collections.

## Inbuilt age

It was concluded from Chapter 2 that inbuilt age is unlikely to significantly affect the radiocarbon age of an animal. It is considered prudent, however, to obtain an estimate of the possible error that could occur. Both barracouta and red cod are short lived species. Most adult barracouta range between three to ten years of age (Paul 1986:120). Similarly, red cod take about four years to mature, with few fish living longer than 10 years (Doak 1978:20; Horn 1995:1, 4-5). Snapper may, on the other hand, reach ages in excess of 60 years (Paul 1992:7). The age of younger snapper (< 10 years) can, however, be determined from average age-length (fork length) growth curves which have been developed for separate populations from different regions around New Zealand (Paul 1992:7). This is less accurate for older fish.

The fork length of snapper cranial bones, selected from Houhora and Twilight Beach, were measured following the technique outlined in Leach and Boocock (1995). The five paired cranial bones (*i.e.* dentary, articular, quadrate, premaxilla and maxilla) were measured and a series of regression coefficients (Table A3.1), calculated from a modern comparative osteological collection (see Leach and Boocock 1995:2, figure 1, 21-22, table 3), applied to the "optimum estimator" (the largest measured dimension) (Appendix 3). Leach and Boocock (1995:11) have suggested that this method is accurate to within 20 mm. Measurements of the Rotokura snapper were obtained from Leach and Boocock (1994). The calculated fork length values of snapper from Twilight Beach, Houhora and Rotokura were then compared with Paul's (1992:10) graph of snapper growth versus age. These results are given in Figure 5.15.

Leach and Boocock (1994:77, 79, figure 7a and table 2) estimated that the fork length of snapper from Rotokura, Layer 4 ($n$ = 198) was between 362 and 746 mm with a mean of 557 mm ± 5.4 mm and a mode of 550 mm (Figure 5.15a). For snapper from Tasman Bay this equates to an estimated age of between 5 and >40 years, with a mean of 16 years and a mode of 16 years. Snapper from the boundary of layers 3 and 4 ($n$ = 118) had a fork length between 138 and 813 mm (2 to >40 years), with a mean of 552 mm ± 9.0 mm (16 years).

Snapper from Houhora ($n$ = 171) range between approximately 280 to 819 mm in length, with a mode of 490 mm and a mean of 493 mm (Figure 5.15b and Table A3.6 and A3.7). For snapper on the east coast of the North Island this equates to a range of *ca.* 4 to >40 years, a mode of 27 years and a mean of 28 years. This implies a slightly older population than suggested by Nichol (1988:193-194, figure 7.3) who, using a larger sample from Houhora, estimated that the snapper recovered had a size range of

250 to 700 mm (*i.e. ca.* 3 to >40 years), and the most common fork lengths were between 400 and 450 mm (*i.e.* 10 to 17 years).

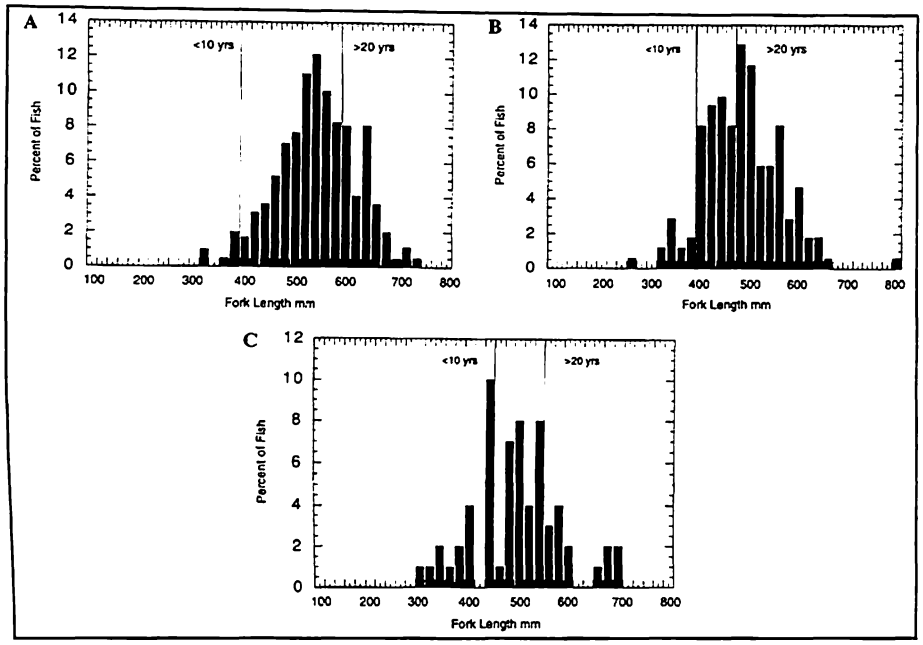



Figure 5.15: Size-frequency of snapper using fork length at a) Rotokura (from Leach and Boocock 1994:77, figure 7a), b) Houhora, and c) Twilight Beach, showing Paul's (1992:10) estimated age range of snapper based on snapper populations in Tasman Bay, and along the East coast and West coast of New Zealand respectively.

The Twilight Beach snapper ($n$ = 63) range between approximately 312 to 713 mm, with a mode of 450 mm and a mean of 507 mm (Figure 5.15c and Table A3.2-A3.5). Using Paul's (1992:10) growth curve for snapper on the West coast of New Zealand, a population ranging between 4 to >40 years is suggested, with a mode of *ca.* 10 years and a mean of 14 years. Previous reconstructions of the live length of the Twilight Beach snapper by Nichol have not been fully reported. Taylor (1984:177) noted, however, that the largest individual had an estimated length of 108 cm (*i.e.* >40 years), while the average weight of the snapper from Twilight Beach was calculated to be 2.8 kg (*i.e.* >40 years) (see Paul's (1992:10) average age-weight growth curves).

These figures suggest that snapper from all three sites are predominantly older than 10 years, and that snapper older than 40 years of age are possible. Snapper from Houhora appear to have largest inbuilt age. This inbuilt error is, however, likely to be significantly less than the calculated mode of 25 years as only *ca.* 10 years is required for complete replacement of collagen. In any case, fork length values of snapper from Twilight Beach, Houhora and Rotokura are within the standard error inherent in charcoal radiocarbon determinations (McFadgen, Knox and Cole 1994).

## Depleted $\Delta^{14}C$

A more likely cause of erroneous results will be via the introduction of $^{14}C$ depleted carbon from deep water, either as a result of habitat depth, upwelling, or from migration through depleted waters.

Below *ca.* 200 m in the Pacific (between 15-50°N and S) (Lassey, Manning and O'Brien 1990:124) a gradient in the dissolved inorganic carbon (DIC) has been noted which may influence those fish that live and feed in deep water (*e.g.* Pearcy and Stuiver 1983; Williams, Druffel and Smith 1987). Because barracouta and snapper occupy surface waters above 200 m, they should not be seriously affected by this gradient, though barracouta have been recorded at depths of 350 m (Hurst and Bagley 1989:105; Paul 1986:120; 1992:5). Red cod have a greater possibility of incorporating depleted carbon from deep water because this species range from 50 m in rocky areas down to about 550 m depth (Ayling 1982:143). If present, the introduction of depleted carbon should be apparent by older ages for archaeological fish bone samples compared to terrestrial samples.

Terrestrial organic carbon, or a hardwater effect may also be introduced into fish collagen via diet, especially where deposit feeders or deep water organisms have been sampled. Higham (1993:137) and Schmidt (1996:178) have, however, concluded that hardwater does not appear to be a significant source of error in radiocarbon determinations of shell from New Zealand archaeological sites. This remains to be fully tested. Such influences are, therefore considered to be minimal for barracouta, a carnivorous species which generally feeds on a variety of mid-water organisms (Paul 1986:120). Snapper, on the other hand, are omnivorous feeders eating fish, crustaceans, worms, gastropods and bivalves (Paul 1992:5-6) and may feed on shellfish with depleted $\Delta^{14}C$ values. Anomalous $\Delta^{14}C$ values are, however, more likely to affect red cod as they are bottom feeders, eating crabs, shrimps and other crustaceans, small fishes, squid and shellfish (Doak 1978:20; Ayling 1982:142).

## Regional variation

Neither snapper nor barracouta move outside New Zealand waters and it is possible to identify distinct snapper and barracouta populations around the New Zealand coastline. This enables a fairly accurate assessment of the fish stock and influencing water masses, or the effects of upwelling.

Because snapper make net movements of <50 km (Kalish 1993:551) they can be tied closely to the particular region in which they were caught. Distinct snapper populations have been identified in Tasman Bay and along the west coast of the North Island of New Zealand. These populations are genetically similar to, but distinct from the East Cape/Bay of Plenty and Hawkes Bay stocks (Paul 1992:11)(see Figure 5.1). Although barracouta are migratory fish, Hurst and Bagley (1989:105,110) have also tentatively suggested the presence of distinct spawning stocks centred along the east coast of the North and South Islands and west coast of the South Island, with an unclear relationship of west coast North Island and southern South Island barracouta.

Barracouta from the east coast of the South Island (*i.e.* Pleasant River, Shag River Mouth and Long Beach barracouta samples) live in waters influenced by the Subtropical Convergence (STC). The STC separates Subtropical surface water from offshore Subantarctic surface waters (Habib 1975:5-6; Heath 1985:87). This convergence is continuous around southern New Zealand (Figure 5.16) and along the continental shelf off the eastern coast of the South Island (where it is called the Southland Front) before turning west just south of the Chatham Rise (Heath 1985:87). At the STC depleted $^{14}C$ values mark the transition from the mixed Subtropical to Subantarctic surface waters (Sparks *et al.* 1992:729) (Figure 5.17). Upwelling also occurs at Kaikoura where $^{14}C$ depleted Antarctic water (from below 1000 m) is forced upwards (Sparks *et al.* 1992:732). Depleted carbon may, therefore influence radiocarbon measurements of barracouta excavated from Long Beach, Pleasant River, and Shag River Mouth. At present no depleted carbon signature has been detected in marine shell determinations from along this coastline (Higham 1993; Schmidt 1996).

Fish remains from Rotokura and Tata Beach are most likely to have come from coastal waters on the west coast of the North Island as well as Tasman and Golden Bays. These coastlines are influenced by subtropical water from the D'Urville Current, which is derived from the Westland Current (Heath 1985:114) (Figure 5.16). Upwelling is also common along the west coast due to convergence between inshore and offshore waters. Specifically, upwelling occurs at the north western corner of South Island near Cape Farewell and off the north Taranaki Bight (Ayling 1982:17; Heath 1985:114) (see Figure 5.1).

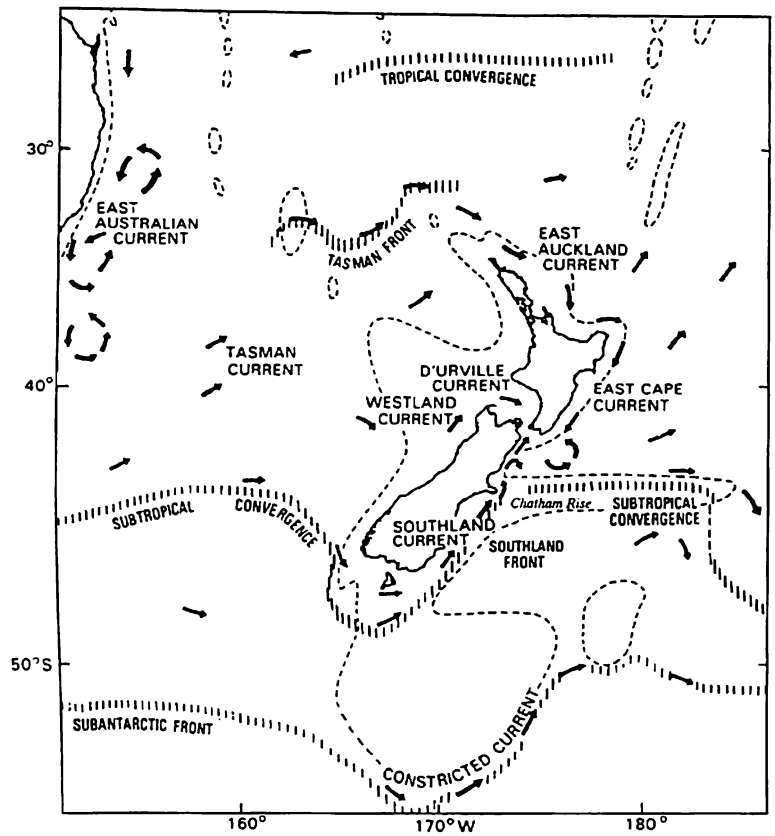



Figure 5.16: General circulation around New Zealand (from Heath 1985:82, figure 2).

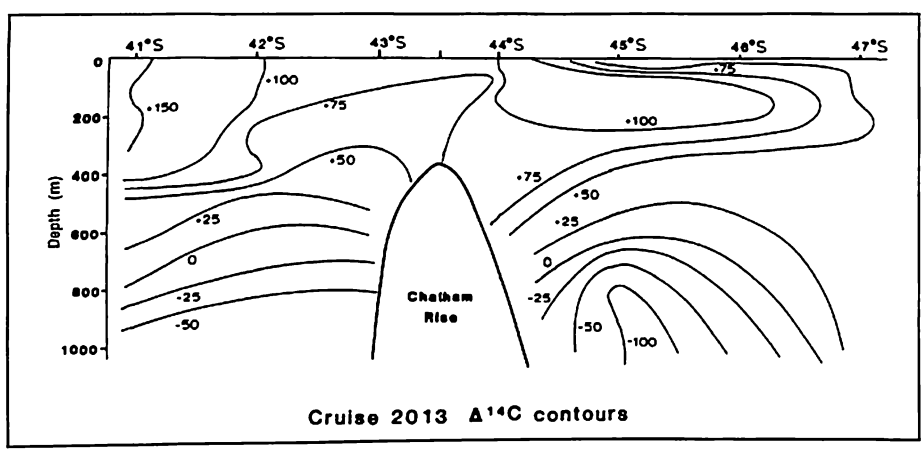



Figure 5.17: Plot of variation in $\Delta^{14}C$ along 179°E in the South Pacific Ocean east of New Zealand (figure adapted from Sparks *et al.* 1992:731, figure 3).

The East Cape Current and the East Auckland Current affect waters and snapper populations on the east coast of the North Island, around Houhora, and at the very top of the island, near Twilight Beach (Figure 5.16). Both of these currents are derived

from the Tasman Current via a zonal jet that connects waters off the eastern coast of Australia to the flow east of New Zealand (Heath 1985:87-88). Otoliths from modern and historic snapper collected in this region (Kalish 1993) compare favourably with surface water DIC values, modern shellfish samples (Higham 1993:131-2) and historic shell data reported by McFadgen and Manning (1990) (Figure 5.18).

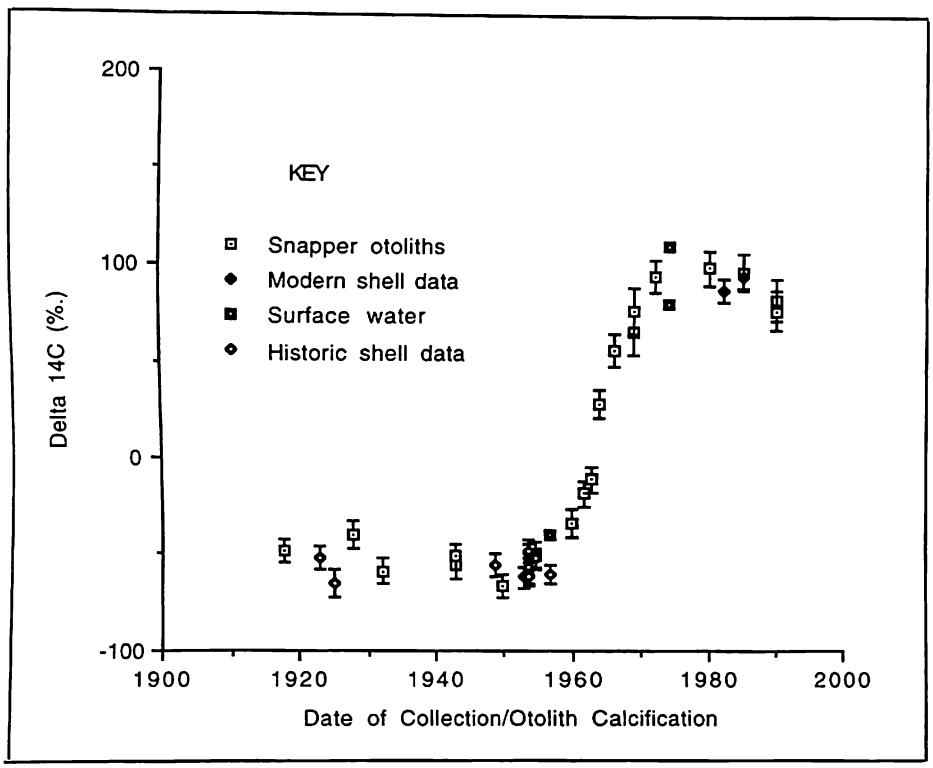



Figure 5.18: Comparison of $\Delta^{14}C$ in known age snapper otoliths (Kalish 1993:550, table 1), surface water DIC values (Kalish 1993:552, table 2), historic shell data (McFadgen and Manning 1990:230, table 1) and modern shell data (Higham 1993:133, table 9.3) from 1918 to 1990.

Higham and Hogg (1995) used McFadgen and Manning's (1990) historic shell data and Kalish's (1993) otolith data to calculated a new estimate of $\Delta R$ for New Zealand (-25 ± 15 $^{14}C$ years). This value was tested by comparison with a local $\Delta R$ calculated for the archaeological site of Shag River Mouth from mean charcoal and marine shell determinations. This local $\Delta R$ was statistically indistinguishable from the new New Zealand $\Delta R$ (Higham and Hogg 1995:415).

On the basis of this limited comparison of fish and shellfish data, as well as the evidence of oceanic currents around New Zealand, it is suggested that fish from the New Zealand mixed surface waters (above 200 m) should have a $\Delta R$ similar to molluscan shell. The modelled marine calibration curve developed by Stuiver and

Braziunas (1993) should, therefore yield acceptable calendrical ages for fish bone collagen determinations from New Zealand archaeological sites.

## ENVIRONMENT

Bone degradation and contamination may also affect $^{14}C$ values. These factors are dependent on biological activity, pH, water and temperature that are in turn related to the immediate climate, site geology, as well as cultural influences pre- and post-deposition. Information relating to site taphonomy and chemistry, as well as interpretation of past activities may, therefore be important in assessing the potential of any particular bone to yield accurate radiocarbon determinations.

### Site environment

There is little information available on environmental conditions for the sites which have been selected for analysis in this dissertation. Observations of bone preservation state have only been made for Twilight Beach and Shag River Mouth.

The Twilight Beach midden is situated within Pleistocene dunes which, at the time of excavation, had been eroded into a pedestal (Taylor 1984:34). Though no chemical data exists for the site, a number of taphonomical features of the deposit were given by Taylor (1984). Taylor (1984:199) noted that Layer 3 was relatively impervious, a factor which had resulted in water ponding on its surface causing a corresponding increase in the density of the layer above (Layer 2). The preservation state of the bones also varied with depth (*i.e.* cracking and root damage increased with midden depth, while splitting and flaking decreased). This was interpreted to be in-part the result of exposure to acidic conditions at the surface, which were neutralised by the shell midden in the lower layers. The influence of exaggerated wetting and drying cycles at the surface were also suggested as a cause (Taylor 1984:121-122). In addition, pitting on the larger mammal bones was noted and Taylor (1984:157, 234) attributed this to algal growth during previous exposure. Smaller bones were not pitted, possibly due to quick reburial. As a whole, Taylor (1984:198-199) identified little evidence of advanced weathering among the excavated remains. These observations suggest a porous environment, with diminishing biological activity and fluctuating acidity.

Information on site chemistry is available from Shag River Mouth. Chemical analyses of soil samples taken from near the SM/C:Dune excavation indicated roughly neutral to moderate alkaline conditions (pH = 6.77 - 8.35), with calcium levels that were

medium to high, possibly the result of shell leaching (Anderson, Worthy and McGovern-Wilson 1996:208, table 14.6). Anderson, Worthy, and McGovern-Wilson (1996:207) suggested these conditions were conducive to long-term bone survival. This conclusion was supported for the sand dunes by the results of hand specimen analysis that identified relative low levels of weathering in this area (67% in an "unweathered" condition and 86% better than Stage 3[8]) (Anderson, Worthy and McGovern-Wilson 1996:207-209).

Nicholson (1998), however, stresses that hand specimen analysis is an imprecise means of identifying bone preservation state. Hand specimen identifications are, therefore virtually useless in predicting the ability to accurately measure the $^{14}C$ of a sample. Nicholson (1996b:79, 89) also notes that soil pH and drainage are not paramount in determining bone survival, because a wide range of variables are involved (Nicholson 1996b:89). For example, although a pH of up to 7.9 tends to preserve bones, the activity of micro-organisms is also greatest between a pH of 7.0 and 8.0 (Garlick 1969:504, 506). In addition, a deposit is unlikely to be characterised by one pH (Linse 1992:329).

## Climate

Water and temperature have been identified as two major influences on the survival of bone in archaeological sites (see Chapter 2). Both water and temperature are closely tied in with climatic variables. The seven sites under examination in this dissertation are situated in widely differing climatic regions (Table 5.2), therefore a range in bone preservation states are to be expected. Houhora and Twilight Beach are Northland sites where the regional climate is subtropical to mild temperate, and humid conditions exist. Tata Beach and Rotokura, at the top of the South Island, are affected by differing climatic conditions. The climate at Tata Beach is mild and cool temperate with high rainfall (*ca.* 1270 to 1524 mm annually), whereas Rotokura is characterised by slightly lower rainfall (*ca.* 1016 to 1270 mm annually). Pleasant River, Shag River Mouth and Long Beach fall into one climatic region where mild and cool temperate conditions prevail, and annual rainfall is lower than regions further north.

It is unknown what affect these different environmental conditions will have on bone preservation, though higher rainfall and temperature are likely to be detrimental to bone survival. Therefore, depending on intra-site variations and cultural influences, bone

[8] The weather stages used were not defined by Anderson, Worthy and McGovern-Wilson (1996:207), except that Stage 1 represented unweathered bone, and Stage 5 represented bone on the point of disintegration.

material from Pleasant River, Shag River Mouth and Long Beach should produce better preserved bone than sites further north.

Table 5.2: Climatic conditions (Soil Bureau Bulletin 1968:8,36, figure 1.3.1 and table 2.7.2).

| Site | Annual rainfall† | Mean annual temperature† | Moisture class | Thermal efficiency Class |
|---|---|---|---|---|
| Twilight Beach Layer 3 | 1016-1270 mm | 13.9-14.4°C | Humid | Subtropical and mild temperate |
| Houhora Layer 2b? | 1016-1270 mm | 14.4-15°C | Humid | Subtropical and mild temperate |
| Rotokura Layer 3/4 | 1016-1270 mm | 11.7-12.2°C | Subhumid to humid | Mild and cool temperate |
| Tata Beach | 1270-1524 mm | 11.7-12.2°C | Subhumid to humid | Mild and cool temperate |
| Shag River Layer 4 | 508-635 mm | 10.6-11.1°C | Subhumid to humid | Mild and cool temperate |
| Pleasant River Layer 1/2a | 508-635 mm | 10.6-11.1°C | Subhumid to humid | Mild and cool temperate |
| Long Beach Layer 2 | 762-1016 mm | 10.6-11.1°C | Subhumid to humid | Mild and cool temperate |

† Rainfall and temperature at sea level (from McLintock 1960:map 8).

## Cultural influences

A wide range of fish preparation methods have been recorded in New Zealand, including drying, roasting, steaming, boiling and uncooked (*i.e.* filleted prior to cooking) (see Best 1977). Archaeological evidence of such cultural influences on bone is unfortunately limited, except in extreme cases where bone has been charred or heated sufficiently to effect a colour change. At Shag River Mouth for example, a large proportion of Layer 4 had been burnt *in situ* following deposition (Anderson and Smith 1996b:278) and a large quantity of bone was visibly burnt. Little evidence of burning was apparent in any of the other sites, though an ash lens is present in, and around square G2 at Long Beach (Figure 5.14).

Patterns of deposition provide additional evidence of food processing activities. During the analysis of the faunal material from Houhora, Shawcross (1972:608) noted a discrepancy in the proportions of cranial relative to post-cranial bones amongst snapper remains (the pattern for other fish species suggested consumption whole on site). A similar discrepancy in cranial bones relative to body parts was noted by Taylor (1984:177) for Twilight Beach. This was attributed to removal of bodies either for consumption or preservation, though Taylor (1984:177) suggested attrition by dogs or differential preservation may also be responsible. At Pleasant River a total of 399 barracouta were represented by the second pharyngobranchial, compared to 16 barracouta suggested by remains of mouth parts. This was interpreted tentatively as the result of processing activity that involved removing the gills (presumably while

cleaning the fish) prior to preservation (I. Smith, *pers. comm.* 5/3/96). At Long Beach, Fyfe (1982:70-71) also concluded that the bulk of the catch was being preserved, with the "frames" of barracouta being discarded, presumably before cooking.

## DISCUSSION

Barracouta and snapper are the predominant fish species found in New Zealand archaeological middens. The occurrence of these species in midden sites around New Zealand (snapper in the north, and northern South Island, and barracouta in the south), in both Archaic and Classic occupations, makes fish bone potentially an extremely useful sample type for radiocarbon analysis. Seven sites have been selected with snapper or barracouta remains for radiocarbon assay from the North and South Islands.

Snapper and barracouta both occupy coastal, surface waters around New Zealand. On the basis of limited analysis of fish $\Delta^{14}C$ values it is suggested that these species should be subject to a similar reservoir correction as marine shell. This is currently untested. Errors may be introduced from variation in dietary $\Delta^{14}C$ and upwelling, but inbuilt age and depleted $\Delta^{14}C$ values associated with depth are considered to be minor influencing factors.

The survival of bone following discard and burial is also influenced by a multitude of variables. These include intra-site differences and the effects of cultural practices on the bone. Prediction of bone survival is, therefore extremely complex and should be accompanied by analytical data. Unfortunately, information on bone preservation states and environmental conditions at each of the sites analysed here is virtually non-existent. Because all sites are located in coastal, sandy environments, climatic influences are likely to be influential in bone survival. Those sites located in the southern South Island should, therefore produce bones of better preservation state due to the lower temperatures and rainfall encountered in this region.

# CHAPTER 6

# PRETREATMENT AND ASSESSMENT

## INTRODUCTION

When investigating the potential of a novel material for radiocarbon dating, it is necessary to test for contamination and choose an effective pretreatment that will remove the contamination. In this chapter the results of a range of methods used to assess each bone sample selected in this dissertation for radiocarbon analysis are presented. The interpretation of these results and the expected reliability of the $^{14}C$ measurement on each sample are also examined.

Following the discussion of bone radiocarbon pretreatments and assessment given in Chapter 3, it was hypothesised that:

- Well-preserved "Class II" bones (*i.e.* between 0.9 and 3.5% nitrogen) (after Stafford, Brendel and Duhamel 1988:2258), less than 1000 years old, should give reliable $^{14}C$ determinations when gelatinised following a NaOH wash. Bones with less than 0.9% nitrogen (*i.e.* Class III) may require more rigorous pretreatment.

- It is suggested, however, that around 8% contamination can remain following gelatinisation (van Klinken and Hedges 1995:268). In a sample of 600 BP this equates to a possible error of 42 years if contaminated by modern carbon, or 680 years if contaminated by $^{14}C$ free carbon (*c.f.* Table 2.3). At 900 BP contamination by 8% modern carbon may be of greater concern (*i.e.* a possible 77 year error).

- Contamination at this level can often be recognised analytically when the sample is well-preserved (*i.e.* of "good" preservation) (Hedges and van Klinken 1992:284). This can be assessed using a combination of isotopic, yield information and infrared analysis of whole bone, collagen and gelatin fractions.

- For problem samples (*i.e.* low levels of remaining collagen, an anomalous infrared spectrum, and/or spurious radiocarbon results) the measurement of $^{14}C$ in tripeptides is presently considered to be one of the most reliable methods available for dating collagenous samples (van Klinken and Hedges 1995:269). There is

currently no reliable method for dating non-collagenous samples (*i.e.* below 0.5% nitrogen; Class IV and V).

## PRELIMINARY ASSESSMENT

A number of tests were undertaken prior to pretreatment in order to assess the reliability of each sample to be dated. These include hand specimen analysis, percent nitrogen and whole bone Fourier transform infrared analysis (FTIR). Samples of barracouta bone from Long Beach (LONG), Tata Beach (TATA bar) Pleasant River (PIR) and Shag River Mouth (SRM), snapper bone from Rotokura (ROTO), Twilight Beach (TWB), and Houhora (HC8), and red cod from Tata Beach (TATA rc) were analysed. Modern barracouta and snapper standards were also prepared for comparison (see Appendix 4 and Tables A5.3 and A5.4).

### Physical appearance

The physical characteristics of each bone sample were examined to assess the usefulness of hand specimen methods in the selection of bone for radiocarbon dating. On the basis of these descriptions, "Class" designations were assigned following Stafford, Brendel and Duhamel (1988:2258, table 1)(see Table 3.2). The results are given in Table 6.1.

Table 6.1: Physical characterisation of archaeological fish bone.

| Site | Physical appearance | Munsell colour of bulk sample | Class |
|---|---|---|---|
| TWB | Mottled surfaces. Exterior soft, some splitting. | 10YR 7/3: dull yellow orange | II |
| HC8 | Exterior soft, some splitting. | 7.5YR 7/4: dull orange | II |
| TATA bar | Bone soft. | 7.5YR 7/3: dull orange | III |
| TARA rc | Bone soft | 7.5YR 5/4: dull brown | III |
| ROTO | Moderately hard, some splitting. Evidence of burning. | 7.5YR 7/4: dull orange | II |
| SRM | Moderately hard. Evidence of burning. | 7.5Y 6/4: dull orange | II |
| PIR | Hard, translucent. | 7.5YR 6/4: dull orange | I |
| LONG | Moderately hard. | 10YR 8/4: light yellow orange | II |

### Percent nitrogen: Total collagen content

The amount of nitrogen (N%) remaining in individual skeletal elements and bulk ground bone was measured at the Waikato Stable Isotope Unit, University of Waikato, on a Dumas elemental analyser (Europa Scientific™ ANCA-SL) interfaced to an isotope mass spectrometer (Europa Scientific™ Tracermass). Instrument error for nitrogen analysis (both N% and $\delta^{15}N$, see below) was ± 1‰. All bone was cleaned

with a razor blade and dental pick, then ultrasonicated in distilled water for 30 minutes, air dried, shaken and then ground to a fine powder.

Measurements on individual bones were undertaken to give an indication of sample heterogeneity. Three samples from each site were selected and compared to bulk values (Tables 6.2 and A5.1). These bulk N% estimates were used to assign each sample to a particular preservation state; Class I to V, as defined by Stafford, Brendel and Duhamel (1988:2258, table 1)(see Table 3.2). The proportion of remaining protein in each archaeological sample and the amount of bone required for each radiocarbon measurement was calculated on the basis that modern fish bone has on average 4.12% nitrogen (see Table A5.4), and approximately 50 g of bone is required for a conventional determination[1].

Table 6.2: Nitrogen, bone requirements and class designation.

| Sample | Individual bones | | | Mean + sd | Bulk value | Estimated | Class |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | | | bone wt (gm) | |
| HC8 | 1.90 | 1.66 | 1.59 | 1.72 ± 0.16 | 2.11 | 97.6 | II |
| TWB | 2.37 | 2.11 | 2.24 | 2.24 ± 0.13 | 1.64-1.78 ($n$ = 2) | 125.6-115.7 | II |
| ROTO | 1.63 | 2.25 | 2.24 | 2.04 ± 0.36 | 1.96 | 105.1 | II |
| TATA bar | 2.12 | 3.24 | 1.36 | 2.24 ± 0.95 | 1.66 | 124.1 | II |
| TATA rc | 1.21 | 0.69 | 1.54 | 1.15 ± 0.43 | 0.94 | 219.2 | II / III |
| PIR | 3.19 | 3.47 | 2.19 | 2.95 ± 0.67 | 2.97-3.09 ($n$ = 2) | 69.4-66.7 | II |
| SHAG | 2.87 | 3.06 | 1.57 | 2.50 ± 0.81 | 2.12-2.68 ($n$ = 3) | 76.9-97.2 | II |
| LONG | 2.15 | 2.65 | 2.80 | 2.53 ± 0.34 | 2.60-2.50 ($n$ = 2) | 79.2-82.4 | II |

## Fourier Transform Infrared analysis (FTIR): Whole bone

FTIR analyses were determined on the ground bulk bone to assess the degree of alteration to the bone structure (both collagen and hydroxyapatite). Spectra of archaeological fish bone were compared to spectra of modern snapper and barracouta standards (Figure 6.1). Bone apatite is characterised by $CO_3$ vibration bands at 870, 1415 and 1460 $cm^{-1}$, and $PO_4$ vibration bands at 565, 1035 and 605 $cm^{-1}$, and there is a protein peak at 1650 $cm^{-1}$. Changes in these peaks give a clear indication of diagenesis. The relative intensity of the protein peak also gives an approximate indication of remaining protein. Additional peaks suggest contamination.

The splitting factor (SF) or crystalinity index, and carbonate/phosphate ratio (C/P) are two techniques used commonly to assess the degree of hydroxyapatite alteration (either burning or weathering) in fossil, sub-fossil and archaeological bones. The splitting factor is measured by taking the average height of the $PO_4$ absorption peaks at 565 $cm^{-1}$ and 605 $cm^{-1}$ (baseline drawn between 425 and 795 $cm^{-1}$), divided by the height of

[1] *i.e.* 4.12 ÷ N% x 50 = estimated bone weight.

the low point between them. The higher the SF value, the larger and/or more ordered the crystals. Consequently, the crystalinity index is lowest for the amorphous structure of fresh bone (*e.g.* SF = 2.5 - 2.9). As recrystalisation proceeds, these two absorption peaks become increasingly separated from one another because crystal size increases (Weiner and Bar-Yosef 1990; Stiner *et al.* 1995:227-228; Wright and Schwarcz 1996:936).

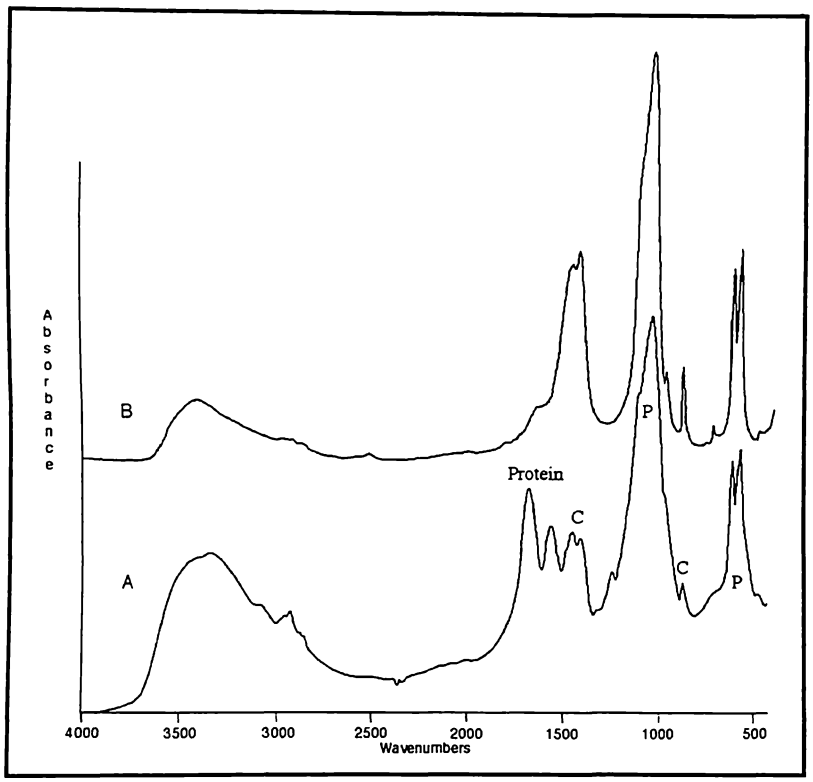



Figure 6.1: Infrared spectrogram of a) modern bone showing protein, carbonate (C) and phosphate (P) peaks; b) non-collagenous severely altered bone. Note anomalous peak *ca.* 1420 - 1460 $cm^{-1}$ (wavenumbers) and absence of protein peaks.

The relative carbonate content of the mineral phase can be semi-qualitatively estimated by measuring the ratio of the carbonate absorption peak at 1454 - 1460 $cm^{-1}$ compared to the phosphate peak at 1034 - 1039 $cm^{-1}$, following baseline correction between 1900 $cm^{-1}$ and 795 $cm^{-1}$ (*c.f.* Rink and Schwarcz 1995). This technique has, however, had limited success as there is only a weakly defined correlation between the FTIR carbonate/phosphate peak ratio and the manometrically determined $CO_3$ content (Rink and Schwarcz 1995:253; Wright and Schwarcz 1996:936).

Qualitative FTIR spectra were obtained using a Biorad™ FTS-40 spectrometer at the School of Biological Sciences, University of Waikato. The bone samples were

ground and approximately 0.5 mg mixed with 150 mg of KBr in a mortar and pestle. A twelve millimetre diameter pellet was prepared using a SPENAC™ press 25.001 with an applied load of 8000 kg under vacuum. Individual spectra were obtained using 16 acquisitions before Fourier transform, at a spectral resolution of 4 $cm^{-1}$, using the empty chamber as the background reference spectrum. Absorbance spectra were plotted from 4000 to 500 $cm^{-1}$. The FTIR spectra of archaeological samples analysed are shown in Figures 6.2 to 6.9. CP ratios and SF values are shown in Figure 6.10.

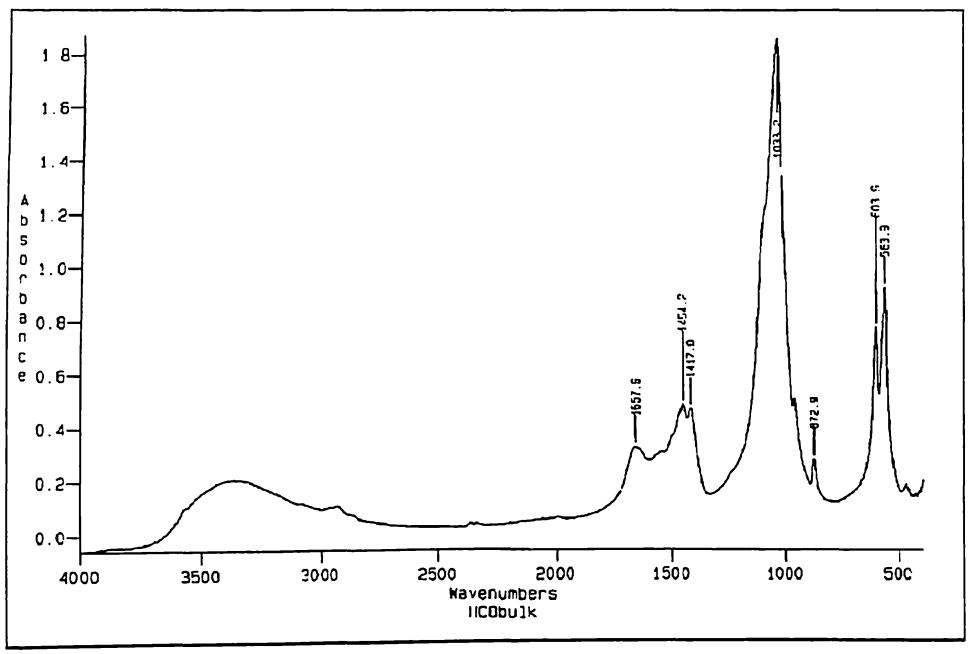



Figure 6.2: Infrared spectrogram of bulk snapper (*Pagrus auratus*) bone from Houhora.

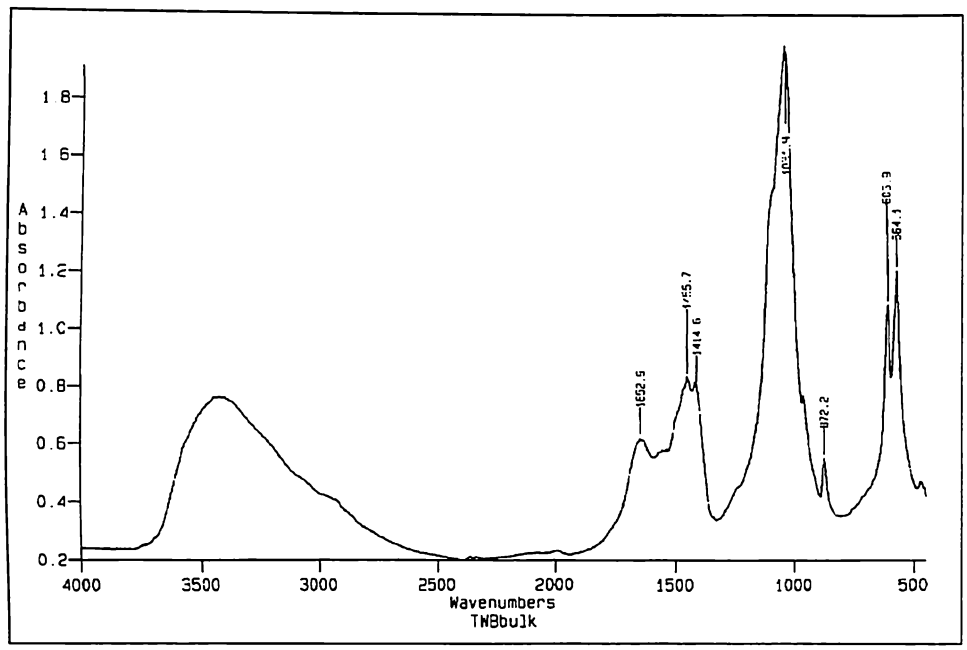



Figure 6.3: Infrared spectrogram of bulk snapper (*Pagrus auratus*) bone from Twilight Beach.

