Waikato Radiocarbon Dating Laboratory

AMS Processing Technical Report

THE UNIVERSITY OF
WAIKATO
Te Whare Wānanga o Waikato

Radiocarbon Dating Laboratory, University of Waikato

2017

The Waikato Radiocarbon Dating Laboratory

The Waikato Radiocarbon Dating Laboratory (WRDL) is part of the Faculty of Science and Engineering at the University of Waikato, based in Hamilton, New Zealand. We are an international radiocarbon facility undertaking both Accelerator Mass Spectrometry (AMS) dating (±15yrs at Modern) and Standard Radiometric Dating (± 30yrs at Modern; High Precision dating ±8yrs at Modern).

AMS Methodology Statement

The WRDL has a fully equipped AMS pretreatment and graphitisation laboratory operated by highly experienced professional staff using equipment dedicated to ^{14}C analysis. The AMS graphitisation and combustion laboratory has been operating since 2002 and by the end of 2017 over 18,000 unknowns (commercial and research samples, excluding standards) had been measured. During this time sample preparation methods have been upgraded to increase sample throughput, precision and accuracy and testing/revision are on-going. Present sample processing capabilities include the treatment, combustion/hydrolysis and graphitisation of organic and carbonate samples. A variety of pretreatment procedures are employed to ensure we date only material of secure chemical origins. Many of these pretreatments are specifically tailored to the sample, contaminant and submitter requirements. The following description of our procedures is therefore intended as a guide only, and detailed step by step routine pretreatment protocols can be provided if requested. WRDL publications using these methodologies are also given.

Please note: All shell/charcoal/wood and bone should be identified to species/element before dating. This is not the responsibility of the dating laboratory. Similarly, we assume that all samples submitted for dating have predetermined relevance to the archaeological or paleo-environmental chronological model determined by the submitter (c.f., Bayliss 2015; Waterbolk 1971). Specific sampling/pretreatment instructions should be discussed prior to submission and clearly indicated on submission forms.

All packages sent to us from overseas must contain a Ministry of Primary Industries (MPI) permit. This is renewed yearly (April) and can be downloaded from www.radiocarbondating.com.

Sample requirements

Recommended sample sizes are given in Table 1. Sample size requirements can vary significantly depending on preservation state, carbon content and contamination. Submitters should consider sending twice the maximum sample sizes when analyses additional to ^{14}C are required (*i.e.,* bone or shell environmental/dietary isotopes, XRD or FTIR evaluations).

Table 1: Routine AMS Sample size requirements (dry weights*).

Material	AMS dating (Recommended weights)
Wood^	20-100 mg
Charcoal^	20-100 mg
Charred residue^	20-100 mg
Carbonates	20-60 mg
Peat^	20 mg -1 g
Bone^	0.5 mg - 1 g
Cremated bone	1 g

* Recommended weights given are for clean, dry material.
^ Ranges reflect varying carbon content. We recommend submitting the higher weight value.

Inspection

On arrival, all samples are inspected under >10x magnification to isolate the most reliable fraction for dating and assess contaminants (*e.g.,* rootlets, labels, *etc*) which are removed by scalpel, drill or by "hand" where possible. The sample is then cleaned (either by scalpel, or for bone and shell by air abrasion with 20-50 µm aluminium oxide powder, and/or by ultrasonification in MilliQ™ water if required) and crushed, or milled to increase the surface area for subsequent pretreatment (<2 mm fragments) and transferred to a test-tube or beaker that has

been pre-baked at 500°C.

Solvent extraction

Where contamination by glue, consolidant, resin or oils is specified or observed, we employ soxhlet extraction using a range of solvents. The solvents used are designed to remove the specific contaminant if known. Where the specific chemistry of the contaminant is unknown (which is normally the case), we use a combination of xylene, toluene, ether, acetone and distilled water (in an elutropic sequence/temperature dependent on solvent). Xylene and toluene should remove most common reversible contaminants (including PVA). Because of the difficulty of removing many chemical contaminants, especially those that may have cross-linked to the sample, it is recommended that options for pretreatment and evaluation are investigated prior to dating. FTIR and isotopic evaluation (David *et al.* 2013; Petchey 1998) of contaminant removal can be undertaken at additional cost.

Charcoal

Charcoal is routinely pretreated using a dilute acid/dilute alkali/dilute acid treatment (commonly termed AAA or ABA). Our routine procedure is 1M HCl at 80°C for 1hr; 1M NaOH at 80°C for 30 mins; 1M HCl at 80°C for 1 hr; 80°C, MilliQ™ water for 5 mins (pH>5), sonicated, then dried at 80°C. The supernatant is removed after each step by pipette. The chemical concentrations, number of NaOH treatments (which continues until the colour is no longer transferred from sample to the liquid), temperature and length of pretreatment will vary depending on the quantity and condition of the sample.

Specialised ABox-SC purification of charcoal following the method of Bird *et al.* (1999) can be performed on request. Before undertaking we recommend careful consideration of sample size requirements, likely contaminants and the use of pretreatment specific secondary standards (Bird *et al*. 2014).

Charred organic residue on potsherds may be from a variety of sources (*e.g.,* soot, charred food residues) and it is recommended that a detailed evaluation of the chemistry is made prior to dating. Charred residues are removed using a scalpel under 10x magnification prior to ABA treatment. Extra care is taken at each step since these residues may not survive the standard chemical concentrations and pretreatment temperatures. $\delta^{13}C$ can be measured on a gas split taken during AMS processing and analysed by CRDS in-house (see below). This value is used to assess if the residue is most likely derived from plant matter (*e.g.,* soot from C_3 plants) or animal derived food residue. Additional elemental/isotopic evaluation can be undertaken if requested. We do not currently process lipid or any fraction specific residues.

Wood/ Plant fragments

Pretreatment of wood varies depending on preservation condition:
Where structural collapse to the cellulose structure of the wood has not occurred, we recommend the holo-cellulose fraction be extracted; 0.5 mm shavings are treated with 1M HCl at 70°C for 30 mins; 1M NaOH at 70°C for 30 mins (repeat until clear); 1M HCl (overnight, RT); 1M $NaClO_2$ for 30 mins at RT; Rinse with MilliQ™ water for 30 mins at 70°C. The supernatant is removed after each step by pipette. We will perform alpha-cellulose extraction (involves an additional treatment with 5M NaOH for 1hr at RT; 1M HCl at 70°C for 30 mins; Rinse with MilliQ™ until pH>6), and solvent extraction using acetone to remove wood resins (Hogg *et al.* 2017) upon request at additional cost.

