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Phil. Trans. R. Soc. Lond. A 1990 **330**, 403-412
doi: 10.1098/rsta.1990.0021

Phil. Trans. R. Soc. Lond. A **330**, 403–412 (1990)
Printed in Great Britain

The ^{14}C record in bristlecone pine wood of the past 8000 years based on the dendrochronology of the late C. W. Ferguson

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When, in 1950, Willard Libby and his coworkers obtained their first radiocarbon (^{14}C) dates, C. W. Ferguson at the University of Arizona Tree Ring Laboratory was working on establishing a continuous tree ring series for the newly discovered bristlecone pine *Pinus aristata*. Before his untimely death in 1986, he had extended the series nearly 8000 years into the past. From the Ferguson series I obtained for ^{14}C determinations wood samples grown at various times. Also, two other laboratories obtained such samples. For B.C. times in particular, our measured ^{14}C-values that deviated consistently from those calculated from tree rings, and the deviations increased with age. This general trend was observed by other laboratories, but the presence of deviations from these trends, of the so-called 'wiggles', was questioned by other workers. To me these wiggles indicated the existence of a most interesting geophysical parameter valid for the whole terrestrial atmosphere. Fourier spectra obtained at my request by Kruse in 1972, and by Neftel, demonstrated the consistency of the results, and supported my contention that the secular variations of ^{14}C in atmospheric CO_2 are related to variations of solar activity.

1. Introduction

When I was offered the opportunity in 1952 to set up a routine radiocarbon counting laboratory at the U.S. Geological Survey in Washington, D.C., I contemplated using acetylene ($HC{\equiv}CH$) as the counting gas. In Germany, more than 10 years before, I had used acetylene to investigate 'hot atom' reactions as they occur in connection with nuclear reactions (Libby 1947; Suess 1939). I therefore expected acetylene to be ideal as a counting gas as it would combine with atoms and radicals that interfere with the counting of radioactive decay. Indeed, I found it to be much less sensitive than CO_2 to the presence of minute quantities of impurities, in particular of parts per million of oxygen in the counting gas. Carbon dioxide is commonly used by physicists as a counting gas. However, it easily can be converted to acetylene by hydrolysing a carbide, such as strontium carbide, obtained from strontium carbonate by reduction with magnesium metal, or lithium carbide obtained by reacting lithium metal with CO_2 gas at sufficiently high temperature. Acetylene has practically no vapour pressure at the temperature of liquid nitrogen. Its purity can be checked easily by measuring its triple point pressure.

From 1952 to 1954, at the U.S. Geological Survey I used acetylene for precision measurements of ^{14}C, dubbed 'radiocarbon' by W. F. Libby in 1952. There I measured the time of the maximum extent of the continental glaciation of North America to be about 20000 radiocarbon years before the present. Also, the dilution of the ^{14}C in the atmospheric CO_2 by the addition of ^{14}C-free anthropogenic CO_2 from the burning of fossil fuels, the so-called Suess effect, was observed.

† Dr Timothy W. Linick died in Tucson, Arizona, on 4 June 1989.

2. Radiocarbon in tree rings

When Willard Libby and his coworkers published their first radiocarbon date list (Arnold & Libby 1951) it was considered most desirable to test their method on samples of wood of precisely known ages. The best samples for this purpose were considered wood samples from trees, for which the time of growth could be determined from tree rings. At that time the California *Sequoia sempervirens* offered such wood. Accurately dated samples of wood close to 2000 years old were available from the University of Arizona Tree Ring Laboratory. Another tree, the bristlecone pine, *Pinus aristata*, discovered by Professor Schulman of the same laboratory, made it possible to derive a tree ring series more than 7000 years into the past. This was done by the late C. W. Ferguson (1968) who for the rest of his life concentrated entirely on this work.

