SHORT-TERM FLUCTUATIONS OF CARBON ISOTOPE LEVELS IN ATMOSPHERIC CARBON DIOXIDE

THESIS

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JOHN G. FARMER

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SUMMARY

Natural ^{14}C fluctuations are known to have occurred over periods of 50 to thousands of years during the last 10 millennia. As the fluctuations represent deviations from the basic assumptions of the radiocarbon dating method, major research programmes have concentrated on the establishment of the main trends of secular ^{14}C variations. Recent work has questioned the assumed constancy of natural ^{14}C levels over shorter time periods of 10 years and has thus implied the reduced effectiveness of present calibration curves to the age-correction of short-lived dating samples.

In this research, annual atmospheric ^{14}C concentrations in the northern hemisphere have been studied through analyses of 19th Century single tree rings. Natural ^{14}C fluctuations of 2% over the 11-year sunspot cycle appear to have occurred in correlation with solar activity. Consequently, an additional error of at least ± 80 years is inevitable in the radiocarbon age determination of dating samples of lifetime 1 year. In addition, the selection of dating samples which incorporate the products of 10 - 11 years' growth (or a multiple of this) is urged by the apparent relationship between annual ^{14}C levels and the 11-year sunspot cycle. It is suggested that the origin of this relationship lies in changes in ^{14}C production and in internal atmospheric mixing through the modulation of incident radiation by variations in solar activity.

Annual atmospheric ^{14}C concentrations in the southern hemisphere during this century have also been studied

through analyses of tree rings, wines, seeds and wool. No correlation between southern hemisphere ^{14}C activity and the 11-year sunspot cycle has been observed. It is believed that the greater surface area of the southern oceans may be responsible for observed ^{14}C differences between hemispheres through enhanced uptake and exchange of atmospheric CO_2.

Variations of the stable carbon isotope composition of atmospheric CO_2 during the 20th Century have been detected by mass-spectrometric measurements of the $^{13}C/^{12}C$ ratios of single tree rings. A decrease of 0.2% has been observed in the atmospheric $^{13}C/^{12}C$ ratio as a result of the input of isotopically lighter CO_2 from fossil fuel combustion. The temporal trend of the $^{13}C/^{12}C$ variations suggests that industrial CO_2 has been removed from the atmosphere at an increased rate during the past few decades. Generally, the study implies non-uniform CO_2 transfer rates across the atmosphere/biosphere/ocean interface during this century.

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CHAPTER 1

INTRODUCTION

1.1 Historical

Within the last 25 years, radiocarbon dating has become firmly established as one of the foremost aids to the determination of the chronological sequence of events during the last 50,000 years. At the same time, however, refinements in experimental technique, an improved understanding of ^{14}C geochemistry and the development of related scientific disciplines have created an awareness of the subtleties and limitations of the method. The precise nature of these constraints on the basic concepts of radiocarbon dating is now the major objective of research in ^{14}C chronology.

The formulation of the basic principles of the dating method is attributed to Libby (1946, 1955) who was influenced by two major scientific findings of the 1930's:

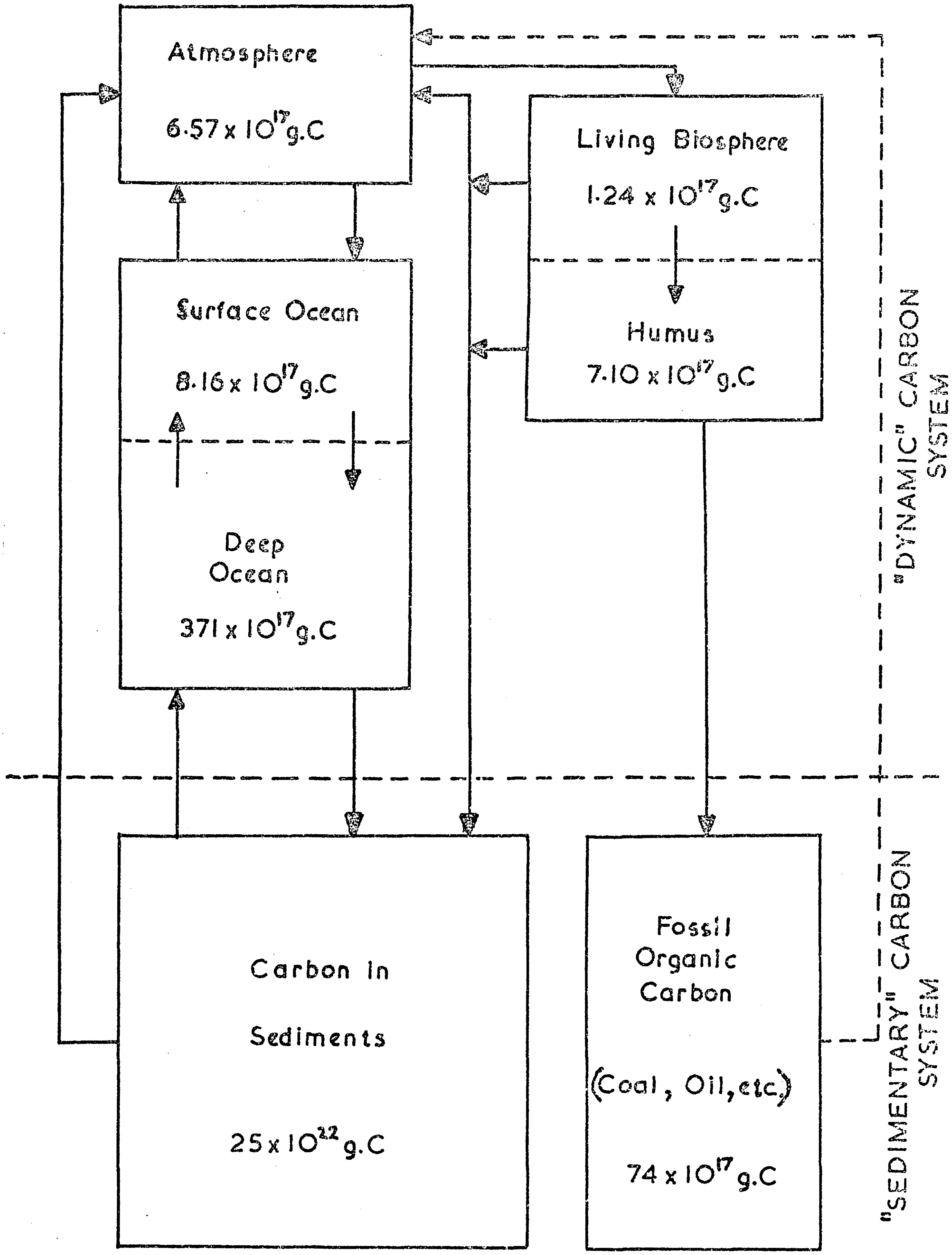
(1) the neutron-induced transmutation of atmospheric nitrogen to radiocarbon ($^{14}N + n \rightarrow {}^{14}C + p$) under laboratory control (Kurie 1934),

(2) the discovery of cosmic-ray produced neutrons in the upper atmosphere (Korff and Danforth 1939).

These facts led to the prediction that, via the same mechanism, radioactive ^{14}C atoms would be produced in the upper atmosphere. Libby postulated that the ^{14}C is rapidly oxidised to $^{14}CO_2$ which, on mixing with inactive atmospheric CO_2, enters the natural carbon cycle (Figure 1.1). The prime assumption of the dating method is that the distribution of ^{14}C in the carbon reservoirs has remained constant throughout the past 50,000 years. This implies constancy

FIGURE 1.1

THE CARBON CYCLE



of the $^{14}C/^{12}C$ ratio in all reservoirs, a premise which is dependent on:

(1) a constant ^{14}C production rate,

(2) constant exchange rates between reservoirs.

Now all living biospheric materials, which assimilate CO_2 by photosynthesis, should possess the same $^{14}C/^{12}C$ ratio as atmospheric CO_2. This ratio remains constant for any biospheric organism throughout the period of its lifetime provided that the fundamental conditions listed above are true. When death occurs, the plant or animal ceases to participate in the CO_2 cycle and the equilibrium radiocarbon activity maintained during life starts to fall at the half-life rate ($t_{\frac{1}{2}}$ = 5,730 ± 40 years). Assay of the residual activity in a sample therefore allows assessment of the time elapsed since death.

Following the initial detection of natural ^{14}C, using a primitive screen-wall Geiger counter (Anderson et al. 1947), efforts were made to test the validity of the dating method. Radiocarbon measurements, statistically precise to ± 250 years, were found to be in agreement with the known ages of historically dated samples (Libby et al. 1949). Thus, the primary assumption of ^{14}C equilibrium was apparently valid. With the subsequent improvement of analytical precision to ± 50 years, significant deviations between radiocarbon dates and historical ages were found. The possibility of such discrepancies had been expected because the ^{14}C method dates the time of removal of the sample from the carbon cycle, rather than the time of usage by man. Also there were doubts as to the accuracy of the Libby half-life of 5,568 years for ^{14}C. Despite these factors, it was generally suspected that the observed deviations reflected a non-equilibrium distribution of ^{14}C in the carbon cycle caused by temporal variations in the controlling geophysical parameters, (1) ^{14}C production rate and/or (2) exchange rates between reservoirs (Figure 1.1). As the atmosphere contains only 1 - 2% of the earth's exchangeable carbon, and the deep ocean response time is several hundred years, any disturbance of the general ^{14}C distribution is necessarily amplified in the atmosphere. Thus it was realised that the difference between a calendar date and a radiocarbon date could be a direct result of this deviation from constancy of the atmospheric $^{14}C/^{12}C$ ratio during the lifetime of the dating material.

These suspicions were soon confirmed by De Vries (1958) whose discovery of secular variations of atmospheric ^{14}C levels initiated a period of intense activity in the precise measurement of past atmospheric $^{14}C/^{12}C$ ratios. As a deviation of only 1% in the atmospheric ^{14}C concentration alters the radiocarbon age by about 80 years, it was evident that a documented record of past ^{14}C levels is of the utmost importance to the ultimate accuracy of the dating method. Furthermore, a knowledge of the magnitude and deviation of ^{14}C variations could improve our understanding of the geochemical and geophysical processes which control ^{14}C production and distribution.

A detailed review of radiocarbon dating has been published elsewhere (Baxter and Farmer 1971).

1.2 Long-term Fluctuations of Natural ^{14}C Concentrations in the Atmosphere

In 1958, De Vries observed that the ^{14}C content of late 17th Century A.D. wood samples was 2% higher than that expected on the basis of a constant "natural" level. The age-corrected ^{14}C activity of late 19th Century wood (i.e. prior to man's influence) was assumed to be the "natural" level. Since the discovery of the "De Vries effect", many ^{14}C analyses have revealed the general trends of atmospheric ^{14}C fluctuations over the last 12,000 years (Figure 1.2).

(a) Method of detection

The annual rings of trees provide the most readily available source of dated material from the past. Using dendrochronological methods, dated rings from one tree can be related to a ring sequence from another older tree of unknown age from the same climatic region. In this way, it is possible to build an extremely accurate tree-ring chronology which extends back into the past. Such chronologies have been established for several species of European (Huber 1970) and American (Ferguson 1968, 1970a) trees. Early ^{14}C measurements (Willis et al. 1960, Suess 1965) were made on dated multiannual sections of both European trees and Sequoia gigantea, a species from California with a well-defined chronology over the last 3,000 years. The development of the 7,104-year bristlecone-pine (Pinus aristata) chronology (Ferguson 1970 a) has, however, permitted ^{14}C assay of 10-year ring sections stretching back to 5,200 B.C. (Suess 1967, 1970a, Damon et al. 1966, 1970, Ralph and Michael 1970). These measurements make possible the calculation of the initial

^{14}C concentration in the sample at the time of formation. Although the bristlecone-pine tree-ring sequence has now been extended to nearly 8,200 years (Ferguson 1970b), it appears rather unlikely that the chronology will be extended much beyond 10,000 years because of the lack of suitable specimens (Ferguson 1970a).

Varve series present a potentially suitable alternative for the study of ^{14}C variations prior to 10,000 years ago. Varves are the annual layers found in clays which originate in the beds of glacial lakes. Seasonal variations in sediment texture permit recognition of annual layers in an analogous manner to the identification of annual tree rings. The Swedish varve chronology of De Geer (1940) has been used in the measurement of ^{14}C levels back to 12,500 years B.P. (Tauber 1970). Although insufficient organic matter was present in these varves, pollen-zone boundary correlations enabled their relation to nearby peat bogs from which satisfactory samples were obtained for ^{14}C assay (Wenner 1968, Fromm 1970). The other major varve series is from Lake of the Clouds, Minnesota. Direct measurements on the organic matter present (Stuiver 1970a, 1970b) provided data on ^{14}C levels during the past 10,000 years.

It is of interest to note that both of the above methods are dependent on particular climatic conditions prevailing at the time of formation of long sequences of annual layers. Such a restriction has limited the development of accurate long-term chronologies on a world-wide basis.

(b) Magnitude of fluctuations

The variations of atmospheric ^{14}C concentrations over the last 12,000 years are shown in Figure 1.2. The solid line representing the tree-ring data is based on over 300 measurements by Suess (1970a). Walton and Baxter (1968) have pointed out a consistently higher activity of about 2% for the period 3,500 B.P. to 5,000 B.P. in the data of Damon et al. (1966, 1970). Despite this, there appears to be general agreement, among the 3 major laboratories involved, about the long-term trends of the bristlecone-pine curve (Wendland and Donley 1971).

Certain major features can be identified from this curve:

(1) atmospheric ^{14}C concentrations over the past 2,500 years have been within a few per cent of the "natural" level,

(2) between 6,000 and 2,500 years B.P. the atmospheric ^{14}C level was reduced from about 11 - 12% above "normal", based on the half-life of 5,568 years (+9% based on the half-life of 5,730 years), to the "natural" level.

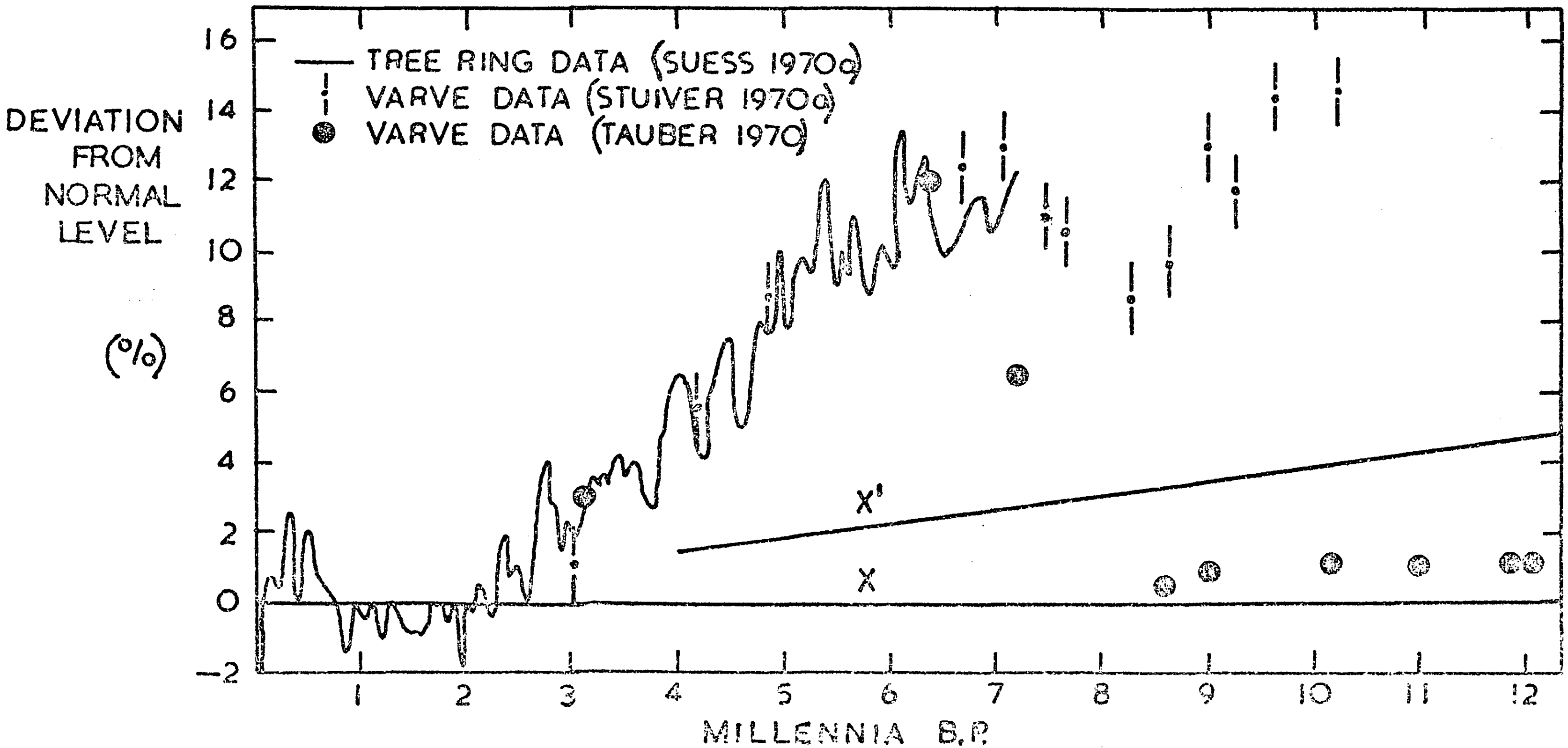
The varve results of both Tauber and Stuiver show good agreement with the bristlecone-pine data from 6,000 B.P. to the present.

Prior to 6,000 B.P., the Swedish varve ^{14}C data indicate a decrease to the "natural" level by 12,000 B.P. This is in complete disagreement with Stuiver's measurements from Lake of the Clouds. There the level decreases to +8% by 8,500 B.P. but increases again to +14% by 10,000 B.P. This discrepancy, unlikely to be real, may be due to errors in either or both of the chronologies.

FIGURE 1.2

SECULAR VARIATIONS OF ATMOSPHERIC ^{14}C CONCENTRATIONS DURING THE LAST 12 MILLENNIA

(Reference axes based on $t_{1/2}$ (a) 5,568 years — X
(b) 5,730 years — X′)



Further extension of the bristlecone-pine chronology will finally resolve the issue although data around 7,000 B.P. already appear to concur with those of Stuiver.

In addition to the long-term features, there are short-term changes of 2 - 3% over 50 - 200 years. A typical example is the "De Vries effect". Suess (1970b) claims that there are also similar ^{14}C variations over 400-year periods.

The implications of the observed fluctuations for radiocarbon dating are significant. The radiocarbon age for a 6,000-year-old sample would be approximately 800 years too young, if uncorrected for the ^{14}C deviation from the normal level. A calibration curve, based on the bristlecone-pine ^{14}C measurements, has been constructed for ready comparison of radiocarbon and calendar ages (Suess 1970a). However, due to the short-term fluctuations of the curve, one radiocarbon age may correspond to more than one calendar date. On the other hand, in certain circumstances, a much more precise date may be obtained. This can occur when the ^{14}C fluctuation pattern of a wood sample containing a "floating" tree-ring sequence of at least 100 years, matches the pattern in the bristlecone-pine curve (Ferguson et al. 1966, Suess and Strahm 1970). The initial general trends of the calibration curve have been verified by dating ancient Egyptian material of known age from the 2nd and 3rd millennia B.C.

The calibration curve applies strictly to the northern hemisphere. Jansen (1970) has shown by measurements on New Zealand and Australian trees that southern hemisphere ^{14}C levels may have been up to 2% lower than those of the northern hemisphere during the last 600 years. The main trends appear to be synchronous in the two hemispheres. Lerman et al. (1969, 1970) have also reported a latitudinal dependence of the ^{14}C content of the atmosphere amounting to a deficiency of 0.5% in the southern hemisphere during the last few centuries.

(c) Causes of the fluctuations

The causes of atmospheric ^{14}C fluctuations were much discussed at the Twelfth Nobel Symposium on Radiocarbon Variations and Absolute Chronology at Uppsala in 1969. More than a decade after the discovery of secular variations of ^{14}C, opinions still differ as to their causes although certain relationships with geophysical parameters appear partially established. The various mechanisms which have been proposed are based on one or both of two major phenomena:

(1) changes in the global production rate of ^{14}C,

(2) changes in the mixing of carbon within the dynamic carbon reservoir.

Bucha (1970) claims that the long-term trend of ^{14}C levels from 8,000 B.P. until the present is associated with variations in the earth's magnetic field intensity. An increase in the earth's magnetic moment is accompanied by a decrease in the cosmic-ray flux at the earth and therefore by a decrease in the production rate of ^{14}C (Elsasser et al. 1956). The reasons for these changes are related to hydro-magnetic processes in the boundary layers of the earth's core and mantle. From archaeomagnetic measurements, Bucha has constructed a curve of the earth's magnetic field intensity during the last 8,500 years. An inverse relationship between ^{14}C level and magnetic moment is evident. Furthermore, Houtermans (1966) has shown that a 50% change in the ^{14}C production rate is required to account for the change in ^{14}C activity over the last 8,000 years. This compares favourably with the observed variation by a factor of about 2 in the intensity of the geomagnetic field. However, Lal and Venkatavaradan (1970) have pointed out that the limited archaeomagnetic data presently available may not reflect variations on a world-wide basis but only regional disturbances.

Superimposed on this long-term trend, fluctuations of 2 - 3% in ^{14}C activity have been observed on a time-scale of 50 - 200 years. These fluctuations are thought to be correlated with solar activity. Stuiver (1961) postulated the existence of an inverse relationship between the level of solar (sunspot) activity and the intensity of cosmic radiation arriving at the earth. Thus at times of high sunspot activity the associated intensification of the weak magnetic field of the solar wind causes a reduction in the cosmic-ray flux near the earth and consequently a decrease in ^{14}C production rate. Direct measurement of cosmic radiation over the last 3 solar cycles (Lingenfelter 1963, Lingenfelter et al. 1970) has confirmed this empirically derived relationship. The correlation between solar activity (sunspot numbers) and ^{14}C levels appears well established and statistically significant for the period since 1600 A.D. (Houtermans 1966) when sunspot numbers were officially recorded for the first time (Schove 1955). Grey (1969) has used a solar-cycle model, based on these records and sunspot number estimates by Schove, to calculate ^{14}C variations for the last 750 years. Excellent agreement is observed with the experimentally observed ^{14}C levels. The occurrence of

^{14}C minima at 400-year intervals over the last 8,000 years (Suess 1970b) may reflect the existence of a 400-year solar cycle.

It is now generally accepted that solar modulation of cosmic radiation can produce variations in the ^{14}C production rate sufficient (~30%) to cause fluctuations of 2 - 3% in ^{14}C levels over 50 to several hundred years. These short-term variations are less pronounced during periods of high geomagnetic activity when the solar-modulated low-energy cosmic-ray flux responsible for ^{14}C production is deflected away from the earth.

Solar activity may further influence the ^{14}C production rate through the positive contribution to the cosmic-ray flux by solar flares. No records exist of the frequency of significant solar flares in the past but Lingenfelter and Ramaty (1970) have estimated from recent direct measurements that sudden short-term increases of 1% in atmospheric ^{14}C activity may be due to these events.

It is possible that solar activity may not only have a direct influence on ^{14}C levels via production rate change but may also induce climatic variations (Suess 1968, Damon 1968) which, in turn, affect the transfer and exchange of carbon within the carbon cycle. Temperature changes can alter the CO_2 distribution between the atmosphere and the carbonate/bicarbonate system of the oceans. However, effects produced by climatic variations tend to counteract each other e.g. a decrease in global temperature leads to a decrease in the partial pressure of CO_2 in the atmosphere giving rise to an increase in the specific activity of atmospheric ^{14}C; at the same time, the temperature inversion layer of the ocean (i.e. the thermocline) will be weakened, resulting in more rapid transport of ^{14}C into the deep ocean. This would produce a decrease in atmospheric ^{14}C.

There are, however, some noteworthy correlations with climate e.g. the Little Ice Age period (15th - 17th Century A.D.) is one of relatively cold climate associated with relatively high atmospheric ^{14}C concentrations ("De Vries effect") compared to the warm period of the 11th - 15th Century. Despite this, the high ^{14}C level is more probably explained by production rate modulation rather than by climatic changes caused by the estimated low sunspot activity at that time (Suess 1968, 1970b).

Lal and Venkatavaradan (1970) have suggested that the high prevailing ^{14}C activity of 10,000 B.P. can be attributed to the last Ice Age. They introduce the concept of direct ^{14}C input into the deep layers of the ocean via the Antarctic surface outcrop. During glacial periods, there would be a reduction in the exchange between the atmosphere and deep ocean outcrop due to coverage of the ocean surface by ice. Hence atmospheric ^{14}C values would rise as a consequence of this reduced exchange of CO_2. It has been suggested further (Schell et al. 1965) that worldwide melting of the glaciers may have caused the long-term decrease of ~10% in atmospheric ^{14}C from ca. 8,000 B.P. through increase in ocean size and in contribution of old carbon locked in the ice. Again it is difficult to assess the effect of such a climatic variation although, in this case, the predicted 2.5% increase in ocean reservoir size appears too small to account for the observed decrease in ^{14}C levels. Indeed, Damon (1970) has concluded that the effect of changes in climate on the ^{14}C content of the atmosphere during the last 8 millennia is of minor importance compared to the effect produced by variations in the intensity of the geomagnetic field.

A simplified overall statement of the causes of secular ^{14}C variations could take the following form:

(1) an initially high ^{14}C activity 10,000 years B.P. as a consequence of the last Ice Age,

(2) a gradual long-term change of amplitude 10% in ^{14}C levels due to geomagnetic moment variations, on a periodic time-scale of 8,000 - 10,000 years,

(3) fluctuations of 2 - 3% in ^{14}C levels over 50 to several hundred years superimposed on general trends and due to heliomagnetic modulation of the cosmic-ray flux.

Information on the constancy of cosmic radiation arriving at the earth can be obtained from studies of other terrestrial cosmic-ray-produced radionuclides e.g. ^{37}Ar ($t_{\frac{1}{2}}$ = 35 days), ^{39}Ar ($t_{\frac{1}{2}}$ = 270 years), ^{81}Kr ($t_{\frac{1}{2}}$ = 210,000 years). The present concentrations of these rare-gas isotopes in the atmosphere (when compared with the expected concentration ratios as deduced from production cross-section data) reflect the cosmic-ray intensity averaged over time periods of the order of these half-lives. Thus the ratio of ^{39}Ar to ^{81}Kr is an indication of the average intensity over the last few hundred years relative to the average over the past few hundred thousand. Measurement of these isotopes in ice cores from deep bore holes in Greenland and Antarctica could indicate past atmospheric concentrations, and hence past levels of cosmic radiation at the earth, during the last 10^5 - 10^6 years. However, present counting techniques are not sufficiently precise to allow the detection of variations comparable to those observed in atmospheric ^{14}C levels (Oeschger et al. 1970). Similar studies of lunar and meteoritic material in the future should permit the resolution of geomagnetic activity and solar activity effects on cosmic radiation since the geomagnetic field does not affect the cosmic-ray flux experienced by such samples. Measurements of ^{36}Cl ($t_{\frac{1}{2}}$ = 308,000 years) and ^{39}Ar ($t_{\frac{1}{2}}$ = 270 years) concentrations in several recently fallen meteorites have led Schaeffer et al. (1963) to conclude that the average cosmic-ray intensity over the past 10^6 years was the same (to within 10%) as the average value during the past 10^3 years.

1.3 Annual Fluctuations of Natural ^{14}C Concentrations in the Atmosphere

Since the early days of radiocarbon dating, it has often been stated that short-term fluctuations of atmospheric ^{14}C may occur in association with the 11-year solar cycle. For example, Fergusson (1958) specifically selected multiannual tree-ring sections for determination of the industrial "Suess effect" (Section 1.4(a)), to avoid the perturbations of any yearly variations. Indeed, the bristlecone-pine ^{14}C data are obtained from measurement of 10-year sections. It has been pointed out that, on its own, modulation of the ^{14}C production rate by solar activity is at least an order of magnitude too small to influence annual ^{14}C activities significantly (Stuiver 1961, Houtermans 1966). Quite naturally, the major research programmes have been concerned with the long-term trends in ^{14}C levels. In recent years, however, studies of annual ^{14}C variations (Dyck 1965, Baxter and Walton 1971) have provoked some uncertainty as to the primary assumption of ^{14}C constancy from one year to the next.

(a) Method of detection

Past annual ^{14}C levels are obtained through analysis of short-lived biospheric materials of not more than 1 year's growth. The samples must be valid indicators of atmospheric ^{14}C activity and be free from contamination by non-contemporaneous carbon. Tree-rings (Dyck 1965), seeds, wool, wines and spirits from plant material (Baxter and Walton 1971) have been used as indicators.

(b) Magnitude of fluctuations

Dyck's ^{14}C data on single rings of fir tree suggested that cyclic fluctuations of up to 3% amplitude occurred during A.D. 822 - 831 and again during A.D. 1616 - 1627. Baxter and Walton's analysis of 20th Century materials revealed cyclic fluctuations through 3% over 6 consecutive solar cycles. Schaeffer and Schaeffer (1971) have reported significant annual ^{14}C variations in North American single tree rings for the period 1940 - 1954. In addition, Lerman (1970) has tentatively suggested that early 20th Century ^{14}C levels fluctuated within a cycle of amplitude 0.6%.

The available data is meagre with respect to both time and latitude. All results apply to the higher latitudes of the northern hemisphere and only Dyck's refer to pre-20th Century levels. Further studies of annual ^{14}C levels for previous centuries and different latitudes seem necessary for a more definite assessment of this effect.

One consequence of the observed magnitude of variation is that any radiocarbon dating sample of lifetime in the order of 1 year (e.g. grain, straw, seeds, single tree rings, roots, twigs, egg shells, leaves, sheep's wool) is susceptible to a dating error of ± 120 years.

(c) Causes of the fluctuations

The annual variations observed by Baxter and Walton were attributed to a combination of isotope production-rate modulation by solar activity and of variable injection of ^{14}C from its stratospheric source into the troposphere at the latitude of sampling. Solar records are not available on an annual basis for the short time periods covered by Dyck who used the concept of an active climate-sensitive biosphere to explain the observed fluctuations. Obviously the lack of ^{14}C data severely hinders the proposal of a valid mechanism for annual fluctuations of atmospheric ^{14}C.