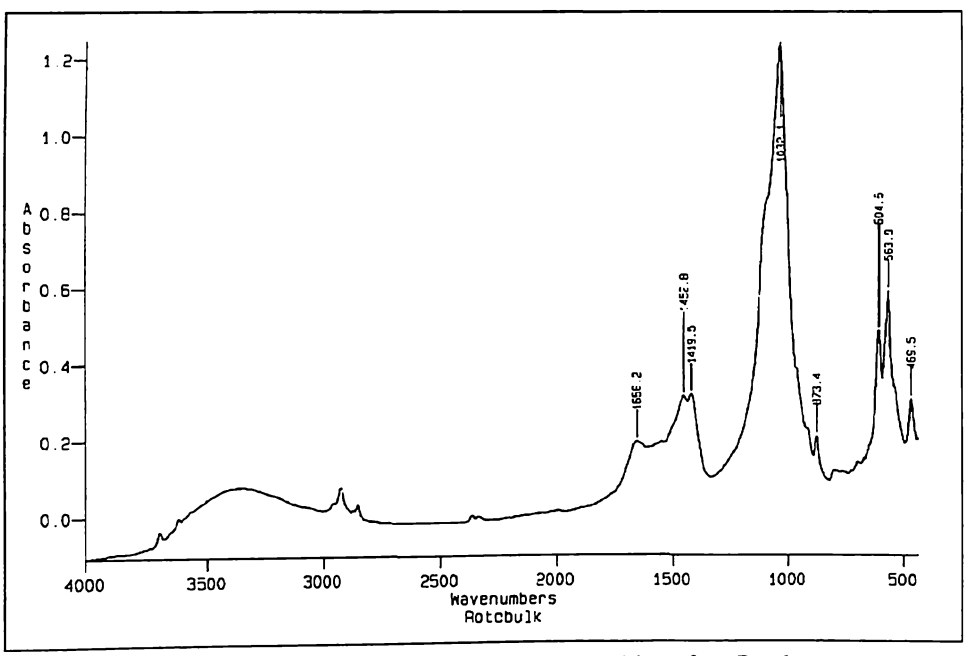



Figure 6.4: Infrared spectrogram of bulk snapper (*Pagrus auratus*) bone from Rotokura.

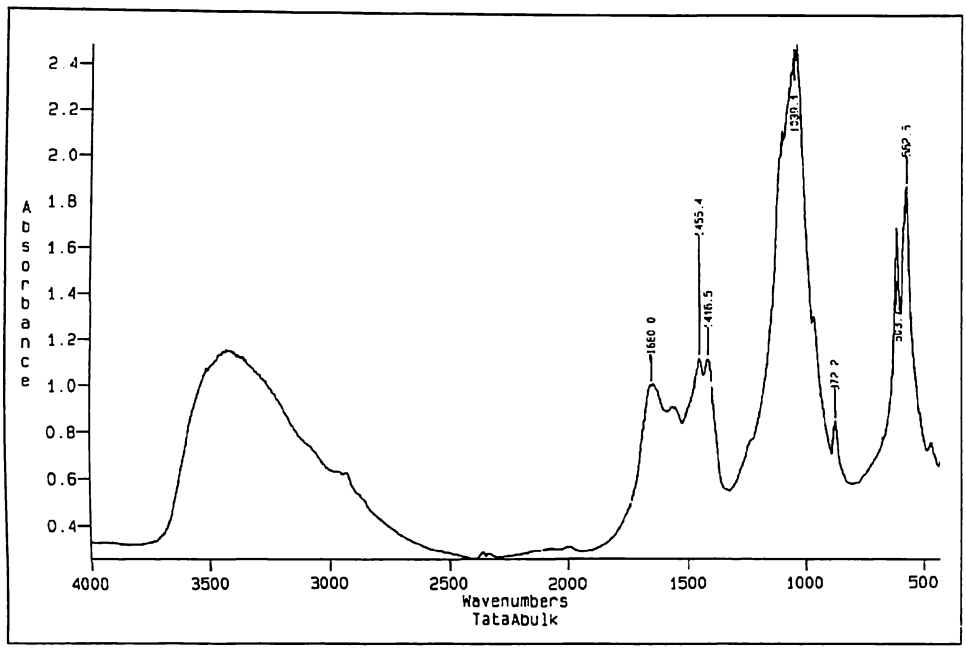



Figure 6.5: Infrared spectrogram of bulk barracouta (*Thyrsites atun*) bone from Tata Beach.

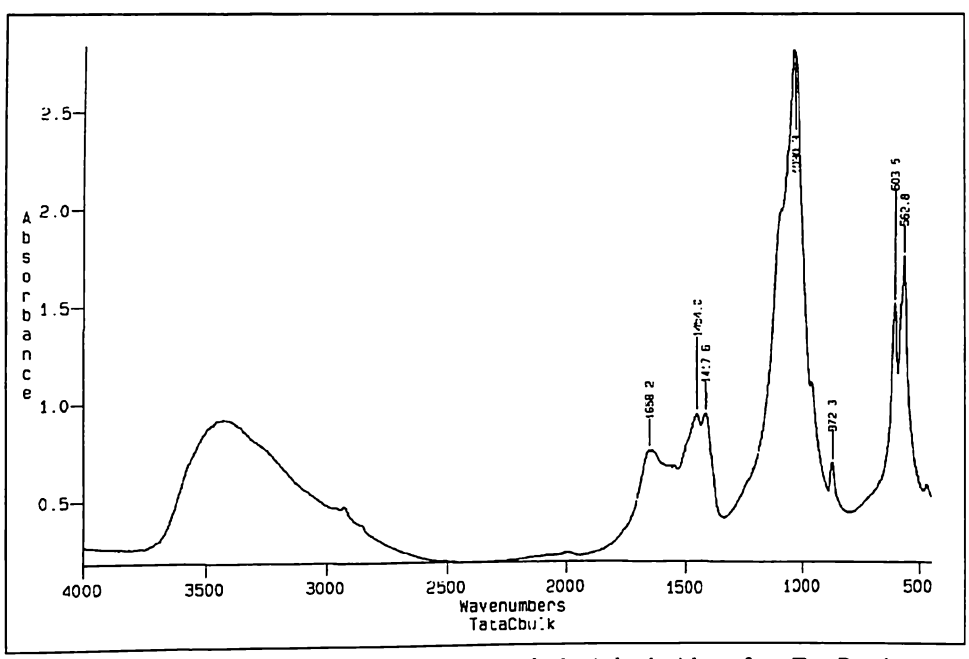



Figure 6.6: Infrared spectrogram of bulk red cod (*Pseudophycis bachus*) bone from Tata Beach.

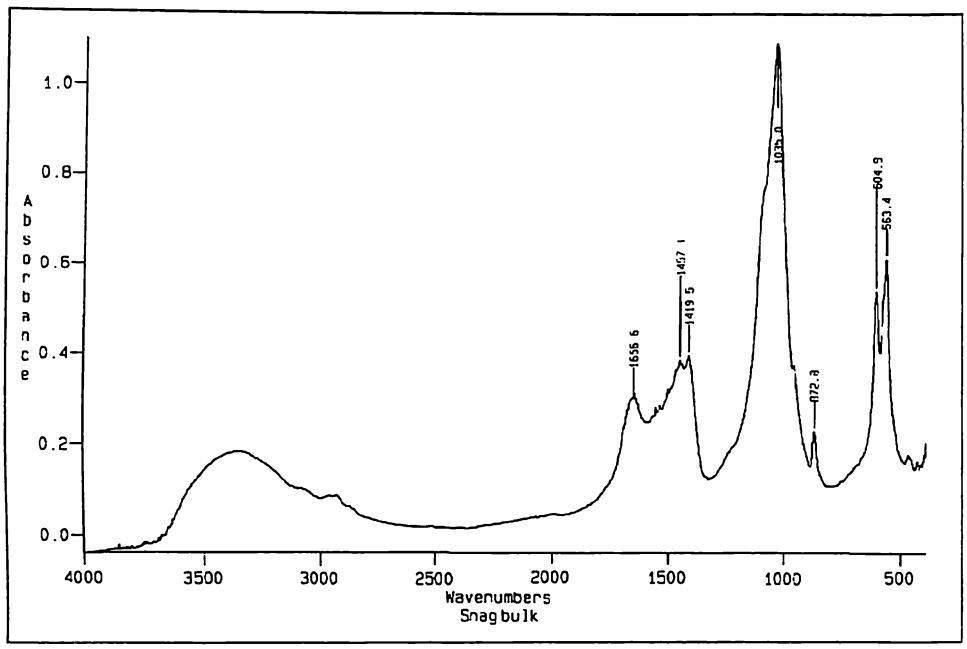



Figure 6.7: Infrared spectrogram of bulk barracouta (*Thyrsites atun*) bone from Shag River Mouth.

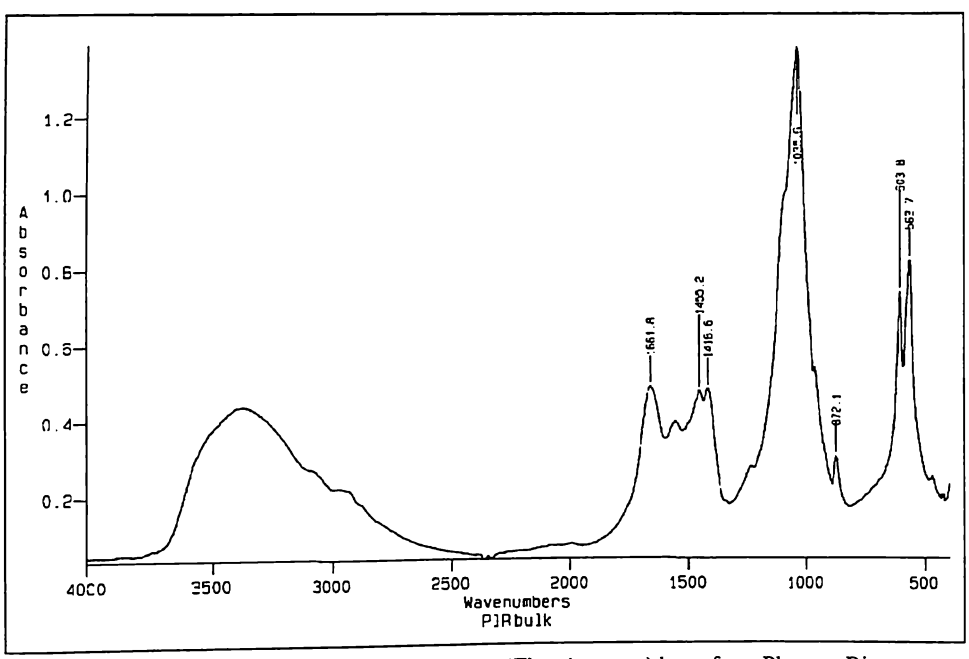



Figure 6.8: Infrared spectrogram of bulk barracouta (*Thyrsites atun*) bone from Pleasant River.

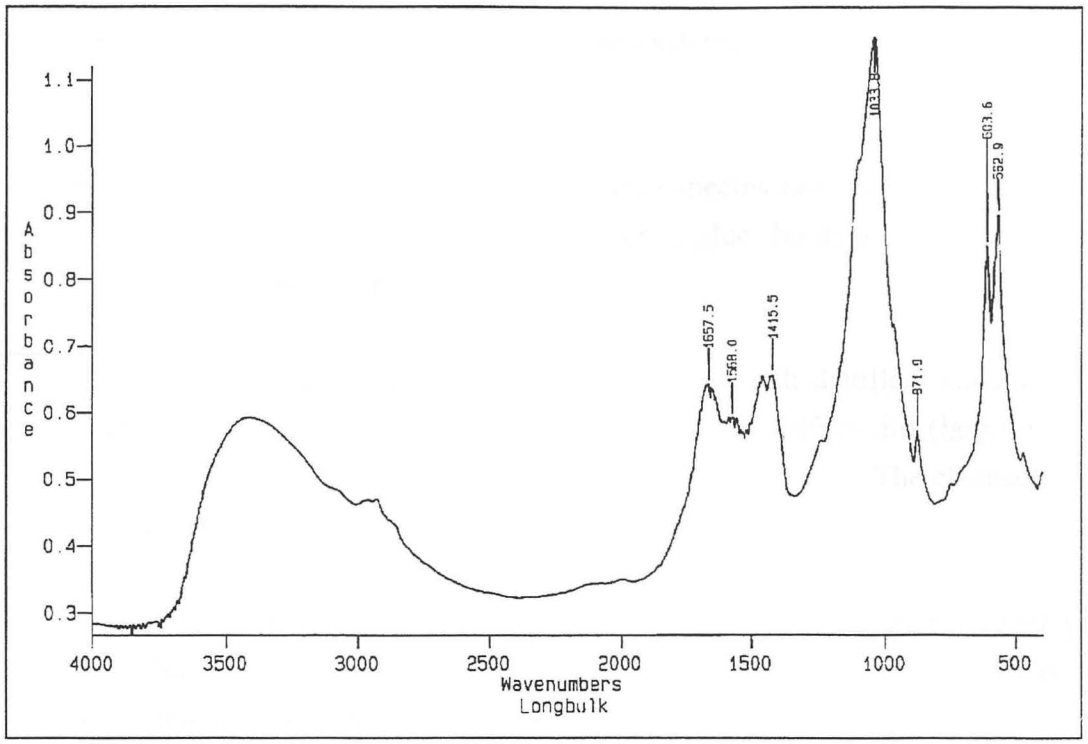



Figure 6.9: Infrared spectrogram of bulk barracouta (*Thyrsites atun*) bone from Long Beach.

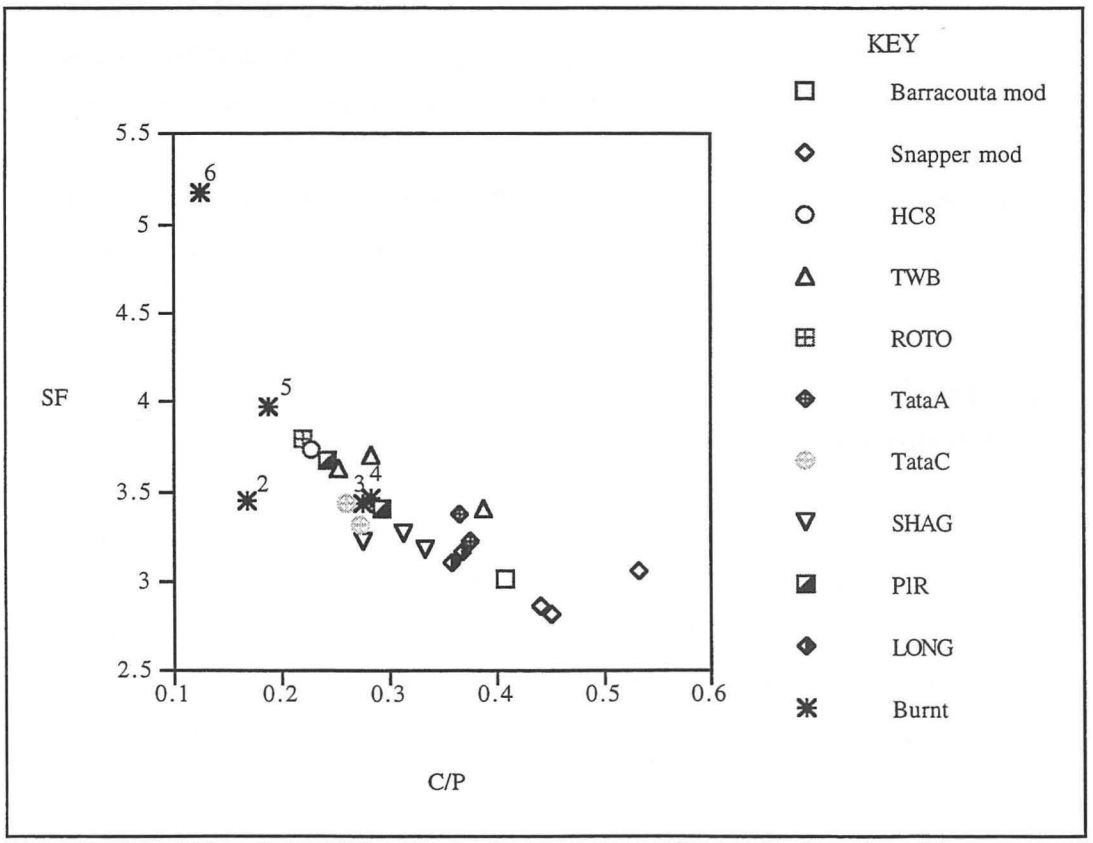



Figure 6.10: Splitting factor (SF) versus carbonate content (CP ratio) of modern fish bone, bulk archaeological bone from sites sampled, and burnt bone (Samples 2 - 6, see Table 6.6) from Shag River Mouth.

## BONE PRETREATMENT

Following analysis of N% and FTIR spectra, bones defined as well-preserved ("Class II") were pretreated in the following manner:

a) Samples of bulk fish bone were sorted into species and any fragments with obvious contamination removed (*e.g.* labels, glue, burnt bone and/or bones belonging to different species).

b) The dry bone was cleaned in an ultrasonic bath with distilled water for 15 minutes, then scrubbed with a stiff brush to remove surface dirt (larger bones were broken up to enable easy cleaning of interior surfaces). The cleaned bone was air-dried at 40 - 50°C.

c) When dry, the bone was ground in a Wiley mill to ≤ 2 mm. The ground sample was then put through a sample splitter until a specified amount of bone (determined by bulk N% (Table 6.2)) was obtained.

d) Each sample was decalcified in 2% HCl (approximately 1000 ml per 100 g of bone) at 4°C for 2 to 4 days, or until degassing stops. This varied with the amount of bone, contaminating carbonates and the type of bone (cortical versus spongy). The acid was replaced when frothing stopped, or after 24 hours.

e) This **"acid-insoluble collagen"** was then filtered through Whatman GF/C glass microfibre filter paper with six litres of RO (reverse osmosis) water.

f) The acid insoluble collagen was leached in 2% NaOH (approximately 500 ml per 100 g of bone) at room temperature for 1 hour, then either filtered through Whatman GF/D glass microfibre filter paper with 6 litres of distilled water, or centrifuged at 1000 rpm[2] for 15 minutes (x5).

The filtrate was removed and pH adjusted to 1. The acid adjusted filtrate was left to settle for 1 hour, centrifuged for 15 minutes at 1000 rpm, 2% HCl added and then centrifuged again. The precipitated **"humic acids"** were dried at 80°C and retained for stable isotope analysis.

[2] Revolutions per minute.

g) The alkali washed collagen was then acidified in 2% HCl at room temperature for 1 hour and filtered through Whatman GF/C microfibre filter paper.

h) The pH of this **"crude collagen"** was adjusted to 3 and heated at 90°C on a heating mantle for 4 hours. The sample was continuously stirred and pH monitored. The gelatin mixture was then centrifuged for 15 minutes at 1000 rpm, after which the supernatant was removed and freezedried (**"gelatin"**). Any **"residue"** remaining after centrifugation of the gelatin mixture was dried at 80°C and retained for analysis.

i) Radiocarbon estimates were measured at the University of Waikato Radiocarbon Dating Laboratory. Residual $^{14}C$ activity was measured by the Liquid Scintillation Counting (LSC) method, following the procedures outlined by Hogg (1982) and Hogg, Lowe and Hendy (1987), and counted in a Wallac LKB 1220 "Quantulus"™ spectrometer.

j) Where anomalous results were obtained, samples were sent for collagenase digestion and HPLC separation of tripeptides (Figure 6.11) to the Radiocarbon Accelerator Unit, Research Laboratory for Archaeology and the History of Art, Oxford. Details of pretreatment are given in van Klinken and Hedges (1992:292-3) and van Klinken, Bowles and Hedges (1994:2545-2546). Combustion and radiocarbon measurement were performed using the methods described by Hedges *et al.* (1989) and Hedges *et al.* (1992).

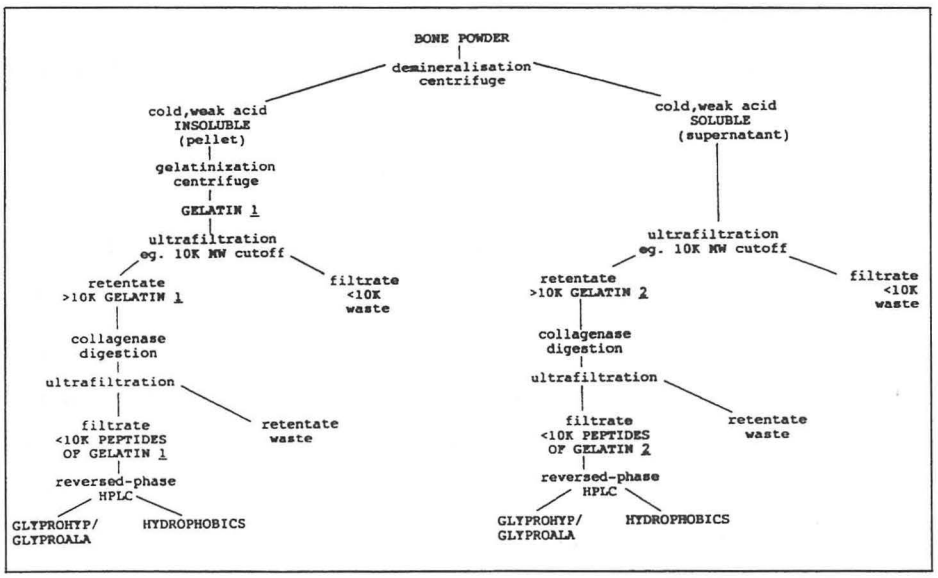



Figure 6.11: Chemical procedure for tripeptide separation (from van Klinken and Hedges 1992:193, figure 1).

## PRETREATMENT ASSESSMENT

During pretreatment a number of tests were undertaken to monitor the "clean up" of the samples, including measurement of yield, stable isotopes and FTIR analysis of the acid washed collagen and gelatin fractions.

### Collagen concentrations (Yield)

Table 6.3: Gelatin and "residue" yields.

| Site | Gelatin yield wt% | % extractable protein | Actual bone requirements (gm) | Residual % |
|---|---|---|---|---|
| HC8 batch A | 6.71 | 39 | 128.2 | 0.96 |
| HC8 batch B | 6.94 | 39 | 128.2 | 1.29 |
| TWB batch A | 6.63 | 37 | 135.1 | 1.26 |
| TWB batch B | 7.65 | 41 | 122.0 | 1.26 |
| TWB batch C | 8.84 | 44 | 113.6 | 2.08 |
| TWB batch D | 10.49 | 44 | 113.6 | 4.84 |
| ROTO batch A | 9.14 | 49 | 118.0 | 1.52 |
| TATA batch A (barracouta) | 6.65 | 37 | 135.1 | 1.82 |
| TATA batch B (barracouta) | 6.01 | 29 | 172.4 | 1.76 |
| TATA batch C (red cod) | – | – | – | – |
| TATA batch D (red cod) | 4.91 | 27 | 185.2 | 1.26 |
| TATA batch E (mix) | 6.03 | 32 | 156.3 | 1.33 |
| SRM batch A | 10.55 | 57 | 87.7 | 1.78 |
| SRM batch B | 9.50 | 53 | 94.3 | 1.10 |
| SRM batch C | 9.86 | 54 | 92.6 | 1.86 |
| SRM batch D | 9.20 | 52 | 96.2 | 1.58 |
| SRM batch E | 7.97 | 50 | 100.0 | 1.49 |
| PIR batch A | 12.53 | 69 | 72.5 | 1.69 |
| PIR batch B | 12.41 | 70 | 71.4 | 1.89 |
| PIR batch C | 11.89 | 64 | 78.1 | 3.85 |
| LONG batch A | 11.10 | 58 | 86.2 | 3.85 |
| LONG batch B | 11.14 | 62 | 80.7 | 2.49 |
| LONG batch C | 11.19 | 63 | 79.4 | 2.47 |
| LONG batch D | 11.46 | 63 | 79.4 | 2.29 |

Crude gelatin yields were measured as a percentage wrt bone. Interpretation of the preservation state of the bone (*i.e.* "good", "poor" or "non-collagenous") was based on recommendations by Hedges and van Klinken (1992:282, 284) (see Chapter 3). The amount of extractable protein was adapted according to the yields obtained for modern fish bone following the pretreatment described above. Using this method it was calculated that 18 g of protein could be extracted per 100 g of modern bone. To avoid variations caused by incomplete dryness of the freeze-dried gelatin, this value ("extractable protein") was corrected according to the yield of $CO_2$, following combustion of the sample. Where >20% of the original collagen could be extracted the bones were considered to be of "good preservation". Where less than 10% of the original protein could be extracted the bone is considered to be of "poor preservation". Bones falling between 10 and 20% are considered here to be "transitional" and may

require additional purification. The crude gelatin yield and extractable collagen value are given in Table 6.3. Losses incurred during pretreatment are assumed to be constant.

Yield measurements were also calculated from the insoluble residue (wrt bone) remaining following gelatinisation. Mook and Waterbolk (1985:40-41) recommend that this value should be below 10%.

## Stable $\delta^{13}C$ and $\delta^{15}N$ isotopes

Stable isotope values (*i.e.* $\delta^{13}C$ and $\delta^{15}N$) were obtained on various fractions removed during pretreatment, including the gelatin (Tables 6.4 and A5.2), humic acid and residue fractions (Table 6.5). These results were compared with modern snapper and barracouta standards (Table A5.3).

Table 6.4: Stable carbon and nitrogen measurements for gelatin.

| Sample | no. | $\delta^{13}C$ | $\delta^{15}N$ |
|---|---|---|---|
| Snapper modern | 3 | -11.56 | 13.77 |
| HC8 | 1 | -13.55 | 13.33 |
| TWB | 2 | -11.35 | 11.58 |
| ROTO | 2 | -12.23 | 15.59 |
| Barracouta modern | 2 | -14.10 | 12.73 |
| PIR | 2 | -13.24 | 12.73 |
| TATA b | 1 | -13.21 | 13.24 |
| SHAG | 4 | -13.57 | 12.45 |
| LONG | 2 | -13.29 | 13.85 |
| Red Cod modern† | | -11.2* | |
| TATA rc | 1 | -14.13 | 14.71 |

† Isotope value for red cod bone "collagen"[3] given in Leach, Quinn and Lyon (1996:46, table 7).

Table 6.5: Stable isotope measurements: Humic and residue fractions.

| Sample | no. | Humics | | Residue | |
|---|---|---|---|---|---|
| | | $\delta^{13}C$ | $\delta^{15}N$ | $\delta^{13}C$ | $\delta^{15}N$ |
| HC8 | 1 | -17.34 | 14.39 | -13.55 | 14.08 |
| TWB | 1 | -17.36 | 14.46 | -15.12 | 13.54 |
| ROTO | 1 | -18.92 | 16.79 | -14.91 | 16.06 |
| PIR | 1 | -20.27 | 14.99 | -19.19 | 14.51 |
| TATA b | 1 | -20.74 | 15.67 | -17.28 | 15.05 |
| TATA rc | 1 | -19.87 | 15.60 | -17.11 | 15.10 |
| SHAG | 1 | -19.38 | 15.28 | -17.21 | 12.98 |
| LONG | 1 | -21.62 | 14.38 | -18.60 | 14.48 |

$\delta^{15}N$ and $\delta^{13}C$ were measured at the Waikato Stable Isotope Unit, University of Waikato on a Dumas elemental analyser (Europa Scientific™ ANCA-SL) interfaced to an isotope mass spectrometer (Europa Scientific™ Tracermass). Sample error for

[3] Pretreatment not specified.

$\delta^{13}C$ (combination of machine error plus sample heterogeneity) = ± 0.5. $\delta^{13}C$ and $\delta^{15}N$ values are given in ‰ versus VPDB[4] and AIR, respectively.

## Fourier Transform Infrared analysis: Collagen and gelatin

Various organic fractions obtained during pretreatment, including acid-insoluble collagen, crude collagen, and gelatin were analysed using qualitative FTIR spectroscopy. Both the acid-insoluble collagen and gelatin (Figure 3.2) are characterised by the amide I band at 1650 $cm^{-1}$, amide II at 1550 $cm^{-1}$, and proline absorption at 1456 $cm^{-1}$ (Stiner *et al.* 1995:234). Contaminants cover a wide range of values and can be confused by the overlapping of individual absorptions, especially humic absorption peaks (Schnitzer and Khan 1972:71-72). Generally, contamination may be indicated by a large absorption feature centred around 1040 $cm^{-1}$, possibly the result of humic acid-like materials, poorly preserved collagen, or clay (Weiner and Bar-Yosef 1990:193, figure 4; Law *et al.* 1991:308, 311, figure 3a). This may indicate a "transitional" or "bad prehistoric" collagen. Bad prehistoric collagen was identified by DeNiro and Weiner (1988a:2205) as having neither collagen peaks (proline, amide I and II) nor polysaccharide peaks (Figure 3.1). Conversely, most synthetic polymers give diagnostic "fingerprint" spectra (Law *et al.* 1991:308).

Acid-insoluble fractions for FTIR analysis were prepared by grinding bone to a fine powder. The powder was then decalcified with 2% HCl for two days, centrifuged at 3500 rpm for 5 minutes and washed with distilled water (repeated 5x). The decalcified insoluble residue was then dried at 80°C for 24 hours to remove water that may cause problems with the FTIR spectra. The dried, decalcified residue was then reground. Gelatin samples were removed following the standard pretreatment of bone for radiocarbon analysis. Similar machine parameters were used to obtain gelatin and acid-insoluble spectra as for whole bone FTIR spectra, except absorbance spectra were plotted from 2000-500 $cm^{-1}$. Archaeological FTIR spectra of acid-insoluble collagen and gelatin fractions are shown in Figures 6.12 to 6.19.

[4] Pee Dee Belemnite.

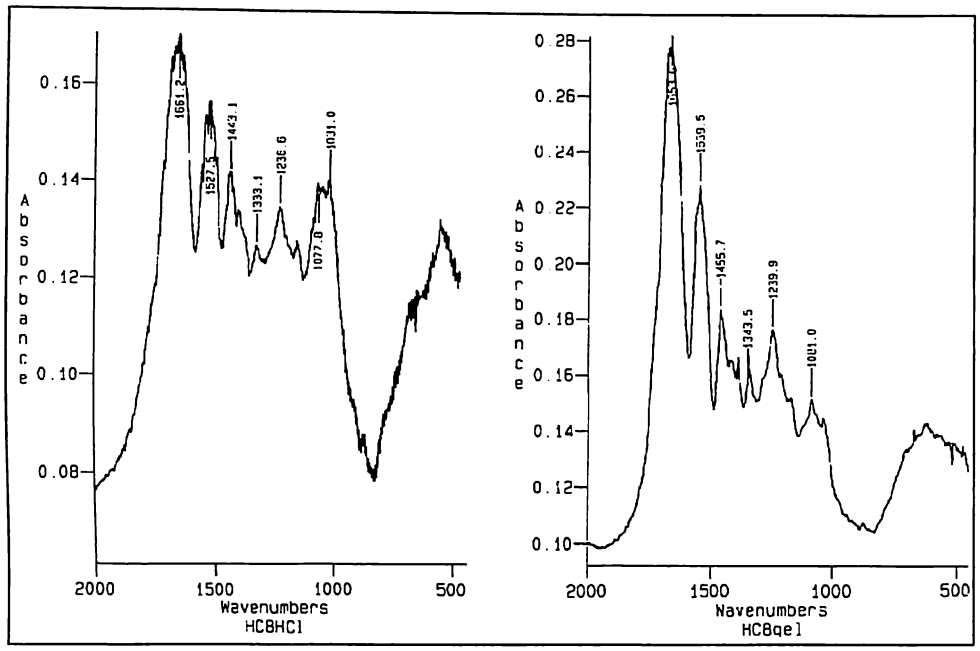



Figure 6.12: Infrared spectrograms of acid-insoluble collagen (HC8HCl) and gelatin (HC8gel) from Houhora snapper.

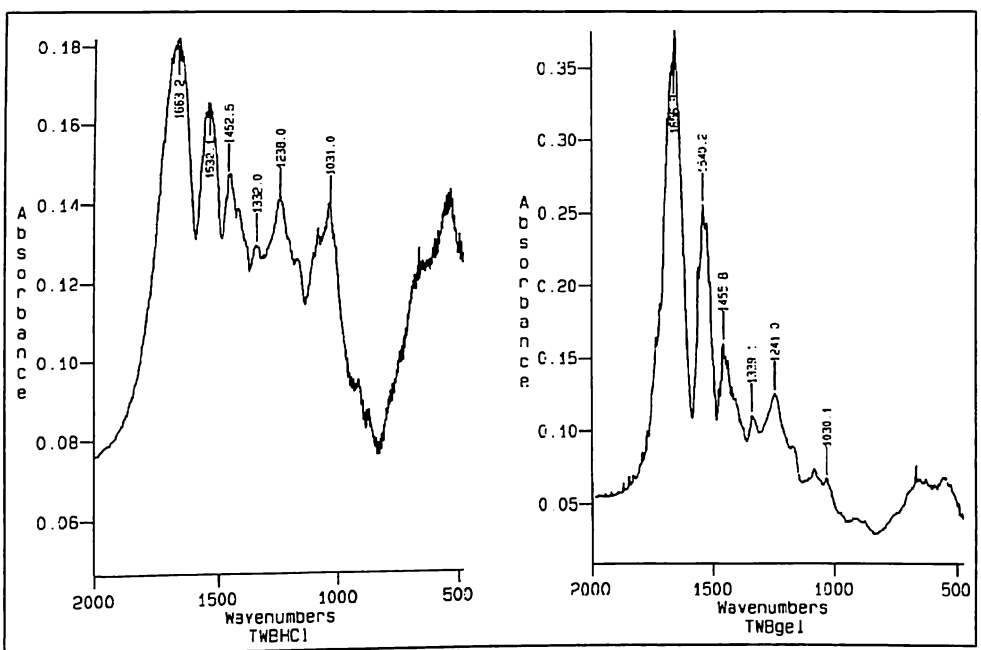



Figure 6.13: Infrared spectrograms of acid-insoluble collagen (TWBHCl) and gelatin (TWBgel) from Twilight Beach snapper.

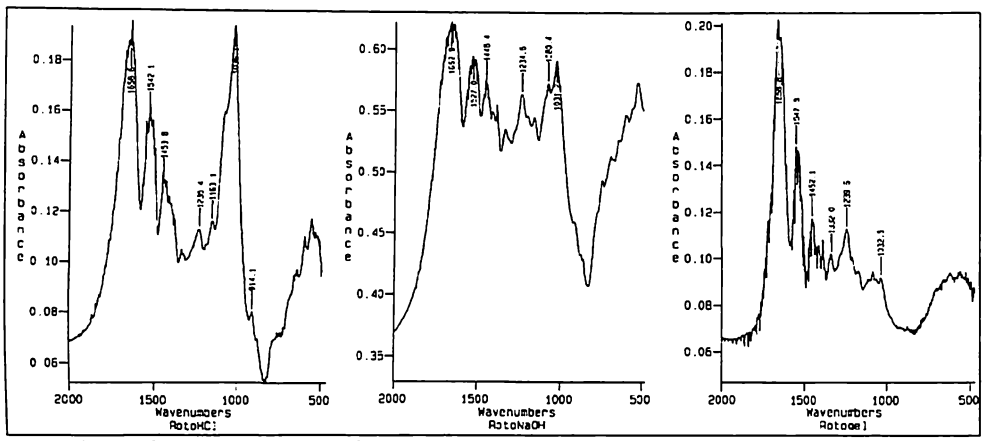



Figure 6.14: Infrared spectrograms of acid-insoluble collagen (RotoHCl), NaOH treated "crude collagen" (RotoNaOH) and gelatin (Rotogel) from Rotokura snapper.

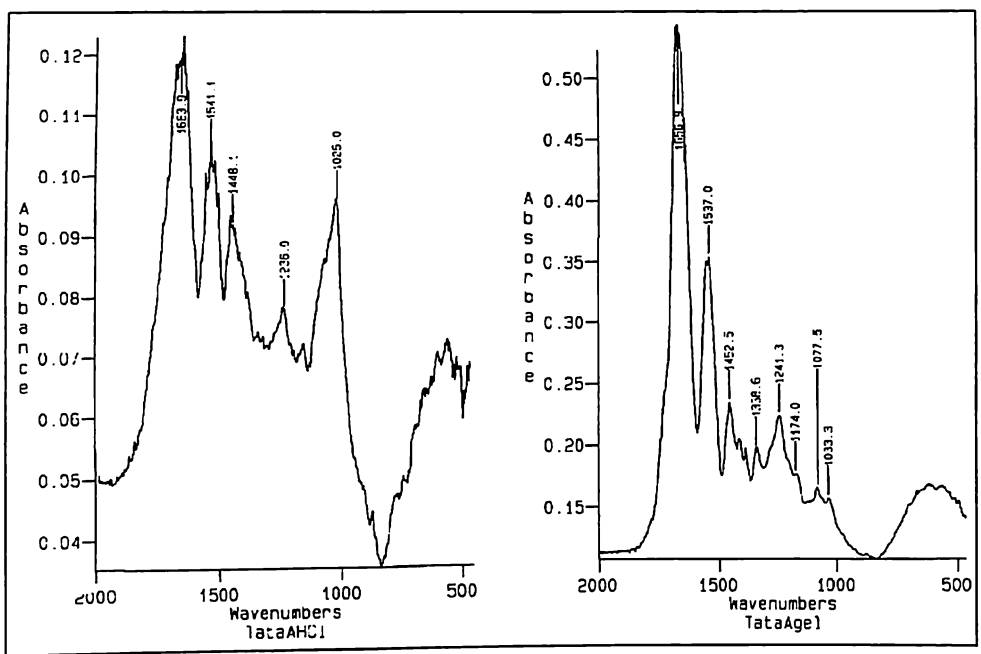



Figure 6.15: Infrared spectrograms of acid-insoluble collagen (TataAHCl) and gelatin (TataAgel) from Tata Beach barracouta.

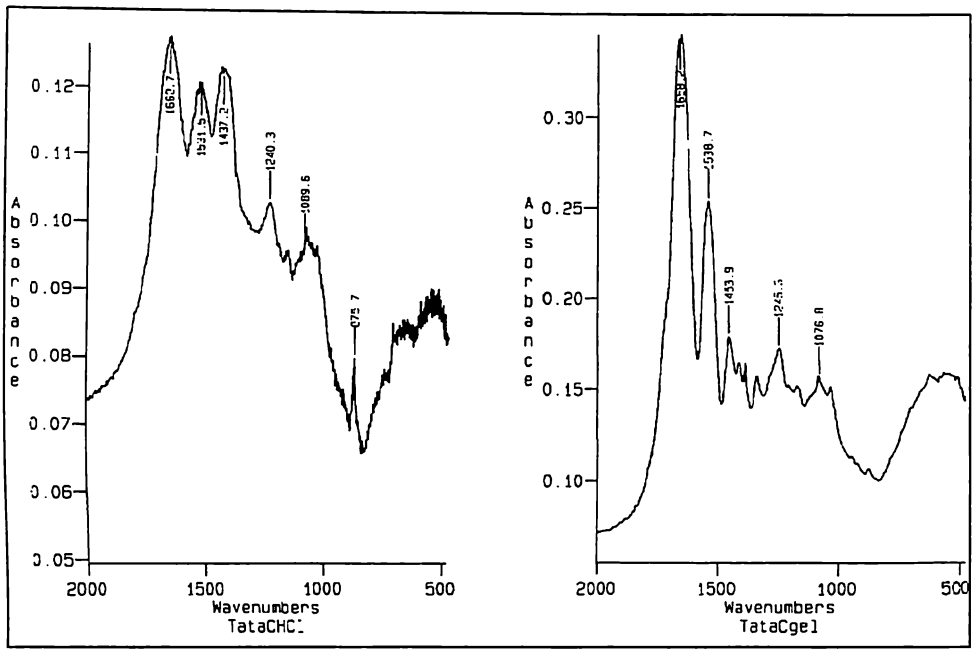



Figure 6.16: Infrared spectrograms of acid-insoluble collagen (TataCHCl) and gelatin (TataCgel) from Tata Beach red cod.

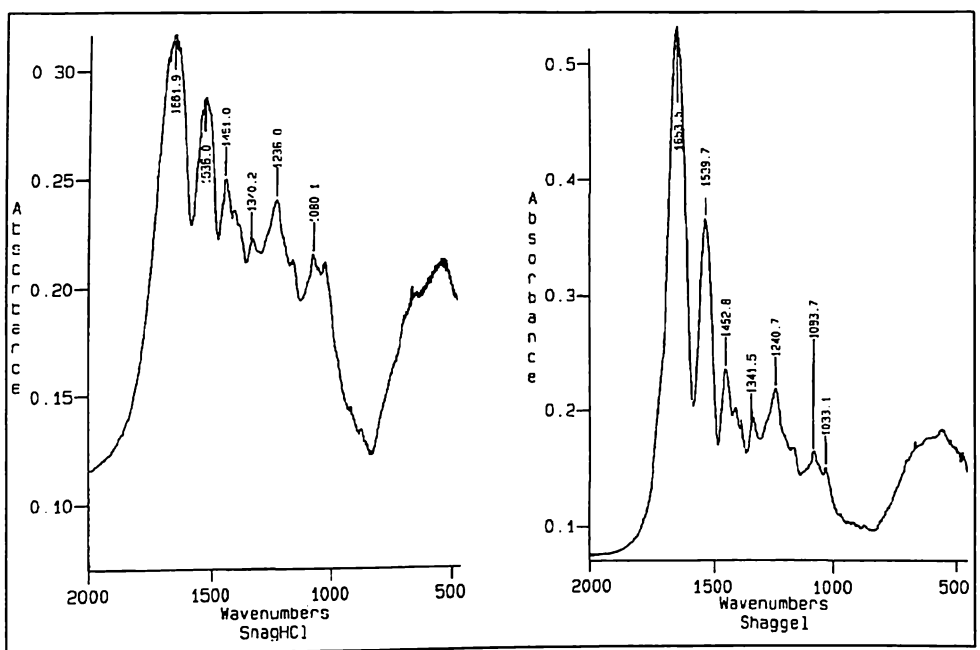



Figure 6.17: Infrared spectrograms of acid-insoluble collagen (ShagHCl) and gelatin (Shaggel) from Shag River Mouth barracouta.