For all other wood/plant fragment samples, we use an ABA treatment as outlined above. We are not currently equipped to isolate pollen fractions for dating, but can combust/graphitise pre-prepared material.

Bone

Gelatine is extracted from the bone using a modified Longin (1971) protocol, whereby the sample is decalcified in 1M HCl for up to 4 days depending on preservation condition, rinsed with MilliQ™ water, then gelatinised by heating in weakly acidic water (pH 3 at 90°C for 4 hr). The supernatant (**"**gelatine**"**) is removed, ultrafiltered (pre-cleaned Centriprep®, Ultracel YM-30 filters using Oxford lab protocols), and frozen at **–**75**°**C before being freeze-dried using a Labconco FreeZone Triad freeze-dryer backed by an Edwards nXDS10i series oil-free pump for a minimum of 48 hours.

The amount of extractable protein (% ultrafiltered gelatine) is used as a guide to the reliability of the ^{14}C results, whereby any sample yielding <0.5% of the starting weight of bone powder is treated with caution (Petchey *et al*. 2014). The quality of the prepared gelatine is further assessed using quality assurance (QA) measurements (%N, %C and C/N) following the recommendations of van Klinken (1999). Both QA measurements and $\delta^{15}N$, $\delta^{13}C$ values for dietary calibration correction are measured by Isotope Ratio Mass Spectrometry (IRMS) at Iso-trace Research Department of Chemistry, University of Otago on a Carlo Erba NA 1500 elemental analyser (EA),

coupled with either a Europa Scientific '20/20 Hydra' or a Thermo Finnigan Delta Plus Advantage using reference (USGS-40, USGS-41) and control (EDTA-OAS and IAEA MP152) materials providing precision of ~0.2‰ for $\delta^{15}N$ and $\delta^{13}C$. $\delta^{15}N$ and $\delta^{13}C$ measurements provide information on trophic level and ^{14}C reservoir – both essential for date interpretation and calibration as outlined in Carvalho and Petchey (2013), Clark *et al.* (2013) and Petchey *et al*. (2011).

White to light grey cremated bone is pretreated by a modified Lanting *et al.* (2001) method whereby finely ground bone powder is treated with 1M acetic acid (CH_3COOH) until frothing stops (~ 2 days), centrifuged 6 times with MilliQ™ water, dried and double combusted to remove undesirable gases that can prevent graphitisation. Dietary $\delta^{13}C$ for cremated bone (Petchey *et al.* 2015) is measured on a gas split taken during AMS processing and analysed by CRDS in-house (see below).

Other materials (hair/wool/silk/skin, *etc*)

Delicate materials are individually assessed. Our routine procedure is 1M HCl at RT for 1 hr; [then if sufficiently robust 1M NaOH at RT for 15-30 mins; 1M HCl at RT for 1 hr]. Extra care is taken at each step since these samples may not survive the standard chemical concentrations.

Soil and Peat

Sediments are carefully evaluated under 10x magnification to see if plant macrofossils can be isolated either by floatation or hand picking, and treated as per wood/plant fragments (see above). Typically, the humin fraction is isolated from peat and soil using the ABA method. The sample is then rinsed in ultra-pure water until pH is >5, then dried at 80°C (Turney *et al.* 2017). If requested we can isolate and date the total organic fraction and/or the humic fraction of the sample. The total organic fraction is isolated using 1M HCl at 80°C for 1hr; rinsed with MilliQ™ water to pH>5, and dried at 80°C. Humic acids are isolated by collecting the NaOH filtrate which is carefully acidified to pH 1.5 with HCl to precipitate the humics, centrifuged to remove liquid, and dried. Where the sediment is fine, a combination of pipette and centrifuge may be used to remove the chemical solutions.

Shells

To aid in our identification of secondary carbonate contamination it is important that shells are identified to taxa (genera) as a minimum in order to ascertain which polymorph(s) of calcite should be naturally present. It is further recommended that all shells are identified to species for interpretation of environmental ^{14}C variation (Petchey *et al.* 2012, 2013, 2016).

WRDL methods used to routinely pre-screen aragonitic or naturally mixed aragonite/calcite shells and coral for contamination rely on visible inspection (cracking across growth rings indicative of the formation of large calcite crystals associated with burning, or softening/powdering of shell surface associated with dissolution and precipitation) and Feigl staining (Friedman 1959) which has the benefit of being able to see natural patterns in shell composition and identify specific areas where secondary recrystallisation may occur. XRD analysis can be undertaken if required to ensure quantitative estimates to secondary contamination at detection of better than 1% calcite. Detection of secondary contamination in shells that are naturally calcitic (*e.g.,* oysters) relies on visible inspection and the presence of a pearly lustre.

Where possible a sample ~10 mm-long and ~4 mm-wide is taken parallel to the margin/lip of each shell. This sample size is designed to avoid seasonal ^{14}C variation (Petchey *et al.* 2012, 2013). Shell (< 3 mm fragments, 35–45 mg) are etched in 1M HCl to remove ~45% of the surface, then dried. For samples >20 Ka because of the possibility of a higher solubility of bio-aragonite relative to secondary carbonate, stepped hydrolysis and dating of different hydrolysis fractions, following the method of Burr *et al.* (1992) and Bird *et al.* (2003), may be necessary to evaluate the removal of contamination. This requires ~55 mg of sample in order to remove 8-10 CO_2 fractions. 4 ml ~40% H_2PO_4 is injected into the evacuated reaction vessel. Evolved CO_2 is monitored and periodically withdrawn once sufficient CO_2 (~0.5 mgC) has been collected. Unused fractions can be stored for later graphitisation.

Water and Methane (AMS only)

We date the dissolved inorganic carbon (DIC) fraction of water which is isolated following the method of Gao *et al.* (2014). Methane gas is converted to CO_2 at 975°C and the CO_2 is cryogenically collected and converted to graphite following the methodology of Pack *et al.* (2015).

