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THE NEW ZEALAND KAURI (*AGATHIS AUSTRALIS*) RESEARCH PROJECT: A RADIOCARBON DATING INTERCOMPARISON OF YOUNGER DRYAS WOOD AND IMPLICATIONS FOR INTCAL13

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ABSTRACT. We describe here the New Zealand kauri (*Agathis australis*) Younger Dryas (YD) research project, which aims to undertake $\Delta^{14}C$ analysis of ~140 decadal floating wood samples spanning the time interval ~13.1–11.7 kyr cal BP. We report ^{14}C intercomparison measurements being undertaken by the carbon dating laboratories at University of Waikato (Wk), University of California at Irvine (UCI), and University of Oxford (OxA). The Wk, UCI, and OxA laboratories show very good agreement with an interlaboratory comparison of 12 successive decadal kauri samples (average offsets from consensus values of –7 to +4 ^{14}C yr). A University of Waikato/University of Heidelberg (HD) intercomparison involving measurement of the YD-age Swiss larch tree Ollon505, shows a HD/Wk offset of ~10–20 ^{14}C yr (HD younger), and strong evidence that the positioning of the Ollon505 series is incorrect, with a recommendation that the ^{14}C analyses be removed from the IntCal calibration database.

INTRODUCTION

The Younger Dryas (YD) stadial, from ~12.95 to 11.6 kyr cal BP, represents an abrupt Northern Hemisphere (NH) cooling episode, punctuating the general warming trend from the Last Glacial Maximum (LGM; ~21 kyr cal BP) to the Holocene (~11.7 kyr cal BP, Walker et al. 2009; Blockley et al. 2012). The YD represents the end of the last glacial period in the Atlantic region of the NH and ended with rapid warming at high latitudes accompanied by several as yet unexplained, large, prolonged changes in atmospheric ^{14}C concentration. Crucially, the YD is also an important period of time for ^{14}C calibration in that it links the younger absolute extended tree-ring chronology (Friedrich et al. 2004; Hua et al. 2009) with the older floating European Lateglacial Pine (LGP, Kromer et al. 2004) and Central European Lateglacial Master (CELM, Kaiser et al. 2012) chronologies.

By extending the European absolute tree-ring chronology (Friedrich et al. 2004) from 12.4 to 12.56 kyr cal BP and linking it to the floating LGP data set using a 617-yr-long floating sequence of tree rings of huon pine (*Lagarostrobos franklinii*) from Tasmania, Australia, Hua et al. (2009) made an important contribution towards improving ^{14}C calibration across this time period. However, the huon pine sequence, which is composed of only 4 logs, could not be cross-matched by ring-width

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correlations, and therefore relied on ^{14}C wiggle-matching alone, introducing potential uncertainties in the chronology. Unfortunately, the situation is exacerbated by the limited overlap between the older LGP/CELM series and younger Preboreal Pine Chronology (PPC, Friedrich et al. 2004).

We present here a new initiative using New Zealand kauri (*Agathis australis*), which will not only significantly improve linkage of the floating LGP record to the extended absolute tree-ring chronology, but will also increase the sample density of both records. The Northland subfossil kauri resource represents one of the world's foremost archives of atmospheric records during the last 60 kyr (Turney et al. 2007). Kauri logs are buried in bogs scattered over a 300-km stretch of northern New Zealand, with the anaerobic conditions resulting in a remarkable state of preservation of the wood (Ogden et al. 1992; Palmer et al. 2006). Some of the buried trees are of enormous proportions, with diameters greater than 4 m and individual ages of more than 2 kyr. Living tree cores from a network of sites have been collected (Buckley et al. 2000; Fowler et al. 2000), and this chronology was recently linked to late Holocene subfossil sites (Boswijk et al. 2006). At the same time, a collection of significantly older subfossil kauri has been obtained from 16 different locations, and several floating tree-ring chronologies are in varying stages of development (Turney et al. 2010). This wood contains an immense, high-resolution store of information about past environmental conditions, including climate and landforms. The timespan covered (>60 kyr) and the potentially detailed climatic reconstructions possible from the long series of annual rings preserved in these trees (Buckley et al. 2000; Fowler et al. 2000, 2012) means that this wood is a scientific resource of international significance (Turney et al. 2007).

The 1450-yr-long New Zealand YD kauri chronology, which is constructed from 30 trees from Towai in Northland (35°30.393′S, 174°10.376′E; Figure 1), is also floating and presently spans the time interval ~13.1–11.7 kyr cal BP. Here, we present dendrochronological data showing that approximately 1150 yr are securely cross-matched, with efforts continuing to increase replication for the remaining 150 yr at either end of the record.