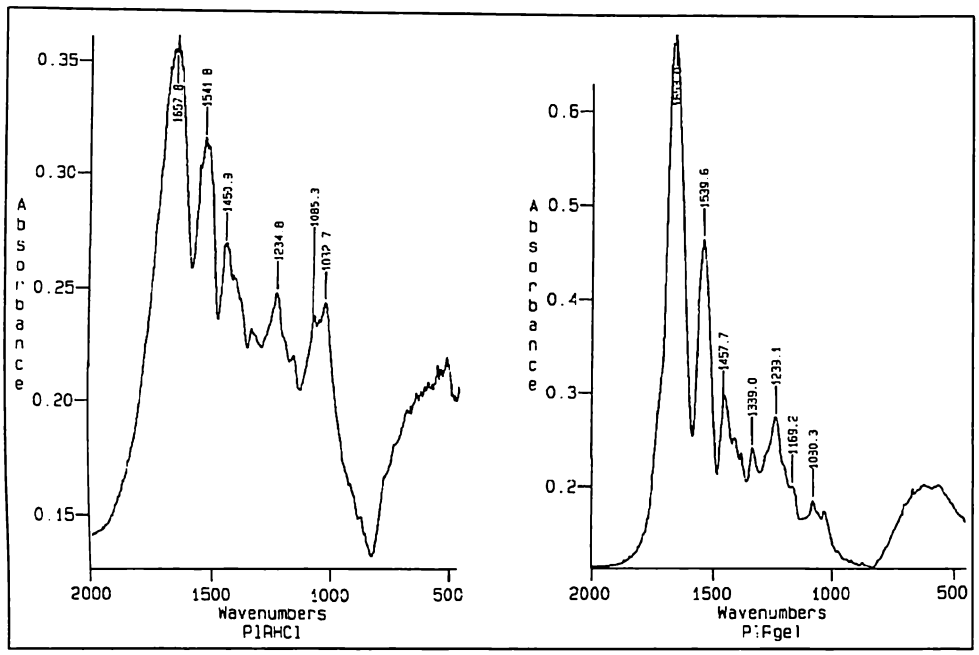



Figure 6.18: Infrared spectrograms of acid-insoluble collagen (PlRHCl) and gelatin (PlRgel) from Pleasant River barracouta.

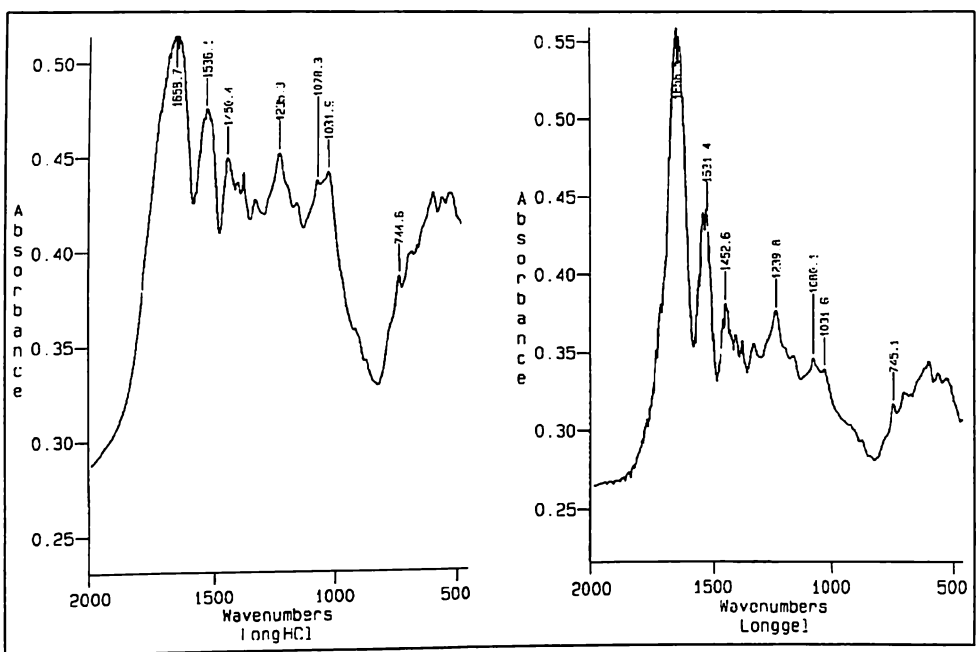



Figure 6.19: Infrared spectrograms of acid-insoluble collagen (LongHCl) and gelatin (Longgel) from Long Beach barracouta.

## OVERVIEW

### Houhora

Bone from Houhora had a soft exterior indicative of a moderate degree of alteration (Table 6.1). Analysis of the FTIR of bulk fish bone (Figure 6.10) suggests a significant loss of $CO_3$ (decrease in CP ratio) compared to modern snapper bone, and an increase in crystalinity (increase in SF). Although the sample was not charred, ovens near square C8 attest to the possibility that this alteration may be heat induced. The FTIR spectrum of whole bone also shows considerable loss of protein (Figure 6.2).

The total bulk N% values (2.11%) suggest that over half the original collagen remains. Nitrogen values for individual fish elements indicate the snapper bone from Houhora is fairly homogenous with a mean of 1.72%. All bone analysed belongs to Class II on the Stafford, Brendel and Duhamel (1988) scale. Nitrogen values are given in Table 6.2. Crude gelatin yields were uniform at around 7% (Table 6.3). This equates to approximately 39% extractable protein remaining which, although being fairly low, suggest that this sample is of "good" preservation. Residual yields were also low (0.96-1.29%).

The FTIR spectrum of the acid-insoluble collagen fraction from Houhora has a small peak at 1040 $cm^{-1}$ indicative of "transitional" or "bad" collagen (Figure 6.12). The gelatin spectrum is, however, typical of modern bone, thus indicating that gelatinisation has removed most of this contamination, though the tan colour of the sample suggests that some remains. Stable isotope results on the gelatin ($\delta^{13}C$ = -13.55‰; $\delta^{15}N$ = 13.33‰) are similar to modern snapper (Table 6.4) and there is no noticeable contamination present in the isotopic analysis of the residue ($\delta^{13}C$ = -13.55‰), though the humic acid $\delta^{13}C$ is depleted by comparison ($\delta^{13}C$ = -17.34‰) (Table 6.5).

### Twilight Beach

The SF and CP ratio derived from the Twilight Beach FTIR bone spectrum, indicate a loss of $CO_3$ and an increase in crystalinity (SF) compared to modern snapper bone (Figure 6.10). These results also suggest that there is some variability in preservation state. The soft exterior identified by hand specimen analysis supports this conclusion, and the mottled surfaces of some bones are constant with differential exposure

(bleaching) (Table 6.1) which may have hastened the decay process in some bones, imparting the variability noted.

The FTIR spectrum of whole bone also indicates some loss of protein (Figure 6.3). This is supported by the total bulk N% values (1.64 - 1.78%) shown in Table 6.2, which suggest that just under half of the original bone protein remains. The Twilight Beach sample can, therefore be classified as well-preserved (Class II) bone. Crude gelatin yields were fairly uniform (7 - 8%), with the exception of Batch D (10.49%); a sample of scrap bone, the gelatin of which was brown and powdery, possibly the result of contamination hindering the gelatinisation process (Ambrose 1990:436). Residual yields were also variable (1.26 - 4.84%) with the highest level of contamination measured in Batch D. The variation in gelatin yield was evened out when $CO_2$ correction was taken into account, with a possible 37 - 44% of the original collagen being extracted as shown in Table 6.3. The sample is, therefore considered to be of "good" preservation.

There is no indication of contamination in either the acid-insoluble collagen or gelatin infrared spectra (Figure 6.13). The stable isotope result on the gelatin ($\delta^{13}C$ = -11.58‰) is also within the parameters for modern snapper (Table 6.4), though both the residue and humic acid isotope values ($\delta^{13}C$ = -15.12‰ and -17.36‰ respectively) are depleted relative to the gelatin (Table 6.5).

**Rotokura**

Analysis of the infrared spectrum of bulk snapper bone from Rotokura (Figure 6.4) shows greater alteration to hydroxyapatite (C/P and SF) than is evident at either Houhora or Twilight Beach. This may be due to heating, which is upheld by the presence of charred samples in the Rotokura sample (Table 6.1). "Unburnt" elements also had a soft exterior suggestive of moderate weathering. Contaminating peaks in the bone FTIR spectra occur at 469 and 873 $cm^{-1}$. These peaks may be due to contamination by clay as the samples were removed from below a clay lens. The protein peak at 1650 $cm^{-1}$ is also significantly reduced, but the total bulk nitrogen value (1.96%), given in Table 6.2, identifies the Rotokura snapper as Class II bone. Following pretreatment, approximately 49% of the original protein could be extracted and the residual yield was low (1.52%). It is, therefore suggested that this sample is of "good" preservation (Table 6.3).

The acid-insoluble collagen spectrum for Rotokura shows a pronounced peak at 1037 $cm^{-1}$. This peak is likely to be the result of clay contamination rather than by any

extensive protein degradation, as this is not supported by the results given above. The vibration band at 1037 $cm^{-1}$ is significantly reduced in the infrared spectra of crude collagen (NaOH leached collagen), and the gelatin FTIR is typical of modern bone (Figure 6.14). The $\delta^{13}C$ result on the gelatin (-12.23‰) is also similar to modern snapper (Table 6.4). A fraction of the Rotokura gelatin was powdery, possibly a result of contamination hindering the gelatinisation process (see Ambrose 1990:436). The $\delta^{13}C$ of the residual fraction (-14.91‰) and humic acids (-18.92‰) suggest that the contaminating material removed is depleted in $\delta^{13}C$ (Table 6.5).

## Tata Beach

*a) Barracouta*

The infrared spectrum of bulk bone from Tata Beach, given in Figure 6.5, indicates a minor loss of $CO_3$ compared to modern barracouta bone, and a slight increase crystalinity (SF) (Figure 6.10). The total bulk N% for barracouta bone (1.66%) suggests just under half of the original collagen remains (Table 6.2), though considerable variation is present with individual skeletal elements ranging from 1.36 to 3.24% nitrogen. This implies that anything from approximately 25% to 75% of the original protein is present and places the Tata Beach barracouta in Stafford, Brendel and Duhamel's (1988) Class II preservation category. The low crude gelatin yields, shown in Table 6.3, necessitate the use of greater quantities of bone for each radiocarbon determination than estimated from N% (*i.e.* approximately 135 - 172 g required compared to 124.1 g estimated) with only approximately 29 - 37% of the original protein remaining. The gelatin samples were also of a powdery texture, possibly as a result of contamination (Ambrose 1990:436). Residual yields are, however, low (1.76 - 1.82%) and all samples still fall within the parameters of Hedges and van Klinken's (1992:284) "good" preservation state.

Infrared spectra of barracouta protein fractions are shown in Figure 6.15. The infrared spectrum of the acid-insoluble collagen residue shows an anomalous peak at *ca.* 1040 $cm^{-1}$. This is most likely the result of severe collagen degradation or contamination by humic acids, and may explain the high N% value and low gelatin yield. There is, however, no indication of contamination in the gelatin FTIR spectrum. The stable isotope results for the residue ($\delta^{13}C$ = -17.28‰) and the humic fractions ($\delta^{13}C$ = -20.74‰) (Table 6.5) are depleted in $\delta^{13}C$ relative to the gelatin (-13.21‰), which is indistinguishable from modern barracouta gelatin (Table 6.4).

*b) Red cod*

The infrared spectrum of red cod bone from Tata Beach shows a more extreme loss of $CO_3$ than is evident in the barracouta bone (Figures 6.6 and 6.10). The protein peak is also reduced by comparison. A loss of protein is upheld by the total bulk N% for red cod (0.94%) which suggests only 25% of the original collagen remains (Table 6.2). Considerable variation is present within the site, with as little as 0.69% but up to 1.54% N measured in individual bone elements. These values suggest that red cod bone is borderline Class II or III. This level of distinction is not apparent from the hand specimen analysis, the results of which are given in Table 6.1. The Tata Beach red cod bone appears, however, to be of "good" preservation because around 27% of the original protein could be extracted by gelatinisation (Table 6.3).

The infrared spectrum of the acid-insoluble collagen residue, shown in Figure 6.16, has two anomalous peaks at *ca.* 1437 and 875.7 $cm^{-1}$. FTIR diagrams for pretreatment batches C, D and E did not have these peaks, but did have a distinct anomaly at 1040 $cm^{-1}$. No contamination was visible in the gelatin FTIR spectrum, though the stable isotope results of the residue ($\delta^{13}C$ = -17.11‰) and humic acids ($\delta^{13}C$ = -19.87‰) imply the presence of contamination depleted in $\delta^{13}C$ (Table 6.5). The stable isotope result on the gelatin ($\delta^{13}C$ = -14.13‰) (Table 6.4) is also within the parameters for modern marine fish (Table 2.2) and the red cod collagen value given in Leach, Quinn and Lyon (1996:46).

**Shag River Mouth**

Analysis of the physical appearance of the bone from Shag River Mouth indicated that fish remains were moderately dense and well-preserved (Table 6.1), though a large proportion of the sample was rejected for radiocarbon analysis due to burning. The total bulk N% (2.12 - 2.68) values for "unburnt" specimens (Table 6.2) suggest that over half the original collagen remains, supporting the bulk FTIR spectrum (Figure 6.7). This places the Shag River Mouth barracouta in Class II on the Stafford, Brendel and Duhamel (1988) scale. This "unburnt" bone is, therefore considered to be of "good" preservation.

The acid-insoluble collagen and gelatin spectra (Figure 6.17) for the Shag River Mouth "unburnt" sample are equivalent to modern spectra. The gelatin $\delta^{13}C$ value of -13.57‰ is also similar to modern barracouta (Table 6.4), though the humic acid and residue contaminants are more depleted in $\delta^{13}C$ (-19.38‰ and -17.21‰ respectively)(Table 6.5).

Further tests were run on samples of burnt bone to correlate burning with N% estimates and stable isotope data. The results of N% and stable isotope analysis on the burnt bone, along with class designation are shown in Table 6.6. From these results it is apparent that burning significantly reduces the protein content making such bone impractical to date (*i.e.* Sample 2 = 355.2 g expected bone requirements). Burning also affects the stable isotope results. Extensive burning alters the $\delta^{15}N$ values of the bone even when protein still remains, possibly due to increased exposure to contamination or differential loss of amino acids in the collagen. Alteration to $\delta^{13}C$ appears after minor burning (Sample 2). On the basis of the parameters established for this research, samples 2,3, 5, 6 and 7 in Table 6.6 fall into Classes III, IV and V and would be unsuitable for dating. Although Sample 4 is designated a Class II bone, it has anomalous stable isotope values.

Table 6.6: Shag River Mouth burnt whole bone samples.

| Sample | Description (after Stiner *et al.* 1995:226). | Munsell colour of powder. | N% | $\delta^{15}N$ | $\delta^{13}C$ | Expected bone requirements (gm) | Class |
|---|---|---|---|---|---|---|---|
| Mod | Hard Waxy | | ~4.12 | ~12.73 | ~-14.1 | ~50.0 | I |
| 1 | Not burned, moderately dense | 7.5Y 6/4 dull orange | 2.12-2.68 | 15.85 | -14.05 | ~76.9-97.2 | II |
| 2 | Slightly burned: localised and <half carbonised | 7.5YR 5/4 dull brown | 0.58 | 15.20 | -18.51 | 355.2 | III |
| 3 | Lightly burned: > half carbonised | 5YR 3/4 dark reddish brown | 0.54 | 16.78 | -18.25 | 381.5 | III |
| 4 | Fully carbonised (completely black) | 2.5YR 2/2 v. dark reddish brown | 0.82 | 16.17 | -18.65 | 251.2 | II |
| 5 | Localised < half calcined (more black than white) | 7.5YR 4/1 brownish grey | 0.29 | 16.75 | -18.98 | 710.4 | IV |
| 6 | >half calcined (more white than black) | 2.5YR 6/1 reddish grey | 0.23 | 18.23 | -15.94 | 895.7 | IV |
| 7 | Fully calcined (completely white) | 7.5Y 7/1 light grey | 0.14 | 16.54 | -- | 1471.4 | V/IV |

The effects of burning are clearly visible in the FTIR spectra of whole bone samples (Figure 6.20). As burning damage intensifies the carbonate peaks at 1460 $cm^{-1}$, 1415 $cm^{-1}$, and 870 $cm^{-1}$, and the protein peak at 1650 $cm^{-1}$ decrease, while peaks at 960 $cm^{-1}$ and 630 $cm^{-1}$ appear due to increased crystalinity (*c.f.* Sillen 1989; Weiner and Bar-Yosef 1990; Stiner *et al.* 1995:227). This alteration to the hydroxyapatite fraction can be clearly seen using C/P and SF calculations, the results of which are shown in Figure 6.10. The "unburnt" fish bone has a lower CP ratio compared to modern barracouta bone and only a slight increase in crystalinity (SF). The FTIR spectra of burnt samples, however, display a marked decrease in C/P values and increase in SF as burning damage intensifies (*c.f.* Stiner *et al.* 1995). A trend is apparent when modern bone, "unburnt" bone and burnt bone from Shag River Mouth are compared. This method cannot adequately ascertain whether this is the result of burning or

weathering (Stiner *et al.* 1995:223). Because Anderson and Allingham (1996:43-44) suggested that a large proportion of the Layer 4 midden had been burnt *in situ*, it is considered likely, however, that all samples have been subjected to some degree of heating.

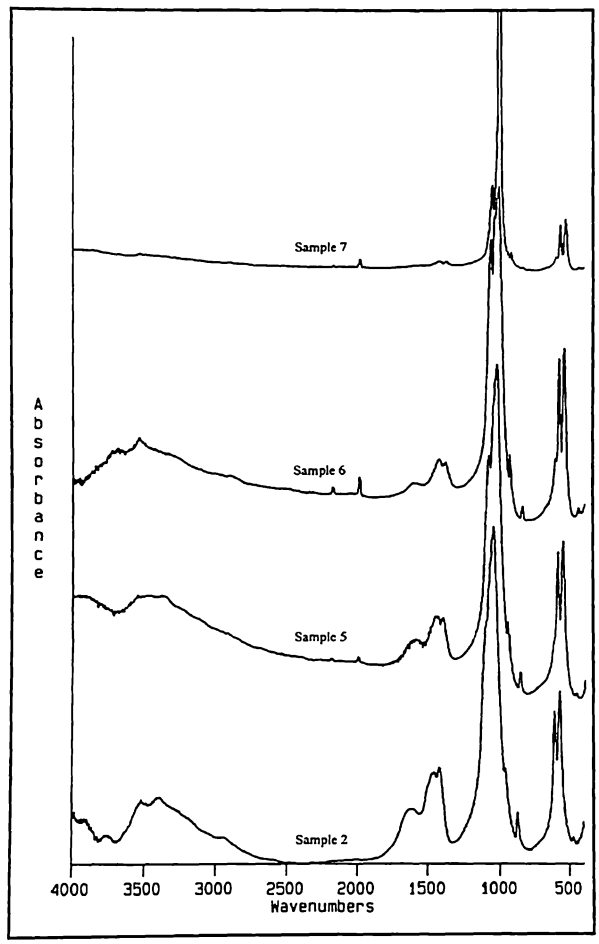



Figure 6.20: Changes to infrared spectra with burning (burnt samples 2, 5, 6 and 7 from Shag River Mouth).

## Pleasant River

Barracouta bone from Pleasant River has a translucent quality and is fairly dense (Table 6.1), characteristics which are typical of well-preserved bone (*c.f.* Nicholson 1996a:527). This is supported by the whole bone FTIR spectrum of barracouta from Pleasant River (Figure 6.8) which indicates that substantial protein remains when compared to the modern fish bone (Figure 6.1). No major change is evident in the SF, though the CP ratio suggests some loss of $CO_2$ compared to modern barracouta (Figure 6.10).

Total bulk N% (2.97 - 3.08%), given in Table 6.2, upholds this suggestion of minimal protein loss, and places the Pleasant River barracouta bone in the Class II preservation state. The protein yield after pretreatment (Table 6.3) is also high and uniform (11.58 - 12.64). Following conversion for $CO_2$ yield this equates to approximately 64 - 70% extractable collagen and implies that this sample is of "good" preservation. Residual yields are, however, variable with the largest yield (3.85%) recovered from PlR batch C (barracouta pharyngobranchials), most likely due to sand which had been held within the bone structure.

No indication of contamination is present in either the acid-insoluble collagen or gelatin FTIR fractions, both of which are characteristic of modern bone derivatives (Figure 6.18). The gelatin isotopic value ($\delta^{13}C$ = -13.14‰) is equivalent to modern barracouta bone gelatin, but both the residue and humic fractions indicate that contamination has an depleted $\delta^{13}C$ value (-19.19‰ and -20.27‰ respectively). In such a well-preserved sample it is possible that this depleted $\delta^{13}C$ value may be due to lipids, which can be up to 7% more negative than bone protein (Liden, Takahashi and Nelson 1995:321). Isotope values are given in Tables 6.4 and 6.5.

## Long Beach

The physical appearance of the barracouta bone from Long Beach suggests that these remains are well-preserved (Table 6.1). The whole bone FTIR spectrum of barracouta from Long Beach supports this conclusion (Figure 6.9). Both C/P and SF are similar to modern barracouta and surviving protein levels are high (Figure 6.10). There is no evidence of burning, despite the presence of an ash lens close to square F1 (see Figure 5.14), and it is possible that fish were filleted prior to cooking (Fyfe 1982:70-71).

The total bulk nitrogen value of 2.5 - 2.6% for the Long Beach samples (Table 6.2) falls within the Class II designation of Stafford, Brendel and Duhamel (1988). Crude gelatin and residual yields were uniformly 11.1 - 11.46% and 2.20 - 3.85% respectively. This equates to around 58 - 63% extractable collagen, and suggest that this sample is of "good" preservation (Table 6.3).

The acid-insoluble collagen and gelatin spectra for Long Beach show no indication of contamination (Figure 6.19). The $\delta^{13}C$ result on gelatin (-13.29‰) is comparable to modern barracouta, though both the residue ($\delta^{13}C$ = -18.60‰) and humic acid ($\delta^{13}C$ = -21.62‰) values suggest contamination by a depleted source. Isotope values for gelatin, residue and humic fractions are given in Tables 6.4 and 6.5.

## Moa bone

*a) Shag River Mouth*

The Shag River moa bone sample was very hard, and an unusual light grey colour (10YR 8/2). This sample had a low nitrogen level of 0.67%, which places the bone at the boundary of Stafford, Brendel and Duhamel's (1988) Class II and III designations. Given the low percentage of remaining protein, NaOH treatment was omitted. Therefore, yield comparisons between the fish bone and this moa bone sample are problematic, but it is suggested that the extractable collagen falls below the calculated 19.3% (crude gelatin yield = 3.48%). This places the moa bone in Hedges and van Klinken's (1992) "transitional" preservation category. No sign of contamination is present, however, in either the acid-insoluble collagen nor gelatin infrared spectra (Figure 6.21). Stable isotope results on the gelatin attest to the terrestrial nature of the sample ($\delta^{15}N$ = 8.32‰; $\delta^{13}C$ = -22.71‰), but no modern comparison is possible to assess this data. Residual yields were low (0.85%) and $\delta^{13}C$ is comparable to the gelatin (-23.78‰), though $\delta^{15}N$ is enriched (13.59‰).

Given the lack of modern comparison material, the whole bone spectrum of Wk-5433 (Figure 6.22) was compared to a second moa bone from Layer 4. This second moa sample showed the same general trend as the fish bone, namely a low CP ratio (0.3199) and high SF (4.4). Wk-5433, on the other hand, had a higher carbonate content relative to the second moa (C/P = 0.3507), but no significant increase in crystal size was evident (SF = 3.01). This is consistent with $CO_3$ substitution for $PO_4$ which produces smaller crystals (Wright and Schwarcz, 1996:936).

The dense nature of the bone, the whole bone FTIR spectrum and the highly reactive effervescence during decalcification attest to the extent of carbonate alteration. This is in contrast to the barracouta bone from the same area. Combined, this data implies significant alteration to both the collagen and carbonate fractions. These differences may be attributable to variation in depositional environment, possibly even a sub-fossil origin for this sample, which could have been collected in prehistory and subsequently discarded within the site. The identification of sub-fossil bone on the basis of mineralisation is, however, notoriously inaccurate (Trotter and Malthus 1967; Scarlett 1974:3).

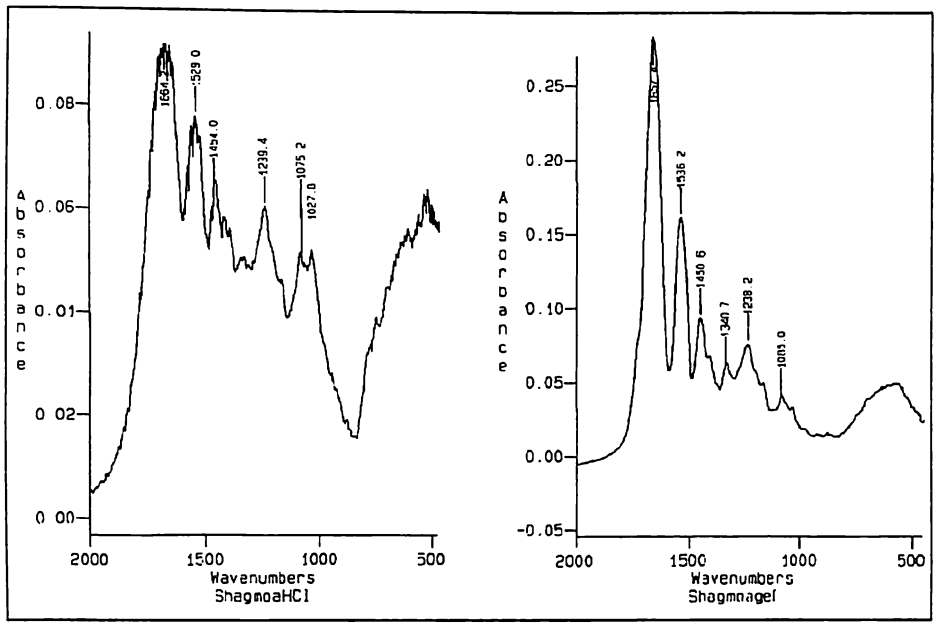



Figure 6.21: Infrared spectrograms of acid-insoluble collagen (ShagmoaHCl) and gelatin (Shagmoagel) from Shag River Mouth moa bone.

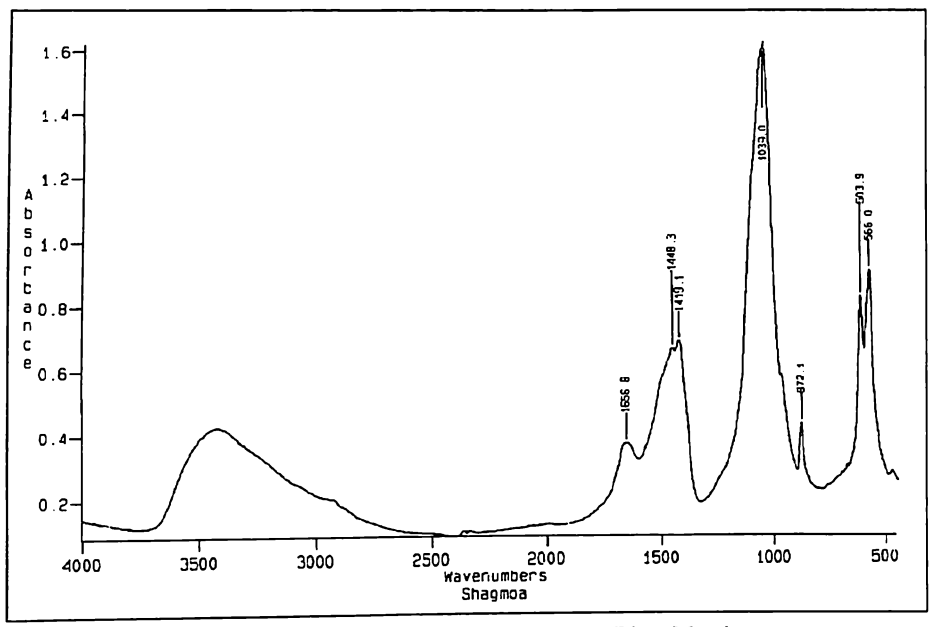



Figure 6.22: Infrared spectrogram of bulk moa bone from Shag River Mouth.

*b) Pleasant River*

Two samples of moa bone were assessed from Pleasant River, one from Layer 2b (PlR 1059) and the other from Layer 2a, square A3 (PlR 1038-BM-1) - in direct

association with the barracouta bone. PIR 1059 has a N% of 1.12 (*i.e.* Class II). PIR 1038-BM-1 consisted of two moa bone samples; Moa A and Moa B. Moa A had a N% of 1.15 - 1.42 and Moa B had a N% of 1.16. These values are surprisingly similar to a moa bone sample (PIR 1059) from Layer 2a and at odds with values on barracouta from the same layer (*i.e.* N% = 2.97 - 3.08). Crude gelatin yields for PIR 1038 were low at 4.02% (residual yield = 1.88%), and it was calculated that 22.3% of the original collagen could be extracted following pretreatment. This is just within Hedges and van Klinken's (1992:284) "good" collagen definition.

Stable isotope results on the gelatin for PIR 1038 attest to the terrestrial nature of the sample ($\delta^{15}N$ = 6.86‰; $\delta^{13}C$ = -23.86‰). Humic contaminants are depleted in $\delta^{13}C$ and enriched in $\delta^{15}N$ (-25.02‰ and 10.69‰ respectively). This variation is also evident in the isotope values of the residue ($\delta^{15}N$ = 9.89‰ and $\delta^{13}C$ = -24.52‰). The isotopic, yield data and FTIR spectra (Figures 6.23 and 6.24), therefore suggest that moa bone from Pleasant River should be reliable, though stratigraphic displacement may have occurred.

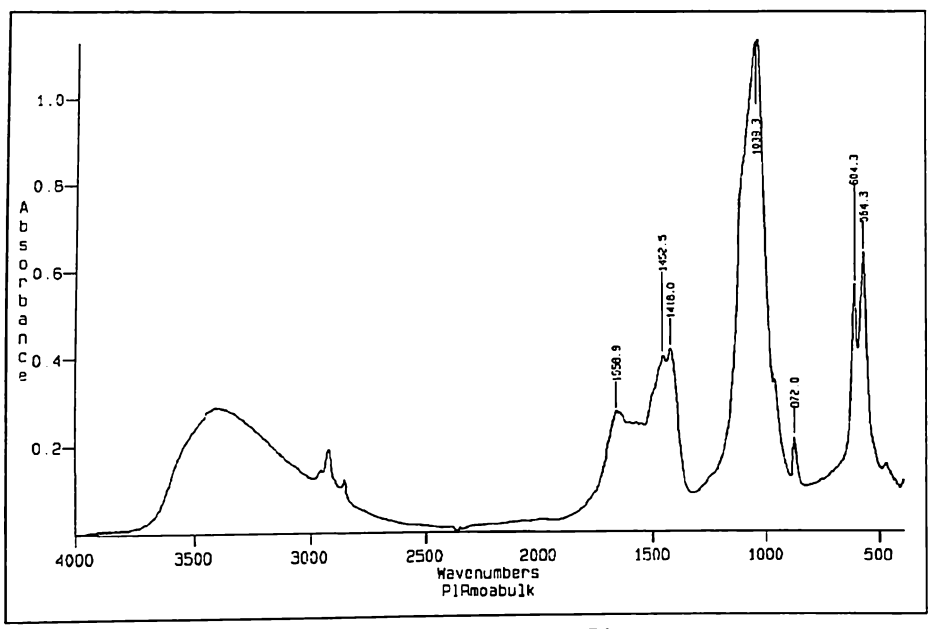



Figure 6.23: Infrared spectrogram of moa bone from Pleasant River.

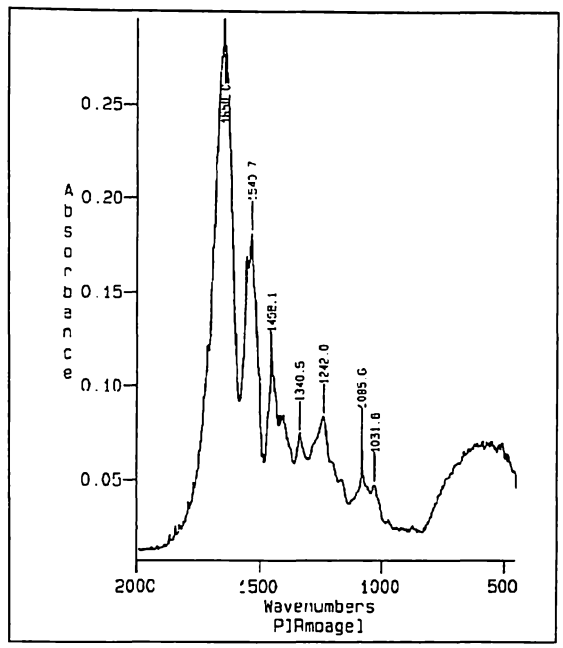



Figure 6.24: Infrared spectrogram of moa gelatin from Pleasant River.

## Tripeptide separations

Samples for tripeptide separation and dating were selected from Tata Beach and Rotokura. Contamination had been detected in the FTIR crude collagen spectra of bone from both of these sites. Material was also submitted from the Shag River Mouth site as a control sample for South Island barracouta (*i.e.* to check for contamination masking $\Delta^{14}C$ values influenced by the Subtropical Convergence), and from Houhora in order to evaluate the influence of inbuilt age in snapper (see Chapter 5).

Initial attempts to isolate collagenase were undertaken on samples of gelatin that had been prepared at Waikato according to the method outlined above. All four samples had reasonably high yields in the enzyme step, indicating that they were predominantly collagenous (van Klinken[5], *pers. comm.* 15/8/1997). For all samples 50% of the ultrafiltration yield was, however, of small molecular weight (van Klinken, *pers. comm.* 21/8/1997), possibly caused by gelatinisation, a process which will break down the protein structure. The gelatin samples from Houhora, Shag River Mouth and Rotokura were not useable because the collagen specific GlyProHyp and

[5] Dr. G.J. van Klinken, formerly of the Radiocarbon Accelerator Unit, Research Laboratory for Archaeology and the History of Art, Oxford, England.

GlyProAla peaks (Table 2.1) were not present following elution from the HPLC column (van Klinken, *pers. comm.* 14/8/1997). Under such circumstances it was impossible to tell if the sample was degraded or contaminated.

A second batch of whole bone samples (except Tata Beach which had been decalcified) were submitted for treatment. TATA A (OxA-7568), HC8 A (OxA-7569) and ROTO 3/4 (OxA-7570) all had identifiable GPA/GPX peaks (*i.e.* hydrophilic peptides; mainly GlyProHyp and GlyProAla) in the collagenase chromatogram and during the preparative separations the eluting peptides were isolated for $^{14}C$ measurement (Figures 6.25 - 6.27). The peaks of the SHAG A (OxA-7793) sample were not as well defined, with the "hydro-phobics" merging into the GPA/GPX peak (Figure 6.28). It was suggested that this poorer separation may have been the result of a recently changed buffer solution (C. Bronk-Ramsey[6], *pers. comm.* 2/4/1998). The Shag River Mouth sample was successfully reseparated and $^{14}C$ measured (OxA-7593). The results of these tripeptide determinations are presented in Chapter 7.

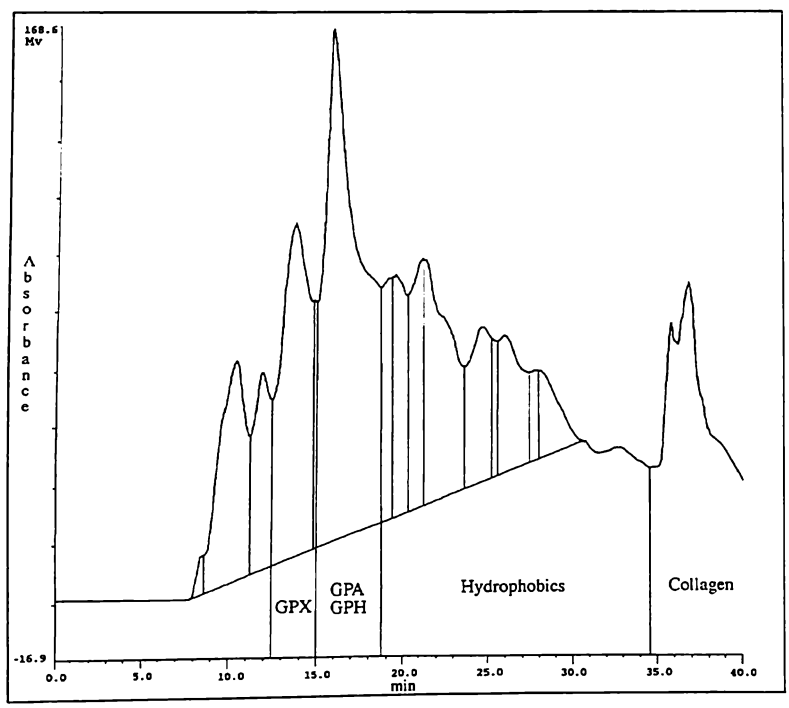



Figure 6.25: Chromatogram of collagenase peptides from the Tata Beach (ESW/5) barracouta.

[6] Dr. C. Bronk-Ramsey, Radiocarbon Accelerator Unit, Research Laboratory for Archaeology and the History of Art, Oxford, England.

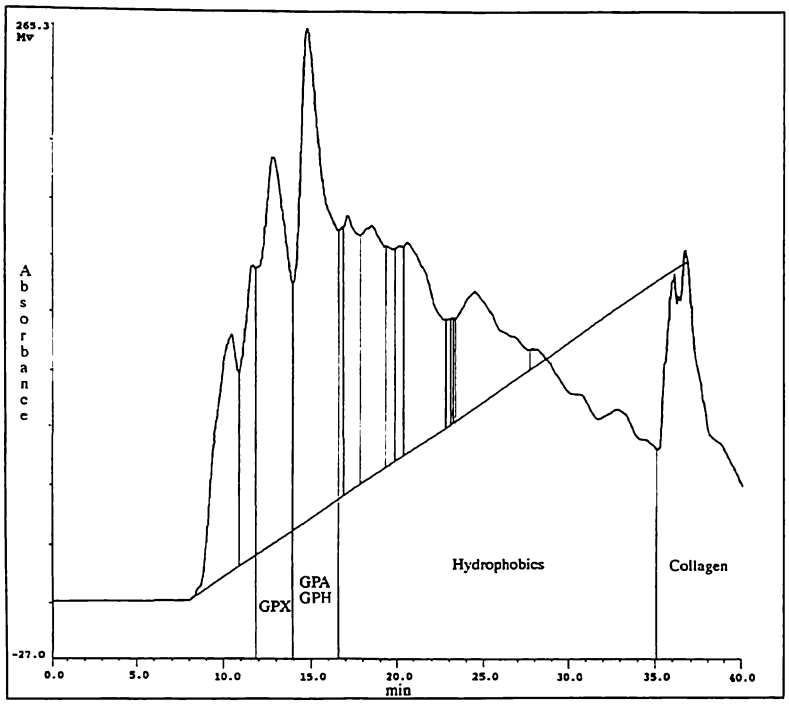



Figure 6.26: Chromatogram of collagenase peptides from the Houhora snapper.

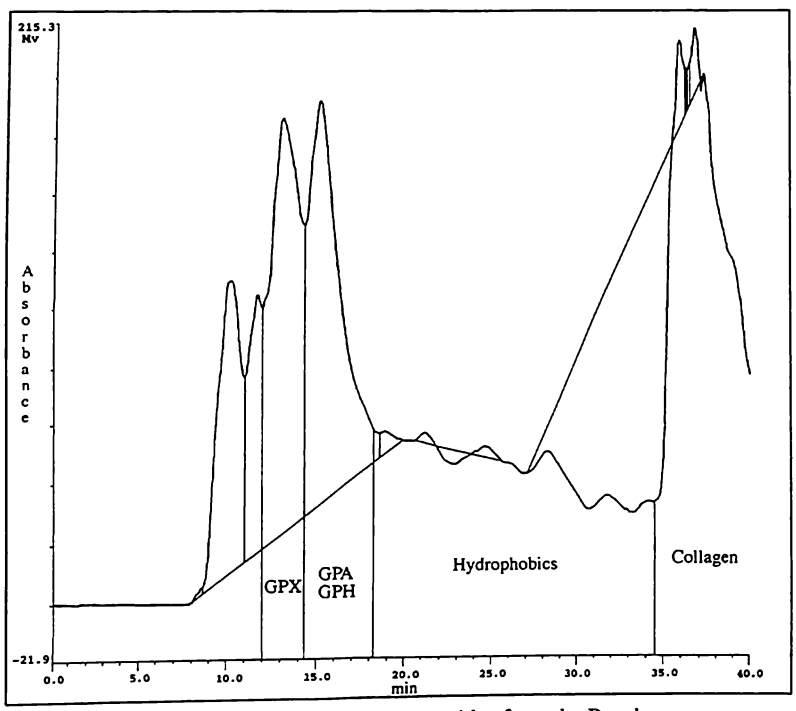



Figure 6.27: Chromatogram of collagenase peptides from the Rotokura snapper.

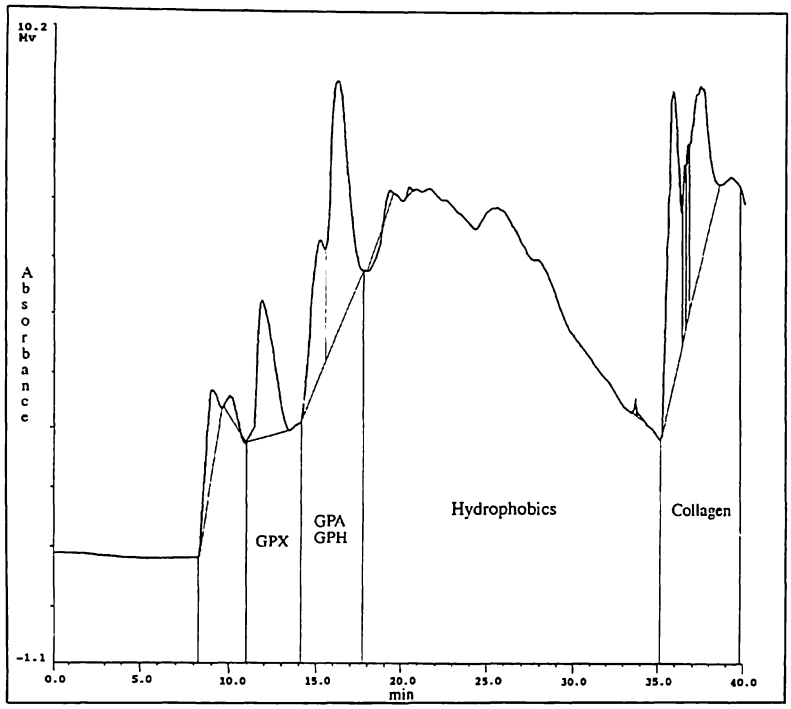



Figure 6.28: Chromatogram of collagenase peptides from the Shag River Mouth barracouta.