Environmental isotopes (in house):

$\delta^{13}C$ and $\delta^{18}O$ values are measured on solid sample (shell) or CO_2 gas prepared on WRDL AMS vacuum lines using a cavity ring-down CO_2 isotope analyser (CRDS) (Los Gatos Research model CCIA-46). Phosphoric acid (102%) is added to each ground shell sample (0.42-0.5 mg) to evolve CO_2. Samples are heated (72°C, ≥1 hr) to promote hydrolysis before analysis of the $\delta^{18}O$ and $\delta^{13}C$ values. IAEA International Atomic Energy Agency standards NBS-18 (calcite) and NBS-19 (limestone) are used to construct a two-point isotope calibration curve ($\delta^{13}C$=-5.014‰, $\delta^{18}O$ =-23.2‰ and $\delta^{13}C$=1.95‰, $\delta^{18}O$=-2.20‰ respectively) and further evaluated using BDH ($\delta^{13}C$=-24.95‰, $\delta^{18}O$ =-13.99‰) and Sigma ($\delta^{13}C$=-14.18‰, $\delta^{18}O$ =-20.07‰) synthetic $CaCO_3$ standards (Beinlich *et al*. 2017, Table 2). A drift correction is made after every two samples using 1500ppm CO_2 reference gas. $\delta^{13}C$ and $\delta^{18}O$ values are reported as ‰ V-PDB. Routine precision of 0.3‰ or better is typical as determined using sample reproducibility of duplicate measurements.

Combustion and Graphitisation

The WDRL AMS facility has dedicated glass vacuum lines each connected by Ultra-Torr® Swagelok® Cajons and maintained under vacuum by Pfeiffer HiCube 80 turbo drag pumps.

One line with 21 Cajon fittings is dedicated to the evacuation of tubes for the combustion of organic samples using pre-combusted 9mm quartz tubing. These lines can be adapted for the evacuation of septa-sealed vials and injection of acid needed for carbonate hydrolysis. Organic samples (charcoal, wood, peat/soil and bone gelatine) are converted to CO_2 by oxidation at 800°C overnight in the presence of pre-baked CuO wire (JT Baker) and silver wire. CO_2 is collected from shells and cremated bone by reaction with 85% phosphoric acid (H_3PO_4) under vacuum at 70°C/~30 mins and 80°C/~4 hrs respectively (cremated bone/H_3PO_4 brought up to temperature prior to mixing to prevent fractionation - *cf.* Brock *et al.* 2010).

We have three CO_2/graphitisation lines, each with 8 hydrogen reduction units (reactors) that routinely graphitise 0.5mgC – 0.2mgC targets following the method outlined in Santos *et al.* (2004). The reaction vessel is attached to a vacuum line consisting of (in sequence) a glass cracker or needle transfer port, a water trap, one standard volume glass ampoule with attached pressure transducer, and 8 graphite reactors. Each reactor consists of a three-way Cajon attached to a 0-30 psi transducer and two quartz 6 mm tubes; one containing pre-baked BDH Fe powder and the other Alfa Aesar $Mg(ClO_4)_2$ to remove water from the reaction. Each reactor has a dedicated 550°C furnace for reduction of the CO_2 to graphite which is monitored in real-time using a customised LabView program to ensure quick determination of reaction completion and reducing the possibility of fractionation due to methane production. All three lines can be adapted to process <0.04mgC targets easily by reduction to the graphitisation reactor volumes and the use of 0-5 psi transducers.

On completion, the cooled graphite is pressed to 350psi using a NEC cathode press. The pressed graphite is stored in a wet cabinet with NaOH reservoir to reduce CO_2 concentration prior to being packaged and sent to the Keck AMS Radiocarbon Dating Laboratory (UCI Irvine). Samples are stored for no more than 4 weeks before being analysed. Both primary and secondary standard are pretreated and graphitised at the same time as unknowns to prevent any storage offset (see Beverly *et al.* 2010).

Analysis

Pressed graphite is analysed at the Keck Radiocarbon Dating Laboratory, University of California on a NEC 0.5MV 1.5SDH-1 AMS system coupled with an in-house modified ion source (Beverly *et al.* 2010). A total of 60 graphite samples are included in each AMS wheel – composition varies but approximates as follows: six primary OxII standards are used to setup and tune the AMS system as well as to normalize the $^{14}C/^{12}C$ ratios (c.f., Santos *et al*. 2007); for every 10-17 unknowns there are one blank (Carrara Marble/ Ancient Wood, No Name Charcoal or Ancient Bone) and one in-house secondary standard of similar age, material and pretreatment (Dugong Bone, Oak Wood, Kiri Wood or Tridacna Shell) used for background correction and quality control respectively.

Data analysis is undertaken at the Keck facility as per Santos *et al.* (2007). All ^{14}C results are fractionation-corrected using the measured on-line AMS $\delta^{13}C$ values. These are <u>not reported</u> because they are heavily fractionated and intended for ^{14}C fractionation correction, as per the recommendations of Stuiver and Polach (1977). Environmental $\delta^{13}C$ (and $\delta^{18}O$ – carbonates only) values are recommended for shell and cremated bone (see above) and are measured in house by CRDS. Charcoal, wood and peat environmental $\delta^{13}C$ values can be obtained if requested. $\delta^{13}C$ /$\delta^{15}N$, C/N, C% and N% for bone gelatine are measured by IRMS and are included in the bone pricing (see above).

Quality Assurance

1. Standards

A range of standards are used at the WRDL (Table 2). The secondary standards and blanks are chosen to match the unknown sample type and expected age, and undergo the same chemical steps as unknowns. All pretreatment and graphite preparation for samples, Modern and Background standards and Continuity standards is undertaken in the WRDL. Monitoring of standards and blanks allows graphite production issues to be resolved immediately. In addition, long-term trends permit analysis of accuracy and precision. This enables us to maintain a constant check on the accuracy of different pretreatment and CO_2 purification processes. Moreover, our Background standards are also sample and pretreatment specific and therefore better reflect the true background limits.

Table 2: Waikato AMS In-house standards.

Standard name/pretreatment	Source	Independent Measured Age (LSC)	LSC Wk- number	AMS Mean±GSD[#]	4D Code
Background standards ($F^{14}C$%)					
Ancient Bone (UG)	Brogga Peninsula, Svalbard	0.088 ± 0.054*	Wk-27800	0.213±0.916^ (31/5/16-26/7/17)	MV
No Name Charcoal (ABA)(>0.5mgC)	No Name Beach, Australia	0.090± 0.061	Wk-17466	0.186±0.029 (4/4/17 -24/10/17)	MR
No Name Charcoal (ABA) (0.2-0.5mgC)				0.231±0.084 (10/3/15-17/10/17)	
No Name Charcoal (ABA) (0.04-0.07mgC)				0.765±0.104 (16/7/15-2/10/17)	
Ancient Wood (ABA)	Manukau (OIS7), NZ	0.043 ± 0.012	Wk-17031	0.157±0.061 (17/8/16-24/7/17)	MW
Ancient Wood (α-cellulose)				0.146±0.053 (23/9/16-8/8/17)	
Carrara Marble (AW)	Unknown	Estimated >Background	na	0.172±0.047 (2/6/16-17/10/17)	MM
Secondary standards (BP)					
Oak charcoal (ABA)	Rathnew, Ireland	3796 ± 44	Wk-20690	3848±14 (21/4/17-24/10/17)	MX
Dugong Bone (UG)	Botany Bay, Australia	5520 ± 70*	Wk-8616	5608±15 (22/3/16-29/9/17)	MZ
Kiri wood (ABA)	Kirikopuni, NZ	3521 ± 44	Wk-20225	3552±14 (1/9/16-26/7/17)	MD
Rotomohana charcoal (ABA)	Lake Rotomahana, NZ	12,445 ± 25	Wk-20724	12453±40 (22/12/14-15/817)	MU
Tridacna shell (AW)	Bourewa, Fiji	3027 ± 40	Wk-28029	3028±16 (16/3/17-29/9/17)	MY