Ferguson wisely decided to distribute 10 g samples of his wood, consisting of 10 annual growth rings each, to three ^{14}C-dating laboratories, at the University of Pennsylvania, at the University of Arizona in Tucson, and at the Scripps Institution of Oceanography of the University of California in La Jolla. There, commencing in 1955, I used acetylene as the counting gas. For precision measurements I used two ultra low background counters of the Houtermans–Oeschger type (1955), that Dr Oeschger kindly had ordered made by his institute shop.

It soon became obvious that the measured ^{14}C values indeed deviated consistently from those calculated, using ages derived by Ferguson from tree-ring counting. For the past 2000 years the magnitudes of the deviations were relatively small but increased in B.C. times. ^{14}C values for the oldest dendrochronologically dated wood samples were nearly 10 % too high, i.e. their ^{14}C ages up to 800 years too young. It was therefore necessary to answer the following questions.

1. Are the tree ring ages, the so-called 'Dendro-ages', correct?
2. Do wood samples from different kinds of trees, grown at different geographic locations and having the same tree-ring age, show the same ^{14}C content?
3. Can the ^{14}C content of wood samples change through contamination, irradiation, or in any other way?

Much careful work was done during the following years, and we can trust now that these questions are reliably answered. The ^{14}C in the cellulose present in wood in a given annual ring corresponds remarkably well to that in the CO_2 of the atmosphere at the time of the growth of the ring if one corrects for isotope fractionation during photosynthesis. Other organic compounds, such as the sap and lignin in sapwood, may migrate into older rings. This has been studied by Cain in detail (Cain & Suess 1976), making use of bomb ^{14}C present after 1955 in atmospheric CO_2 as tracer.

If data are normalized as discussed above, one finds that the ^{14}C-content of the cellulose in wood grown at the same time is practically independent of geographic location and altitude. An exception seems to be a slight difference of a few per mille in ^{14}C in air from the two hemispheres. Cellulose from wood from the Northern Hemisphere seems to have a slightly higher ^{14}C content than that from the Southern Hemisphere (see, for example, Baxter & Walton 1971).

In any case, we can assume that the differences between calculated and measured ^{14}C are essentially a unique function of their ages. The general trend of this function, as determined by the La Jolla Laboratory, can be seen in figure 1. This general trend was soon confirmed by other laboratories.

About half of all the ^{14}C measurements by the La Jolla laboratory during the time of its existence from 1956 to 1981 were carried out for the purpose of determining this function. These measurements showed consistently relatively small deviations from a smooth curve, the so-called 'wiggles' that were superimposed upon the general trends. These wiggles, in general with amplitudes of less than 1%, were not important for radiocarbon dating, but appeared most interesting for ^{14}C-geophysics.