1.4 Artificial Fluctuations of Atmospheric ^{14}C Concentrations

Twentieth Century atmospheric ^{14}C levels have been significantly affected by two of man's activities:

(1) the burning of fossil fuels,

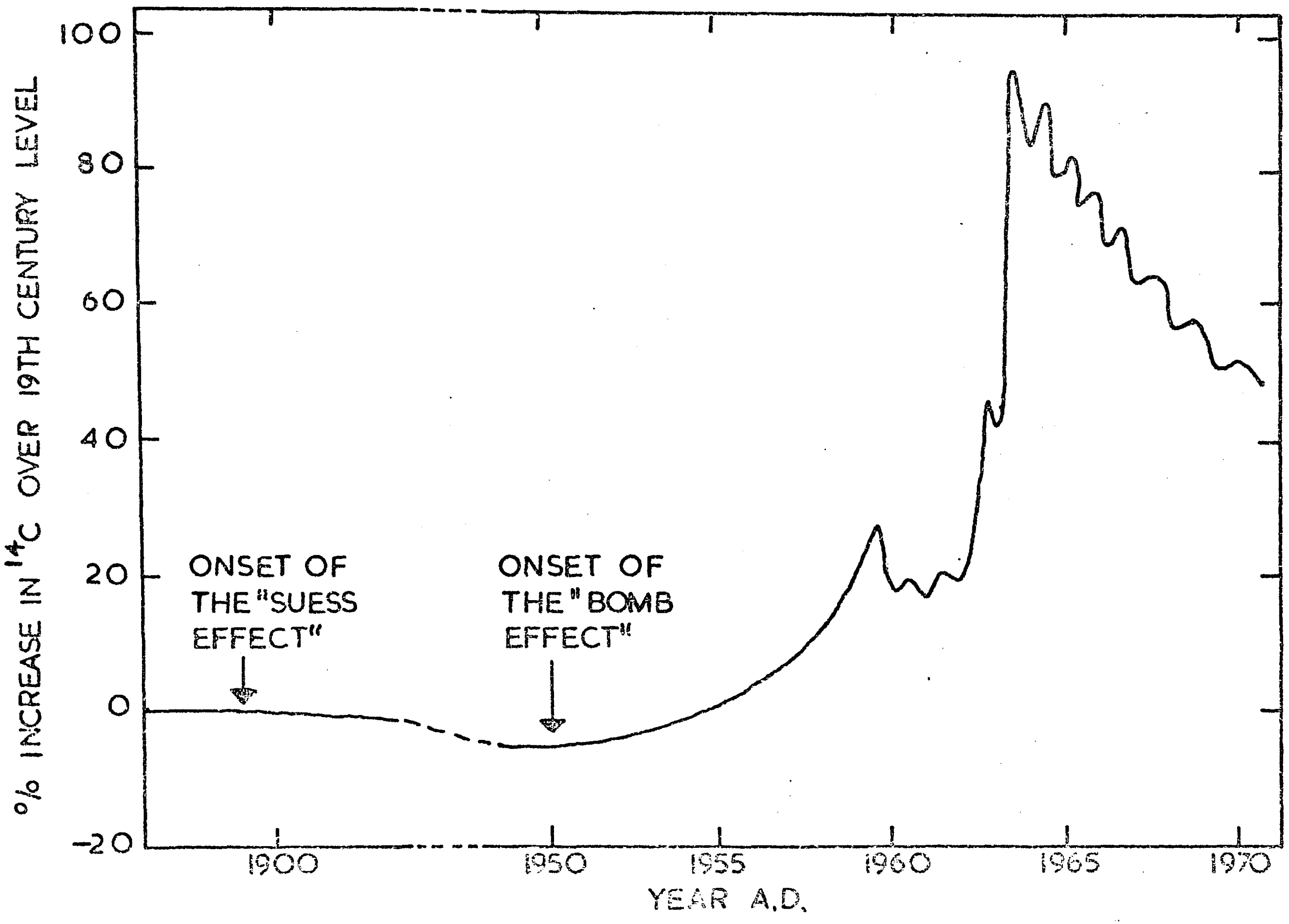
(2) the testing of nuclear weapons.

(a) The "Suess effect"

The "Suess effect" is the decrease in atmospheric ^{14}C concentrations caused by the combustion of large quantities of ^{14}C-free fossil fuels (Figure 1.3). This effect was estimated by Suess (1955) to have caused a depression of about 3% in northern hemisphere atmospheric ^{14}C concentrations by 1950. Fergusson (1958) obtained a corresponding value of 2% for the southern hemisphere. Both figures were derived from the comparisons of ^{14}C measurements of 20th Century and middle 19th Century wood. One important

FIGURE 1.3

ATMOSPHERIC ^{14}C CONCENTRATIONS IN THE
NORTHERN HEMISPHERE DURING THE PAST CENTURY



consequence of the discovery of the "Suess effect" has been the need to employ a universal ^{14}C standard, N.B.S. oxalic acid, based on 19th Century levels, instead of the former 20th Century wood standards.

The annual input to the atmosphere of CO_2 from fossil fuels can be estimated from records of the production of coal, petroleum, lignite, natural gasoline and natural gas. The rate of input has risen rapidly since 1860 with a doubling time of 15 - 20 years except for a noticeable slowing during the economic depression and the 2 world wars (Revelle 1965). Such estimates have been employed in theoretical determinations of the "Suess effect" at particular times in the past (Revelle and Suess 1957, Fergusson 1958, Baxter and Walton 1970). The values obtained can be used to correct measured 20th Century annual ^{14}C levels so that any natural ^{14}C fluctuations are apparent (Baxter and Walton 1971).

The dynamic equilibrium existing among the major carbon reservoirs has been disturbed by the fossil CO_2. Indeed, the magnitude of the atmospheric "Suess effect" depends on the distribution of this excess CO_2 through the carbon cycle which, in turn, has enabled calculations of the exchange parameters between the various reservoirs (Craig 1957a, Revelle and Suess 1957, Bolin and Eriksson 1959, Bolin and Keeling 1963). More recent calculations have been based on the distribution of excess ^{14}C from nuclear weapon testing (Section 1.4(b)).

The atmospheric CO_2 concentration has increased from about 290 p.p.m. in 1890 (Callendar 1958) to 320 p.p.m. (Bolin and Bischof 1970). During the last decade, the average annual rate of increase of CO_2 content has been

0.7 ± 0.1 p.p.m./year (Bolin and Bischof 1970). The acceleration in the consumption of fossil fuels implies an atmospheric concentration of about 375 p.p.m. by the end of the 20th Century (Revelle 1965, Bolin and Bischof 1970, Baxter and Walton 1970). Since CO_2 is a strong absorber and back-radiator of infra-red radiation, especially in the wavelength range 12 - 18 μ, an increase of atmospheric CO_2 could cause an increase in global surface temperatures (Callendar 1938, Plass 1956, 1961, Kaplan 1960). The evaluation of this effect is rather difficult because of associated changes in cloud cover and atmospheric dust levels. Nevertheless, it is quite possible that the predicted increases of atmospheric CO_2 will appreciably change the climate over the next few centuries and, for this reason, the effect merits further study at this time.

(b) The "bomb effect"

The "bomb effect" is the result of the addition to the atmosphere of considerable quantities of ^{14}C produced through the activation of atmospheric nitrogen by "bomb" neutrons released during nuclear weapon tests. Table 1.1 presents the total ^{14}C production from 1945 - 1970. The total production of ^{14}C to date is estimated at 95.6×10^{27} atoms, based on a yield of 2×10^{26} ^{14}C atoms/M ton. fission or fusion for an air burst, and 1×10^{26} ^{14}C atoms/M ton. fission or fusion for a ground burst (Machta 1959).

Figure 1.3 includes a profile of the irregular increase of atmospheric ^{14}C concentrations for the period 1950 - 1970 for the northern hemisphere troposphere (Broecker and Walton 1959, Broecker and Olson 1960, Nydal 1963, 1967, 1968, Lal and Rama 1966, Young and Fairhall 1968, Walton et al. 1970, Telegadas 1971).

TABLE 1.1

ESTIMATED "BOMB" ^{14}C PRODUCTION 1945 - 1970

Period	^{14}C Yield (10^{27} atoms)
1945 - 1951	0.1
1952 - 1954	6.0
1955 - 1956	3.9
1957 - 1958	14.2
1959 - 1960	0
1961	24.0
1962	43.4
1963	0
1964 - 1970	4.0
Total	95.6

Since the majority of the artificial ^{14}C was injected into the northern hemisphere stratosphere, the highest levels of northern tropospheric concentrations occurred in 1963 and 1964, about 2 years after the period of maximum production. The finite stratospheric residence time of CO_2 accounts for this lag. Since the maximum levels were attained, ^{14}C concentrations have gradually decreased through mixing with the southern troposphere and absorption by the oceans and biosphere. This exchange of artificial "tracer" ^{14}C has afforded an opportunity for the determination of the exchange parameters controlling carbon distribution.

The "box-model" approach has been widely used to interpret the extensive ^{14}C data gathered in recent years (Lal and Rama 1966, Nydal 1968, Walton et al. 1970, Rafter and O'Brien 1970). A typical model consists of the division of the carbon cycle into compartments e.g. stratosphere, troposphere, biosphere, surface ocean, deep ocean. The complexity of the model depends on the number of boxes. If differences in the latitudinal distribution of excess ^{14}C are taken into account, more boxes are required and there is a corresponding increase in complexity. A knowledge of both the total carbon and excess ^{14}C content of each reservoir employed is necessary for evaluation of exchange rates or the corresponding residence times.

Such studies have provided basic information on exchange rates between the component reservoirs of the carbon cycle. Despite intense activity in this field, however, some uncertainty still exists regarding exchange values (Table 1.2). Disagreement may reflect significant variations of atmospheric CO_2 exchange rates both temporally

TABLE 1.2

MEAN RESIDENCE TIMES (YEARS) OF CO_2 IN VARIOUS CARBON RESERVOIRS (Based on "Bomb" ^{14}C Studies)

Source	Stratosphere to Troposphere	Troposphere to Surface Ocean
Lal and Rama (1966)	0.8 ± 0.3	4
Münnich and Roether (1967)	–	5.4
Bien and Suess (1967)	–	25
Nydal (1967)	3.5 ± 0.8	–
Young and Fairhall (1968)	1.5	2.5
Nydal (1968)	2.0 ± 0.5	5 - 10
Walton et al. (1970)	4.0	9.3
Rafter and O'Brien (1970)	–	12.0

and latitudinally. These are certainly observed on an annual basis in the northern hemisphere where the seasonally varying injection of excess ^{14}C from the stratosphere has produced the "spring peaks" shown in Figure 1.3.

"Bomb" ^{14}C distribution has interesting applications in other fields of research e.g. plants and animals living after 1962 should reflect the large increase in ^{14}C in tropospheric air. Thus the suitability of a particular material (e.g. tree-ring component) as an indicator of atmospheric ^{14}C levels can be tested. The study of natural ^{14}C fluctuations is critically dependent on valid sample material of known age.

"Bomb" ^{14}C is, however, a significant source of contamination for old dating samples, particularly inorganic material which may have undergone ion-exchange with carbonate of atmospheric origin. Nuclear-era ^{14}C levels of 100% above normal obviously constitute an even greater threat than natural "pre-bomb" levels to the integrity of old carbon samples (Table 2.1).

As the excess ^{14}C distribution tends further to equilibrium, future observations should allow increased accuracy in exchange-rate studies. The influence of an increasing "Suess effect" must be taken into account, however, in the future decreasing ^{14}C levels of the atmosphere. From a consideration of both artificial effects, it has been estimated that atmospheric ^{14}C levels should return to normal by 2000 A.D. (Harkness 1970).

1.5 Aims of Research Project

During the last 20 years, radiocarbon dating has progressed through improvements in analytical precision and in identification of the magnitude and direction of long-term ^{14}C fluctuations. Indeed, the bristlecone-pine calibration is perhaps the method's most important contribution to the improved determination and interpretation of past events. However, if significant short-term ^{14}C variations have occurred over periods of 1 - 10 years, neither of these major developments can aid the necessary age-correction of short-lived dating samples. It follows that the basic philosophy of sample selection for dating would require revision if such ^{14}C fluctuations were identifiable in past centuries. The discovery of 3% fluctuations in atmospheric ^{14}C concentrations over the 11-year solar cycle is comparatively recent and conflicts with the traditional view shared by many radiocarbon chronologists that deviations of this magnitude (± 1.5%) are impossible on a time-scale of $\sim$11 years. Thus, an investigation of past annual ^{14}C concentrations, preferably during a period undisturbed by artificial influences such as the "Suess effect", is of immediate concern and relevance to the radiocarbon dating method.

The study of southern hemisphere ^{14}C concentrations has been almost completely ignored in the calibration of the radiocarbon time-scale. Indeed, no systematic study of past annual atmospheric ^{14}C levels in the southern hemisphere has ever been undertaken. The few existing data suggest possible differences in ^{14}C content between hemispheres over periods of a few hundred years. Recent "bomb" ^{14}C studies suggest these interhemispheric variations may be a result of latitudinal variations in CO_2 exchange. In view of these differences, an investigation of past annual ^{14}C concentrations in the southern hemisphere is of major importance to the dating method. Furthermore, annual ^{14}C data from both hemispheres should improve our understanding of the parameters controlling ^{14}C production and distribution.

The release of significant quantities of inactive CO_2 through fossil fuel combustion has significantly depressed atmospheric ^{14}C concentrations during the 20th Century (the "Suess effect"). Initial evaluations of the "Suess effect" were based merely on ^{14}C depletion, an approach which ignores possible natural variations of atmospheric ^{14}C. Subsequent estimates have been made through a theoretical consideration of the distribution of fossil CO_2 within the dynamic carbon cycle, assuming constant exchange rates between carbon reservoirs. This assumption is perhaps unrealistic in view of the disturbance of the equilibrium conditions of the carbon cycle by the addition of fossil CO_2 to the atmosphere. A reassessment of the methods of determination of the "Suess effect" and of past atmospheric CO_2 levels seems necessary both for correction of 20th Century ^{14}C data and for the investigation of possible CO_2 exchange variations.

The basic objectives of the research were therefore:

(1) the measurement of annual concentrations of atmospheric ^{14}C in both hemispheres during recent times,

(2) the evaluation of the importance of this short-term ^{14}C data with respect to the radiocarbon dating method,

(3) the assessment of the implications of ^{14}C and CO_2 concentrations for the geochemical and geophysical processes controlling ^{14}C and CO_2 distribution.

CHAPTER 2

EXPERIMENTAL METHODS IN RADIOCARBON ASSAY

2.1 Introduction

The measurement of environmental ^{14}C requires sophisticated chemical and physical procedures. These are necessary for the following reasons:

(1) ^{14}C is a weak beta emitter (maximum energy 0.158 MeV.),

(2) ^{14}C is present in natural carbon in extremely low concentrations. A specific activity of 13.56 ± 0.07 d.p.m./g.C (Karlen et al. 1964) corresponds to approximately 1 atom $^{14}C/10^{12}$ atoms C.

It is thus imperative that the ^{14}C detector has a high efficiency and that sample activities are statistically high compared to the background count rate.

Furthermore, long-term stability of both the detection efficiency and background count rate are necessary because (1) the determination of ^{14}C concentrations relative to the natural level involves the precise intercomparison of modern standard and sample activities and (2) relatively long counting times ($\sim$1 day) are employed to reduce the statistical uncertainty. The background count rate must be stable over such periods.

A ^{14}C counting system, therefore, must display the following features:

(1) high beta detection efficiency,

(2) low background count rate,

(3) long-term stability of beta detection efficiency and background.

The early ^{14}C counting systems (Libby 1955) of quarter of a century ago involved the coating of the inner wall of a screen-wall Geiger counter with elemental carbon prepared from the sample. The total detection efficiency was only 5% and the "carbon black" was subject to contamination from ambient "fallout" isotopes. The method was soon rendered obsolete by the development of internal gas proportional counting techniques.

The proportional, rather than the Geiger, region is favoured for the now common counting gases (CO_2, CH_4, C_2H_2). In detecting low levels of activity more precise data can be obtained by energy analysis of the counter pulses. In the Geiger region, all output pulses are uniform in size, independent of the initiating event; in the proportional region, the height of each output pulse is a measure of the energy absorbed by the counting gas. Thus, with a proportional counter, it is possible to monitor only the energy range of interest through rejection of lower or higher energy pulses.

Over the last 20 years, improvements in the performance of gas proportional counting of CO_2 (De Vries et al. 1952, Fergusson 1955, Olsson 1958), of CH_4 (Burke and Meinschein 1955, Fairhall et al. 1961, Sharp and Ellis 1965) and of C_2H_2 (Suess 1954) have established the technique as a reliable method of measuring environmental ^{14}C.

Liquid scintillation counting of benzene is the other major method of ^{14}C assay. Many new radiocarbon laboratories utilise liquid scintillation techniques because of:

(1) the general improvement made in component performance (e.g. increase in figure of merit E^2/B

from 150 in 1960 to 800 in 1970),

(2) the appeal of automatic sample counting with its time saving advantage and consequently lower cost per date obtained in commercial laboratories.

Nevertheless, gas proportional counting continues to offer a basically sound counting system with excellent features of stability, efficiencies greater than 90%, background count rates of the order of 1 - 5 c.p.m. ($E^2/B \sim 3000$) and less involved chemical procedures. In general, gas counting techniques can handle small samples (<2g.C) more conveniently while liquid scintillation techniques are more suitable for large samples. At the outset of this research, it was considered that gas proportional counting provided the more reliable and appropriate system with respect to the size of samples involved.

Methane was chosen as the counting gas for the following reasons:

(1) the counting characteristics of CH_4 are less sensitive to electronegative impurities than those of CO_2 (Burke and Meinschein 1955). Extreme purification procedures are therefore unnecessary.

(2) CO_2 to CH_4 conversion is rapid, quantitative and non-hazardous (Fairhall et al. 1961) whereas CO_2 to C_2H_2 conversion involves rather tedious chemical procedures.

(3) CH_4 is safe to handle, store and count at high pressures in contrast to C_2H_2, which, while having the theoretical advantage of incorporating two carbon atoms per molecule, tends to explode at pressures greater than 1.5 atm.

The counting gas must be prepared in high yield to avoid isotopic fractionation. At the same time, it should be of the required purity, with a minimal level of electronegative impurities. Thus, the chemical procedures employed in the conversion of sample carbon to CH_4 must be highly efficient and capable of consistently producing a pure counting gas i.e. the demanding requirements of the counting system necessitate correspondingly sophisticated chemical preparation techniques.

Figure 2.1 presents a block diagram of the routine analytical procedures employed with approximate times required for each operation.

2.2 Chemical Preparation System

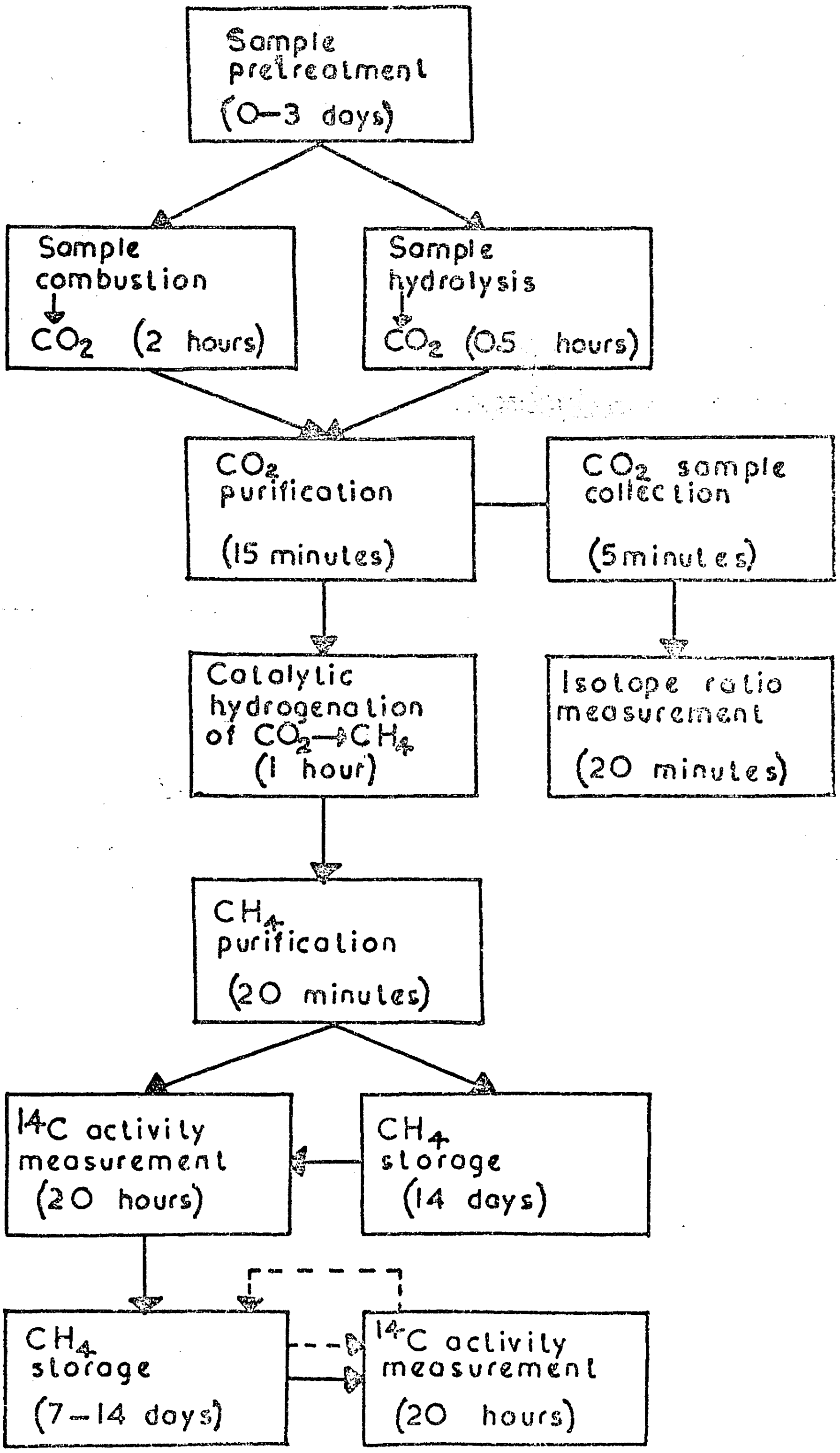
(a) Sample pretreatment

It is most important in ^{14}C studies that the sample contains the original carbon atoms present at the time of isolation from the carbon exchange cycle. In the time period between removal from the exchange reservoir and analysis, the sample may become contaminated with foreign carbonaceous materials. The type of contamination a particular sample may undergo depends on its chemical structure and its environment in the years following removal from the carbon cycle. Thus the carbon of an inorganic sample (e.g. bone or shell carbonates) may be replaced by ion-exchange with the carbonates of ground waters. Organic samples are generally not subject to this type of "chemical" alteration.

"Superficial" contamination involving impregnation of the sample by non-contemporaneous material does affect its organic constituents. Rootlets, humic acids, carbonates,

FIGURE 2.1

BLOCK DIAGRAM OF LABORATORY PRACTICE



sand and soil are typical contaminating agents. They are usually introduced into the sample through ground water infiltration, but do not enter into ion-exchange processes or chemical bonding with the sample.

The presence of non-contemporaneous carbon atoms can introduce errors in sample activities which, in dating, become increasingly significant with increasing sample age. Table 2.1 indicates the magnitude of the errors caused in old and nuclear era samples by contamination with varying amounts of recent and inactive carbon.

Pretreatment of old organic samples which are submitted for dating generally consists of a visual examination for intrusive rootlets followed by successive boilings in distilled water, 5% HCl, distilled water, 5%NaOH, distilled water, 5% HCl and distilled water. In this way the elimination of carbonate and humic acid contaminants is ensured. The pretreatment of charcoal, a particularly useful dating material, can be relatively severe, since charcoal is composed primarily of chemically inert carbon atoms. Strong alkali and acid washing can be employed in contrast to the milder conditions required for the pretreatment of structurally unstable materials e.g. peat. Inorganic materials such as shells and marbles are leached in acid to remove 20% by weight. Removal of this portion of the external shell carbonate is generally successful in freeing samples from carbonate contamination.

In this research, various pretreatment procedures are performed on the wood of individual tree rings. Removal of non-contemporaneous resins is attempted by acid/base treatment or by Soxhlet extraction with an organic solvent. The cellulose component can be isolated through

TABLE 2.1

ERRORS CAUSED BY SAMPLE CONTAMINATION

(a) Contamination of Old Samples by Modern Carbon

True age of sample (years)	Radiocarbon age of sample (years) Degree of contamination with modern carbon 1%	 0.1%	 0.01%
5,570	5,490	5,560	5,570
11,140	10,900	11,120	11,140
22,280	21,080	22,160	22,270
44,560	32,260	42,760	44,350

(b) Contamination of Nuclear Era Samples by Dead Carbon

True ^{14}C concentration of sample (% deviation from normal level)	Observed ^{14}C concentration (% deviation from normal level) Degree of contamination with dead carbon 10%	 5%	 1%
+40.0	+26.0	+33.0	+38.6
+60.0	+44.0	+52.0	+58.4
+80.0	+62.0	+71.0	+78.2
+100.0	+80.0	+90.0	+98.0

bleaching the wood in a $NaClO_2/HCl$ solution. In general, cellulose samples are charred at 500°C prior to combustion in the CO_2 preparation system. The lignin fraction can be obtained by the 72% H_2SO_4 method. (Section 3.3(c)).

Wines and spirits require pretreatment through distillation to remove colouring matter.

(b) Sample combustion

All organic samples are burned in an atmosphere of O_2 to yield CO_2 (Figure 2.2).

$$C + O_2 \rightarrow CO_2$$

Five litre-atm. of CO_2 are usually prepared.

Solid samples are contained in porcelain boats placed as shown within the quartz glass tube. A stream of O_2 and N_2 is passed over the sample which is heated from below by a Meker burner. The nature of the sample material determines the initial O_2 flow rate. For volatile samples (e.g. seeds) the flow rate is 100 - 200 ml./min. with a N_2 flow of 500 ml./min. For more stable samples (e.g. charcoal) the initial O_2 rate is 300 ml./min. An O_2 flow rate of 500 ml./min. is maintained through the sidearm. The rate of combustion is controlled by varying the sample heating rate. A negative pressure gradient of about 5 cm. Hg is maintained throughout the system by controlled pumping to prevent pressure build-up. As the combustion proceeds, the O_2 flow rate over the sample is increased to 500 ml./min., the N_2 flow rate reduced to 100 ml./min. or less and the sample heating rate increased.

For alcohol samples the modified combustion system shown in Figure 2.3 is used. An inner tube packed with cotton wool is fitted inside the outer combustion tube. A 1 mm. aperture at the tip of the inner tube permits the

FIGURE 2.2

COMBUSTION SYSTEM

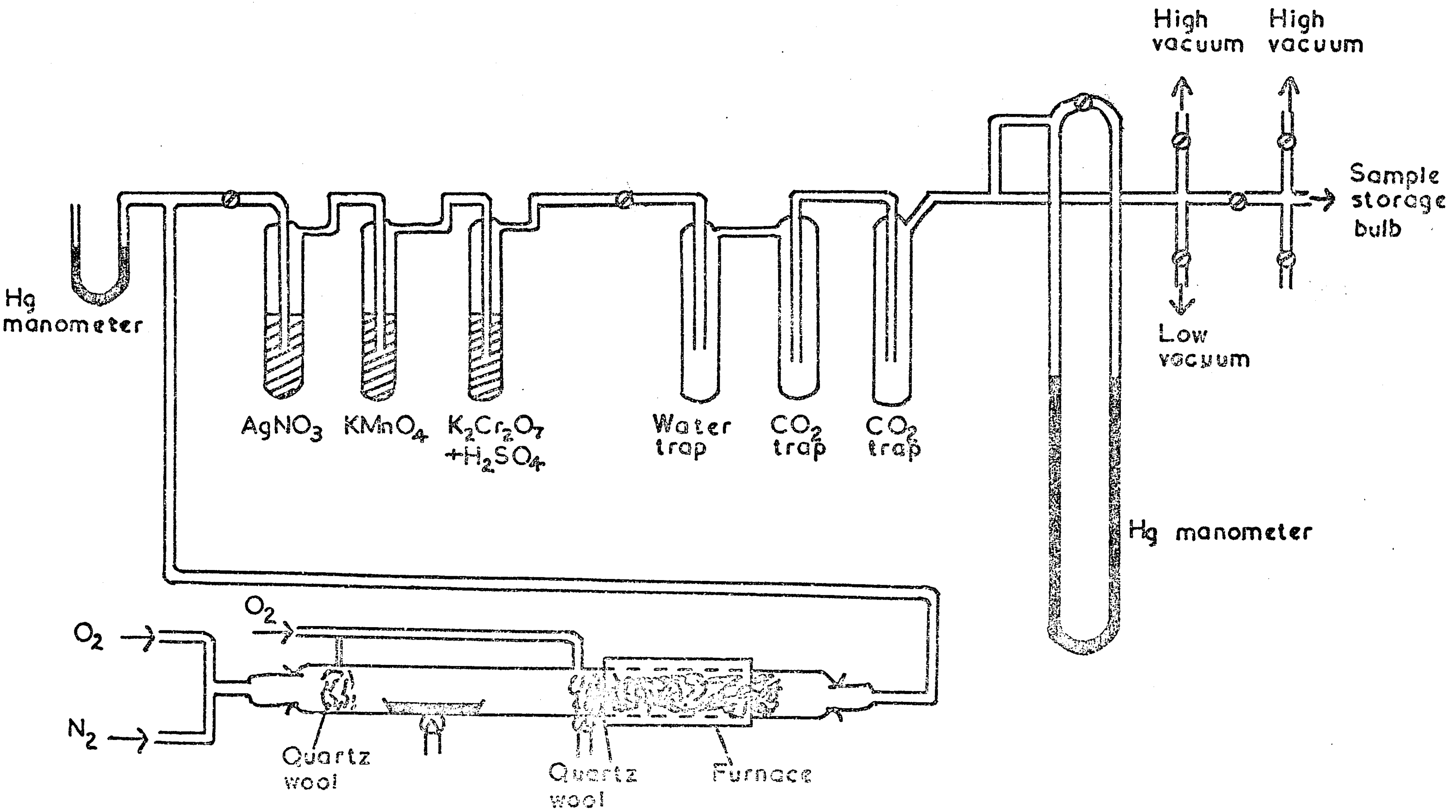
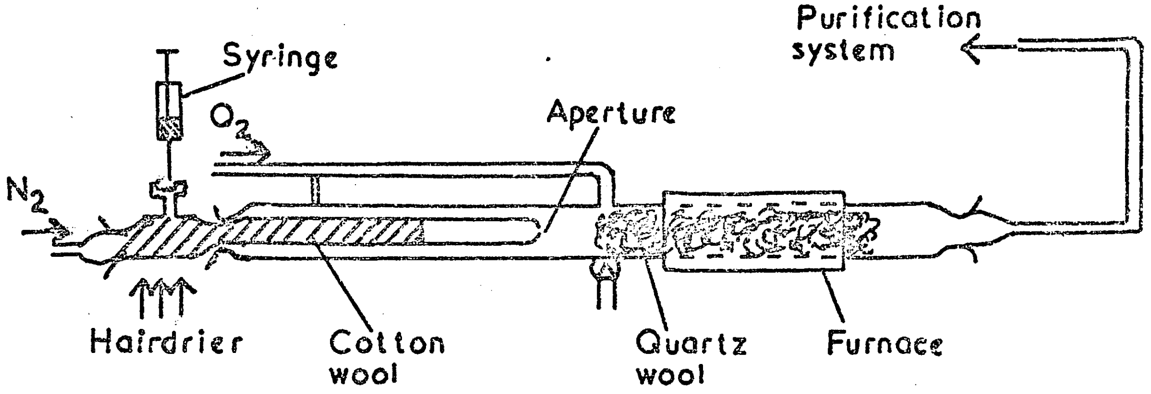


FIGURE 2.3

ALCOHOL COMBUSTION SYSTEM



passage of gases through the system. A stream of N_2 (500 ml./min.) is passed through the inner tube. The alcohol/water mixture from the distillation is injected by a syringe in 1 ml. quantities through a self-sealing septum and is absorbed by the wool. This area is heated gently using a hairdrier and the alcohol vapour is swept along the inner tube and burned at the quartz wool plug.