UG = Ultrafiltered gelatine; ABA = Acid/Base/Acid; AW = Acid wash

* Longin collagen pretreatment

[#] Gaussian standard deviation based on the last 10 wheels (time frames given in brackets)

^GSD raised by abnormal Ancient Bone result: 0.472±0.09 (13/7/16)

2. Precision

The quoted ^{14}C uncertainties (~±15 at Modern) include contributions from the normalising standards, the background subtraction, and from the scatter in the repeated runs on each sample, as well as counting statistics.

The $^{14}C/^{12}C$ measurements as supplied by the UCI Keck AMS laboratory routinely have errors approximating ±15 years at Modern. Our lab error multiplier (reproducibility) is assessed by analysis of appropriate continuity standards that are contained in each wheel. For a particular continuity standard, the ratio between the Gaussian (population) standard deviation derived from the last 10 wheels and individual wheel continuity standard errors, allows calculation of the lab error multiplier for that sample type in that wheel. A screen grab from our database, using the modern (Kiri) wood alpha-cellulose standard as an example, is shown in Figure 1 below. The Gaussian SD, based upon 20 measurements from the last 10 wheels, is ±14 years for this standard, resulting in a lab multiplier of 1.0 for wood alpha-cellulose analyses with errors greater than ±15 yrs. Our Background standards are sample, and pretreatment specific, with backgrounds ~52 kyr BP. For example, the OIS7 alpha-cellulose sub-fossil kauri wood blank ranges from 0.0007 to 0.0023 times Modern (58–49 kyr BP) with a mean of 0.0015 (52 kyr BP). We assume a background uncertainty of ±30%.

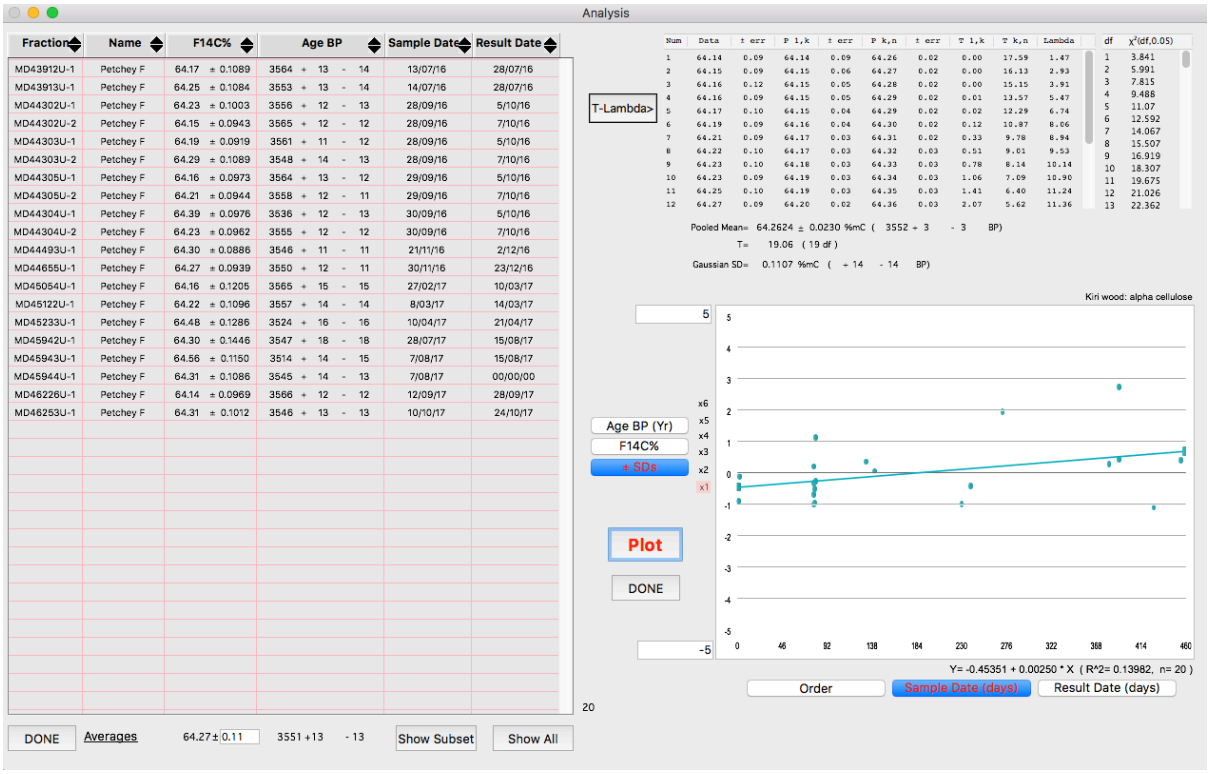

Figure 1. Kiri wood, alpha-cellulose, continuity standard data for the last 10 AMS wheels.

3. Accuracy

The only way to truly assess accuracy is through regular analysis of known calendar age tree-ring samples or through inter-laboratory comparisons (see Scott *et al.* 2018). Although not all of the following publications utilise AMS analysis, Waikato is in a unique position to be able to directly compare AMS with radiometric measurements. Published tree-ring atmospheric ^{14}C studies containing Waikato measurements include both Southern Hemisphere and Northern Hemisphere measurements and encompass the most recent 2 millennia (Hogg *et al.* 2009, 2011, 2016, 2017; Turney *et al.* 2016), Younger Dryas-aged material (Hogg *et al.* 2016), and OIS2-3 samples (Turney *et al.* 2010, Hogg *et al.* 2006, 2007).