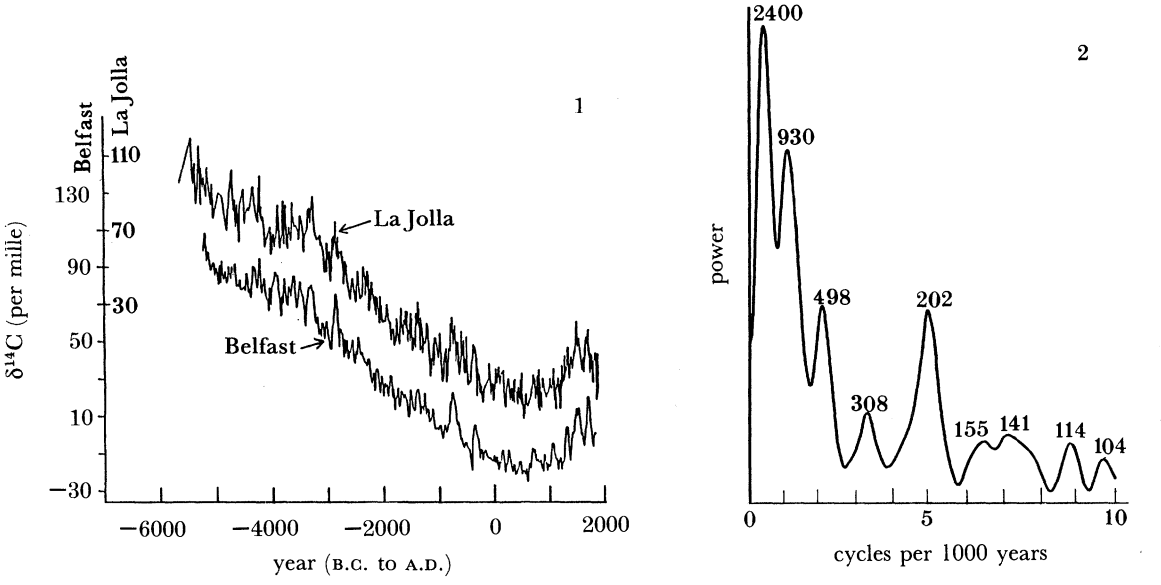

FIGURE 1. Upper curve: δ^{14}C (normalized) as a function of tree ring date, as measured at La Jolla in Ferguson bristlecone pine wood. Lower curve: same as measured in Belfast in Irish Oak wood.

FIGURE 2. Fourier spectrum of the δ^{14}C variations during the period from 5300 B.C. to 1500 A.D. as observed by the La Jolla radiocarbon laboratory in samples from bristlecone pine wood dated by Ferguson according to A. Kruse (see Suess 1980).

The first important question was whether the wiggles represented random variations or were, at least in part, periodic deviations from the smooth trend. The Fourier spectum shown in figure 2 was derived by A. Kruse (see Suess 1980). It confirmed the existence of a conspicuous periodicity of about 200 years.

Unfortunately, the accuracies of the measurements of the other laboratories were insufficient to demonstrate even the existence of 'wiggles'. A statistical analysis by Clark (1975) stated that 'on the basis of all the existing measurements the assumption of wiggles was statistically not justified' (figure 4). Even after a paper by De Jong *et al.* (1980) had appeared entitled 'Confirmation of the Suess wiggles', other experts did not concern themselves with this interesting phenomenon.

Shortly thereafter the U.S. National Science Foundation, Atmospheric Science Section, terminated the financial support of the La Jolla Laboratory, supposedly, because our measurements were 'not sufficiently accurate for the purpose in question'. With no funds for continuing my own research, I personally contacted a number of experts in time series analyses who might possibly be interested in these observations. I asked for help in data reduction and interpretation of data. One of them, Professor C. P. Sonett of the University of Arizona in Tucson, responded.

3. Normalization of data and comparisons of time series

Most authors publish their laboratory results in 'conventional radiocarbon dates', expressed in radiocarbon years, and give their accuracy as one- (or two-) sigma statistical counting errors. Regarding these counting errors (given in general as plus and minus) widespread misconceptions prevail. Therefore, it should be emphasized that these ± numbers do not indicate the maximum but rather the minimum average error of a number of measurements. This means that the average error of a sufficiently large number of measurements can never be smaller, but may well be much larger than what is indicated by these ± values, because the uncertainty of the result of a measurement not only arises from statistical fluctuations but may result from a multitude of other experimental factors.