The gaseous products are purified in the following stages:

(1) an $AgNO_3$ bubbler to extract halogens and their acids,

(2) a $KMnO_4$ bubbler to remove oxides of sulphur and nitrogen,

(3) an $H_2SO_4/K_2Cr_2O_7$ bubbler to extract sulphur and nitrogen oxides and act as a drying agent,

(4) a dry ice trap (-76°C) to remove water vapour.

The CO_2 then largely condenses in the first liquid N_2 trap (-196°C) and is pumped to less than 1μ Hg to remove all gases (especially O_2) which have an appreciable vapour pressure at -196°C. The CO_2 is then distilled into the second trap which may already contain a minor amount of CO_2 not collected by the first trap. Pumping to below 1μ removes any gases present. The CO_2 is then expanded and condensed into a storage bulb of known volume.

In the limited number of cases where the condensed CO_2 is discoloured and is obviously contaminated, the CO_2 is absorbed in KOH solution and released later by acid hydrolysis. Such contamination was evident following the combustion of samples of sewage-containing sediments from the Firth of Clyde (McKenzie 1971). The orange-coloured impurity, probably derived from sulphur-containing compounds, was removed by the above procedure.

The combustion of charcoal and charred cellulose proceeds smoothly; whole wood tree rings, wool, wheat and oat seeds require care because of the rapid release of volatile components on ignition; the combustion of alcohol samples is comparatively time-consuming but trouble-free.

Prior to routine analysis of unknown materials, combustion of oxalic and benzoic acids produced 95 - 100% conversion yields. Blank runs showed that no CO_2 was being produced from impurities in the system (Baxter 1969).

After each combustion the quartz tube is roasted to remove any carbon residues. The section of the combustion line containing the chemical bubblers is completely detachable. This facilitates cleaning of the glassware and changing of the chemicals before the next combustion.

(c) Sample hydrolysis

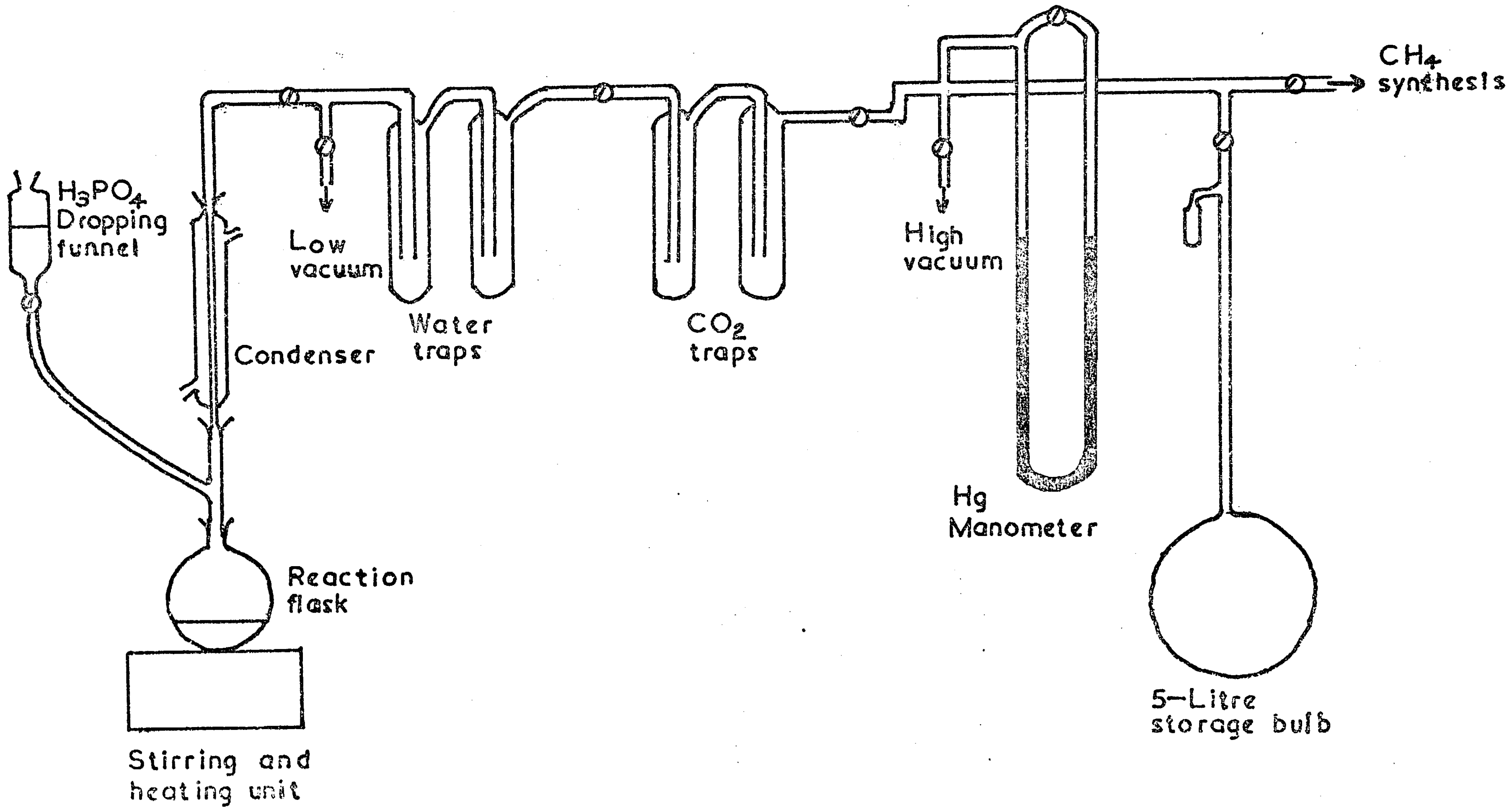
Inorganic materials such as shells and K_2CO_3 are hydrolysed in the apparatus shown in Figure 2.4. Solid samples are fragmented and covered with a small volume of water. Phosphoric acid (50% V/V) is used as the hydrolysing agent.

$$CO_3^{2-} + 2H^+ \longrightarrow CO_2 + H_2O$$

The rate of reaction is controlled by varying the rate of acid addition, the stirring rate and the pressure in the reaction vessel. Usually no heating is required and the pressure is maintained at several cm. Hg by manipulation of the valve between the reaction system and the first water collection trap. Water vapour is removed from the product CO_2 by passage through a condenser and two dry ice traps. The condensed CO_2 is then pumped to less than 1μ, distilled and pumped again to remove occluded impurities.

FIGURE 2.4

HYDROLYSIS SYSTEM



The hydrolysis system is also used for the wet oxidation of standard oxalic acid samples:

$5(COOH)_2 + 2MnO_4^- + 16H^+ \longrightarrow 10CO_2 + 2Mn^{2+} + 8H_2O + 10H^+$

The oxidising agent used is saturated $KMnO_4$ in 0.5 M H_2SO_4 solution. The reaction requires slight heating and is generally allowed to proceed for several hours to eliminate the possibility of isotopic fractionation (Grey et al. 1969).

The CO_2 obtained from hydrolysis or wet oxidation is transferred to a 5 litre bulb for storage. Conversion of pure $CaCO_3$ and oxalic acid samples to CO_2 regularly gave yields of 98 - 100%.

(d) Methane synthesis

Two distinct techniques are available for the catalytic hydrogenation of CO_2 to CH_4 over a ruthenium catalyst,

$$CO_2 + 4H_2 \underset{Ru}{\overset{\Delta}{\rightleftharpoons}} CH_4 + 4H_2O \ :$$

(1) the high pressure batch reactor method of Fairhall et al. (1961). This involves the use of a stainless-steel high pressure reactor fitted with two side arms for the condensation of reactants and products. The reactor is filled with CO_2 and H_2 is added in two stages. Yields of approximately 98% are obtained.

(2) the continuous flow method. The system is constructed almost entirely from glass and is operated at less than 1 atm. pressure. The catalyst is 100g. of 0.5% ruthenium on 1/8 inch alumina pellets (Engelhard Industries Ltd.,New Jersey). A diaphragm pump circulates the mixture of CO_2 and H_2 over the catalyst maintained at a temperature of 375°C.

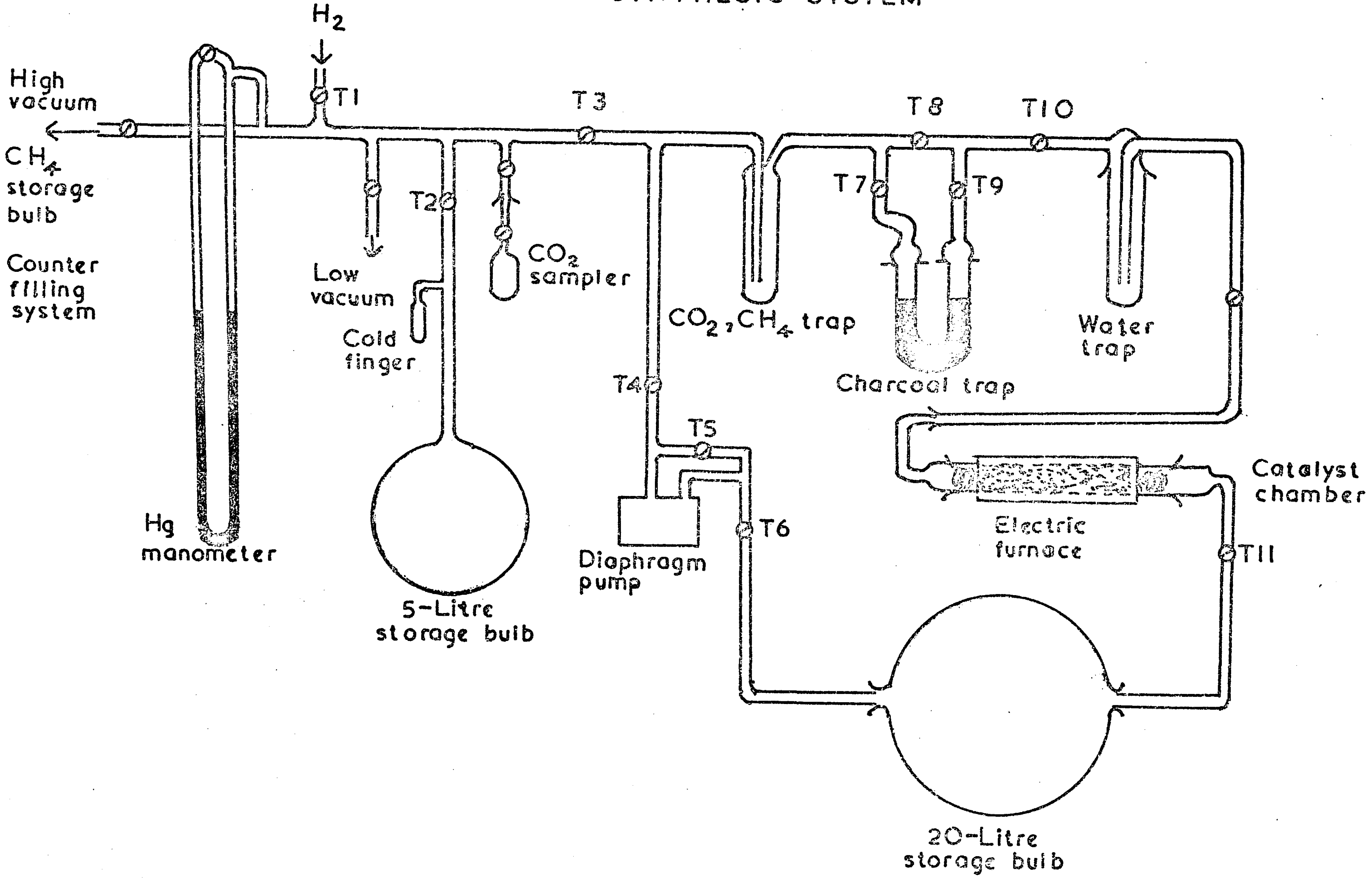
The latter system, a modification of one in use at

I.A.E.A.'s Radiocarbon Laboratory in Vienna (Ergin, 1969), is employed in this research. Due to its very large volume (~231.) the whole system (Figure 2.5) is evacuated in stages to less than 1μHg. The catalyst is heated to 375°C by an electric furnace. After evacuation, stopcocks T4, T6, T7, T9, T10, T11, are all in the closed position, thus isolating the 20 litre bulb, the charcoal trap and the catalyst chamber. Tap T2 is opened and a small aliquot of CO_2 is collected in a 25 ml. sampler for mass-spectrometric measurement of isotopic fractionation. The CO_2 from the storage bulb is then condensed into the first trap.

T2 is closed, T4 and T6 opened, and the calculated amount of H_2 (Messer Griesheim, Dusseldorf) with 5% excess is admitted to the system from a gas cylinder via T1. The gas pressure is held at slightly less than 1 atm. at this stage. If the amount of H_2 required for the reaction would raise the total pressure in the system over 1 atm. it is introduced in two stages. After H_2 has been added, the CO_2 is expanded into the 20 litre bulb as quickly as possible by warming the cold trap with a hairdrier. The final pressure in the system is recorded, the stopcocks T11, T10 on both sides of the catalyst opened, the circulation pump bypass, T5, closed and the diaphragm pump switched on. In about 10 seconds, the pressure begins to drop and water vapour droplets begin to condense in the water trap, which is cooled by an acetone/dry ice mixture, indicating that reaction has commenced. The time usually required for completion of reaction is 40 minutes from the last addition of H_2. The reaction is considered complete when the manometer mercury level remains constant. At this stage, the total pressure should be approximately equal to the

FIGURE 2.5

METHANE SYNTHESIS SYSTEM



original CO_2 pressure plus the excess H_2 pressure. Stopcocks T7, T9 are opened, T8 closed, and the gases passed through the charcoal trap cooled with liquid N_2. For the next 10 minutes, the CH_4 and H_2 are left to adsorb on the charcoal. The circulation pump is then switched off, the bypass opened and the system allowed to stand for a further 10 minutes. The charcoal adsorption trap is necessary for the quantitative recovery of CH_4 due to its high vapour pressure, 11 mm. Hg, at -196°C.

The charcoal trap is then isolated by closing T7 and T9. The 20 litre bulb and catalyst chamber are pumped for about 5 minutes to remove the bulk of the remaining H_2. This enables a more rapid degassing of the catalyst prior to the next synthesis. With T8 and T9 closed, T7 open, the charcoal trap is pumped to less than 200μ Hg, removing adsorbed H_2. T7 is closed and the trap used earlier for the condensation of CO_2 is cooled with liquid N_2. When 1μ Hg has been achieved, T3 is closed, T7 opened and the liquid N_2 container removed from the charcoal trap. The CH_4 is released by heating the charcoal for about 5 minutes and condenses in the liquid N_2 trap. T7 is closed and by opening T3 for one second, the last traces of H_2 are removed from the CH_4.

The CH_4 is then allowed to expand into a calibrated storage bulb where the yield is measured. The gas is then either condensed in the cold finger of the storage bulb or transferred to the counter filling system.

From the pressure changes recorded during the reaction the CO_2 to CH_4 conversion yields are believed to be close to 100%. The finite vapour pressure of CH_4 at -196°C precludes 100% CH_4 recovery but yields of greater than 90% are always obtained approximating to a mean yield of 95%. This compares well with the data obtained by other laboratories (Fairhall et al. 1961, Olson and Nickoloff 1965, Long 1965). It is most important that the yield be above 90% since for poorer yields significant fractionation effects may occur (Long 1965). The purity of the product CH_4 has been confirmed by mass spectrometry. The gas contains no CO_2 and only p.p.m. quantities of hydrocarbons up to molecular weight 140 (Baxter 1969, Ergin 1969).

The catalyst is replaced after about 50 syntheses. After each synthesis the catalyst is degassed to 1μ at 400°C. This procedure requires about 3 hours of pumping but appears sufficient to maintain the catalyst condition and eliminate memory effects. The charcoal is also degassed between syntheses to eliminate the possibility of memory effects and to reactivate the adsorbent. The charcoal is therefore heated by a furnace to 200°C and pumped to 1μ for 1 hour.

2.3 Gas Storage Facilities and Counter Filling System

Storage facilities, in the form of a number of 5 litre bulbs, are necessary because each CH_4 sample is counted at least on two occasions, usually 14 days apart. Statistically consistent sample activities must be obtained before a gas is discarded. The presence of radon (^{222}Rn), an alpha emitter with beta emitter daughters, can introduce significant errors in the CH_4 sample activities. Gases prepared from inorganic materials are most susceptible to this form of contamination because radon commonly originates from the radium content of calcium compounds. Indeed, in a similar system, Baxter (1969) has observed a count rate of 8 c.p.m./litre CH_4 for gas prepared from a mortar sample.

Since ^{222}Rn has a half-life of 3.83 days, a storage period of 14 days will generally suffice to reduce the Rn contamination to immeasurable values for potentially contaminated CH_4 samples.

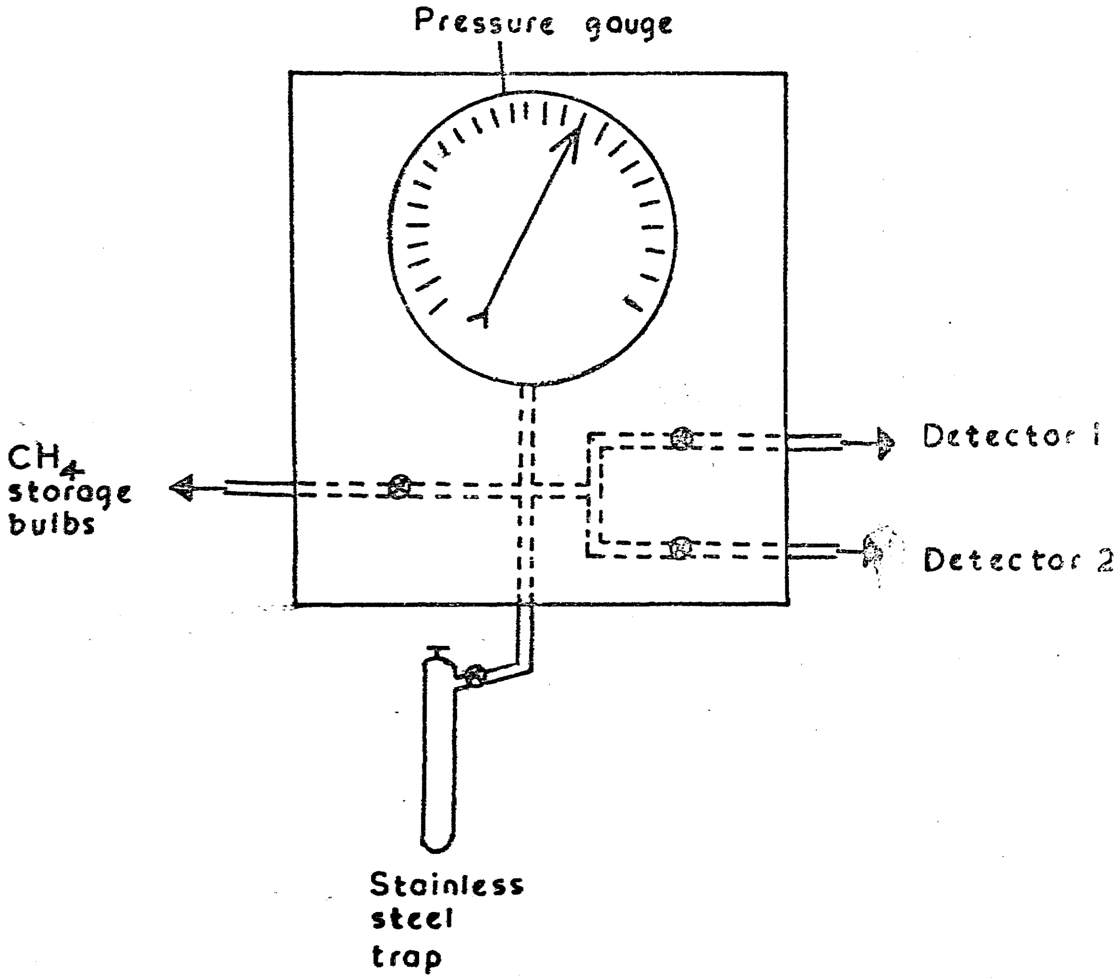
Ten 5 litre bulbs are available for sample storage. Each bulb has a cold finger attached so that sample transfer losses due to the vapour pressure of CH_4 at -196°C are minimised. A manometer in the storage frame allows measurement of bulb filling pressures. Each storage bulb is evacuated to less than 1μ prior to filling.

The counter is filled to the routine filling pressure of 5 atm. through the all-metal system shown in Figure 2.6. The detector is first pumped below 1 μ over a period of about 1 hour. The valve to the detector is closed and the 100 ml. stainless-steel trap is cooled by liquid N_2. Both the counter filling system and sample storage frame are then isolated from vacuum. The sample gas is distilled into the metal trap. After the filling system is isolated from the storage frame via a needle valve, the CH_4 can be expanded into the counter. After 15 minutes, when the gas temperature has reached equilibrium with its surroundings, the excess CH_4 is returned to the storage bulb as the counter filling pressure is adjusted to 5 atm. The filling pressure can be read to an accuracy of 0.2 p.s.i. ($\pm$ 0.25%). The counter valve is closed and the remaining CH_4 is condensed in the storage bulb.

The filling temperature is monitored by a thermometer probe within the counter shield. Since temperature variations between 15°C and 23°C have been observed, all sample activities are normalised to a constant filling temperature of 18°C. The 0.5 litre counter contains approximately

FIGURE 2.6

COUNTER FILLING SYSTEM



1.25 g. C for a 5 atm. fill of CH_4 at 18°C. Thus, in theory, the absolute minimum weight of sample carbon required prior to combustion is 1.25 g. However, a slight excess is necessary because of small losses in gas preparation and incomplete CH_4 recovery due to its slight vapour pressure at -196°C. In practice, where there is sufficient sample carbon, a 100% excess is prepared corresponding to a total CH_4 yield of 5 litre-atm. It should be noted that, by filling the counter to the same pressure with each gas and by normalising ^{14}C activities to 18°C, sample and standard activities can be directly compared without recourse to absolute counter volume or absolute activity measurements.

2.4 Measurement of Isotopic Fractionation

Isotopic fractionation occurs in the transfer of carbon between different phases of the environment. For example, mass-spectrometric studies have shown organic plants to be depleted in ^{13}C by approximately 2% compared to the atmosphere from which they assimilate CO_2 (Craig 1953). This is due to preferential uptake of ^{12}C during photosynthesis. Fractionation may also occur during the laboratory preparation of CO_2 and CH_4 if chemical yields in the preparation stages are less than 100%. A correction for this effect is therefore necessary before measured ^{14}C concentrations can be directly compared with a specified standard activity. It is assumed that the fractionation effect for ^{14}C is twice as large as for ^{13}C (Craig 1954 a).

Unfortunately, CH_4 is not suitable for mass-spectrometric measurement of sample $^{13}C/^{12}C$ ratios. This is partly because interpretation of the spectra would be rather difficult due to the successive loss of hydrogen ions of unit mass. The determinations of $^{13}C/^{12}C$ ratios are carried out on the 25 ml. CO_2 samples collected just before the CH_4 synthesis. No correction is made for any fractionation occurring in CH_4 synthesis, purification or storage. These processes do involve sample losses, as described in Section 2.3, but, since CH_4 synthesis yields are high (greater than 90%) and the majority of samples show activity agreement after 2 counting periods, it appears that fractionation is negligible. Confirmatory evidence is provided by the constancy of the ^{14}C activity of standard oxalic acid samples, even after several counting periods and many distillations (Table 2.2).

Sample $^{13}C/^{12}C$ ratios are measured using a Micromass 602 B mass spectrometer (V.G.Micromass Ltd., Winsford, Cheshire). This spectrometer is fitted with twin ion collectors which permit direct measurement of the deviation in sample $^{13}C/^{12}C$ ratio from the standard ratio. The primary standard is P.D.B. belemnite limestone. In practice, a secondary standard, previously intercalibrated with the belemnite standard, is employed. ^{13}C enrichment values are based on the general formula (Craig 1961):

$$\delta^{13}C = \frac{{}^{13}C/{}^{12}C_{\text{sample}} - {}^{13}C/{}^{12}C_{\text{standard}}}{{}^{13}C/{}^{12}C_{\text{standard}}} \times 1000 ‰$$

The precision of mass-spectrometric measurement of $\delta^{13}C$ is about $\pm$ 0.1‰ ($\pm 2\sigma$).

The use of $^{13}C/^{12}C$ ratios is not confined to the correction of ^{14}C activity measurements but can be of importance in the study of carbon distribution in nature. If there are small variations of $\delta^{13}C$ with time, between and within different reservoirs of the carbon cycle, then ^{13}C can be considered as a stable isotope tracer. Special CO_2 gas preparation techniques appropriate to this application of stable carbon isotope ratios and further mass-spectrometric procedures are discussed in Section 2.8.

2.5 ^{14}C Counting System

The counting system employed has been described by Sharp and Ellis (1965). The sample detector is a 0.5 litre internal gas proportional counter supplied by Beckman Instruments Inc., California. Two detectors can be accommodated within the concentric wall multiple anode anti-coincidence counter but only one is involved in this research project. The whole assembly is encased within a lead shield (J. Girdler & Co., London). Counter electronics, anti-coincidence system and power supply are of Beckman design. A block diagram of the counting system is shown in Figure 2.7.

(a) Detector, guard and shielding assembly

The detector was machined from a solid ingot of OFHC (oxygen free high conductivity) copper providing a 1.8 cm. thick copper wall which acts as a very clean inner lining to the shield (Figure 2.8). The interior surface of the detector is electroplated with pure nickel to absorb any alpha particles from the copper and to eliminate memory effects occasionally observed with pure copper cathodes. The outside of the detector is also nickel plated. Stainless-steel wire (diameter 0.001 in.) stretched to 90% of its elastic limit constitutes the anode. Satisfactory vacuum and pressure holding performances are obtained by using teflon as insulator material and by sealing the endplates of the detector with O-rings. The detector can be operated at gas filling pressures of up to 10 atm. CH_4.