## DISCUSSION

It is apparent that the use of physical appearance to estimate collagen preservation and contamination can be mis-leading, especially given the different responses of collagen and hydroxyapatite to the same environmental conditions and cultural influences.

Caution is also recommended when identifying burnt samples because a visible colour change does not occur in bone until a temperature of 400°C is reached (Shipman, Foster and Schoeninger 1984). Burning will also affect the isotope values, possibly due to loss of protein or as a result of increased susceptibility to contamination. Nicholson (1996:527, 529; 1998:401), however, noted that baked bone (no visible charring) appeared to survive better than uncooked bone under similar environmental conditions. This may be caused by partial dehydration which would increase hydrophobic interactions and strengthen existing inter-chain ionic linkages (Collins *et al.* 1995:181). Therefore, the possibility of undetected minor heating episodes on these samples should not significantly alter the radiocarbon results, and may even aid in preserving the bone.

Bulk nitrogen values are a useful indication of the amount of bone required for each radiocarbon determination. Such measurements reduce unnecessary destruction of bone and aid in assuring sufficient bone is pretreated. A more practical application is to run multiple N % on individual elements which would give an indication of spread, while minimising sample destruction. Unfortunately, N% as an indicator of contamination is limited and this technique should, therefore be supported by additional analytical methods.

FTIR spectra of whole bone give a holistic picture of bone preservation. This technique is, however, limited in the identification of contaminated collagen.

Gelatin yields vary depending on the specifics of pretreatment, including variations in decalcification time, gelatinisation temperature and time, as well as the presence and strength of NaOH (Figure 3.1). The gelatin yield, in combination with N% are useful methods of screening collagen degradation and contamination. This does, however, require careful control over the gelatinisation environment. Residual yields are more variable and depend on the extent of initial physical cleaning.

NaOH treatment appears to reduce contaminants that may hinder subsequent gelatinisation. Levels of contamination high enough to be detected by FTIR analysis may, however, remain following a NaOH wash. This treatment alone is, therefore not recommended for $^{14}C$ analysis. Gelatinisation reduces contamination in well-preserved bone to levels below detection (*i.e.* by FTIR spectra and stable isotope analysis), but may also degrade remaining protein. The degraded protein remnants can then re-complex with humic contaminants that remain after decalcification. Such an outcome is especially problematic for small samples, or where little collagen remains. Lowering the temperature of gelatinisation may significantly decrease protein degradation (*c.f.* Brown *et al.* 1988). This may be important in improving fish gelatin yields given the low environmental temperature of fish and, therefore the low collagen denaturation temperature (*c.f.* Richter 1986).

FTIR analysis of the acid-insoluble fraction increases the chance of identifying problem samples. Where no abnormalities are detected, one can assume that contamination in the gelatin will be below the possible 8% level measured by van Klinken and Hedges (1995:268) in gelatinised collagen samples.

Stable isotope values are of limited use, except where gross contamination is present.

## CONCLUSIONS

The isotopic and FTIR data from Houhora and Twilight Beach suggest that over half the collagen has been lost, and that contamination is minimal. There is no visible indication of burning, though both sites have evidence of cooking activities. Consequently, the majority of diagenesis is thought to be the result of the high annual rainfall (1016 - 1270 mm) and mean annual temperature (13.9 - 15°C) of this region (Table 5.2). It is concluded, therefore that the Houhora and Twilight Beach snapper bone should give reliable $^{14}C$ estimates when pretreated to gelatin.

Both the barracouta and red cod bone from Tata Beach appear to fall within acceptable parameters, as outlined above, for dating via gelatinisation. Caution is, however, suggested as gelatin yields were low, N% was highly variable and contaminating peaks were present in the FTIR spectra. The data also indicates that red cod bone from Tata Beach appears to be of poorer preservation than the barracouta remains. This may reflect differences in bone element chemistry or prehistoric preparation, but is most likely due to differential exposure during deposition. As already noted (Chapter 5) a number of differences were identified between the lower red cod dominated midden and the upper barracouta dominated midden, including evidence of disturbance at the top of the lower lens, in the form of a diffuse intermediate unit. This was interpreted as a hiatus in deposition by Barber (1998:8-9). A longer period of exposure may account for the poorer preservation of the red cod samples. The poorer preservation of fish bone from Tata Beach generally, may be related to the high annual rainfall (1270 - 1524 mm) and mean annual temperature (11.7 - 12.2°C) of the region (Table 5.2). The Tata Beach fish bone is not considered to be a reliable sample for radiocarbon analysis, despite the relatively young age expected for the site (mid 16$^{th}$ century).

Analysis of snapper bone from Rotokura suggests that over half the original collagen has been lost. There is some evidence of burning at the site which may also be evident in the FTIR spectrum. Anomalous peaks in the infrared spectra are probably the result of contamination by clay. This should be removed by the gelatinisation process, but additional purification may be necessary.

The isotopic and FTIR analyses suggest that barracouta bone from Shag River Mouth, Pleasant River and Long Beach is well-preserved (excluding burnt elements). At Pleasant River and Long Beach this could be attributed to the young age of these sites (*i.e.* late 16$^{th}$ century and late 17$^{th}$ to early 18$^{th}$ centuries respectively), or from particularities of prehistoric processing practices (*i.e.* fish from both sites may have been filleted prior to cooking or preservation). The high gelatin yields obtained from

the Shag River Mouth fish samples, however, suggests otherwise. This site was occupied in the mid 14$^{th}$ century, and there is clear evidence of *in situ* burning. Instead it is suggested that the cool, mild climate of the southern region (Table 5.2) has strongly influenced bone preservation at all three sites. On the basis of this analysis it is concluded that barracouta bone from these sites should give reliable radiocarbon results when pretreated to gelatin.

The moa bone samples from Pleasant River and Shag River Mouth are both anomalous. It is suspected that the Shag River moa bone may have a sub-fossil origin. Stratigraphic displacement from a lower moa hunting layer is also a possible explanation for the variation identified among the Pleasant River moa bone. Neither sample is recommended for dating given uncertainties over context.

# CHAPTER 7

# RADIOCARBON RESULTS

## INTRODUCTION

The aim of this study has been to evaluate the reproducibility of radiocarbon determinations of fish bone, specifically snapper (*Pagrus auratus*) and barracouta (*Thyrsites atun*). Neither sample type has been dated previously. It is, therefore crucial, prior to routine radiocarbon analysis, that these species be investigated carefully for accuracy and reproducibility (Higham 1994; Schmidt 1996;154). This dissertation has concentrated on obtaining this information, with specific interest in carbon source and bone preservation, as well as $^{14}C$ analysis of the fish bone.

In this chapter, radiocarbon ages of fish gelatin from Houhora, Twilight Beach, Rotokura, Tata Beach, Shag River Mouth, Pleasant River Mouth and Long Beach are presented along with results on other sample types obtained previously and during the course of this research. Several potential problems were identified with dating bones of this material.

In Chapter 5 it was suggested that snapper and barracouta obtain their carbon indirectly from DIC and should, therefore be subject to a similar reservoir correction as marine shell. Errors could, however, be introduced due to variation in dietary $\Delta^{14}C$ and/or incorporation of depleted carbon, especially where coastal waters are influenced by the Subtropical Convergence or by upwelling along the west coast of New Zealand. The influence of inbuilt age and depleted $\Delta^{14}C$ values associated with depth are another source of error, but are likely to be minor factors.

Collagen degradation and contamination are major problems in the radiocarbon analysis of bone. Assessment of bone given in Chapter 6 suggest that barracouta remains from Shag River Mouth, Pleasant River and Long Beach are well-preserved and should give reliable results when pretreated to gelatin. Snapper bone from Houhora and Twilight Beach are considered to be reliable for dating, despite evidence of moderate protein loss and contamination. The barracouta and red cod bone from Tata Beach also appear to fall within acceptable parameters outlined above for dating using the gelatinisation method. Caution was suggested, however, as gelatin yields were low, N% was highly variable and contaminating peaks were present in the FTIR

spectra. High levels of contamination, probably by clay, were also observed in the Rotokura snapper sample.

## DATING PARAMETERS

All ages are reported as conventional radiocarbon ages BP, based on the Libby half-life and calculated according to the recommendations outlined by Stuiver and Polach (1977:355-363). Conventional radiocarbon ages BP are reported with reference to the net corrected activity of the modern reference standard HOxII (SRM-4990C, NIST HOxII). All age estimates were calibrated using the intercepts method with OxCal v3.0 (Bronk-Ramsey 1995). For terrestrial samples, 27 ± 5 years was subtracted from the conventional radiocarbon age to allow for the southern hemispheric offset (McCormac *et al.* 1998). The decadal curve (Stuiver and Becker 1993) was used to calibrate results on identified charcoal samples, while the bidecadal curve (Stuiver and Pearson 1993) was used to calibrate unidentified charcoal and moa bone collagen measurements given the uncertainties associated with these sample types. Both the shell and fish results were calibrated using the marine curve of Stuiver and Braziunas (1993) with $\Delta R$ set at -25 ± 15 years (Higham and Hogg 1995).

The calibrated $^{14}C$ results for each site are shown in Figures 7.1-7.7 and Tables 7.1 and 7.3-7.8. The prefixes 'NZ' and 'NZA' refer to ages calculated at IGNS, and 'Wk' to those measured at the University of Waikato Radiocarbon Dating Laboratory. Two methods were used to evaluate the radiocarbon determinations:

First, the protocol outlined by Ward and Wilson (1978) was used to determine whether there were statistical grounds for combining the results. A Case I situation occurs where all determinations have the same true mean and any differences between radiocarbon measurements were due to changes in the circumstances under which the determination was made (Ward and Wilson 1978:20). Otherwise radiocarbon determinations are evaluated as Case II examples. The fish bone gelatin results are considered to be acceptable when they are statistically identical and overlap with the calibrated age ranges of other sample types at one standard deviation ($1\sigma$).

The results are also evaluated using OxCal combine probabilities calculations (Bronk-Ramsey 1998). Using this method dates from the same sample are combined prior to calibration using the R Combine method (chi square test). All other $^{14}C$ determinations are calibrated ('prior' distribution), combined, and then assessed in the light of the combined data (the 'posterior' distribution). This posterior distribution is given an agreement index which indicates the extent to which the posterior distribution

overlaps the prior distribution. The agreement index should not fall below 60.0% (<A'c) (an unaltered index = 100%), but can be tested by calculating an overall agreement index for combinations. $A_{overall}$ is the calculated agreement index and An is the value (dependent on n) below which it should not fall. If $A_{overall}$ falls below 60.0% the model should also be questioned. For this dissertation, an overall agreement index was calculated for each sample type (*i.e.* marine shell, charcoal, fish gelatin and tripeptides) and for the $^{14}C$ determinations for the site as a whole.

## Houhora

Radiocarbon determinations for the Archaic Layers at Houhora are shown in Table 7.1. The snapper (*Pagrus auratus*) bone samples were combined, ground and split evenly four ways prior to gelatinisation.

Three charcoal radiocarbon determinations (NZ-914, NZ-915 and NZ-916) were obtained during excavations in 1965-1966. All three charcoal samples were unidentified and likely to have been subject to in-built age, which can result in errors of 300 years or more. Material from two of the original radiocarbon determinations (NZ-914 and NZ-916) were obtained from the IGNS for this research. Analysis of charcoal from these samples (Table 7.2) confirm that they are almost completely composed of long-lived species (R. Wallace, *pers. comm.* May 1997). NZ-914, NZ-915 and NZ-916 are, therefore excluded from the final analysis. A sample of short lived *Myrsine australis* was selected from NZ-916 for dating (Wk-5485).

Anderson and Wallace (1993) submitted six charcoal samples, four of which were removed from latex pulls taken at the time of the 1965-1966 excavation, and two came from bags collected in 1965 and 1972. One of the bagged charcoal samples reported by Anderson and Wallace (1993)(NZ-7921), has since been shown to have come from a nearby site called Houhora Terrace excavated by Swadling in 1972 (L. Furey, *pers. comm.* 6/5/97) and is, therefore not included in this discussion. The identified charcoal results (NZA-2436, NZA-2437, NZA-2438 and Wk-5485) have a pooled mean age of 668 ± 33 BP, which gives a calibrated age range at 1σ of AD 1294-1329 and AD 1347-1393 [$T' = 2.62$; $\chi^2_{3:0.05} = 7.81$].

Table 7.1: Radiocarbon determinations from Houhora: Archaic layers[1].

| Lab No. | Provenance ^ | Material (Batch) | Species | $\delta^{13}C‰$ | CRA (BP) | Cal 95% (AD) |
|---|---|---|---|---|---|---|
| NZ-914§ | Layer 2b, Square G6 | Charcoal | Not identified | -25† | 697±49 | -- |
| NZ-915§ | Layer 3b, Square E4 | Charcoal | Not identified | -25† | 563±61 | -- |
| NZ-916§ | Layer 3b, Square E3 | Charcoal | Not identified | -25† | 775±61 | -- |
| NZA-2436§ | Base of Layer 2b, Square E6. Pull 2. | Charcoal | *Pittosporum* sp. (20%) *Dodonaea viscosa* (40%) *Leptospermum scoparium* (20%) *Beilschmiedia taraire* twig (205) | -26.2 | 632±86 | 1291-1422 |
| NZA-2437§ | Layer 2b, Square C8. Pull 4. | Charcoal | *Olearia* sp. (25%) *Beilschmiedia taraire* twig (25%) *Pseudopanax* sp. (25%) *Leptospermum scoparium* (25%) | -26.3 | 774±87 | 1216-1300 1376-1379 |
| NZA-2438§ | Layer 3, Square A7. Bagged sample from 1972 excavation. | Charcoal | *Coprosma* sp. (36%) *Pittosporum* sp. (43%) *Brachyglottis repanda* (7%) *Hebe* sp. (24%) | -25.2 | 727±86 | 1262-1328 1349-1391 |
| Wk-5485 | Layer 3b, Square E3. | Charcoal | *Myrsine australis* (100%) | -25.5 | 640±40 | 1300-1375 1380-1407 |
| NZ-5007§ | Layer 2c, Square D9. | "Collagen" | *Anomalopteryx didiformis* *Euryapteryx curtus* *Pachyornis mappini* | -21.1 | 563±56 | 1398-1437 |
| NZ-5008§ | Layer 3b, Square D10. | "Collagen" | *Dinornis struthoides* *Anomalopteryx didiformis* *Euryapteryx curtus* *Pachyornis mappini* | -22.5 | 585±46 | 1320-1340 1395-1427 |
| NZ-7920§ | Layer 2b, Square E6. Pull 2 | Shell | *Austrovenus stutchburyi* *Paphies australis* | 0.9 | 812±37 | 1457-1510 |
| Wk-5034 | Layer 2b, Square D6. | Shell | *Lunella smaragda* (100%) | 1.8 | 960±40 | 1341-1426 |
| Wk-5035 | Layer 2b, Square E7. | Shell | *Austrovenus stutchburyi* (100%) | 0.7 | 1060±45 | 1285-1334 |
| Wk-4920 | Square C8. | Gelatin (Batch A) | *Pagrus auratus* (100%) | -13.6[2] | 1010±40 | 1311-1398 |
| Wk-4921 | Square C8. | Gelatin (Batch A) | *Pagrus auratus* (100%) | -14.2 | 1000±40 | 1316-1404 |
| Wk-4968 | Square C8. | Gelatin (Batch B) | *Pagrus auratus* (100%) | -14.4 | 950±40 | 1362-1432 |
| Wk-4969 | Square C8. | Gelatin (Batch B) | *Pagrus auratus* (100%) | -14.8 | 1050±40 | 1293-1338 |
| OxA-7569 | Square C8. | Tripeptides | *Pagrus auratus* (100%) | -10.9 | 1080±50 | 1268-1324 |

§ See Anderson and Wallace (1993). ^ Pull locations after Anderson and Wallace (1993:11) and L. Furey (*pers. comm.* 6/5/97). † $\delta^{13}C$ assumed, not measured.

[1] Isotopic fractionation ($\delta^{13}C$) for each Wk- sample combusted was determined by a VG Micromass 602C™ Mass Spectrometer at the University of Waikato.

[2] Differences in $\delta^{13}C$ of around 2.0-2.5 ppm occur between the tripeptide dates and the Waikato gelatin samples. This is the result of differences in combustion, pretreatment and sample size, and should not significantly affect the dates as the $\delta^{13}C$ value will correct for any fractionation that has occurred (C. Hendy†, *pers. comm.* 19/5/1997). †Dr. C. Hendy, Department of Chemistry, University of Waikato, Hamilton, New Zealand.

Table 7.2: Typical species composition of NZ-914 and NZ-916.

| Lab No. | Species | Lifespan (McFadgen, Knox and Cole 1994:224). |
|---|---|---|
| NZ-914 | *c.f. Vitex lucens*<br>*Metrosideros excelsa*<br>*Lagarostrobus colensoi*<br>*Prumnopitys taxifolia* | Long: >300 yrs |
| NZ-916 | *c.f. Vitex lucens*<br>*Metrosideros excelsa*<br>*Lagarostrobus colensoi*<br>*Prumnopitys taxifolia*<br>*Prumnopitys ferruginea*<br>*Agathis australis* | Long: >300 yrs |
| | *Myrsine australis* | Short: <100 yrs |

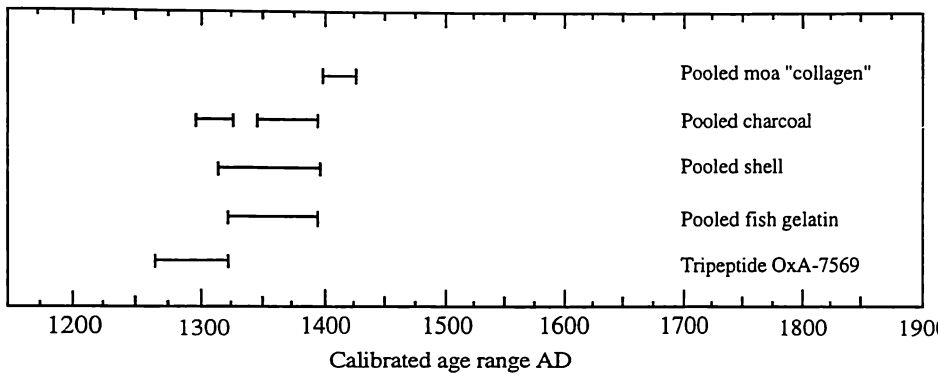
Two more shell determinations were measured at Waikato. These are indistinguishable [$T' = 2.76$; $\chi^2_{1:0.05} = 3.84$] and give a pooled mean age of 1005 ± 31 BP, and a reservoir corrected calibrated age range at 1σ of AD 1317-1396. NZ-7920 was distinguishable from the group [$T' = 19.08$; $\chi^2_{2:0.05} = 5.99$]. This sample was obtained by Anderson and Wallace (1993) from Pull 2, and was considered at the time to be incorrect for some "sample constituent or technical reasons which are not yet understood" (Anderson and Wallace 1993:12). Recent research (Higham 1993; Higham and Hogg 1995; Schmidt 1996) indicates, however, that *Austrovenus stutchburyi* and *Paphies australis* are reliable species for radiocarbon analysis. It is instead suggested that "retouching" of the pulls may have contaminated this sample, as indicated by Coster in correspondence with Anderson and Wallace (1993:11). NZ-7920 is excluded from Figure 7.1.

Two moa bone samples (NZ-5007 and NZ-5008) were collected in 1965-1966 from Layers 2c and 3b (Figure 5.3), but were submitted for dating several years later (Millener 1981). These moa bone "collagen" samples give a pooled mean age of 576 ± 37 BP, and a calibrated age range at 1σ of AD 1399-1427 [$T' = 0.09$; $\chi^2_{1:0.05} = 3.84$]. While the results are statistically indistinguishable, they do not overlap with the pooled charcoal and shell age ranges given in Figure 7.1. Some doubt has been voiced previously about the primary nature of *Anomalopteryx* at Houhora (Millener 1981:240; Anderson 1989a:112), but contamination by modern carbon is considered here to be the most likely cause of this discrepancy. When the radiocarbon content of these bones was measured, the standard pretreatment at IGNS was a simple acid wash.[3] Recent research by van Klinken and Hedges (1995:268) suggests that a significant amount of contamination (possibly > 15%, or > 80 years modern error) could remain following such pretreatment.

[3] Specifically, decalcification with phosphoric acid to remove carbonates (Jansen 1984:29). The resulting residue from such pretreatment is not collagen, but a combination of collagen, its degradation products and contaminants. The composition will, therefore vary depending on pretreatment and preservation state of the bone.

The fish bone gelatin samples have a pooled mean age of 1003 ± 20 BP, and form a coherent group [$T$ = 3.17; $\chi^2_{3:0.05}$ = 7.81], indicating that these results are reproducible. When the standard reservoir correction for marine shell is applied (Stuiver and Braziunas 1993) they give a calibrated result at 1σ of AD 1322-1392. The tripeptide sample (OxA-7569) has a calibrated age range at 1σ of AD 1268-1324, which overlaps with the pooled fish bone gelatin result and is indistinguishable from it [$A'(p)$ = 1014 ± 19 ($T'$ = 5.24; $\chi^2_{4:0.05}$ = 9.49)].

Figure 7.1: Calibrated pooled radiocarbon ages from Houhora, Archaic layers.




Calibrated pooled results of reliable charcoal (NZA-2436, NZA-2437, NZA-2438 and Wk-5034) and shell ages (Wk-5035 and Wk-5035) are shown in Figure 7.1 along with the reservoir corrected pooled snapper gelatin and moa "collagen" results, and the single tripeptide determination. The moa bone "collagen" measurements are clearly too young. The snapper gelatin pooled result overlaps with the pooled charcoal and shell determinations.

Using the OxCal combined probabilities method the combined moa collagen determinations are in poor agreement with other sample types [A = 50.7% (<A'c = 60.0%)]. The overall agreement index for all determinations from Houhora is, however, acceptable at 62.4% (An = 31.6%, n = 5). This gives a calibrated age of AD 1315-1335 (64.3%) and 1346-1350 (3.9%) at 1σ. Removing the moa collagen dates from the calculation improves the overall agreement [n = 4, $A_{overall}$ = 81.1% (An = 35.4)] and gives a calibrated age range of AD 1317-1330 and 1348-1376 at 1σ (see Chapter 8).

These results support the hypothesis outlined in Chapter 5 that snapper from the east coast of New Zealand should not be affected by depleted carbon, and suggest that there is no detectable inbuilt age at this level of precision. Contamination also appears to be minimal. Overall, this series of seven new radiocarbon determinations, and

those acceptable published results, indicate that the Archaic occupation at Houhora began during the early to mid 14th century. This is slightly later than the late 13th century occupation suggested by Anderson and Wallace (1993:14), a result probably influenced by inbuilt age in the unidentified charcoal determinations and the high standard errors associated with the AMS measurements.

## Twilight Beach

Conventional radiocarbon ages and calibrated age ranges for Layer 3 at Twilight Beach are shown in Table 7.3. The diagnostic barracouta sample from Twilight Beach came from two locations, and were pretreated separately. Non-diagnostic bone from these locations was combined and dated.

Table 7.3 Radiocarbon determinations for Twilight Beach, Layer 3.

| Lab No. | Provenance | Material (Batch) | Species | $\delta^{13}C‰$ | CRA (BP) | Cal 95% (AD) |
|---|---|---|---|---|---|---|
| NZ-6579§ | Layer IIIc, Sq. P18/5 6. 14. 15. | Shell | *Paphies ventricosa* | 1.9 | 1005±33 | 1316-1397 |
| Wk-5032 | Layer IIIa, Sq. O20, 3-1. | Shell | *Paphies ventricosa* | 1.2 | 900±40 | 1410-1456 |
| Wk-5033 | Layer IIIa, Sq. Q17, 1-1. | Shell | *Paphies ventricosa* | 0.9 | 930±45 | 1390-1443 |
| Wk-5678 | Layer IIIa, Sq. Q17, 1-1. | Shell | *Paphies ventricosa* | 1.2 | 960±40 | 1341-1426 |
| Wk-5437 | Layer IIIa, Sq. O19, O22, O23 . | Gelatin (Batch B) | *Pagrus auratus* (100%) | -15.1 | 940±40 | 1384-1436 |
| Wk-5438 | Layer IIIa, Sq. P25, P24, O19, O22, O23. | Gelatin (Batch C) | *Pagrus auratus* (~92.8%) scraps† | -14.0 | 950±40 | 1362-1432 |
| Wk-5439 | Layer IIIa, Sq. P25, P24, O19, O22, O23. | Gelatin (Batch D) | *Pagrus auratus* (~92.8%) scraps† | -16.0 | 970±40 | 1332-1421 |

§ From the Jansen database. † see Table A2.2

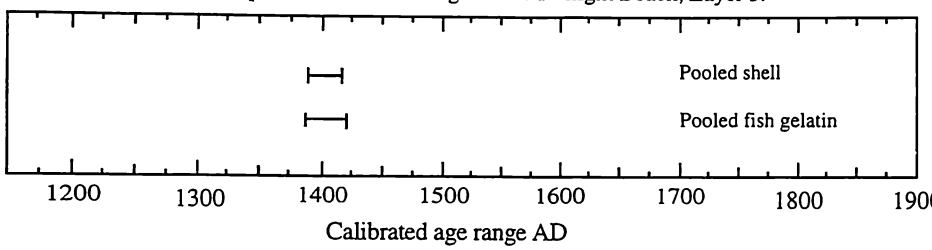
There are four toheroa (*Paphies ventricosa*) determinations from this site. They give a pooled mean age of 956 ± 20 BP (Cal AD 1386-1419 at 1σ [$T' = 4.51$; $\chi^2_{3:0.05} = 7.81$]). Three snapper (*Pagrus auratus*) gelatin results pool at 953 ± 24 BP. This gives a calibrated age range of AD 1385-1423 when the standard marine reservoir correction is applied (Stuiver and Braziunas 1993). The high level of contamination suspected for Batch D (Wk-5439) is not evident in the $^{14}C$ results, with the fish ages being indistinguishable [$T' = 0.29$; $\chi^2_{2:0.05} = 5.99$]. No tripeptide determinations were obtained. The calibrated pooled shell and fish gelatin results are shown in Figure 7.2.

Evaluation of the $^{14}C$ determinations using OxCal suggests that the combined shell and fish gelatin results are in overall agreement [n = 2, $A_{overall}$ = 135.0% (An = 50.0%)].

The combined calibrated age range for Twilight Beach suggests an occupation *ca.* AD 1393-1417 (1σ).

Both methods of comparison, therefore suggest that there is minimum inbuilt age and/or contamination present in the gelatin samples, as suggested in Chapter 6. This series of six new $^{14}C$ results and one existing determination supports the deposition of Layer 3 at Twilight beach in the late 14th to early 15th centuries.

Figure 7.2: Calibrated pooled radiocarbon ages from Twilight Beach, Layer 3.




## Rotokura

Radiocarbon determinations for Rotokura, Layer 3/4 are shown in Table 7.4. The snapper bone gelatin results were derived from a single bulk ground bone sample. The charcoal samples measured at Waikato (Wk-5482, Wk-5483 and Wk-5484) were derived from one sample spit three ways. A charcoal sample previously obtained for this site (NZ-1105) was also used for comparison.

Three $^{14}C$ estimates were taken on identified charcoal removed from archived material belonging to the original NZ-1105 sample. This sample appears to be entirely composed of short lived species (*i.e. Dodonaea viscosa, Melicytus ramiflorus,* and *Coprosma* sp.). This is consistent with Schmidt's (1996:58) observation that the environment around Nelson/Marlborough is conducive to rapid decay, which reduces the possibility of inbuilt age in the charcoal samples. Three charcoal determinations were obtained on this archived material. These three results are statistically indistinguishable [$A(p) = 559 \pm 24$ ($T = 1.69$; $\chi^2_{2:0.05} = 5.99$)]. On the basis of this identification NZ-1105 is also accepted in the following analysis. When pooled all four charcoal samples are indistinguishable [$A'(p) = 565 \pm 29$ ($T' = 0.20$; $\chi^2_{3:0.05} = 7.81$)] and result in a calibrated age range of AD 1405-1428 at 1σ.

Table 7.4: Radiocarbon determinations for Rotokura, Layer 3/4.

| Lab No. | Provenance | Material (Batch) | Species | $\delta^{13}C‰$ | CRA (BP) | Cal 95% (AD) |
|---|---|---|---|---|---|---|
| NZ-1105§ | Layer 4 (middle of layer), Sq. O/63. | Charcoal | Not identified | -25.0 | 586±57 | 1327-1351<br>1363-1365<br>1390-1431 |
| Wk-5482 | Layer 4 (middle of layer), Sq. O/63. | Charcoal | *Dodonaea viscosa*<br>*Melicytus ramiflorus*<br>*Coprosma* sp. | -24.7 | 530±45 | 1410-1440 |
| Wk-5483 | Layer 4 (middle of layer), Sq. O/63. | Charcoal | Duplicate of Wk-5482 | -24.3 | 600±40 | 1327-1350<br>1390-1415 |
| Wk-5484 | Layer 4 (middle of layer), Sq. O/63. | Charcoal | Duplicate of Wk-5482 | -24.4 | 540±40 | 1409-1438 |
| Wk-4887 | Layer 4, Sq. O61. | Shell | *Paphies australis*<br>*Protothaca crassicosta*<br>*Lunella smaragda*<br>*c.f. Haliotis iris* | 1.4 | 1040±40 | 1298-1352 |
| Wk-4953 | Layer 3/4, Sq. O61 and N62. | Gelatin (Batch A) | *Pagrus auratus* (100%) | -14.7 | 940±40 | 1384-1436 |
| Wk-4954 | Layer 3/4, Sq. O61 and N62. | Gelatin (Batch A) | *Pagrus auratus* (100%) | -15.2 | 960±45 | 1336-1429 |
| Wk-4955 | Layer 3/4, Sq. O61 and N62. | Gelatin (Batch A) | *Pagrus auratus* (100%) | -16.4 | 910±45 | 1402-1453 |
| OxA-7570 | Layer 3/4, Sq. O61 and N62. | Tripeptides | *Pagrus auratus* (100%) | -11.9 | 1045±45 | 1293-1352 |

§ From Leach and Boocock (1994:70) and Butts (1978:9).

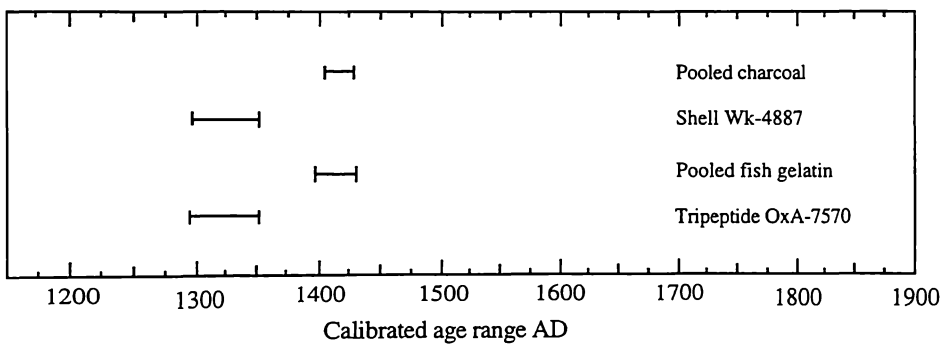
Two samples of shell were selected for analysis from Rotokura, one was analysed by XRD and found to be recrystallised. The second (Wk-4887) yielded a CRA of 1040 ± 40 BP and a calibrated result of AD 1298-1352 at 1σ. This does not overlap with the charcoal determinations (Figure 7.3). Wk-4887 is considered to be suspect for a number of reasons. First, the shell sample was composed of a number of different species (*i.e. Paphies australis, Protothaca crassicosta, Lunella smaragda* and *Haliotis iris*). Although *Paphies australis* is reliable, the other three shell species have not been thoroughly tested. Consequently, Schmidt (1996:161) and Higham *et al.* (in prep) do not recommend the use of samples composed of mixed species until further research has been undertaken. In addition, the storage history of this sample is poorly known. Third, shell needs to be carefully selected for radiocarbon analysis as basal deposits may become mixed with natural beach shells[4] (Schmidt 1996:140-142).

The snapper (*Pagrus auratus*) gelatin results are statistically indistinguishable [$A(p) = 937 \pm 25$ ($T = 0.63$; $\chi^2_{2:0.05} = 5.99$)] and give a pooled mean at 1σ of Cal AD 1397-1432 when the standard reservoir correction for marine shell is applied (Stuiver and Braziunas 1993). The tripeptide determination; OxA-7570 (1045 ± 45 BP) does not overlap the pooled gelatin determination when calibrated at 1σ (AD 1293-1352), and when pooled with the gelatin results, the fish results as a whole are distinguishable [$A'(p) = 966 \pm 24$ ($T' = 4.43$; $\chi^2_{2:0.05} = 3.84$)].

[4] Although a lower layer (Layer 6) was identified at Rotokura, it was of limited distribution. Shell from this layer could also have become incorporated in Layer 4 and although Layer 6 has not been dated, Challis (1991:122-126) has noted a progression in artefact forms between Layer 4 and Layer 6.

The calibrated tripeptide and the single marine shell (Wk-4887) results are shown in Figure 7.3, along with pooled results of the charcoal and reservoir corrected date for the fish bone gelatin. Figure 7.3 clearly demonstrates that the fish gelatin and tripeptide results do not overlap. The tripeptide result is around 100 years older. Inbuilt age alone does not account for this discrepancy, but upwelling on the west coast of New Zealand could have introduced an error of this magnitude. If the tripeptide determination is correct, then a significant level of modern contamination (>10%) is required in the gelatin samples to account for the masking of this effect. Such high levels of contamination are considered to be unlikely for a number of reasons. First, the fish bone gelatin ages overlap with the reliable charcoal results. Second, although contamination was noted in the FTIR of the Rotokura acid insoluble fraction (Chapter 6), gelatinisation alone is considered to remove better than 8% contamination (van Klinken and Hedges 1995:268). If contaminated with modern (1950) carbon this equates to a possible error of <77 years, which could account for this discrepancy. Contamination is likely, however, to be a variety of ages.

Figure 7.3: Calibrated pooled radiocarbon ages from Rotokura, Layers 3/4.




This assessment is supported by the results obtained using the OxCal combined probabilities method. The tripeptide and gelatin results fall below the 60.0% threshold for an acceptable combination [n = 2, $A_{overall}$ = 55.5% (An = 50.0%)], and when combined with other sample types the overall agreement index for Rotokura is 46.0% (An = 35.4%, n = 4). Removing the suspect shell (Wk-4887) and tripeptide determinations increases the overall agreement index for Rotokura [(n = 2, $A_{overall}$ = 138.1% (An = 50.0%)] and gives an acceptable combined calibrated age range of AD 1407-1425 at 1σ.

There is currently insufficient data to adequately evaluate this situation. From the results of charcoal and fish bone gelatin radiocarbon determinations, the deposition of Layer 4 at Rotokura can be placed in the late 14th to early 15th century. This is in

keeping with Millar's (1967:10-11) estimated time of occupation based on artefactual and economic evidence. A date in the late 13th to mid 14th century, as suggested by the tripeptide estimate and Wk-4887 is at variance with the date expected on archaeological evidence.

## Tata Beach

Conventional radiocarbon and calibrated ages for Tata Beach, ESW/5, Layer 3 are shown in Table 7.5. Fish bone was obtained from upper, intermediate and lower lenses, and from a sample of undifferentiated Layer 3 midden. Each sample was pretreated separately.

Table 7.5: Radiocarbon determinations for Tata Beach (ESW/5), Layer 3.

| Lab No. | Provenance | Material (Batch) | Species | $\delta^{13}C‰$ | CRA (BP) | Cal 95% (AD) |
|---|---|---|---|---|---|---|
| Wk-4864 | Lower lens. | Shell | *Paphies australis* | 1.3 | 780±40 | 1473-1536 |
| Wk-4865 | Lower lens. | Shell | *Austrovenus stutchburyi* | 0.7 | 810±40 | 1456-1513 |
| Wk-4866 | Upper lens. | Shell | *Paphies australis* | 1.5 | 840±40 | 1442-1491 |
| Wk-4867 | Upper lens. | Shell | *Austrovenus stutchburyi* | 0.8 | 730±40 | 1509-1633 |
| Wk-4894 | Lower lens. | Charcoal | *Pteridium esculentum*<br>*Cordyline australis*<br>*Metrosideros* sp.<br>*Olearia* sp.<br>*Myoporum laetum*<br>*Pseudopanax colensoi*<br>*Melicytus ramiflorus* | -27.0 | 360±40 | 1490-1644 |
| Wk-4893 | Upper lens. | Charcoal | *Pteridium esculentum*<br>*Cordyline australis*<br>*Metrosideros* sp.<br>*Myoporum laetum*<br>*Melicytus ramiflorus*<br>*Nothofagus* sp. (twig) | -26.8 | 420±40 | 1443-1520<br>1596-1622 |
| Wk-5134 | Upper lens. | Gelatin (Batch A) | *Thyrsites atun* (100%) | -15.7 | 680±40 | 1549-1664 |
| Wk-6033 | Midden. | Gelatin (Batch B) | *Thyrsites atun* (100%) | -17.0 | 750±50 | 1486-1621 |
| Wk-5135 | Intermediate/Lower lens. | Gelatin (Batch C) | *Pseudophycis bachus* (100%) | -16.9 | 680±50 | 1540-1668 |
| Wk-6032 | Midden. | Gelatin (Batch D) | *Pseudophycis bachus* (100%) | -16.2 | 780±45 | 1471-1540 |
| Wk-6034 | Midden. | Gelatin (Batch E) | Fish scrap predominantly red cod | -16.0 | 720±40 | 1516-1640 |
| OxA-7568 | Upper lens. | Tripeptides | *Thyrsites atun* (100%) | -12.3 | 795±45 | 1462-1528 |

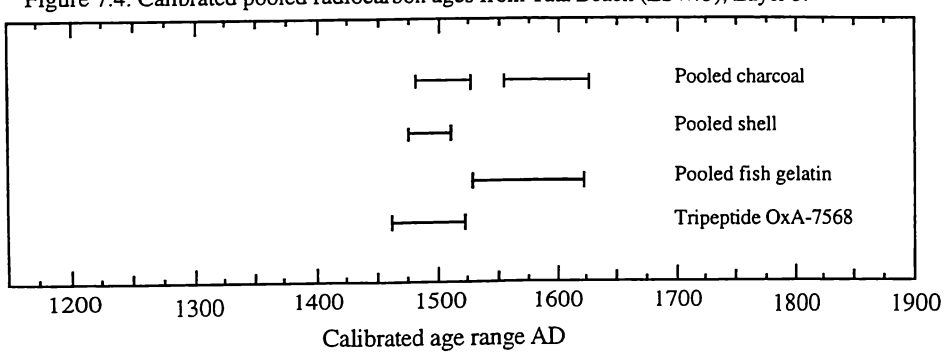
Four shell determinations (two on *Austrovenus stutchburyi* and two on *Paphies australis*) give a pooled result of 789 ± 21 BP [$T' = 4.13$; $\chi^2_{3:0.05} = 7.81$] and a calibrated age range at 1σ of AD 1478-1516. These overlap with the two charcoal estimates from the site [$A'(p) = 387 \pm 30$ ($T' = 1.13$; $\chi^2_{1:0.05} = 3.84$)] which calibrate at AD 1482-1528 and 1558-1632 at 1σ. As already noted (Chapter 5) a number of

differences were identified between the lower, red cod dominated midden and the upper, barracouta-dominated unit. Aside from species composition, these included a change in charcoal composition, and evidence of disturbance at the top of the lower midden, represented by the diffuse intermediate unit. These shell and charcoal results suggest no significant time separation between upper and lower midden units.

The analysis of fish bone from Tata Beach presented in Chapter 6 indicated that bone from the red cod samples was of poorer preservation than the barracouta. This may reflect differences in bone element chemistry between species or prehistoric preparation, but is most likely due to differential exposure during deposition. The fish bone samples (barracouta and red cod) as a group are indistinguishable, however, with a pooled age of 720 ± 20 BP [$T' = 3.78$; $\chi^2_{4:0.05} = 9.49$] and a calibrated result of AD 1529-1625 at 1σ. A barracouta tripeptide result (OxA-7568) was also obtained and gave a calibrated age range at 1σ of AD 1462-1528. This is statistically indistinguishable from the pooled gelatin determinations [$A'(p) = 732 \pm 18$ ($T' = 6.09$; $\chi^2_{5:0.05} = 11.07$)], but does not overlap with them when calibrated.

The pooled shell, charcoal, and fish gelatin results are shown in Figure 7.4 along with the single tripeptide estimate. Although the fish gelatin dates overlap with the upper age range of the charcoal they do not overlap with shell results, and are distinguishable from them [$T' = 5.66$; $\chi^2_{2:0.05} = 3.84$]. This may be a consequence of young contamination as noted in Chapter 6 for the Tata Beach fish bone. This conclusion is supported by the single tripeptide determination which, although being indistinguishable from the gelatin ages, is slightly older and overlaps with both shell and charcoal pooled results. The agreement between the tripeptide determination and these other two sample types suggests that any influence from upwelling, a possible cause of anomalous results for fish caught on the west coast of New Zealand, is insignificant at this level of precision. These results also indicate that error introduced by contamination will be difficult to detect.

Figure 7.4: Calibrated pooled radiocarbon ages from Tata Beach (ESW/5), Layer 3.



Using the OxCal combined probabilities method it is apparent that the tripeptide determination (OxA-7568) does not agree with the fish gelatin results [(A = 53.4% (<A'c = 60.0%)], but overall the fish results are in agreement [n = 6, $A_{overall}$ = 67.3% (An = 28.9%)]. The overall agreement index for Tata Beach, however, is low [(n=4, $A_{overall}$ = 46.4% (An = 35.4%)], and the fish gelatin samples are in poor agreement with all other sample types [A = 24.9% (<A'c = 60.0%)]. Excluding the fish gelatin results improves the overall agreement index for Tata Beach [(n = 3, $A_{overall}$ = 143.6% (An = 4 0.8%)] and the remaining sample types give an acceptable combined calibrated age at 1σ of AD 1484-1510.