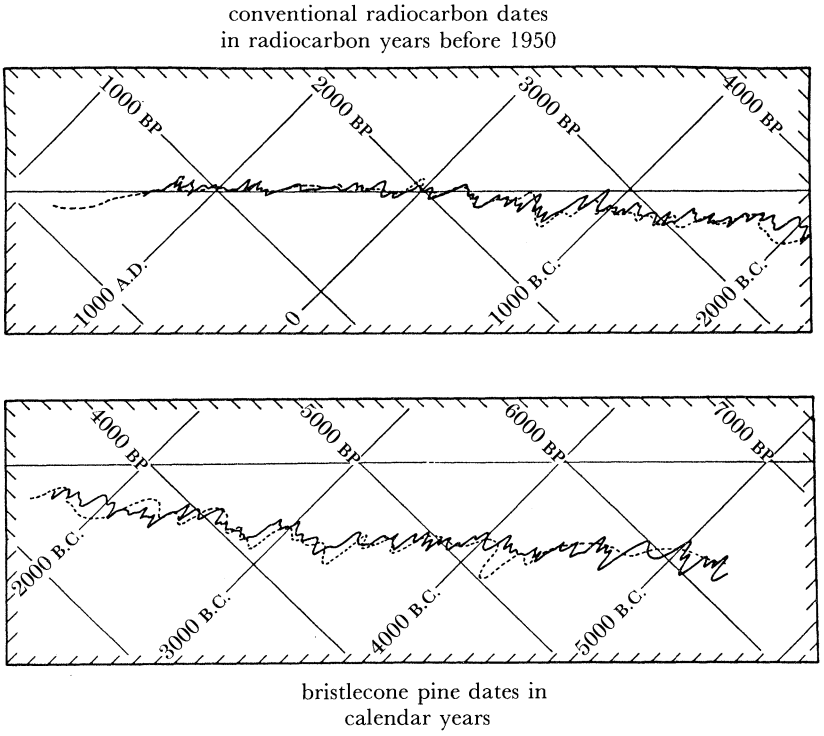

Figure 3. Dendrochronological age as a function of radiocarbon age determined in La Jolla, representing a calibration curve. The dotted line was published by Suess in 1970 to indicate the character of the expected curve. The solid line shows the same, but is based on about 700 individual measurements (Suess 1980). The diagram is tilted 45° to conserve space and a spline curve is drawn through the measured points.

In figure 3 we drew a line through the measured points free-hand with what was called cosmic 'Schwung'. This was taken by some of our colleagues as an indication of inaccuracy. This expression, however, was coined by the late eminent Austrian 'cosmic' (sic!) physicist and oceanographer Albert Defant, who, when plotting the amplitudes of ocean tides, used this expression to indicate that the amplitudes resulted from cosmic, extraterrestrial forces, and also, that these forces did not change abruptly. An ancient dictum, *natura non facet saltum* (nature does not make jumps), expresses this appropriately. Today one might say: the second time-derivative of (macroscopic) quantities in nature does not change abruptly. Therefore, unknown parts of a function in nature can best be approximated by spline functions.

For many reasons archaeologists should not expect ^{14}C data (before and after their calibration) to give more than the correct century, at best. Geophysicists, however, require an optimal precision for the interpretation of the observed data. In this case it is not always simple to compare results from different laboratories, because the numerical results depend on a number of normalizations. These are the following.

1. Radiocarbon ages are given by convention as years before the present (BP). Time zero is taken as 1950 A.D.

2. The measured counting rate is compared with that of a ^{14}C sample prepared by using a sample distributed by the U.S. Bureau of Standards.

3. Normalization of δ^{13}C of the sample to δ^{13}C of the standard, assuming mass-dependent isotope fractionation (Libby 1952). (Mass-independent isotope fractionation has not yet been observed for carbon isotopes (Thiemens 1983).)

4. By agreement, to preserve consistency of published ^{14}C-dates, the 'Libby' or 'conventional' half-life of 5568 years (by definition) is used. The more recently determined 'Cambridge' half-life of 5730 ± 40 years should be used in connection with the physics of ^{14}C decay.

Archaeologists usually report conventional Libby dates. Calibrated dates are expressed, of course, in calendar years. Usually, the uncalibrated conventional Libby dates differ only by a few times ten years because of small differences in normalization. This is negligible for archaeological dates but it may interfere with their interpretation for geophysical purposes.