Both inner and outer walls of the guard counter are heavy wall OFHC copper pipe with a combined wall thickness

FIGURE 2.7

BLOCK DIAGRAM OF COUNTING SYSTEM

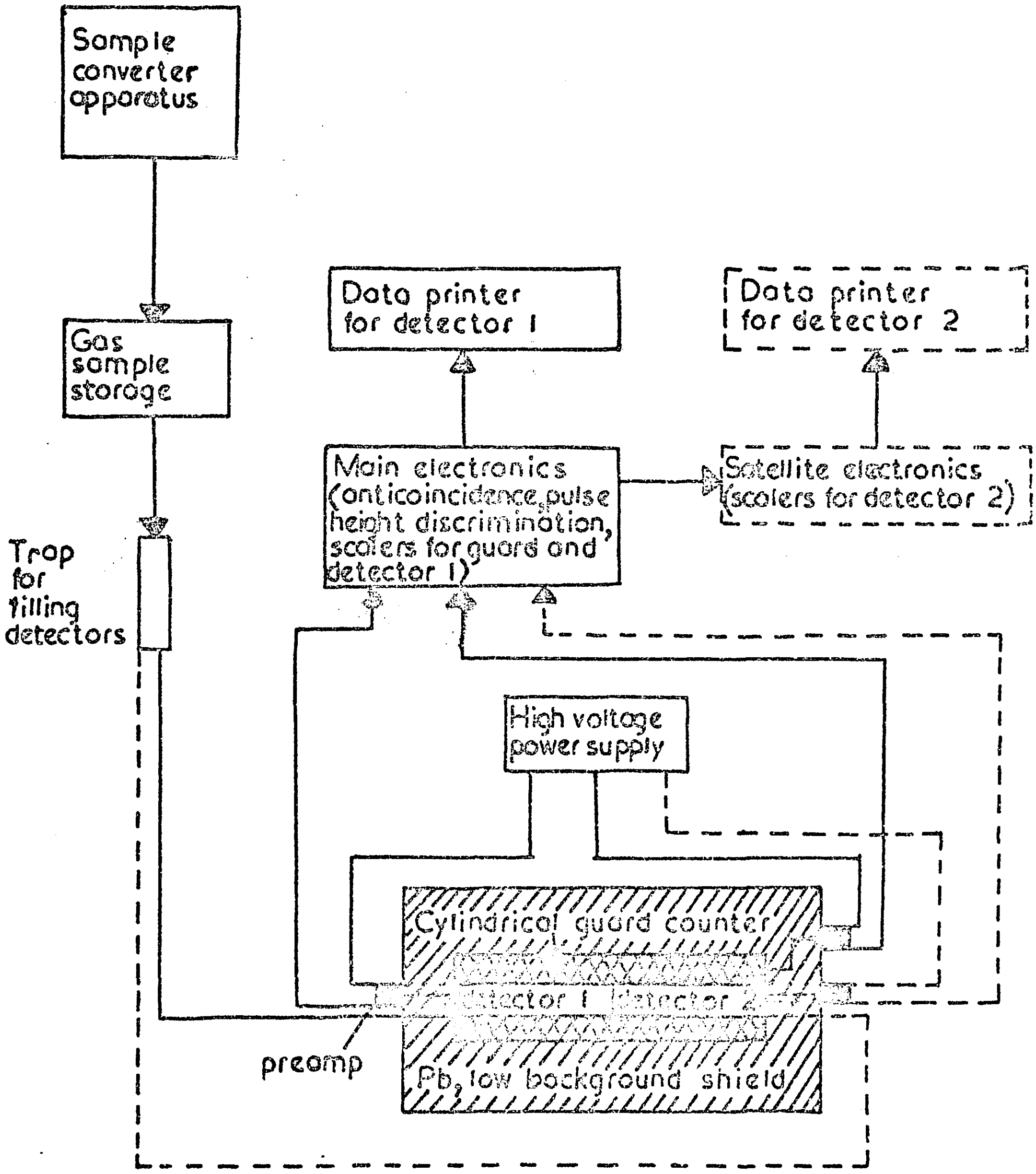
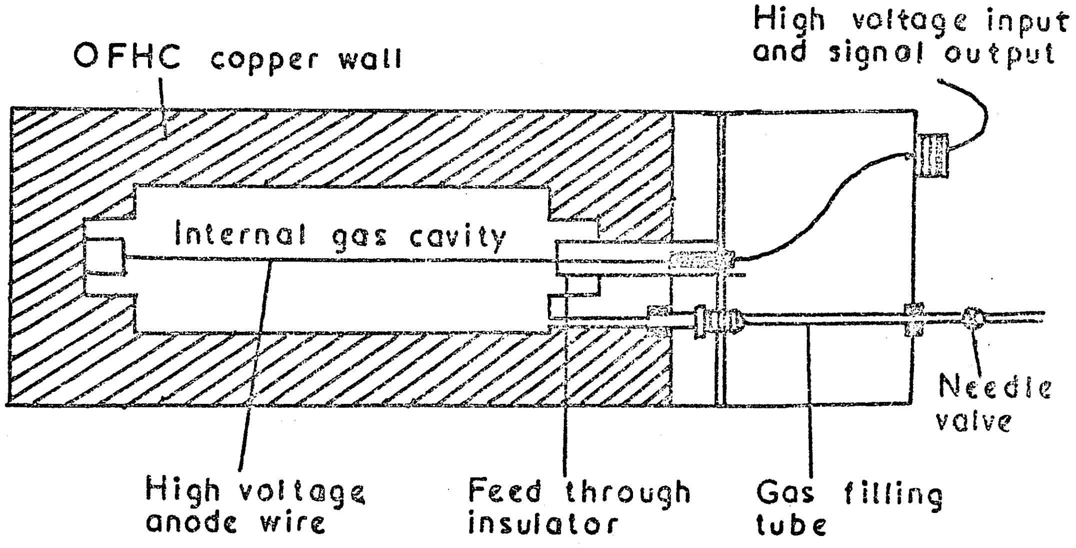


FIGURE 2.8

CROSS-SECTION DIAGRAM OF SAMPLE DETECTOR



of 2.5 cm. Thus, including the detector wall, there is an OFHC copper shield liner over 4 cm. thick surrounding the sample volume. The guard counter fits closely inside the shield to increase the efficiency of interception of the mu-mesons producing gamma showers in the shield. The anode wires, teflon insulators and O-ring seals are similar to those in the detector. The outer sleeve of the guard is easily removable to allow inspection and cleaning of the anode wire assembly.

The guard counter, which operates in the proportional region, is filled to 80 cm. Hg with inactive CH_4, each fill having a lifetime of 6 to 8 months. The use of a proportional guard counter with a proportional detector ensures that the guard channel is at least as sensitive to noise as the detector channel. Thus effective cancellation of simultaneous pulses in both counters is achieved.

The external shield is constructed of 4 in. thick "aged" lead, known to be relatively free from natural radioactivity and fission products. Its overall dimensions are 16 in. x 16 in. x 36 in., with a total weight of 2,960 lb. At each end the shield is fitted with a close-fitting lead plate door which opens freely on a thrust-bearing. This provides ready access to the counter unit inside.

The background count rate of the system largely represents the sum of the following components:

(1) alpha and beta radiation from radioactive contamination of the counter materials,

(2) ionising particles, mainly cosmic-ray mu-mesons, not detected by the guard,

(3) Compton, photo- and pair electrons produced by gamma radiation in the counter wall. The gamma

radiation may originate from radioactive contaminants in the lead shield or be produced by the interaction of cosmic-ray mu-mesons with the lead shield.

The "wall effect", due to the recoil electrons produced by gamma interactions in the counter walls, is believed to contribute 20 - 40% of the background count rate. Oeschger-type counters (Oeschger 1962) with guard and detector combined in a single unit reduce the "wall effect" contribution. The Beckman system, however, compensates for the increased background by a reduction in dead volume.

(b) Electronics and power supply

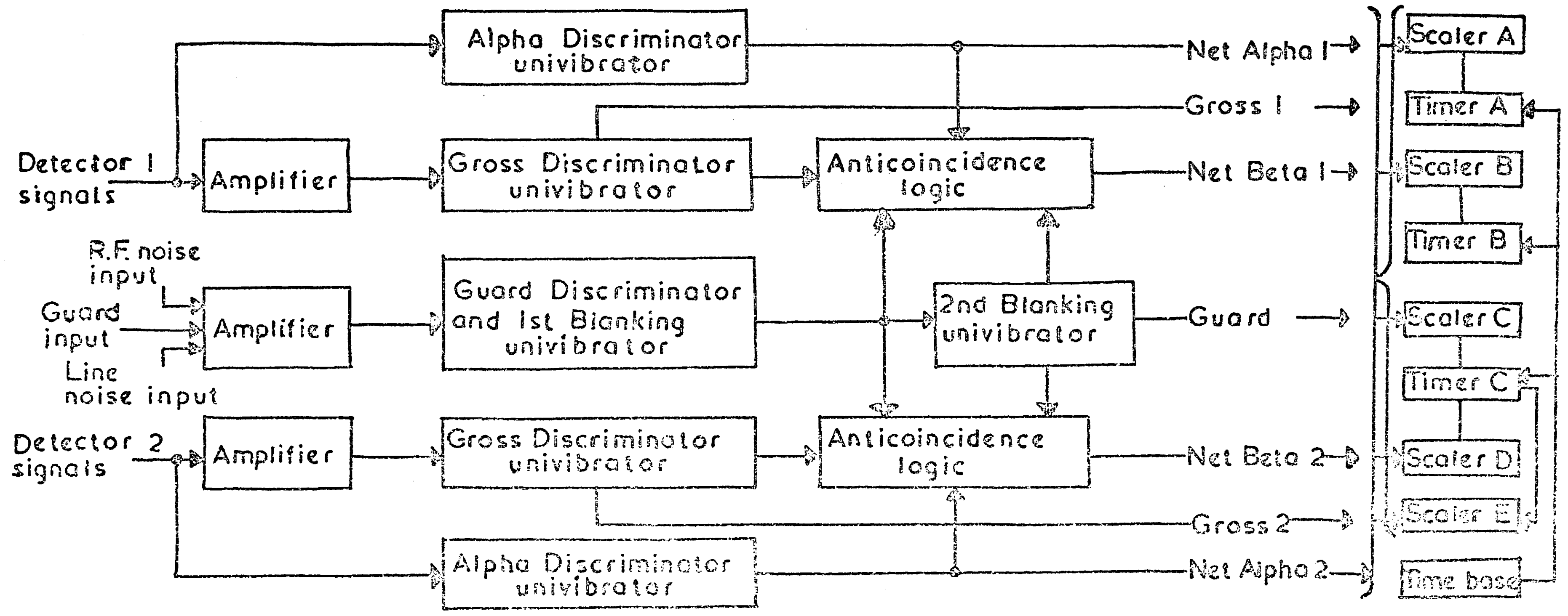
Seven data outputs are provided from the main electronics; net alpha counts, gross unguarded counts and net beta counts for each detector, and guard counts (Figure 2.9). Five scalers are available to switch to any of the seven outputs. The alpha data channels are triggered by an adjustable upper level discriminator. Four of the five scaler units are linked to automatic data printers. A print-out each 30 minutes allows examination of data for statistical reproducibility.

Noise elimination and control is one of the most important features of the electronics design. To eliminate environmental electrical noise the power line and a radio-frequency pickup antenna are coupled into the anticoincidence circuit. This ensures that the anticoincidence circuit is more sensitive to noise than the detectors.

A circuitry test programme is also built into the main electronics unit. Three internal test pulses simulate detector pulses at the detector inputs, mu-meson pulses coincident at the detector and guard inputs, and alpha pulses

FIGURE 2.9

MAIN ELECTRONICS BLOCK DIAGRAM



at the detector inputs. Using the 7 data outputs and 5 scalers a 105 step test programme can thoroughly check every circuit board in a few minutes.

The high voltage power supply provides 3 channels separately adjustable between 1,000 and 10,000 volts.

2.6 Counter Characteristics

(a) Plateaux

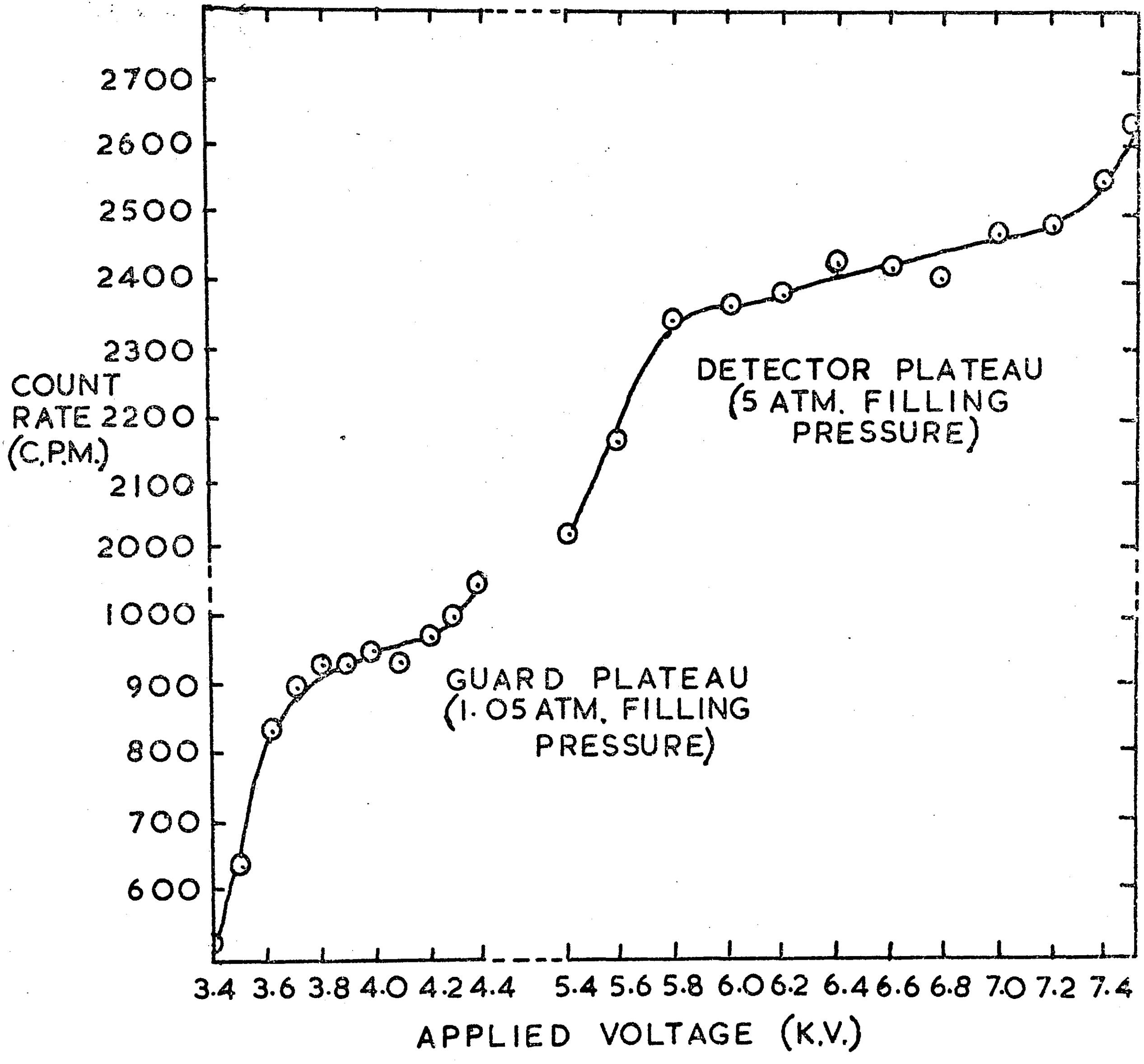
All initial calibration procedures were carried out using "pure tank" CH_4 obtained from Beckman Instruments Ltd., Glenrothes. This source of inactive CH_4 has been shown to be free from radioactive contamination and capable of producing results in excellent agreement with CH_4 synthesised from inactive materials in the laboratory (Baxter 1969, Ergin 1969). Detector plateaux are monitored using an external ^{137}Cs source to increase the count rate and improve statistics. The detector plateaux are commonly 1,500 volts in length with slopes less than 0.5% per 100 volts (Figure 2.10). Guard plateaux are 500 to 1,000 volts long with a slope less than 1% per 100 volts. At the routine filling pressures of 5 atm. and 1.05 atm., the detector and guard working voltages are approximately 6.4 KV. and 4.0 KV. respectively. The optimum detector filling pressure was selected as 5 atm. for the following reasons:

(1) the high voltage power unit was unstable at the continuous operating voltages (>8KV.) required for higher filling pressures (Ergin 1969),

(2) a filling pressure of 5 atm. is in accord with the production rate and handling capacity of the gas preparation system.

FIGURE 2.10

DETECTOR (^{137}Cs SOURCE) AND GUARD (COSMIC-RAY FLUX) PLATEAUX



(b) Operating voltage

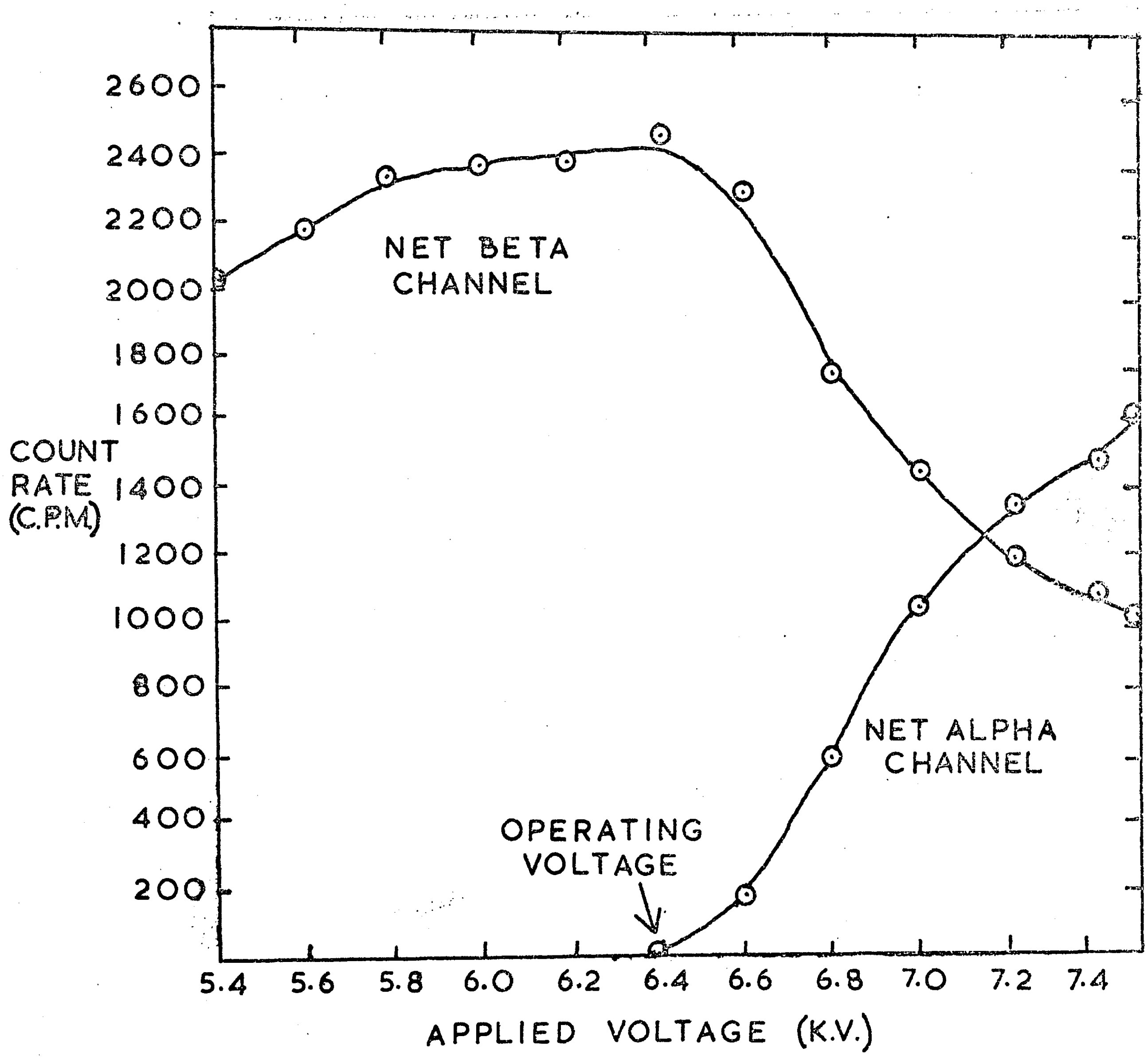
To compare count rates of different sample gases, it is necessary to operate at a constant gas gain i.e. a constant electron multiplication factor. Trace quantities of electronegative impurities in the counting gas decrease the electron multiplication and hence the distribution and amplitude of pulses in adjacent energy channels. CH_4 is much less susceptible to this effect than CO_2 but small variations in gas purity are unavoidable. Adjustment of the operating voltage compensates for any variation in gas purity. The operating voltage is determined by observing the distribution of counts in the net beta and net alpha channels, produced by an external ^{137}Cs source, as the applied high voltage is increased. (Figure 2.11). The upper discriminator is set so that counts just begin to appear in the net alpha channel at an applied voltage almost at the mid-point of the plateau. This voltage is chosen as the operating voltage. For routine filling pressures the operating voltage is in the range 6.4 ± 0.05 KV. Typically, less than 0.05 c.p.m. is registered in the upper channel for a 24 hour count of a sample gas. This channel is able to detect the presence of the alpha emitter ^{222}Rn in the counting gas.

(c) Background data

Background measurements are made weekly with a minimum of 4,000 counts recorded per run. The "tank" methane supplied by Beckman is used as the background gas. Inactive gases prepared from marble and anthracite have yielded data in agreement with those of "tank" methane (Baxter 1969, Ergin 1969). Similarly, in this research, CH_4 prepared from the hydrogenation of "tank" CO_2 (Messer Griesheim) recorded identical background levels.

FIGURE 2.11

DISTRIBUTION OF EVENTS INITIATED BY EXTERNAL ^{137}Cs SOURCE — DETERMINATION OF OPERATING VOLTAGE



An inverse linear relationship is evident between the background count rate and barometric pressure. At high pressures, the physical resistance of the atmosphere to the passage of cosmic-ray derived particles is greater than at low pressures. Hence, periods of high atmospheric pressure correspond to low background count rates and vice versa. Atmospheric pressure, continuously recorded by a laboratory barograph, ranged from 980 mb. to 1,040 mb. during the total period of sample counting. The mean barometric pressure is calculated for each sample counting period.

The linear regression for any series of data was calculated by computer analysis using the method of least squares fit. Figure 2.12 shows such an analysis for the period October 1969 - June 1971. The background count rate varies with atmospheric pressure by -0.12 c.p.m./cm. Hg or -0.009 c.p.m./mb. at 5 atm. filling pressure. The corresponding calculations are detailed in Appendix 1.

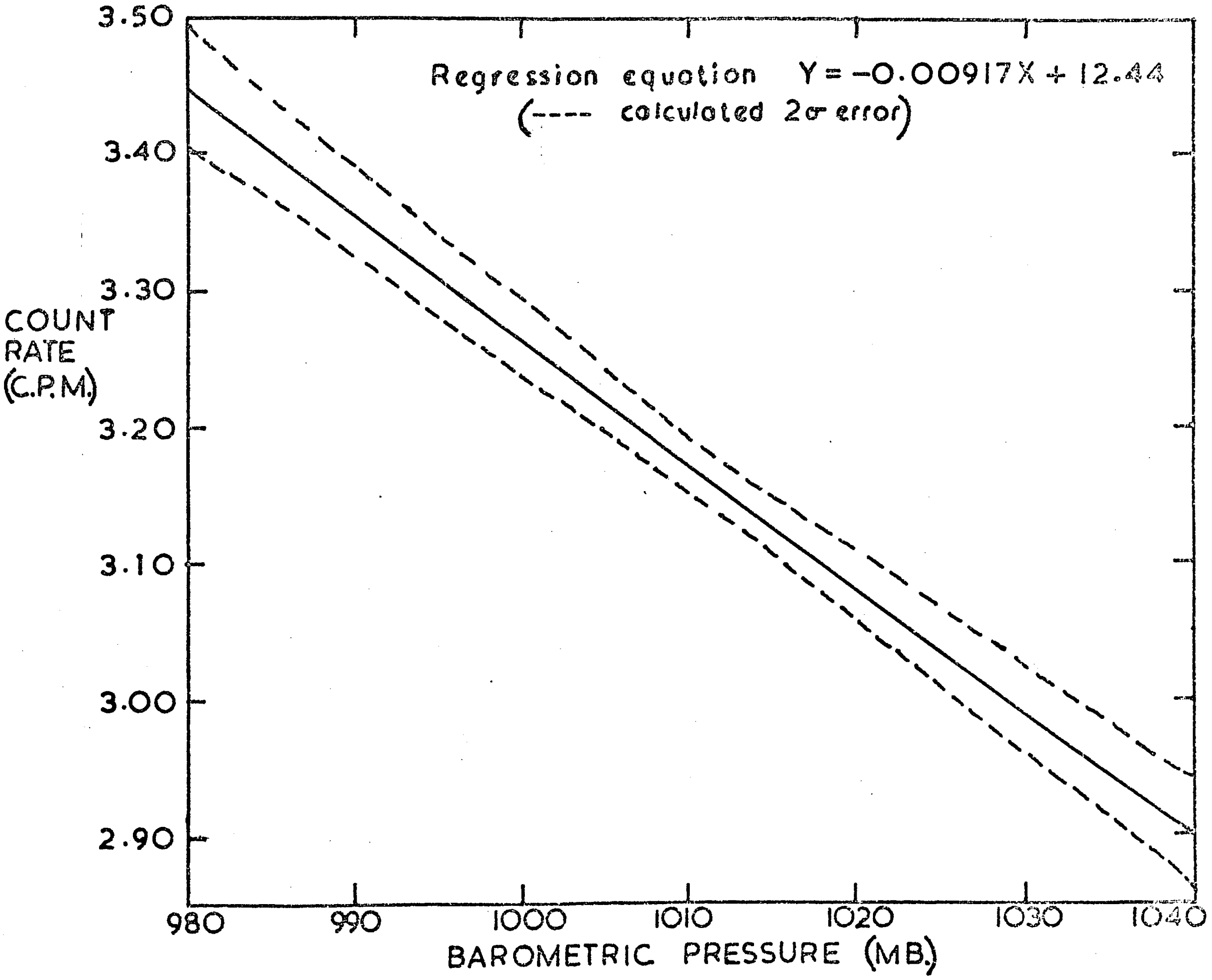
A small increase in background count rate has been observed since June 1971. This increase may reflect an enhanced cosmic-ray flux or may have resulted from minor modifications of the counting equipment. Regular monitoring of the background allows the gas counting programme to be divided into periods determined by the statistical agreement between series of background measurements.

(d) Modern standard count rates

The standard used is oxalic acid (National Bureau of Standards). The "natural" level is assumed equal to 95% of the ^{14}C concentration of this oxalic acid standard. The factor of 0.95 is based on the observation that 95% of the N.B.S. standard ^{14}C activity in 1958 equals the decay-corrected ^{14}C activity of 1890 wood samples (Broecker and

FIGURE 2.12

VARIATION OF BACKGROUND COUNT RATE
WITH BAROMETRIC PRESSURE
(OCTOBER 1969 — JUNE 1971)



Olson 1959). These wood samples are assumed free from the "Suess effect."

Where possible, measurements of the standard are made fortnightly. After correction of each standard count rate for background and filling temperature normalisation, the following additional corrections are made for radioactive decay and isotopic fractionation:

(1) 95% of the standard activity at 1st January, 1958 (t_o) is used as the international standard. Thus present day activities of N.B.S. oxalic acid must be corrected for ^{14}C decay since that time. The decay rate is 0.12‰ per year. Thus

$$A' = A\left[1 + \frac{0.12\ (t-t_o)}{1000}\right] -$$

where A' is the decay corrected activity (c.p.m.) and A is the measured activity (c.p.m.) at time t years.

(2) the isotopic fractionation correction is based on the mean value of -19‰ for $\delta^{13}C$ of N.B.S. oxalic acid relative to P.D.B. belemnite (Craig 1961). All modern standard activities are therefore corrected for fractionation relative to -19‰. Thus,

$$A_o = A'\left[1 - \frac{2\ (\delta^{13}C + 19)}{1000}\right]$$

where A_o is the final corrected modern activity (c.p.m.) and $\delta^{13}C$ is the $^{13}C/^{12}C$ ratio in the CO_2 relative to that of the P.D.B. belemnite.

Table 2.2 lists the activities of three of the N.B.S. oxalic acid modern standard gases used during this research. The consistency of the results confirms that the counting

TABLE 2.2

N.B.S. OXALIC ACID MODERN STANDARD ACTIVITIES

Sample No.	Date	Activity	
45	8-10-70	18.32 ± 0.14	
	15-10-70	18.43 ± 0.26	
	22-10-70	18.21 ± 0.26	
	5-11-70	18.58 ± 0.26	
	10-11-70	18.22 ± 0.26	
	24-11-70	18.45 ± 0.26	
	7-12-70	18.38 ± 0.26	
	9-01-71	18.20 ± 0.26	
		Mean 18.35 ± 0.09	(± 2σ)
82	23-04-71	18.60 ± 0.16	
	12-05-71	18.58 ± 0.26	
	19-05-71	18.42 ± 0.26	
	26-05-71	18.39 ± 0.26	
	24-06-71	18.32 ± 0.23	
	20-07-71	18.40 ± 0.28	
	28-07-71	18.67 ± 0.18	
	5-08-71	18.39 ± 0.26	
		Mean 18.47 ± 0.08	(± 2σ)
135	22-12-71	18.50 ± 0.27	
	28-12-71	18.47 ± 0.17	
	8-01-72	18.60 ± 0.26	
	19-01-72	18.19 ± 0.27	
	5-02-72	18.41 ± 0.18	
	22-02-72	18.41 ± 0.26	
	2-03-72	18.53 ± 0.26	
	22-03-72	18.36 ± 0.25	
	6-04-72	18.48 ± 0.26	
		Mean 18.44 ± 0.08	(± 2σ)

system and counting efficiency are stable.

(e) Sample gas count rates

Each gas is counted at least twice with a minimum cumulative total of 50,000 counts. The count rates are corrected for background, normalised to 18°C filling temperature and corrected for radioactive decay if the age of the sample is known. A mean value is then calculated for net counting rates which agree within $\pm\, 2\sigma$ counting limits.

2.7 Calculation of ^{14}C Concentrations

(a) Calculation of Δ

^{14}C concentrations are calculated relative to 95% of the N.B.S. oxalic standard. They are expressed in terms of $\delta^{14}C$ and Δ. The former term refers to the measured ^{14}C concentration prior to correction for isotopic fractionation. Using the method of Broecker and Olson (1961), calculations are performed as follows:

$$\delta^{14}C = \left[\frac{A_s}{0.95\ A_m} - 1 \right] \times 1000\ ‰$$

$$\Delta = \delta^{14}C - (2\delta^{13}C + 50)\left(1 + \frac{\delta^{14}C}{1000}\right) ‰$$

where A_s is the mean sample count rate (c.p.m.),

A_m is the mean modern standard count rate (c.p.m.) and

$$\delta^{13}C = \frac{{}^{13}C/{}^{12}C_{\text{sample}} - {}^{13}C/{}^{12}C_{\text{P.D.B.}}}{{}^{13}C/{}^{12}C_{\text{P.D.B.}}} \times 1000\ ‰$$

Thus a typical pre-"Suess effect" $\delta^{13}C$ value of −25‰ for wood brings the Δ value of 1890 wood close to zero.

$\delta^{14}C$ and Δ are usually quoted to $\pm\, 1\sigma$ error which relates solely to the random uncertainties associated with sample, modern, background and mass-spectrometric measurements.

The error on $\delta^{14}C$ is calculated from the relationship,

$$\pm\ 1\sigma = \pm \frac{1000\ A_s}{0.95\ A_m}\left[\left(\frac{\sigma_{A_s}}{A_s}\right)^2 + \left(\frac{\sigma_{A_m}}{A_m}\right)^2\right]^{\frac{1}{2}}$$

The error on Δ is calculated using the formula of Callow et al. (1965),

$$\pm\ 1\sigma = \left[\left(1 - \frac{(2\delta^{13}C + 50)}{1000}\right)^2 \sigma^2(\delta^{14}C) + 4\left(1 + \frac{\delta^{14}C}{1000}\right)^2 \sigma^2(\delta^{13}C)\right]^{\frac{1}{2}}$$

(b) Age determination

By a decision of the 1962 Cambridge Conference on Radiocarbon Dating, 5,568 years is still used as the half-life of ^{14}C despite improved measurements giving a mean value of 5,730 years (Godwin 1962). This decision was taken to avoid the confusion which would arise if the volumes of published dates required revision. If necessary, ^{14}C ages can be converted to dates based on the 5,730 year half-life through multiplication by the factor 1.03.