The WRDL has also been involved in laboratory inter-comparisons, including an international 5-lab ^{14}C inter-comparison in 2013 (Hogg *et al.* 2013). The labs analysed 12 successive decadal kauri samples ~10,000 ^{14}C years in age with the high-resolution sampling providing laboratory offset information previously unavailable in other inter-comparisons. The WRDL results (both radiometric and AMS) were found to be highly consistent with the other labs (see Figure 2).

To measure laboratory reproducibility and crosscheck our results, we are also involved in inter-calibration exercises with the radiocarbon community. We have participated in all of the Glasgow University programs (including the recent 6th international radiocarbon inter-comparison) and the earlier International Atomic Energy Agency (IAEA) inter-comparison exercise. Results of the Glasgow inter-comparisons are given in Table 3 below and show a high level of agreement between the WRDL determinations and consensus values.

The WRDL is also participating in a large 8-laboratory atmospheric, single-ring, AMS inter-comparison study lead by Lukas Wacker (ETH Zurich). This work is not yet published but the Waikato offset to the 8-lab mean data is summarised in Table 4. All samples were pretreated to alpha-cellulose, which although may prove to be unnecessary for oak samples, is essential for many species, especially for samples >10 ka BP. These results are preliminary only. Because the Waikato dating was done on the smaller alpha-cellulose fraction, the measurements were done on 2-ring (not single-ring) samples.

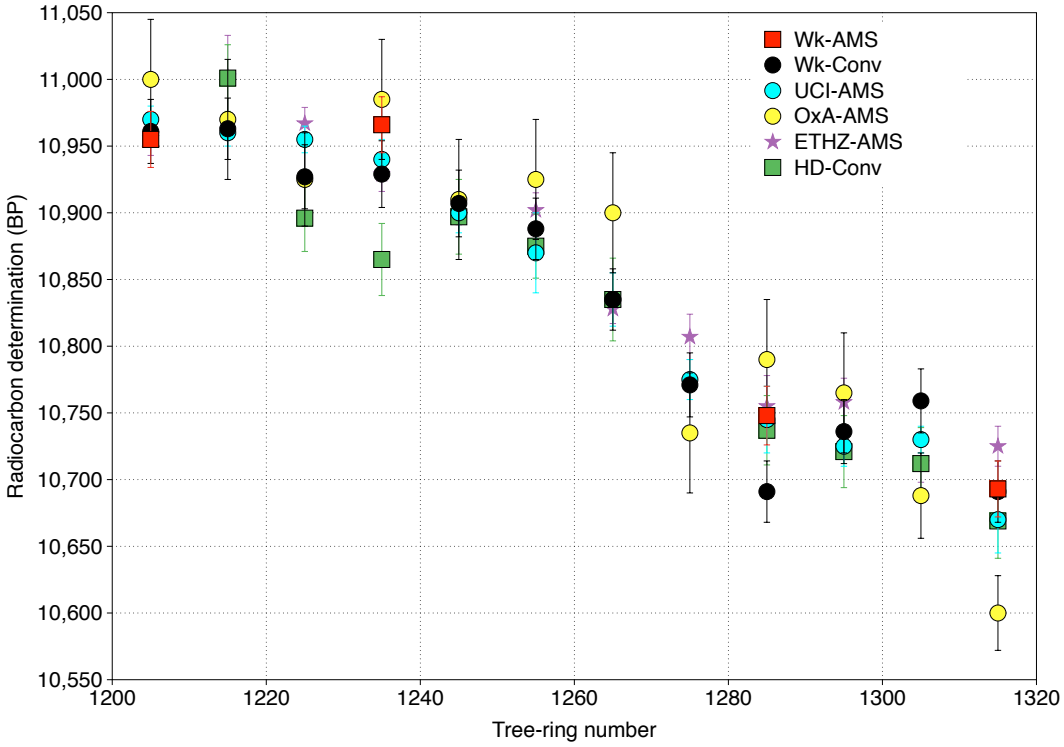

Figure 2: Inter-comparison results for 12 successive ~10 kyr BP subfossil Kauri sample. (OxA = University of Oxford; ETHZ = Laboratory of Ion Beam Physics; Wk = University of Waikato-conventional; Waikato-AMS; HD = University of Heidelberg-conventional; UCI = University of California at Irvine).

Table 3: University of Glasgow Inter-comparisons (2008) showing consensus values vs. WRDL results.

	WRDL Results*		
VIRI Sample	- Standard Radiometric	- AMS	**VIRI consensus values**
Sample A (barley mash)	109.2 ± 04 yr BP	109.5 ± 0.53 yr BP	109.1 ± 0.4 pMC
Sample B (seed charred)	2855 ± 32 yr BP	2802 ± 33 yr BP	2820 ± 3.3 yr BP
Sample C (barley mash)	111.0 ± 0.4 pMC	111.02 ± 0.42 pMC	110.7 ± 0.04 pMC
Sample D (seed charred)	2842 ± 33 yr BP	2804 ± 32 yr BP	2836 ± 3.3 yr BP
Sample E (mammoth bone)	38347 ± 511 yr BP	40,809 ± 2239 yr BP	39,305 ± 121 yr BP
Sample F (horse bone)	2545 ± 30 yr BP	2477 ± 37 yr BP	2513 ± 5 yr BP
Sample G (human bone)	-	1035 ± 32 yr BP	969 ± 5 yr BP
Sample H (whale bone)	9491 ± 45 yr BP	9617 ± 49 yr BP	9528 ± 7 yr BP
Sample I (whale bone)	8360 ± 37 yr BP	8318 ± 43 yr BP	8331 ± 6 yr BP
Sample J (humic acid)	-	41,795 ± 1860	43226 ± 140 yr BP
Sample K (wood)	0.04 ± 0.04 pMC	0.09 ± 0.1 pMC	0.058 ± 0.06 pMC
Sample L (wood)	2269 ± 26 yr BP	2241 ± 30 yr BP	2234 ± 5 yr BP
Sample M (wood)	-	2442 ± 30 yr BP	2430 ± 4 yr BP
Sample N (cellulose)	-	2417 ± 36 yr BP	2436 ± 5 yr BP
Sample O (cellulose)	99 ± 25 yr BP	75 ± 30 yr BP	125 ± 5 yr BP
Sample P (charcoal)	1751 ± 27 yr BP	-	1747 ± 9 yr BP
Sample Q (charcoal)	-	600 ± 30 yr BP	636 ± 5 yr BP
Sample R (shell)	2469 ± 26 yr BP	2419 ± 30 yr BP	2491 ± 4 yr BP
Sample S (barley mash)	110.46 ± 0.36 pMC	110.2 ± 0.4 pMC	109.96 ± 0.04 pMC
Sample T (humic acid)	-	3335 ± 30 yr BP	3360 ± 4 yr BP
Sample U (humic acid)	11829 ± 41 yr BP	11746 ± 87 yr BP	11778 ± 6 yr BP

* Inter-comparison standard errors are considerably higher than 2017 date precision.
pMC = Percent Modern Carbon.