The reliable shell and charcoal results suggest an occupation at Tata Beach, ESW/5 in the late 15th to early 16th century. This is in-keeping with Barber's (1998:11) hypothesis of a 15th to 16th century deposition for layer 3 on the basis of radiocarbon determinations of comparable sites nearby. The fish gelatin results suggest an occupation in the mid to late 16th century, an estimate slightly later, but still within the charcoal and shell age ranges.

## Shag River Mouth

Conventional radiocarbon ages and calibrated dates from Shag River Mouth, Layer 4 are shown in Table 7.6. Fish bone selected for analysis came from three locations; a bulk sample from squares E7, E8, F7 and F8, and smaller samples from square J8 and square H8. These were pretreated separately.

A single charcoal sample (NZ-7761) from Shag River Mouth, layer 4, gave a CRA of 600 ± 50 BP and a calibrated age range of AD 1325-1353, 1359-1368 and 1389-1420 (1σ).

Two moa bone determinations were obtained by Anderson, Smith and Higham (1996). NZ-7743 a moa bone "collagen" result, was 600 years older than expected and is, therefore discarded from the following analysis (for discussion of this sample and radiocarbon results from other areas of Shag River Mouth see Chapter 8). The second moa bone determination (Wk-5433) on moa gelatin resulted in a calibrated age range of AD 1300-1375 and 1380-1407 at 1σ [CRA = 640 ± 40 BP]. The preservation state of this moa bone sample was described as anomalous in Chapter 6, and therefore probably originated from a sub-fossil deposit. The result is apparently satisfactory, but until further research is carried out anomalous samples such as Wk-5433 should be avoided.

Table 7.6: Radiocarbon determinations for SM/C:Dune, Layer 4.

| Lab No. | Provenance | Material (Batch) | Species % | $\delta^{13}C‰$ | CRA (BP) | Cal 95% (AD) |
|---|---|---|---|---|---|---|
| NZ-7761 | Sq. E7. | Charcoal | *Hoheria* (37)<br>*Pittosporum* (23)<br>*Coprosma* (20)<br>*Myrsine australis* (10)<br>*Pseudopanax* (7)<br>*P. eugenioides* (3). | -26.0 | 600±50 | 1325-1353<br>1359-1368<br>1389-1420 |
| NZ-7743 | Sq. H8. | "Collagen" | Medium sized moa proximal L. tibiotarsus | -24.9 | 1201±38 | 816-846<br>856-893<br>918-953 |
| Wk-5433 | Sq. G8 upper. | Gelatin | Unidentified sp. | -26.2 | 640±40 | 1300-1375<br>1380-1407 |
| Wk-2751 | Sq. F7. | Shell | *Austrovenus stutchburyi* | 1.0 | 960±45 | 1336-1429 |
| Wk-2410 | Sq. F7. | Shell | *Austrovenus stutchburyi* | 1.5 | 1020±50 | 1302-1398 |
| Wk-2411 | Sq. F7. | Shell | *Austrovenus stutchburyi* | 0.8 | 990±45 | 1318-1412 |
| Wk-2412 | Sq. F7. | Shell | *Austrovenus stutchburyi* | 1.2 | 980±45 | 1323-1418 |
| Wk-2362 | Sq. G8. | Shell | *Austrovenus stutchburyi* | 1.3 | 1010±50 | 1307-1403 |
| NZ-7805 | Sq. H8. | Shell | *Austrovenus stutchburyi* | 0.7 | 965±26 | 1350-1417 |
| Wk-2508 | Sq. H8. | Shell | *Austrovenus stutchburyi* | -0.7 | 1060±45 | 1285-1334 |
| Wk-2632 | Sq. J5. | Shell | *Paphies australis* | 1.4 | 980±40 | 1326-1415 |
| Wk-2752 | Sq. J5. | Shell | *Mytilus edulis aoteanus* | 1.0 | 1040±45 | 1296-1371 |
| Wk-2856 | Sq. J5. | Shell | *Austrovenus stutchburyi* | 1.0 | 980±40 | 1326-1415 |
| Wk-2857 | Sq. J5. | Shell | *Austrovenus stutchburyi* | 1.0 | 950±45 | 1348-1434 |
| Wk-2440 | Sq. J5. | Shell | *Austrovenus stutchburyi* | 0.7 | 1050±50 | 1288-1351 |
| Wk-2441 | Sq. J5. | Shell | *Austrovenus stutchburyi* | 1.0 | 1070±45 | 1279-1327 |
| Wk-4930 | Sqs. E7/E8/F7/F8. | Gelatin (Batch A) | *Thyrsites atun* (~67.95%)† | -16.3 | 880±40 | 1421-1467 |
| Wk-4971 | Sqs. E7/E8/F7/F8. | Gelatin (Batch A) | *Thyrsites atun* (~67.95%)† | -16.7 | 870±40 | 1427-1473 |
| Wk-4970 | Sqs. E7/E8/F7/F8. | Gelatin (Batch B) | *Thyrsites atun* (~67.95%)† | -15.6 | 940±40 | 1384-1436 |
| Wk-5131 | Sqs. E7/E8/F7/F8. | Gelatin (Batch C) | *Thyrsites atun* (~67.95%)† | -16.0 | 1040±45 | 1296-1371 |
| Wk-5434 | Sq. H8, upper spit 2. | Gelatin (Batch D) | *Thyrsites atun* (~67.95%)† | -16.4 | 910±45 | 1402-1453 |
| Wk-5435 | Sq. J8, upper. | Gelatin (Batch E) | *Thyrsites atun* (~67.95%)† | -16.2 | 990±40 | 1320-1409 |
| OxA-7793 | Sqs. E7/E8/F7/F8. | Tripeptide | *Thyrsites atun* (~67.95%)† | -14.1 | 1155±55 | 1191-1292 |
| OxA-7593 | Sqs. E7/E8/F7/F8. | Tripeptide | *Thyrsites atun* (~67.95%)† | -13.1 | 1155±45 | 1203-1287 |

All radiocarbon determinations except those on fish and Wk-54533 from Anderson, Smith and Higham 1996:table 17.1). † see Table A2.5.

There are fourteen shell determinations from layer 4. All *Amphibola crenata* results have been excluded because this species is unreliable (Anderson, Smith and Higham 1996; Higham and Hogg 1995:409). One estimate on *Haliotis iris* differed from that expected by 300 years and is also excluded from Table 7.6. The remaining 13 shell

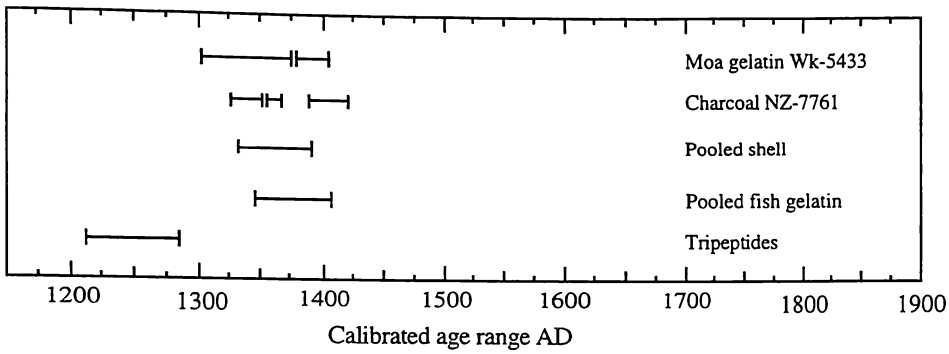
determinations pool at 999 ± 12 and give a calibrated age range at 1σ of AD 1328-1390 [$T' = 10.73$; $\chi^2_{12:0.05} = 21.03$].

Six barracouta (*Thyrsites atun*) gelatin estimates were obtained during this analysis. Wk-4930 and Wk-4971 both came from pretreatment batch A and gave results 100 years younger than previously established for the Shag River Mouth site. These dates were also distinguishable from the rest of the fish bone gelatin results [$T' = 12.19$; $\chi^2_{5:0.05} = 11.07$]. No contamination was identified in the FTIR spectrum of the Shag River Mouth acid-insoluble fraction (see Chapter 5), and it is hypothesised that laboratory related error or operator inexperience is responsible as these were among some of the first bones pretreated. Determinations belonging to pretreatment batch A are, therefore discarded. The remaining four barracouta gelatin results are indistinguishable and have a pooled mean of 970 ± 22 BP [$T' = 5.01$; $\chi^2_{3:0.05} = 7.81$], and a reservoir corrected calibrated age range at 1σ of AD 1348-1412.

Two tripeptide determinations were also obtained (OxA-7593 and OxA-7793). These are indistinguishable and pool at 1155 ± 35 [$T = 0.0$; $\chi^2_{1:0.05} = 3.84$]. The tripeptide results do not, however, agree with the gelatin results [$A'(p) = 1022 \pm 21$ ($T' = 20.03$; $\chi^2_{5:0.05} = 3.84$)].

The calibrated pooled results for reliable shell, fish gelatin and tripeptides are presented in Figure 7.5 along with the charcoal $^{14}C$ estimate (NZ-7761) and the moa bone gelatin determination (Wk-5433). The fish gelatin and tripeptide ages do not overlap. In Chapter 5 it was noted that the barracouta along the east coast of the South Island may be influenced by $^{14}C$ depleted subantarctic waters at the Subtropical Convergence which could account for the discrepancy in the Shag River Mouth samples. In order to mask an additional *ca.* 100 year ΔR the gelatin samples would require modern contamination at levels greater (*i.e.* 10%) than typically expected following gelatinisation (< 8%). While theoretically possible, this is not supported by the results given in Chapter 5 which indicate no detectable contamination in the FTIR spectra. Further, at this level of precision the fish bone gelatin ages overlap with the single charcoal and the pooled shell results for Layer 4. If depleted $\Delta^{14}C$ values had affected the Shag River Mouth barracouta samples, then other sites along this coastline should also have anomalous $^{14}C$ determinations. This does not appear to be the case at Pleasant River and Long Beach (see below). Because fish remains from both of these sites were well-preserved, contamination masking a reservoir effect is also considered to be unlikely.

Figure 7.5: Calibrated pooled radiocarbon ages from SM/C:Dune, Layer 4.




The Shag River Mouth determinations were also evaluated using OxCal combined probabilities method. The 6 fish gelatin estimates are not in agreement [n = 5, $A_{overall}$ = 33.2% (An = 31.6%)], with the batch A gelatin and Wk-5131 falling below the 60% threshold for intrusive results [A = 32.4% (<A'c = 60.0%) and A = 23.7% (<A'c = 60.0%) respectively]. Combination following the removal of the batch A gelatin determinations results in better agreement between the remaining gelatin results [n = 4, $A_{overall}$ = 67.8% (An = 35.4%)]. They do not, however, combine with the combined tripeptide result [n = 5, $A_{overall}$ = 3.8% (An = 31.6%)].

The overall agreement index for Shag River Mouth (excluding batch A samples) is 3.9% (An = 31.6%, n = 5) which falls well below the required 60.0%. Only the tripeptide samples are considered, however, to be in poor agreement with the other sample types [A = 0.1% (<A'c = 60.0%)]. When the tripeptide determinations are excluded the remaining sample types are in agreement [n = 4, $A_{overall}$ = 96.2% (An = 35.4%)] and give a combined calibrated age range of AD 1340-1370 (1$\sigma$).

Anderson, Smith and Higham (1996:67) have concluded previously that Shag River Mouth was occupied in the mid 14$^{th}$ century for a period of perhaps 20-50 years, with no apparent difference between the base of the SM/C:Dune excavation and the top layers, nor in the broad areal extent of the site. The barracouta gelatin results support the existence of fishing activities at the site at this time. The tripeptide dates appear to be erroneous. Futher research is required to understand the precise reason for this anomalous result.

## Pleasant River

Radiocarbon determinations for Areas 3 and 7 at Pleasant River are shown in Table 7.7. Two fish bone samples were selected from Layer 2a; a sample of barracouta pharyngobranchials and fish spines. These were pretreated separately.

Table 7.7: Radiocarbon determinations for Pleasant River, Areas 3 and 7.

| Lab No. | Provenance | Material (Batch) | Species | $\delta^{13}C‰$ | CRA (BP) | Cal 95% (AD) |
|---|---|---|---|---|---|---|
| NZA-2802 | Area 3 Layer 1, Sq. A1. | Charcoal | *Olearia* sp. (100 %) | -25.1 | 494±62 | 1414-1452<br>1460-1479 |
| NZA-3740 | Area 7 Layer 2a, Sq. B2. | Charcoal | *Discaria toumatou* | -27.4 | 624±65 | 1298-1415 |
| Wk-3509 | Area 7 Layer 1, Sq. A4. | Shell | *Austrovenus stutchburyi* | 1.0 | 760±40 | 1486-1558 |
| Wk-3510 | Area 7 Layer 2a, Sq. A5/B4-5. | Shell | *Austrovenus stutchburyi* | 0.5 | 720±40 | 1516-1640 |
| Wk-5169 | Area 7 Layer 2a, Sq. A3 and B4. | Gelatin | *?Eu. geranoides*<br>Moa ?sp. | -26.2 | 580±45 | 1330-1346<br>1392-1429 |
| Wk-4956 | Area Layer 2a/ 1, Sq. A4. | Gelatin (Batch A) | *Thyrsites atun* (>65.71%)† | -16.0 | 790±40 | 1468-1528 |
| Wk-5031 | Area 7 Layer 2a/ 1, Sq. A4. | Gelatin (Batch B) | *Thyrsites atun* (>65.71%)† | -16.8 | 680±40 | 1549-1664 |
| Wk-5036 | Area 7 Layer 2a/ 1, Sq. A4. | Gelatin (Batch C) | *Thyrsites atun* (100% ) | -16.4 | 780±40 | 1473-1536 |
| NZ-8099 | Area 7 Layer 2b, Sq. B6-7. | Charcoal | *Ribbonwood %?*<br>*Discaria toumatou*<br>*Pittosporum sp.*<br>*Myrsine australis*<br>*Olearia sp.*<br>*Hebe sp.* | -28.0 | 624±37 | 1317-1370<br>1386-1410 |

All $^{14}C$ determinations, except those on fish and Wk-5169, from I. Smith (*pers. comm.* to T. Higham 15/9/1995). † see Table A2.6.

Two shell estimates have been obtained for Area 7, Layer 1 (Wk 3509) and Layer 2a (Wk 3510). These are statistically indistinguishable ($A'(p)$ = 740 ± 28 BP [Cal AD 1509-1583 at 1σ ($T'$ = 0.05; $\chi^2_{1:0.05}$ = 3.84 )].

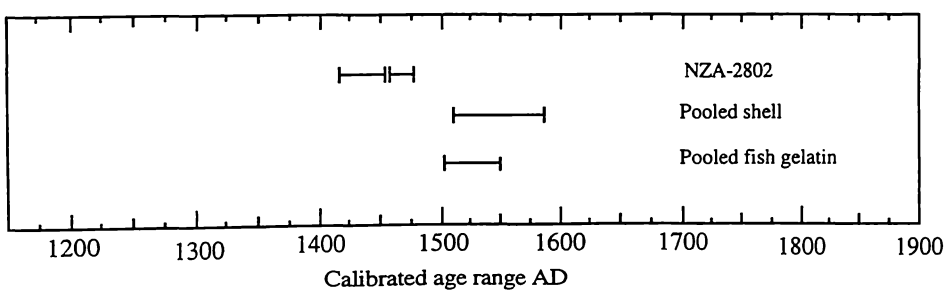
The charcoal determinations (NZA-2802 and NZA-3740) are also statistically indistinguishable [$A'(p)$ = 531 ± 47 ($T'$ = 2.10, $\chi^2_{1:0.05}$ = 3.84)] and gave a calibrated pooled range of AD 1410-1441 at 1σ. They do not, however, overlap with the shell results from the same layer. It is possible that both charcoal samples may be affected by inbuilt age because *Discaria toumatou* and *Olearia* sp. may live to between 100 and 300 years (McFadgen, Knox and Cole 1994:224, table 1). It is likely, however, that NZA-3740 dates the earlier occupation (Smith, *pers. comm.* 23/10/96) because the result is identical to a charcoal determination (NZ-8099) from the lower horizon (Layer 2b, Area 7), and because NZA-3740 comes from a square noted for less dense midden surrounding an old excavation. Although NZA-2802 is removed from this disturbance and is in better agreement with the shell results, with a calibrated age range of AD

1414-1452 and 1460-1479 at 1σ, they do not overlap. Both charcoal estimates are excluded as unreliable.

The moa bone (PLR-1038) sample selected for dating despite its apparent removal from Layer 2a, gives a CRA of 580 ± 45 BP and a calibrated age range of AD 1330-1346 and 1392-1429 at 1σ. This is closer to results obtained from Layer 2b (Table 7.7). Contextual mis-placement is suggested, either from modern or prehistoric disturbance. This is supported by anomalous N% values (see Chapter 5) and evidence of disturbance elsewhere at the site, including thinning of the layers to the south, which may also be responsible for the anomalous NZA-2802 result (I. Smith, *pers. comm.* 23/10/96). Unfortunately, because this sample included several moa bones, the inclusion of moa from different periods of occupation cannot be discounted. Wk-5169 is, therefore excluded from this analysis.

Three barracouta (*Thyrsites atun*) gelatin determinations have been obtained. These are statistically indistinguishable, pooling at 750 ± 23 BP [$T' = 4.63$; $\chi^2_{2:0.05} = 5.99$]. When the marine reservoir correction is applied they give a calibrated age range of AD 1504-1550 at 1σ. This overlaps the pooled shell result (Figure 7.7). These determinations uphold the assessment that the Pleasant River bone was well-preserved and, that no additional reservoir effect is present. No tripeptide results were obtained.

Figure 7.6: Calibrated pooled radiocarbon ages from Pleasant River, Layers 1 and 2a.




When all dates from Pleasant River, Layers 1 and 2a are combined using the OxCal combined probabilities method the overall agreement falls below that expected for an acceptable grouping [n = 3, $A_{overall}$ = 0.2% (An = 40.8%)]. This upholds the suggestion, given above, that the site has been disturbed.

When the fish gelatin determinations are combined separately Wk-5031 appears to be intrusive [A = 55.9% (<A'c = 60.0%)]. As a whole, however, the fish gelatin determinations are in agreement [n = 3, $A_{overall}$ = 61.0% (An = 40.8%)]. When

compared with the shell results from Pleasant River the overall agreement index is 122.8% (An = 50.0%, n = 2). The combined shell and fish gelatin results give an acceptable calibrated result of AD 1509-1554 (1σ).

These radiocarbon results on shell, barracouta and moa bone gelatin support the previous hypotheses that post-depositional disturbance has affected radiocarbon results at Pleasant River. They also support the suggestion that Layers 1 and 2a in Areas 3 and 7, represent an occupation in the early to mid 16th century which concentrated on fishing and gathering activities (I. Smith, *pers. comm.* 23/10/96).

## Long Beach

Radiocarbon determinations for Long Beach, Layer 2 are shown in Table 7.8. Fish bone for dating was selected from two squares and sorted into diagnostic and non-diagnostic fish bone (scrap), which were pretreated and dated separately.

Table 7.8: Radiocarbon determinations for Long Beach, Layer 2.

| Lab No. | Provenance | Material (Batch) | Species | $\delta^{13}C‰$ | CRA (BP) | Cal 95% (AD) |
|---|---|---|---|---|---|---|
| NZ-4702§ | Sq. 2Z? | Charcoal | *Leptospermum* (dominant) *Hebe* (minor) *Coprosma* (subdominant) *Myrsine* | -24.1 | 305±82 | 1496-1511 1516-1599 1618-1673 1780-1801 1944-1948 |
| NZ-4703§ | Sq. 2Y? | Charcoal | *Podocarpus totara* (minor) *Myrsine* sp. (dominant) *Hoheria* or *Plagianthus* sp. (minor) *Coprosma* sp. (minor) *Pittosporum* sp. (minor) | -22.2 | 440±56 | Old wood |
| Wk-5636 | Sq. 3E. | Shell | *Paphies australis* | 1.7 | 650±40 | 1627-1678 |
| Wk-5637 | Sq. 3E. | Shell | *Paphies australis* | 1.7 | 620±45 | 1647-1694 |
| Wk-5679 | Sq. 3E. | Shell | *Paphies australis* | 1.8 | 570±40 | 1676-1732 |
| Wk-5680 | Sq. E5. | Gelatin (Batch A) | *Thyrsites atun* (~63.64%) scrap† | -15.9 | 600±40 | 1661-1702 |
| Wk-5681 | Sq. F1. | Gelatin (Batch B) | *Thyrsites atun* (~73.68%) scrap† | -15.9 | 570±40 | 1676-1732 |
| Wk-5682 | Sq. F1. | Gelatin (Batch C) | *Thyrsites atun* (~73.68%) scrap† | -15.0 | 540±30 | 1694-1813 |
| Wk-5683 | Sqs. F1 and E5. | Gelatin (Batch D) | *Thyrsites atun* (100%) | -15.9 | 550±40 | 1684-1813 |

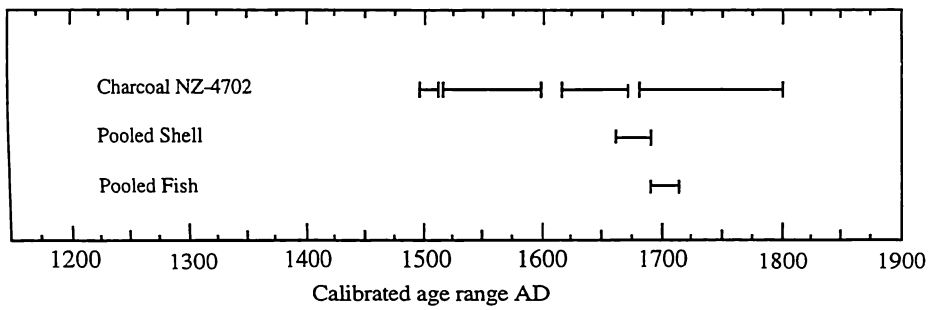
§ From Anderson 1991:774, table 1 and Hamel and Leach 1979:12). † see Tables A2.7 and A2.8.

Two charcoal determinations have been obtained for Layer 2. NZ-4703 contained samples of totara (*Podocarpus totara*), a long lived species, and has been discarded.

NZ-4702 gives a calibrated age range of AD 1496-1511, 1516-1599, 1618-1673, 1780-1801 and AD 1944-1948 at 1σ. Three pipi (*Paphies australis*) shell samples were measured for comparison. They give a pooled mean age of Cal AD 1661-1688 at 1σ [$A'(p)$ = 614 ± 24 ($T'$ = 2.04; $\chi^2_{2:0.05}$ = 5.99)].

The barracouta (*Thyrsites atun*) gelatin samples were reproducible and resulted in a marine reservoir corrected calibrated age range of AD 1688-1717 at 1σ [$A'(p)$ = 561 ± 18 ($T'$ = 1.57; $\chi^2_{3:0.05}$ = 7.81)]. No tripeptide determinations were obtained.

Figure 7.7: Calibrated pooled radiocarbon ages from Long Beach, Layer 2.




The reservoir corrected, calibrated pooled results of shell and barracouta gelatin ages and NZ-4702 are shown in Figure 7.7. From Figure 7.7 it can be seen that the fish bone gelatin pooled result overlaps with the pooled charcoal and shell determinations. 'Wiggles' in the atmospheric calibration curve have, however, resulted in the artificial spreading of the calibrated results of charcoal sample NZ-4702 (McFadgen, Knox and Cole 1994). The marine samples do not display this variation because the dilution effect of the oceanic reservoir smooths the marine calibration curve allowing more precise calender ages to be obtained (Higham 1993:120).

Following evaluation with OxCal the overall agreement index for Long Beach is low at 55.3% (An = 40.8%, n = 3); Cal AD 1679-1696 at 1σ], and the charcoal sample is considered to be an intrusive determination [A = 47.7% (<A'c = 60.0%)]. When NZ-4702 is excluded the overall agreement improves [n = 2, $A_{overall}$ = 81.8% (An = 50.0%)] and the shell and fish gelatin results suggest an occupation *ca.* AD 1682-1699 (1σ).

The marine determinations support an occupation of Long Beach, Layer 2 in the late 17th century. This is in keeping with Leach and Hamel's (1981:112) assessment based on evidence of material culture.

## CONCLUSION

From analyses presented in Chapter 5 it was suggested that fish bone from Long Beach, Pleasant River and Shag River Mouth should all produce accurate and reproducible results. It was also concluded that snapper bone from Houhora and Twilight Beach should give reliable dates when pretreated to gelatin as they were both moderately well-preserved, though low levels of contamination were identified in the acid insoluble fraction. These conclusions are upheld by the suite of reproducible fish gelatin estimates that were comparable to results of other sample types. Two samples from Shag River Mouth, however, produced results 50 to 100 years too young, possibly the result of laboratory-based pretreatment or sample preparation error.

The preservation state of fish bone from Tata Beach and Rotokura was suspect due to the identification of high levels of contamination in the acid-insoluble FTIR spectra of these samples. In the case of Rotokura, this was attributed to clay contamination, which should have been largely removed by the gelatin process. This conclusion is supported by the gelatin determinations, which are indistinguishable from charcoal found at the site. Bone from Tata Beach was the least well-preserved sample analysed (barracouta = 29 - 37% collagen remaining; red cod = 27% collagen remaining), and bordered on the Class III preservation state not recommended for radiocarbon analysis. The Tata Beach results were variable and distinguishable from associated marine shell results.

Tripeptide determinations obtained on bone samples from Houhora, Rotokura, Tata Beach and Shag River Mouth do not support these conclusions. In every case the Oxford results were older than associated fish gelatin ages and at Shag River Mouth and Rotokura they were statistically different from the fish gelatin and other sample types. It is possible that this is the result of contamination in the gelatin samples masking reservoir effects or an inbuilt age (snapper only). The evidence does not support this conclusion. First, all gelatin results, both snapper and barracouta are indistinguishable or only slightly younger (*i.e.* Tata Beach) than reliable ages on other sample types. Second, at Rotokura and Shag River Mouth an error of up to 100 years is suggested by the tripeptide estimates. Such high levels of modern contamination (*ca.* 10%) should have been detected by assessment methods used in Chapter 5 and although the bone from Rotokura was suspect, no contamination was identified in the Shag River Mouth fish bone. Third, the gelatinisation method should leave no more than 77 years modern contamination in a sample of 1000 BP. This is a maximum error and would be extremely unlikely. Fourth, no inbuilt age or reservoir effect was

noted in other samples from comparable locations. Fifth, the separation and dating of tripeptides is still largely experimental. There are few published accounts on samples of comparable age to those run here, and none of equal precision[5]. The possibility of laboratory induced contamination has also been noted (van Klinken, Bowles and Hedges 1994:2548).

Taken together these results support the use of the marine reservoir curve (Stuiver and Braziunas 1993) to calibrate the snapper and barracouta gelatin radiocarbon estimates. In addition, at the level of precision associated with the radiocarbon analyses, contaminants are either negligible in their impact, or their effects are masked by higher standard errors. These results, therefore indicate that gelatinisation will give reliable $^{14}C$ determinations on archaeological bone, though it is suggested that results should be viewed with caution where yields are low (*i.e.* <40%) and where contamination is evident in the acid-insoluble FTIR spectra. Less rigorous pretreatment involving only an acid wash, or acid followed by NaOH is not recommended, except for extremely well-preserved bone (*i.e.* Class I). Where bone is of poor preservation (Class III or <20% remaining protein) greater purification may be required.

5 Most published tripeptide dates are >3000 BP. Tripeptide dates <1000 BP have been obtained of human remains from Castledyke and the skeleton of St. Timotheus from St. Emmeram Church (van Klinken, Bowles and Hedges 1994:2549). The tripeptide date on Castledyke did not agree with archaeological expectation, but is not considered to be the result of laboratory error. The sample from St. Emmeram church gave a result in accordance with two other burials from the church of the same period, but cannot be considered to be securely provenanced. Problems have also been encountered with the measurement of tripeptides from bog bodies (van Klinken and Hedges 1998:54).

# CHAPTER 8

# DISCUSSION AND CONCLUSIONS

## OVERVIEW

The reliability of different samples for radiocarbon dating is a key archaeological issue in New Zealand because of the brevity of prehistoric occupation. Fish bone is one material that has received little attention, although the ability to measure the $^{14}C$ content of fish accurately has a number of advantages for New Zealand archaeologists. Notably, fish bone is common in archaeological sites around New Zealand, from the early Archaic to the later Classic phases. This dissertation has examined the potential of fish bone for providing accurate radiocarbon results. This necessitated not only an understanding of the primary origin and $\Delta^{14}C$ of the carbon in the bone, but also the origin and influence of contamination and the effectiveness of various pretreatments.

In Chapter 2, bone and isotopic influences on collagen were examined. Collagen was identified as the main bone fraction analysed by radiocarbon laboratories, due in part to its highly conservative, relatively stable structure *in vivo*. It was also shown that in marine animals the carbon in collagen is either directly, or indirectly derived from DIC via the diet. Consequently, it is likely that fish bone is subject to similar uncertainties with radiocarbon content as marine shell, including possible anomalies introduced by uptake of organic terrestrial carbon, upwelling, or a hardwater effect, with additional complications caused by the vertical and geographical distribution of many fish species. It is, therefore necessary to select fish species for $^{14}C$ analysis only after careful consideration of their habitat, distribution and diet.

Despite the stability of collagen *in vivo*, it was noted that bone protein is subject to alteration following the death of the animal through a combination of chemical, physical and biological factors. Further, although collagen decay is initiated by the breakdown of soft tissue, in the long term it is dependent on the environment of deposition. This decay process is manifest as a loss of collagen and a corresponding increase in susceptibility to humic as well as non humic contaminants that can alter the apparent age of the sample.

In Chapter 3, the methods currently available for the pretreatment of bone samples prior to analysis for $^{14}C$ content, were investigated. From this summary it was

apparent that there is no ideal method of pretreatment. The isolation of bone specific fractions does, however, hold promise (*e.g.* tripeptides), though these and other highly technical pretreatment methods are expensive, not routinely performed by radiocarbon laboratories, and may not significantly improve the result. A more economic and balanced approach is to select an appropriate pretreatment according to the preservation state of the bone (*i.e.* the amount of surviving collagen and contamination) and age of the sample. It was also concluded that the accuracy of any radiocarbon determination on bone can be enhanced using assessment techniques, such as infrared, isotopic, and amino acid analysis, obtained prior to, and at various stages during pretreatment.

In Chapter 4, bone $^{14}C$ analyses undertaken in New Zealand were examined. This included the different pretreatments adopted, radiocarbon results and some of the implications of those dates. In particular, the results of a number of tests undertaken at IGNS over the past forty years were described, including research into the reliability of different species and various preservation states. From this review it was concluded that the interpretation of radiocarbon determinations has been hampered by the limited published information available for each sample. Most notably, the fractions analysed have often been reported incorrectly, while the chemical steps used in pretreatment have not been specified in each case, thus preventing replication and assessment of the method used. In addition, there is a dearth of information on the preservation state of the bones themselves. Therefore, despite the apparently definitive opinion in the literature that bone is an inherently bad sample type for dating New Zealand's prehistory, it was shown that little is known about the reliability of bone radiocarbon estimates undertaken so far.

A number of recommendations can, however, be made on the basis of early tests, including that:

- The carbonate fraction of bone is unreliable as it will exchange with atmospheric $CO_2$;
- Burnt bone gives inconsistent results;
- The $\Delta^{14}C$ of bone collagen can be affected by reservoir differences that may vary according to diet. It has been suggested, therefore that rat, human, dog, sea bird, whale and seal are unsuitable species for $^{14}C$ analysis. Further tests on these animals are however, required;
- The identification of sub-fossil moa bone is a major problem in the interpretation of moa ages.

In Chapter 5, the type and context of samples selected for radiocarbon assay in this dissertation were considered. It was concluded that snapper (*Pagrus auratus*) and barracouta (*Thyrsites atun*) should be suitable for radiocarbon analysis because they occupy New Zealand's coastal waters and have either a small inbuilt age, or one which may be measured. In addition, barracouta and snapper have been identified as the predominant fish species in New Zealand archaeological midden sites. Several areas of uncertainty were noted, however, including the effects of terrestrial organic carbon, hardwater and depleted carbon introduced by upwelling. The influence of these factors was considered to be minimal because no such effects have been detected in marine shell from archaeological sites around New Zealand. Fish from surface waters should, therefore have a comparable $\Delta R$ to marine shellfish.

Seven sites with snapper or barracouta remains were chosen from Classic and Archaic archaeological contexts from around New Zealand, including Houhora and Twilight Beach in the northern North Island, Rotokura and Tata Beach in the northern South Island, and Shag River Mouth, Pleasant River and Long Beach in the southern South Island. The stratigraphy, regional climate, intra-site variation and material culture of each site were discussed.

In Chapter 6 the pretreatment and assessment of the bone samples selected for radiocarbon assay were described. On the basis of conclusions given in Chapter 3 it was suggested that well preserved bones, (defined as those bones with greater than 18% extractable protein) from New Zealand archaeological sites (*i.e.* less than 1000 years old) should, following an alkali wash and gelatinisation, result in accurate radiocarbon determinations. Because such pretreatment could leave around 8% contamination, the amount and purity of bone protein were assessed prior to, and during pretreatment.

Results of these analyses demonstrated that measurement of the bone nitrogen content enabled a more accurate assessment of bone preservation and intra-site variability than hand specimen identification. Further, nitrogen values could be used within a single site to aid in the identification of sub-fossil bone or site disturbance. The nitrogen determinations did not, however, necessarily confirm the preservation state of the bone. It was also concluded that $\delta^{13}C$ and $\delta^{15}N$ stable isotope analyses were limited for identification of contamination, except in severe cases. Infrared analysis was, however, a useful tool for indicating alteration to hydroxyapatite as well as degradation and contamination of the collagen. This range of assessment techniques, combined with gelatin yield data, was used to build up a picture of bone preservation which aided in the identification of bones that could give problematic radiocarbon estimates.

The range of analytical data applied also gave an insight into environmental conditions and bone taphonomy not readily apparent from hand specimen analysis. From these assessments it was concluded that the preservation state of bone was directly related to environmental conditions, with the better preserved material coming from the mild, cool temperate environs around Otago, and material of poorer preservation coming from regions further north where the climate is subtropical and mild temperate with high rainfall.

Following sample assessment it was suggested that bone from most of the sites investigated should give reliable radiocarbon results. Bones from Tata Beach were, however, considered to be potentially problematic because gelatin yields were low and the presence of contamination was identified. High levels of contamination were also noted in the Rotokura samples.

In Chapter 7 the results of radiocarbon determinations were given. The snapper and barracouta gelatin results were reproducible and, following calibration with the marine reservoir curve of Stuiver and Braziunas (1993), were comparable to ages of other sample types. This supported the hypotheses, given in Chapter 6, that the gelatin pretreatment had reduced contamination to undetectable levels, with the possible exception of laboratory induced error (Shag River Mouth) and contaminated samples with low collagen yield (Tata Beach). The results also suggested that no significant impact on the radiocarbon determination was introduced by upwelling of old carbon, a hardwater effect or inbuilt age at the level of precision used in this research.

These conclusions were not, however, supported by a limited number of results on tripeptides. All five tripeptide determinations (from Rotokura, Tata Beach, Houhora and two from Shag River Mouth) were older than associated dates on fish gelatin, and significantly older in the case of Shag River Mouth, Rotokura and Tata Beach. This may be the result of contamination masking the influence of inbuilt age, or more likely a reservoir effect. The lack of concordance of the tripeptide results generally with $^{14}C$ estimates of other sample types and the degree of contamination necessary to alter the gelatin determinations suggested, however, that a problem may exist with the tripeptide technique. Overall, these results suggest that for well-preserved bones (less than 1000 years old) purification beyond gelatin is uneconomical at the level of precision obtained in the Waikato Radiocarbon Dating laboratory for samples described in this dissertation.

The importance of careful screening of all samples before radiocarbon analysis, and appraisal of existing determinations was highlighted by problems encountered with

other sample types, including recrystallisation of shell, inbuilt age in charcoal, and post depositional disturbance or insecure provenance.

## NEW ZEALAND BONE DATING REVISITED: "CHRONOMETRIC HYGIENE" PROTOCOL FOR BONE

A culling protocol has been devised to appraise comprehensively all bone determinations measured in New Zealand given the discussion of bone and of ages on different fractions of bone given in Chapters 2-4, and the results of dating and analyses given in Chapters 6 and 7. The aim is to isolate "acceptable" bone radiocarbon determinations and consider whether there are sufficient grounds for doubting radiocarbon determinations of bone collagen, as suggested by Anderson and McGovern-Wilson (1990:44-45), Anderson, Smith and Higham (1996:64), Anderson (1991:777, 779).

The databases of the University of Waikato and IGNS radiocarbon dating laboratories were searched for all known New Zealand archaeological bone determinations (this list does not include results of bones measured overseas or the fish bone estimates from this research). Information relating to samples analysed at IGNS was obtained from a preliminary compilation of archaeological determinations by Dr. McFadgen[1], the fossil record forms (FRF), radiocarbon result sheets held by IGNS, and the "Jansen" database. Most of these radiocarbon measurements have been recalculated with respect to modern standards by IGNS and may, therefore differ from published accounts. A few early determinations have not been recalculated due to the obvious inaccuracy of the results - these are instead reported according to the reference cited at the bottom of Table 8.1. A number of more recent bone $^{14}C$ estimates were also obtained from a search of the literature. This list may, therefore be incomplete. Radiocarbon results of other sample types associated with the bone determinations are listed in Appendix 6.

From Table 8.1, it is apparent that several different fractions of bone have been dated in New Zealand. "Collagen" or bone has been used as a generic label for most determinations published. This has resulted in considerable confusion. Often the specific pretreatment used for each sample has not been identified and laboratory reports provide only a general indication of the fraction analysed. Mis-identification of the measured fraction has been compounded by the simultaneous analysis of carbonate and collagen (or "fixed carbon") results in the period 1956-1972. The first series of

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radiocarbon estimates measured at IGNS have the same NZ number for carbonate and collagen fractions, further confusing this issue. For example, carbonate results for Tautuku and Papatowai have been continually mis-reported as "collagen" (*i.e.* Anderson 1989:174; Anderson and McGovern-Wilson 1990:52) since being first published as "moa bone" determinations by Lockerbie (1959). Poor communication between the laboratory and submitter has also often led to incorrect reporting of the fraction analysed, for example NZ-510, a charcoal sample from Paremata, was reported by Sinclair (1977:158) to be a mix of moa, dog and seal bone. It has since become apparent that charcoal was removed from the mix of moa, dog and seal bone, collected by Sinclair (Davidson 1978b:214).

To distinguish between different pretreatments and fractions isolated, bone determinations in Table 8.1 are described variously as:

1. "Fixed carbon" - the protein fraction pretreated as outlined by Rafter (1955:23).
2. "Collagen" - the fraction remaining after an acid wash (using either hydrochloric or phosphoric acid) or a combination of acid and alkali treatment.
3. "Gelatin" - where gelatinisation has been used to purify the sample.
4. "Carbonate" - the inorganic fraction isolated by acid hydrolysis of whole bone.

In addition, both the laboratory number (Wk- or NZ-) and "run number" (*R*-) are supplied, where possible, to assist in the identification of carbonate and protein fractions.

## BONE DISCARD PROTOCOL

The discard protocol for "bone" determinations is as follows;

*1. Carbonate dates*

Whole bone or carbonate results are rarely reliable because the carbonate fraction of bone may exchange with atmospheric $CO_2$ (*e.g.* Rafter *et al.* 1972:638; Stafford *et al.* 1991:62; Hedges and van Klinken 1992:285). From Table 8.1 it is apparent that the majority of carbonate radiocarbon estimates give younger results than the associated "collagen" determinations, and around 40% of those are modern. Therefore, all carbonate ages are rejected. This includes; NZ-56 (*R*199), NZ-59 (*R*197), NZ-60, NZ-137 (*R*192/1), NZ-138, NZ-139, NZ-140, NZ-142, NZ-146 (*R*192/2), NZ-460, NZ-480, NZ-424, NZ-425, NZ-514, NZ-558, NZ-751, NZ-753, NZ-755, NZ-757, NZ-759, NZ-765, NZ-784, NZ-917, NZ-927, NZ-929, NZ-931, NZ-1112, NZ-1298, NZ-2464, and NZ-4652.

