Exploration of age offset between radiocarbon dating and dendrochronology

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Ayaz Khan

Supervisors

Dr. Kristina Stenström

Associate Professor
Department of Physics,
Division of Nuclear Physics, Lund University

Dr. Raimund Muscheler

Associate Professor
Dept. of Earth and Ecosystem Sciences,
Division of Geology, Lund University

Dedication

"I dedicate this thesis to my mother, the most precious gift God has given to me"

Abstract: Radiocarbon dating requires calibration by an independent dating technique. An ideal method used to calibrate radiocarbon results is dendrochronology, because tree-rings are almost perfect archives of the atmospheric radiocarbon level and dendrodating can be very accurate. However, an age offset between the calibrated ^{14}C and dendrochronologically-dated ages has been observed for certain pine-tree samples studied at Lund University. It was observed that the ^{14}C ages of the samples are older than their ages determined dendrochronologically. The aim of this master thesis was to investigate the apparent age offset between the two methods and study the processes that could lead to the age offset. To probe the age offset, trees recovered from the peat bog Hällarydsmossen, Southern Sweden, were dendrochronologically dated via a German bog-pine chronology. The ^{14}C ages of the samples were measured using the accelerator mass spectrometry (AMS) technique. The samples for AMS measurement were prepared by using the cellulose extraction method. The results do not suggest any systematic age offset between radiocarbon dating and dendrochronology, as observed previously. However, the study verifies the reliability of the radiocarbon dating calibration by dendrochronology.

Key words: Radiocarbon dating, Dendrochronology, AMS, Radiocarbon calibration, ^{14}C wiggle matching.

Sammanfattning: Åldersbestämning med ^{14}C-metoden kräver kalibrering med hjälp av en oberoende dateringsteknik. En idealisk metod som idag används för kalibreringen är dendrokronologi, eftersom trädens årsringar utgör ett nästan perfekt arkiv av ^{14}C-halten i atmosfären och eftersom dendrodatering är en mycket exakt metod. Bakgrunden till detta arbete är ett forskningsprojekt vid Lunds universitet, där man i trädringsprover från tall i en torvmosse observerat att dendrodatering och ^{14}C-datering inte gav samstämmiga resultat; ^{14}C-dateringen gav högre ålder än dendrodateringen. Syftet med denna uppsats var att vidare undersöka eventuella åldersskillnader mellan de två metoderna och studera de processer som kan leda till en förskjutning av åldern. I arbetet användes träd funna i torvmossen Hällarydsmossen (södra Sverige) som dendrodaterats via en tysk tall-kronologi. ^{14}C-åldern på proverna mättes med tekniken acceleratormasspektrometri (AMS). Cellulosa extraherades ur trädringsproverna före AMS-mätning. Resultaten tyder inte på någon systematisk åldersskillnad mellan ^{14}C-datering och dendrokronologi, i motsats till tidigare observationer. Resultaten verifierar istället tillförlitligheten av ^{14}C-kalibreringen genom dendrokronologi.
Nyckelord: ^{14}C-datering, dendrokronologi, AMS, ^{14}C-kalibrering, "wiggle matching".

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1. Introduction

Radiocarbon dating is used worldwide to date carbonaceous material by measuring its $^{14}C/^{12}C$ ratio. The results need to be calibrated by an independent technique, because the production of ^{14}C and its distribution among different carbon reservoirs has been changing in the past, resulting in fluctuations in the atmospheric radiocarbon level. The tree–ring cellulose provides a direct measure of the atmospheric ^{14}C level. Dendrochronology is therefore the preferred source of radiocarbon calibration (Kromer, 2009). However, an age difference between the radiocarbon dating method and dendrochronology has been found at the Lund University Radiocarbon Dating Laboratory. In a PhD research project (PhD student Johannes Edvardsson), tree samples recovered from the peat bog Hällarydsmossen, Southern Sweden were first dendrochronologically dated via a German Bog pine chronology and then their ^{14}C ages were determined with the help of accelerator mass spectrometry (AMS) measurements. It was observed that the radiocarbon ages of the samples are different from the expected values inferred from dendrochronology. The unpublished results from the experiment are given in Table1 below.

Table1. Previous results of the ^{14}C measurements of tree samples from the peat bog Hällarydsmossen, Southern Sweden.

Sample	Calibrated ^{14}C age(BP)	Dendro age(BP)	Age offset (± 2σ)
TM451	6558±118	6413± 5	145 ± 118
TM451	6390±90	6199± 5	191 ± 90
TM468	6113±163	5973± 5	140 ± 163
TM453	6054±133	5832± 5	222 ± 133

Table 1 represents the calibrated ^{14}C ages, dendro ages and the age offset between the ^{14}C and dendro ages of the samples. Each calibrated ^{14}C age is the mean age of the probable age distribution within two standard deviations (± 2σ). The dendro age of each sample is the mean of an eleven years range (e.g. 6413± 5 represent the range 6408-6418). The weighted mean of these results show that the ^{14}C ages of the samples are older than their dendro ages by 179±59 years. The inconsistency of these results was confirmed by using defined sequence analysis technique of a calibration program OxCal, which showed an age difference of about 160 years between the ^{14}C ages and dendro ages of the samples. The samples were

cleaned chemically, and re-measured to see if the age difference was due to contamination, but almost the same results were obtained. The reason for the offset was not clear. Either all trees do not represent the exact level of atmospheric ^{14}C or there are other processes that effect the radiocarbon concentration in trees-rings. This master thesis project was conducted to probe this apparent age offset between radiocarbon dating and dendrochronology and to investigate the processes behind it.

The discrepancy was investigated by taking pine trees samples recovered from the peat bog Hällarydsmossen, Southern Sweden. The samples consisted of two tree-ring sequences; (1) samples from different trees in one chronology and (2) samples from one tree. The aim of the first sequence was to examine the age offset for different trees in the sequence and compare the results with the radiocarbon calibration curve. The second series from one tree was analyzed to study if the offset is age dependent. For example the tree could have taken more respirated/old carbon from the soil when it was small or it might have taken more radiocarbon from the atmosphere as it was grown up.

The samples were cleaned chemically to avoid contamination followed by cellulose extraction and graphitization processes. All the samples were thus converted into elemental carbon. The ^{14}C ages of the samples were measured using the AMS technique. Two different methods were used to transform ^{14}C years into calendar ages; (1) calibration of individual ^{14}C dates and (2) wiggle matching technique.

The calibration of individual ^{14}C dates as well as wiggle matching was performed by using a computer program OxCal (Ramsey et al., 2001).

2. Radiocarbon Dating

Carbon has three naturally occurring isotopes ^{12}C, ^{13}C and ^{14}C. ^{12}C and ^{13}C are stable, while ^{14}C is radioactive having a half-life 5730 years (Hua, 2009). Radiocarbon is naturally produced by the interaction of the secondary neutrons from cosmic rays with nitrogen in the upper atmosphere according to the reaction, $^{14}N + n \rightarrow ^{14}C + p$. After its production, ^{14}C is rapidly oxidized forming $^{14}CO_2$, which is dispersed in the whole atmosphere, the hydrosphere and the biosphere (Hua, 2009). Living organisms take up ^{14}C via the food chain and through metabolic process. As long as an organism is alive, it is in equilibrium with $^{14}C/^{12}C$ ratio of its environment. The decay of radiocarbon content in the organisms is compensated via exchange with the environment. However, when an organism dies, its exchange of radiocarbon with the environment is stopped, thus the organism no longer takes up radiocarbon. Consequently the radiocarbon concentration in the deceased organism starts to decrease at a rate given by the radiocarbon half-life (Hua, 2009).The time t passed since the organism stopped the exchange of radiocarbon with the environment is determined by the formula,

$$t = \frac{T_{1/2}}{\ln 2} \ln\left(\frac{N(t)}{N_0}\right) = \frac{1}{\lambda} \ln\left(\frac{N(t)}{N_0}\right) \qquad (1)$$

where $T_{1/2}$ is the half-life of radiocarbon, N_0 represents the original ^{14}C concentration in the organism, $N(t)$ is the ^{14}C concentration left at time t and λ is the decay constant (equals $\ln 2/T_{1/2}$). The conventional radiocarbon age of a material is determined by using eq (1) and the so called Libby half-life of 5568 (Stuiver and Polach, 1977).

Two different methods are used to measure the ^{14}C concentration in a sample. One method is to measure the activity A of the sample or the number of β^- particles emitted per unit time, known as decay counting. The number of β^- particles emitted by a sample is proportional to the number of ^{14}C atoms in it.

$$A = \left|\frac{dN}{dt}\right| = \frac{d}{dt}\left|N_0 e^{-\lambda t}\right| = \lambda N_0 e^{-\lambda t} = A_0 e^{-\lambda t} \qquad (2)$$

Thus ^{14}C is measured by detecting these particles, using either gas proportional or liquid scintillation counters. The second method is called accelerator mass spectrometry (AMS), which counts ^{14}C atoms directly in a sample relative to the stable carbon isotopes ^{13}C and ^{12}C (Hua, 2009; Linick et al., 1989). Both methods perform similar measurements on modern

reference standards to establish the initial activity or concentration ratio of ^{14}C (Bowman, 1990). The AMS technique used in this project work is described in more detail in chapter 4.