A sample age, T years, is obtained from:

$$T = 8033 \log_e \frac{1}{1 + (\Delta \times 10^{-3})}$$

where $$8033 = \frac{t_{\frac{1}{2}}}{0.693}$$

Limits of the age are given by:

$$(T + t_1, T - t_2) = 8033 \log_e \frac{1}{1 + \left[(\Delta \pm \sigma(\Delta)) \times 10^{-3}\right]}$$

It is customary procedure, as employed in the journal Radiocarbon, to report all ages in years B.P. (before present), where the present is taken as 1950.

(c) Intercalibration of counting system

Several interlaboratory calibration samples were measured to check the validity of the laboratory and counting techniques. Good agreement was obtained, within statistical uncertainty, with the data of other radiocarbon laboratories (Table 2.3). These samples were run periodically to confirm the long-term reliability of the system.

2.8 Mass Spectrometry

A study was made of 20th Century variations of $^{13}C/^{12}C$ ratios in the wood of annual tree rings (Section 5.3(c)). The following experimental procedures were employed.

(a) Sample preparation

A simple combustion system is used for preparing CO_2 from small quantities of sample material (Figure 2.13). The combustion system used in the preparation of samples for ^{14}C assay (Figure 2.2) is unsuitable because of the small size of CO_2 samples required for mass-spectrometric measurements and the need for consistent 100% yields in isotopic fractionation studies. A suitable weight of sample (35 mg. wood) is placed in a quartz boat which is inserted into the quartz tube. A stream of CO_2-free O_2 is passed over the sample which is heated from below by a burner. The gases formed then pass through quartz wool heated by a burner and 2 furnace-heated sections of the tube separated by quartz wool. A few inches in length of CuO, to complete the oxidation, are maintained at 700°C by the first furnace. Similarly, MnO_2, to remove oxides of nitrogen, is held at 500°C by the second furnace. The gases pass through 2 dry ice/acetone spiral traps to

TABLE 2.3

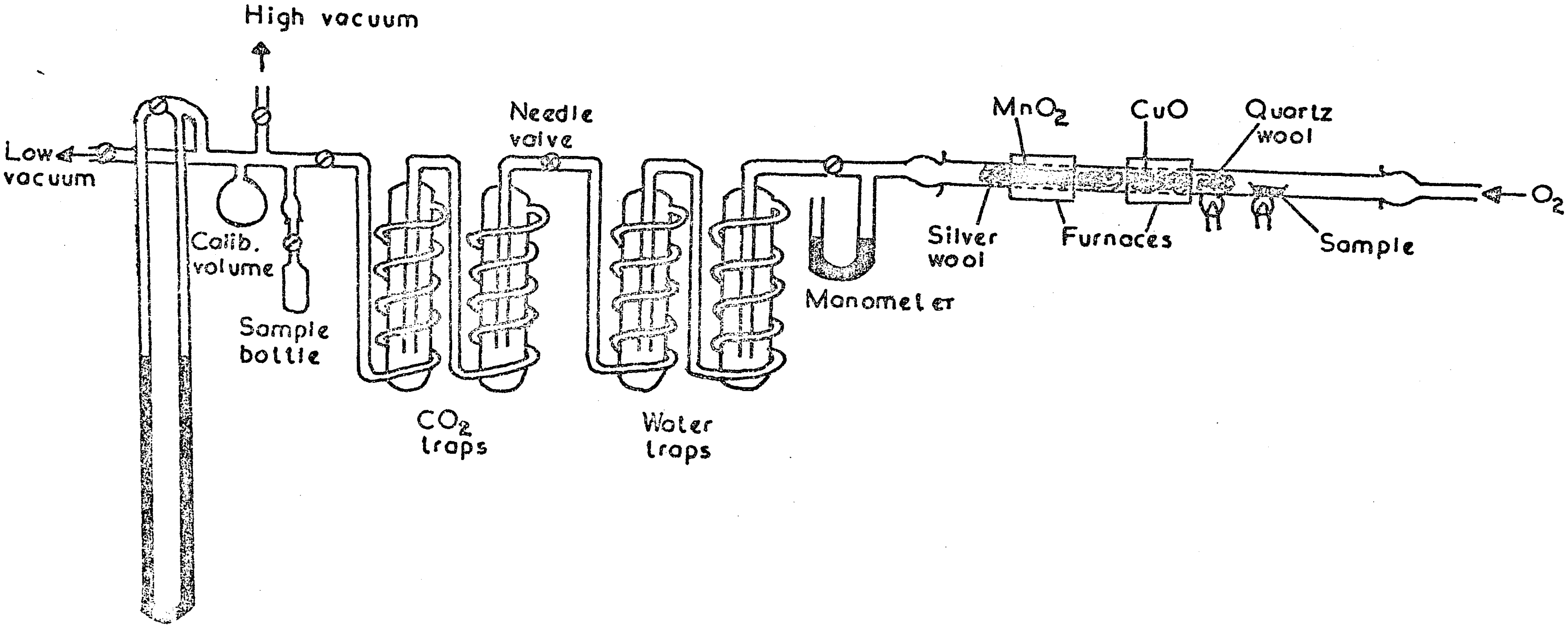
INTERCALIBRATION DATING SAMPLES

Sample	Age (Years B.P.) ±1σ This Laboratory	Other laboratories
Kilphedir Hut Circles Charcoal	2,038±49	2,100±80 (S.R.R.C., Lamont)
Wood Calder	2,630±57	2,569±80 (S.R.R.C.) 2,585±100 (Stockholm)
Oxbow Wood	4,289±53	4,280±100 (Stockholm)
Wadji Wood	4,695±57	4,656±60 (S.R.R.C.) 4,496±80 (B.M.)

S.R.R.C.	Scottish Research Reactor Centre, East Kilbride
B.M.	British Museum, London

FIGURE 2.13

MICRO-COMBUSTION SYSTEM
(PREPARATION OF MASS-SPECTROMETRIC CO_2 SAMPLES)



remove any water vapour present.

A needle valve separates the combustion section from the CO_2 collection line. Pumping through the valve maintains a negative pressure gradient of about 4 cm. Hg. The CO_2 is condensed in 2 liquid N_2 spiral traps. When combustion is considered complete, usually 10 minutes after ignition of the sample, the needle valve is closed and the 2 collection traps pumped to 1μ. After isolation from the pump, the first liquid N_2 trap is removed and the CO_2 distilled into the second trap which is again pumped to 1μ. The CO_2 is then condensed in the calibrated bulb. The tap to the CO_2 collection traps is closed and the CO_2 expanded in the known volume for measurement of yield. The sample gas is then condensed into a 25 ml. glass sampler for mass-spectrometric measurement.

Combustion of spectrographic pure graphite samples, under the above conditions, confirmed that yields are consistently close to 100%.

(b) Measuring technique

The abundance ratio measurements of C and O are carried out on the prepared CO_2. The $^{13}C/^{12}C$ and $^{18}O/^{16}O$ values are deduced from the beam intensity ratios 45/44 and 46/44+45 respectively,

where m/e 44 represents $^{12}C^{16}O^{16}O$ (98.42%)
m/e 45 " $^{12}C^{16}O^{17}O$ (0.08%) + $^{13}C^{16}O^{16}O$ (1.1%)
m/e 46 " $^{12}C^{16}O^{18}O$ (0.4%) + $^{12}C^{17}O^{17}O$ (~ 0%) + $^{13}C^{16}O^{17}O$ (~ 0%)

As before, deviations with respect to a standard sample are measured, not the absolute isotopic ratios. All isotopic analyses are carried out using the double collecting, 90° deflection, 6 cm. radius Micromass 602 B mass spectrometer mentioned previously (Section 2.4). A double gas all-metal inlet system allows a rapid comparison between sample and standard. The dimensions of capillary leak and the inlet pressure (~6 cm. Hg) are such that the inlet gas flow is viscous, preventing isotopic fractionation in the sample vessel (Brunnée and Voshage 1964). Ratios are obtained on a digital output connected to a pen recorder.

About 8 successive differences of sample and standard ratio are measured on the 45/44 ion beam. Only 3 differences are measured on the 46/44+45 ion beam; analysis of these enables a correction to be applied for ^{17}O contribution by $^{12}C^{16}O^{17}O$ to the mass 45 peak.

(c) Evaluation of $\delta^{13}C$

The averages of the sample 45/44 ratios, standard 45/44 ratios and differences are expressed as R_1', R_0' and Δ' respectively. An initial correction is applied for the slight amount of mixing of the sample and standard gases in the inlet system. Thus, the corrected ratios, R_1 and R_0, are obtained. Δ, the corrected difference in the mass 45/44 ratios of the sample and standard gas, is obtained from:

$$\Delta = \Delta' \left[\frac{R_1 - R_0}{R_1' - R_0'} \right]$$

The measured deviation, $\delta^{13}C_m$, of the sample from the standard is given by

$$\delta^{13}C_m = \frac{\Delta}{R_0} \times 1000 ‰ .$$

Since R is actually the ratio $(^{13}C^{16}O^{16}O + {}^{12}C^{16}O^{17}O)/{}^{12}C^{16}O^{16}O$, a correction factor must be applied for the abundance of ^{17}O. Since enrichments for ^{17}O and ^{18}O differ by a factor of 2 (Craig 1957b) measurements of the 46/44+45 ion beam enables a correction to be applied to $\delta^{13}C_m$ through $\delta^{18}O$. For correction of $\delta^{13}C_m$, $\delta^{18}O$ is given by

$$\delta^{18}O = \frac{\Delta''}{R''} \times 1000 \text{‰}$$

where Δ'' represents the mean of the difference in 46/44+45 ratios of the sample and standard gases,

and R'' represents the mean 46/44+45 standard ratio.

Then the corrected value, $\delta^{13}C_{corr}$, relative to the working standard is

$$\delta^{13}C_{corr} = 1.065\ \delta^{13}C_m - 0.0325\ \delta^{18}O$$

(derived from Craig 1957b).

To express the result relative to the primary P.D.B. belemnite standard, the following formula is invoked:

$$\delta^{13}C_{sample} = \delta^{13}C_{corr} - \delta^{13}C_{std} + 10^{-3}(\delta^{13}C_{corr} \times \delta^{13}C_{std})$$

(Craig 1957b),

where $\delta^{13}C_{sample}$ is the fully corrected $\delta^{13}C$ relative to P.D.B.,

and $\delta^{13}C_{std}$ is the fully corrected $\delta^{13}C$ of the working standard relative to P.D.B.

Appendix 2 gives details of the computer programme for obtaining $\delta^{13}C_{corr}$ and $\delta^{18}O$ with associated statistical errors. Typical precision of measurement is 0.05‰ (± 1σ).

(d) Calibration and reproducibility

The working standard gas was derived from the combustion of a sample of human brain. The calibration of the brain CO_2 was performed by comparison with Solenhofen limestone, the N.B.S. reference sample No.20. Using a value for NBS 20 relative to P.D.B. of $\delta^{13}C_{PDB}$(NBS 20) = -1.03‰ (Craig 1957b), $\delta^{13}C_{PDB}$(brain CO_2) was calculated to be -20.67‰ (Table 2.4).

TABLE 2.4

CALIBRATION OF WORKING STANDARD (BRAIN CO_2) FOR ISOTOPIC FRACTIONATION MEASUREMENTS

Date	$\delta^{13}C_{PDB}$(brain CO_2)‰
1-07-71	-20.86
16-08-71	-20.74
2-09-71	-20.55
16-12-71	-20.51
3-02-72	-20.56
3-03-72	-20.81
	Mean -20.67 ± 0.17

Similarly, the N.B.S. reference sample No.21, spectrographic graphite, was compared with NBS 20. A value of -26.19‰ was obtained. Thus $\delta^{13}C_{PDB}$(NBS 21) was calculated to be -27.22‰, in reasonable agreement with other workers' results (Craig 1957b, Ault 1959, Holt 1960).

It was shown that fractionation at the inlet system is negligible by analysing several aliquots from the same sample bottle at different times.

Replicate analyses performed on pure graphite samples indicated the overall precision of measurement to be of the order of ± 0.2‰ (Table 2.5). This was possibly due to slight inhomogeneity in the samples.

TABLE 2.5

REPLICATE ANALYSES OF PURE GRAPHITE RELATIVE TO BRAIN STANDARD

Sample	$\delta^{13}C_{Brain}$ (Graphite)‰
1	-4.51
2	-4.17
3	-4.76
4	-4.49
5	-4.35
6	-4.71
Mean	-4.50 ± 0.2

CHAPTER 3

TREE RINGS AND OTHER PLANT MATERIALS AS INDICATORS OF ATMOSPHERIC ^{14}C CONCENTRATIONS

3.1 Introduction

A study of past atmospheric ^{14}C concentrations requires samples of known age which accurately reflect the prevailing atmospheric ^{14}C activity at their time and place of growth. For the measurement of annual ^{14}C levels it is imperative that samples indicate the mean atmospheric ^{14}C concentration during a time period of 1 year or less. In addition, there must not have been any exchange of carbon between "death" (i.e. removal from the carbon exchange cycle) and analysis.

Plant materials which grow predominantly during the summer months seem the most obvious source of suitable sample carbon for the study of annual ^{14}C levels. The direct fixation of atmospheric CO_2 for cell synthesis suggests that plant ^{14}C levels will be closely related to those of the atmosphere. However, the uptake of soil CO_2 derived from decaying vegetation and carbonate materials in the soil may disturb the anticipated correlation. Previous studies (Broecker and Walton 1959, Broecker and Olson 1960, Nydal 1963, Walton et al. 1967, Tauber 1967, L'Orange and Zimen 1968, Baxter and Walton 1971) have shown that there is a close correlation between nuclear-era ^{14}C levels in atmospheric CO_2 and short-lived biospheric samples (grain, tree seeds, spirits from grain samples, wines from grapes). Thus, root uptake of soil CO_2 appears insignificant for these sample types. Provided that this type of contamination is avoided by rejecting materials grown on predominantly limestone soils, short-lived biospheric samples are valid indicators of annual atmospheric ^{14}C concentrations. Indeed, Baxter and Walton's survey of 20th Century annual ^{14}C levels was based on the analysis of old wines, spirits and seeds. (1971). For previous centuries, this method of approach is obviously impracticable through lack of documented grain and alcohol samples.

Individual tree rings provide the most readily available source of carbonaceous material for the study of pre-20th Century annual ^{14}C levels. Ten-year sections have, of course, been extensively used in the bristlecone-pine calibration of the radiocarbon time-scale. It is , however, necessary to establish the validity of single rings as indicators of annual ^{14}C concentrations in the atmosphere. Baxter and Walton (1971) questioned the use of single tree rings for their work because of the possibility of carbon exchange between adjacent rings in the outer sapwood layer (Broecker and Olson 1961). The marked variations in atmospheric ^{14}C content caused by nuclear weapon testing now present an ideal opportunity for the study of transfer processes within trees and for an assessment of individual tree rings as reliable annual ^{14}C indicators.

3.2 Single Tree Rings as Annual Atmospheric ^{14}C Indicators

(a) Tree ring growth

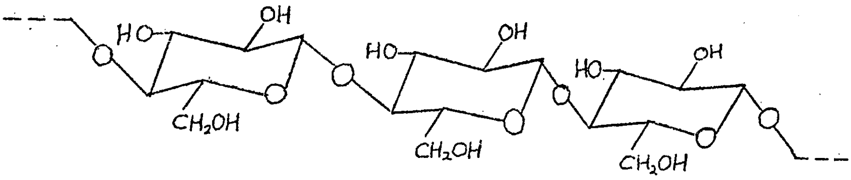
Wood from the temperate zone is generally characterised by growth rings resulting from variations in growing conditions which affect the size and wall thickness of cells. These rings are formed annually as a result of the contrast between the last-formed summerwood (latewood) of one year and the first-formed springwood (earlywood) of the following year. The first wood cells formed by the cambium in the spring of the year usually have larger cavities and thinner walls than latewood cells, providing a contrast which is commonly evident to the naked eye.

Wood can be subdivided into sapwood and heartwood, the former typical of younger wood, the latter of the inner core of older wood. Sapwood contains living parenchyma cells and is the physiologically active wood of the tree. The parenchyma are usually thin-walled cells which function as the physiologically active living tissue in the sapwood and provide for food storage. Most of the parenchyma are found in wood rays that radiate from the centre outward to the bark. These rays also provide a means of lateral communication between the wood cells, cambium and living bark. In some species, the parenchyma may carry resins and gums. As the sapwood becomes older, its cells die and are infiltrated with various substances which darken the colour of the wood. This heartwood contains no living cells, is less permeable to liquids and is more resistant to decay and insect attack. Its main function is the physical support of the tree.

(b) Chemical composition of wood

Wood is a composite of several complex organic compounds. On complete degradative analysis it is found to consist of approximately 50% carbon, 6% hydrogen and 44% oxygen. The cell wall is composed of a framework of interconnected chain molecules of cellulose encrusted with other carbohydrates called hemicelluloses, lignin and a number of extraneous materials. The cementing substance between cells consists largely of calcium and magnesium pectate and within the cell cavities, particularly in heartwood, there is often appreciable accumulation of materials such as resins, gums, fats, tannins, pigments and minerals.

Cellulose, which constitutes about 45 - 60% of wood, is a glucose polymer of high molecular weight (50,000 - 1,000,000) and is the main structural material of all plants. It is believed that cellulose is completely linear and that the glucose units are joined by 1 - 4 linkages i.e.



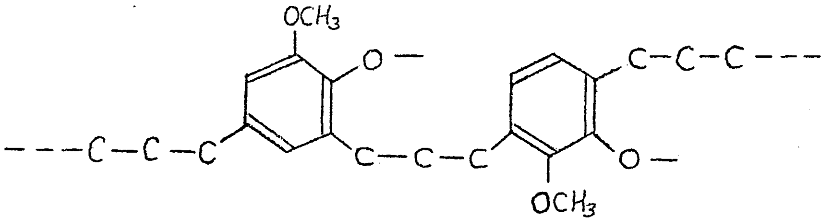
The long chains lie side by side to form "bundles" which are held together by hydrogen bonding between the neighbouring hydroxyl groups in different molecules. These "bundles" are twisted together to form rope-like structures which are themselves grouped to form macroscopically visible cellulose fibres. In wood the cellulose "ropes" are embedded in lignin which stiffens the structure and is responsible for most of the physical strength of the wood.

The principal reaction of cellulose involves the hydroxyl groups and it therefore undergoes reactions typical of alcohols. Cellulose, however, is soluble in base since the hydroxyl groups are more acidic than those of simple alcohols because of substituent effects exerted by neighbouring oxygen atoms. Treatment of cellulose with very strong acid or very strong base therefore gives degradation by cleavage of the glycoside linkages.

Hemicelluloses, the closely related carbohydrate compounds which constitute 15 - 25% of wood, are degraded in rather less severe conditions e.g. by aqueous acid.

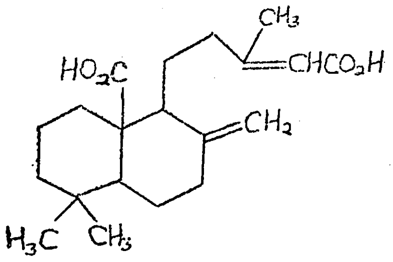
In view of the structure and molecular weight of cellulose in natural wood it may be assumed that it will be insoluble in virtually any liquid in the wood. Since extreme conditions are required for cleavage of the glycoside linkages, degradation of cellulose in wood under natural conditions should not occur. It is therefore reasonable to assume that, once formed, no transfer of cellulose will occur within a tree.

Lignin, which constitutes about 15 - 35% wood, is a non-carbohydrate polymer whose structure has not yet been completely defined. Degradative studies have led to the proposal that the basic unit of lignin is of the form:

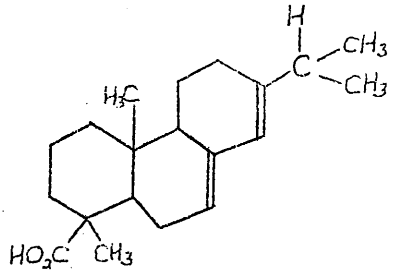


The low reactivity and complete insolubility of lignin in inert solvents suggest that it will remain essentially localised in wood and will not transfer between rings.

The amount of extraneous materials, or extractives, in wood depends largely upon the species and varies from sapwood to heartwood. The term resin will be used here to represent the mixture of compounds that can be extracted from wood with inert solvents. Resin compounds are mainly polyisoprenoids and an important group are the resin acids. These are diterpenes (C_{20} compounds) such as agathic acid and abietic acid.



Agathic acid



Abietic acid

Resins, in contrast to cellulose and lignin, are composed of small molecules and are soluble in inert solvents. Also resin molecules contain fairly reactive sites such as the carboxyl groups in the above compounds. Therefore transfer of resins between individual tree rings could possibly occur.

(c) Factors affecting the validity of single tree rings as indicators of atmospheric ^{14}C concentrations

The use of individual tree rings as indicators of annual atmospheric ^{14}C levels can only be considered valid if the following conditions are fulfilled:

(1) the wood comprising a tree ring, or some isolable and identifiable component, must have a ^{14}C content identical to the atmospheric concentration at the time of formation,

(2) no gain or loss of ^{14}C must occur, other than by radioactive decay, after the formation of the ring.

There are several factors which could invalidate the use of single tree rings as annual atmospheric ^{14}C indicators:

(1) if the tree can store a food supply, in the roots or wood rays for example, and use this as a nutrient material to build new rings, then

^{14}C which has been stored for some time may be incorporated in the outermost ring. Then the ^{14}C content would differ from the atmospheric level.

(2) if the roots take in CO_2 or dissolved organic materials from the soil in which the tree is growing, then significant differences in ^{14}C content could occur between the outermost ring and the atmosphere.

(3) if there is any transfer of material from outer rings to inner rings, then the inner rings could be contaminated with additional amounts of ^{14}C from the younger outer rings. It is possible that resin is quite mobile within a tree and may be transferred by means of the radial wood rays. It is extremely improbable that solid cellulose and lignin would undergo transfer in this way.

(4) the conversion of soft, light-coloured, living sapwood to hard, dark-coloured, dead heartwood may alter the ^{14}C content of a ring.

(5) in the biogenetic processes which build up the wood of a tree, isotopic fractionation occurs i.e. there is discrimination against ^{13}C and ^{14}C in favour of ^{12}C. Consequently, there is a lower ^{14}C concentration in the outermost ring than in the atmosphere. This effect is corrected by stable isotope mass spectrometry.

(6) for a tree growing at high altitudes, such as the bristlecone pine, interaction with cosmic radiation may produce ^{14}C in situ through

(n,p) reaction on the nitrogen contained in the tree. (Berger 1970).

The quantitative assessment of these effects is important both for the use of single rings as annual ^{14}C indicators and for the long-term bristlecone-pine calibration of the radiocarbon time-scale.

(d) Previous data

Fairhall and Young (1970) have found that the outer sapwood rings of a western redcedar from the U.S.A. showed an increase in "bomb" ^{14}C which lagged slightly behind the levels of ^{14}C prevailing in the atmosphere. This lag they attributed to a holdover of food supply extending over several years. Acetone extractives from the darker outermost heartwood rings (1943 - 49) showed significant amounts of excess ^{14}C e.g. the ^{14}C activity of the 1949 heartwood-ring extractive was comparable with that of the outermost sapwood ring. It was concluded that the extractives are formed as metabolites in the outermost growth ring and are deposited in the dead cells at the periphery of the heartwood.

However, an initial study by Wilson (1961) on the ^{14}C levels of components of recent radiata-pine tree rings from New Zealand showed close agreement between the cellulose fraction and the acetone/ethyl acetate heartwood extractives. Furthermore, the ^{14}C activity of the extractives differed markedly from that of the atmosphere at the time of heartwood formation. On the basis of these results, Wilson suggested that the sapwood of a pine tree ring always contains the material which constitutes the heartwood extractives after sapwood to heartwood conversion has taken place. Later work by Wilson (1963a) indicated a significant difference between the cellulose fraction and acetone extractives (resin) of recent outer rings. As the ^{14}C activity of the resin of each ring was considerably lower than that of the atmosphere at the time of felling the tree, Wilson concluded that the lateral circulation through resin canals is rather slow. Additional work showed that the cellulose of each ring is not in dynamic equilibrium with the metabolism of the tree but that, once synthesised, remains fixed. However, the ^{14}C levels of the corresponding water-soluble carbohydrate fractions were higher than those of the cellulose fractions. This may be due to the metabolism of some of the parenchyma cells in the wood rays (Wilson 1963b).

Olsson et al. (1970, 1972) have observed a "bomb" ^{14}C effect in the organic solvent extract of tree rings of pine from Sweden grown 1945 - 1950. This effect was attributed to radial movement of nutrients in the parenchyma cells. It is interesting to note that the ^{14}C activity of the inorganic base extract, while reflecting bomb levels, was lower than that of the organic extract. Olsson commented that standard treatment with inorganic solvents may be insufficient for precise work e.g. calibration of the radiocarbon time-scale.

Berger (1970) has also measured "bomb" ^{14}C in recent tree rings. His studies on bristlecone pine and European oak indicated a close correlation between atmospheric ^{14}C levels and tree-ring ^{14}C content for both species. Thus any holdover of food supply was not apparent. In addition, he concluded that, at most, transfer of ^{14}C between rings represents a minor effect for these species.

The above data serve to indicate the lack of agreement about the extent of food holdover and resin transfer within trees. Furthermore, there is a wide range of opinion as to the solvents which should be used in the pretreatment of wood samples. Some laboratories employ both organic (e.g. acetone, ethyl acetate) and inorganic (e.g. HCl, NaOH) solvents. Others consider either an organic or inorganic pretreatment as sufficient. There is therefore a need for more research to determine the validity of single tree rings as indicators of atmospheric ^{14}C levels and to establish a standard pretreatment system for radiocarbon analysis of wood.

3.3 ^{14}C Content of Nuclear Era Tree Rings

(a) Aims

An essential part of this research programme was the measurement of the distribution of "bomb" ^{14}C within recent tree rings. The aims of the project were:

(1) to determine the effects of resin transfer and food holdover in the tree and hence to assess the validity of single tree rings as indicators of atmospheric ^{14}C content at the time of their formation,

(2) to study different wood fractions and extraction techniques and to assess their value in the pretreatment of wood for radiocarbon analysis.

(b) Sample selection

The samples studied were single tree rings from a Scottish silver fir (Abies nobilis) obtained from the Forestry Commision. The tree, from the Glengarry Forest, Inverness-shire (57°N, 5°W) was planted in 1937 and felled in 1970. This particular species was selected because it has a rapid growth rate giving rise to wide rings. It was hoped that this would allow sufficient wood to be obtained for a given year to permit separation of different fractions. The section of the tree was taken from above waist-height to ensure that no soil CO_2 had been incorporated in the wood under study. The area from which the tree was obtained is free from any localised "Suess effect". The age of a given ring was obtained by assuming each ring represents 1 year's growth. This assumption was justified by the fact that the total number of rings was equal to the number of years for which the tree was known to grow.

The sapwood rings studied were all from the nuclear era. Marked variations in atmospheric ^{14}C concentrations from year to year throughout this period (Figure 1.3) ensure that any food storage or resin transfer in the tree should introduce a discrepancy between recorded atmospheric ^{14}C levels and measured wood ^{14}C concentrations.

(c) Sample pretreatment

The sections taken from the tree were allowed to dry for a few months prior to the separation of the individual rings by chisel. The following pretreatment procedures were employed:

(1) for whole wood ^{14}C analysis, about 6 g. were splintered for combustion.

(2) samples of 1958, 1962, 1963, 1964 and 1969 wood were extracted with petroleum ether (40 - 60°C boiling range). The wood was finely divided before extraction in a Soxhlet apparatus for at least 24 hours. After extraction, samples were dried at 100°C for at least 24 hours to remove any traces of solvent. The extractives

from the 1964 and 1969 wood were collected by evaporation of the solvent.

(3) samples of 1963 and 1964 wood were extracted using acetone as solvent.

(4) the cellulose fraction was obtained from each of the 1962, 1963, 1964, and 1969 rings. Initial extraction of the wood with petroleum ether was followed by heating the extracted wood to 70°C in a solution of 110 ml. of 1N HCl plus 80 g. $NaClO_2$ in 3 l. of distilled water. This process dissolves all components of the wood except cellulose. Additional quantities of HCl and $NaClO_2$ were added if bleaching was incomplete. After 36 - 48 hours the soft, white cellulose was collected, washed with distilled water, oven-dried (100°C) and finally charred at 500°C prior to combustion.

(5) the lignin fraction was obtained from the 1963 ring by the 72% H_2SO_4 method. The ether-extracted wood was weighed and 15 ml. 72% H_2SO_4 /g. wood were added. The mixture was stirred until gelatinization was complete and then allowed to stand, with occasional stirring, at room temperature for 48 hours. After dilution of the reaction product with water, the lignin was filtered off and washed until almost free of H_2SO_4. The product was then heated in 0.5% HCl on a steam bath for several hours to remove any combined H_2SO_4 and to hydrolyse any remaining carbohydrate material. After filtration, the dark-coloured lignin was washed and dried

before combustion.

(6) a sample of 1963 wood was boiled for 4 hours in 4% HCl and then for 4 hours in 1% NaOH. The strengths of the acid and base were chosen to correspond to those employed by Lerman et al. (1970) in the pretreatment of tree rings.

(7) a sample of 1963 wood was extracted with acetone and then treated with acid and base as in (6).