Table 8.1. Bone determinations from New Zealand archaeological sites measured at the Waikato Radiocarbon Dating Laboratory and IGNS.

| Site name | Lab no. Run no. | Provenance | Sample type | CRA | $\delta^{13}C$ | Reference |
|---|---|---|---|---|---|---|
| | AA3474[1] | Cow bone protein | | standard | -29.4 | Rafter 1955; Rafter *et al.* 1972:639 |
| | AA3474 | Cow bone $CO_3^{2-}$ | | standard | -16.4 | |
| Ahuriri Lagoon | NZ-5608 *R*9541/1 | | Human collagen | 429 ± 55 | -16.43 | |
| | NZ-5609 *R*9541/2 | | Human collagen | 497 ± 55 | -16.60 | |
| Avoca Point | NZ-2717 *R*4863/3 | Cultural layer | Seal collagen | 436 ± 156 | -23.10 | Trotter 1980a:283; Challis 1991:132-133 |
| | NZ-3164 *R*4857 | Cultural layer: Oven | *Anomalopteryx didiformis* collagen | 952 ± 192 | -25.29 | |
| | NZ-4155 *R*5157/4 | Cultural layer: Oven | *Anomalopteryx* collagen | 703 ± 85 | -22.90 | |
| Avoca Point, Fyffe Site | NZ-6496 *R*9810/1 | Base of wall: Early occupation | *Anomalopteryx didifornis* collagen | 529 ± 42 | -22.85 | Challis 1991:133 |
| | NZ-6566 *R*9810/3 | Outside wall: Early occupation | *Anomalopteryx didifornis* collagen | 745 ± 59 | -22.70 | |
| Awamoa | NZ-4872 *R*5927/1 | Cultural deposit: Test pit | *Euryapteryx gravis* collagen | 671 ± 55 | -22.70 | Trotter 1980b:185 |
| Cascade Cove, Fiordland | NZ-784 *R*1526/1A | Floor of cave | Human carbonate | -100 ± 61 | -6.29 | Begg and Begg 1966:214-215; Moore and Tiller 1976:153; Coutts 1972:527 |
| | NZ-785 *R*1526/1B | Floor of cave | Human collagen | 802 ± 48 | -12.91 | |
| | NZ-786 *R*1526/2B | Floor of cave | Burnt human collagen | 720 ± 49 | -12.91 assumed | |
| | NZ-787 *R*1526/3B | Floor of cave | Human collagen | 574 ± 60 | -12.91 assumed | |
| Cross Creek | NZA-576 *R*11758/3 | Layers 7, 8 and 9 | Moa collagen | 751 ± 58 | -23.45 | Sewell 1986:229; 1988:8 |
| False Island | NZ-142 *R*192/15 | Midden | Fish carbonate | 516 ± 73 | -4.80 | Fergusson and Rafter 1959:220-221; Lockerbie 1959:106; Grant-Taylor and Rafter 1963:136 |

| Site name | Lab no. Run no. | Provenance | Sample type | CRA | $\delta^{13}C$ | Reference |
|---|---|---|---|---|---|---|
| Hampden | NZ-755 *R*1641/1A | Occupation layer (Sq. F8 and G9) | *Euryapteryx gravis* carbonate | 355 ± 48 | -10.67 | Trotter 1967b:140; Trotter 1967c:59 |
| | NZ-756 *R*01641/1B | Occupation layer (Sq. F8 and G9) | *Euryapteryx gravis* collagen | 503 ± 70 | -23.34 | |
| | NZ-757 *R*1641/2A | Occupation layer (Sq. F8 and G9) | Burnt *Euryapteryx* ? carbonate | 437 ± 81 | -16.23 | |
| | NZ-758 *R*1641/2B | Occupation layer (Sq. F8 and G9) | Burnt *Eurtyapteryx* collagen | 519 ± 60 | -24.22 | |
| Hawksburn | NZ-59 AA2550/2 *R*197 | Occupation layer: Oven 1 | Burnt *Dinornithidea* carbonate | 470 ± 55^ | -13 | Rafter 1955:36; Fergusson and Rafter 1957:744-745; Lockerbie 1959:106; Grant-Taylor and Rafter 1963:126-127; Rafter *et al.* 1972:639 |
| | NZ-59 *R*198 AA2550/2 | Occupation layer: Oven 1 | Burnt *Dinornithidea* "fixed carbon" | 440 ± 55^ | -25.7 | |
| | NZ-60 AB1502/15 | Occupation layer: Oven 2 | *Euryapteryx gravis* carbonate | 293 ± 64 | -- | |
| Hot Water Beach | NZ-1298 *R*4068/3A | Layer 4 | Fish carbonate | -100 ± 104 | -4.34 | Leahy 1974:71-72 |
| | NZ-1299 *R*4068/3B | Layer 4 | Fish collagen | 647 ± 92 | -13.89 | |
| | NZA-583 *R*11758/1 | Layer 6 | Moa collagen | 549 ± 74 | -23.25 | |
| Houhora | NZ-5007 *R*9107/1 | Layer 2c (Sq. D9) | *Anomalopteryx didiformis, Euryapteryx curtus, Pachyornis septentrunalis* collagen | 563 ± 56 | -21.10 | Millener 1981:847; Anderson and Wallace 1993:10 |
| | NZ-5008 *R*9107/2 | Layer 3b (Sq. D10) | *Dinornis struthoides, Anomelopteryx didiformis, Euryapteryx curtus, Pachyornis septentrionalis* collagen | 585 ± 46 | -22.50 | |
| Hurunui River Mouth | NZ-1839 *R*4745/6 | Occupation layer: Oven | *Euryapteryx* collagen | 646 ± 85 | -23.60 | McCulloch and Trotter 1975a:17; Moore and Tiller 1975:103 |

| Site name | Lab no. Run no. | Provenance | Sample type | CRA | $\delta^{13}C$ | Reference |
|---|---|---|---|---|---|---|
| Kaupokonui | NZ-3931 *R*5055/1 | Layer 4d (Cassels 1974); Layer 4 (Buist 1963) | *Pachyornis* sp. collagen | 568 ± 49 | -22.70 | Buist 1963; Cassels nd:9-13; Foley 1980:3, table A1.1 |
| | NZ-3934 *R*5054/1 | Layer 4f (Cassels 1974); Layer 6 (Buist 1963) | Moa collagen | 618 ± 57 | -25.60 | |
| Lagoon Flat | NZ-1834 *R*4745/1 | Burial 4 | Human collagen | 437 ± 57 | -16.50 | McCulloch and Trotter 1975b:110; 1975a:3, 17; Trotter 1982:97 |
| Makara | NZ-480 *R*700/3 | Beach midden | *Dinornis* carbonate | -100 ± 144 | -0.44 | Davis 1962:149; Rafter *et al.* 1972:639 |
| Ototara | NZ-753 *R*1640/A | Occupational layer | *Euryapteryx gravis* carbonate | 308 ± 93 | -6.90 | Trotter 1965:113; Trotter 1967b:138 |
| | NZ-754 *R*1640/B | Occupational layer | *Eurayspterx gravis* collagen | 435 ± 70 | -25.00 | |
| Papatowai | NZ-137 *R*192/1 | Middle layer | *Euryapteryx gravis* carbonate | 309 ± 46 | -25.60 | Fergusson and Rafter 1959:220-221; Lockerbie 1959:106; Grant-Taylor and Rafter 1963:136; Hamel 1978a:54 |
| | NZ-137 *R*192/1A | Middle layer | *Euryapteryx gravis* "fixed carbon" | 707 ± 61 | -25.68 | |
| | NZ-138 *R*192/8 | Upper layer | *Dinornis maximus* carbonate | 571 ± 75 | -8.50 | |
| | NZ-139 *R*192/9 | Upper layer | *Euryapteryx gravis* carbonate | 399 ± 60 | -10.90 | |
| | NZ-140 *R*192/3 | Upper layer | *Euryapteryx gravis* carbonate | 690 ± 59 | 2.19 | |
| Parker's Midden | NZA-557 *R*11758/2 | Layer 4 | *Euryapteryx* sp collagen | 510 ± 58 | -22.57 | |
| Pauatahanui | NZA-7411 | Midden 2 | *Rattus exulans* gelatin | 452 ± 69[f] | -- | Sparks, Beavan and Redvers-Newton 1997:207 |
| | NZA-7044 | Midden 4 | *Rattus exulans* gelatin | 361 ± 69[f] | -- | |
| | NZA-7410 | Midden 9 | *Rattus exulans* gelatin | 439 ± 71[f] | -- | |
| Pawhetau Pa, Kawakawa | NZ-3903 *R*2548 | Burial | Human crude collagen | 350 ± 80[#] | | Moore and Tiller 1976:153; Fox 1974:20 |

| Site name | Lab no. Run no. | Provenance | Sample type | CRA | $\delta^{13}C$ | Reference |
|---|---|---|---|---|---|---|
| Peketa Pa | NZ-4154 *R*5157/3 | Floor of pit house | Dog collagen | 508 ± 83 | -12.70 | Challis 1991:133 |
| | NZ-4296 *R*5343 | Floor of pit house | Dog collagen | 222 ± 241 | -19.40 | |
| Pleasant River : Trotter 1979 excavation | NZ-5013 *R*9096/1 | Black soil containing occupational material | Moa collagen | 408 ± 56 | -24.70 | Anderson 1989:222 |
| Pleasant River: Area 1 | NZA-6536 | Layer 2, Sq. A2 | *Rattus exulans* gelatin | 1591 ± 71‡ | -22 | Smith and Anderson 1998:90 |
| Pleasant River: Area 2 | NZA-6532 | Layer 4, Sq. C4 | *Rattus exulans* gelatin | 1039 ± 69‡ | -21.6 | Smith and Anderson 1998:90 |
| Pleasant River: Area 7 | Wk-5169 | Layer 2a, Sq. A3 and B4 | *Eu. geranoides ?* Moa sp. ? gelatin | 580 ± 45 | -26.2 | This thesis |
| Port Jackson | NZ-4883 *R*5965 | Deflation hollow under midden | *A. didifornis, P.mappii, D. stuthioides* collagen | 606 ± 56 | -23.10 | Millener 1981:848; Anderson 1991:775 |
| Poukawa | NZ-2464 *R*2540/A | "Natush property" | Human carbonate | -100 ± 45 | -12.04 | |
| | NZ-2467 *R*2540/B | "Natush property" | Human collagen | 315 ± 35 | -18.08 | |
| Pounawea | NZ-56 AA2550/1b *R*199 | Middle layer | Seal carbonate | 520 ± 55~ | -- | Rafter 1955:36; Fergusson and Rafter 1957:742-743; Lockerbie 1959:106; Grant-Taylor and Rafter 1963:126; Anderson 1989:222 |
| | NZ-56 AA2550/1c *R*200 | Middle layer | Seal "fixed carbon" | 550 ± 55~ | -- | |
| | NZ-1796 *R*4451/1 | Lowest layer | *Dinornis maximus* collagen | 699 ± 105 | -23.73 | |
| | NZ-1797 *R*4451/2 | Lowest layer | Moa collagen | 668 ± 60 | -25.10 | |
| | NZ-1798 *R*4451/3 | Lowest layer, base of oven | Moa collagen | 772 ± 66 | -26.00 | |
| | NZ-1866 *R*4544/3 | Lowest layer, base of oven | Burnt *Dinornis maximus* collagen | 1465 ± 79 | -25.80 | |
| | NZ-4438 *R*5437 | Lowest deposit | Moa collagen | 602 ± 47 | -25.60 | |

| Site name | Lab no. Run no. | Provenance | Sample type | CRA | $\delta^{13}C$ | Reference |
|---|---|---|---|---|---|---|
| Rakaia River Mouth | NZ-927 *R*2068/1A | Middle layer | Burnt *Euryapteryx gravis* carbonate | 215 ± 120 | -16.23 | Trotter 1972b:135 |
| | NZ-930 *R*2068/1B+ 2B | Middle layer | Burnt moa collagen | 556 ± 71 | -25.39 | |
| | NZ-929 *R*2068/2A | Middle layer | White burnt moa carbonate | 924 ± 112 | -20.42 | |
| | NZ-931 *R*2068/3A | Middle layer | *Euryapteryx* ? carbonate | -100 ± 82 | -10.77 | |
| | NZ-932 *R*2068/3B | Middle layer | *Euryapteryx* ? crude collagen | 487 ± 88 | -25.10 | |
| Redcliffs: Hamilton's Deposit | NZ-1112 *R*1936/2A | Occupation layer | *Euryapteryx gravis* carbonate | -100 ± 94 | -7.55 | Trotter 1968:87; 1975c:204 |
| | NZ-1113 *R*1936/2B | Occupation layer | *Euryapteryx gravis* collagen | 701 ± 60 | -20.76 | |
| Redcliffs: Sewer Trench Pit | NZ-1162 *R*2553/6 | Occupational deposit: 9.84 to 19.79 cm depth | *Euryapteryx, Emeus* and *Anomalopteryx* collagen | 622 ± 44 | -23.83 | Trotter 1968:87; 1975c:204 |
| | NZ-1376 *R*2553/7 | Occupational depost: 9.84 to 19.79 cm depth | *Euryapteryx, Emeus* and *Anomalopteryx* collagen | 537 ± 45 | -24.91 | |
| Redcliffs: Hine's oven | NZ-460 *R*1052/2-3 | Top of oven | *Euryapteryx* carbonate | 480 ± 84 | -13.01 | Trotter 1975c:204; Duff 1963:10 |
| Redcliffs: Moa Bone Point Cave | NZ-514 *R*1090/2 | Post fill | *Euryapteryx gravis* carbonate | 515 ± 64 | -16.12 | Duff 1963:10; Trotter 1967a; 1975c:203 |
| Shag River Mouth: Trotter 1979 testpit | NZ-5016 *R*9096/4 | Ashy layer below midden | Moa collagen | 641 ± 85 | -23.50 | Anderson 1991:776; Anderson and Smith 1996a:9 |
| Shag River Mouth: SM/A | NZ-7741 *R*11838/8 | Layer 2 | Moa collagen | 522 ± 37 | -25.20 | Anderson, Smith and Higham 1996:61-63 |
| Shag River Mouth: SM/B:FHA | NZ-7742 *R*11838/9 | Layer 2 | Moa collagen | 530 ± 36 | -23.70 | Anderson, Smith and Higham 1996:61-63 |

| Site name | Lab no. Run no. | Provenance | Sample type | CRA | $\delta^{13}C$ | Reference |
|---|---|---|---|---|---|---|
| Shag River Mouth: SM/C:Dune | NZA-781 *R*11838/5 | Layer 2 | Moa collagen | 630 ± 82 | -24.40 | Anderson 1996:179; Anderson, Smith and Higham 1996:61-63; This thesis |
| | NZ-7743 *R*11838/10 | Layer 4 | Moa collagen | 1201 ± 38 | -24.90 | |
| | NZA-5719 | Layer 4 | *Rattus exulans* gelatin | 1487 ± 87† | -21.5 | |
| | Wk-5433 | Layer 4 | Moa gelatin | 640 ± 40 | -26.2 | |
| | NZ-7737 *R*11838/4 | Layer 5 | Moa collagen | 1170 ± 70 | -24.95 | |
| | NZA-5936 | Layer 5 | *Rattus exulans* gelatin | 2040 ± 68† | -19.6 | |
| | NZ-7736 *R*11838/3 | Layer 6 | *Emeus* or *Euryapteryx* collagen | 634 ± 58 | -24.50 | |
| | NZA-5926 | Layer 6 | *Rattus exulans* gelatin | 1578 ± 88† | -21.1 | |
| | NZA-780 *R*11838/2 | Layer 7 | Moa collagen | 509 ± 72 | -23.50 | |
| | NZ-7666 *R*11722 | Layer 11 | *Emeus* or *Euryapteryx* sp collagen | 787 ± 72 | -26.88 | |
| | NZA-5720 | Layer 11 | *Rattus exulans* gelatin | 1862 ± 86‡ | -21.2 | |
| Shag River Mouth SM/D:1 | NZ-7739 *R*11838/6 | Layer 5 | *Euryapteryx* sp collagen | 370 ± 38 | -24.00 | Anderson, Smith and Higham 1996:61-63 |
| Shag River Mouth SM/D:3 | NZ-7740 *R*11838/7 | Layer 2 | Moa collagen | 477 ± 53 | -24.67 | Anderson, Smith and Higham 1996:61-63 |
| Skippers midden | NZA-575 *R*11758/6 | Beach midden | Moa collagen | 417 ± 56 | -24.19 | |
| Station Bay, Motutapu Island | NZ-4346 *R*5407/1 | Davidson undefended site | Human crude collagen | 451 ± 45 | -15.00 | Davidson 1972; 1978a:15 |
| | NZ-4347 *R*5407/2 | Leahy undefended site | Human collagen | 562 ± 41 | -18.20 | |
| | NZ-4348 *R*5416 | Pa site: Burial 1 on floor of kumera pit | Human collagen | 367 ± 61 | -25.00 | |
| Stewart Island Old Neck | NZ-424 *R*780/3 | Oven | *Euryapteryx* carbonate | 261 ± 81 | -9.6 | Rafter *et al.* 1972:639 |
| | NZ-425 *R*780/4 | Oven | Moa carbonate | 1 ± 59 | -9.10 | |

| Site name | Lab no. Run no. | Provenance | Sample type | CRA | $\delta^{13}C$ | Reference |
|---|---|---|---|---|---|---|
| Tairua | NZA-558 *R*11758/4 | Layer 2: oven | *Dinornis struthiodes* collagen | 460 ± 55 | -24.35 | Schmidt and Higham, in prep |
| Tai Rua | NZ-558 *R*1371/1A | Main occupation (Layers 5, 5a and 6) | *Euryapteryx gravis* carbonate | -100 ± 33 | -10.0 | Trotter 1967b:139; 1979:226-227; Rafter *et al.* 1972:639 |
| | NZ-559 *R*1371/1B | Main occupation (Layers 5, 5a and 6) | *Euryapteryx gravis* collagen | 473 ± 37 | -25.9 | |
| | NZ-578 *R*1544/1B | Main occupation (Layers 5, 5a and 6) | *Euryapteryx gravis* collagen | 473 ± 37 | -24.7 | |
| | NZ-751 *R*1639/3A | Main occupation (Layers 5, 5a and 6) | *Eurapteryx gravis* carbonate | -100 ± 55 | -9.21 | |
| | NZ-752 *R*1639/3B | Main occupation (Layers 5, 5a and 6) | *Euryapteryx gravis* collagen | 513 ± 36 | -24.51 | |
| | NZ-765 *R*1661/1A | Main occupation (Layers 5, 5a and 6) | *Euryapteryx gravis* carbonate | -100 ± 47 | -8.33 | |
| | NZ-766 *R*1661/1B | Main occupation (Layers 5, 5a and 6) | *Euryapteryx gravis* collagen | 363 ± 48 | -24.22 | |
| Takahanga Pa | NZ-4464 *R*5492/1 | Burial 4 | Human collagen | 646 ± 83 | -13.70 | Challis 1991:132; Trotter 1974; 1982:100 |
| | NZ-4465 *R*5492/2 | Cremation K52 | Burnt human collagen | 171 ± 81 | -21.80 | |
| | NZ-4525 *R*5658/1 | Burial 4 | Human collagen | -100 ± 30 | -13.80 | |
| | NZ-4526 *R*5658/2 | Burial 1 | Human collagen | 419 ± 45 | -14.70 | |
| | NZ-4635 *R*5742 | Burial 4 | Human collagen | 477 ± 56 | -13.70 | |
| Takahe Valley, Rockshelter A | NZA-2227 | Layer A: Surface | *Megalapteryx didinus* collagen | 623 ± 39 + | -- | O'Regan 1992:174 |
| Tautuku | NZ-146 *R*192/2 | Occupation deposit below human bone | *Dinornis torosus* carbonate | 391 ± 59 | -9.50 | Fergusson and Rafter 1959:220-221; Lockerbie |
| | NZ-146 *R*192/2A | Occupation deposit below human bone | *Dinornis torosus* "fixed carbon" | 530 ± 67 | -25.78 | 1959:106; Grant-Taylor and Rafter 1963:136 |
| Timpendean, Weka Pass | NZ-917 *R*2251/1A | Lower occupation level | *Euryapteryx gravis* carbonate | 252 ± 86 | -8.04 | McCulloch and Trotter 1975a:5; 1975b:110; Trotter |
| | NZ-918 *R*2251/1B | Lower occupation level | *Eyrapteryx gravis* collagen | 1192 ± 62 | -24.81 | 1972a:45, 49; Moore and Tiller 1975:103 |

| Site name | Lab no. Run no. | Provenance | Sample type | CRA | $\delta^{13}C$ | Reference |
|---|---|---|---|---|---|---|
| Titirangi Beach | NZ-4236 *R*5159/1 | Lowest occupational deposit (240 cm depth) | *Euryapteryx geranoides* collagen | 792 ± 148 | -22.80 | Trotter 1977b:9; 1982:90-91; Challis 1991:130 |
| Tumbledown Bay | NZA-338 *R*11690/3 | Layer 3 | *Dinornis novaezealandiae* collagen | 307 ± 85 | -21.90 | |
| Waimataitai Mouth | NZ-5015 *R*9096/3 | Eroded section of main occupational deposit | *Emeus crassus* collagen | 686 ± 173 | -24.10 | Anderson 1991:776 |
| Wairau Bar | NZ-1835 *R*4745/2 | Burial 42 | Human collagen | 700 ± 142 | -20.90 | Moore and Tiller 1975:103; McCulloch and Trotter 1975a:12; Trotter 1975a:80; 1975b:90; Challis 1991:131 |
| | NZ-1838 *R*4745/5 | Main phase of occupation | *Euryapteryx* collagen | 547 ± 58 | -23.90 | |
| | NZ-4442 *R*5433/1 | Burial 3 | Human collagen | 575 ± 45 | -19.70 | |
| | NZ-4443 *R*5433/2 | Burial 5 | Human collagen | 598 ± 56 | -18.70 | |
| | NZ-4444 *R*5433/3 | Burial 35 | Human collagen | 329 ± 46 | -23.10 | |
| Wakanui | NZ-1766 *R*4002/1 | Oven, in ash matrix | Burnt *Euryapteryx gravis* collagen | 629 ± 58 | -25.58 | Trotter 1975b:90; McCulloch and Trotter 1975a:6 |
| | NZ-1767 *R*4002/2 | Oven, in ash matrix | *Euryapteryx gravis* calcined bone | 558 ± 69 | -24.71 | |
| | NZ-1768 *R*4002/3 | Oven, in ash matrix | *Euryapteryx gravis* collagen | 383 ± 58 | -24.70 | |
| Whakamoenga Cave | NZA-577 *R*11758/5 | Occupation 1: Period 1 | *Euryapteryx curtus* collagen | 4750 ± 81 | -24.78 | McFadgen 1989 |
| Woolshed Flat | NZ-759 *R*1692/1A | Occupation layer | *Pachyornis* and *Euryapterx* sp. carbonate | -100 ± 47 | -13.20 | Trotter 1967b:139; 1968:87; McCulloch and Trotter 1975a:6 |
| | NZ-760 *R*1692/1B | Occupation layer | *Pachyornis* and *Euryapterx* sp. collagen | 544 ± 70 | -20.03 | |

^Rafter *et al.* (1972:639); # Fox (1974:20); ~Fergusson and Rafter (1957:126) includes 120 year industrial correction; + O'Regan (1992:174); ƒ Sparks, Beavan and Redvers-Newton (1997:207);‡Smith and Anderson (1998:90);†Anderson (1996:179).

[1] AA and AB are early IGNS reference numbers.

*2. Burnt bone*

Burning significantly reduces the protein content and increases the porosity of the mineral phase. Thus charred bone is an impractical sample type to analyse for $^{14}C$ content because of the large sample sizes required and the increased reactivity of collagen with contaminants (see Table 6.6). In addition, burnt bone tends to give inconsistent stable isotope results and radiocarbon determinations (Tamers and Pearson 1965:1055; Polach and Golson 1966:31; Rafter *et al.* 1972:643; Stafford *et al.* 1991:63, table 12).

"Collagen" ages on samples that have been burnt in prehistory are, therefore rejected. This includes; NZ-59 (*R*198) from Hawksburn; NZ-758 from Hampden Beach; NZ-930 from Rakaia River Mouth; NZ-1866 from Pounawea; and NZ-1766 and NZ-1767 from Wakanui. Because there may be other $^{14}C$ measurements of burnt samples which have not been identified by either the submitter or laboratory, it is recommended that samples selected from firescoops or ovens, or from sites where extensive burning has been noted in the associated layer generally, should be interpreted with caution.

*3. Old dates*

Old $^{14}C$ estimates have been variously identified as the result of contamination or as a consequence of dating sub-fossil bone. An attempt is made here to clarify this situation. Determinations significantly older (removed by more than $2\sigma$) from results of associated samples are discarded. The most likely cause of these anomalous results (*i.e.* as the result of contamination or the inclusion of sub-fossil remains), is also discussed.

Trotter initially submitted the bone for NZ-918 from Weka Pass/Timpendean because fractures appeared to have been applied when fresh (Trotter to Rafter 28/1/1969). The estimated date for this sample (1192 ± 62 BP) is, however, older than the anticipated 15$^{th}$ century occupation. Trotter (1972a:45) later suggested that the bone analysed was of suspect cultural origin because sub-fossil moa remains were discovered in the cave. NZ-918 is excluded.

NZA-557 from Whakamoenga Cave was considered initially to date the remains of a moa brought into the cave by humans. A result of 4750 ± 81 BP raised doubt about this interpretation. McFadgen (1989:257) has since suggested that NZA-557 dates either a dead bird washed into the lake when water levels were higher, or an old moa nesting site. NZA-557 is excluded from further analysis.

NZ-7743 (1201 ± 39 BP) and NZ-7737 (1170 ± 70 BP) from Shag River Mouth (SM/C:Dune) both yielded results approximately 600 years older than the established date of occupation. Both samples were carefully selected on the basis of exhibiting butchery marks (Anderson, Smith and Higham, 1996:60, 64; I. Smith, *pers. comm.* 30/6/1997), and the anomalous results have been attributed either to variability in the rates of preservation, inadequate pretreatment or to the use of sub-fossil bone in prehistory. One of these samples (NZ-7743) was lightly burnt (*i.e.* "blackened on outside, but still robust") (I. Smith, *pers. comm.* 30/6/1997), a factor that could also have affected the radiocarbon estimate. A shift in age of 600 years would, however, require around 8% contamination by $^{14}C$ free carbon, a result that is extremely unlikely in conventional sized samples from this site (Higham, *pers. comm.* 7/5/98). It is suggested, therefore, that these samples are sub-fossil bones which were collected in prehistory and subsequently discarded within the site.

*4. Uncertain provenance*

All acceptable $^{14}C$ determinations must come from samples in direct stratigraphic association with an archaeological event. Where displacement has occurred, either by a natural occurrence or human disturbance, the $^{14}C$ age estimate is discarded because the provenance and chronological integrity of the sample cannot be proven.

A number of anomalous moa collagen determinations were obtained of material from Poukawa. Unfortunately, shrinkage following drying out of the Poukawa Lake bed mixed cultural and natural moa deposits (McFadgen 1978:177). All moa bone crude collagen determinations from Poukawa are undoubtably from natural deposits. These results have not been included in Table 8.1.

NZ-4236 from Titirangi Beach is significantly older (792 ± 148 BP) than three shell determinations which suggest a 16$^{th}$ century occupation. All four samples come from the lower occupation deposit, 90 cm above the moa bone sample. It is, therefore possible that different events are being dated. NZ-4236 is considered here to belong to sub-fossil moa remains, though the large standard error makes assessment difficult.

NZ-4883 from Port Jackson came from a deflation hollow under a midden (FRF *R*5965). This sample is discarded due to questionable cultural association.

Wk-5169 from Pleasant River Area 7, Layer 2a, yielded a CRA closer to that expected for Area 7, Layer 2b (see Chapters 6 and 7). Because there is evidence of disturbance

at the site (I. Smith, *pers. comm.* 23/10/96), contextual mis-placement either from modern or prehistoric disturbance is likely.

NZ-5013 also from Pleasant River was submitted by Trotter in 1979. Exactly what the stratigraphic and chronological relationship between this and other excavated areas at Pleasant River is unclear (I. Smith, *pers. comm.* 23/4/1998). Given the possibility of disturbance elsewhere at Pleasant River (Higham 1993:143, 157), this sample is excluded from further discussion.

NZ-6496 and NZ-6566 from Fyffes, Avoca Point are discarded. These samples came from outside the concentration of prehistoric debris identified by Trotter (1980a:278-279) as undisturbed. Schmidt (1996:51-52) has previously discussed shell sample NZ-6525 from this provenance and concluded that disturbance may be responsible for the anomalous ages. This is based on an observation by McFadgen (1987) that sub-fossil material from a natural beach ridge formation at the site may have become mixed with cultural remains. Trotter (1980a:281) also noted natural faunal remains to the west of the "*in situ* " deposit. The older of the two moa collagen determinations; NZ-6566 (745 ± 59 BP) may, therefore be of sub-fossil material.

NZ-1838 dates a sample of moa bone obtained from Duff's excavations at Wairau Bar. The exact provenance of this sample is unknown, but appears to have come from Layer 4 (*i.e.* the "main layer") which, according to Wilkes (1964:4), was in places disturbed by subsequent agricultural activity. This sample is discarded given the present uncertainties surrounding its context.

*5. Unsuitable species*

Several species have been considered to be unsuitable for $^{14}C$ analysis due to dietary or reservoir influences. Radiocarbon estimates on these species are discarded until research is carried out to suggest they are reliable.

Radiocarbon results of marine species known to migrate into depleted Antarctic waters are rejected due to the possibility of wide variations in reservoir correction (*i.e.* up to 1400 years)(Law 1981:234-235; Ambrose and Norr 1993:31; Gordon and Harkness 1993). Similarly, species that feed in the deep ocean are rejected due to the possible incorporation of old carbon (Pearcy and Stuiver 1983; Williams, Druffel and Smith 1987). For example, NZ-56 (*R*200); a "fixed carbon" seal bone determination from Pounawea; and NZ-2717, a collagen measurement from Avoca Point. Contra to the expected outcome, both of these results are too young. This is likely to be the result of

inadequate pretreatment (see below). The reliability of this seal bone cannot, therefore be adequately assessed at present.

While the results of this research suggest that snapper and barracouta are reliable species for radiocarbon dating, this may not be the case for all fish species (*e.g.* ling, a deep sea fish). Therefore, determinations of fish species which have not been identified are also discarded. This includes NZ-1299 from Hot Water Beach.

Results on omnivorous species known to incorporate marine and terrestrial diet components are also excluded. This includes dog bone collagen measurements NZ-4154 and NZ-4296. These determinations, both from Peketa Pa, have anomalous $\delta^{13}C$ values (-12.7‰ and -19.40‰ respectively) suggestive of variable marine input. Human bone collagen results are also suspect due to a varied diet. This hypothesis is supported by the range of $\delta^{13}C$ values evident (from -12.91‰ to -25.00‰) (see Chapter 2). All human bone determinations are discarded including NZ-785, NZ-786 and NZ-787 from Cascade Cove; NZ-2467 from Poukawa; NZ-3903 from Pawhetau Pa; NZ-1834 from Lagoon Flat; NZ-5608 and NZ-5609 from Ahuriri Lagoon; NZ-4346 from Station Bay N38/37; NZ-4347 from Station Bay N38/30; NZ-4348 from Station Bay N38/25; NZ-4464, NZ-4465, NZ-4525, NZ-4526 and NZ-4635 from Takahanga Pa; and NZ-1835, NZ-4442, NZ-4443 and NZ-4444 from Wairau Bar.

Radiocarbon determinations on archaeological rat bone are highly variable. Anomalous determinations on modern samples of *Rattus exulans* also suggest variation introduced through diet, though laboratory induced contamination or inadequate pretreatment appear to be the most likely cause of erroneous results on archaeological bone (Anderson 1998; Smith and Anderson 1998; Petchey and Higham, in prep)(see Chapter 4). All rat bone radiocarbon estimates are, therefore rejected. This includes: NZA-5719, NZA-5620, NZA-5926, and NZA-5936 from Shag River Mouth; NZA-6536 and NZA-6532 from Pleasant River, Areas 1 and 2 respectively; and NZA-7411, NZA-7044 and NZA-7410 from Pauatahanui.

*6. Contamination*

Radiocarbon estimates are excluded if the sample analysed has been noted by the laboratory or researcher to have been, or was at risk of being contaminated. This includes: NZ-766 from Tai Rua which was contaminated with dieldrin, a carbon compound (Trotter to Rafter 24/1/67); and NZ-7666 and Wk-5433 from Shag River Mouth. NZ-7666 was contaminated with "electronegative impurities" and required further purification through a molecular sieve (Anderson, Smith and Higham

1996:64). The exact method of purification is unclear and NZ-7666 is, therefore considered to be questionable. The preservation state of Wk-5433 was anomalous. Excessive recrystallisation of the hydroxyapatite fraction (see Chapter 6) compared to other bones from Shag River Mouth implies that this sample was not in primary deposition. It is suspected that this sample may have a sub-fossil origin.

*7. Single radiocarbon determinations*

All measurements on bone without contemporary paired radiocarbon determinations of reliable samples are rejected from this assessment because their accuracy cannot be determined at present. This includes: NZ-146 (*R*192/2A) from Tautuku; NZ-756 from Hampden; NZ-932 from Raikaia River Mouth; NZ-1162 and NZ-1376 from Sewers Trench, Redcliffs; NZ-1839 from Hurunui River Mouth; NZA-557 from Parker's Midden; NZA-575 from Skipper's Midden; NZ-1763 from Wakanui; and NZA-583 from Hot Water Beach, Layer 6.

Radiocarbon ages are also excluded from further analysis where the matching charcoal or shell pairs can be rejected following the protocols given in Schmidt (1996:161-162) and Higham *et al.* (in prep), or where the reliability of the sample type is unknown (see Appendix 5). This includes: NZ-559, NZ-578 and NZ-752 from Tai Rua; NZ-760 from Woolshed Flat; NZA-2227 from Takahe Valley; NZ-4872 from Awamoa; and NZ-3934 and NZ-3931 from Layer 4 at Kaupokonui.

## BONE, CHARCOAL AND SHELL PAIRS

A total of eleven sites with bone and matching charcoal and or marine shell determinations out of 46 sites with bone results remain after application of the above discard protocol (Table 8.2). All calibrated ages are calculated according to the parameters given in Chapter 7.

Table 8.2: Bone, charcoal and marine shell radiocarbon ages from New Zealand archaeological sites remaining following application of discard protocol.

| Site name | Lab no. Run no. | Provenance | Sample type | CRA | Cal 95% (AD) |
|---|---|---|---|---|---|
| Mt Camel/ Houhora | NZ-5007 | Layer 2c | Moa collagen | 563 ± 56 | 1398-1437 |
| | NZ-5008 | Layer 3b | Moa collagen | 585 ± 46 | 1320-1340<br>1395-1427 |
| | NZA-2436 | Layer 2b | Charcoal | 632 ± 86 | 1291-1422 |
| | NZA-2437 | Layer 2b | Charcoal | 774 ± 87 | 1216-1300<br>1376-1379 |
| | NZA-2438 | Layer 3 | Charcoal | 727 ± 86 | 1262-1328<br>1349-1391 |

| Site name | Lab no. Run no. | Provenance | Sample type | CRA | Cal 95% (AD) |
|---|---|---|---|---|---|
| Mt Camel/ Houhora | Wk-5485 | Layer 3b | Charcoal | 640 ± 40 | 1300-1375<br>1380-1407 |
| | Wk-5034 | Layer 2b | Shell | 960 ± 40 | 1341-1426 |
| | Wk-5035 | Layer 2b | Shell | 1060 ± 45 | 1285-1334 |
| Cross Creek | NZA-576 | Layers 7, 8 and 9 | Moa collagen | 751 ± 58 | 1273-1300 |
| | NZ-6800 | Layer 7 | Shell | 1035 ± 28 | 1304-1344 |
| Tairua | NZA-558 | Layer 2, oven | Moa collagen | 460 ± 55 | 1434-1484 |
| | Wk-5444 | Layer 2 | Shell | 1000 ± 50 | 1311-1409 |
| | Wk-5445 | Layer 2 | Shell | 1090 ± 50 | 1258-1319 |
| | NZ-1875 | Layer 2 | Shell | 885 ± 58 | 1409-1474 |
| Avoca Point, (Old Pier Point) | NZ-4155 | Cultural layer: Oven | Moa collagen | 703 ± 85 | 1280-1398 |
| | NZ-3164 | Cultural layer: Oven | Moa collagen | 952 ± 192 | 898-909<br>964-1286 |
| | NZ-2719 | Cultural layer | Shell | 1174 ± 33 | 1192-1270 |
| | NZ-2718 | Cultural layer | Shell | 1183 ± 29 | 1187-1259 |
| | Wk-4000 | Cultural layer | Eggshell | 700 ± 70 | 1282-1330<br>1346-1393 |
| | Wk-4001 | Cultural layer | Eggshell | 740 ± 70 | 1262-1305<br>1312-1317<br>1371-1385 |
| Redcliffs: Hamilton's Deposit | NZ-1113 | Occupation layer | Moa collagen | 701 ± 60 | 1285-1316<br>1344-1393 |
| | NZ-1111 | | Shell | 924 ± 42 | 1396-1444 |
| Tumbledown Bay | NZA-825 | Layer 3 lower | Moa collagen | 307 ± 85 | 1490-1602<br>1616-1674<br>1778-1799<br>1945-1948 |
| | NZ-7656 | Layer 3 hut site | Charcoal | 418 ± 47 | 1443-1522<br>1582-1626 |
| | NZ-7654 | Layer 3 | Shell | 706 ± 50 | 1520-1655 |
| | NZ-7745 | Layer 3 lower | Shell | 686 ± 38 | 1545-1660 |
| Ototara | NZ-754 | Occupational layer | Moa collagen | 435 ± 70 | 1436-1521<br>1566-1629 |
| | NZ-560 | | Shell | 838 ± 59 | 1434-1506 |
| Shag River Mouth: Trotter 1979 testpit | NZ-5016 | Ashy layer below midden | Moa collagen | 641 ± 85 | 1293-1416 |
| | NZ-5017 | Ashy layer below midden | Shell | 994 ± 33 | 1322-1404 |
| Shag River Mouth: SM/C:Dune | NZA-781 | Layer 2 | Moa collagen | 630 ± 82 | 1296-1421 |
| | NZ-7758 | Layer 2 | Charcoal | 580 ± 47 | 1300-1347<br>1392-1430 |
| | Wk-2751 | Layer 4 | Shell | 960 ± 45 | 1336-1429 |
| | Wk-2410 | Layer 4 | Shell | 1020 ± 50 | 1302-1398 |
| | Wk-2411 | Layer 4 | Shell | 990 ± 45 | 1318-1412 |
| | Wk-2412 | Layer 4 | Shell | 980 ± 45 | 1323-1418 |
| | Wk-2362 | Layer 4 | Shell | 1010 ± 50 | 1307-1403 |
| | NZ-7805 | Layer 4 | Shell | 965 ± 26 | 1350-1417 |
| | Wk-2508 | Layer 4 | Shell | 1060 ± 45 | 1285-1334 |
| | Wk-2632 | Layer 4 | Shell | 980 ± 40 | 1326-1415 |
| | Wk-2752 | Layer 4 | Shell | 1040 ± 45 | 1296-1371 |
| | Wk-2856 | Layer 4 | Shell | 980 ± 40 | 1326-1415 |
| | Wk-2857 | Layer 4 | Shell | 950 ± 45 | 1348-1434 |

| Site name | Lab no. Run no. | Provenance | Sample type | CRA | Cal 95% (AD) |
|---|---|---|---|---|---|
| Shag River Mouth: SM/C:Dune | Wk-2440 | Layer 4 | Shell | 1050 ± 50 | 1288-1351 |
| | Wk-2441 | Layer 4 | Shell | 1070 ± 45 | 1279-1327 |
| | NZ-7761 | Layer 4 | Charcoal | 600 ± 50 | 1325-1353<br>1359-1368<br>1389-1420 |
| | NZ-7757 | Layer 5 | Charcoal | 537 ± 44 | 1409-1439 |
| | Wk-2416 | Layer 5 | Eggshell | 600 ± 50 | 1325-1353<br>1359-1368<br>1389-1420 |
| | NZ-7736 | Layer 6 | Moa collagen | 634 ± 58 | 1303-1411 |
| | NZ-7756 | Layer 6 | Charcoal | 670 ± 47 | 1291-1331<br>1344-1395 |
| | Wk-2417 | Layer 6 | Eggshell | 560 ± 45 | 1334-1341<br>1399-1435 |
| | NZA-780 | Layer 7 | Moa collagen | 509 ± 72 | 1406-1465 |
| | NZ-7755 | Layer 7 | Charcoal | 646 ± 47 | 1296-1407 |
| | Wk-2589 | Layer 7 | Charcoal | 630 ± 35 | 1306-1371<br>1385-1408 |
| | NZ-7806 | Layer 7 | Shell | 1022 ± 29 | 1310-1378 |
| | Wk-2604 | Layer 8 | Eggshell | 570 ± 45 | 1332-1344<br>1395-1432 |
| | NZ-7771 | Layer 11 | Charcoal | 660 ± 46 | 1293-1332<br>1342-1401 |
| | NZA-1175 | Layer 11 | Shell | 974 ± 49 | 1324-1423 |
| Shag River Mouth: SM/D:1 | NZA-888 | Layer 3 | Charcoal | 585 ± 93 | 1301-1374<br>1382-1439 |
| | NZ-7739 | Layer 5 | Moa collagen | 370 ± 38 | 1480-1640 |
| Shag River Mouth: SM/D:3 | NZ-7740 | Layer 2 | Moa collagen | 477 ± 53 | 1429-1475 |
| | NZA-887 | Layer 2 | Charcoal | 626 ± 95 | 1291-1429 |
| Shag River Mouth: SM/A | NZ-7741 | Layer 2 | Moa collagen | 522 ± 37 | 1412-1442 |
| | NZ-7759 | Layer 2 | Charcoal | 627 ± 40 | 1304-1371<br>1385-1410 |
| Shag River Mouth: SM/B:FHA | NZ-7742 | Layer 2 | Moa collagen | 530 ± 36 | 1410-1440 |
| | NZ-7760 | Layer 2 | Charcoal | 582 ± 47 | 1329-1348<br>1392-1429 |
| Waimataitai | NZ-579 | | Shell | 940 ± 32 | 1391-1433 |
| | NZ-5015 | | Moa collagen | 686 ± 173 | 1224-1435 |
| Pounawea | NZ-4438 | Lowest layer | Moa collagen | 602 ± 47 | 1312-1349<br>1390-1416 |
| | NZ-1796 | Lowest layer | Moa collagen | 699 ± 105 | 1276-1404 |
| | NZ-1797 | Lowest layer | Moa collagen | 668 ± 60 | 1292-1400 |
| | NZ-1798 | Lowest layer, base of oven | Moa collagen | 772 ± 66 | 1236-1298 |
| | NZ-5031 | Layer 1, Sq. H21 | Charcoal | 582 ± 77 | 1322-1370<br>1387-1437 |
| | NZ-1864 | Lower layer | Shell | 1095 ± 41 | 1261-1312 |
| | NZ-1867 | Lower layer | Shell | 1028 ± 41 | 1302-1385 |
| | NZ-1868 | Middle layer | Shell | 905 ± 41 | 1407-1453 |
| | NZ-1869 | Middle layer | Shell | 1025 ± 41 | 1304-1388 |
| | NZ-1870 | Lower layer | Shell | 1012 ± 41 | 1310-1398 |
| | NZ-1871 | Lower layer | Shell | 926 ± 41 | 1395-1443 |

| Site name | Lab no. Run no. | Provenance | Sample type | CRA | Cal 95% (AD) |
|---|---|---|---|---|---|
| Pounawea | NZ-1872 | Lower layer | Shell | 919 ± 41 | 1399-1446 |
| Papatowai | NZ-137 (*R*192/1A) | Middle layer | Moa "fixed carbon" | 707 ± 61 | 1284-1314<br>1346-1391 |
| | NZ-1333 | Bottom layer | Shell | 1051 ± 45 | 1290-1342 |
| | NZA-1415 | Upper shell layer | Charcoal | 570 ± 66 | 1328-1349<br>1391-1437 |
| | Wk-1761 | Lower cultural layer | Charcoal | 650 ± 45 | 1296-1406 |
| | Wk-1762 | Lower cultural layer | Charcoal | 640 ± 45 | 1298-1408 |

## Considerations

Despite the use of a discard protocol, not all determinations are indistinguishable from their associated pairs (see below). There are six documented possibilities for these anomalous results;

- variation in dietary $\Delta^{14}C$;
- incorporation of sub-fossil bone;
- inadequate pretreatment or unremoved contamination;
- contextual misplacement;
- poor bone preservation (including burning); or
- statistical variation.