In his book *Radiocarbon dating* Professor R. Ervin Taylor (1987) has presented graphically the results of calibration measurements from several laboratories, including those obtained in La Jolla, and has plotted them as we had done previously (Suess 1970, 1980). As far as we know there exist now two complete series of precision ^{14}C measurements of wood samples with times of growth of the past 7000 years. Figures 3 and 4 show the La Jolla bristlecone pine and the Belfast Irish oak series respectively. The agreement is most remarkable. The two series were obtained completely independently at different times during the past 20 year, using two different methods of ^{14}C determination: (*a*) acetylene counting of bristlecone pine samples from California and (*b*) scintillation counting of oak samples from Ireland. What is measured is a steady-state concentration of ^{14}C in wood. This concentration reflects the ^{14}C in the CO_2 of air, which is a function of its cosmic ray production rate and the rate by which it equilibrates with the world's oceans, where most of it decays (Houtermans *et al.* 1973). The similarities of the two time series, as shown in figures 1, 3 and 4, are easily recognized. Errors in the measured data, or in data reduction, can never produce this kind of resemblance.

The curve by Clark (1975) in figure 5 was derived by statistically evaluating the measurements by various authors assuming, however, that all the data have the same accuracy, which is certainly not the case. One sees that with this assumption, no fine structure and no wiggles result and all the irregularities are smoothed out. Also, the smooth curve in figure 6 was drawn in such a way as to eliminate most of the structure.

Perhaps even more convincing are the Fourier spectra of the two time series. They both show the by now well-known prominent spectral line around 205 years, first recognized visually in the La Jolla series as early as 1970, and confirmed by Fourier analyses by Kruse (figure 2) and then by Neftel (Neftel *et al.* 1981). As expected, the 200-year line is present in the Belfast Irish oak spectrum and can also be recognized now in other time series.

According to Sonett, the empirical average standard error sigma of our measurements is 7.8