In this paper, we describe a collaborative research program between 6 universities (University of Waikato, University of New South Wales, University of California at Irvine, University of Oxford, University of Exeter, and University of Auckland) and the Gondwana Tree-Ring Laboratory, Canterbury, New Zealand, aimed at providing a floating, high-precision (±2–3‰), high-resolution (decadal), atmospheric $\Delta^{14}C$ record covering the YD chronozone. It will test the integrity of the European extended absolute tree-ring chronology, some of the linkages of which are considered "tentative" (Friedrich et al. 2004) and will provide a more secure overlap with the older floating LGP record. We describe our methodology, including the efficacy of various pretreatment regimes (ABA, holocellulose, and α-cellulose) for removing modern contamination from subfossil wood. We also present the results of 2 intercomparison studies designed to identify any interlaboratory differences. The first involves analysis of 12 successive decadal YD-age kauri samples, with the University of Waikato (Wk), University of California at Irvine (UCI), and University of Oxford (OxA) radiocarbon laboratories joined by the radiocarbon laboratories at the University of Heidelberg (HD) and the Laboratory of Ion Beam Physics at the Swiss Federal Institute of Technology Zurich (ETHZ). The second intercomparison is between the Wk and HD laboratories, to assist with aligning the Southern Hemisphere (SH) kauri data set with IntCal data. It consists of >30 new analyses from the Swiss larch tree Ollon505 (Friedrich et al. 2004; Kaiser et al. 2012) for comparison with 13 previous ^{14}C measurements incorporated into IntCal04 (Reimer et al. 2004) and IntCal09 (Reimer et al. 2009). We also discuss the impact of these analyses on IntCal04, IntCal09, and IntCal13 (Reimer et al., this issue) for this important time period.

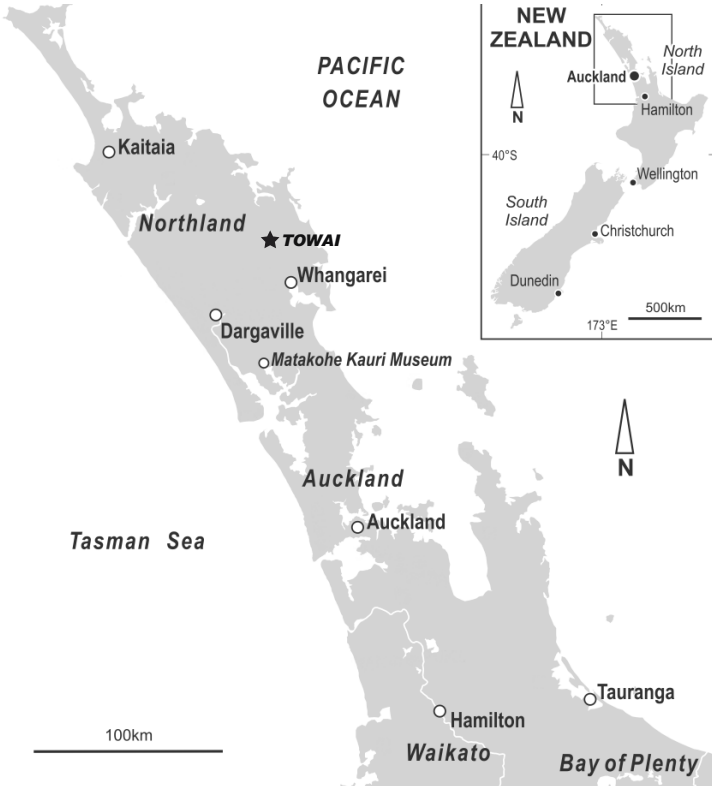

Figure 1 Location of Towai site containing YD-age kauri

METHODS

Dendrochronology

It is crucial that calibration data sets are obtained from securely cross-dated and well-replicated tree-ring sequences. Kauri trees used for the measurements were excavated from a farm site at Towai, Northland, New Zealand. A total of 30 logs were collected, from which 77 radial series were measured to produce a chronology that spans 1451 yr. The average length of the series is 551 yr, with an average ring-width of 1.13 mm, with only 0.63% missing rings. The average cross-correlation coefficient between all the series is 0.71. The number of logs measured per tree-ring number is shown in Figure 2.

The 1451-yr series has a declining number of samples at each end. In tree-ring research, a major emphasis is placed on ensuring chronologies are well replicated in an effort to avoid any dendrochronological dating errors. A frequently used criterion for establishing if sufficient replication is present is the expressed population signal, or EPS (Wigley et al. 1984). With an EPS threshold of >0.85 applied to the Towai kauri chronology, the first 115 yr (i.e. oldest rings) and the last 164 yr (i.e. youngest rings, see Figure 2) have inadequate sample depth. The intervening 1172 yr is thought to have adequate replication and the subset of 12 samples selected for the kauri laboratory intercomparison was taken from this interval (Figure 2). The lack of replication at the younger end of the Towai kauri series weakens linkages with the NH extended absolute tree-ring chronology, and efforts are currently underway to extract new kauri logs to increase the sample depth for this part of the chronology.