In order to obtain the $N\,(t)/N_0$ ratio of equation (1) the ^{14}C of a sample is measured relative to ^{14}C content of modern standard samples, Oxalic Acid I or Oxalic Acid II having known $^{14}C/^{12}C$ ratios (Hajdas, 2006). The internationally accepted radiocarbon dating reference value is defined as 95% of the radiocarbon concentration, in AD 1950, of Oxalic Acid I (Stuiver and Polach, 1977). 1950 is year 0 BP by convention in radiocarbon dating and is defined as "present".

In order to get accurate ^{14}C results it is also necessary to have an accurate background level, obtained from materials that have no ^{14}C, known as background blanks. Usually ancient wood or ancient carbonates are used as "dead" carbon sources for this purpose (Hogg, 2004). The ancient wood blanks do not only give a measure of the level but also the variability of any contaminating radiocarbon introduced in the sample preparation or in the measurement (Hogg et al., 2007). In radiocarbon dating, the mean radiocarbon activity of the background sample is determined and is subtracted from the measured ^{14}C activity of the sample and standards (Hogg et al., 2007).

The ^{14}C concentration in the atmosphere varies through time due to variations in the production rate of radiocarbon in the atmosphere. The production rate of ^{14}C in the atmosphere varies due to changes in the Earth´s geomagnetic field intensity, solar activity and carbon cycle (Fairbanks et al., 2005). Because of these variations, the conventional radiocarbon ages obtained by eq (1) are not equivalent to calendar ages. Hence, it is essential to convert radiocarbon results into calendar years. The calibration process converts ^{14}C age (±error) into the corresponding calendar age ranges (Hajdas, 2006), using a calibration curve, which describes the atmospheric ^{14}C concentration in the past measured in precisely and independently dated materials (Hua, 2009). The latest radiocarbon calibration curve is shown in Fig 1.
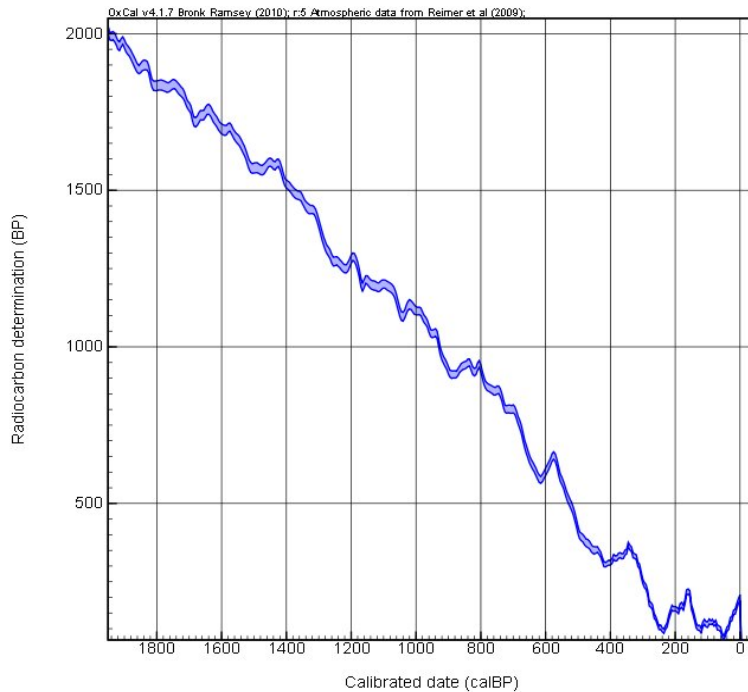
Fig 1. Radiocarbon calibration curve covering the age 0-2000 BP (Reimer et al., 2009).

There are many useful archives such as tree-rings, corals, laminated sediments and stalagmites used to develop radiocarbon calibration curves (Hajdas, 2006). Dendrochronologically dated records give a direct measure of the atmospheric radiocarbon on an absolute time scale. The annual growth ring patterns of trees provide an almost exact calendar age and also the same material can be directly examined for the radiocarbon content (Staff et al., 2010). Therefore, soon after the development of the radiocarbon method, the ^{14}C measurements of known-age tree samples were suggested as a method to calibrate the radiocarbon ages.

However, the tree-ring based radiocarbon calibration curve only dates back to 12,590 calendar years BP (Reimer et al., 2009). The curve has been extended beyond the tree ring time scale by using corals laminated sediments and stalagmites which provide reconstruction of the atmospheric radiocarbon over the last 50-60 thousand years (Hajdas, 2006). The latest calibration curve IntCal09 provides the possibility to calibrate ^{14}C ages from 0-50,000 calendar years BP (Reimer et al., 2009).

Several calibration programs such as CalPal, Calib and OxCal have been developed by radiocarbon experts (Hajdas, 2006). The computer program OxCal, developed by (Ramsey et

al.,2001) not only calibrates ^{14}C ages but also provides the possibility of statistical analysis of data and allows development of age models (Ramsey et al., 2001). The probability distribution generated by OxCal shows the probable age ranges of the dated material.

The calibration of a single radiocarbon date from ^{14}C age to the real calendar age may however not be always precise. The reason is that the calibration curve (See Fig.1), which is a function R dependent on time t with an uncertainty δR, given by $r = R(t) \pm \delta R(t)$ is not smooth and monotonic (Ramsey et al., 2001). Thus there is no single valued, differentiable, inverse function for calibration.

However, if several different points with known age separation are sampled on this curve, the ^{14}C data can be fitted to the shape of the function $R\ (t)$.This method of matching radiocarbon dates to the 'wiggles' of the calibration curve where the age difference between the ^{14}C dates is known, is referred to as wiggle matching (Ramsey et al., 2001). In wiggle matching one can see where the data fits the curve and how good that fit is.

The wiggle matching technique can be used in case of tree rings, where the rings have known age separation and the radiocarbon measurements can be chosen to be corrected over several hundred years (Ramsey et al., 2001). The program OxCal is also used to perform wiggle matching and calculate the probability distribution for samples in sequence (Ramsey, 1995).

3. Dendrochronology

Dendrochronology is a scientific technique mainly used to determine the age of wooden objects by studying tree-rings patterns in wood. The growth variability and the relative ages of different trees are determined by comparison and measurement of their annual rings (Schweingruber, 1988) There are seven principles that govern the application of dendrochronology (Smith and Lewis, 2007). However, the most important one is the principle of cross dating, which is a process of matching variations in ring widths or other ring characteristics among several tree ring series that helps to identify the exact year of formation of each ring (Haneca et al., 2009). Cross dating of a sample of unknown age is shown in Fig 2.
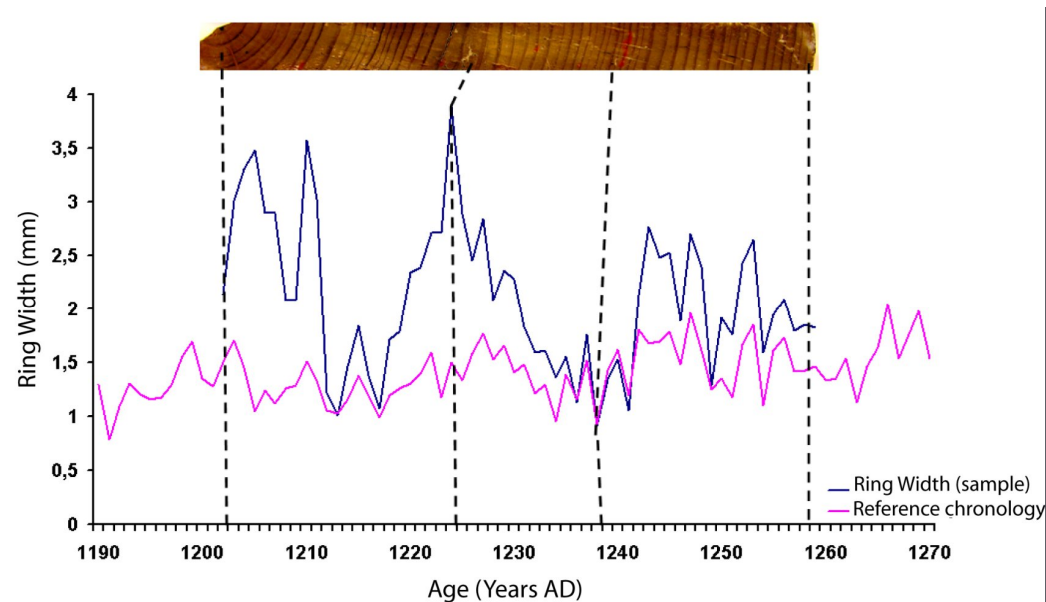

Fig 2. Cross dating of a sample of unknown age against a reference chronology (Photo by Edvardsson).