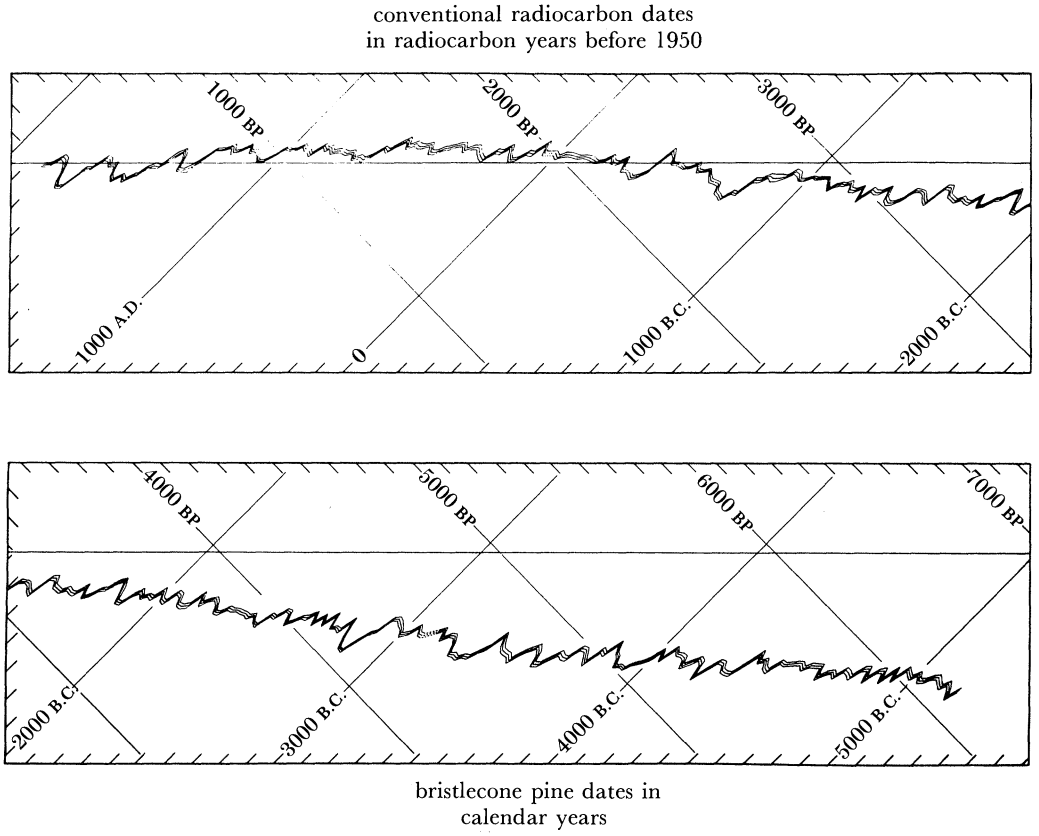

FIGURE 4. Same as figure 3, but with data from the Belfast laboratory. After Pearson *et al.* (1986), normalized in the same way as figure 3. Empirical values are connected by straight lines. The parallel lines indicate statistical one sigma limits. The graph is adapted from R. E. Taylor (1987) to conform with figure 3 and published here with permission.

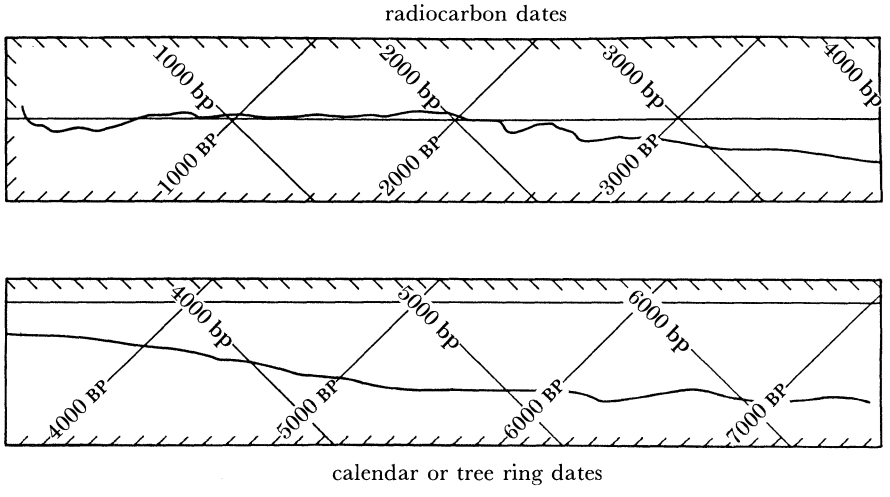

FIGURE 5. Calibration lines after Malcolm Clark (1975). The average values of published results of many measurements are calculated assuming they have the same experimental errors. With this assumption the depicted smooth line appears 'statistically justified'. Adapted to conform with the other figures by R. E. Taylor and published here with his permission.