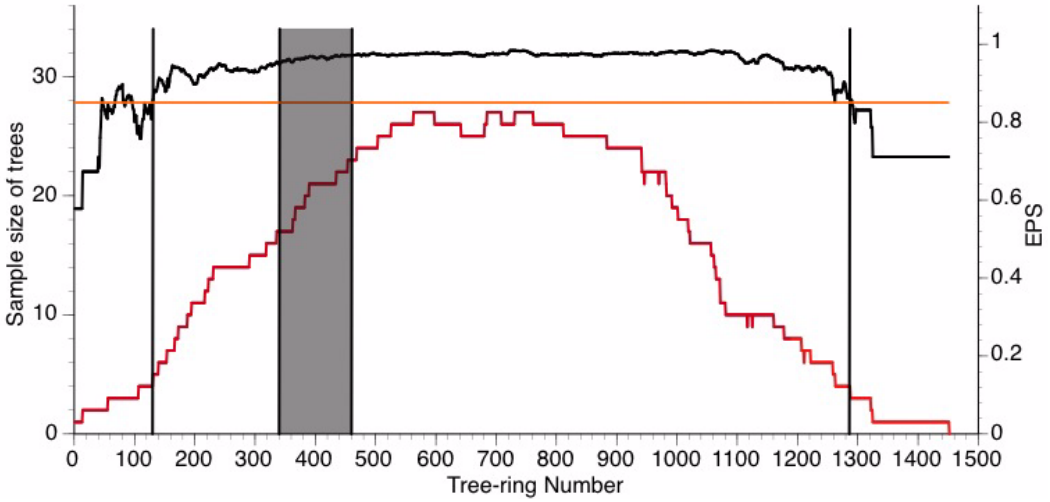

Figure 2 Number of tree samples per yr plotted against tree-ring number: gray (red) curve. The vertical lines indicate the start and end of where there are sufficient tree samples for a robust chronology. The shaded area indicates the 120-yr window where the decadal samples were taken for the intercalibration study. For the intercomparison period, there were between 17 and 23 log samples per year, ensuring a secure tree-ring chronology for this interval. The right scale shows the EPS (expressed population signal), which is a frequently used criterion for establishing if sufficient replication is present. An EPS value of >0.85, shown by the horizontal gray (orange) line, is considered satisfactory replication (Wigley et al. 1984). Colors in parentheses relate to the online version of this article.

Wood Pretreatment for $\Delta^{14}C$ Measurement

It is important that the wood component chosen for ^{14}C dating of any particular tree species is representative of ambient atmospheric $\Delta^{14}C$ levels at the time of growth. It is generally accepted that all resin fractions should be discarded, and Hoper et al. (1998) recommend isolating highly pure α-cellulose, by removing lignin and hemicelluloses as well, to avoid species-specific differences resulting from variable lignin fractions. They showed that while bleaching with acidified $NaClO_2$ was capable of removing lignin in English oak (*Quercus petraea*), it was insufficient for New Zealand cedar (*Libocedrus bidwillii*), which required an additional base extraction. Variations in sample size, associated with analysis method, also need to be considered, with chemical pretreatment of small accelerator mass spectrometry (AMS)-sized samples (<50 mg) more effective because of surface area than for liquid scintillation counting (LSC) and gas proportional (GP) samples, which can be more than 1000 times larger (e.g. 70 g). Before embarking upon a large-scale calibration study, researchers may wish to compare results from different pretreatment methods to ascertain whether or not the additional effort extracting α-cellulose is warranted. Pretreatments used by the Wk/UCI/OxA research group are presented in some detail below.

University of Waikato

Wood pretreatment protocols employed at the University of Waikato are modified from those outlined in Hogg et al. (2011). The 70-g samples were chipped and ground in a Thomas Wiley intermediate mill to pass a 20-mesh sieve. Resins were extracted by refluxing in a Soxhlet apparatus, using a 2-step process (acetone, 6 hr; distilled water, 6 hr). The wood was then bleached in acidified $NaClO_2$ (15 g/L) repeatedly until the wood component was white in color. It was then stirred in 5% NaOH in a N_2 gas atmosphere for 30 min, followed by acidification in 5% HCl and washing in distilled water. Final material is white in color and represents ~40% of the initial weight of the wood.

University of California at Irvine

Fine shavings (<0.5 mm thick) were subsampled from the decadal wood blocks, producing samples of 20–40 mg. Acid-base-acid (ABA) pretreatment was carried out in 13 × 100 mm test tubes covered with vented closures, on a heat block at 70 °C. Samples were treated with aliquots of ~6 mL of 1N HCl for 30 min, followed by successive 1-hr treatments with 6 mL of 1N NaOH until the liquid remained clear, ending with another 30-min 1N HCl wash.

Isolation of holocellulose was carried out in 13-mm test tubes at 70 °C using equal volumes of 1N HCl and 1M $NaClO_2$. Some 2.5 mL of bleach and 2.5 mL of acid was usually sufficient to bleach up to 40 mg of wood over 3–6 hr, though bleaching times varied and a second short treatment was required for a few of the larger samples. After bleaching, the holocellulose was washed several times with ultrapure water (Milli-Q™ 30 min, 70 °C) to pH > 6. Samples were then air-dried at 70 °C; vacuum drying was not used because tests showed that backgrounds are higher in vacuum-dried cellulose samples.

For α-cellulose extractions, the bleached holocellulose was washed once with ultrapure water, followed by treatment with 6 mL of 5N NaOH for 1 hr at room temperature. This was followed by a 30-min treatment with 1N HCl at 70 °C to remove any absorbed atmospheric CO_2, followed by multiple ultrapure water washes and drying as above.

University of Oxford

ABA method (laboratory code UW). Following the routine ORAU pretreatment protocol for wood (Brock et al. 2010), samples (~70 mg) were washed sequentially with 1N HCl (80 °C, 20 min); 0.2N NaOH (80 °C, 20 min); 1N HCl (80 °C, 1 hr); and 5% w/v NaO_2Cl (80 °C, up to 30 min). They were rinsed with ultrapure water 3 times after each stage.