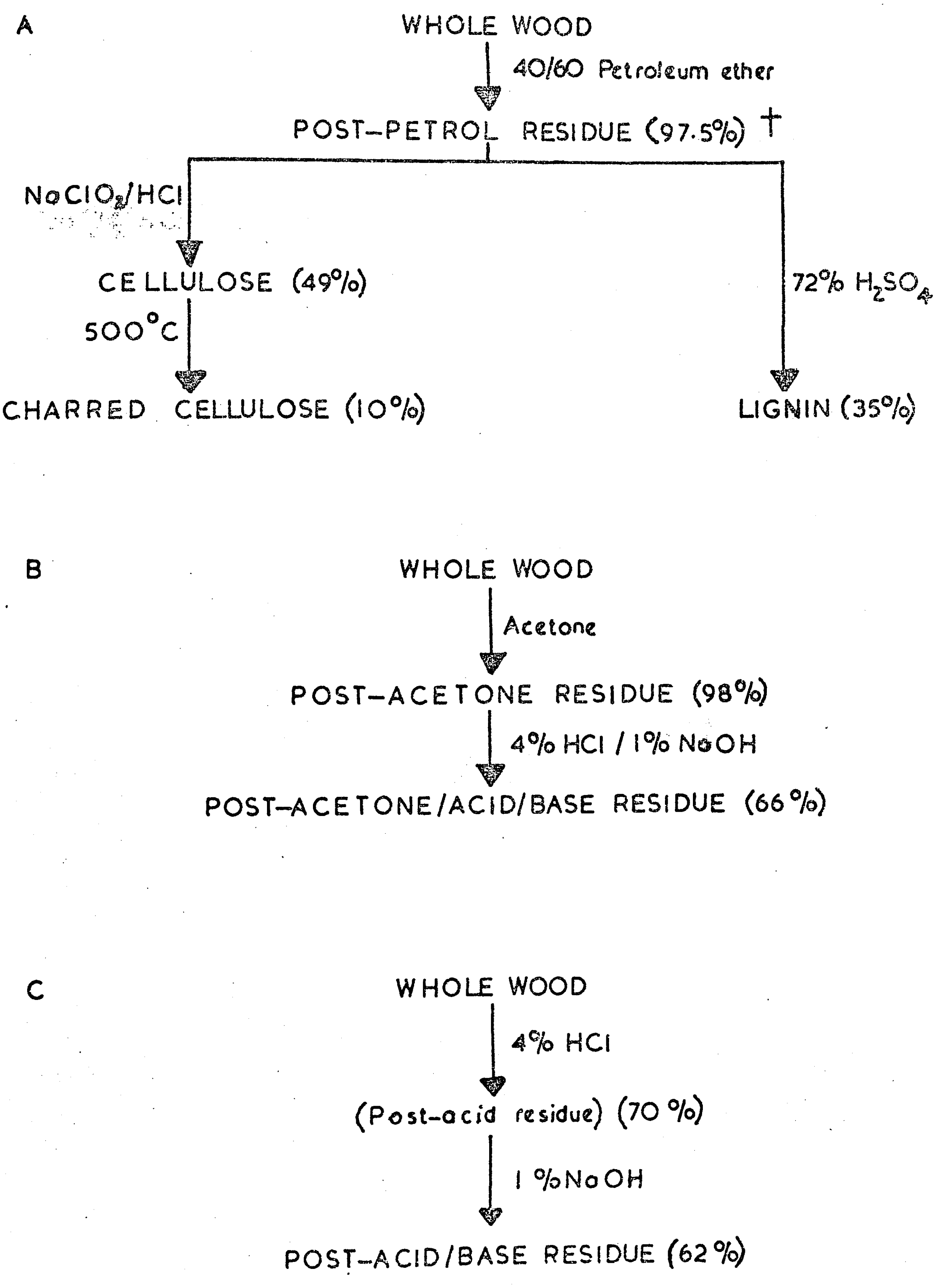
The reaction scheme for the 1963 ring is shown in Figure 3.1 where the approximate chemical yields are also listed.

(d) <u>^{14}C analysis</u>

The results of the ^{14}C measurements of the annual tree-ring components are shown in Table 3.1. Figure 3.2 shows the Δ values calculated for the different wood fractions relative to the corresponding recorded atmospheric Δ values. In all cases, the Δ value for each fraction overlaps the range of Δ recorded for the atmosphere in the year of ring growth. Baxter and Walton (1971) have calculated a curve for the atmospheric levels of ^{14}C in which they average the direct measurements of ^{14}C levels to obtain Δ values for the "growth" (April - September) and "winter" seasons of grains. The atmospheric ^{14}C concentrations were derived from analyses of CO_2 samples collected in the middle and upper latitudes of the northern hemisphere (Broecker and Walton 1959, Broecker and Olson 1960, Münnich and Roether 1967). These data were chosen because of the rapid mixing believed to occur in the troposphere within the 42°N to 78°N latitude band (Lal and Rama 1966). Excellent agreement was observed between the averaged atmospheric ^{14}C activities and the

FIGURE 3.1

PRETREATMENT PROCEDURES FOR SILVER FIR 1963 TREE RING



† Each yield is expressed as a percentage of the weight of initial whole wood.

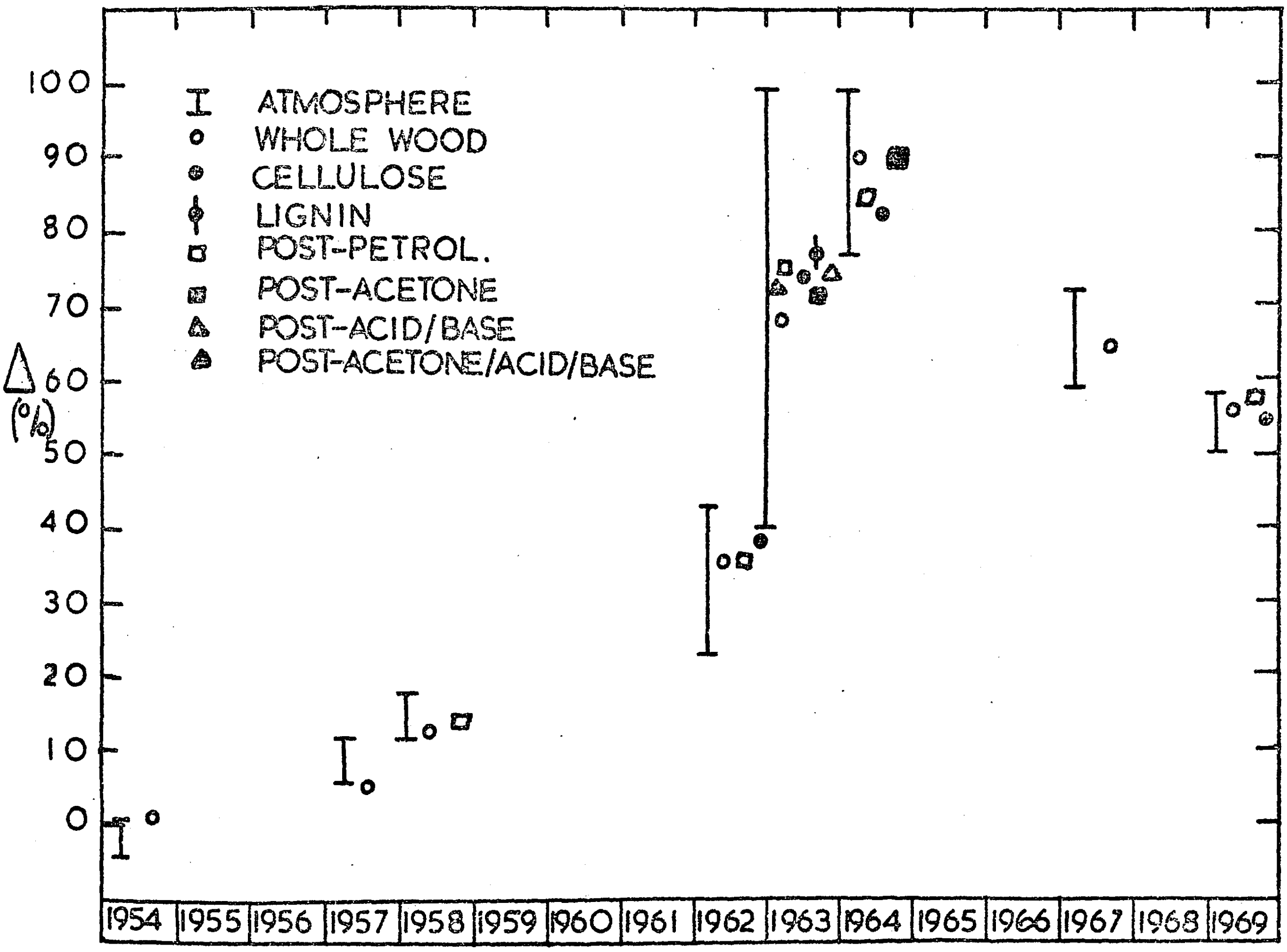
TABLE 3.1

^{14}C CONCENTRATIONS OF NUCLEAR ERA TREE-RING COMPONENTS

Year	Fraction	δ^{14}C(%) ±1σ	δ^{13}C(‰) ±0.1‰ (2σ)	Δ(%) ±1σ
1954	Whole wood	0.69±0.60	-28.71	1.43±0.60
1957	Whole wood	4.35±0.58	-29.72	5.33±0.58
1958	Whole wood	12.29±0.65	-28.81	13.15±0.65
1958	Post-petrol. residue	13.44±0.64	-28.10	14.14±0.64
1962	Whole wood	34.41±0.76	-28.61	35.37±0.76
1962	Post-petrol. residue	34.76±0.73	-28.36	35.67±0.73
1962	Cellulose	36.99±0.71	-27.75	37.75±0.71
1963	Whole wood	67.03±0.74	-28.24	68.11±0.74
1963	Post-petrol. residue	73.62±0.92	-28.67	74.90±0.92
1963	Post-acetone residue	70.13±0.88	-28.19	71.21±0.88
1963	Cellulose	72.94±0.75	-27.34	73.75±0.75
1963	Lignin	74.94±1.09	-28.95	76.33±1.09
1963	Post-acid/base residue	72.94±0.90	-28.81	74.25±0.90
1963	Post-acetone/ acid/base residue	71.45±0.87	-29.07	72.84±0.87
1964	Whole wood	87.99±0.92	-28.71	89.39±0.92
1964	Post-petrol. residue	83.36±0.94	-28.62	84.69±0.94
1964	Post-acetone residue	88.68±1.18	-28.29	89.92±1.18
1964	Cellulose	81.42±0.87	-27.73	82.41±0.87
1967	Whole wood	63.07±0.88	-28.42	64.18±0.88
1969	Whole wood	54.60±0.79	-28.60	55.72±0.79
1969	Post-petrol. residue	56.32±0.81	-28.52	57.42±0.81
1969	Cellulose	53.97±0.79	-27.69	54.80±0.79

FIGURE 3.2

CORRELATION BETWEEN ^{14}C CONCENTRATIONS IN ATMOSPHERIC CO_2 AND SILVER FIR TREE-RING COMPONENTS

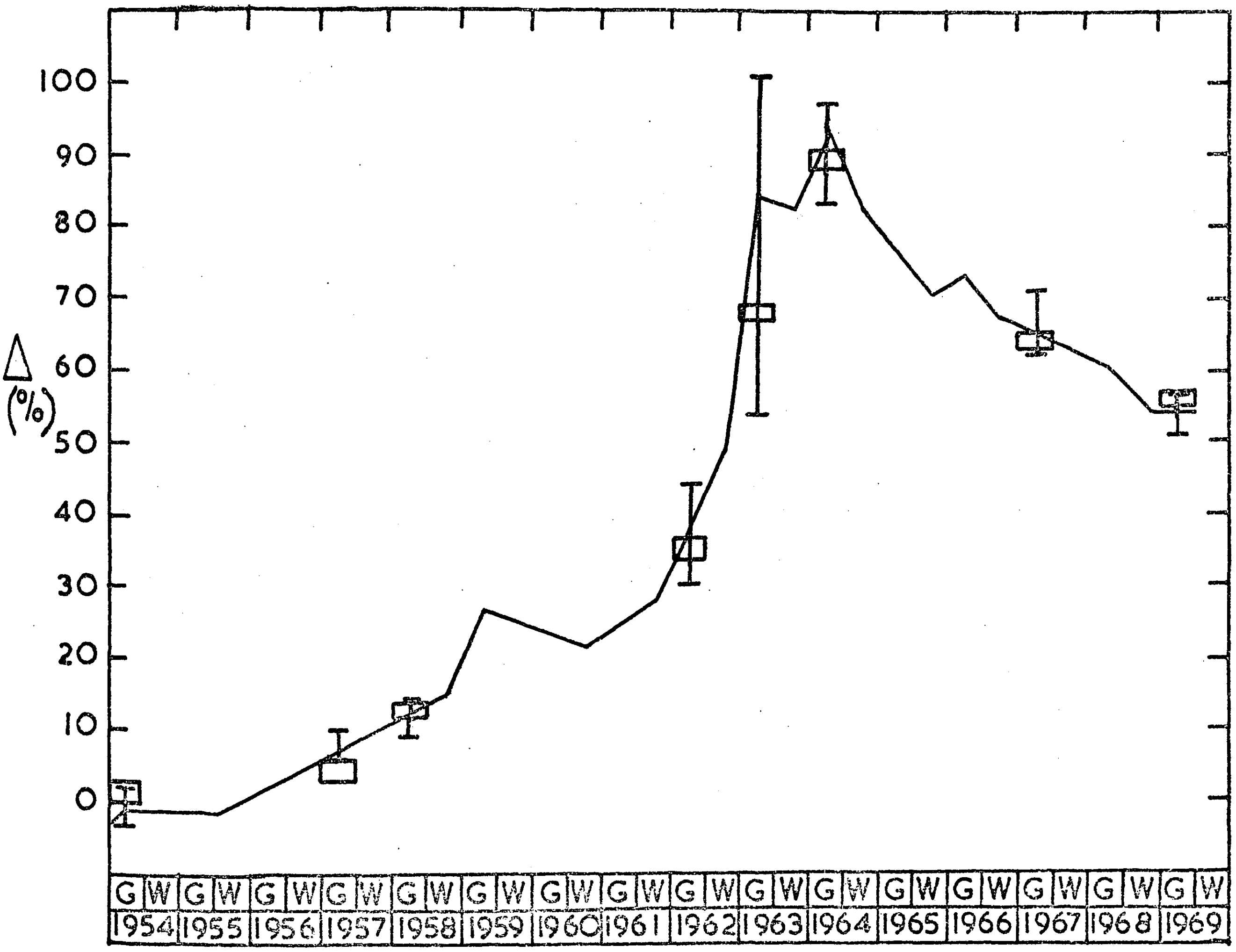


sample ^{14}C levels. Assuming that the growth seasons of wood and grains are approximately coincident, the Δ values for wood should follow the averaged atmospheric curve as calculated by Baxter and Walton. Figures 3.3 - 3.5 present a comparison of the averaged atmospheric and wood fraction ^{14}C activities. Atmospheric Δ values for 1968 and 1969 were calculated from the data of Ergin et al. (1970). In Figures 3.3 - 3.5 the brackets indicate the total ^{14}C activity range within each growth season. Each wood-component ^{14}C concentration is accompanied by a shaded area whose ordinate represents the standard deviation associated with the ^{14}C measurement.

In Figure 3.3 the whole wood values fit the curve reasonably well although the value for 1963 is low. It is unlikely that food storage could explain this value as there is no supporting evidence from the ^{14}C data on the other rings. Figure 3.4 shows the relationship of the Δ values of the extracted wood fractions to the averaged atmospheric levels of ^{14}C. The Δ values of the post-petroleum ether residues for 1963 and 1964 do not coincide with the averaged curve but fall well within the range of Δ values observed in the atmosphere for those years. Figure 3.2 shows that there is no systematic difference between the whole wood Δ values and the corresponding post-petroleum residues. Indeed excellent agreement is observed for 1958, 1962 and 1969. The general conclusion from the post-petroleum results is that any material being removed by the petroleum (<3% for the 1963 ring) is having a negligible effect on the ^{14}C content of the wood. Similarly, the 1963 post-acetone residue Δ value is low but the 1964 value overlaps with the 1964 whole wood Δ value.

FIGURE 3.3

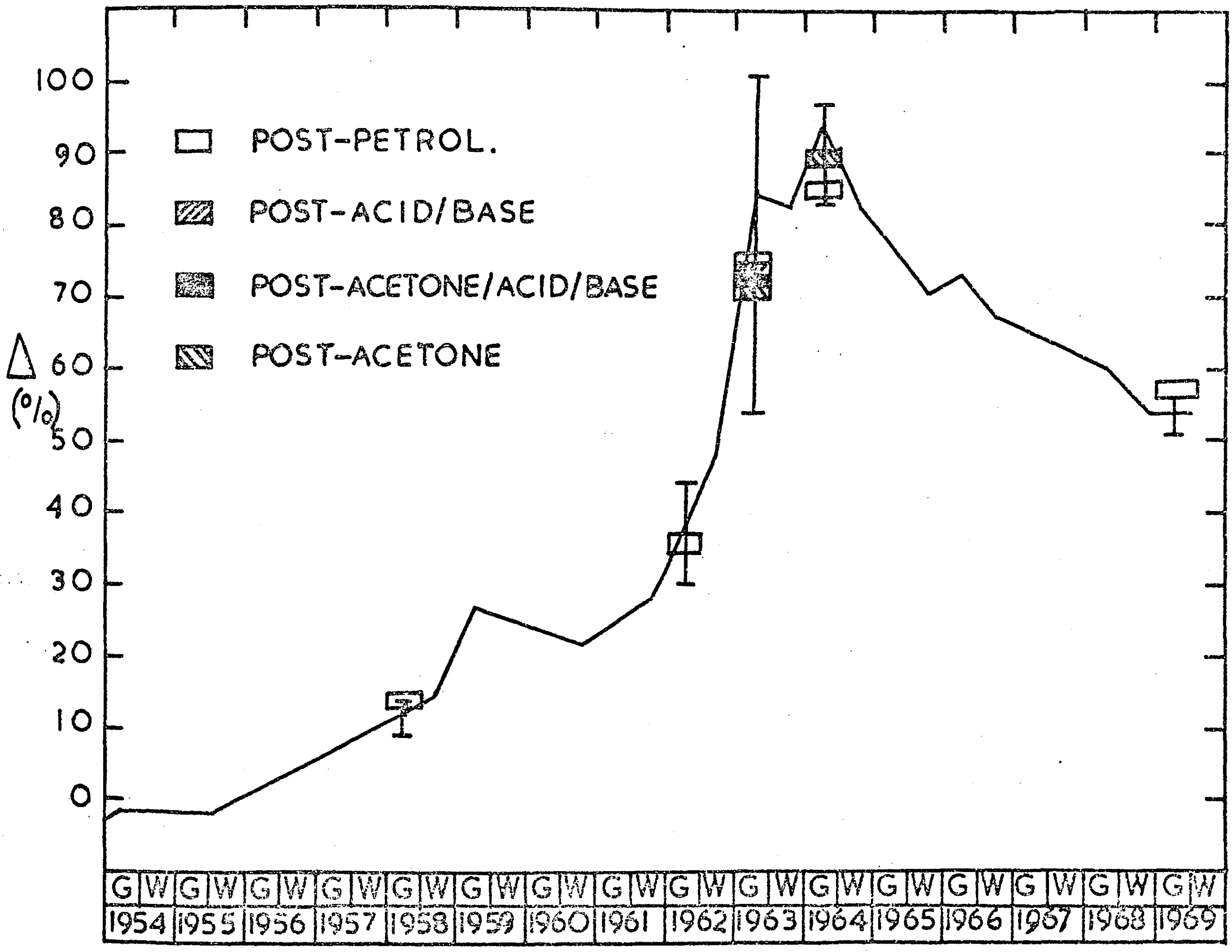
CORRELATION BETWEEN ^{14}C CONCENTRATIONS IN ATMOSPHERIC CO_2 AND SILVER FIR —WHOLE WOOD



G TREE GROWTH SEASON
W CORRESPONDING "WINTER" SEASON

FIGURE 3.4

CORRELATION BETWEEN ^{14}C CONCENTRATIONS IN ATMOSPHERIC CO_2 AND SILVER FIR —POST-EXTRACTION RESIDUES



G TREE GROWTH SEASON
W CORRESPONDING "WINTER" SEASON

Therefore it does not appear that any material removed by the acetone can have a significant effect on the ^{14}C content of the wood. The Δ values for the acid/base and acetone/acid/base residues are grouped closely with the acetone and petroleum ether residues.

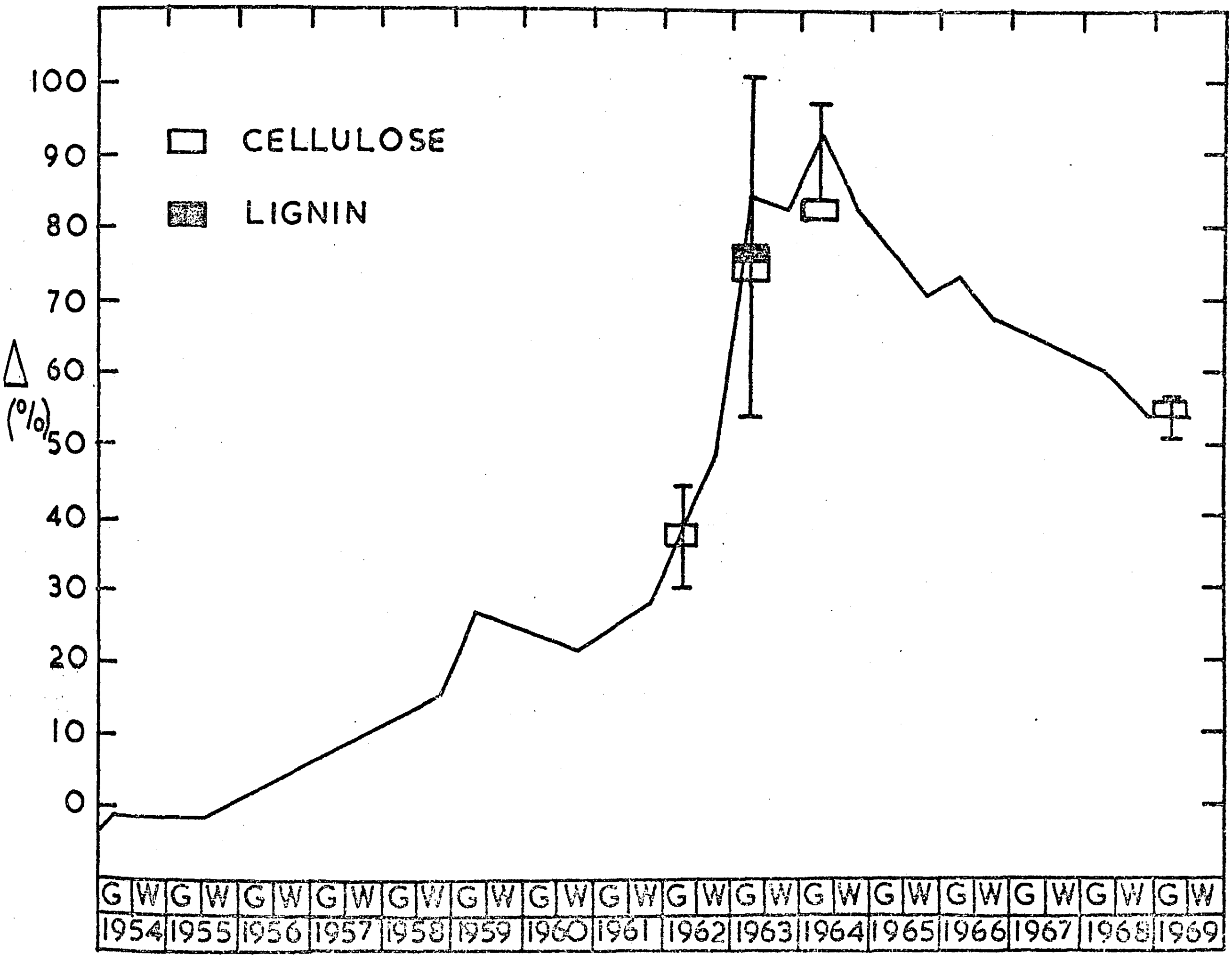
Of the 4 cellulose results shown in Figure 3.5, the 1962 and 1969 Δ values fit the averaged atmospheric curve well but the 1963 and 1964 values, like those of most other fractions, are a few per cent below the averaged values. A food storage effect could explain this since the atmospheric ^{14}C levels in the growth periods of 1962 and 1963 were lower than those in the growth periods of 1963 and 1964 respectively. This theory is not supported by the 1962 and 1969 cellulose Δ values. All Δ values for the different wood fractions in 1963 and 1964 are lower than the corresponding averaged atmospheric levels. This may simply reflect slightly different growth seasons for the tree as compared with the other biospheric samples of Baxter and Walton. As atmospheric ^{14}C concentrations both changed rapidly and attained their highest levels in 1963 and 1964, it is quite probable that slight variations in growth season are responsible for the observed small deviations from the averaged curve. It is of interest that the only significant variations in the Δ values of different wood fractions occur:

(1) in 1963, when there was a range of about 8% in the Δ values, the whole wood having the lowest and the lignin fraction the highest value,

(2) in 1964, when there was a range of about 7% in the Δ values, the cellulose fraction having the lowest value and the post-acetone residue and

FIGURE 3.5

CORRELATION BETWEEN ^{14}C CONCENTRATIONS IN ATMOSPHERIC CO_2 AND SILVER FIR —CELLULOSE AND LIGNIN



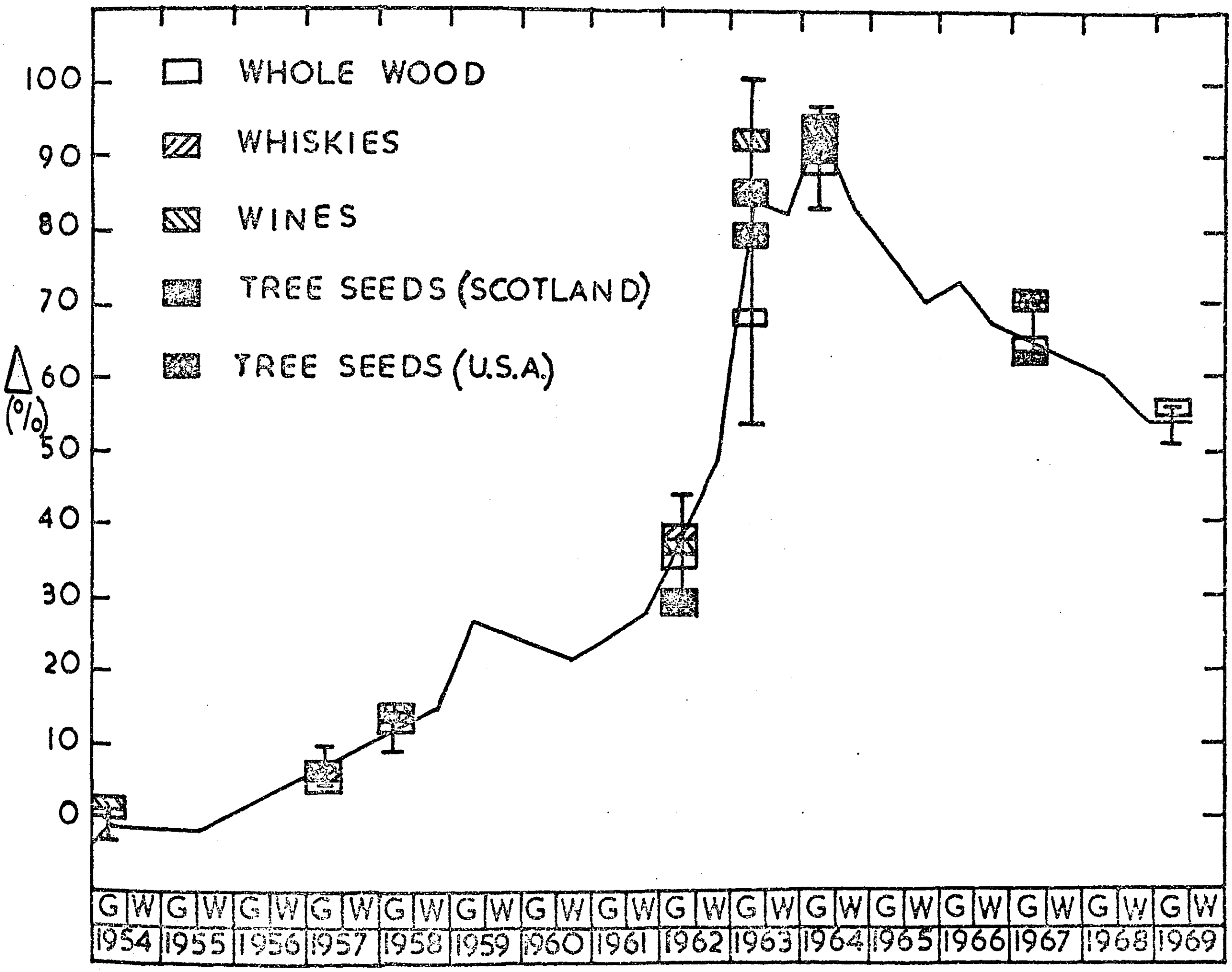
G TREE GROWTH SEASON
W CORRESPONDING "WINTER" SEASON

the whole wood the highest values. Experimental errors such as incomplete removal of organic solvents could account for some of the observed differences but there is no evidence for this from other samples which underwent exactly the same pretreatment processes. Another reason could be a non-homogeneous distribution of the initial wood material for each pretreatment procedure. However, every precaution was taken to ensure complete random mixing of the wood splinters so that each prepared fraction was derived from a wood sample representative of the whole growth season.

Figure 3.6 shows the whole wood Δ values in relation to the Δ values obtained for seeds, wines and whiskies of known age by Baxter and Walton (1971). Differences in Δ values among the various materials are probably attributable to variations in growth seasons. Also photosynthetic activity within the growth season of a particular sample type may alter from year to year depending on climatic conditions. This factor hinders the calculation of a completely reliable averaged curve for atmospheric ^{14}C levels during the growth seasons of these materials. However, it is obvious from Figure 3.6 that the whole wood Δ values reflect the atmospheric values as well as any of the other materials. Hence the general conclusion can be drawn for this particular species of tree, that single tree rings are good indicators of atmospheric ^{14}C levels and that food holdover and resin transfer do not play a significant part in determining the ^{14}C content of the wood constituting a given ring.

FIGURE 3.6

CORRELATION BETWEEN ^{14}C CONCENTRATIONS IN ATMOSPHERIC CO_2 AND VARIOUS BIOSPHERIC SAMPLES



G SAMPLE GROWTH SEASON
W CORRESPONDING "WINTER" SEASON

(e) Assessment of pretreatment procedures

Neither of the organic solvents used removed large amounts of resin from the wood. The largest extract came from the petroleum ether extraction of the 1963 whole wood but amounted to less than 3% of the total weight. Possible reasons for the minimal yields are:

(1) the wood splinters used may have been too large. Although the splinters were only 2 cm. long and 1 - 2 mm. thick, it is possible that the solvent did not remove the resin from within the splint.