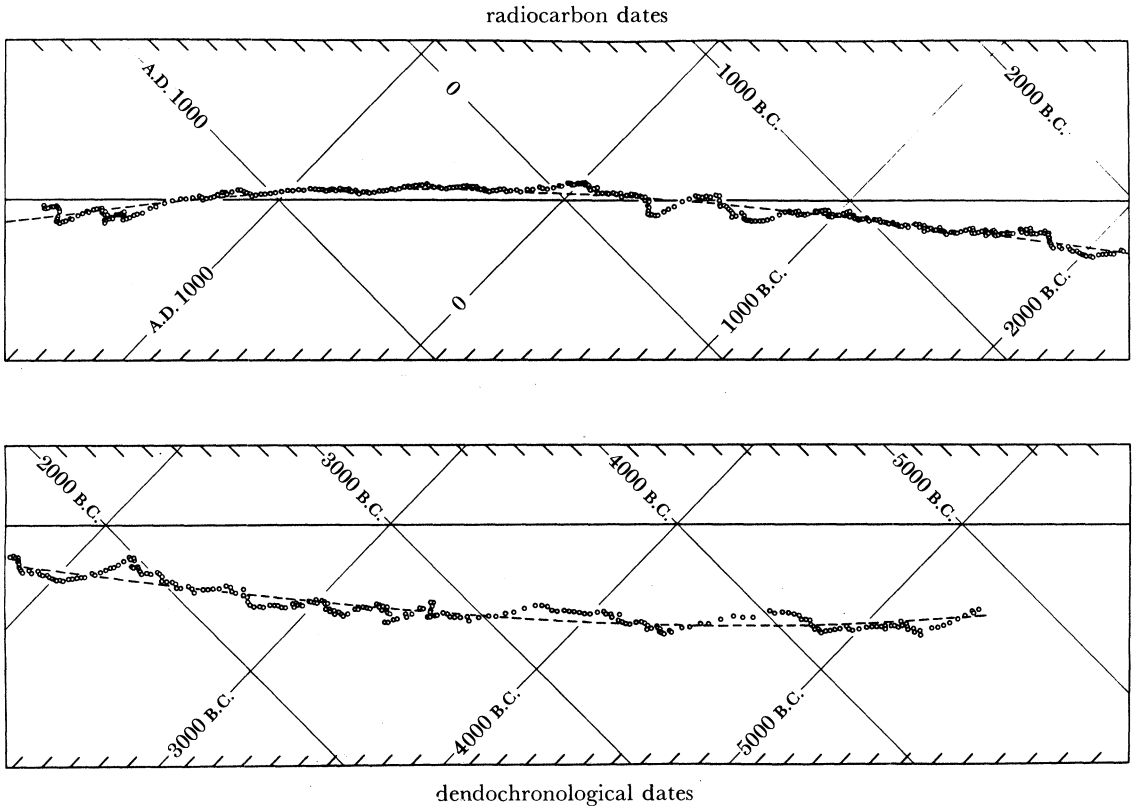

FIGURE 6. 'MASCA' calibration curve according to Ralph *et al.* (1973) derived by calculating 'running means' to eliminate the noise and thus the fine structure. Redrawn by R. E. Taylor and published here with his permission.

per mille. This is quite good, considering a statistical counting error for each measurement between 4 and 8 per mille (depending on age) and the fact that the La Jolla measurements were carried out over a period of nearly 20 years at two different locations of the UCSD campus. Professor Sonett's paper (this Symposium) concerns this. We list in table 1 the strongest lines in the spectra obtained by Sonett.

TABLE 1

La Jolla		Belfast	
period/years	power spectrum densities	period/years	power spectrum densities
2266.8	53870	2387.6	40530
504.5	18872	508.6	18464
358.2	9977	352.8	12988
201.5	14953	206.9	12218
158.5	8849	149.5	10143

The measured ^{14}C values reflect steady-state concentrations, which essentially depend on the cosmic ray production rate and the rate by which ^{14}C is equilibrated with the world's oceans, where most of it decays. If the production rate varies, then the steady state concentration varies, whereby the ocean $\rightleftharpoons$ atmosphere system acts as a low pass filter (see figure 7).

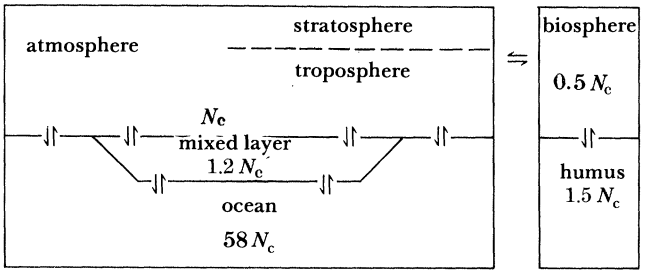

FIGURE 7. Carbon exchanging reservoirs on the surface of the Earth. N_c denotes the relative amounts of exchangeable carbon in each reservoir, with the amount in the atmosphere equal to one. Radiocarbon is produced by cosmic rays in the atmosphere. Most of it decays in the oceans. The concentration of ^{14}C in the total carbon, the $\delta^{14}C$, is measured in wood. It is a function of the $\delta^{14}C$ in the atmospheric CO_2. The ^{14}C in the atmospheric CO_2 roughly depends on (1) the cosmic ray production rate, (2) the relative amounts N_c in the different reservoirs, and (3) the exchange and transfer rate of carbon between the different reservoirs (Libby 1952).