α-cellulose method (laboratory code UA*). This is a method that was specifically developed for this project. A Dionex® ASE 100 (accelerated solvent extraction) system was used to remove the mobile phases (principally resins) from the wood (70–80 mg samples). This operates at 100 °C and 116 atmospheres using 2 × 5 min static cycles, 150% flush volume of acetone, followed by 2 × 5 min static cycles, 150% flush volume of ultrapure water. After drying, the samples were transferred to 12-mL glass tubes and subjected to a bleaching stage (1.5% w/v NaO_2Cl plus 6 mL/L HCl at 70 °C, repeated 4 times over 24 hr), followed by a single ultrapure water rinse. A more rigorous ABA methodology was then applied (as compared with the regular UW pretreatment protocol). This consisted of a 4% (1.12N) HCl treatment (at 70 °C for 20 min), followed by a 17.5% w/v NaOH treatment (at room temperature for 60 min, with ultrasonication, under a constant N_2 environment), and followed by a 5% (1.4N) second HCl treatment (at 70 °C for 10 min). After each successive stage, ultrapure water rinses were performed to ensure effective removal of the acid and base washes (typically, 3 rinses after the initial acid, 5 rinses after the base, and a further 5–6 after the final acid). Additionally, the pH was checked to confirm removal of the base.

Following treatment, all samples were subsequently freeze-dried prior to combustion and graphitization as described by Brock et al. (2010).

^{14}C Measurement

To obtain high resolution, accuracy, and precision, we have employed replicate measurement by both LSC (Wk) and AMS (UCI, OxA) laboratories on decadal wood samples. All ^{14}C ages were calculated according to Stuiver and Polach (1977).

University of Waikato

The University of Waikato carbon dating laboratory utilizes liquid scintillation spectrometry to measure $\Delta^{14}C$ and optimizes each step of the process to achieve high levels of precision (1σ errors average ±24 yr at 10 kyr BP). α-cellulose samples of 35 g were combusted in an oxygen stream, forming CO_2, which was reacted with molten lithium metal to form Li_2C_2. This was then hydrolyzed to form acetylene gas, and converted to benzene by vanadium-activated catalytic trimerization. The benzene was synthesized in vacuum lines preconditioned for activities of approximately 2 half-lives, with 7.5-g benzene samples measured in "Waikato" synthetic silica counting vials (Hogg 1993) for 10k min in LKB Wallac Quantulus™ spectrometers optimized for high-precision dating (Hogg et al. 2007). Background and modern activities were individually determined for each scintillation vial. Background ^{14}C levels were initially calibrated with scintillation-grade Spectrobenzene, with background correction achieved by multiple analysis of the α-cellulose fraction of the Waikato OIS7 kauri standard (~140 kyr cal BP subfossil kauri, Hogg et al. 2006), to account for *in situ* contamination or extra activity added or removed in the laboratory, during either pretreatment or benzene synthesis. Background blank activity was equivalent to 0.00071 ± 0.00005 times Modern (58.2 kyr BP, Hogg et al. 2006). Oxalic acid II (HOxII) was used for individual modern calibration of counting vials. It was combusted in a similar manner to the cellulose samples, using a throughflow combustion system. This method of HOxII CO_2 preparation results in typical $\delta^{13}C$ values (–17.33 ± 0.14‰) with no evidence of isotopic fractionation. The secondary standard ANU sucrose (IAEA C-6) was used as a check on long-term reproducibility, with Waikato measurements (1.5033 ± 0.0005 times Modern) producing statistically indistinguishable values from those recently published by Xu et al. (2010), 1.5023 ± 0.0013 times Modern (with Waikato/Hogg data removed) and significantly less than the international consensus value of 1.5061 ± 0.000011 times Modern (Rozanski et al. 1992). Isotopic fractionation correction was achieved by measuring $\delta^{13}C$ for all samples using a Europa Scientific Penta 20/20 isotope ratio spectrometer.

University of California at Irvine

^{14}C measurements were carried out with an NEC compact (1.5SDH) AMS system, using a running mean of results on 6 aliquots of oxalic acid 1 (HOx1) as the normalizing standard. Each mg-sized carbon sample was measured multiple times (typically 8–12 runs) over a 24-hr period. Samples of holocellulose from the Waikato OIS7 kauri background standard and an internal laboratory standard (SR7269, 11,980 ± 30 BP) were prepared and measured with each batch of unknowns, usually with one OIS7 and one SR7269 in each set of 12 samples graphitized. Typically, 2 aliquots of holocellulose were prepared separately from each decadal Towai kauri sample, and in many cases, additional duplicates were measured on new combustions of the remaining cellulose. $\delta^{13}C$ fractionation correction was achieved with measurements obtained from the AMS spectrometer itself. Results on the OIS7 blank ranged from 0.0007 to 0.0022 times Modern (58–49 kyr BP) with a mean of 0.0012 (54 kyr BP). The mean of results from OIS7 aliquots graphitized and measured with a given batch of unknowns was used as the best estimate of the blank for that set, with an assumed uncertainty of ±30%. The quoted ^{14}C uncertainties include contributions from the normalizing standards, the background subtraction, and from the scatter in the repeated runs on each sample, as well as counting statistics.

University of Oxford

All Oxford samples were measured as reported in Bronk Ramsey et al. (2004). Wood samples were combusted in a CHN analyzer with GC purification of the evolved CO_2. The CO_2 was then converted to graphite using H_2 and an Fe catalyst, and loaded into aluminum target holders for the

HVEE 846 ion source. Batches of targets including standards and backgrounds were measured with a 3MV HVEE Tandetron, correcting for isotopic fractionation using the $^{13}C/^{12}C$ ratio from the AMS. The background correction routinely used for wood samples in the Oxford laboratory is made up of 2 components: an AMS background that is determined at run-time using graphitized CO_2 of fossil origin, and a sample-size dependent combustion background determined through multiple measurements of background standards (principally nylon) covering a wide range of sizes. Multiple analyses of the Waikato OIS 7 kauri background returned results statistically indistinguishable from the estimated backgrounds using the standard procedure.