Table 4: Preliminary results from 8-laboratory Inter-comparison study.

Wood series	Wood source	Approximate age	WRDL mean offset - ^{14}C years
H-Series	GBD-A101 (oak, Bridestowe)	~200 BP	4
A-Series	Q451 (oak, Armagh)	~1700 BP	-10
G (R)-Series	Gaed5 (oak, Gaedheim)	~7600 BP	-8

General laboratory protocols & procedures relating to required turn-around time

The WRDL utilises a multi-relational 4th Dimension database to manage sample information, turn-around times and for quality assurance (QA) purposes. The database comprises 9 tables – Samples, Fractions, ^{13}C fractionation, Name & Address, Invoices, WebSub, AMS import and others. The Samples table (Figure 3) contains information about sample provenance, expected age, date acquired and deadline. All samples submitted to the WRDL have a unique laboratory (Wk) number which is released to the client with the age report.

The Fractions table contains all related analytic data covering pretreatment (pretreatment details, operator and dates), CO_2 generation (line number, line pressures, operator, dates) and graphitisation (size, operator, dates). This table also includes bone C and N isotope data and elemental ratios. Different materials (*e.g.,* SP = Peat; SS=Shell; SB= Bone, Charcoal = SC; Wood = SW) have different fraction codes and are associated with pretreatment codes (*e.g.,* A = AMS ABA pretreatment; E= AMS shell pretreatment).

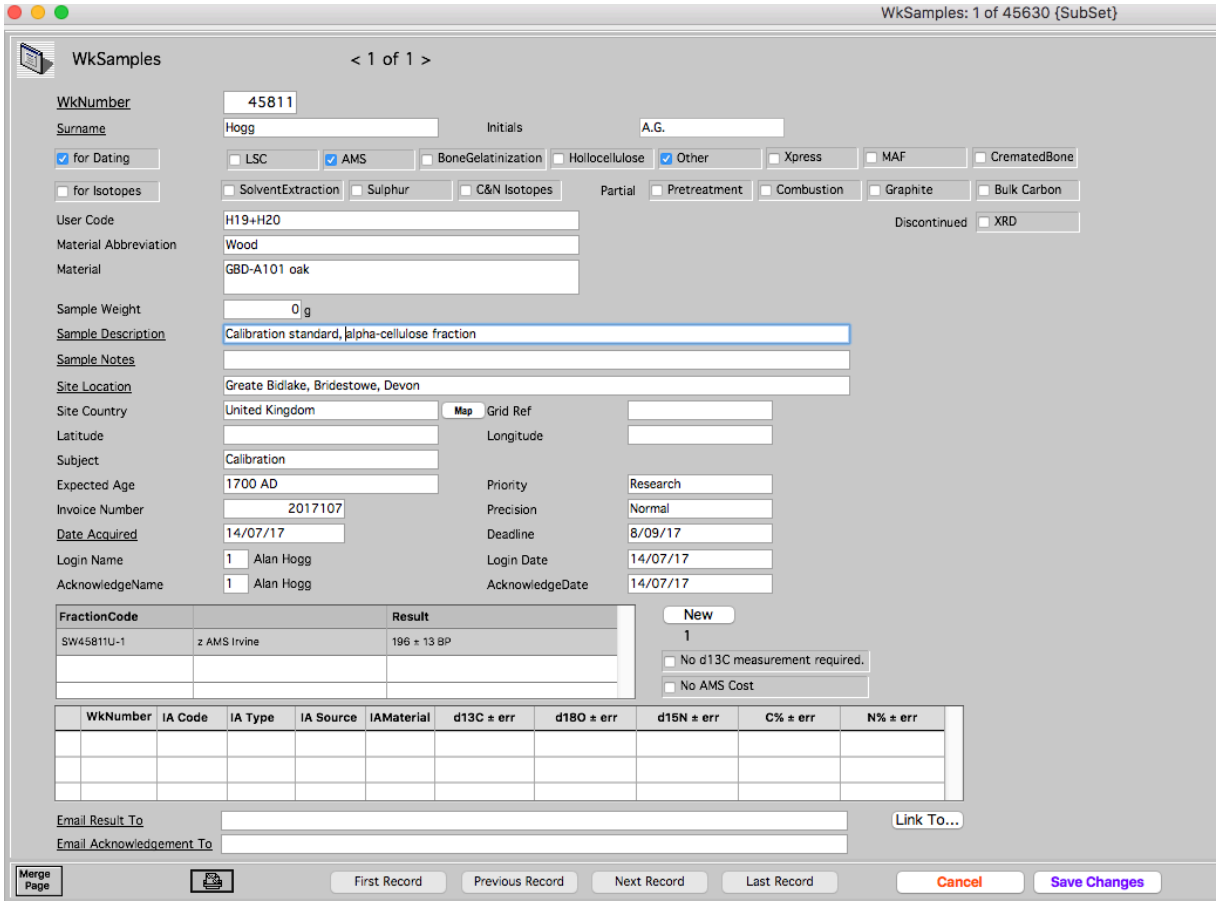

Figure 3: 4th Dimension 'Samples' table example.

Turnaround Times

Turnaround time fluctuates with demand. Between 2013 and 2017 our turn-around averaged 6.4 weeks (Figure 4). Longer turnaround times shown are predominantly bone samples which have longer processing times (typically 8-12 weeks).