Typically two ring-width series are shifted along each other having one-year intervals between them. At different points, correlation values between the two series are calculated, and statistically significant values are used to characterize the exact position for an undated series on a dated chronology (Haneca et al., 2009). Thus crossdating assigns an absolute

value to each ring in a tree-ring series of unknown age by matching the undated ring-with patterns to those of a known series. Crossdating is also used to measure errors and false or missing rings (Smith and Lewis, 2007). In general trees produce valuable climate data as their growth is limited by e.g. temperature or precipitation. This generates similar growth variability between different individual trees which makes it possible to cross date them (Schweingruber, 1988). Apart from similar growth variability the trees must produce anatomically distinct and visible annual rings. Obviously, tree-ring series are not identical. Statistics and the calculation of correlation values are used in crossdating to assess the common variability of two tree-ring series. Typically; tree-ring dating is started by measuring the tree-ring widths at individual trees. These tree-ring series can thereafter be cross dated, that leads to development of a tree-ring chronology. Ring-width chronologies have successfully been used for the calibration of the radiocarbon curve, which is the most important part of this study.

4. Materials and methods

Two tree-ring sequences of pine trees recovered from the peat bog Hällarydsmossen close to Stockaryd, a small village in Southern Sweden, were examined in order to probe the age offset.

Fig 3. Picture of the peat bog Hällarydsmossen, Southern Sweden (Photo by Edvardsson).

The absolutely dated bog-pine ring-width chronology analyzed in this study was dendrochronologically cross dated with a German bog-pine chronologies (Edvardsson et al., In press). The first series consisted of 11 samples from different trees, covering the period 5700BP to 6300 BP, with age gaps of 60 years between consecutive samples. The second sequence contained 8 samples from one tree (see Fig 4) having dendrochronologically dated ages from 6111BP to 6464 BP.

Fig 4. Picture of the tree TM 463 from which 8 samples were taken for analysis.

The samples in the second series are separated by age gaps of 50 years. The age of each sample is the mean of an 11 years range as described in the introduction part. The statistical methods used for the age determination of the samples include *t*-value test and Gleichläufigkeit (Schweingruber, 1988), which are normal procedures in dendrochronology. Also, calculation of the Pearson correlation coefficient (*r*) and visual comparison between the different chronologies have been performed (Edvardsson et al., In press). The modern radiocarbon standard used in this study was Oxalic acid II. Brown coal was utilized as the background sample for the AMS measurement. The ^{14}C concentration was measured in graphite made up from CO_2 produced by combustion of the samples (Goslar and Czernik, 2000). The process performed to produce elemental carbon from wood samples is outlined in section 4.1 and Appendix.

4.1. Sample preparation

First the samples (as shown in Fig 5) were examined under the microscope and were brushed to remove surface dust and other undesirable organic materials.

Fig 5. Picture of a sample cut out from a tree.

The samples might have absorbed carbonates from percolating ground water, and they may contain humic acids, which is deposited in the vicinity of the sample matrix. The result of the contamination is that carbonates contaminated samples appear too old, while samples contaminated with humic acids appear too young (Hellborg and Skog, 2008).

To avoid any kind of contamination, the tree-ring samples were cleaned chemically. First, the samples were cut to small pieces (see Fig 6) and were heated at 80°C for 5 hours in 2% sodium hydroxide (NaOH) solution in order to remove humic acids.

Fig 5. Thin pieces of a sample before chemical pre-treatment.

Then the samples were rinsed to neutral pH with de-ionized water. The samples were then kept in 3% HCl solution at the same temperature (80^oC) in the oven for more than 12 hours to extract carbonate contamination (Goslar and Czernik, 2000). Thereafter, the sample material was washed with de-ionized water again until got neutral.

In ^{14}C studies of trees cellulose extraction is carried out to remove resins, lignins and other mobile wood fractions that can contaminate the sample with translocated carbon which is not removed by conventional pre-treatment (Southon and Magana, 2010).

The extraction of cellulose makes sure that the fraction of the sample isolated for dating is a representative of prevailing atmospheric conditions at the time of growth (Hogg et al., 2007). In order to obtain the cellulose, each sample was put in 16 ml of water in a clear glass jar which was kept in a water bath at temperature between 65^oC-95^oC. 0.1gram of 80% sodium chlorite ($NaClO_2$) and two drops of 3% hydrochloric acid (HCl) were added to each sample in order to remove lignins (Southon and Magana, 2010). After half an hour, the amount of sodium chlorite and that of hydrochloric acid was increased to 0.2 grams and three drops respectively to accelerate the cellulose extraction. The process of putting the above mentioned chemicals after each hour was repeated three times. However it was found that the samples still contained lignin. To isolate cellulose, sodium chlorite and hydrochloric acid were used two more times. Thus very fine and completely white cellulose was obtained from each sample (see Fig 7).

Fig 7. Picture of the cellulose obtained from sample RAI-18a.

The cellulose was then washed with water and dried in an oven at 80^oC for 10 hours. 2 to 2.5 mg dried cellulose were taken from each samples and placed in small quartz tubes (length 30

mm, diameter 7mm) containing 200 mg of copper oxide (CuO) powder. These quartz tubes were then placed in large quartz tubes (length 180 mm, diameter 9.5mm). Thereafter the large tubes were evacuated with a vacuum system and sealed with a torch (see Fig 8).
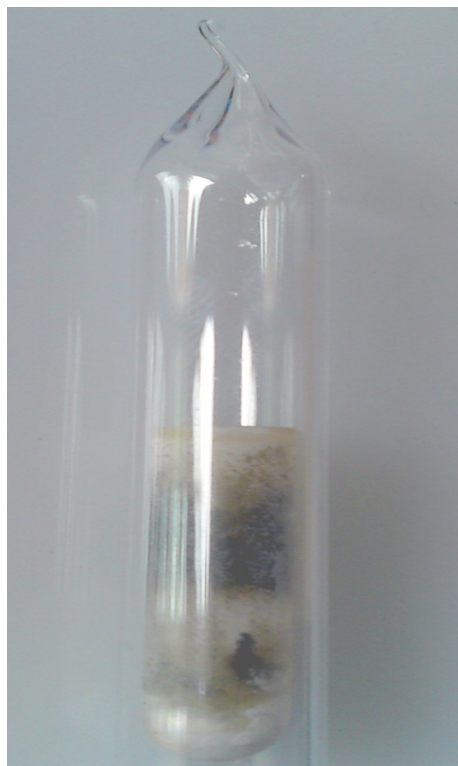

Fig 8. A sealed quartz tube containing the sample.

The sealed tubes were heated in an oven at 950°C for 2 hours in order combust the sample to CO_2.The sample tubes were then cooled to room temperature and fitted one by one in the sample holder of the graphitization system (see Fig 9).
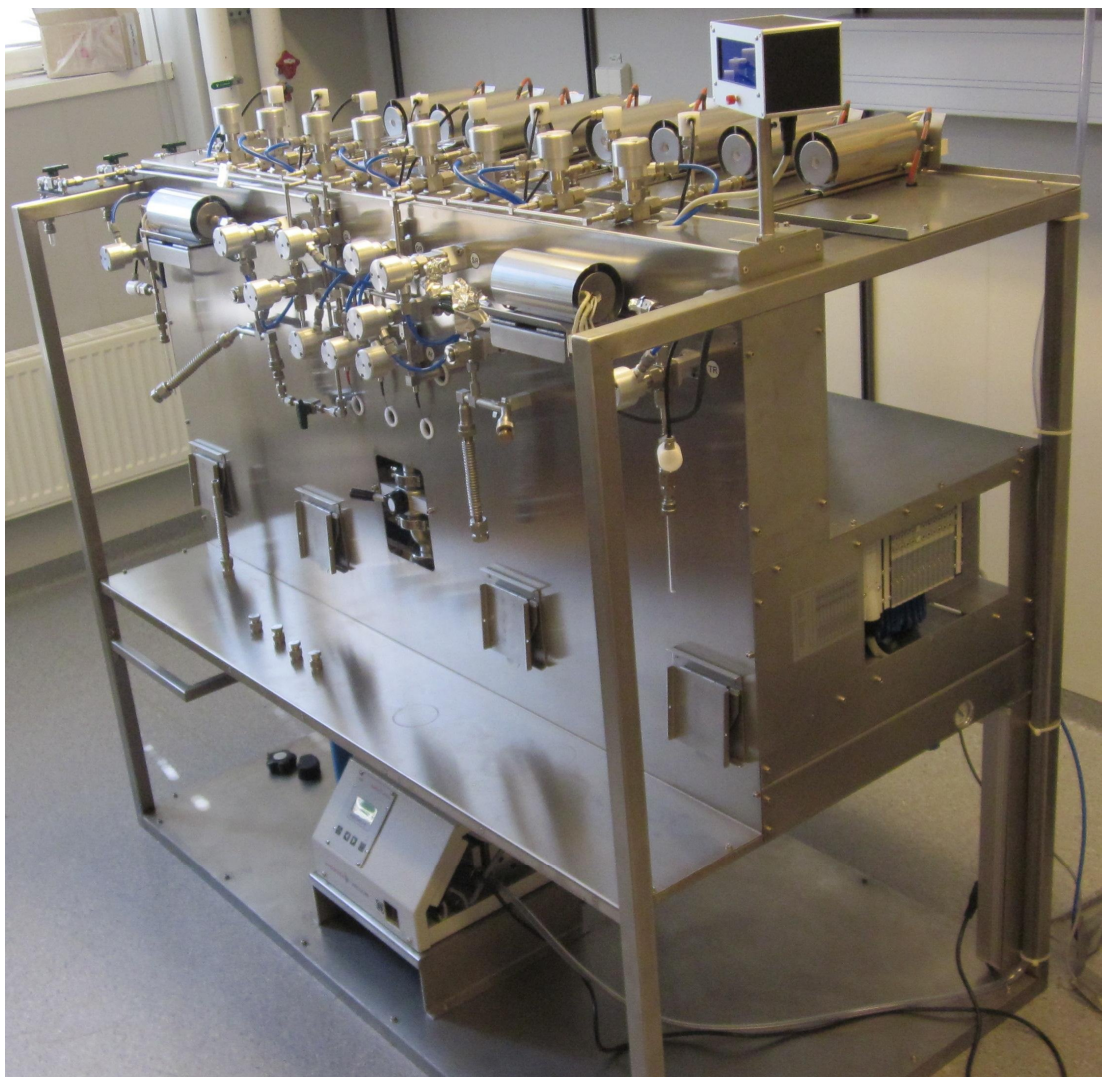
Fig 9. Graphitization system at Lund University Radiocarbon Laboratory.