INTERCOMPARISON RESULTS

Two separate intercomparison studies were undertaken as part of this research program. The first involved 5 laboratories (Wk, UCI, OxA, together with HD and ETHZ) measuring $\Delta^{14}C$ in 12 successive YD-age decadal kauri samples to determine if the various laboratory protocols produced consensus values. The second intercomparison was confined to the Waikato and Heidelberg radiometric laboratories and involved high-precision measurement of $\Delta^{14}C$ levels in the ~10 kyr BP Swiss larch tree Ollon505, to investigate potential offsets between the Wk/UCI/OxA research group and previous Heidelberg YD measurements incorporated into IntCal04 (Reimer et al. 2004) and IntCal09 (Reimer et al. 2009).

The Five-Laboratory intercomparison

The 5 contributing laboratories listed above analyzed 12 successive decadal kauri samples with mid-ring numbers 346.5–456.5. Error-weighted mean values and average laboratory differences were calculated for each decade (Table 1).

Table 1 Initial weighted mean values and interlaboratory differences for 12 successive decadal kauri samples (initial weighted mean age minus laboratory age). All errors represent the population standard deviations.

Mid-ring nr	Initial weighted mean values (yr BP)	ETHZ mean difference (^{14}C yr)	HD mean difference (^{14}C yr)	OxA mean difference (^{14}C yr)	UCI mean difference (^{14}C yr)	Wk mean difference (^{14}C yr)
346.5	10,961 ± 22	–15 ± 36	—	–40 ± 50	13 ± 28	–1 ± 33
356.5	10,965 ± 29	–37 ± 43	–37 ± 38	–6 ± 53	32 ± 34	2 ± 37
366.5	10,943 ± 43	–58 ± 51	47 ± 49	–42 ± 66	–2 ± 45	16 ± 49
376.5	10,917 ± 46	–38 ± 56	52 ± 53	–68 ± 64	7 ± 49	–12 ± 52
386.5	10,891 ± 19	–23 ± 34	–6 ± 34	–19 ± 49	24 ± 26	–16 ± 31
396.5	10,870 ± 49	–85 ± 57	–5 ± 55	–55 ± 67	44 ± 52	–18 ± 54
406.5	10,842 ± 32	–33 ± 45	7 ± 45	–58 ± 55	17 ± 38	7 ± 39
416.5	10,764 ± 20	–31 ± 35	—	—	9 ± 25	–7 ± 31
426.5	10,728 ± 49	–74 ± 55	–10 ± 56	–63 ± 67	23 ± 52	37 ± 54
436.5	10,737 ± 26	–36 ± 35	16 ± 38	–28 ± 52	22 ± 33	1 ± 36
446.5	10,719 ± 26	–5 ± 35	7 ± 37	31 ± 41	5 ± 28	–40 ± 35
456.5	10,677 ± 69	–58 ± 73	8 ± 74	127 ± 82	22 ± 72	–14 ± 72
Average offset (^{14}C yr)		–41	8	–20	18	–4
Population standard error		23.4	26.1	56.8	12.7	19.0

Initial results showed significant variation, particularly amongst the AMS labs, which showed differences from mean values ranging from 41 ^{14}C yr older to 18 ^{14}C yr younger. Because of the unexpectedly large variation in results, all laboratories carefully scrutinized their wood pretreatment and Δ^{14}C analysis protocols, with the AMS laboratories undertaking some new analyses (Table 2).

Table 2 Final consensus values and interlaboratory differences for 12 successive decadal kauri samples (consensus age minus laboratory age). All errors represent the population standard deviations.

Mid-ring nr	Final consensus values (yr BP)	ETHZ mean difference (^{14}C yr)	HD mean difference (^{14}C yr)	OxA mean difference (^{14}C yr)	UCI mean difference (^{14}C yr)	Wk mean difference (^{14}C yr)
346.5	10,966 ± 20	9 ± 24	—	–34 ± 49	–4 ± 22	5 ± 31
356.5	10,968 ± 21	–34 ± 37	–33 ± 32	–2 ± 50	8 ± 23	5 ± 31
366.5	10,951 ± 28	–16 ± 30	55 ± 37	26 ± 45	–4 ± 30	24 ± 37
376.5	10,928 ± 43	–1 ± 45	63 ± 51	–57 ± 62	–12 ± 45	–1 ± 50
386.5	10,901 ± 7	1 ± 11	4 ± 29	–9 ± 46	1 ± 16	–6 ± 26
396.5	10,893 ± 22	–9 ± 26	18 ± 33	–32 ± 50	23 ± 37	5 ± 32
406.5	10,833 ± 30	5 ± 32	–2 ± 43	–67 ± 54	–2 ± 36	–2 ± 38
416.5	10,783 ± 29	–24 ± 34	—	48 ± 54	8 ± 33	12 ± 38
426.5	10,735 ± 36	–20 ± 43	–2 ± 44	–55 ± 57	–10 ± 44	44 ± 42
436.5	10,737 ± 20	–21 ± 27	16 ± 33	–28 ± 49	12 ± 25	1 ± 31
446.5	10,725 ± 26	12 ± 30	13 ± 38	37 ± 41	–5 ± 28	–34 ± 36
456.5	10,690 ± 46	–36 ± 48	21 ± 54	90 ± 54	20 ± 52	–1 ± 51
Average offset (^{14}C yr)		–11	15	–7	3	4
Population standard error		16.4	27.8	48.2	11.3	18.4