The fact that there exist two time series of radiocarbon measurements obtained by completely different experimental methods, namely, acetylene counting and scintillation counting, of wood ^{14}C from two different kinds of trees that grew at different altitudes and continents makes it possible to recognize reliably worldwide global fluctuations in the ^{14}C-level of atmospheric CO_2.

4. The three causes of secular ^{14}C fluctuations

Professor Sonett and we have looked into the possibilities of explaining these observations. We agree now that most of the spectral lines must be a result of periodic variations of the intensity of the ^{14}C-producing radiation that reaches the Earth. Its important galactic component is attenuated by magnetic fields of the Sun and also by the magnetic dipole moment of the Earth. Changes in the carbon distribution in the ocean $\rightleftharpoons$ atmosphere system on the surface of the Earth are unimportant at the present time but were important during glacial and early postglacial times. To obtain more information on cosmogenic radioisotopes during these periods of time is a most desirable research objective that promises to answer many important questions on solar activity and global climate. The following three causes of ^{14}C variations are being discussed in the literature:

(1) changes in the magnetic field of the Earth;

(2) changes in the size and exchange rates of the carbon reservoirs on the surface of the Earth (figure 7);

(3) changes in the intensity of the components of the galactic (and solar) radiations that give rise to the ^{14}C formation on Earth.

The spectral lines must result from periodic variations of the intensity of the ^{14}C-producing radiation that reaches the Earth.

In addition to the two series of measurements discussed here in detail, many so-called precision, high-precision, or ultra-high-precision measurements have been published during the past few years (see, for example, Kra 1986). However, to our knowledge analyses of the spectra of their time series and comparison with our, or Dr Pearson's, results have not been

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made yet in most cases. We hope very much that this will be done soon by the respective authors. Many details presented here graphically need explanations.

5. Concluding remarks

When, in 1958, H. de Vries published his paper 'Variation in concentration of radiocarbon with time and location on Earth', it appeared probable, and soon certain, that the overall concentration of this carbon isotope had not remained constant, but had changed both slowly on a timescale of several thousand years and also more rapidly on a timescale of some hundred years. We have considered here the more rapid variations, fluctuations, or 'de Vries wiggles', as they were called by some investigators. Mostly they were considered rare stochastic phenomena, in some way connected with the occurrence of climatic change. However, it was possible to show less than 20 years later that bristlecone pine wood, dated by its tree rings by C. W. Ferguson, showed ^{14}C-variations throughout the investigated time range, albeit with greatly varying amplitudes (Suess 1970). These variations were then shown to exhibit a well-defined time spectrum with a prominent line at slightly more than 200 years.

For more than 10 years now the majority of experimental workers has been most skeptical regarding the existence of periodicities in the natural ^{14}C record and of meaningful spectral lines in the observed secular variations of the cosmic ray produced ^{14}C on the surface of our planet. It was pointed out by Damon *et al.* (1978) that 'no single de Vries type fluctuation (prior to the Medieval Warm Epoch) has been confirmed by two or more laboratories', and also that 'wiggles of the type reported by Suess (1970) have not been confirmed'. This, and probably other factors, then led the U.S. National Science Foundation to deny repeated requests for further financial support. Now, thanks to the outstanding success of the experimental work at Belfast, headed by Dr Gordon Pearson, and the sophisticated theoretical evaluation of the results by Professor Sonett at the University of Arizona, there cannot be any doubt that these wiggles are real and reflect periodic occurrences. They constitute an unexpected, important source for new scientific information. Unfortunately, it will be too late for me to participate in its exploration, but hopefully still in time to enjoy the findings of my colleagues.

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