Breaking the tube inside the sample holder, the CO_2 from the sample is transferred into a small reaction volume for graphitization. 4-5 mg Iron (Fe) was used in each reactor tube as catalyst. The graphitization of CO_2 with H_2 on iron powder was used to prepare graphite targets for the ^{14}C measurements by AMS (Wacker et al., 2010b). The graphitization took place at 580^oC using the catalytic Bosch reaction (Hellborg and Skog, 2008)**.**

given as

$$CO_2 + 2H_2 \xrightarrow{Catalyst(Fe)} C + 2H_2O$$
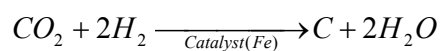
Thus after 3 hours carbon was obtained on the surface of hot Fe catalyst. In graphite form (iron/carbon mixture) each sample was pressed into a sample holder. The sample holders were then mounted on a target wheel (see Fig 10) for AMS measurement together with standard samples of known activity, secondary standard (test samples) of known ^{14}C age and background samples processed in the same way.
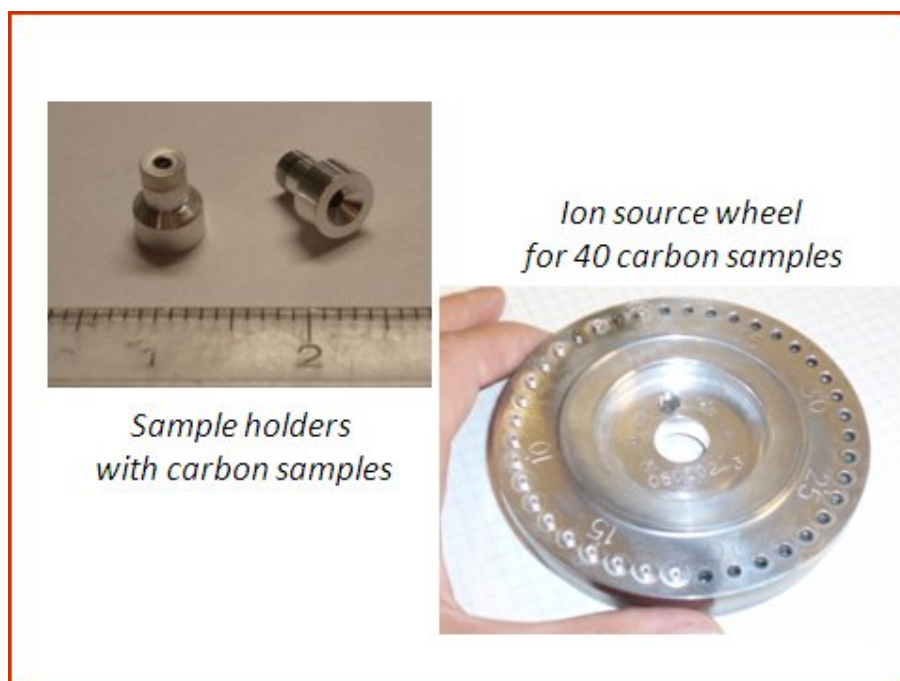

Fig 10. Target wheel with 40 carbon sample holders.

A protocol developed for the sample preparation part can be seen in appendix.

4.2. Accelerator Mass Spectrometry (AMS)

Accelerator Mass Spectrometry (AMS) is a highly sensitive technique of counting atoms and is used to determine the ratio of the abundant to rare isotopes. Isotopes that can be analyzed by AMS include ^{10}Be, ^{14}C, ^{26}Al, ^{36}Cl, ^{41}Ca, ^{129}I and many others (Linick et al, 1989). However, ^{14}C is the most widely used isotope studied with AMS (Hellborg and Skog, 2008). Using AMS, sub-milligram-size small samples can be measured in a short interval of time, which is not possible by radiometric methods (Hellborg and Skog, 2008). In AMS the ^{14}C atoms are detected directly and one does not have to wait for them to decay.
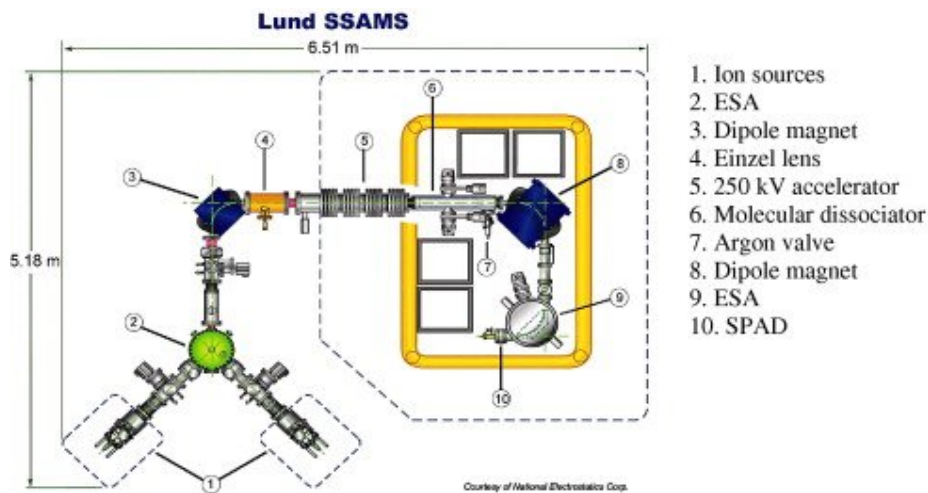

Fig 11. The SSAMS system at Lund University. (Reproduced with permission from NEC)

The Single Stage Accelerator Mass Spectrometry (SSAMS) system at Lund University is shown in Figure 11. It is equipped with two MC-SNICS (Multi-Cathode Source of Negative Ions by Cesium Sputtering) ion sources (1). To measure ^{14}C, the graphite samples, mounted on a 40 position target wheel (see Fig 10), are loaded into one of the ion sources. In the ion source, the sample material is transformed into a singly charged negative ion beam consisting of $^{12}C^-$, $^{13}C^-$ and $^{14}C^-$ as well as molecules like $^{13}CH^-$ and $^{12}CH_2^-$ by a process known as sputtering (Klody et al., 2005). A 45° rotatable spherical electrostatic analyzer (ESA) (2) is used to switch between the ion sources, improve the energy resolution of the injected beam, limits the injected ion beam to a narrow energy range and leads the beam to the first dipole magnet (3). The low energy bending magnet (LEBM) or dipole magnet (3) is placed after the ESA, to analyze the isotopes by their mass to charge ratio. The $^{12}C^-$ and $^{13}C^-$ can be measured

after the dipole magnet (3) but not the $^{14}C^-$, since at this stage; the beam contains a lot of other molecules having the same mass as $^{14}C^-$. To get rid of these molecules the beam needs to be accelerated and passed through a molecular dissociator. The Einzel lens (4) close to the entrance of the acceleration tube (5) keeps the beam envelope as small as possible. The isotopes of carbon are inserted to the accelerator in a sequence with the vacuum chamber of the LEBM adjusted to predetermined voltages (*ca. 0.2 kV for ^{14}C, 3.5 kV for ^{13}C and 7 kV for ^{12}C*) (Hellborg and Skog, 2008). A Faraday cup is located off-axis after the injection magnet, which sequentially monitors $^{12}C^-$ and $^{13}C^-$ during the sequential injection of all three carbon isotopes into the accelerator. After the acceleration, the beam is injected into a molecular dissociator (stripper) (6), where the negative ions pass through an *Ar* gas cell. Now at a high energy, the negative ions lose electrons and thus neutral and positively charged $^{12}C,$ ^{13}C and ^{14}C ions are produced. The molecular ions are dissociated in the stripper by the interaction of these molecules with *Ar* gas. The positive ions beam is then analyzed by a 90° high energy bending magnet (HEBM) (8) that removes the molecular fragments from the ^{14}C beam. Two Faraday cups are used to measure the $^{12}C^+$ and $^{13}C^+$ beams after the high energy dipole magnet. Another electrostatic spherical analyzer (ESA) (9) is used at 90° before the sequential post-accelerator deflector (SPAD) (10). The (SPAD) consisting of two parallel plates is used to deflect scattered $^{14}C^+$ ions and direct the beam to a surface barrier detector, placed at the end of the beam line (Hellborg and Skog, 2008).