An initial 15–20 ^{14}C yr UCI offset to younger kauri ages was found to be due to previously unrecognized dead time in the data processing electronics, additional to the known software-corrected dead time that affected high ^{14}C count rates from recent samples and normalizing standards. These and other factors contributing to the initial interlaboratory differences will be described in detail elsewhere. The Oxford laboratory corrections appear to be related to issues with the new α-cellulose pretreatment method. Excess material from the first pretreatment from a few samples was re-acidified in 0.5N HCl and rinsed 5–6 times with deionized water, to ensure that the samples had reached neutrality, and combusted and dated again. Two samples were pretreated again from the original wood sample material and redated. The repeated ETHZ measurements followed a stricter process control for chemical pretreatment and cellulose storage. Samples, standards and background blank materials were prepared and measured over a shorter time interval to avoid possible storage contamination issues. The mean ^{14}C age of the repeated measurements (Table 2) is ~30 ± 7 ^{14}C yr younger than the initial analyses (Table 1). As the reason for the initial offset could not finally be resolved, all ETHZ measurements are included in the second data set. The final interlaboratory results are summarized in Figure 3.

The final AMS consensus values had equivalent or significantly reduced population standard errors. The Waikato/UCI/Oxford results are very consistent, with offsets of –7 to +4 ^{14}C yr and with mean population standard deviations consistent with stated analytical errors. The HD results are slightly younger than the Wk/UCI/OxA consensus values and this potential offset will need to be considered when the YD-kauri data set is ^{14}C wiggle-matched against the extended absolute tree-ring chronology.

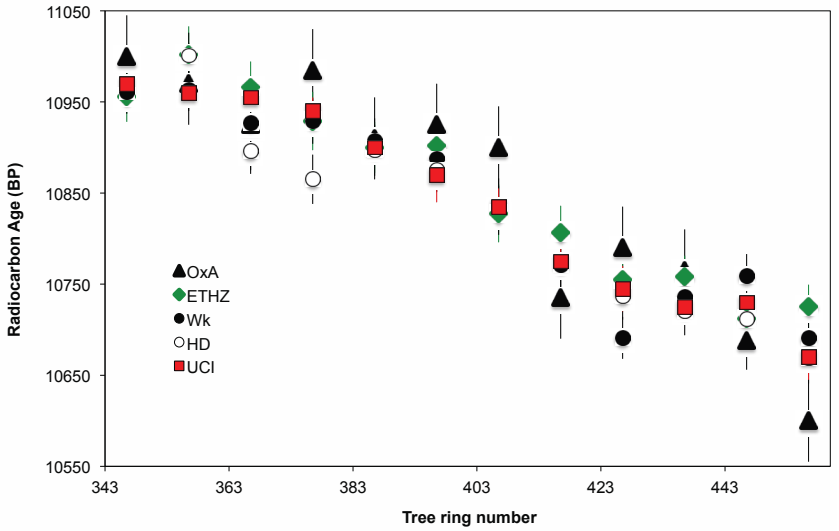

Figure 3 Intercalibration results for 12 successive YD-aged kauri samples—final results (OxA, University of Oxford; ETHZ, Laboratory of Ion Beam Physics; Wk, University of Waikato; HD, University of Heidelberg; UCI, University of California at Irvine).

The Waikato/Heidelberg Intercomparison

Waikato and Heidelberg undertook a second intercomparison to investigate further the possibility of an offset (OxA, UCI, Wk dates older) that might influence the accuracy of wiggle-matching the YD-kauri data set to IntCal09 data. A Swiss larch tree, Ollon505 (Friedrich et al. 2004; Kaiser et al. 2012), was chosen because it contains 363 rings and offered sufficient quantities of wood for both LSC and GP $\Delta^{14}C$ analysis. The HD and Wk laboratories undertook new analyses (11 and 20 measurements, respectively), with previously published IntCal09 HD measurements given in Table 3A and the new HD/Wk data sets in Table 3B.

Table 3A Previously published IntCal09 HD dendrochronology mid-ring numbers and ^{14}C analyses for the Swiss larch tree Ollon505 (data from IntCal09 supplementary files: http://www.radiocarbon.org/IntCal09.htm).

Ring nr (range)	Mid-ring nr	HD lab nr	IntCal09 dendro BP mid-ring nr	HD age (yr BP)
1–30	15.5	16184	12,127.5	10,313 ± 55.9
30–40	35	16185	12,108.0	10,343 ± 71.4
40–60	50	16847	12,093.0	10,335 ± 33.3
60–80	70	16825	12,073.0	10,282 ± 34.5
80–100	90	16641	12,053.0	10,291 ± 32.1
100–120	110	16823	12,033.0	10,218 ± 29.8
140–160	150	17325	11,993.0	10,257 ± 26.2
180–200	190	17304	11,953.0	10,140 ± 29.8
220–240	230	16779	11,913.0	10,179 ± 25
260–280	270	16812	11,873.0	10,160 ± 28.6
280–300	290	17757	11,853.0	10,227 ± 33.3
320–337	328.5	17026	11,814.5	10,088 ± 44
342–355	348.5	16092	11,794.5	10,138 ± 28.6

Table 3B New HD and Wk ^{14}C analyses of the Swiss larch tree Ollon505.