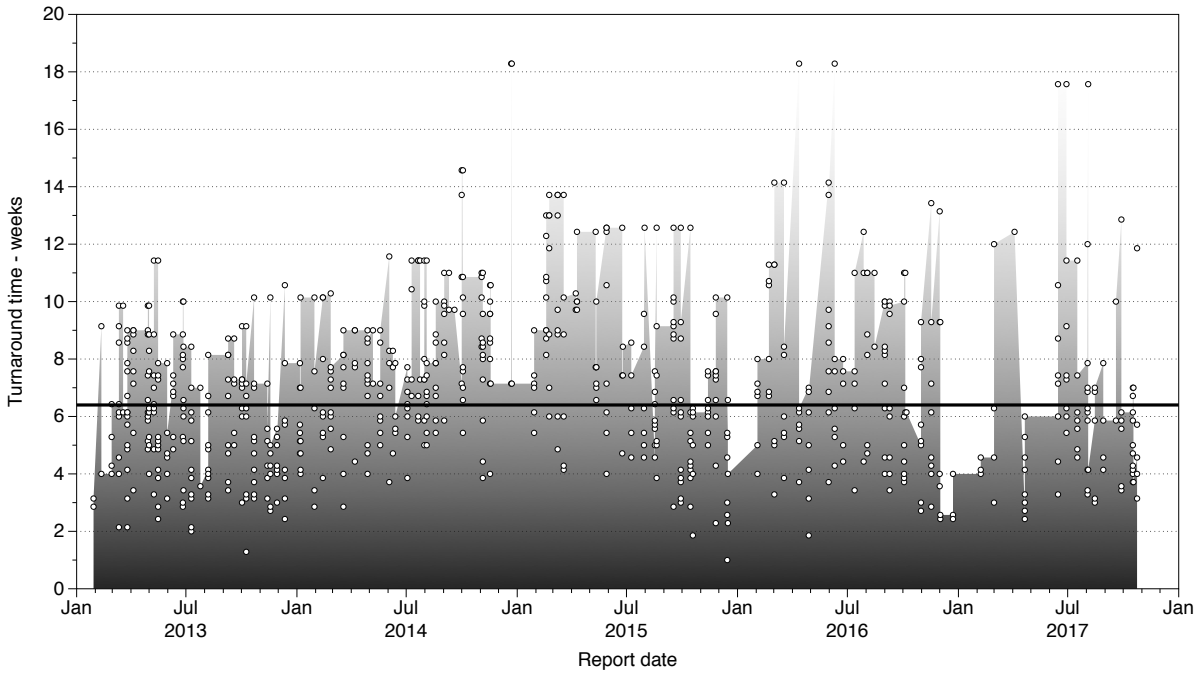

Figure 4: Turn-around time for dated samples (from date of acknowledgment to date reporting). The black line is the average turn around for the period given (6.4 weeks).

References

Bayliss A, 2015. Quality in Bayesian chronological models in archaeology. World Archaeology; doi:10.1080/00438243.2015.1067640

Beinlich, A, SLL Barker, G Dipple, M Gupta, D Baer, 2017. Stable isotope ($\delta^{13}C$, $\delta^{18}O$) analysis of sulfide-bearing carbonate samples using laser absorption spectrometry. *Economic Geology*, 112(3):693-700; doi:10.2113/econgeo.112.3.693.

Beverly, RK, W Beaumont, D Tauz, KM Ormsby, K F von Reden, GM Santos, JR Southon. 2010. The Keck Carbon Cycle AMS Laboratory, University of California, Irvine: Status Report. *Radiocarbon*, 52(2–3):301–309.

Bird, MI, V Levchenko, PL Ascough, W l Meredith, CM Wurster, A Williams, EL Tilston, CE Snape, DC Apperley, 2014. The efficiency of charcoal decontamination for radiocarbon dating by three pre-treatments – ABOX, ABA and hypy. *Quaternary. Geochronology,* 22:25–32.

Bird, MI, LK Ayliffe, LK Fifield, CSM Turney, RG Cresswell, TT Barrows, B David. 1999. Radiocarbon dating of "old" charcoal using a wet-oxidation, stepped-combustion procedure. *Radiocarbon,* 41(2):127–40.

Bird, MI, CSM Turney, LK Fifield, MA Smith, GH Millere, RG Robertsg, JW Mageeh, 2003. Radiocarbon dating of organic- and carbonate-carbon in Genyornis and Dromaius eggshell using stepped combustion and stepped acidification. *Quaternary Science Reviews*, 22:1805–1812.

Brock, F, T Higham, P Ditchfield, C Bronk-Ramsey, 2010. Current pre-treatment methods for AMS radiocarbon dating at the Oxford Radiocarbon Accelerator Unit (ORAU). *Radiocarbon*, 52(1):103–112.

Burr, GS, RL Edwards, DJ Donahue, ERM Druffel, FW Taylor, 1992. Mass spectrometric ^{14}C and U-Th measurements in coral. *Radiocarbo*n, 34(3):611-618.

Carvalho, AF, **F Petchey,** 2013. Stable isotope evidence of Neolithic palaeodiets in the coastal regions of southern Portugal. *Journal of Island and Coastal Archaeology,* 8(3):361-383.

Clark, G, **F Petchey,** S Hawkins, C Reepmeyer, I Smith, WB Masse, 2013. Distribution and extirpation of pigs in Pacific Islands: a case study from Palau. *Archaeology in Oceania*, doi: 10.1002/arco.5012.

David, B, B Barker, **F Petchey,** J-J Delannoy, J-M Geneste, C Rowe, M Eccleston, L Lamb, R Whear, 2013. A 28,000-year-old excavated painted rock from Nawarla Gabarnmang, northern Australia. *Journal of Archaeological Science,* 40:2493-2501; doi.org/10.1016/j.jas.2012.08.015.

Friedman, GM, 1959. Identification of carbonate minerals by staining methods. *Journal of Sedimentary Research,* 29, 87–97.

Gao, P, X Xu, L Zhou, MA Pack, S Griffin, GM Santos, JR Southon, K Liu, 2014. Rapid sample preparation of dissolved inorganic carbon in natural waters using a headspace-extraction approach for radiocarbon analysis by accelerator mass spectrometry. *Limnology and Oceanography: Methods* 12:174-190.

Hogg, A, L Fifield, C Turney, J Palmer, R Galbraith, M Baillie, 2006. Dating ancient wood by high sensitivity liquid scintillation counting and accelerator mass spectrometry - Pushing the boundaries. *Quaternary Geochronology* 1:241-248.

Hogg, A, L Fifield, J Palmer, C Turney, R Galbraith, 2007. Robust radiocarbon dating of wood samples by igh-sensitivity liquid scintillation spectroscopy in the 50-70 kyr age range. *Radiocarbon,* 49(2):379-391.

Hogg, A, J Palmer, G Boswijk, P Reimer, D Brown, 2009. Investigating the interhemispheric ^{14}C offset in the 1st Millennium AD and assessment of laboratory bias and calculation errors. *Radiocarbon,* 51(4):1177-1186.

Hogg, A, J Palmer, G Boswijk, C Turney, 2011. High-precision radiocarbon measurements of tree-ring dated wood from New Zealand: 195 BC – AD 995. *Radiocarbon*, 53(3):529-542.