5. Results

All the samples were measured twice in order to get more accurate results. Each ^{14}C measurement is accompanied by an experimental uncertainty which is referred to as the statistical error. So a "± "term is added as a suffix to all ^{14}C age estimates and is usually expressed as ± one sigma or one standard deviation (±σ) (Taylor, 1995). The "±1σ"implies that there is a 68.3% chance that the true result will lie within ±1σ of the experimental result. Similarly there is a 95.4% chance within ±2σ and 99.7% within ±3σ (Bowman, 1990). To estimate the error, it is assumed that the Gaussian or normal probability function holds for radiocarbon measurements.

The conventional ^{14}C ages of the samples and the relevant $^{12}C^-$ current obtained from AMS for the 11 samples from different trees covering the calendar age period 5700 BP to 6300 BP with age gaps of 60 years between consecutive samples are shown in Table2 below.

Table2. Conventional ^{14}C ages and $^{12}C^-$ currents obtained from AMS for the first sequence

Tree ID	Sample	$^{12}C^-$ current (μA)		Conventional ^{14}C age (BP)	
		Run-1	Run-2	Run-1	Run-2
TM414	RAI-11a	22.2	18.9	4968 ± 51	5021 ± 53
TM414	RAI-12a	15.1	13.4	5014 ± 59	5052 ± 61
TM478	RAI-13a	23.9	22.5	5019 ± 50	5080 ± 50
TM466	RAI-14a	18.5	11	5066 ± 55	5064 ± 67
TM453	RAI-15a	21.8	20.4	5138 ± 52	5130 ± 58
TM437	RAI-16a	12.7	5.6	5142 ± 65	5450 ± 94
TM468	RAI-17a	21.2	19.5	5099 ± 52	5316 ± 53
TM468	RAI-18a	20.6	16.7	5297 ± 53	5294 ± 57
TM464	RAI-19a	22.8	21.2	5283 ± 52	5381 ± 52
TM436	RAI-20a	4.4	1.5	5275 ± 104	5132 ± 173
TM447	RAI-21a	12	13.8	5459 ± 67	5459 ± 67

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In Table 2, the samples "RAI-11a" and "RAI-12a" have been taken from one tree "TM 414". Also the samples "RAI-17a" and "RAI-18a" belong to one tree "TM468" The samples that

gave a $^{12}C^-$ current below 10 μA were rejected as the samples have large uncertainties and are not considered reliable for analysis. However those samples that showed the $^{12}C^-$ current above 10 μA in either run were included in the analysis. For example the sample "RAI-20a" that showed the $^{12}C^-$ current as 4.4 μA and 1.5 μA respectively in the two runs of AMS was rejected, however the sample "RAI-16a" was analyzed based on the value of $^{12}C^-$ current obtained from the first run of AMS.

Table 3 represents the conventional ^{14}C ages and the $^{12}C^-$ currents of the 8 samples from one tree "TM 463" having dendrochronologically dated ages from 6111 BP 6464 BP.

Table 3. Conventional ^{14}C ages and $^{12}C^-$ currents obtained from AMS for the second sequence

Tree ID	Sample	$^{12}C^-$ current (µA)		Conventional ^{14}C age (BP)	
		Run-1	Run-2	Run-1	Run-2
TM463	RAI-29	18.2	13.8	5339 ± 56	5442 ± 62
TM463	RAI-30	21.5	20.6	5206 ± 69	5289 ± 58
TM463	RAI-31	22.3	20.4	5499 ± 52	5425 ± 53
TM463	RAI-32	22.6	20.8	5284 ± 52	5372 ± 52
TM463	RAI-33	7.4	14.6	5612 ± 94	5572± 60
TM463	RAI-34	15.4	18.3	5685 ± 61	5442 ± 55
TM463	RAI-35	14.3	13.6	5696 ± 62	5653 ± 63
TM463	RAI-36	23.4	22.8	5729 ± 52	5777 ± 51

Here the sample "RAI-33" was rejected because of the small $^{12}C^-$ current in the first run. However in the second run the $^{12}C^-$ current obtained for this sample was 14.6 μA as shown in Table 3.Hence the ^{14}C age based on this value was taken into account.

Table 4 shows the values of conventional ^{14}C ages and $^{12}C^-$ currents of the test samples used in ^{14}C - AMS measurements.

Table 4 .Conventional ^{14}C ages and $^{12}C^-$ currents obtained from AMS for the test samples (secondary standard)

Number	Sample	$^{12}C^-$ current (µA)		Conventional ^{14}C age (BP)	
		Run-1	Run-2	Run-1	Run-2
1	RAI-22a	13.7	15.2	311±49	270±46
2	RAI-23a	20.8	19.0	272±42	196±43

.

Both the test samples "RAI-22a" and "RAI-23" used in the measurements were taken from the same tree rings and have a known ^{14}C age of 340 BP.

In order to analyze the results, the weighted mean ^{14}C age and the mean uncertainty were calculated for each sample from the two runs of AMS. The weighted mean ^{14}C age and the respective uncertainty were calculated by using eq (3) and eq (4) respectively and are presented in Table 5 and Table 6 as conventional ^{14}C ages.

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i / \sigma_i^2}{\sum_{i=1}^{n} 1 / \sigma_i^2} \tag{3}$$

$$\sigma_{\bar{x}}^2 = \frac{1}{\sum_{n=1}^{n} \left(1 / \sigma_i^2 \right)} \tag{4}$$

Using the computer program OxCal; all ^{14}C dates were then calibrated individually. The aim of this calibration was to get a probability distribution of the ^{14}C date along the calendar axis. The midpoint of the total error range ($\pm 2\sigma$) on the calendar scale of each calibrated ^{14}C date was taken as the most probable date. This is an approximation since the probability distribution of calibrated ^{14}C ages can very have different shapes and it is usually not symmetric. Table 5 shows the results for the samples of the first sequence.

Table 5. Conventional ^{14}C ages, calibrated ^{14}C ages, dendro ages and age offset between the calibrated ^{14}C ages and dendro ages of the samples from the first sequence

Tree ID	Sample	Conventional ^{14}C age(BP)	2σ range(95%) years(BP)	Calibrated age (BP) ± 2σ	Dendro age(BP)	Age offset (years) = calibrated ^{14}C age - dendro age ± 2σ
TM 414	RAI-11a	4986± 37	4912-5060	5748 ± 139	5700 ± 5	48 ± 139
TM 414	RAI-12a	5045±42	4961-5129	5785 ± 122	5760 ± 5	25 ± 122
TM 478	RAI-13a	5037±35	4967-5105	5782 ± 119	5820 ± 5	-38 ± 119
TM 466	RAI-14a	5091±42	5007-5175	5830 ± 90	5880 ± 5	-50 ± 90
TM 453	RAI-15a	5105±39	5027-5183	5836 ± 90	5940 ± 5	-104 ± 90
TM 437	RAI-16a	5142±65	5012-5272	5947 ± 227	6000 ± 5	-53 ± 227
TM 468	RAI-17a	5200±37	5126-5274	6037 ± 136	6060 ± 5	-23 ± 136
TM 468	RAI-18a	5302±39	5224-5380	6070 ± 135	6120 ± 5	-50 ± 135
TM 464	RAI-19a	5339±37	5261-5417	6133 ± 135	6180 ± 5	-47 ± 135
TM 436	RAI-20a	rejected	Rejected	rejected	6240 ± 5	rejected
TM 447	RAI-21a	5415±45	5325-5505	6262 ± 141	6300 ± 5	-38 ± 141