Ring nr (range)	Mid-ring nr	HD lab nr	HD age (yr BP)	Wk lab nr	Wk age (yr BP)	Difference (^{14}C yr) HD–Wk
127–136	131.5	29108	10,215 ± 22	27115	10,231 ± 23	–16 ± 32
137–146	141.5	29109	10,232 ± 19	27116	10,223 ± 22	9 ± 29
147–156	151.5	—	—	27117	10,233 ± 21	—
157–166	161.5	29191	10,150 ± 21	27118	10,223 ± 21	–73 ± 30
167–176	171.5	—	—	27119	10,208 ± 22	—
177–186	181.5	—	—	27120	10,203 ± 22	—
187–196	191.5	—	—	27121	10,152 ± 22	—
197–206	201.5	—	—	27122	10,167 ± 22	—
207–216	211.5	—	—	27123	10,152 ± 22	—
217–226	221.5	28914	10,154 ± 19	27124	10,159 ± 22	–5 ± 29
227–236	231.5	28919	10,149 ± 20	27125	10,173 ± 22	–24 ± 30
237–246	241.5	28920	10,182 ± 18	27126	10,150 ± 19	32 ± 26
247–256	251.5	28927	10,120 ± 20	27127	10,165 ± 22	–45 ± 30
257–266	261.5	29000	10,100 ± 20	27128	10,094 ± 22	6 ± 30
267–276	271.5	29042	10,113 ± 20	27129	10,127 ± 23	–14 ± 30
277–286	281.5	28997	10,066 ± 22	27130	10,113 ± 22	–47 ± 31
287–296	291.5	29028	10,111 ± 21	27131	10,169 ± 24	–58 ± 32
297–306	301.5	—	—	27132	10,090 ± 24	—
307–316	311.5	—	—	27133	10,067 ± 23	—
317–326	321.5	—	—	27134	10,063 ± 23	—
					Average offset (^{14}C yr)	–21

The differences between the 11 new Ollon505 sample pairs are shown in Table 3B, last column. The average difference of 21 ^{14}C yr reinforces the view that there may be a systematic offset between the HD and Wk laboratories of ~10–20 ^{14}C yr, with HD analyses younger. Differences of this magnitude will only be significant when comparing a very high-precision data set, such as the new kauri measurements, obtained from combining many replicate analyses. It may be necessary to consider this offset, perhaps by increasing the error limits for the interhemispheric offset, when the new floating kauri YD data set is wiggle-matched against the ^{14}C absolute extended tree-ring chronology, which is dominated by HD measurements for this time period.

The combined previously published and new Ollon505 data sets (Tables 3A and 3B) based upon the IntCal09 calendar ages are plotted alongside IntCal09 in Figure 4. Although the original 13 Ollon505 measurements conform to, and indeed define, IntCal09 (see Figure 4), the new measurements are clearly offset towards younger ages. To investigate this further, we created a revised IntCal curve (hereafter called IntCal09^{-}) by stripping out the published Ollon505 measurements, and ^{14}C wiggle-matched the new combined HD and Wk Ollon505 data set against IntCal09^{-}. The new Ollon505 measurements show high agreement (A_{comb} = 233.5%, A_n = 15.8%) with IntCal09^{-} (Figure 5), but in a time interval some 145 yr younger than the calendar ages given in IntCal09.

This strongly suggests that Ollon505 is incorrectly positioned in both IntCal04 and IntCal09. The Ollon505 data set has therefore been omitted from the IntCal13 update (Reimer et al., this issue). Removal of the Ollon505 measurements from IntCal09 creates a significant paucity of data with only 1 measurement (from the Cottbus chronology) between ~12.15 and 11.94 kyr cal BP (Figure 5).

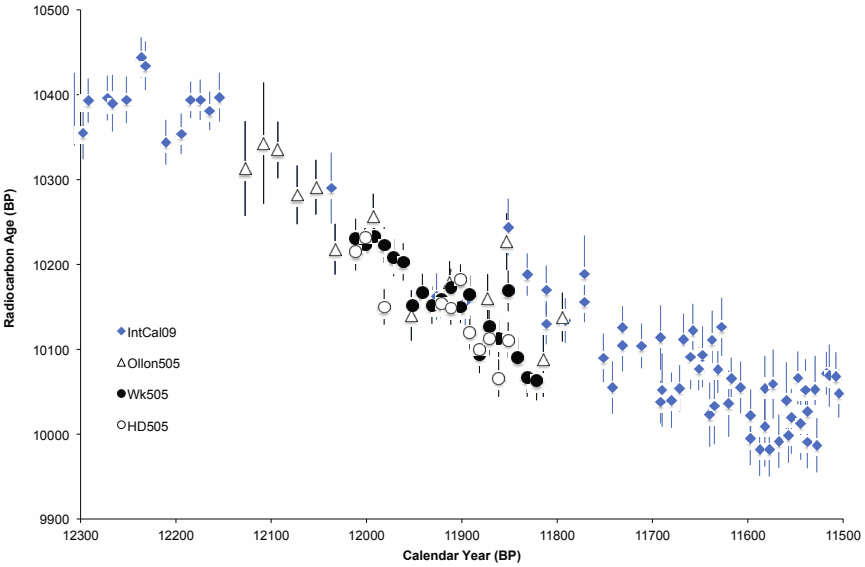

Figure 4 Ollon505 measurements graphed with IntCal09. All ^{14}C results plotted using the IntCal09 calendar ages. Previously published Heidelberg analyses shown as Ollon505. New analyses shown as HD505 (Heidelberg) and Wk505 (Waikato). Although the previous Ollon505 measurements from the inner rings (older ages) conform to the shape of the IntCal09 curve, the new measurements, mostly from the outer rings (younger ages), are significantly younger.