(2) the extraction time may have been too short.

(3) initial volatile resins may have been lost during the storage of the wood for drying after the section was cut from the tree.

In addition to the low loss of weight on extraction, difficulty was encountered in efficiently separating the solvent from the resin without loss of the product resin. Thus insufficient resin was obtained for analysis of the ^{14}C content.

It was also observed that the 2 organic solvents extracted different materials from the wood. The petroleum extract was pale-yellow in contrast to the dark-brown colour of the acetone extract. The nature of the material extracted depends on the polarity of the solvent used. Therefore for complete removal of the resin from a wood sample it may be necessary to use a range of solvents of increasing polarity e.g. petroleum ether, diethyl ether, ethyl acetate, acetone and water. This would be a lengthy process and is impractical as a pretreatment technique for ^{14}C analysis of wood. Successive boilings in HCl and NaOH solutions caused the wood to darken in colour. This suggests that some carbohydrate material was removed by the inorganic pretreatment. Thus it is difficult to evaluate the efficiency of resin removal by inorganic acids and bases.

The isolation of cellulose from wood is a straightforward process with good yields. For the 4 rings from which cellulose was extracted the average yield was 53%, within the anticipated range. The lignin fraction for the 1963 ring amounted to 35% by weight of the whole wood. The process, which destroys all carbohydrate material to leave only lignin, is more troublesome to handle on a routine laboratory basis because of the large quantities of concentrated H_2SO_4 that are involved.

(f) Conclusions

The results of this study show that single tree rings are valid indicators of atmospheric ^{14}C levels. Therefore their use in the measurement of past annual ^{14}C concentrations in the atmosphere is readily justifiable.

However, several factors must be borne in mind when selecting the appropriate wood component of tree rings for a study of annual ^{14}C levels:

(1) other species of tree may exhibit different properties to the silver fir studied here particularly with regard to resin transfer from younger to older rings. Jansen (1970), for example, observed that Δ values for resin samples from a New Zealand rimu (600 - 400 B.P.) were 2.6% higher than those of cellulose samples from the corresponding years. The presence of wood rays or resin canals in abundant supply may seriously affect the ^{14}C indicator validity

of the whole wood itself through the contribution of non-contemporaneous material.

(2) the silver fir tree rings of this study were all part of the outer sapwood layer. Studies of past atmospheric ^{14}C concentrations are largely based on rings from the heartwood portion of trees. The possibility of changes occurring during sapwood to heartwood conversion (Fairhall and Young 1970) suggests that the heartwood may be contaminated with younger material.

(3) chemical extraction by organic or inorganic solvents may be incapable of removing all non-contemporaneous substances from whole wood.

The above factors suggest that the use of wood fractions such as cellulose or lignin may be more valid than whole wood in the study of past annual ^{14}C levels. Both components remain fixed within a given tree ring after formation and the time-consuming nature of their chemical isolation is probably justified by a resultant minimisation of the risk of contamination by older or younger carbon. In this respect, as already mentioned previously, the isolation of the cellulose fraction is easier to handle on a routine laboratory basis.

3.4 Other Biospheric Materials

It has already been conclusively demonstrated by Baxter and Walton (1971) and others that short-lived biospheric materials such as wines, whiskies, seeds, wool etc. are valid indicators of annual atmospheric ^{14}C concentrations. Nearly all of the previous measurements were carried out on material from the northern hemisphere. It is to be expected that similar short-lived biospheric samples from the southern hemisphere are reliable indicators of annual ^{14}C levels. Several ^{14}C analyses were performed on recent samples from the southern hemisphere and the results compared with the corresponding prevailing atmospheric ^{14}C activities (Rafter 1965, Rafter and O'Brien 1970) in Table 3.2. The anticipated correlation was obtained. Thus the types of sample used by Baxter and Walton (1971) in their study of 20th Century annual atmospheric ^{14}C levels in the northern hemisphere can be justifiably employed in a similar project for the southern hemisphere.

TABLE 3.2

COMPARISON OF RECENT ^{14}C CONCENTRATIONS IN BIOSPHERIC MATERIALS AND THE ATMOSPHERE IN THE SOUTHERN HEMISPHERE

Year*	Sample$^{\emptyset}$	δ^{14}C(%) $\pm 1\sigma$	δ^{13}C(‰) $\pm$0.1‰ (2σ)	Δ(%) $\pm 1\sigma$	† Atmospheric Range Δ (%)
1960	Whisky	16.78±0.60	-24.42	16.65±0.60	15-19
1963	Whisky	27.39±0.65	-24.20	27.18±0.65	22-28
1967	Whisky	56.39±0.83	-24.25	56.16±0.83	52-62
1967	Wine	52.81±0.81	-27.53	53.58±0.81	52-62
1969	Wine	52.08±0.68	-27.94	52.97±0.68	51-54
1971	Wool	47.70±0.84	-27.87	48.55±0.84	47-50

* Calendar year refers to year of sampling e.g. the designation 1960 whisky refers to barley grown late 1959 - early 1960.

$\emptyset$ Whisky samples from Melbourne (37°52'S, 145°8'E), Australia.
Wine samples from Santiago (33°S, 71°W), Chile.
Wool sample from Otago (46°S, 168°E), New Zealand.

† Range of atmospheric ^{14}C concentrations up to 1967 based on Rafter (1965) and Rafter and O'Brien (1970). Values for 1969 and 1971 are estimated.

CHAPTER 4

ANNUAL ATMOSPHERIC ^{14}C CONCENTRATIONS (1829 - 1865)

4.1 Preliminary Investigations

(a) Sample selection criteria

The investigation of annual atmospheric ^{14}C concentrations (19th Century) required samples which satisfied the following criteria:

(1) known sample age and location of growth,

(2) sample growth periods of less than 1 year,

(3) atmospheric ^{14}C indicator validity.

On the basis of these criteria, accurately dated individual tree rings were considered the most suitable, and indeed the most readily available, source of sample material. Furthermore, the single rings of a particular tree preserve a record of past atmospheric ^{14}C levels at one fixed geographical location. This factor, itself, perhaps gives individual tree-ring ^{14}C studies an advantage over corresponding studies based on other short-lived biospheric materials from varying locations. These latter investigations may suffer from differing atmospheric ^{14}C concentrations at the various sample sites due to either natural or artificial local environmental effects.

Accordingly, with the cooperation of the Forestry Commission, Coleford, a 15 inches thick cross-section was cut from the trunk (above head-height) of an oak (Quercus robur; planted 1810, felled July 1970) grown in Russell's Enclosure, Forest of Dean (51°48'N, 2°37'W), Gloucestershire, England.

(b) Dendrochronological dating of the Forest of Dean oak

The cross-section of oak was sawn into four 90° discs, each of the original thickness, to facilitate drying of the wood. After 3 months, these discs were sawn into smaller discs of 1 - 1.5 inches thickness. After a further 2 - 3 days' drying the discs were polished on a sander so that the annual rings might be readily identified. It was initially contemplated that each ring be assigned to a calendar year by successively counting back from the outermost ring which corresponded to the date of felling (assuming the 1 year - 1 ring relationship typical of oak and of trees from the northern temperate zone in general). Unfortunately, this particular oak had unusually narrow annual growth rings from about 1915 onwards. It was thus impossible to date the rings on a simple ring-counting basis and recourse to the more elaborate techniques of dendrochronological dating was essential. Eventual identification of the rings in terms of calendar years was accomplished in conjunction with F.S. Walker and J.M. Fletcher (Research Laboratory for Archaeology and the History of Art, Oxford) as described below.

Successive rings prior to 1915 were fixed in date by comparison of the oak ring-width curve with those of 2 other oaks recently felled in Russell's Enclosure. One of these had also been planted in 1810 in the same compartment (529/30); the other was planted in 1848 in a nearby compartment (536a). Both had relatively wide rings for the years after 1915 until 1971 and 1968, the respective dates of felling. All 3 oaks had relatively wide rings for the years 1880, 1884-85, 1895, 1897, 1901 and 1914, with 1880 appearing as a particularly sharp peak. In all 3 there were relatively narrow rings for the years 1881-82, 1892, 1896, 1910 and 1915-16. The correlation coefficients (W) in the increase/decrease ratio of the successive widths of the annual rings of the oak used in this ^{14}C study compared to those of the other 2 oaks were:-

pre-1915 years: with the 1810 oak, 70.5% (over 68 years)
" " 1848 " , 71% (over 47 years)
post-1915 years: with the 1810 oak, 75% (over 54 years)
" " 1848 " , 75% (over 53 years).

These values lie towards the upper limit of the range of values typically found for different oaks growing in the same forest (Bauch at al. 1967).

(c) Sample pretreatment

Each 1 - 1.5 inches thick 90° disc was further subdivided into 5 sectors through the original centre of the complete 360° cross-section to facilitate the separation of individual rings which varied from 1 - 7 mm. in thickness. The rings were split out by slicing through the low density earlywood, adjacent to the previous ring's latewood, with a chisel or sharp knife. The ring sequence 1846-48 was too narrow for satisfactory individual-ring separation and the 3 rings were thus cut out as a group.

Although whole-wood oak appears to be a reliable indicator of atmospheric ^{14}C levels (Berger 1970), it was decided to perform the ^{14}C analyses on the cellulose fractions of the individual rings for reasons already given in Section 3.3. The pretreatment schedule consisted of a 24-hour extraction of $\geqslant$50 g. splintered wood with 40 - 60 petroleum ether, followed by the extraction and charring of cellulose as described in Sections 2.2(a) and

3.3(c). Mean yields of 44% and 9% relative to the initial whole wood were obtained for the cellulose and charred cellulose fractions respectively. Gas preparation and counting procedures were as described in Sections 2.2 and 2.6.

4.2 Atmospheric ^{14}C Concentrations (1829 - 1865)

(a) ^{14}C analysis

The annual atmospheric ^{14}C concentrations (Δ) for 1829 - 1865 are shown in Table 4.1 (Farmer at al. 1972). The value for 1846 - 1848 was obtained from ^{14}C assay of the corresponding 3-year ring section (Section 4.1(c)). Figure 4.1 includes the best straight line fit through the data, defined by $\Delta_T = 110.62 - 0.06T$, where T is in calendar years. The reduction in Δ of ~0.06%/year is a general trend which has previously been observed for this time period from analyses of multi-ring tree sections (Lerman et al. 1970).

(b) Natural fluctuations of atmospheric ^{14}C concentrations (1829 - 1865)

The observed points (Figure 4.1) are scattered well outside statistical errors. For example, the 1836 and 1843 ^{14}C activities differ by 2.49 ± 0.8(1σ)% and there is a similar 2.79 ± 0.8(1σ)% discrepancy between 1850 and 1853 values. In addition, there appears to be a general cyclic trend through the data with maxima around 1836, 1850 and 1858, and minima for 1834, 1843, 1853 and 1864. The almost constantly periodic nature of this trend suggested a possible relationship with the 11-year solar cycle. Furthermore, the need for investigation of this possibility was supported by the recent establishment of

TABLE 4.1

ATMOSPHERIC ^{14}C CONCENTRATIONS 1829 - 1865

Year	δ^{14}C(%) $\pm 1\sigma$	δ^{13}C(‰) $\pm$0.1‰ (2σ)	Δ(%) $\pm 1\sigma$
1829	+2.01±0.56	-23.37	+1.68±0.56
1830	+0.86±0.51	-23.64	+0.59±0.51
1831	+1.43±0.59	-24.09	+1.25±0.59
1832	+0.11±0.56	-24.17	-0.06±0.57
1833	+0.75±0.49	-24.27	+0.60±0.49
1834	-0.29±0.76	-24.95	-0.30±0.76
1835	+0.59±0.60	-24.61	+0.51±0.60
1836	+2.01±0.56	-23.60	+1.72±0.56
1837	+1.80±0.59	-24.05	+1.61±0.54
1838	+1.20±0.45	-24.77	+1.15±0.45
1839	+0.17±0.56	-24.74	+0.12±0.56
1840	+0.69±0.54	-23.85	+0.46±0.54
1841	+0.57±0.56	-23.95	+0.36±0.56
1842	-0.34±0.56	-24.26	-0.49±0.56
1843	-0.69±0.58	-24.61	-0.77±0.58
1844	-0.34±0.52	-24.19	-0.50±0.52
1845	-0.42±0.53	-24.89	-0.44±0.53
1846	-0.06±0.54	-24.36	-0.19±0.54
1847			
1848			
1849	+0.17±0.51	-23.41	-0.15±0.51
1850	+0.17±0.59	-24.59	+0.09±0.59

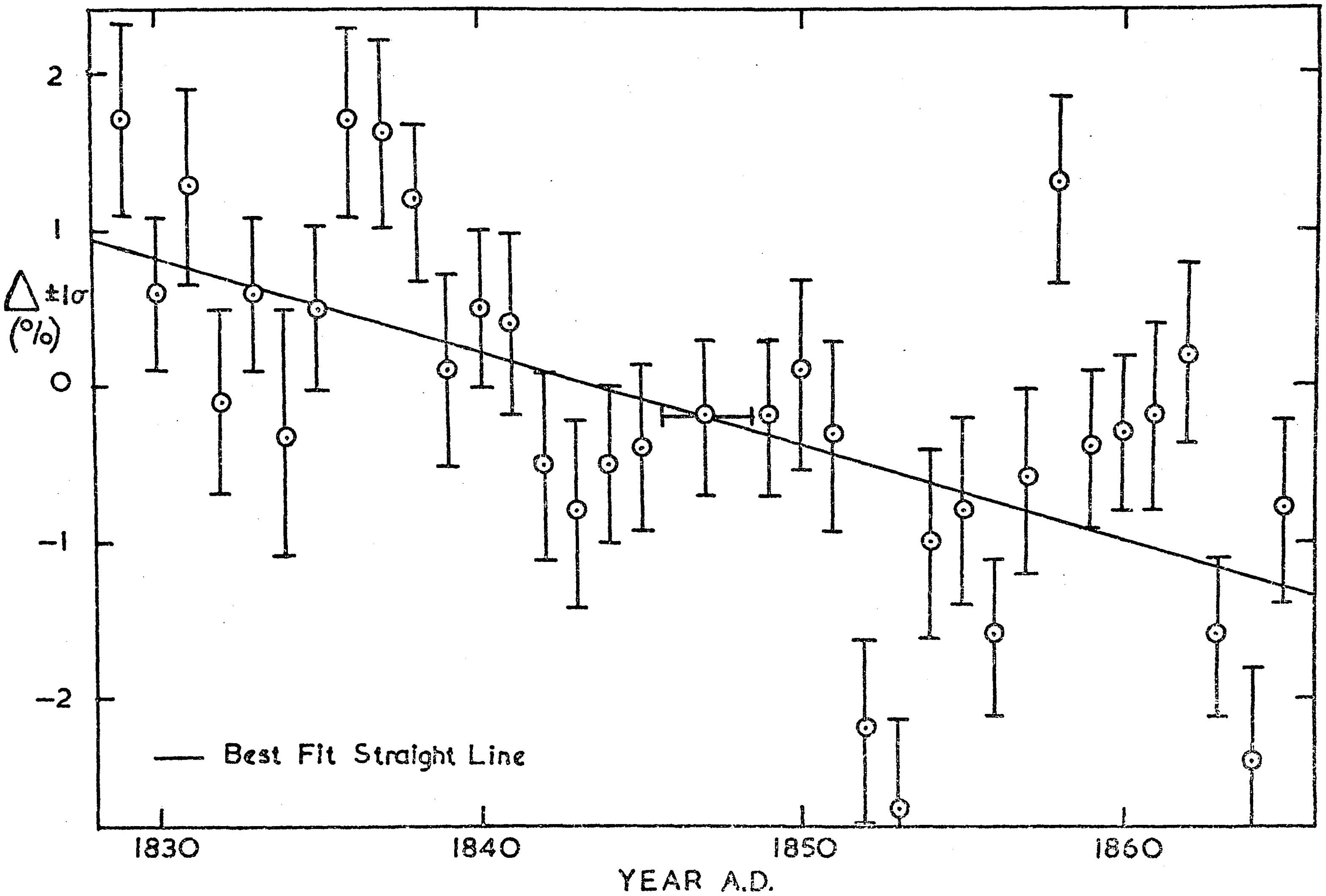
TABLE 4.1 (CONTD.)

ATMOSPHERIC ^{14}C CONCENTRATIONS 1829 - 1865

Year	δ^{14}C(%) $\pm 1\sigma$	δ^{13}C(‰) ± 0.1‰ (2σ)	Δ(%) $\pm 1\sigma$
1851	-0.29±0.60	-25.04	-0.28±0.60
1852	-1.95±0.56	-23.86	-2.17±0.56
1853	-2.75±0.56	-25.25	-2.70±0.56
1854	-0.69±0.57	-23.26	-1.04±0.57
1855	-0.46±0.56	-23.27	-0.81±0.56
1856	-1.38±0.54	-23.90	-1.60±0.54
1857	-0.46±0.56	-24.49	-0.56±0.56
1858	+1.49±0.59	-24.24	+1.34±0.59
1859	-0.29±0.50	-24.24	-0.44±0.50
1860	-0.23±0.50	-24.45	-0.34±0.50
1861	-0.06±0.59	-24.41	-0.18±0.59
1862	+0.29±0.59	-24.44	+0.18±0.59
1863	-1.26±0.51	-23.43	-1.57±0.51
1864	-2.01±0.56	-22.87	-2.43±0.56
1865	-0.57±0.57	-23.84	-0.80±0.57

FIGURE 4.1

ATMOSPHERIC ^{14}C CONCENTRATIONS (1829–65)



a connection between annual 20th Century natural ^{14}C levels and the 11-year solar cycle (Baxter and Walton 1971). A plot of ^{14}C data and the corresponding mean annual Wolf sunspot numbers (Schove 1955) for 1829 - 1865 is shown in Figure 4.2.

The dependence of the ^{14}C data on sunspot number was tested via the null hypothesis, b = 0, within the general expression:

$$\Delta_T = a + bR_T + cT + \text{error}$$

where Δ_T is the value of Δ at time T,

R_T is the mean Wolf sunspot number at time T,

T is the calendar year,

and a, b, c are constants.

A reduction in the residual sum of squares, using conventional least mean squares analysis procedures, from 41.05 ($b = 0$, $c = 0$) to 31.74 ($c = 0$) was observed, corresponding to a significant F value of 9.68 at the 5% level. Hence, the null hypothesis, b = 0, was disproved and a relationship between Δ_T and R_T was evident.

For the 35 pairs of ^{14}C and sunspot data, the correlation coefficient, r, was 0.45. Further correlation analysis revealed a maximum correlation, $r = -0.54$, at a phase shift such that sunspot minima preceded Δ maxima by 5 years. The variation of the correlation coefficient with phase shift is shown in Figure 4.3. Despite the high degree of serial correlation which exists in both the sunspot and ^{14}C data, the maximum correlation ($r = -0.54$) remains highly significant corresponding to a probability of only 1 in 1,000 that Δ and sunspot number are unrelated.

Similar statistical tests to the above were applied within the expression:

FIGURE 4.2

ATMOSPHERIC ^{14}C CONCENTRATIONS (Δ) AND
MEAN ANNUAL SUNSPOT NUMBERS (R) (1829–65)

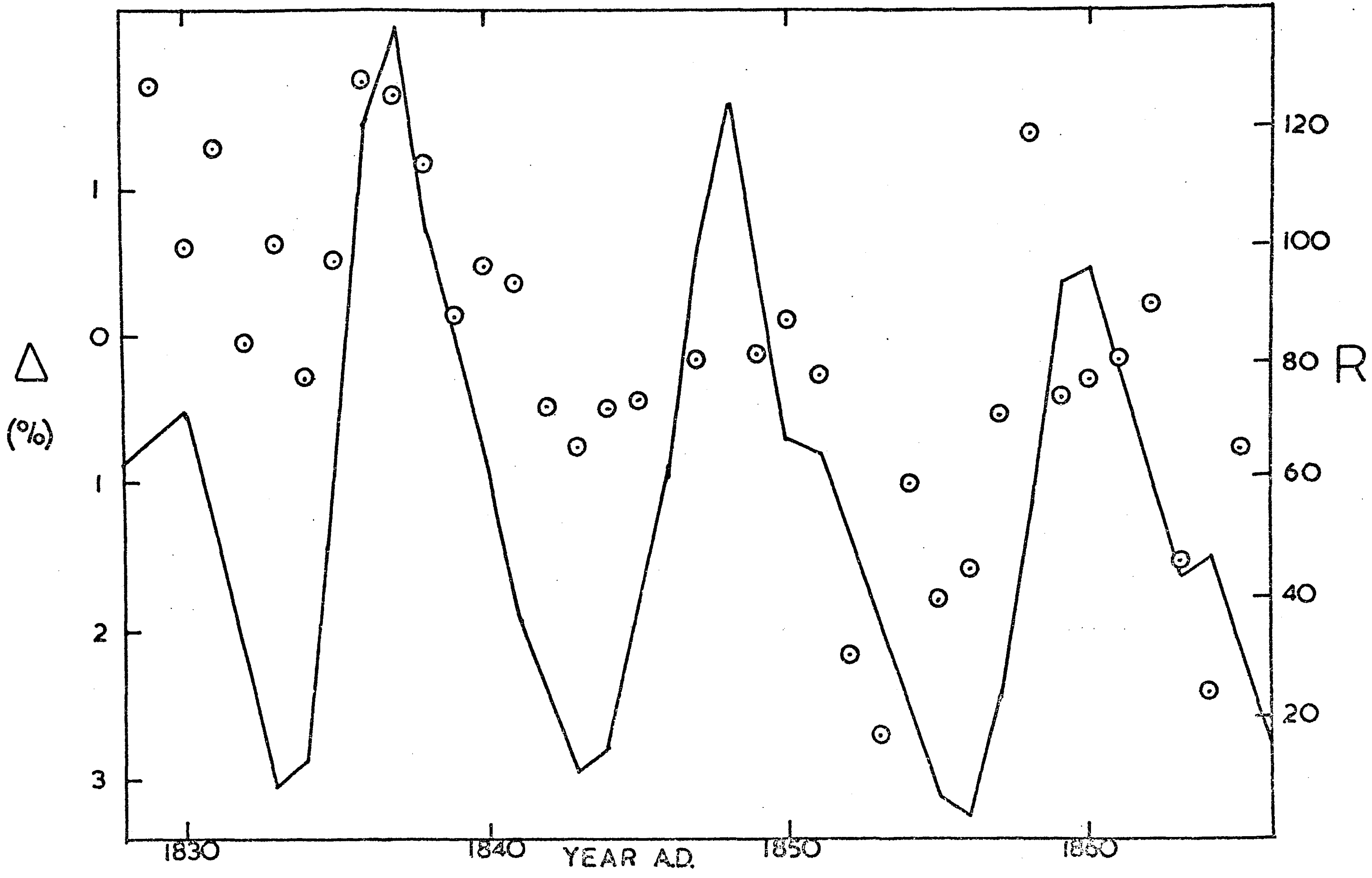
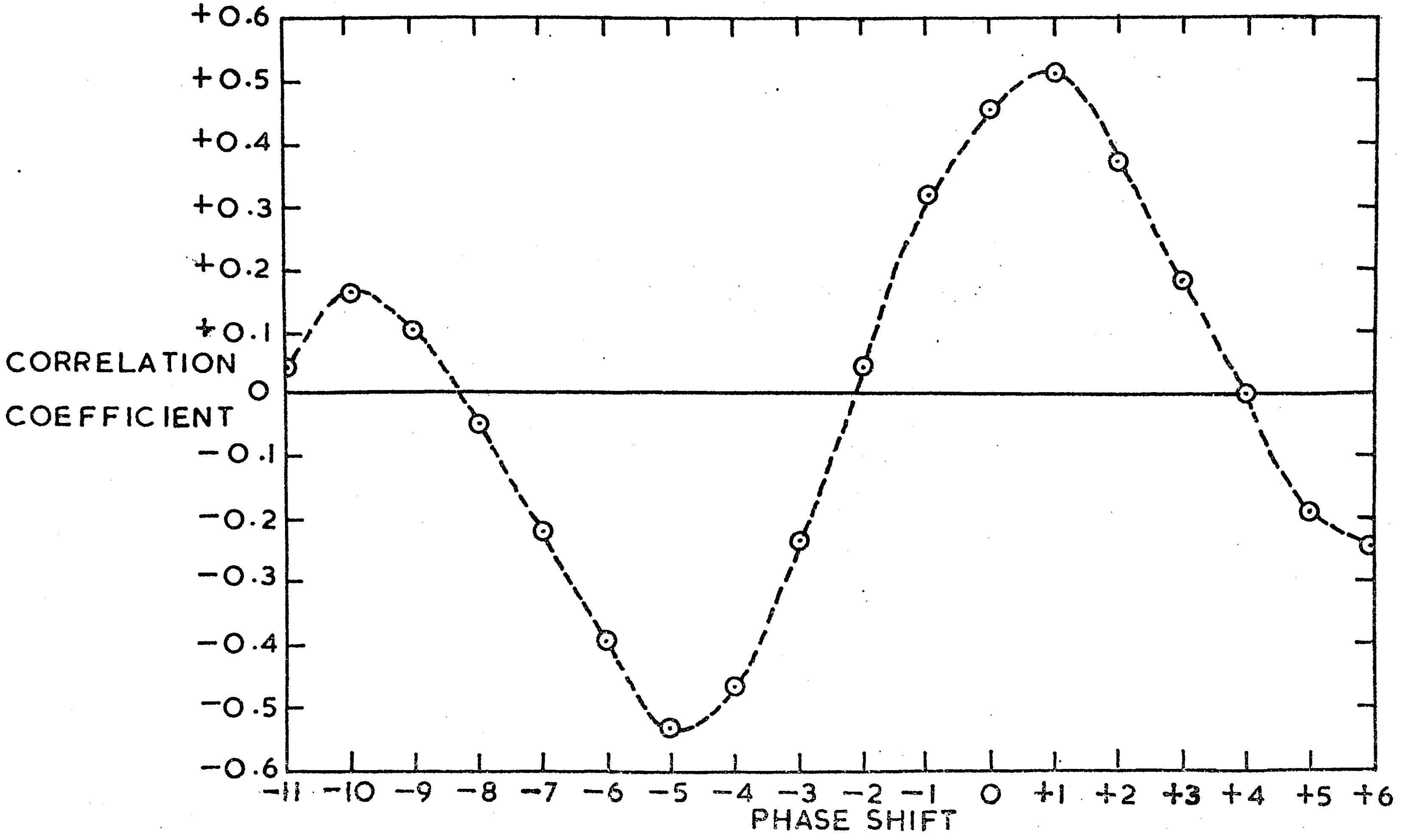


FIGURE 4.3

VARIATION OF CORRELATION COEFFICIENT WITH PHASE SHIFT

1829–65



$$\Delta_T = a + bR_{T-5} + cT + \text{error}.$$

A reduction in the residual from 41.05 ($b = 0$, $c = 0$) to 28.71 ($c = 0$) was observed corresponding to a significant F value of 14.18 at the 5% level. Thus, as expected, $b = 0$ was disproved. The null hypothesis, $c = 0$, was then tested within the above expression. A reduction from 28.71 to 13.10 was found, with an F value of 38.23. Evaluation of the parameters, a, b, c yielded the following expression for Δ_T in terms of R_{T-5} and T:

$$_T = 127.88 - 0.0141R_{T-5} - 0.0689T.$$

The curve relating to this equation was plotted with the ^{14}C data points as shown in Figure 4.4. Fluctuations of amplitude up to 2% over 1 solar cycle are evident.