Hogg, A, C Turney, J Palmer, J Southon, B Kromer, C Bronk Ramsey, G Boswijk, P Fenwick, A Noronha, R Staff, M Friedrich, L Reynard, D Guetter, L Wacker, R Jones, 2013. The New Zealand kauri (*Agathis australis)* research project: A radiocarbon dating inter-comparison of Younger Dryas wood and implications for IntCal13. *Radiocarbon,* 55(4):2035-2048.

Hogg, A, J Southon, C Turney, J Palmer, C Bronk Ramsey, P Fenwick, G Boswijk, U Buntgen, M Friedrich, G Helle, K Hughen, R Jones, B Kromer, A Noronha, F Reinig, L Reynard, R Staff, L Wacker, 2016. Decadally-resolved Late glacial radiocarbon evidence from New Zealand kauri. *Radiocarbon*, 58(4):709-33.

Hogg, AH, W Gumbley, G Boswijk, **F Petchey**, T Roa, J Southon, A Anderson, L Donaldson, 2017. The first accurate and precise calendar dating of New Zealand Maori Pā, using Otāhau Pā as a case study. *Journal of Archaeological Science: Reports*, *12*:124-133; doi:10.1016/j.jasrep.2017.01.032

Lanting, JN, AT Aerts-Bijma, J van der Plicht, 2001. Dating of cremated bones. *Radiocarbon*, 43(2A):249–254.

Longin, R. 1971. New method of collagen extraction for radiocarbon dating. *Nature,* 230:241–2.

Pack, MA, X Xu, M Lupascu, JD Kessler, CI Czimczik, 2015. A rapid method for preparing low volume CH_4 and CO_2 gas samples for ^{14}C AMS analysis. *Organic Geochemistry,* 78:89-98.

Petchey, F, 1998. Radiocarbon Analysis of a Novel Bone Sample Type: Snapper and Barracouta Bone from New Zealand Archaeological Sites. Unpublished D.Phil thesis, University of Waikato.

Petchey, F, M Spriggs, F Leach, M Seed, C Sand, M Pietrusewsky, **K Anderson**, 2011. Testing the human factor: Radiocarbon dating the first peoples of the South Pacific. *Journal of Archaeological Science*, 38:29-44

Petchey, **F**, S Ulm, B David, IJ McNiven, B Asmussen, H Tomkins, T Richards, C Rowe, M Leavesley, H Mandui, J Stanisic, 2012. Radiocarbon marine reservoir variability in herbivores and deposit-feeding gastropods from an open coastline, Papua New Guinea. *Radiocarbon*, 54(3-4):1-11.

Petchey, F, S Ulm, B David, IJ McNiven, B Asmussen, H Tomkins, N Dolby, K Aplin, T Richards, C Rowe, M Leavesley, H Mandui, 2013. High-resolution radiocarbon dating of marine materials in archaeological contexts: radiocarbon marine reservoir variability between *Anadara*, *Gafrarium*, *Batissa*, *Polymesoda* and *Echinoidea* at Caution Bay, Southern Coastal Papua New Guinea. *Archaeological and Anthropological Science,* 5(1):69–80.

Petchey, F, M Spriggs, S Bedford, F Valentin, H Buckley, 2014. Direct radiocarbon dating of burials from the Teouma Lapita cemetery, Efate, Vanuatu. *Journal of Archaeological Science,* 50:227–242.

Petchey, F, M Spriggs, S Bedford, F Valentin, 2015. The chronology of occupation at Teouma, Vanuatu: Use of a modified chronometric hygiene protocol and Bayesian modelling to evaluate midden remains. *Journal of Archaeological Science: Reports* 4:95-105.

Petchey, F, C Geoffrey, O Winter, P O'Day, M Litster, 2016. Colonisation of Remote Oceania: New dates for the Bapot-1 site in the Mariana Islands. *Archaeology in Oceania*, doi:10.1002/arco.5108

Santos, GM, JR Southon, KC Druffel-Rodriguez, S Griffin, M Mazon, 2004. Magnesium perchlorate as an alternative water trap in AMS graphite sample preparation: a report on sample preparation at KCCAMS at the University of California, Irvine. *Radiocarbon,* 46(1):165–73.

Santos, GM, RB Moore, JR Southon, S Griffin, E Hinger, D Zhang, 2007. AMS ^{14}C sample preparation at the KCCAMS/UCI facility: status report and performance of small samples. *Radiocarbon,* 49(2):255–269.

Scott, M, P Nasmith, G Cook, 2018. Why do we need ^{14}C inter-comparisons? The Glasgow-^{14}C inter-comparison series, a reflection over 30 years. *Quaternary Geochronology,* 43:72-82.

Stuiver M, HA Polach, 1977. Discussion: reporting of ^{14}C data. *Radiocarbon,* 19(3):355–63.

Turney, CSM, RT Jones, SJ Phipps, Z Thomas, **A Hogg**, AP Kershaw, CJ Fogwill, J Palmer, C Bronk Ramsey, F Adolphi, R Muscheler, KA Hughen, RA Staff, M Grosvenor, NR Golledge, SO Rasmussen, DK Hutchinson, S

Haberle, A Lorrey, G Boswijk, A Cooper, 2017. Rapid global ocean-atmosphere response to Southern Ocean freshening during the last glacial *Nature Communications*, 8:520; doi:10.1038/s41467-017-00577-6

Turney, C, J Palmer, **A Hogg**, C Fogwill, R Jones, C Bronk Ramsey, P Fenwick, P Grierson, J Wilmshurst, A O'Donnell, Z Thomas, M Lipson, 2016. Multi-decadal variations in Southern Hemisphere atmospheric ^{14}C: Evidence against a Southern Ocean sink at the end of the Little Ice Age CO_2 anomaly. *Global Biogeochemical Cycles*, 30(2):211-218.

Turney, C, K Fifield, **A Hogg**, J Palmer, K Hughen, M Baillie, R Galbraith, J Ogden, A Lorrey, S Tims, R Jones, 2010. The potential of New Zealand kauri (*Agathis australis*) for testing the synchronicity of abrupt climate change during the Last Glacial Interval (60,000-11,700 years ago). *Quaternary Science Reviews*, doi:10.1016/j.quascirev.2010.08.017.

van Klinken, GJ, 1999. Bone collagen quality indicators for palaeodietary and radiocarbon measurement. *Journal of Archaeological Science,* 26:687–695.

Waterbolk, HT, 1971. Working with Radiocarbon Dates. *Proceedings of the Prehistoric Society,* 37:15–33; doi:10.1017/S0079497X00012548.