All remaining $^{14}C$ determinations given in Table 8.2 are of moa bone. Because moa feed mainly on C3 plants (Anderson, 1991:777) they are considered to have been in equilibrium with atmospheric $\Delta^{14}C$ values. Variation introduced by dietary $\Delta^{14}C$ should not, therefore significantly influence the radiocarbon estimates.

Seperating sub-fossil moa from cultural moa remains often relies on the presence of butchery marks. The recognition of bone associated with cultural activity has, however, been a major problem with $^{14}C$ analysis of moa bone as the identification of sub-fossil bone appears to "rely on experience rather than any objective criteria" (Anderson 1989:112), and butchery marks can be easily mis-interpreted (Andrews 1995;148). Because sub-fossil bone may have been imported into a site for tool manufacture (Anderson 1989:112; Millener 1981:240), or stock piled for fuel (Kooyman 1985:99, 116), and because archaeological sites may be located on sub-fossil deposits, it is argued that samples for radiocarbon measurement should be considered on a site by site basis.

Identification of contextual misplacement relies on initial evaluation during excavation and is difficult to detect if not noted at the time. This remains a problem with any

anomalous determination, especially where there is no, or only a preliminary published site report.

Inadequate pretreatment and variable preservation state have been suggested as possible reasons for anomalous collagen determinations (*i.e.* Anderson 1991:777, 779; Anderson, Smith, Higham 1996:64; Beavan and Sparks 1997:8). Neither viewpoint has been adequately assessed in the New Zealand situation. Indeed, a variety of bone pretreatment methods have been applied at IGNS (Table 4.1). Research overseas (Stafford *et al.* 1991:62-64; van Klinken and Hedges 1995) and the results given in Chapter 6, suggest that many of these pretreatments are not of equal validity.

- Rafter (1955) devised a pretreatment technique to isolate both the protein ("fixed carbon") and carbonate portions of bone. The "fixed carbon" fraction is, in effect, the residue remaining following decalcification of bone. There have been no comparisons made between this and other pretreatments, though it is speculated that the success of such "fixed carbon" determinations are similar to those that have undergone an acid wash (see below).

- The "fixed carbon" method was superseded at IGNS by a more conventional acid wash pretreatment (Rafter 1965; Rafter *et al.* 1972; Jansen 1984). An acid wash (HCl or phosphoric acid) can leave a considerable amount of contamination (>15%) (van Klinken and Hedges 1995:268). This could result in a possible error of greater than 80 years in a sample of 600 BP when contaminated by modern carbon (Table 2.3). Therefore, bone pretreated in this manner will generally give a minimum age (Stafford *et al.* 1991:63, table 12). The presence of contamination can clearly be seen in the FTIR spectra of some acid-insoluble fractions isolated for this research (see Chapter 6).

- In the late 1980's, a NaOH wash was added to the routine bone pretreatment method at IGNS (McFadgen and Manning 1989). An alkali washed, acid-insoluble fraction may leave up to 10 - 15% humic contamination (van Klinken and Hedges 1995:268). This equates to a possible error of 55 - 80 years in a sample 600 years old when contaminated by modern carbon (Table 2.3). In most cases, an error of this magnitude would go undetected.

- A gelatinisation step was added to the pretreatment at IGNS in 1993 (Redvers-Newton and Coote 1994). Van Klinken and Hedges (1995:268) have demonstrated that gelatinisation of heavily contaminated collagen can leave around

8% humic contamination. This can result in an error of around 42 years in a sample 600 years old, or 680 years too old when contaminated with $^{14}C$ free carbon (Table 2.3). Both scenarios are, however, unlikely because contamination is usually a mix of ages. It is generally agreed that such pretreatment improves the possibility of an accurate radiocarbon estimate on well-preserved bone (>20% collagen remaining), but that contamination should be tested for prior to analysis (Stafford *et al.* 1991:64, table 12; Hedges and van Klinken 1992:286). Redvers-Newton (1995:113) concluded that gelatin pretreatment would not give accurate results for Class III bones (0.9-0.4 %N).

- A NaOH wash before gelatinisation can improve the accuracy of radiocarbon measurements depending on the level and type of contamination (Gurfinkel 1987: 51; Arslanov and Svezhentsev 1993:389). All Waikato samples (Wk-) were treated with NaOH prior to gelatinisation. This method has been shown to be successful in most cases for Class II bones (Chapters 6 and 7) and should reduce contamination to levels below the 8% of gelatinisation alone.

All the remaining bone determinations, given in Table 8.2, were of an acid or an acid /alkali washed fraction. The results of this dissertation suggest that where bone is very well-preserved, the remaining contamination following pretreatment will be invisible at the level of precision used to date most archaeological sites. Where the bone is of "poor" or "transitional" preservation it is likely that significant contamination will remain following the pretreatment and be responsible for anomalous results. This begs the question then, which bones were poorly preserved ?

The importance of environmental and climatic conditions has already been noted. Unfortunately, microclimate information for the sites listed in Table 8.2 is virtually non-existent. From Chapter 5 it was suggested that, all things being equal, bones were of better preservation when they came from sites located in the southern South Island where the climate is cool and rainfall is low (Table 8.3). Therefore, it is hypothesised that bone from sites in Otago should give reliable radiocarbon results. Bone determinations from sites further north may have been of poor preservation state and, therefore did not receive sufficient pretreatment.

It should also be noted that statistical variation may play a part in explaining some of the smaller discrepancies identified between bone determinations and more reliable sample types. Van Klinken and Hedges (1998), for instance, have suggested that a shift in age of 1-2$\sigma$ between identical repeat dated samples may be due either to the effects of contamination or inbuilt age, or it might reflect simple statistical variation in a

Gaussian distribution. A shift in age of 3σ or greater is more clear in implying a contamination effect. Difficulty in reliably assessing the accuracy of many of the determinations discussed below is exacerbated further by larger standard errors.

Table 8.3: Climatic information for sites with bone determinations following application of discard protocol.

| Site | Annual rainfall (mm)† | Mean annual temperature (°C)† |
|---|---|---|
| Houhora | 1016-1270 | 14.4-15.0 |
| Cross Creek | 1270-1524 | 13.9-14.4 |
| Tairua | 1524-2032 | 13.9-14.4 |
| Avoca Point | 1016-1270 | 11.7-12.2 |
| Redcliffs | 635-762 | 11.1-11.7 |
| Tumbledown Bay | 635-762 | 11.1-11.7 |
| Ototara | 508-635 | 10.6-11.1 |
| Shag River Mouth | 508-635 | 10.6-11.1 |
| Waimataitai Mouth | 508-635 | 10.6-11.1 |
| Pounawea | 1270-1524 | 9.4-10 |
| Papatowai | 1016-1270 | 9.4-10 |

† Rainfall and temperature at sea level (from McLintock 1960:map 8).

## RESULTS AND ANALYSIS

Bone, charcoal and marine shell determinations remaining following this analysis are considered to be acceptable (at the level of precision encountered) when they are statistically identical and overlap with the calibrated age ranges of other sample types at one standard deviation (1σ). Due to the small number of determinations present for many sites, and given the uncertainties with preservation state and effectiveness of pretreatment, the determinations are also assessed according to geographical location, site details (where available), and pretreatment.

1. Houhora: There is a total of 8 "acceptable" $^{14}C$ determinations from Houhora, two of which are of moa bone. The moa bone "collagen" samples from Houhora (NZ-5007 and NZ-5008) give a pooled mean age of 576 ± 37 BP, and a calibrated age at one sigma of AD 1399-1427. While these two determinations are statistically indistinguishable [$T' = 0.09$; $\chi^2_{1:0.05} = 3.84$], they do not overlap with the pooled charcoal and shell age ranges for the site (see Chapter 7). Evaluation of these results using OxCal combined probabilities method suggests that there is poor overall agreement between moa, charcoal and shell [n = 3, $A_{overall}$ = 59.9% (An = 40.8%)] and that the moa determinations are the outliers with A = 50.8% (<A'c = 60.0%).

   There is some doubt about the primary nature of the *Anomalopteryx* bones at Houhora (Anderson 1989:112)(both NZ-5007 and NZ-5008 include remains of *Anomalopteryx*) (Millener 1981:240). Following the analysis of material from

Houhora given in Chapter 7, it is considered more likely that these young estimates are the result of contamination that remained after the acid wash.

2. Cross Creek: The calibrated moa collagen $^{14}C$ estimate for NZA-576 does not overlap the calibrated result of the shell (NZ-6800) at 1σ. They are, however, very close, being separated by only four calendrical years. Using the OxCal combine probabilities method these two dates are in agreement [n = 2, $A_{overall}$ = 75.3% (An = 50.0%)] and give a combined calibrated age of AD 1289-1320 (37.5%) and 1351-1381 (30.7%) at 1σ.

   Sewell (in Higham *et al.* in prep) has suggested that it is impossible to be certain whether the moa was hunted or brought to the site for industrial purposes, though Anderson (1989:111-112) considered it likely that the moa bone had been imported. The slightly older moa determination could support this hypothesis. Conversely, the Cross Creek midden is situated within a sand dune in a region with high annual rainfall (1270 - 1524 mm) and temperature (13.9 - 14.4°C) (Table 8.3). Under such circumstances it is possible that this bone sample was of "poor" preservation. This cannot be adequately evaluated at this level of precision.

3. Tairua: The calibrated moa collagen determination for NZA-558 (Cal AD 1433-1484) does not overlap the pooled value of two Wk- shell results [$A'(p)$ = 1045 ± 36; Cal AD 1297-1340 at 1σ ($T'$ = 1.62; $\chi^2_{1:0.05}$ = 3.84)][2].

   Tairua falls into the highest rainfall region (1524 - 2032 mm) of any of the sites given here (Table 8.3). Although the Tairua midden is located within a well-drained sand dune (McFadgen to IGNS, 6/8/73), it is suggested that the bone used for NZA-558 may have been of poor preservation. Schmidt and Higham (in prep) concluded that Tairua had been occupied in the late 13th to early 14th century. The moa bone sample suggests a 15th century occupation.

4. Avoca Point: There are two collagen results for Avoca Point; NZ-4155 and NZ-3164. These are indistinguishable [$A'(p)$ = 744 ± 78 ($T'$ = 1.41; $\chi^2_{1:0.05}$ = 3.84)]. NZ-3164 does, however, have a very large standard error making any

[2] The three shell determinations are statistically distinguishable (T' = 7.17; $\chi^2_{2:0.05}$ = 5.99). Combination of the three shell determinations using OxCal also suggests they are in poor agreement [n = 3, $A_{overall}$ = 33.9% (An = 40.8%)]. Schmidt and Higham (in prep) suggest there may be a problem with NZ-1875 due to the inclusion of *Cellana denticulata*, an estuarine and subtidal species which may be subject to $^{14}C$ enrichment (see Hogg, Higham and Dahm 1988). When excluded, the remaining shell estimates are in agreement [n = 2, $A_{overall}$ = 82.1% (An = 50.0%)], though the overall agreement for the Tairua moa and "acceptable" shell samples is poor [n = 2, $A_{overall}$ = 18.5% (An = 50.0%)].

conclusion regarding accuracy problematic. The calibrated age ranges of the moa collagen at one sigma (AD 1256-1307 and AD 1358-1384) overlap with the pooled calibrated shell results of NZ-2718 and NZ-2719 [$A'(p)$ = 1179 ± 26; Cal AD 1193-1261 at 1σ ($T'$ = 0.04; $\chi^2_{1:0.05}$ = 3.84)], and the pooled eggshell determinations [$A'(p)$ = 720 ± 52; Cal 1σ AD 1282-1320 and 1370-1386 ($T'$ = 0.16; $\chi^2_{1:0.05}$ = 3.84)]. These radiocarbon estimates suggest an occupation in the 13th to 14th centuries.

Evaluation of the suite of $^{14}C$ determinations using OxCal suggests that they are in poor agreement with the overall index falling below the 60% threshold for an acceptable result [n = 3, $A_{overall}$ = 52.5% (An = 40.8%)].

The Avoca Point collagen determinations may be suspect for a number of reasons. First, the occupation layer at Avoca Point is located at the edge of swampy ground and Trotter (1980a:281, 283) has suggested that at one point midden material had been deliberately dumped into a swamp at the time of occupation. In addition, at the eastern extent of the site there had been a natural accumulation of faunal remains. Although the moa bones selected for analysis came from squares (squares 9 and 10) several metres away from the natural accumulations and swamp deposits (Trotter 1980a:283), it should be kept in mind that sub-fossil material may have been selected or that excessive bone degradation may have occurred.

5. Hamilton's deposit, Redcliffs: The moa bone collagen result for NZ-1113 does not overlap when calibrated at one sigma with the single shell determination (NZ-1111). The calibrated ages for these two samples are, however, only separated by 3 calendrical years. The OxCal combined probabilities method suggests these two dates are in agreement [n = 2, $A_{overall}$ = 74.1% (An = 50.0%)] and give a combined calibrated age of AD 1352-1400 (1σ).

   Although Redcliffs is located in a low temperature and rainfall area (Table 8.3), swampy conditions on the flat (Trotter 1975c:190) may be responsible for the discrepancy in calendrical ages. The possibility of disturbance at the site also cannot be ruled out because both samples were collected in 1966 when Trotter renewed excavations approximately 60 cm away from where previous $^{14}C$ samples had been collected in 1957 (Trotter 1975c:192, 197). There is insufficient information at present to evaluate these results.

6. Tumbledown Bay: Tumbledown Bay is located in a sand dune environment (FRF). No information has been published concerning this excavation. The

calibrated moa bone collagen result for NZA-825 overlaps associated shell and charcoal determinations. Evaluation of the combined results from Tumbledown Bay using OxCal indicates that all $^{14}C$ estimates are in agreement [n = 3, $A_{overall}$ = 101.7% (An = 40.8%)], yielding a calibrated age range at 1σ of AD 1564-1631. This is a late date for a site with evidence of moa butchery. Ten percent modern contamination in a site 400 years old is, however, unlikely to be statistically significant at this level of precision.

7. Ototara: When calibrated, the moa bone collagen determination (NZ-754) from Ototara overlaps with the calibrated result of the single shell radiocarbon estimate for the site (NZ-560). Using the OxCal combine probabilities method, these two $^{14}C$ estimates are in agreement [n = 2, $A_{overall}$ = 122.8% (An = 50.0%)], and suggest an occupation *ca.* AD 1440-1502 (1σ). This is in-keeping with Trotter's (1965:113) description of the site as having intermediate to "typical" Archaic and Classic Maori remains. According to Trotter (1965), however, there is evidence of bone working for industrial purposes. There is, therefore some doubt about whether NZ-754 dates a butchered moa (Higham *et al.* in prep). Contamination by modern carbon is also unlikely to be statistically significant in a site of this age, at this level of precision. The location of the Ototara midden in a low rainfall and temperature region, under a limestone overhang (Trotter 1965:109) suggests, however, that this should be an accurate radiocarbon measurement. There is, unfortunately, insufficient data to evaluate these results adequately.

8. Shag River Mouth: When considered as a set, the moa bone collagen determinations from Shag River Mouth are statistically distinguishable and are highly variable when compared to other sample types that indicate a mid 14$^{th}$ century occupation (Anderson, Smith and Higham 1996:67). This implies some form of contamination, despite all submitted bone samples being in "good" condition, being robust and relatively dense, with no obvious visual sign of weathering (I. Smith, *pers. comm.* 30/6/1997). In addition, because archaeological investigations at Shag River Mouth covered a wide area incorporating both dune and estuarine environments it is suggested that bone preservation will vary depending on the excavation area. It is also likely that hand specimen identification may not have been sufficient to detect problem samples (Nicholson 1996a, 1998) as suggested by the results given in Chapter 6. The additional purification required for NZ-7666 (see above) supports this idea of poor preservation. Consequently, the existing radiocarbon determinations are analysed on an area by area basis (see below).

*a) Test pit, Trotter (1979):*

Moa bone (NZ-5016) and shell samples (NZ-5017) were collected from a test pit on the southern margin of Shag River Mouth by Trotter in 1979 (Anderson and Smith 1996a:9). Both NZ-5016 and NZ-5017 overlap when calibrated and suggest a 14th century occupation. Evaluation using OxCal indicates that these two determinations are in agreement [n = 2, $A_{overall}$ = 113.0% (An = 50.0%)]. The calibrated age range of AD 1332-1394 (1σ) is also consistent with the expected age for the occupation at Shag River Mouth (see below).

*b) SM/A and SM/B*

Two bone samples were obtained in these areas; NZ-7741 from SM/A and NZ-7742 from SM/B:FHA. Although NZ-7741 from area SM/A is indistinguishable [$T'$ = 3.72; $\chi^2_{1:0.05}$ = 3.84] to a charcoal determination from a similar stratigraphic horizon (NZ-7759), and are in agreement when combined using OxCal [n = 2, $A_{overall}$ = 61.9% (An = 50.0%); Cal AD 1402-1426 (1σ)], the calibrated age ranges do not overlap. Conversely, NZ-7742 from SM/B:FHA is comparable with the calibrated age range of its paired charcoal result (NZ-7760) and is in agreement following combination [n = 2, $A_{overall}$ = 114.3% (An = 50.0%); Cal AD 1408-1432 (1σ)].

Both bone samples indicate a later occupation than the 14th century suggested by Anderson, Smith and Higham (1996:67). It is possible that SM/B:FHA and SM/A were occupied later than SM/C:Dune (see below). These determinations are, however, likely to have been on bone of poor preservation. SM/A and SM/B, although separated by almost 200 m, are located close to the boundary of the *Salicornia* mud flats, near the surface of the water table (Allingham and Anderson 1996:35, figure 4.1). According to Anderson, Worthy and McGovern-Wilson (1996:207, 209, 210), both SM/A and SM/B:FHA are also characterised by a higher degree of weathering and burning compared to material from the dunes.

*c) SM/C:Dune*

Anderson, Worthy, and McGovern-Wilson (1996:207) suggested that the soil matrix at the SM/C:Dune excavation is conducive to long-term survival of bones. The results presented in Chapters 6 and 7 of this research support this conclusion. There is, therefore no reason to suggest that bone from the high dune area will be degraded or unsuitable for radiocarbon analysis, with the possible exception of

excessively burnt bone. Such bone does not appear to have been submitted from SM/C:Dume (I. Smith, *pers. comm.* 30/6/1997).

In general, the bone samples from this area appear to be acceptable for $^{14}C$ analysis, with the exception of NZ-7666, NZ-7743, NZ-7737 and Wk-5433 (see above). The remaining acceptable samples are indistinguishable [$A'(p) = 596 \pm 40$ ($T' = 2.06$; $\chi^2_{2:0.05} = 5.99$)] and give a calibrated age of Cal AD 1318-1342 and 1394-1416 at one sigma. This average overlaps with the pooled shell [$A'(p) = 993 \pm 11$; Cal AD 1332-1394 at 1σ ($T' = 8.03$; $\chi^2_{12:0.05} = 21.03$)], eggshell [$A'(p) = 575 \pm 29$; Cal AD 1334-1341 and 1397-1425 at 1σ ($T' = 0.37$; $\chi^2_{2:0.05} = 5.99$)] and charcoal ($A'(p) = 618 \pm 18$ ($T' = 6.70$; $\chi^2_{6:0.05} = 12.59$; Cal AD 1327-1350 and 1390-1408 at 1σ) results from SM/C:Dune. Using OxCal's combined probabilities method the radiocarbon determinations from SM/C:Dune are in agreement [n = 4, $A_{overall} = 92.4\%$ (An = 35.4%)] and result in an acceptable calibrated age range of AD 1332-1344 at 1σ.

*d) SM/D*

One sample of moa bone (NZ-7739) from Layer 5 in SM/D:1 has been dated. When calibrated, this determination does not overlap at one sigma with charcoal sample NZA-888 from Layer 3, is statistically distinguishable [$T' = 4.58$; $\chi^2_{1:0.05} = 3.84$], and the agreement index, when combined using OxCal, falls below the acceptable 60% threshold [n = 2, $A_{overall} = 30.5\%$ (An = 50.0%)].

The large sample size requirement of bone (349.18 g compared to around 200 g [see Anderson, Smith and Higham 1996] for other conventional collagen determinations from Shag Mouth with comparable standard errors) implies lower yields and carbon content, and therefore possible poorer preservation for this sample. This conclusion is supported by the location of SM/D:1 on the edge of wave eroded bank and close to the mud flats, where the water table is significantly higher (Smith 1996:52), even though weathering was apparently limited and the matrix at SM/D:1 was similar to the high dunes (Anderson, Worthy and McGovern-Wilson 1996:207-209).

One moa bone was dated from SM/D:3. The calibrated ages of this sample (NZ-7740) and its associated charcoal result (NZA-887) overlap by 1 calender year, and are statistically indistinguishable [$T' = 1.88$; $\chi^2_{1:0.05} = 3.84$]. When combined using OxCal they are in agreement [n = 2, $A_{overall} = 76.2\%$ (An = 50.0%)] and give a calibrated age range of AD 1405-1450 (1σ). This result is late compared

with other dating evidence from Shag River Mouth, and although acceptable at this level of precision, the result considered to be suspect.

The moa bone sample was collected from the base of an oven apparently protected from the extensive fossicking at the top of layer 2 (Smith 1996:57-58). It is, possible that the sample may have been burnt. Indeed, a higher degree of burning was noted at this location, with just under 50% of bone unburnt but blackened (considered to be the result of being buried in oven rake-out), and just under 10% completely calcined (Anderson, Worthy and McGovern-Wilson 1996:210). This area is also close to the *Salicornia* mud flats and although there is no evidence of a continuation of the swamp deposit evident to the west of the excavation (Smith 1996:51), a higher water table in this area could affect the preservation state of bone. This is supported by Anderson, Worthy and McGovern-Wilson's (1996:207-209) observation that 51% of the bones belonged to Weathering Stage 3.

9. Waimataitai Mouth: The calibrated range of a single shell determination (NZ-579) overlaps the calibrated moa bone collagen result for NZ-5015. These two determinations are also in agreement following combination using OxCal [n = 2, $A_{overall}$ = 121.5% (An = 50.0%)] and give a calibrated age range of AD 1374-1433 (1$\sigma$)]. The large standard error of the collagen radiocarbon estimate makes any conclusion regarding accuracy impossible. Because the main deposit at Waimataitai Mouth was continually damp, and only approximately 5 cm above the water level of the lagoon (Trotter 1955:296), it is likely, however, that this sample was of poorer preservation.

10. Pounawea: Four moa collagen determinations were measured from Pounawea (NZ-4438, NZ-1796, NZ-1797 and NZ-1798) and the calibrated results are indistinguishable [$A'(p)$ = 663 ± 32 ($T'$ = 4.54; $\chi^2_{3:0.05}$ = 7.81)]. When pooled (Cal 1$\sigma$ AD 1300-1322 and AD 1338-1396) they overlap the calibrated pooled result of the shell samples submitted by Lockerbie ($A'(p)$ = 988 ± 16; Cal 1$\sigma$ AD 1333-1400 ($T'$ = 18.14; $\chi^2_{6:0.05}$ = 12.59)]), and the single reliable charcoal determination (NZ-5031) from a later excavation by Hamel. Evaluation using OxCal's combined probabilities method results in an acceptable calibrated age range of AD 1344-1371 (53.2%) and 1384-1392 (15.0%) [n = 3, $A_{overall}$ = 107.2% (An = 40.8%)].

Despite the poor agreement between shell determinations from the site [n = 7, $A_{overall}$ = 17.3% (An = 26.7%)] (see also the chi squared test above), radiocarbon

estimates of all three sample types support Hamel's (1980:16) suggestion of a short period of occupation sometime in the 14th century (Higham *et al.* in prep). Further, there is no indication of a sequence that may suggest multiple occupation, as implied by Anderson (1991:787) who suggested that only the basal layer of Pounawea was inhabited prior to the 13th century. The overall agreement of bone determinations suggests the bone is reliable despite the fact that Pounawea lies in a high rainfall area (though the mean annual temperature is low and the site is generally well-drained (Lockerbie 1959:82)).

11. Papatowai: The moa "fixed carbon" result (NZ-137, *R*192/1A) collected by Lockerbie (1959) overlaps the calibrated age range of the single acceptable shell sample (NZ-1333) for the site taken from a later excavation (Hamel 1977), and the three charcoal dates ($A'(p)$ = 630 ± 30; Cal 1σ AD 1317-1370 and 1386-1407 ($T'$ = 1.07; $\chi^2_{2:0.05}$ = 5.99)] from Anderson and Smith's (1992) excavation. The overall agreement between the different sample types, following combination using OxCal, is 100.9% [An = 40.8%, n = 3], and gives an acceptable calibrated age range of AD 1302-1332 (33.5%) and 1341-1370 (34.7%) at 1σ. This supports Anderson and Smith's (1992:151) suggestion of a short period of occupation in the 14th century.

**Overview**

Bone collagen radiocarbon estimates from Tairua, SM/D:1 and Houhora are clearly erroneous. At these sites it is apparent that an acid wash pretreatment was not adequate to remove contamination, and that the bone is likely to have been poorly preserved. Bone collagen determinations from Hamilton's deposit (Redcliffs), Cross Creek, SM/A, SM/D:3 are also suspect, but there is insufficient data to form a conclusive indication of the reliability of these results. Tairua, Cross Creek and Houhora are, however, in high rainfall and temperature regions. The swampy depositional environment at Redcliffs Flat and some areas at Shag River Mouth (and Waimataitai) also appear to be non-conducive to bone preservation.

The remaining determinations from Papatowai, Pounawea, SM/C:Dune, Ototara, Tumbledown Bay and Waimataitai appear to be reliable at the level of precision encountered. Bone collagen determinations from the relatively young sites of Ototara and Tumbledown Bay are, however, unlikely to have high enough levels of contamination to be statistically visible. Problems with other sample types at Avoca Point and Pounawea may also be masking problematic bone determinations.

These results suggest that moa bone can be reliably dated, but that existing bone determinations may be suspect given the limited collagen extraction and purification methods used. Careful assessment of preservation state, intra-site environmental conditions, as well as the routine use of a gelatinisation pretreatment to purify radiocarbon samples, will significantly improve the reliability of bone determinations.

## RECOMMENDATIONS AND FUTURE WORK

This research has highlighted a number of deficiencies in the selection and analysis of bone for radiocarbon dating. The following recommendations for future application of radiocarbon analysis of bone in New Zealand are given below.

1. The development of routine techniques to aid in the selection and assessment of bone material prior to selection of a suitable radiocarbon pretreatment.

2. A greater emphasis on site chemistry would also aid in the selection of bone suitable for radiocarbon dating, as well as with the interpretation of site taphonomy.

3. All $^{14}C$ estimates should be routinely compared with contemporary multiple sample types of secure provenance. This is especially important before any rigorous assessment of sample accuracy or comprehensive New Zealand prehistoric chronology can be developed.

4. There is considerable misunderstanding and a range of misconceptions about bone and radiocarbon bone pretreatments. Better communication with the archaeological public is vital.

## CONCLUSIONS

This research lends support to the following conclusions:

1. Snapper (*Pagrus auratus*) and barracouta (*Thyrsites atun*) bone can be used for dating New Zealand archaeological sites. Inbuilt age, hardwater effect, terrestrial carbon effect, and old carbon introduced by upwelling do not appear to be a potential source of error for radiocarbon analysis of these fish species at the level of precision used in this study. It is likely that the $^{14}C$ content of other coastal marine fish can be measured, but this needs to be tested.

2. The Stuiver and Braziunas (1993) modelled marine curve provides reliable calibrated ages for archaeological fish bone gelatin.

3. Gelatinisation of NaOH washed bone should provide reliable radiocarbon determinations on samples <1000 years old where >40% gelatin can be extracted. Such bones should, however, have additional confirmation of their reliability by one (or preferably several) assessment techniques. In most cases more rigorous pretreatment methods are not necessary at the level of precision commonly used, and do not warrant the additional cost involved. Indeed, where bones are of poor preservation or Class III and below, it is considered doubtful whether the radiocarbon estimate will be accurate.

4. There is no conclusive proof that moa bone from New Zealand archaeological sites cannot be dated accurately by radiocarbon. It is apparent, however, that previous pretreatment methods were not always successful, especially when the bones were of poor preservation. Careful assessment of the bone and site environment are, therefore vital for improving the accuracy and security of the determination. The identification of sub-fossil moa bone is also considered to be one of the major uncertainties with moa bone results, though contextual security is also important.

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*GCA = Geochimica et Cosmochimica Acta*
HPT = New Zealand Historic Places Trust.
*JAS = Journal of Archaeological Science.*
*JPS = Journal of the Polynesian Society.*
*JRSNZ = Journal of the Royal Society of New Zealand*
*NZAA = New Zealand Archaeological Association Newsletter.*
*NZJA = New Zealand Journal of Archaeology.*
*NZJGG = New Zealand Journal of Geology and Geophysics*
*RAIM = Records of the Auckland Institute and Museum.*
*RCM = Records of the Canterbury Museum.*

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# APPENDIX 1

# BAG LABELS

**TWILIGHT BEACH, Layer IIIa†**

**Fish Bone**

TWILIGHT BCH [123]
N1&2 /976
SQ P25/1 Layer 1
Quad NW Spit 1
BK2 P28

N1&2 /976 [12]
SQ O22/11
Quad SW Layer 3
Spit 1
Bk 7 P9
FISH

N1+2 /976 [75]
O23/5 NW
3-1
FISH

N1+2 /976 [26]
O19/5 S.E.
Layer 3
Bk 1 p11
Fish

N1+2 /976
O23/8 SW
3-1
FISH

NZ+2 /976 [76]
O23/6 SW
3-1
FISH

N1&2 /976 [71]
SQ O22/8 NE Quad
Layer 3, Spit 1
Bk 7 P9
FISH

N1&2 /976
O22/10 Quad NW
Layer 3 Spit 1
Bk7 P9
Fishbone [72]

N1&2 /976
SQ P25/7 Layer 1
Quad SE Spit 1
Bk 2 P30

N1&2 /976
SQ P25/5 Layer 1
Quad NE Spit 1
Bk2 P29

N1+2 /976 [119]
P24/7 NE
LAYER 1 SPIT 1
FISH

N1+2 /976
P24/8 SE
Layer 1 Spit 1
FISH.

N1+2 /976
P24/3 NW
LAYER 1 SPIT 1
FISH.

N1&2 /976
SQ P25/2 Layer 1
Quad SW Spit 1
BK 2 P28

N1&2 /976 Bags 1 + 2
SQ O19/16
Quad SE Layer 3
Bk1 pg14
Fish bone [24]

**Shell**

N1+2 /976
O20/8 SE
3-1
Toheroa

N1+2 /976
Q17/1 NW
Layer 1 Spit 1
Toheroa hinges + frags.

**SHAG RIVER MOUTH, Layer 4**

**Fish Bone**

S.M./C Sorted
❑ E.8
L.4
c.26-11-88

Sorted
❑ F.8
L.4. ✔
Layer 4

S.M./C Sorted
❑ E7
Layer 4
24-11-88

Sorted
❑ F.7
Layer 4

Sorted
S.M. 13/12/88
❑ H8
Upper L.4
Spit 1

SHAG MOUTH sorted
14-12-88
❑ H8
Layer 4. (upper)
Spit 2

Shag Mouth sorted
15-12-88
❑ H8
upper L.4
Spit 4

† Layer designation according to M. Taylor (*pers. comm.* 29/1/97).

Shag Mouth sorted
❑ G8
Upper Layer 4
Spit 5
15/12/88

SHAG MTA sorted
J8
L4 UPPER
9/12/88
MATRIX ONLY

Sorted
❑ G8 -L4
*102 (upper)
Shag mouth

SHAG MOUTH sorted
14-12-88
❑ H8
L.4 (upper)
Spit 3

**Moa**

SM
sq G8
upper layer 4
Bag 1056.
BM766-1

**HOUHORA**

**Fish Bone**

C8 MC/65 DD
fossick .A.
premaxilla (L)

C8 MC/65 DB
fossick A
atlas

C8 No label
dentaries (R)

C8 MC/65
.FW.

C8 MC/65 DF
fossk A
Maxilla (R)

C8 No label
premaxilla (R)

C8 No label
dentaries (L)

C8 MC/65 DG
fossick A
Maxilla (L)

**Shell**

Houhora
E-7
2b
SE corner
Shell

Houhora
D-6
2b
2nd Hangi
shell

**ROTOKURA**

**Test samples: Fish bone**

Roto
P61
L-2
AB083

Roto
Q61
L-2
AB086

Roto
N61
L-2
AB091

Roto
N61
L-4
AB093

Roto
N61
L-2
AB095

Roto
P61
L-2
AB099

Roto
P63
L-4
AB103

Roto
P63
L-2
AB104

Roto
P63
L-2
AB106

Roto
O63
L-2
AB108

Roto
O63
L-2
AB109

Roto
O63
L-2
AB112

Roto
N62
L-2
AB114

Roto
P62
L-2
AB115

Roto
P60
L-2
AB127

Roto
O64
L-2
AB136

Roto
O57
L-2
AB157

Roto
O58
L-4
AB162

Roto
O58
L-2
AB163

RotoP63
L-4
AB190

Roto
O60
L-4
AB230

**Radiocarbon samples:**
**Fish Bone**

Roto
O61
L-3 +4
AB088

Roto
N62
L-3 +4
AB131

**Shell**

Roto
O61
L-4
Paphies australis
Protothaca crassicosta
Turbo smargdas
c.f. Haliotis iris

Roto
O61
L-4
Struthiolaria papulosa

**TATA BEACH**

**Fish Bone**

Tata - int.
Red cod sample

Tata - lower
Red cod sample

Tata Beach
ESD/W - 5(N)-east
lower

Tata Beach
Red cod sample
ESD/W-5
trunk line

Tata Beach
Barracouta sample
ESD/W-5
trunk line

Tata Beach
16-5-96
ESD/W-5(N)-west
midden-lower

Tata- upper
Barracouta sample

Tata Beach
18-5-96
ESD/W-5 (N) east
lower

Tata Beach
ESD/W-5 (N) east
17-5-96 Upper

Tata Beach 17-5-96
ESD/W-5 (N) east

ESD/W-5 (N)
fareast
upper

Tata Beach
ESD/W-5 (N) west
midden-upper

Tata Beach
17-5-96
ESD/W-5(N) east
upper
Bulk non diagn. bone

**Charcoal**

Tata Beach
Lower-west
C14 sample

Tata Beach - Golden Bay
upper west
C14 sample 9gms

**Shell**

Tata Beach 17 May 96
ESD/W-5 (N)-East
Upper
Shell

Tata Beach 18 May 96
ESDW-5(N)-east
lower shell

Tata Beach 16 May 96
ESD/W-5(N)-west
Upper
pipis

**PLEASANT RIVER**

**Fish Bone**

PLR 1039-BF-56
-57
Area 7 layer 2a
Sq A4
Barracouta 2nd
Pharyngobranchial
R(bag 56) -15.6gm
L (bag 57)-16.3gm

PLR 1042-BF-40
-41
Area 7 Layer 2a
Sq B4
Barracouta -2nd
Pharyngobranchial
R (bag 40)-24.6gm
L (bag 41)-24.9gm

PLR
1039
BF. 49
1 of 3

PLR
1039
BF. 49
2 of 3

PLR
1039
BF. 3 of 3
49

**Moa**

PLR 1042-1
40.6g
Moa ? sp
R. tarsometatarsus
distal fragment

PLR 1057-2
26.4g
Moa ? sp
pubis fragments

PLR 1038-BM-1
Area 7 Layer 2a
Sq. A3
Moa ? Eu. geranoides
L. Tibiotarsus prox.
182.7gm

PLR 1057-1
62.5g
Moa ? sp.
Ischium fragment

**LONG BEACH**

**Fish Bone**

LB/D EH
1/12/77
1F/L2

LB/D/E5
L-2 IWGS
7/12/77

**Shell**

622.18g
LB/D/3E
L-2
VON

# APPENDIX 2

# Fish Minimum Number of Individuals (MNI)

Table A2.1: Houhora: Fish MNI (from Nichol 1988:192).

| Taxon | Common Name | MNI | Percentage |
|---|---|---|---|
| *Pagrus auratus* | Snapper | 2207 | 91.24 |
| *Pseudocaranx dentex* | Trevally | 132 | 5.98 |
| *Arripis trutta* | Kahawai | 55 | 2.27 |
| *Trachurus declivis* | Jack Mackerel | 10 | 0.41 |
| *Parika scaber* | Leatherjacket | 3 | 0.12 |
| *Labridae* sp. | Labrid | 2 | 0.08 |
| *Thysites atun* | Barracouta | 2 | 0.08 |
| *Nemadactylus macropterus* | Tarakihi | 1.5 | 0.06 |
| *Latris lineata* | Trumpeter | 1.5 | 0.06 |
| *Zeus japonicus* | John Dory | 1.5 | 0.06 |
| *Chelidonichthys kumu* | Red Gurnard | 1 | 0.04 |
| *Seriola grandis* | Kingfish | 1 | 0.04 |
| *Allomycterus jaculiferus* | Porcupine Fish | 1 | 0.04 |
| *Nemadactylus douglasi* | Porae | 0.5 | 0.02 |
| - | Eel | p | - |
| *Pseudophycis bachus* | Red Cod | p | - |
| *Girella tricuspidata* | Parore | p | - |
| *Parapercis colias* | Blue Cod | p | - |
| Total | | 2419 | |

p = present

Table A2.2: Twilight Beach: Fish MNI (from Taylor 1984:103-104 and Leach 1989:37-38).

| Taxon | Common Name | MNI | Percent |
|---|---|---|---|
| *Pagrus auratus* | Snapper | 592 | 93.08 |
| *Pseudolabrus* sp. | Wrasses | 18 | 2.83 |
| *Arripis trutta* | Kahawai | 11 | 1.73 |
| *Nemadactylus macropterus* | Tarakihi | 4 | 0.63 |
| *Pseudocaranx dentex* | Trevally | 2 | 0.32 |
| *Cheilodactylus spectabilis* | Red moki | 2 | 0.32 |
| *Parapercis colias* | Blue cod | 1 | 0.16 |
| *Allomycterus jaculiferus* | Porcupine fish | 1 | 0.16 |
| *Trachurus novaezelandiae* | Horse Mackerel | 1 | 0.16 |
| *Parika scaber* | Leatherjacket | p | - |
| *Zeus japonicus* | John dory | p | - |
| *Chelidonichthys kumu* | Red gurnard | p | - |
| Unidentified sp. | – | 4 | 0.63 |
| Total | | 636 | |

p = present

Table A2.3: Rotokura, Layer 4: Fish MNI (from Butts 1977:figures 16 and 19 and Appendix).

| Taxon | Common Name | MNI | Percent |
|---|---|---|---|
| *Pagrus auratus* | Snapper | 94 | 77.05 |
| *Pseudolabrus* sp. | Wrasses | 9 | 7.38 |
| *Thysites atun* | Barracouta | 3 | 2.46 |
| *Navadon convexirostris* | Rough leatherjacket | 3 | 2.46 |
| *Pseudophycis bachus* | Red cod | 3 | 2.46 |
| *Nemadactylus macropterus* | Tarakihi | 2 | 1.64 |
| *Latridopsis ciliaris* | Blue moki | 2 | 1.64 |
| *Parapercis colias* | Blue cod | 2 | 1.64 |
| *Genypterus blacodes* | Ling | 1 | 0.82 |
| *Chelidonichthys kumu* | Red gurnard | 1 | 0.82 |
| *Helicolenus percoides* | Sea perch | 1 | 0.82 |
| *Myliobatus tenuicaudatus* | Eagle Ray | 1 | 0.82 |
| Total | | 122 | |

Table A2.4: Tata Beach, ESW/5: Barracouta and red cod numbers - selected bags (from Barber 1998:10, table 2).

| Taxon | Fish numbers |
|---|---|
| | Upper Unit |
| *Pseudophycis bachus* | 12 |
| *Thysites atun* | 28 |
| | Intermediate Unit |
| *Pseudophycis bachus* | 52 |
| *Thysites atun* | 6 |
| | Lower Unit |
| *Pseudophycis bachus* | 57 |
| *Thysites atun* | 16 |

Table A2.5: SM/C:Dune, Layer 4: Fish MNI (from Anderson and Smith 1996:239, table 17).

| Taxon | Common Name | MNI | Percent |
|---|---|---|---|
| *Thysites atun* | Barracouta | 604 | 67.95 |
| *Pseudophycis bachus* | Red cod | 200 | 22.50 |
| *Pseudolabrus* sp. | Wrasses | 33 | 3.71 |
| *Paranotothenia magellanica* | Black cod | 14 | 1.58 |
| *Genypterus blacodes* | Ling | 12 | 1.35 |
| *Parapercis colias* | Blue cod | 12 | 1.35 |
| *Polyprion oxygeneios* | Hapuku | 4 | 0.45 |
| *Scorpaena cardinalis* | Scorpion fish | 3 | 0.34 |
| *Latris lineata* | Trumpeter | 3 | 0.34 |
| *Rexea solandri* | Gemfish | 2 | 0.23 |
| *Nemadactylus macropterus* | Tarakihi | 1 | 0.11 |
| *Helicolenus percoides* | Sea perch | 1 | 0.11 |
| Unidentified sp. | – | - | - |
| Total | | 889 | |

Table A2.6: Pleasant River, Upper Layers, Areas 3 and 7: Fish MNI (I. Smith,*pers. comm.* 5/3/96).

| Taxon | Common Name | MNI | Percent |
|---|---|---|---|
| *Thysites atun* | Barracouta | 46 | 65.71 |
| *Pseudophycis bachus* | Red cod | 16 | 22.86 |
| *Pseudolabrus* sp. | Wrasses | 2 | 2.86 |
| *Parapercis colias* | Blue cod | 1 | 1.43 |
| *Paranotothenia magellanica* | Black cod | 1 | 1.43 |
| *Genypterus blacodes* | Ling | 1 | 1.43 |
| Fam. *Carangidae* | – | 1 | 1.43 |
| Unidentified sp. | – | 2 | 2.86 |
| Total | | 70 | |

Table A2.7: Long Beach, Layer 2, Square F1: Fish MNI (from Leach and Boocock 1993:203, table 44).

| Taxon | Common Name | MNI | Percent |
|---|---|---|---|
| *Thysites atun* | Barracouta | 14 | 73.68 |
| *Pseudophycis bachus* | Red cod | 3 | 15.79 |
| *Parapercis colias* | Blue cod | 1 | 5.26 |
| *Polyprion oxygeneios* | Hapuka | 1 | 5.26 |
| Total | | 19 | |

Table A2.8: Long Beach, Layer 2, Square E5: Fish MNI (from Leach and Boocock 1993:202, table 43).

| Taxon | Common Name | MNI | Percent |
|---|---|---|---|
| *Thysites atun* | Barracouta | 14 | 63.64 |
| *Pseudophycis bachus* | Red cod | 4 | 18.18 |
| *Genypterus blacodes* | Ling | 2 | 9.09 |
| *Notothenia angustata* | Maori chief | 1 | 4.55 |
| *Polyprion oxygeneios* | Hapuka | 1 | 4.55 |
| Total | | 22 | |

# APPENDIX 3

## Fork Length Measurements

The fork length of snapper (*Pagrus auratus*) was determined following procedures outlined by Leach and Boocock (1995). A number of measurements were taken from five pared cranial bones (dentary (D), articular (A), quadrate (Q), premaxilla (P), and maxilla (M)) (see Leach and Boocock 1995:2, figure 1). Multiple measurements were made on each skeletal element to compensate for broken bones, but only the largest dimension (the "optimum estimator") was used, because this gives the most reliable estimate of fish size (Leach and Boocock 1995:3). Using the "optimum estimator" for each bone an appropriate regression model is applied depending on the specific bone (Table A3.1). Each regression model has been pre-determined on the basis of modern snapper populations (Leach and Boocock 1995).