The age offset between the calibrated ^{14}C ages and dendro ages of the samples presented in Table 5 is shown graphically in Fig 12.
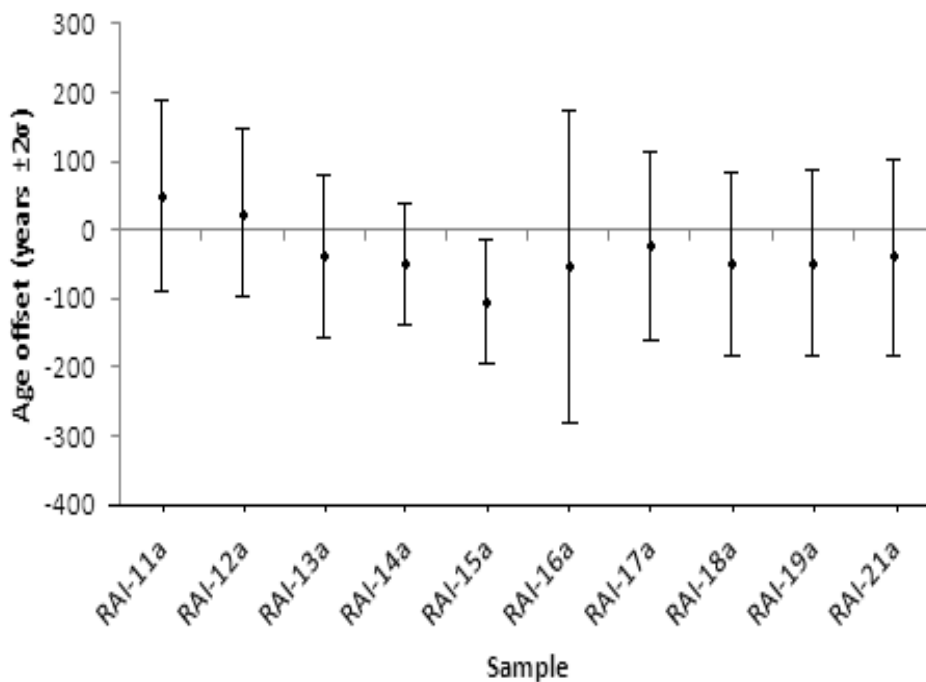

Fig 12. Age offset between the calibrated ^{14}C ages and dendro ages of the samples from the first sequence.

The weighted mean age difference between the calibrated ^{14}C ages and dendro ages of the samples is 37±48.In other words the ^{14}C age of the samples is younger than their dendro age by 37 years. However, the 37 years age difference lies within the standard uncertainty ± 48 (±2σ). Also from Figure 12 it is clear that the age offset of all samples except "RAI-15a" lies within 2 standard deviation and "RAI-15a" lies within 3 standard deviation. This implies that the ^{14}C and dendro ages of the samples are consistent with each other.

The results for the samples of second sequence having dendrochronologically dated ages from 6111 BP to 6464 BP are presented in Table 6.

Table 6. Conventional ^{14}C ages, calibrated ^{14}C ages, dendro ages and age offset between the calibrated ^{14}C ages and dendro ages of the samples from the second sequence

Tree ID	Sample	Conventional ^{14}C age(BP)	2σ range(95%) years(BP)	Calibrated age(BP) ± 2σ	Dendro age(BP)	Age offset (years) = calibrated ^{14}C age - dendro age ± 2σ
TM463	RAI-29	5381±42	5297-5465	6145 ± 140	6111 ± 5	34 ± 140
TM463	RAI-30	5247±44	5159-5335	6049 ± 131	6161 ± 5	-112 ± 131
TM463	RAI-31	5462±37	5388-5536	6252 ± 61	6211 ± 5	41 ± 61
TM463	RAI-32	5324±37	5250-5398	6128 ± 135	6261 ± 5	-133 ± 135
TM463	RAI-33	5572±60	5452-5692	6382 ± 102	6311 ± 5	71 ± 102
TM463	RAI-34	5552±40	5472-5632	6348 ± 61	6361 ± 5	-13 ± 61
TM463	RAI-35	5675±44	5587-5763	6469 ± 148	6411 ± 5	58 ± 148
TM463	RAI-36	5750±36	5678-5822	6545 ± 95	6464 ± 5	81 ± 95

The age offset between the calibrated ^{14}C ages and dendro ages of these samples are plotted as shown in Fig 13.
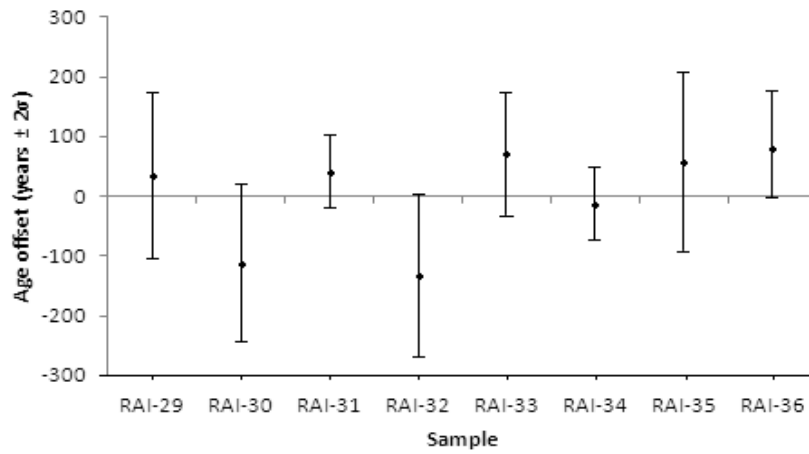

Fig 13. Age offset between the calibrated ^{14}C ages and dendro ages of the samples from the second sequence

For the series presented in Table 6, the weighted mean age difference between the calibrated ^{14}C ages and dendro ages of the samples is 72±72 years. Thus the ^{14}C ages and dendro ages of the samples in this series are also consistent with each other as the 72 years age difference lies within ± *2σ* range. It can be also seen in Fig 13 that the age offset between the calibrated ^{14}C ages and dendro ages of the entire samples lie within 2 standard deviation. This means that the ^{14}C ages and dendro ages of the samples are in agreement with each other.

Table 7. Measured ^{14}C age, calibrated ^{14}C age and known ^{14}C age of the test samples

Number	Sample	Measured ^{14}C age (BP)	2σ range(95%) years(BP)	Calibrated age(BP) ± 2σ	Known ^{14}C age (BP)
1	RAI-22a	288±34	220-356	310±152	340±8
2	RAI-23a	235±30	175-295	209±213	340±8

Table 7 represents the results for the test samples of known age used in the experiment .The measured ^{14}C age of the test sample "RAI-22a" is consistent with the known age within $\pm$ 2σ. However the age of the sample "RAI-23a" lies outside $\pm$ 3σ range. The weighted mean of the measured ^{14}C age of the test samples is 258±22. This is younger than the known age by 16 years while considering $\pm$ *3σ* range in the measurement. In other words one can also say that the measured ^{14}C age is younger than the expected value by about 80 years and lies outside $\pm$ *3σ* range. This could indicate that all results show the same offset. However an alternative ^{14}C data evaluation technique (see discussion part) shows that the measured ^{14}C age is in agreement with the known age within the $\pm$ *2σ*.

For each date the calibration process gives a multi-mode probability distribution, which cannot be characterized properly by a single age estimate such as the weighted average of the probability distribution (Yeloff et al., 2006). The wiggle-match method is used to circumvent this problem. The reason behind the process is that plants that were growing on the surface of peat bogs preserved the same fluctuations in the atmospheric ^{14}C concentration as the trees that were used for the formation of ^{14}C calibration curve (Blaauw et al., 2004), even if there was a slight offset in the ^{14}C ages. The wiggle matching measurements on tree-rings were performed by using D_Sequence of the calibration program OxCal using known age separation of 60 years between samples (Ramsey, 1995). The age gap between RAI-19 and RAI-21 is 120 years, since RAI-20 is rejected because of small ^{12}C current. The wiggle match ages and the dendro ages of the first series of samples from different tree are given in Table 8 along with the age difference between the wiggle match ages and dendro ages of the series.

Table 8. Wiggle match ages and dendro ages of the samples from the first sequence

Tree ID	Sample	Wiggle Match Age (BP) ± 2σ	Dendro Age(BP)	Age offset (years) ± 2σ
TM 414	RAI-11a	5638 ±35	5700 ±5	62±35
TM 414	RAI-12a	5698 ±35	5760 ±5	62±35
TM 478	RAI-13a	5758 ±35	5820 ±5	62±35
TM 466	RAI-14a	5818 ±35	5880 ±5	62±35
TM 453	RAI-15a	5878 ±35	5940 ±5	62±35
TM 437	RAI-16a	5938 ±35	6000 ±5	62±35
TM 468	RAI-17a	5998 ±35	6060 ±5	62±35
TM 468	RAI-18a	6058 ±35	6120 ±5	62±35
TM 464	RAI-19a	6118 ±35	6180 ±5	62±35
TM 436	RAI-20a	rejected	6240 ±5	rejected
TM 447	RAI-21a	6238 ±35	6300 ±5	62±35