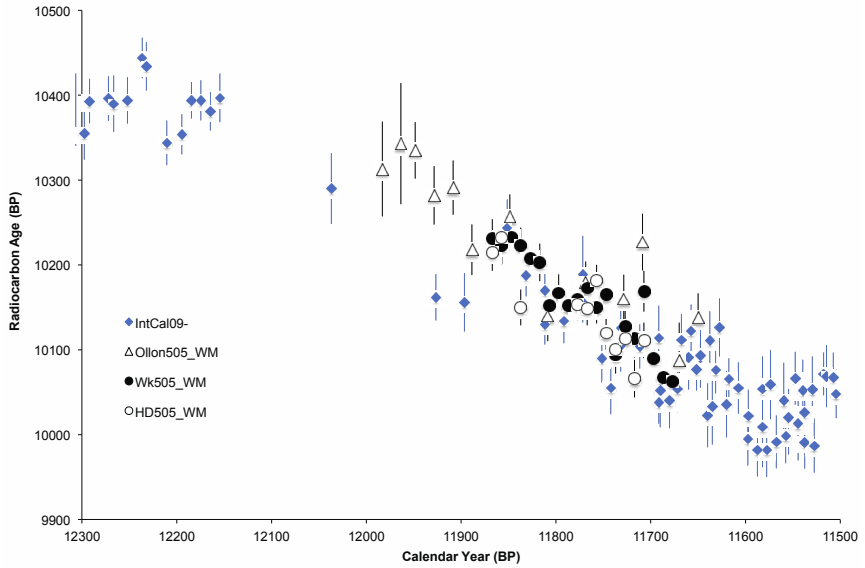

Figure 5 New HD- and Wk- Ollon505 measurements ^{14}C wiggle-matched against IntCal09^{-} (IntCal09 stripped of the original IntCal Ollon505 data set). All ^{14}C results plotted using the new ^{14}C wiggle-matched calendar ages. Previously published Heidelberg analyses now shown as Ollon505_WM. New analyses now shown as HD505_WM (Heidelberg) and Wk505_WM (Waikato). The new measurements now agree very well with IntCal09^{-} but are displaced towards younger ages by ~145 yr. Note that the tentative 2004 dendro-linkage of Ollon to the absolute tree-ring chronology has since been reevaluated (M Friedrich, K F Kaiser, personal communications) and is no longer believed to be correct.

The dendrochronological linkage between the Zurich and Cottbus dendrochronological series is described as "tentative" in Friedrich et al. (2004) because of the small number of trees in the Zurich series, the dependence on chronologies from different regions far away from each other (NE Germany and NE Switzerland), and the length of the overlap between the chronologies, which is relatively short (~130 yr), considering the distance between the sites.

Based upon tree-ring measurements, the 415-yr Swiss Avenches chronology (20 pines) extends from 12,057–11,642 cal BP, and overlaps with the PPC by 299 yr. The German Cottbus chronology (28 pines, 12,325–11,927 cal BP) in turn overlaps with Avenches by 130 yr, and finally Zurich (YD-B, 7 pines, 12,594–12,195 cal BP; Hua et al. 2009) overlaps with Cottbus by another 130 yr. These overlaps are more than sufficient for decadal resolution, high-precision ^{14}C wiggle-matching, but we consider confirmation of these linkages desirable in order to improve the integrity of this part of the calibration curve.

The international research funding bodies should be encouraged to support efforts for obtaining new measurements from these series to increase the sample density for this time range. Furthermore, the dendrochronology of the larch tree Ollon505 and other floating Swiss Younger Dryas and Preboreal pine series from nearby Zurich (Kaiser 1993; Kaiser et al. 2012) should be re-examined to see if a statistically valid younger dendrochronological fit of Ollon505 is possible.

CONCLUSIONS

We describe here the wood pretreatment and $\Delta^{14}C$ analytical protocols adopted for the Younger Dryas kauri research project, with replicate analyses to be performed by the Wk, UCI, and OxA ^{14}C dating laboratories across ~145 decadal floating New Zealand kauri (*Agathis australis*) samples spanning the time interval ~13.1–11.7 kyr cal BP. The initial interlaboratory intercomparison exercise (which also included the HD and ETHZ laboratories) highlighted inconsistencies in AMS sample pretreatment or $\Delta^{14}C$ measurement, which after correction resulted in very good agreement between all 5 participating laboratories. A HD/Wk intercomparison involving measurement of the YD-age Swiss larch tree Ollon505 showed a HD/Wk offset of ~10–20 ^{14}C yr (Heidelberg younger) and strong evidence that the IntCal04 and IntCal09 calendar ages for the Ollon505 series are incorrect. This series has therefore been removed from IntCal13. The dearth of measurements from ~12.15–11.91 kyr cal BP should be rectified by adding new data points, at decadal resolution, from dendrochronologically dated chronologies of this time period.

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