Logarithmic Fit: $Y = A + B^* \ln(X)$

Power Curve Fit: $Y = A * X^B$

Linear Fit: $Y = A + B * X$

where A= constant, B= slope (Leach and Boocock 1995:6).

Table A3.1: Best fit coefficients for live length estimates from bone fragments of snapper (from Leach and Boocock 1995:21, table 3).

| Fit | Bone measurement† | Constant (A) | Slope (B) | Standard error |
|---|---|---|---|---|
| Right elements (R-): | | | | |
| Power | RA1 | 13.80103 | 0.9773467 | 12 |
| Power | RD1 | 14.09165 | 0.9586253 | 12 |
| Power | RD2 | 21.13147 | 0.9330199 | 11 |
| Linear | RD3 | 0.0 | 41.06181 | 13 |
| Linear | RM1 | 0.0 | 10.61411 | 12 |
| Power | RM2 | 27.40638 | 1.003567 | 14 |
| Power | RP1 | 14.40536 | 0.9450058 | 14 |
| Linear | RP2 | 0.0 | 31.58893 | 14 |
| Linear | RQ1 | 0.0 | 19.43539 | 9 |
| Left elements (L-): | | | | |
| Power | LA1 | 13.91409 | 0.9744805 | 13 |
| Power | LD1 | 13.87569 | 0.9625565 | 13 |
| Power | LD2 | 21.21984 | 0.934607 | 11 |
| Linear | LD3 | 0.0 | 41.18091 | 17 |
| Power | LM1 | 12.70081 | 0.951515 | 11 |
| Linear | LM2 | 0.0 | 27.45226 | 15 |
| Power | LP1 | 14.40358 | 0.9448532 | 14 |
| Linear | LP2 | 0.0 | 31.49918 | 14 |
| Linear | LQ1 | 0.0 | 19.56692 | 11 |

† See Leach and Boocock (1995:2, figure 1) for measurement parameters.

Table A3.2: Twilight Beach Layer IIIa (Spit 1, Layer 3): Measurements (mm) of five paired cranial bones (optimal estimator given in bold).

| RD1 | RD2 | RD3 | LD1 | LD2 | LD3 | RP1 | RP2 | LP1 | LP2 | RM1 | RM2 | LM1 | LM2 | RQ1 | LQ1 | RA1 | LA1 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| - | **33.67** | 17.64 | - | - | **17.05** | - | **14.44** | - | **19.15** | **43.00** | - | - | - | **23.46** | - | - | - |
| - | - | - | **56.16** | 36.20 | - | - | **17.38** | - | - | - | **11.30** | - | - | | - | - | - |
| - | - | **12.61** | - | - | - | **28.80** | 10.65 | - | **15.46** | | | - | **16.31** | | - | - | |
| - | **35.16** | 14.42 | - | - | **9.27** | **29.73** | 11.62 | - | **19.19** | | | **39.15** | - | | - | - | |
| **36.46** | 24.99 | 11.67 | **42.98** | - | - | - | **17.12** | - | - | | | - | - | | | - | |
| - | **21.87** | - | - | - | **12.39** | - | - | **40.21** | 14.96 | | | - | - | | | | |
| | | | - | - | - | - | **13.94** | - | **14.55** | | | - | **12.14** | | | | |
| | | | - | - | - | - | **14.54** | | | | | | | | | | |
| | | | - | **35.05** | 14.74 | | | | | | | | | | | | |
| | | | - | **30.97** | - | | | | | | | | | | | | |

Total no. of elements = 52



Table A3.3: Twilight Beach Layer IIIa (Spit 1, Layer 1): Measurements (mm) of five paired cranial bones (optimal estimator given in bold).

| RD1 | RD2 | RD3 | LD1 | LD2 | LD3 | RP1 | RP2 | LP1 | LP2 | RM1 | RM2 | LM1 | LM2 | RQ1 | LQ1 | RA1 | LA1 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **49.00** | 35.51 | - | **47.5** | 32.62 | - | - | **16.93** | **60.67** | 23.12 | - | - | **47.61** | 19.02 | - | - | - | - |
| **45.15** | 32.39 | - | **44.18** | 30.28 | 13.21 | - | **15.68** | - | - | - | - | - | - | - | - | - | - |
| **46.94** | 33.70 | 13.90 | - | - | - | **62.08** | 23.6 | - | **16.35** | | | | | - | - | - | - |
| - | **29.61** | 12.58 | - | - | - | - | **16.34** | **33.75** | 13.53 | | | | | - | - | - | - |
| - | - | **13.06** | - | - | - | **59.42** | 21.24 | - | **17.65** | | | | | - | - | - | **40.59** |
| - | - | - | **40.45** | - | 11.79 | **37.94** | 15.2 | - | **15.23** | | | | | - | - | - | |
| - | - | - | - | - | - | - | **18.61** | - | **17.49** | | | | | - | | | |
| - | - | **9.89** | - | - | - | - | **17.44** | **32.45** | 13.00 | | | | | - | | | |
| - | - | - | **42.10** | 29.76 | 12.40 | **41.42** | - | - | **17.21** | | | | | - | | | |
| - | - | - | **37.61** | 24.96 | - | - | - | | | | | | | - | | | |
| | | | - | - | - | **41.71** | 15.60 | | | | | | | | | | |
| | | | **45.37** | 27.93 | 11.99 | | | | | | | | | | | | |

Total no. of elements = 73

Table A3.4: Twilight Beach, Layer IIIa (Spit 1, Layer 3): Estimated Fork Length from optimum estimator.

| RD1 | RD2 | RD3 | LD1 | LD2 | LD3 | RP1 | RP2 | LP1 | LP2 | RQ1 | RM1 | RM2 | LM1 | LM2 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 404 | 562 | 518 | 680 | 589 | 703 | 345 | 456 | 472 | 603 | 456 | 456 | 312 | 416 | 448 |
| | 585 | | 518 | 525 | 382 | 355 | 549 | | 487 | | | | | 333 |
| | 376 | | | | 510 | | 541 | | 605 | | | | | |
| | | | | | | | 440 | | 458 | | | | | |
| | | | | | | | 459 | | | | | | | |

Table A3.5: Twilight Beach, Layer IIIa (Spit 1, Layer 1): Estimated Fork Length from optimum estimator.

| RD1 | RD2 | RD3 | LD1 | LD3 | RP1 | RP2 | LP1 | LP2 | LA1 | LM1 |
|---|---|---|---|---|---|---|---|---|---|---|
| 588 | 499 | 536 | 570 | 544 | 713 | 535 | 697 | 515 | 514 | 502 |
| 543 | | 406 | 532 | | 684 | 495 | 400 | 556 | | |
| 564 | | | 489 | | 448 | 516 | 386 | 480 | | |
| | | | 508 | | 486 | 588 | | 551 | | |
| | | | 456 | | | 551 | | 542 | | |
| | | | 546 | | | | | | | |

Table A3.6: Houhora, Square C8: Measurements (mm) of five paired cranial bones (optimal estimator given in bold).

| RD1 | RD2 | RD3 | LD1 | LD2 | LD3 | RP1 | RP2 | LP1 | LP2 | RM1 | RM2 | LM1 | LM2 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| - | - | - | **45.70** | 31.17 | 11.75 | **41.56** | 15.32 | - | - | - | - | - | - |
| **38.42** | 26.70 | 14.36 | **42.77** | 30.15 | 13.11 | **39.20** | 13.18 | - | **16.40** | - | **17.05** | - | - |
| - | **24.79** | - | - | - | - | **35.62** | 14.03 | **45.96** | 15.46 | - | **18.36** | - | - |
| - | - | - | **47.75** | 33.15 | - | **35.89** | 13.45 | **38.62** | 14.71 | - | **19.92** | - | - |
| - | **33.49** | 14.29 | - | - | - | **36.55** | 14.15 | **32.41** | 12.71 | - | - | - | **16.04** |
| **42.57** | 28.21 | - | **54.94** | 39.33 | - | **39.79** | 14.35 | **44.81** | 15.75 | - | **18.12** | - | **21.66** |
| - | - | - | - | - | - | - | **15.68** | **42.14** | 16.85 | - | **17.02** | **41.24** | 17.38 |
| - | **32.10** | - | - | - | - | **39.90** | 14.63 | - | - | - | **20.79** | - | **23.36** |
| **47.93** | - | 13.31 | - | - | **10.41** | - | **15.30** | - | **15.36** | - | **24.05** | - | - |
| - | - | - | **40.94** | 26.84 | 11.24 | - | **19.02** | **44.30** | 15.77 | - | - | - | **18.90** |
| - | **37.37** | - | **47.21** | - | 19.89 | - | **14.21** | - | **16.93** | - | - | - | - |
| **39.44** | - | 11.85 | - | **32.11** | - | - | - | **37.85** | 13.57 | - | **15.86** | - | - |
| - | - | - | - | - | **13.34** | **46.34** | 16.82 | - | - | - | - | - | - |
| - | **23.72** | - | - | - | - | - | **14.28** | - | **18.59** | **42.84** | - | - | **18.36** |
| **34.88** | - | 10.24 | **46.06** | - | - | - | **18.27** | - | - | - | - | - | **15.03** |
| - | **28.43** | - | - | **29.24** | - | - | - | - | **16.80** | - | - | | |
| **41.88** | - | 11.99 | - | - | - | **44.48** | 13.86 | **38.73** | 15.63 | - | - | | |
| - | - | **11.53** | - | - | - | **40.92** | 15.35 | - | **15.44** | - | - | | |
| - | **33.08** | 14.72 | **38.56** | - | - | - | - | **34.57** | 12.41 | **58.44** | 22.21 | | |
| - | - | **15.38** | - | - | **12.57** | **51.29** | 19.08 | - | **13.57** | **53.91** | - | | |
| **44.10** | 30.37 | 12.69 | - | - | - | **43.89** | 16.51 | **28.38** | 10.45 | - | **18.57** | | |
| - | - | - | **37.37** | 26.18 | 12.95 | **43.06** | 14.23 | - | - | - | **16.99** | | |
| **40.39** | - | - | - | **21.34** | - | - | **14.00** | **50.07** | 16.70 | - | - | | |
| - | - | - | - | - | - | - | - | - | **13.33** | - | - | | |
| - | - | - | - | - | - | **44.70** | 16.53 | - | **12.26** | - | - | | |
| - | - | - | - | - | - | - | - | - | **11.15** | - | - | | |
| **29.15** | 18.23 | 8.18 | **42.11** | - | 14.73 | - | **18.88** | **36.64** | 12.95 | - | **11.98** | | |
| **41.77** | 23.40 | 13.47 | **30.80** | - | - | **52.67** | 20.69 | - | **18.21** | - | - | | |
| **50.92** | - | 13.90 | **37.47** | 25.74 | - | - | **15.53** | - | - | | | | |
| **48.07** | 30.75 | 13.50 | - | - | - | - | **16.31** | - | - | | | | |
| - | - | **13.77** | - | - | - | - | **18.14** | - | - | | | | |
| - | - | - | - | - | - | **35.91** | 13.14 | - | - | | | | |
| - | **23.56** | - | - | **28.56** | - | - | **16.14** | - | **15.48** | | | | |

Table A3.6: Houhora, Square C8: Measurements (mm) of five paired cranial bones continued.

| RD1 | RD2 | RD3 | LD1 | LD2 | LD3 | RP1 | RP2 | LP1 | LP2 | RM1 | RM2 | LM1 | LM2 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **40.62** | - | - | - | - | - | - | - | - | **10.85** | | | | |
| **47.05** | 30.98 | - | - | - | **15.42** | - | **13.24** | - | **13.19** | | | | |
| - | - | - | - | - | - | - | - | **37.70** | 13.54 | | | | |
| - | **28.18** | - | **36.22** | 24.78 | - | - | **15.56** | - | - | | | | |
| - | **26.85** | - | **41.55** | 31.50 | 14.59 | **48.16** | 17.51 | - | **15.74** | | | | |
| **31.47** | 21.23 | 9.02 | - | - | **10.94** | - | - | - | **12.79** | | | | |
| - | **29.10** | - | - | - | - | - | - | - | **11.78** | | | | |
| **33.89** | 24.44 | - | - | - | - | - | - | - | **15.79** | | | | |
| - | - | - | - | - | - | - | **17.88** | - | - | | | | |
| **53.61** | 35.71 | - | - | - | **11.60** | - | **13.40** | - | **13.94** | | | | |
| - | - | - | - | - | - | **48.69** | 17.07 | - | **14.34** | | | | |
| - | - | - | **40.16** | - | - | - | **13.22** | - | - | | | | |
| **35.69** | - | - | - | - | **13.47** | - | **16.99** | - | - | | | | |
| - | - | **11.20** | - | - | **9.81** | **34.56** | 11.83 | - | **11.26** | | | | |
| **28.31** | - | 7.58 | **32.87** | 22.74 | - | - | **19.58** | - | **8.88** | | | | |
| - | - | **11.71** | - | - | **10.27** | **39.42** | 13.35 | | | | | | |
| - | - | **11.09** | - | - | **13.48** | - | **15.25** | | | | | | |
| | | | | | | - | **19.08** | | | | | | |
| | | | | | | - | **16.78** | | | | | | |
| | | | | | | - | - | | | | | | |
| | | | | | | - | **15.79** | | | | | | |
| | | | | | | **29.23** | 10.07 | | | | | | |
| | | | | | | - | **13.14** | | | | | | |
| | | | | | | - | **16.25** | | | | | | |
| | | | | | | - | - | | | | | | |

Total no. of elements = 249

Table A3.7: Houhora Square C8: Estimated Fork Length from optimum estimator.

| RD1 | RD2 | RD3 | LD1 | LD2 | LD3 | RP1 | RP2 | LP1 | LP2 | RM1 | RM2 | LM1 | LM2 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 641 | 620 | 632 | 656 | 543 | 819 | 610 | 619 | 581 | 586 | 620 | 667 | 437 | 641 |
| 610 | 559 | 565 | 573 | 498 | 635 | 595 | 603 | 536 | 574 | 572 | 616 | | 595 |
| 576 | 553 | 481 | 567 | 487 | 607 | 567 | 601 | 523 | 533 | 455 | 576 | | 519 |
| 577 | 538 | 473 | 554 | 371 | 555 | 561 | 596 | 518 | 529 | | 552 | | 504 |
| 565 | 491 | 460 | 550 | | 555 | 541 | 577 | 494 | 517 | | 514 | | 440 |
| 531 | 480 | 455 | 516 | | 549 | 523 | 573 | 456 | 503 | | 508 | | 413 |
| 514 | 476 | | 508 | | 518 | 520 | 565 | 455 | 496 | | 502 | | |
| 506 | 455 | | 501 | | 478 | 514 | 537 | 446 | 488 | | 472 | | |
| 504 | 423 | | 494 | | 451 | 504 | 530 | 445 | 486 | | 471 | | |
| 491 | 406 | | 485 | | 429 | 488 | 515 | 433 | 484 | | 470 | | |
| 488 | 403 | | 467 | | 423 | 481 | 513 | 410 | 455 | | 439 | | |
| 477 | | | 454 | | 404 | 469 | 510 | 385 | 452 | | 331 | | |
| 466 | | | 453 | | | 468 | 499 | 340 | 439 | | | | |
| 434 | | | 439 | | | 464 | 495 | | 427 | | | | |
| 424 | | | 400 | | | 462 | 492 | | 420 | | | | |
| 413 | | | 377 | | | 432 | 491 | | 416 | | | | |
| 385 | | | | | | 425 | 483 | | 403 | | | | |
| 357 | | | | | | 425 | 482 | | 386 | | | | |
| 347 | | | | | | 422 | 451 | | 371 | | | | |
| | | | | | | 410 | 449 | | 351 | | | | |
| | | | | | | 350 | 442 | | 342 | | | | |
| | | | | | | | 423 | | 280 | | | | |
| | | | | | | | 418 | | | | | | |
| | | | | | | | 418 | | | | | | |
| | | | | | | | 415 | | | | | | |

# APPENDIX 4

## Modern Standards

The modern fish (snapper and barracouta) standards for N%, stable isotope analysis, yield calculations and FTIR analysis were prepared in the following manner:

1) Samples were obtained fresh, and frozen until needed. The fish were filleted and the bones boiled for 15 minutes in tap water to soften the flesh, which was removed.

2) Any adhering flesh was removed by macerating the samples in cold distilled water for 5 days. The water was changed daily and the bones washed under high pressure before being air dried. This dislodged any remaining flesh from cavities and enabled easy disarticulation of the bones (especially vertebrate).

3) The defleshed sample was ground by hand in a pestle and mortar, and the coarsely powdered bone (0.5 - 1.5 mm) defatted with diethyl ether for 1 hour. The bone was then ground to $\leq$0.5 mm and again defatted with diethyl ether for 2 hours. This ground, defatted bone was refrigerated until needed.

Note: Boiling is known to denature the collagen in bones (see Chapter 2). Contamination by fungi, bacteria are also possible during maceration. Neither of these factors, however, are considered to be problematic to the results presented here. First, archaeological fish bones are the remains of food preparation and processing activities, and are, therefore likely to have been cooked. Second, the bone will have been subjected to bacterial and fungal decay following discard into the middens.

# APPENDIX 5

# Isotope Data

Table A5.1: Nitrogen results: Archaeological bulk whole bone.

| Sample | $\delta^{15}N$ | N% |
|---|---|---|
| TWB A bulk | 11.94 | 1.64 |
| TWB B bulk | 11.21 | 1.78 |
| SHAG E bulk | 13.18 | 2.12 |
| SHAG D bulk | 12.91 | 2.44 |
| SHAG ABC bulk | 15.85 | 2.68 |
| TATA A bulk (bar) | 13.78 | 1.66 |
| TATA C bulk (red cod) | 13.21 | 0.94 |
| LONG A bulk | 13.28 | 2.60 |
| LONG B bulk | 13.65 | 2.50 |
| HC8 A bulk | 12.90 | 1.59 |
| PlR B bulk | 13.44 | 2.97 |
| PlR C bulk | 14.71 | 3.09 |
| ROTO A bulk | 16.39 | 1.96 |

Table A5.2: Gelatin stable isotope values.

| Sample | $\delta^{15}N$ | $\delta^{13}C$ | N% |
|---|---|---|---|
| TWB A gel | 11.83 | -11.13 | 15.33 |
| TWB B gel | 11.33 | -11.57 | 14.69 |
| SHAG D gel | 11.24 | -13.24 | 15.93 |
| SHAG E gel | 11.63 | -13.51 | 14.99 |
| SHAG A gel | 13.53 | -13.81 | 15.83 |
| SHAG A gel | 13.41 | -13.71 | 15.26 |
| PlR A gel | 13.59 | -13.42 | 14.58 |
| PlR C gel | 11.86 | -13.06 | 15.27 |
| TATA A gel | 13.24 | -13.21 | 14.83 |
| TATA B gel | 14.71 | -14.13 | 12.36 |
| LONG A gel | 13.82 | -13.29 | 14.59 |
| LONG C gel | 13.88 | -13.14 | 15.66 |
| HC8 A gel | 13.33 | -11.24 | 15.43 |
| ROTO A gel | 15.74 | -12.31 | 13.02 |
| ROTO A gel | 15.43 | -12.15 | 14.68 |

Table A5.3: Modern fish bone gelatin stable isotope values.

| Sample | $\delta^{15}N$ | $\delta^{13}C$ | N% |
|---|---|---|---|
| Snapper 1 gel | 14.17 | -11.65 | 15.16 |
| Snapper 2 gel | 12.79 | -11.52 | 15.43 |
| Snapper 3 gel | 14.36 | -11.51 | 15.40 |
| Barracouta 1 gel | 13.51 | -13.60 | 15.94 |
| Barracouta 2 gel | 11.94 | -14.60 | 15.43 |

Table A5.4: Nitrogen results: Modern bulk fish bone.

| Sample | $\delta^{15}N$ | $\delta^{13}C$ | N% |
|---|---|---|---|
| Barracouta A | 12.36 | -14.90 | 4.31 |
| Barracouta B | 13.52 | -14.60 | 3.96 |
| Snapper A | 17.12 | -11.68 | 4.05 |
| Snapper B | 16.17 | -11.66 | 4.17 |

# APPENDIX 6

# Associated Radiocarbon Samples

Table A6.1: Radiocarbon results of different sample types associated with bone determinations given in Table 8.1.

| Site Name | Lab no. | Provenance | Sample Type | CRA | Rejection Criteria - where applicable |
|---|---|---|---|---|---|
| Avoca Point | NZ-2716 (NZ-3827) | Cultural layer | Charcoal id. | 840 ± 60^ | Not recalculated |
| | NZ-2718 | Cultural layer | *Lunella smaragda*† | 1183 ± 29 | B |
| | NZ-2719 | Cultural layer | *Protothaca crassitesta*† | 1174 ± 33 | B |
| | NZ-2720 | Cultural layer | Matrix | 498 ± 41 | Unidentified |
| | NZ-6525 | Outside wall | *Austrovenus stutchburyi* | 800 ± 32 | Questionable context |
| | Wk-4000 | Cultural layer | Eggshell | 700 ± 70Ω | B |
| | Wk-4001 | Cultural layer | Eggshell | 740 ± 70Ω | B |
| Awamoa | NZ-926 | Charcoal from eroding oven | Charcoal sp.? | 991 ± 49 | Unidentified |
| | NZ-4873 | Cultural deposit: Test pit | Shell sp.? | 982 ± 56 | Unidentified |
| Cross Creek | NZ-6800 | Layer 7 | *Paphies subtriangulatum* | 1035 ± 28 | B |
| False Island | NZ-141 | Midden | *Paphies australe* | 789 ± 39 | A |
| | NZ-144 | Midden | Charcoal sp.? | 404 ± 39 | Unidentified |
| | NZ-143 | Midden: oven | Charcoal sp.? | 361 ± 39 | Unidentified |
| | NZ-145 | Midden: oven | Charcoal sp.? | 265 ± 39 | Unidentified |
| Hawksburn | NZ-5047 | HB/M/6, Layer 1 | Charcoal id | 611 ± 33 | A |
| | NZ-61 | Bottom layer | Charcoal sp.? | 590 ± 50 | Unidentified |
| | NZ-5051 | HB/FA/15, Layer 2 | Charcoal id | 668 ± 33 | A |
| | NZ-62 | Occupation layer | Charcoal sp.? | 633 ± 65 | Unidentified |
| | NZ-5046 | HB/I/23, Layer 1 | Charcoal id | 714 ± 33 | A |
| | NZ-5048 | HB/FB/8, Layer 1 | Charcoal id | 691 ± 33 | A |
| | NZ-5044 | HB/H/14, Layer 1 | Charcoal id | 692 ± 33 | A |
| | NZ-5050 | HB/M/14, Layer 1 | Charcoal id | 720 ± 33 | A |
| | NZ-5052 | HB/L/10, Layer 3 | Charcoal id | 663 ± 28 | A |
| | NZ-5049 | HB/L/5, Layer 3 | Charcoal id | 652 ± 33 | A |
| | NZ-5045 | HB/H/8, Layer 1 | Charcoal id | 709 ± 33 | A |
| | NZ-5053 | HB/E/2, Layer 1 hearth | Charcoal sp.? | 592 ± 33 | Unidentified |
| Hot Water Beach | NZ-1169 | Layer 4, oven | Charcoal sp.? | 437 ± 44 | Unidentified |
| | NZ-1170 | Layer 4 | Soil charcoal | 492 ± 87 | Unidentified |
| | NZ-1171 | Layer 4, oven | "Grease" | 185 ± 86 | Unreliable sample |
| | NZ-1296 | Layer 4, oven | *Amphibola crenata* | 762 ± 44 | Unreliable species |
| | NZ-1297 | Oven , Layer 4 | *Paphies australis* | 832 ± 44 | A |
| Houhora | NZ-914 | Layer 2b, Sq.G6 | Charcoal sp.? | 697 ± 49 | Unidentified |
| | NZ-915 | Layer 3b, Sq.E4 | Charcoal sp.? | 563 ± 61 | Unidentified |
| | NZ-916 | Layer 3b, Sq. E3 | Charcoal sp.? | 775 ± 61 | Unidentified |
| | NZA-2436 | Layer 2b, Sq.E6, Pull 2 | Charcoal id | 632 ± 86 | B |
| | NZA-2437 | Layer 2b, Sq. C8, Pull 4 | Charcoal id | 774 ± 87 | B |
| | NZ-7920 | Layer 2b, Sq. E6, Pull 2 | *Austrovenus stutchburyi* *Paphies australis* | 812 ± 37 | Uncertain context |

| Site Name | Lab no. | Provenance | Sample Type | CRA | Rejection Criteria |
|---|---|---|---|---|---|
| Houhora cont. | Wk-5485 | Layer 3b, Sq. E3 | Charcoal id | 640 ± 40$^{\Delta}$ | B |
| | Wk-5034 | Layer 2b, Sq. D6 | *Lunella smaragda*$^{\dagger}$ | 960 ± 40$^{\Delta}$ | B |
| | Wk-5035 | Layer 2b, Sq. E7 | *Austrovenus stutchburyi* | 1060 ± 45$^{\Delta}$ | B |
| 1972 excavation | NZA-2438 | Layer 3, Sq. A7 | Charcoal id | 727 ± 86 | B |
| Kaupokonui | NZ-3935 | Layer 4c(Cassels1974); Layer 4 (Buist 1963) | Dog coprolites | 325 ± 83 | Unknown reliability |
| Makara | NZ-653 | Beach midden: Oven C | Charcoal sp.? | 442 ± 87 | Unidentified |
| | NZ-654 | Beach midden: Oven A | Charcoal sp.? | 987 ± 74 | Unidentified |
| Ototara | NZ-560 | Occupation layer | *Lunella smaragda*$^{\dagger}$ | 838 ± 59 | B |
| Papatowai | NZ-1332 | Bottom layer | Charcoal sp.? | 916 ± 88 | Unidentified |
| | NZA-1415 | PPT, layer 3 midden (upper shell layer) | Charcoal id | 570 ± 66 | B |
| | NZ-4269 | Middle layer | Charcoal id | 661 ± 71 | Old wood |
| | NZ-134 | Bottom layer | Charcoal sp.? | 825 ± 41 | Unidentified |
| | NZ-4271 | Upper layer: Oven 2 | Charcoal id | 576 ± 57 | Old wood |
| | NZ-4270 | Upper layer: Shell lens | Charcoal id | 560 ± 57 | Old wood |
| | NZ-4267 | Bottom layer | Charcoal id | 853 ± 67 | Old wood |
| | NZ-4268 | Bottom layer | Charcoal id | 760 ± 57 | Old wood |
| | NZ-136 | Bottom layer | Charcoal sp.? | 702 ± 40 | Unidentified |
| | NZ-135 | Bottom layer | Charcoal sp.? | 762 ± 40 | Unidentified |
| | NZ-4272 | Upper layer: Oven 1 | Charcoal id | 577 ± 57 | Old wood |
| | NZ-1333 | Bottom layer | *Paphies australis* | 1051 ± 45 | B |
| | Wk-1761 | THK1, top of layer 5 (lower cultural layer) | Charcoal id | 650 ± 45$^{\Diamond}$ | B |
| | Wk-1762 | THK 9, base of layer 5 (lower cultural layer) | Charcoal id | 640 ± 45$^{\Diamond}$ | B |
| Pauatahanui | NZ-4861 | Midden 2 | *Austrovenus stutchburyi* | [335± 46]$^{\#}$ | A |
| | NZ-4859 | Midden 4 | *Austrovenus stutchburyi* | [410± 50]$^{\#}$ | A |
| | NZ-4855 | Midden 9 | *Austrovenus stutchburyi* | [349± 46]$^{\#}$ | A |
| Peketa Pa | NZ-4152 | Floor of pit house | *Haliotis iris* | 599 ± 40 | Possibly recrystallised |
| | NZ-4153 | Floor of pit house | *Haliotis iris* | 682 ± 40 | Possibly recrystallised |
| Pleasant River Trotter 1979 excavation | NZ-5014 | Black soil with moa bones | *Amphibola crenata* | 1341 ± 29 | Unreliable species |
| Pleasant River: Area 1 | Wk-2506$^{\ddagger}$ | Layer 2 | *Austrovenus stutchburyi* | 930 ± 45$^{f}$ | A |
| | Wk-2753 | Layer 2 | *Austrovenus stutchburyi.* | 910 ± 45$^{f}$ | A |
| | Wk-2851 | Layer 2 | *Austrovenus stutchburyi* | 970 ± 35$^{f}$ | A |
| | NZ-7960 | Layer 2 | Charcoal id | 507 ± 64$^{\S}$ | A |
| Pleasant River: Area 2 | NZ-7962 | | Charcoal id | pooled mean | A |
| | NZ-7963 | | Charcoal id | = | A |
| | NZ-7964 | | Charcoal id | 638 ± 33$^{\S}$ | A |

| Site Name | Lab no. | Provenance | Sample Type | CRA | Rejection Criteria |
|---|---|---|---|---|---|
| Pounawea | NZ-58 | Bottom layer | Charcoal sp.? | 810 ± 60@ | Unidentified |
| | NZ-5031 | Shell mound. Layer 1, Sq H21 | Charcoal id | 582 ± 77 | B |
| | NZ-5032 | Lowest layer 2, Sq J21 | Charcoal id | 816 ± 78 | Old wood |
| | NZ-55 | Middle layer | Charcoal sp.? | 520 ± 55@ | Unidentified |
| | NZ-54 | Top layer | Shell sp.? | 290 ± 60@ | Unidentified |
| | NZ-57 | Bottom layer | Shell sp.? | 500 ± 60@ | Unidentified |
| | NZ-1864 | Lower layer | *Paphies australis* | 1095 ± 41 | B |
| | NZ-1867 | Lower layer | *Paphies australis* | 1028 ± 41 | B |
| | NZ-1868 | Middle layer | *Austrovenus stutchburyi* | 905 ± 41 | B |
| | NZ-1869 | Middle layer | *Austrovenus stutchburyi* | 1025 ± 41 | B |
| | NZ-1870 | Lower layer | *Paphies australis* | 1012 ± 41 | B |
| | NZ-1871 | Lower layer | *Paphies australis* | 926 ± 41 | B |
| | NZ-1872 | Lower layer | *Austrovenus stutchburyi* | 919 ± 41 | B |
| Redcliffs: Hamilton's Deposit | NZ-438 | Occupation layer | Charcoal sp.? | 1167 ± 91 | Unidentified |
| | NZ-1111 | Occupation layer | *Austrovenus stutchburyi* | 924 ± 42 | B |
| Redcliffs: Hine's Oven | NZ-459 | Top of oven | Charcoal sp.? | 777 ± 87 | Unidentified |
| Redcliffs: Moa Bone Point Cave | NZ-437 | Post butt 1 | Charcoal sp.? | 642 ± 88 | Unidentified |
| | NZ-511 | Outter portion of post butt 2 (associated with moa) | Charcoal sp.? | 633 ± 38 | Unidentified |
| | NZ-512 | Inner portion of post butt 2 | Charcoal sp.? | 706 ± 62 | Unidentified |
| Shag River Mouth: SM/A | NZ-7759 | Layer 2 | Charcoal id | 627 ± 40 | B |
| Shag River Mouth: SM/B:FHA | NZ-7760 | Layer 2 | Charcoal id | 582 ± 47 | B |
| Shag River Mouth: SM/C:Dune | NZ-7758 | Layer 2 | Charcoal id | 580 ± 47 | B |
| | Wk-2632 | Layer 4 | *Paphies australis* | 980 ± 40$^{\delta}$ | B |
| | Wk-2633 | Layer 4 | *Amphibola crenata* | 1070 ± 80$^{\delta}$ | Unreliable species |
| | Wk-2752 | Layer 4 | *Mytilus edulis aoteanus*$^{\dagger}$ | 1040 ± 45$^{\delta}$ | B |
| | Wk-2856 | Layer 4 | *Austrovenus stutchburyi* | 980 ± 40$^{\delta}$ | B |
| | Wk-2857 | Layer 4 | *Austrovenus stutchburyi* | 950 ± 45$^{\delta}$ | B |
| | Wk-2440 | Layer 4 | *Austrovenus stutchburyi* | 1050 ± 50$^{\delta}$ | B |
| | Wk-2441 | Layer 4 | *Austrovenus stutchburyi* | 1070 ± 45$^{\delta}$ | B |
| | NZ-7804 | Layer 4 | *Haliotis iris* | 747 ± 38 | Anomalous date |
| | Wk-2751 | Layer 4 | *Austrovenus stutchburyi* | 960 ± 45$^{\delta}$ | B |
| | Wk-2410 | Layer 4 | *Austrovenus stutchburyi* | 1020 ± 50$^{\delta}$ | B |
| | Wk-2411 | Layer 4 | *Austrovenus stutchburyi* | 990 ± 45$^{\delta}$ | B |
| | Wk-2412 | Layer 4 | *Austrovenus stutchburyi* | 980 ± 45$^{\delta}$ | B |
| | Wk-2362 | Layer 4 | *Austrovenus stutchburyi* | 1010 ± 50$^{\delta}$ | B |

| Site Name | Lab no. | Provenance | Sample Type | CRA | Rejection Criteria |
|---|---|---|---|---|---|
| SM/C:Dune cont. | Wk-2367 | Layer 4 | *Amphibola crenata* | 1160 ± 50Ô | Unreliable species |
| | NZ-7805 | Layer 4 | *Austrovenus stutchburyi* | 965 ± 26 | B |
| | Wk-2508 | Layer 4 | *Austrovenus stutchburyi* | 1060 ± 45Ô | B |
| | NZ-7761 | Layer 4 | Charcoal id | 600 ± 50 | B |
| | NZ-7757 | Layer 5 | Charcoal id | 537 ± 44 | B |
| | Wk-2416 | Layer 5 | Eggshell | 600 ± 50Ô | B |
| | Wk-2417 | Layer 6 | Eggshell | 560 ± 45Ô | B |
| | NZ-7756 | Layer 6 | Charcoal id | 670 ± 47 | B |
| | NZ-7806 | Layer 7 | *Haliotis iris* | 1022 ± 29 | B |
| | NZ-7755 | Layer 7 | Charcoal id | 646 ± 47 | B |
| | Wk-2589 | Layer 7 | Charcoal id | 630 ± 35Ô | B |
| | Wk-2604 | Layer 8 | Eggshell | 570 ± 45Ô | B |
| | NZA-1175 | Layer 11 | *Haliotis iris* | 974 ± 49 | B |
| | NZ-7771 | Layer 11 | Charcoal id | 660 ± 46 | B |
| Shag River Mouth: SM/D:1 | NZA-888 | Layer 3 | Charcoal id | 585 ± 93 | B |
| | NZA-900 | Layer 5 | Charcoal id | 2720 ± 95 | Anomalous determination |
| Shag River Mouth: SM/D:3 | NZA-887 | Layer 2 | Charcoal id | 626 ± 95 | B |
| Shag River Mouth: Trotter 1979 testpit. | NZ-5017 | Ashy layer below midden | *Austrovenus stutchburyi* | 994 ± 33 | B |
| Station Bay N38/25 | NZ-4349 | Pit fill associated with burial | Charred bracken fronds | 35 ± 66* | Modern |
| Stewart Island | NZ-422 | Oven (associated with moa bones) | Charcoal sp.? | 687 ± 40 | Unidentified |
| Tairua | NZ-595 | Layer 2: Oven | Charcoal sp.? | 449 ± 44 | Unidentified |
| | NZ-594 | Layer 2: Oven | Charcoal sp.? | 885 ± 52 | Unidentified |
| | NZ-1875 | Layer 2: Oven | *Lunella smaragda*†, *Cellana denticulata*† | 885 ± 58 | B |
| | Wk-5444 | Layer 2 | *Austrovenus stutchburyi* | 1000 ± 50® | B |
| | Wk-5445 | Layer 2 | *Lunella smaragda*† | 1090 ± 50® | B |
| Tai Rua | NZ-750 | Main occupation (Layer 5, 5a and 6) | Charcoal sp.? | 657 ± 37 | Unidentified |
| | NZ-749 | Main occupation (Layer 5, 5a and 6) | *Haliotis iris* | 798 ± 37 | Possibly recrystallised |
| Takahe Valley, Rockshelter A | NZA-2228 | | Burnt feather, tussock and beach leaves | 611 ± 51¶ | Unknown reliability |
| | NZ-51 | | Tussock | 289 ± 63 | Uncertain context |
| | NZ-52 | | Totara bark | 857 ± 48 | Old wood |
| Timpendean, Weka Pass | NZ-892 | Lower occupation level | *Paphies australis, Paphies subtriangulatum, Mytilus edulis*†, *Perna canaliculus* | 744 ± 58 | A |
| | NZ-893 | Lower occupation level | *Hyridella* sp. | 811 ± 61 | Fresh water shell |
| Titirangi Beach | NZ-4237 | Lower occupation deposit 150 cm | *Mytilus edulis*† | 846 ± 40 | A |
| | NZ-4238 | Lower occupation deposit 150 cm | *Lunella smaragda*† | 820 ± 40 | A |
| | NZ-4239 | Lower occupation deposit 150 cm | *Paphies subtrianulatum* | 762 ± 56 | A |

| Site Name | Lab no. | Provenance | Sample Type | CRA | Rejection Criteria |
|---|---|---|---|---|---|
| Tumbledown Bay | NZ-7656 | Layer 3, hut site | Charcoal id | 418 ± 47 | B |
| | NZ-7654 | Layer 3 | *Paphies subtriangulatum* | 706 ± 50 | B |
| | NZ-7745 | Layer 3, lower | *Haloitis australis* | 686 ± 38 | B |
| Waimataitai | NZ-579 | lowest cultural layer | *Lunella smaragda*†, *Mytilus edulis*† | 940 ± 32 | B |
| | NZ-580 | lowest cultural layer | Protein fraction of NZ-579 | 874 ± 45 | Unknown reliability |
| | NZ-1249 | Bottom layer | Charcoal sp.? | 715 ± 45 | Unidentified |
| Wairau Bar | NZ-50 | Upper layer | Charcoal sp.? | 909 ± 48 | Unidentified |
| | NZ-1837 | "Main phase of occupation" | *Paphies australis* | 1029 ± 41 | Uncertain context |
| | Wk-4967 | Wilkes layer 4 | *Austrovenus stutchburyi* | 1060 ± 40[¢] | A |
| | Wk-4458 | Wilkes layer 3 | *Austrovenus stutchburyi* | 1110 ± 50[¢] | A |
| | Wk-4459 | Wilkes layer 4 | *Austrovenus stutchburyi* | 1090 ± 40[¢] | A |
| Whakamoenga Cave | NZ-648 | Occupation 1: Period 1 | Charcoal sp.? | 1011 ± 62 | Unidentified |
| | NZ-686 | Occupation 1: Period 1 | Charcoal sp.? | 610 ± 61 | Unidentified |
| Woolshed Flat | NZ-798 | Occupation level: Oven | Charcoal sp.? | 867 ± 40 | Unidentified |
| | NZ-783 | Occupation level: Oven | Charcoal sp.? | 816 ± 61 | Unidentified |

All NZ- and NZA- determinations recalibrated by IGNS in 1988 except: *Davidson (1978:15); @ Lockerbie (1959:106); ^ The recalculated value for NZ-2716 is questionable (NZ-3827: 6787 ± 100 BP) . The value as reported by Challis (1991:132) is given instead; §Smith and Anderson (1998:88); ; ¶ O'Regan (1992:174).

Ω Unpublished data courtesy Dr. T.F.G. Higham; [Δ] This thesis; [ƒ] Higham (1993:Appendix 1); [◊] Anderson and Smith 1992; [Ó] Anderson, Smith and Higham 1996:61-63; [®] Schmidt and Higham, in prep; [¢] Higham, Anderson and Jacomb, in press.

Note: † Untested or suspect shell species (see Schmidt 1996:178 and Hogg and Higham, in prep), which are accepted in this analysis, but further research required; ‡ Wk-2506 is a re-run of anomalous Wk-2370 (see Higham 1993:Appendix 1); # These are not CRA's but calibrated dates with marine correction of 30 ± 13 (Sparks, Bevan and Redvers-Newton 1997:207).

A = Associated bone $^{14}C$ determination rejected (see Chapter 8 - discard protocol).
B = Samples associated with bone radiocarbon ages remaining after application of discard protocol.