The ^{14}C dates of the samples were plotted on the IntCal 09 in order to compare the ^{14}C dates of the samples with the wiggles in the calibration curve as shown in Figure 14.
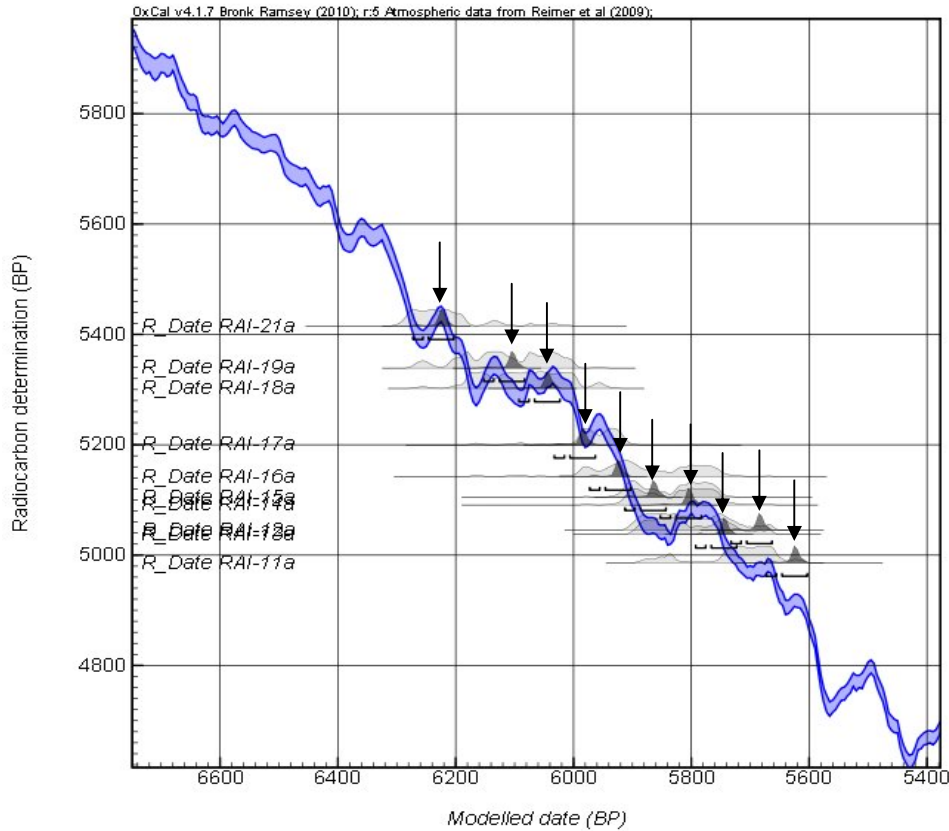
Fig 14. ^{14}C ages of the samples from the first sequence plotted on IntCal 09.

The result shows that there is an age difference of 62 years with ± 2σ as shown in the Table 9 above. However, using the results obtained from the program "BATS" (see discussion part) this age difference was reduced to 39 ±28 years. From the graph in Fig 14, it is clear that the sequence of the ^{14}C dates of the series fits the calibration curve. It means that the ^{14}C results obtained are reliable. Again using OxCal the wiggle matching measurements on tree-rings were carried out for the second series with known age gap of fifty years between samples (Ramsey, 1995). The wiggle match ages and dendro ages of the samples from one tree are presented in Table 9.

Table 9. Wiggle match ages and dendro ages of the samples from the second sequence

Tree ID	Sample	Wiggle Match age (BP) ± 2σ	Dendro Age(Bp)	Age offset (years) ± 2σ
TM463	RAI-29	6118 ±13	6111±5	7±13
TM463	RAI-30	6168 ±13	6161±5	7±13
TM463	RAI-31	6218 ±13	6211±5	7±13
TM463	RAI-32	6268 ±13	6261±5	7±13
TM463	RAI-33	6318 ±13	6311±5	7±13
TM463	RAI-34	6368 ±13	6361±5	7±13
TM463	RAI-35	6418 ±13	6411±5	7±13
TM463	RAI-36	6468 ±13	6464±5	7±13

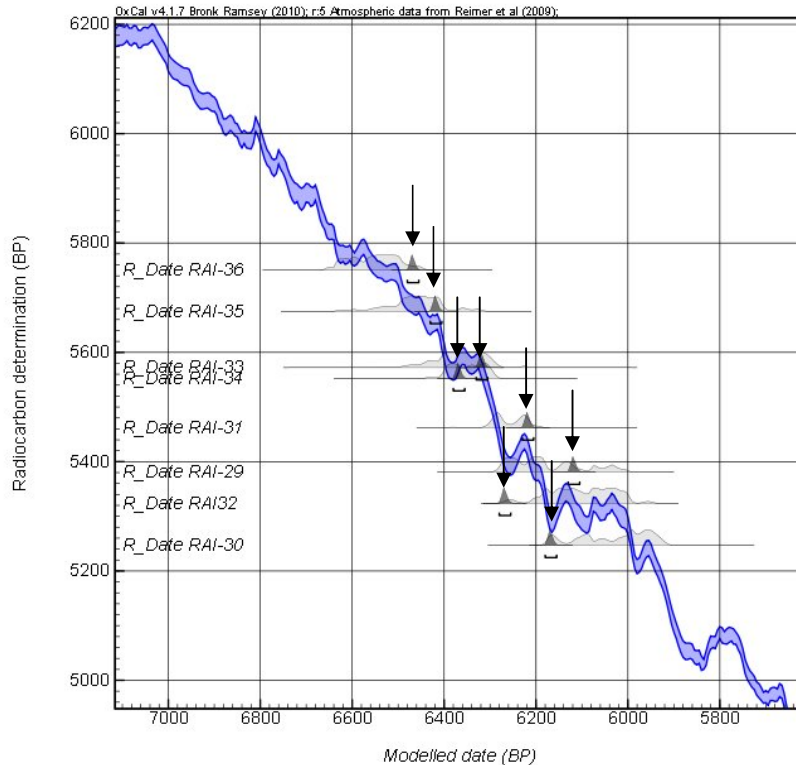The ^{14}C ages of these samples plotted on IntCal 09 are shown in fig 15.

Fig 15. ^{14}C ages of the samples from the second sequence plotted on IntCal 09.

The results show that the wiggle match ages of the samples are older than their dendro ages only by 7 years. However this age difference lies within the uncertainty of ±13 (±2σ). Also the dendro age of each sample covers an eleven years range. So if the uncertainties in the wiggle match ages and dendro ages are taken into account, then it can be conclude that the ages of the samples measured by these two methods are the same. The graph in Fig 15 shows that the ^{14}C data fits well the shape of the IntCal 09. Hence the results obtained are correct.

6. Discussion

Two of the samples that showed an age offset previously belonged to the trees "TM 453" and "TM468". In this study three samples "RAI-15a", "RAI-17a" and "RAI-18a" were taken from these tress (See Table 2). However the results did not show an age offset between the radiocarbon ages and dendro ages of the samples as observed previously. Also the ^{14}C ages of all other samples in the two series are consistent with their dendro ages within the standard uncertainties. Thus these results do not give a clue to solve the mystery of the age offset between radiocarbon dating and dendrochronology observed previously. The study however, suggests that the single date calibration may not be reliable always. As discussed earlier, the midpoint of the total error range ($\pm 2\sigma$) on the calendar scale of each calibrated ^{14}C date is taken as the most probable age of the sample. This midpoint however, does not always match with one of the local maxima in the probability distribution on the calendar scale (Blaauw et al., 2004).
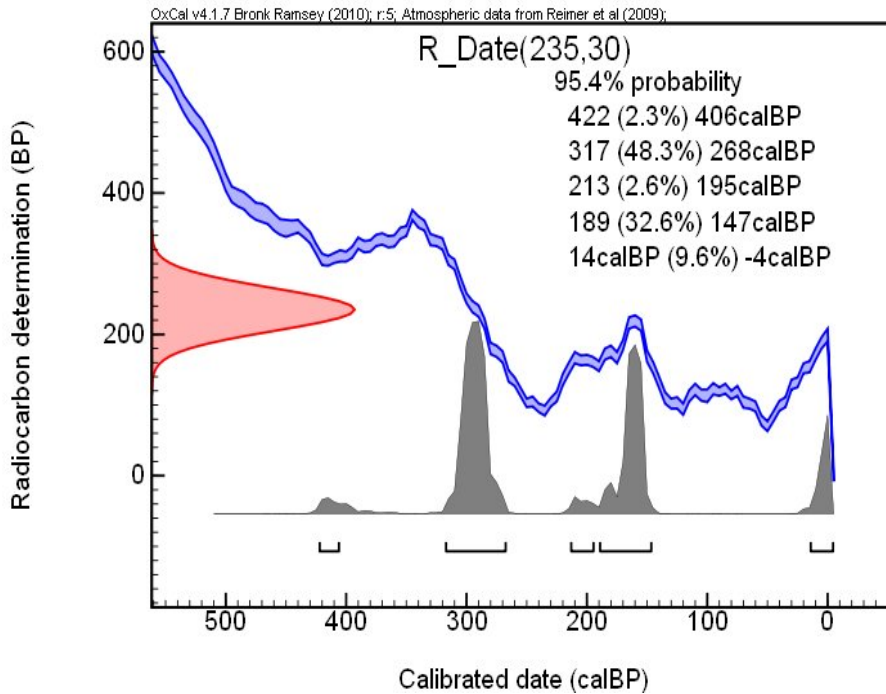

Fig 16. Single ^{14}C date calibration of the sample RAI-23 with known ^{14}C age of 340BP.

For example the midpoint of the total error range for the test sample "RAI-23a" gives 209 as a near age, whereas the most probable age is 268 cal BP as shown in Fig 16.

The study also suggest that along with "ABC" ^{14}C data evaluation program provided by National Electrostatics Corporation (NEC) with the AMS system, other ^{14}C data evaluation programs like "BATS" developed at ETH Zurich (Wacker et al., 2010a) can be used to check the reliability of the results which is clear from the results of the known samples.

The results obtained by from "BATS" for the test samples are given in Table 10 below.

Table 10. Measured ^{14}C ages and known ^{14}C age of the test samples obtained from ^{14}C data evaluation program "BATS" (personal communication with Raimund).

Number	Sample	Measured ^{14}C age (BP)	Known ^{14}C age (BP)
1	RAI-22a	377± 96	340±8
2	RAI-23a	270±96	340±8

From table 10, the weighted mean ^{14}C age of the test samples is 322± 68, which is more close to the known age of the samples as compared to the age obtained from the program "ABC" (see Table 7). Here the age difference between the measured ^{14}C age and known ^{14}C age is 18± 68 years which lies clearly within ± 1σ.

The program "BATS" was also successful in reducing the age difference between the wiggle match ages and dendro ages of the samples belonged to the first series (RAI-11a to RAI-29a) covering the age 5700BP-6300BP from 62 ± 35 years to 39 ± 28 years. However, the case is opposite for the second sequence. The age difference between the wiggle match ages and dendro age of the samples obtained from "BATS" is 13±13.This shows a large age offset as compared to the result obtained from "ABC" which is 7±13. Also the ^{14}C results obtained from "BATS" for the second series (RAI-29 to RAI-36) are in poor agreement with the dendro ages as compared to the results obtained from the program "ABC".

The results however both from the programs "ABC" and "BATS" showed no age offset between the ^{14}C ages and dendro ages of the samples as observed previously.

Regarding the age offset between radiocarbon dating and dendrochronology, one may also think that the dendro ages of the samples might not be correct. In order to examine the dendro ages of the samples, the atmospheric ^{14}C concentration (known as Δ^{14}C) in the samples was calculated according to $\Delta^{14}C = \left\{ \exp\left(\dfrac{calenderage}{8267} - \dfrac{^{14}Cage}{8033} \right) - 1 \right\} * 1000$ per mile (Stuiver and Polach, 1977). The $\Delta^{14}C$ values of the samples from one tree are plotted on dendro time scale as shown in Fig 17.
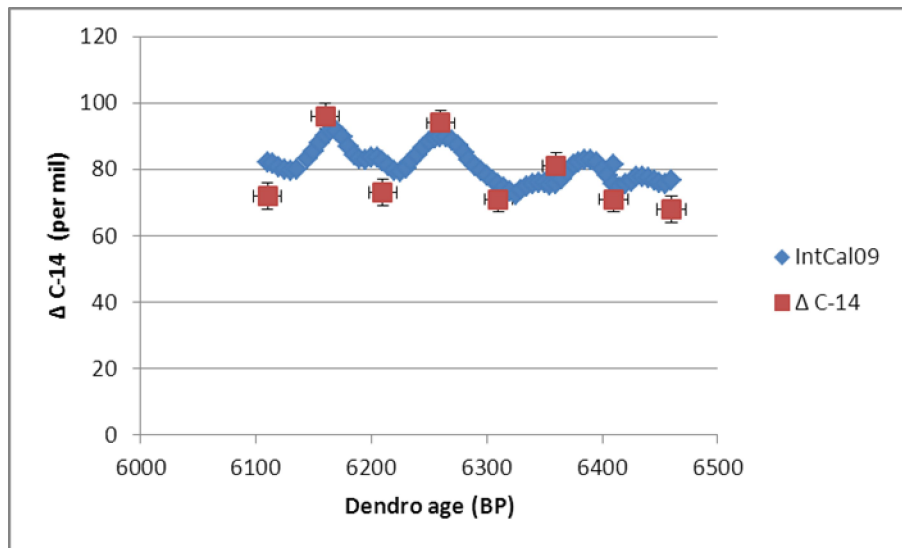

Fig 17. $\Delta^{14}C$ values of the samples from one tree plotted on dendro time scale on the tree ring age referred from dendro dating (Edvardsson et al., In press).

The graph shows that the calculated $\Delta^{14}C$ values are consistent with the dendro time scale. Also the variations in the measured $\Delta^{14}C$ values are the same as in IntCal 09. It means that the tree-rings represent the expected level of atmospheric ^{14}C concentration and hence the dendro ages of the samples can be considered as correct.

7.Conclusion

The ^{14}C ages of the pine tree samples recovered from peat bogs were measured using AMS technique. The radiocarbon dates obtained from AMS were first calibrated individually and then matched to the 'wiggles' of the calibration curve IntCal09 via a computer program OxCal. The single date calibrated ^{14}C ages are in agreement with the dendro ages of the samples. Wiggle matching the first series of samples (RAI-11a to RAI-29a) showed an age difference of 62±35 years between the wiggle match ages and dendro ages of the samples. However, this age difference was reduced to 39±28 years by using another ^{14}C data evaluation program "BATS". For the second series (RAI-29 to RAI-36) no age difference was found between the wiggle match ages and dendro ages of the samples. However the ^{14}C dates of both series fit well on the calibration curve IntCal09. This implies that the ^{14}C dates obtained for both series are correct within uncertainties. The dendro ages of the samples were also confirmed by calculating the atmospheric ^{14}C concentration ($\Delta^{14}C$) in these samples. Thus, these results do not suggest any systematic age offset between radiocarbon dating and dendrochronology. In other words these results do not solve the mystery of the age offset between radiocarbon dating and dendrochronology, as observed previously. However the study confirms the reliability of the radiocarbon dating technique and the calibration of ^{14}C dates via dendrochronology.

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Appendix

A brief review of the step by step process of sample preparation for AMS at Lund University Radiocarbon Dating Laboratory is outlined below.

*Chemical pre-treatment

(1) Take 100mg -250mg wood sample and cut it into small pieces.

(2) Heat it at 80°C for five hours in approximately 20 ml 2% NaOH solution.

(3) Wash it with deionized water until it gets neutral.

(4) Put the sample in approximately 20 ml 3% HCl and keep it in the oven at 80°C for twelve hours.

(5) Wash the sample again to become neutral.

*Cellulose extraction:

(6) Keep the sample in16 ml water and heat it at 75° C in a water bath.

(7) Add 0.1 gram 80% NaClO$_2$ and 2 drops of 3% HCl to the sample solution keeping the temperature between 65° C-95°C for 30 minutes.

(8) Add 0.2 g of 80% NaClO$_2$ and 3 drops of 3% HCl and wait for an hour at the same temperature (65°C-95°C).

(9) Repeat step (8) 3 times. However, the process can be repeated more than three times, if the cellulose is not extracted in 3 times repetition of step (8).

(10) Wash the sample to make it neutral again.

(11) Dry the sample in the oven for 10 hours at 80°C.

*Graphitization

(12) Take 2 to 2.5 mg cellulose and mix it with 200 mg of copper oxide (CuO) powder in a quartz tube (length 30mm, diameter 7mm).

(13) Put the small tube in large quartz tube (length 180 mm, diameter 9.5mm).

(14) Evacuate the quartz tube with help of vacuum pump.

(15) Seal the quartz tube.

(16) Heat it from room temperature to 950°C during two hours.

(17) Keep the sealed quartz tube in the oven at 950°C for one hour. The sample is now

combusted to CO_2 .

(18) Put 4-5 mg of iron powder in the reactor tube (length 111mm, diameter 7mm).

(19) Evacuate the reactor tube containing iron powder at room temperature for 1 hour.

(20) Heat the iron powder to 570° C.

(21) Evacuate the system for three hours keeping the temperature at570^oC.

(22) Lower the temperature to 400^oC and add 700mbar Oxygen gas for 15 minutes.

(23) Evacuate the system for 10 minutes.

(24) Add 700 mbar Hydrogen gas for 30 minutes.

(25) Evacuate the system again. The system is now ready for graphitization.

(26) Take out the sealed tube that was kept at 950^oC for one hour and is cooled now to room temperature.

(27) Scratch the tube with knife to make it easier to break.

(28) Fit the tube in the sample holder of the reactor machine.

(29) Break the tube inside the sample holder.

(30) Trap the CO_2 with help of liquid nitrogen.

(31) Evacuate the system again.

(32) Transfer the CO_2 to the reactor tube.

(33) Measure the CO_2 pressure.

(34) Look at the computer where the hydrogen gas needed is displayed. The hydrogen is calculated according the formula; pressure of CO_2 *2.2 mbar H_2*0.74, where 0.74 is called cooling factor.

(35) Add hydrogen gas to the reactor.

(36) Heat the reactor tube containing CO_2, H_2, and Fe at 580^oC.

The graphitization takes place according to the reaction

$CO_2+H_2+Fe \rightarrow C+H_2O+Fe$
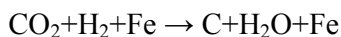
The carbon is obtained on the surface of hot iron catalyst.