(c) The correlation of 19th and 20th Century annual ^{14}C fluctuations with the 11-year sunspot cycle

The discovery of cyclic fluctuations of 2% in atmospheric ^{14}C levels for 1829 - 1865, significantly correlated with the 11-year sunspot cycle, is supported by the 20th Century ^{14}C data and corresponding solar-cycle correlations of Baxter and Walton (1971). They found cyclic fluctuations of up to 3% in natural ^{14}C levels to 1950, also strongly correlated with the 11-year solar cycle (Figure 4.5). Thus both studies clearly provide evidence of significant variations of 2 - 3% in atmospheric ^{14}C concentrations over periods of a decade. Furthermore, there is a marked relationship between annual ^{14}C levels and mean annual sunspot numbers for both investigated time periods. However, as Figures 4.3 and 4.5 show, there appears to be a difference in the phase shift of the maximum correlations e.g. during the period 1829 - 1865 (Figure 4.3), maximum ^{14}C levels are attained 5 years after sunspot minimum

FIGURE 4.4

ATMOSPHERIC ^{14}C CONCENTRATIONS (1829-65)
(RELATIONSHIP WITH SUNSPOT NUMBERS R)

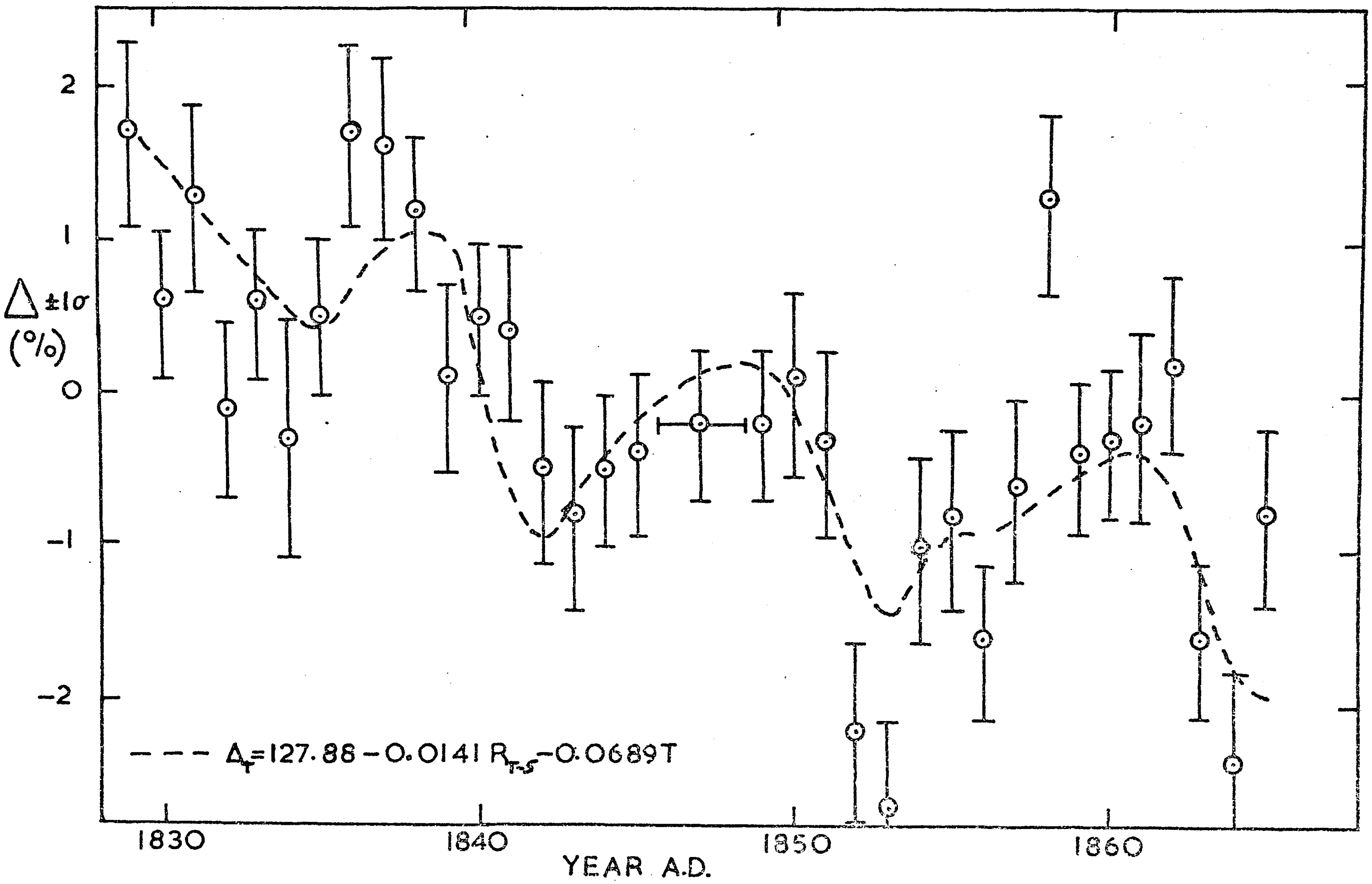
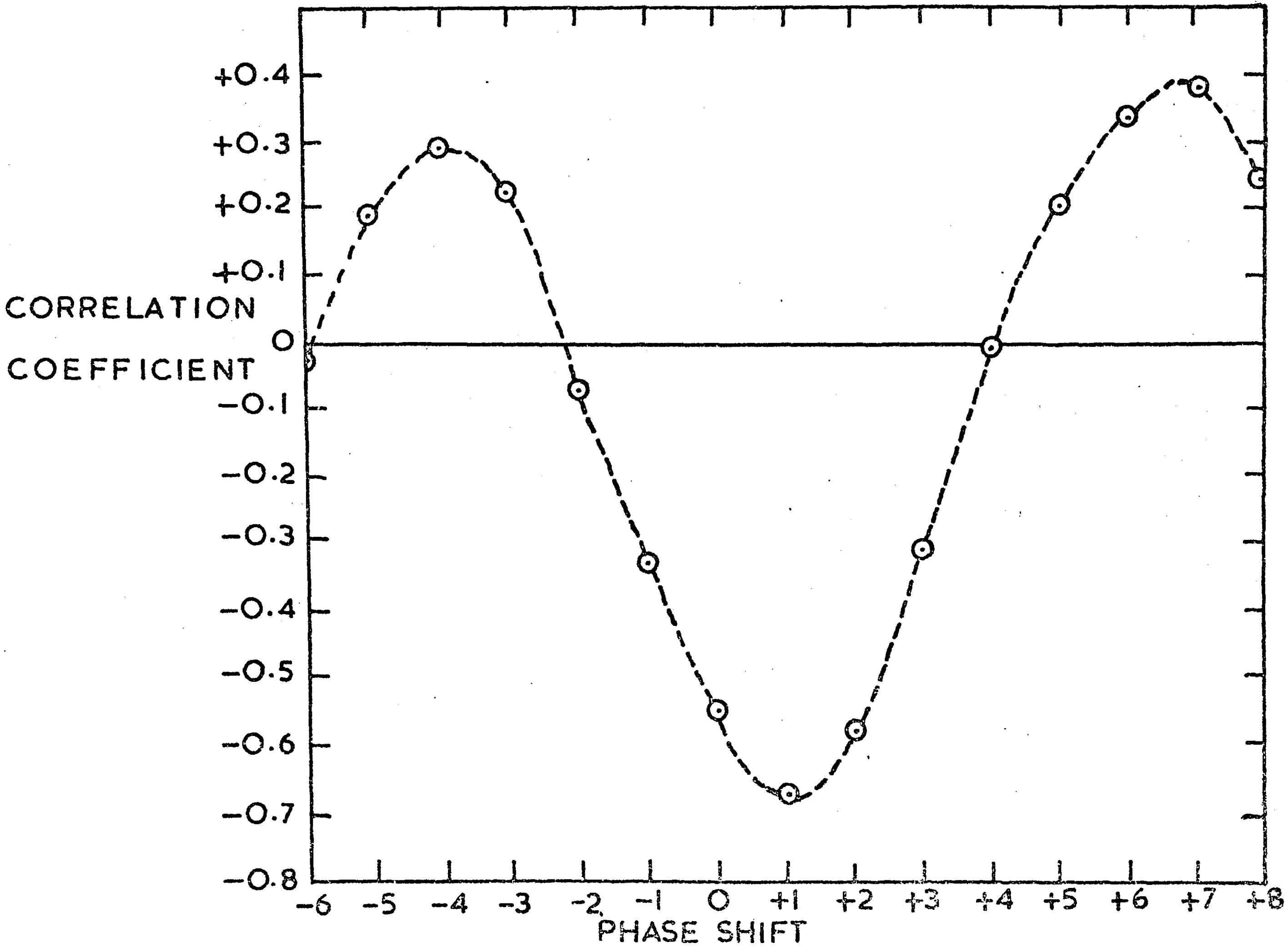


FIGURE 4.5

VARIATION OF CORRELATION COEFFICIENT WITH PHASE SHIFT

1890–1950

(Baxter and Walton 1971)



(or ~1 year before sunspot maximum) whereas, during the period 1890 - 1950 (Figure 4.5), maximum ^{14}C levels are attained 1 year before sunspot minimum. This 180° difference in phase shift is discussed later (Section 4.3) within the general context of the possible causes of the observed natural ^{14}C fluctuations. However, the discrepancy may be partially attributable to the following potential sources of error:

(1) the experimental ^{14}C data of Baxter and Walton (1971) were derived from the ^{14}C assay of a variety of short-lived biospheric materials (whiskies, wines, seeds, cereals and wool) from varying geographical locations in the northern temperate zone. Thus the possibility of a distortion in the general trend due to local variations in ^{14}C concentrations cannot be discounted. This possibility does not arise in the present study because all samples were derived from the same tree.

(2) the ^{14}C data of Baxter and Walton required correction for the "Suess effect" in order that the natural ^{14}C variations could be measured. Potential defects in the theoretical models used in the estimation of the "Suess effect" are discussed in Chapter 5. Furthermore, this factor emphasises the conclusion of (1) that local environmental effects may have influenced the trend of ^{14}C variations observed in the 20th Century data. The measured ^{14}C concentrations for 1829 - 1865 do not require any correction for the "Suess effect" as the

amount of fossil fuel CO_2 released to the atmosphere can be considered relatively insignificant for that period.

(3) the dendrochronological dating of the Forest of Dean oak could be in error. Thus each measured ^{14}C concentration may have been assigned to the wrong calendar year. The extent of the error may in part be responsible for the observed discrepancy in phase shift between the 2 sets of ^{14}C data relative to sunspot numbers.

However, the high degree of correlation observed between 20th Century ^{14}C levels and sunspot numbers (Figure 4.5) would itself be most improbable if factors (1) and (2) were capable of significantly distorting the cyclic trends in the 20th Century ^{14}C data. Furthermore, the established tree-ring chronology of Forest of Dean oak almost certainly precludes the possibility of a tree-ring dating error of even ±1 year (Fletcher 1972). Thus it can be considered rather unlikely, although by no means impossible, that the difference in phase shift is due to these 3 factors.

4.3 Causes of Annual Atmospheric ^{14}C Fluctuations

(a) Variations in ^{14}C production rate

The 5-year phase shift between sunspot minimum and maximum Δ (Figure 4.3) for 1829 - 1865 initially suggests (incorrectly, as is shown later) that the observed 2% fluctuations in ^{14}C over a solar cycle (Figure 4.4) can be attributed solely to ^{14}C production-rate modulation by solar activity (as measured by mean annual sunspot numbers). This erroneous conclusion is reached through a qualitative consideration of:

(1) the enhanced cosmic-ray ^{14}C production in the upper atmosphere (stratosphere) at sunspot minimum relative to sunspot maximum due to the modulation of the cosmic-ray flux, and hence of the ^{14}C production rate, by the increased interplanetary magnetic fields associated with high solar activity (sunspot maximum) (Lingenfelter 1963),

(2) the residence time of CO_2 (and hence of ^{14}C) in the stratosphere prior to transfer to the lower atmosphere (troposphere). Natural ^{14}C is produced mainly in the stratosphere and its rate of transfer to the troposphere is governed by the rate of exchange of CO_2 across the tropopause, the intermediate transition zone. As the stratosphere/troposphere exchange time has been estimated through "bomb" ^{14}C studies at $\leqslant 4$ years (Walton et al. 1970) it might be expected that maximum tropospheric Δ values would occur several years after the period of maximum ^{14}C production (solar minimum) in the stratosphere.

As already forewarned, this seemingly plausible hypothesis becomes untenable when variations in ^{14}C production rate over a solar cycle are considered on a quantitative basis. For example, Lingenfelter (1963) has shown that the ^{14}C production rate varies according to the expression:

$$Q = 2.61 - 0.53(R - 9.1)/178.4$$

where Q is the ^{14}C production rate in atoms/cm_E^2/sec.

and R is the mean annual sunspot number (Wolf Index). Thus the mean production rate from 1824 - 1865 was 2.48 atoms/cm_E^2/sec. or about 4×10^{26} atoms/year with overall variations from $3.60 - 4.24 \times 10^{26}$ atoms/year. Averaged over the solar cycles from 1824 - 1865 the production rate varied from about $3.74 - 4.22 \times 10^{26}$ atoms/year between solar maximum and solar minimum (about 5 years). Thus, assuming constant atmospheric exchange during this period, the annual variations in ^{14}C input to the stratosphere could have amounted to a maximum of $\sim 1 \times 10^{25}$ atoms/year. However, fluctuations of 2% in tropospheric ^{14}C concentrations during an 11-year solar cycle require overall variations in the ^{14}C inventory of the troposphere by $\sim 0.6 \times 10^{27}$ atoms or $\sim 1 \times 10^{26}$ atoms/year. Therefore, the changes in production rate are too small, by about an order of magnitude, to account for the observed ^{14}C fluctuations.

This conclusion was also reached by Baxter and Walton (1971). Indeed the unexpected 1-year phase shift (Figure 4.5) of their maximum correlation, corresponding to attainment of maximum Δ 1 year before sunspot minimum, was taken as confirmation that variations in production rate were not solely responsible for the observed annual ^{14}C fluctuations from 1890 - 1950.

(b) Variable exchange rates between carbon reservoirs

The observed ^{14}C fluctuations of 2% over individual solar cycles from 1829 - 1865 appear to reflect a variable input (or removal) of ^{14}C into (or from) the troposphere. It has been shown (Section 4.3(a)) that modulation of the ^{14}C production rate over the 11-year solar cycle is not solely responsible for the variations in ^{14}C levels. Therefore, it would appear that the variable input must result from fluctuations of the carbon exchange rate between the troposphere and one or more of the adjacent carbon reservoirs (stratosphere, biosphere, surface ocean). Furthermore, the input mechanism should be sensitive to variations in solar activity in view of the strong correlation between ^{14}C variations and sunspot numbers (Figure 4.3).

(1) Solar-terrestrial relationships

The effects of variations in solar activity are much reduced at lower altitudes so that biospheric and oceanic responses over the 11-year cycle are probably negligible. Thus, although Dyck (1965) has postulated that biospheric activity could be sensitive to solar activity through variations in climate, it appears most unlikely that atmospheric ^{14}C concentrations would be significantly changed over short time periods of the order of 10 years.

However, it seems reasonable to assume that atmospheric circulation and mixing may be affected by solar-activity variations since the movement of air within the atmosphere is controlled by the absorption and dissipation of solar energy. The total amount of solar energy incident on the earth's atmosphere is expressed in terms of the solar constant (2.00 ± 0.04 $cal/cm_E^2/min.$). Recent measurements (Kondratyey 1971) indicate that a relationship may exist between the solar constant and solar activity as determined by the Wolf sunspot number. A maximum value of the solar constant was observed with sunspot numbers of about 80 - 100. Furthermore, a reduction of up to 2.5% in the solar constant was observed as the sunspot number increased (or decreased) from this range. Since the thermal balance of the atmosphere is highly sensitive to the value of the solar constant (Manabe and Wetherald 1967) variations of 2.5% could well have an important effect on atmospheric circulation.

Further evidence of atmospheric effects of solar-activity variations is provided by Schove (1955) who suggests that the pressure gradients, which partly control general atmospheric circulation, are influenced by sunspot activity, particularly at sunspot maximum in cycles of medium strength (R = 80 - 140). However, he observed that the effect of strong solar cycles on atmospheric pressure gradients was most marked in the years preceding sunspot maximum.

These examples indicate that the motion of atmospheric air masses may well be significantly influenced by variations in solar activity. Consequently, the ^{14}C exchange rate between the atmospheric carbon reservoirs (stratosphere, troposphere) could be affected by solar-activity variations e.g. during the 11-year solar cycle. This idea of variable stratospheric/tropospheric exchange is supported by the susceptibility of the tropopause to variations in height and stability and by the known occurrence of variable inputs of air from the stratosphere over a 1-year cycle as shown by the "spring peaks" in tropospheric "bomb" ^{14}C concentrations (Figure 1.3).

(2) <u>Stratosphere/troposphere exchange and ^{14}C/11-year sunspot cycle correlations</u>

The concept of variable stratosphere/troposphere exchange was used by Baxter and Walton (1971) to account for the 3% cyclic fluctuations in natural ^{14}C concentrations over 11-year solar-cycle periods from 1890 - 1950. On the basis of the correlation between sunspot numbers and Δ (Figure 4.5) it was calculated that maximum input of ^{14}C to the troposphere occurs on average within the 2-year period following sunspot maximum, when their measured tropospheric ^{14}C concentrations rose most rapidly. Thus maximum Δ is attained about 1 year before sunspot minimum. It was then postulated that the increased input of ^{14}C to the troposphere after solar maximum could be due to the possible intensification of atmospheric circulation (and hence of stratosphere/troposphere exchange) as a result of the high energy fluxes of U.V. and corpuscular radiation associated with solar maximum. In particular, they quoted the limited evidence for variations in mean tropopause height with the 11-year solar cycle (Lawrence 1965) such that maximum tropopause height (and thus presumably maximum input of ^{14}C to the troposphere) occurs in the years following sunspot maximum.

As previously indicated, there is a 180° difference in phase shifts, for maximum correlation between sunspot numbers and Δ, for the periods 1829 - 1865 and 1890 - 1950 (Figures 4.3 and 4.5). Thus if a variable stratosphere/troposphere exchange mechanism is invoked for 1829 - 1865, the correlation illustrated in Figure 4.3 requires that maximum input of ^{14}C to the troposphere occurs after solar minimum in order that the maximum values of Δ are attained about 1 year before sunspot maximum i.e. in contrast to Baxter and Walton's results for 1890 - 1950. It follows that, if variable exchange between the stratosphere and troposphere is responsible for the annual fluctuations observed in the 19th and 20th Centuries, the solar-sensitive mechanism must itself be subject to temporal variations within the 11-year solar cycle. The causes of such temporal variations may be connected with the intensity of sunspot maxima within individual solar cycles or with the effects later discussed in Section 4.3(c).

The fact that the correlations of the 2 ^{14}C data series with sunspot numbers are mutually 180° out of phase could be regarded as proof that the underlying cause of the fluctuations is unrelated to sunspot-number variations. This infers that the correlations, considered separately, are purely coincidental. In view of the high degree of correlation in both cases, such a conclusion is rather unlikely. However, recent advances in our understanding of solar activity and associated cosmic-ray variations, as outlined in (c) below, suggest that the above correlations and subsequent deductions are rather an over-simplification.

(c) Additional causes of annual ^{14}C fluctuations

(1) Temporal variations of solar-modulated cosmic rays

Lingenfelter (1970) has pointed out that the equation describing the dependence of ^{14}C production on sunspots viz.,

$$Q = 2.61 - 0.53(R - 9.1)/178.4$$

which is an alternative expression of

$$Q(R) = Q_{max.}(\text{sunspot min.})(1 - \alpha R)$$

where $\alpha = 1.14 \times 10^{-3}$ (Lingenfelter 1963),

is based on a simple linearity with sunspot number between solar minimum and solar maximum. In more recent calculations (Lingenfelter and Ramaty 1970) based on direct measurements of the cosmic-ray intensity over the last 3 solar cycles, it has been found that cosmic-ray variations (and hence the ^{14}C production rate) are much more strongly dependent on small changes in sunspot number near solar minimum i.e. α is not constant but can vary within a solar cycle.

Furthermore, Ramaty (1970) has indicated that the recent time history of cosmic rays is somewhat different from that predicted from sunspot data. For example, certain cosmic-ray cycles have double maxima, a feature not generally exhibited in sunspot data.

Although variations in production rate over the 11-year solar cycle may have occurred in the past in accord with these factors (e.g. α may have varied considerably more than deduced for recent solar cycles) it is not suggested here that such variations were alone sufficient to cause the ^{14}C fluctuations observed for 1829 - 1865.

(2) Solar flares

It has recently been shown (Lingenfelter and Ramaty 1970) that the contribution of solar-flare particles must be taken into account in the assessment of ^{14}C production during a solar cycle. Solar flares, as distinct from sunspot activity which merely modulates the galactic cosmic radiation, add particles (mainly protons) to the cosmic-ray flux. Small solar flares, which usually occur in positive correlation with solar activity (i.e. near sunspot maximum), contribute particles with energies up to only 100 MeV. Large flares, as yet inadequately documented to enable correlation with sunspot number(Smith and Smith 1963), contribute very appreciably to the flux at energies $\leqslant$10 GeV. For example, about 50% of the total flux of the solar component at the earth below 10 GeV. in the 10 years after 1956 was due to 1 large flare in 1956

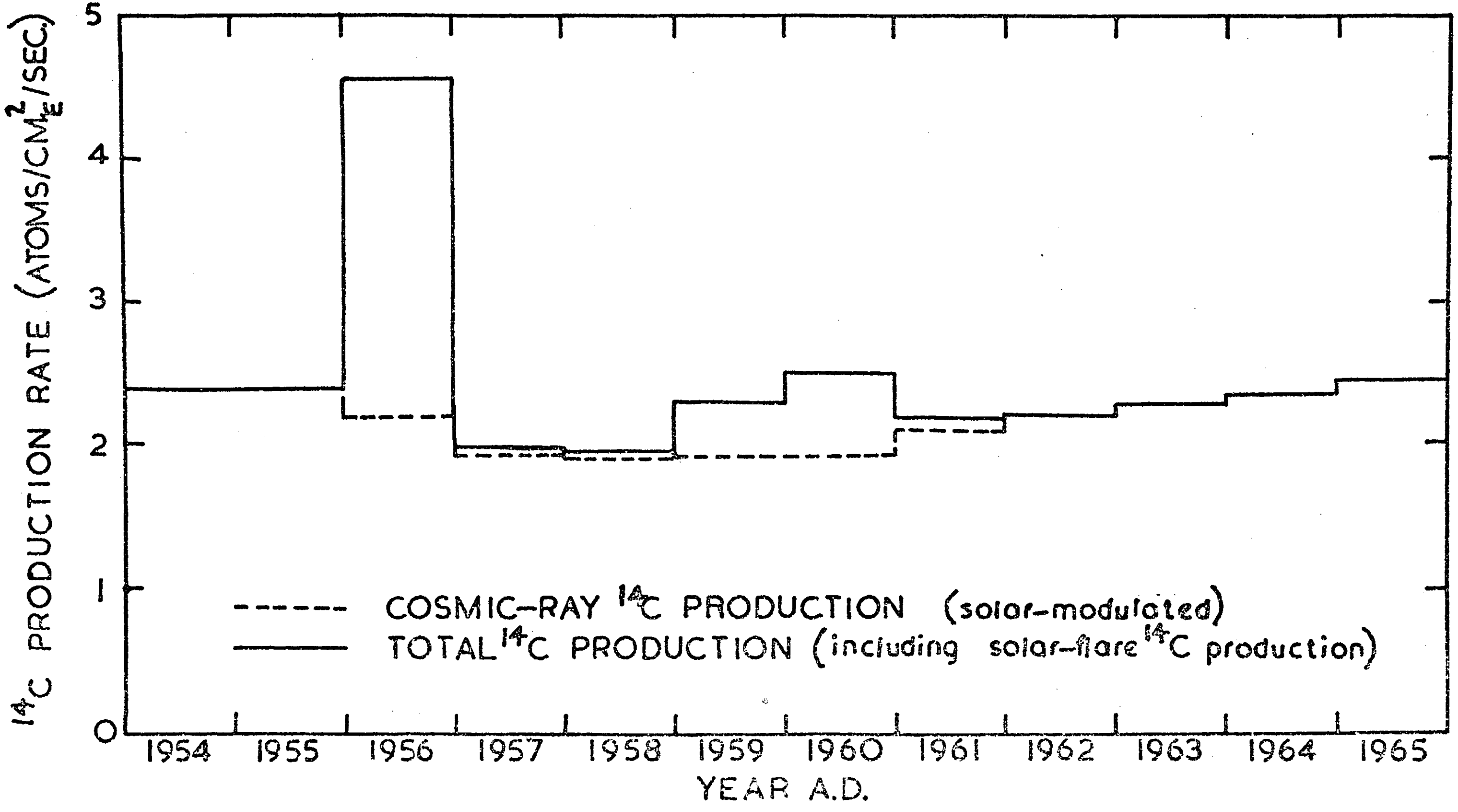
(Oeschger et al. 1970). It is the additional ^{14}C production from flares such as these which is now considered significant. Lingenfelter and Ramaty (1970), using particle-intensity measurements for the major solar flares from 1954 - 1965 (Malitson and Webber 1963), calculated that the solar-flare ^{14}C production averaged over this period was 0.12 - 0.31 atoms/cm_E^2/sec. corresponding to 6 - 14% of the solar-cycle-averaged cosmic-ray ^{14}C production. Moreover, as most of the solar-flare-derived ^{14}C was produced in only a few events, this contribution of ^{14}C was sufficient to modify the solar-cycle dependence of the total ^{14}C production rate (Figure 4.6). Lingenfelter and Ramaty (1970) further estimated that the solar flare of 1956 could have produced an increase of 0.75% in the specific activity of atmospheric ^{14}C. Unfortunately, the excess ^{14}C from nuclear weapon testing has prevented the detection of this effect.

The occurrence of major solar flares is obviously relevant to an understanding of both the magnitude and phase of significant ^{14}C fluctuations over the length of a solar cycle. This is evident from Figure 4.6 which illustrates that, for active solar cycles, the 11-year periodicity in production rate resulting from solar modulation may be completely obscured by solar-flare effects, depending on the time of the solar-flare event within the 11-year cycle. Furthermore, by analogy with the enhanced stratosphere/ troposphere exchange at sunspot maxima due to the atmospheric effects of the increased electromagnetic and corpuscular radiation from associated small flares, it is quite possible that major solar flares may affect not only the ^{14}C production rate, but also the

FIGURE 4.6

VARIATION OF ^{14}C PRODUCTION (1954–65)

(Lingenfelter and Ramaty 1970)



rate of exchange between stratosphere and troposphere.

The first recorded observation of a solar flare was in 1859 but it was not until the invention of the spectrohelioscope by Hale (1926) that the systematic study of flares could be undertaken. The incidence of flares since 1937 correlates positively with sunspot incidence e.g. r = 0.878 for 1937 - 1960 (Smith and Smith 1963). However, for quantitative correlation of flare activity with other solar activity, and especially with geophysical phenomena, incidence alone is an inadequate flare datum. For example, major flares, though relatively few in comparison to small flares, produce ionospheric disturbances of much enhanced intensity. The frequency of major flares is not a sensitive function of solar cycle phase so that the probability that a flare will be of primary importance is not appreciably greater at sunspot maximum than at sunspot minimum (Smith and Smith 1963).

Due to lack of solar-flare records, the evaluation of past solar-flare effects on ^{14}C production and atmospheric exchange processes is rather difficult. However for the period 1829 - 1865, 2 of the solar cycles can be considered highly active with a very strong maximum (R = 138) in 1837 and a strong maximum (R = 124) in 1848 (Figure 4.2). Similarly, a very strong maximum (R = 151.6) occurred in 1947, within the 1890 - 1950 ^{14}C data period of Baxter and Walton (1971). High-energy solar-cosmic-ray events were observed in 1942 (2), 1946 and 1949 (Smith and Smith 1963). It is possible that major solar flares may have been associated with such periods of intense solar activity in the more distant past but, as already discussed, the exact magnitude and timing of these flares within the 11-year solar cycle are unknown.

It can be concluded that significant solar-flare contributions to ^{14}C production and atmospheric exchange processes may have occurred during either or both of the periods 1829 - 1865 and 1890 - 1950. The temporally uncertain occurrence of these flares within individual solar cycles may, in part, be responsible for the observed 180° discrepancy in phase shift between the solar-cycle correlations of this study and that of Baxter and Walton (1971).

4.4 Conclusions

(1) Atmospheric ^{14}C fluctuations of $\sim 2\%$ over individual 11-year solar cycles have been observed for the period 1829 - 1865 in the northern hemisphere.

(2) A correlation exists between mean annual sunspot numbers (R) and annual ^{14}C levels (Δ) such that R_{min} precedes Δ_{max} by 5 years.

(3) The production-rate mechanism suggested by (2) is, on its own, incapable (by a factor of $\leqslant 10$) of causing the observed ^{14}C fluctuations.

(4) The phase of the sunspot number/^{14}C correlation for 1829 - 1865 differs by 180° from the corresponding phase for 1890 - 1950 (Baxter and Walton 1971).

(5) Temporal variations of the solar-sensitive stratosphere/troposphere exchange mechanism within the 11-year solar cycle may account for the observed discrepancy (4). Such variations may be related to variable solar-flare

contributions both to ^{14}C production and to atmospheric exchange processes.

4.5 Implications for Radiocarbon Dating

(a) Dating of short-lived materials

The confirmation of 2 - 3% variations in northern hemisphere atmospheric ^{14}C concentrations over 10-year periods represents a significant deviation from the primary assumption of ^{14}C constancy from one year to the next. Since it is virtually inconceivable that ^{14}C levels can be documented on an annual basis over the period covered by the bristlecone-pine calibration curve, correction of deviant ages for radiocarbon dating samples of lifetime in the order of 1 year will not be readily achievable. Thus short-lived dating samples (e.g. grain, straw, seeds, single tree rings, roots, twigs, egg shells, leaves, sheep's wool) are susceptible to an additional dating error of ± 80 - 120 years corresponding to a ± 1 - 1.5% (Δ) deviation in ^{14}C activity from the "averaged" level as indicated by the conventional calibration curve. For this reason, preference should be given to samples which incorporate the products of many years' growth, ideally 10 - 11 years or a multiple of 10 - 11 years in the case of tree-ring samples.

(b) ^{14}C dating standards

The variations in ^{14}C levels around 1850 emphasise the dangers of using 19th Century wood as a standard for radiocarbon dating. Table 4.1 shows that while Forest of Dean oak from 1849 - 1851 reflects the commonly accepted "natural" ^{14}C level ($\Delta \sim 0$), incorporation of subsequent rings from 1852 - 1858 would depress the average ^{14}C level.

Thus, the use of N.B.S. oxalic acid as the universal ^{14}C dating standard is fully endorsed by the results of this study.

CHAPTER 5

ATMOSPHERIC CO_2 CONCENTRATIONS AND CARBON ISOTOPE LEVELS DURING THE 20TH CENTURY

5.1 Fossil Fuel Consumption since 1860

Prior to development of the Industrial Revolution, the fuels used by man consisted mainly of wood and recent plant remains. The effect of this burning on the content of atmospheric CO_2 was negligible because it only slightly increased the rate of the natural decay processes that continually recycle carbon from the biosphere to the atmosphere. During the last 200 years, however, and especially since the middle of the 19th Century, man has begun to burn the fossil fuels (coal, lignite, petroleum, oil, natural gas) which have been locked in the sedimentary rocks (and thus effectively removed from the dynamic carbon cycle) over hundreds of millions of years. Table 5.1 provides details of the world production of fossil fuels for each decade since 1860 (Revelle 1965). The trend towards liquid hydrocarbons and natural gas as the major sources of energy is reflected in Figure 5.1. The corresponding amounts of CO_2 released to the atmosphere by the combustion of each type of fossil fuel are estimated by assuming that the carbon contents of coal, lignite, liquid hydrocarbons and natural gas are 75%, 45%, 86% and 70% respectively (Table 5.2). The total input of fossil CO_2 to the atmosphere up to the end of the last decade was 4.66×10^{17} g., approximately 21% of the natural atmospheric CO_2 inventory of 2.26×10^{18} g. which is based on a natural atmospheric CO_2 concentration of 290 p.p.m. (Callendar 1958). As the present CO_2 level of ~320 p.p.m.

TABLE 5.1

WORLD PRODUCTION OF FOSSIL FUELS (10^6 Metric Tons)

1860 - 1969

Decade	Coal	Lignite	Liquid Hydrocarbons	Natural Gas	Total
1860-1869	1,660	85	5	–	1,750
1870-1879	2,560	180	15	–	2,755
1880-1889	3,850	285	55	10	4,200
1890-1899	5,405	495	140	40	6,080
1900-1909	8,455	880	310	80	9,725
1910-1919	11,240	1,270	590	155	13,255
1920-1929	11,850	1,875	1,510	285	15,520
1930-1939	11,500	2,135	2,335	485	16,455
1940-1949	13,570	2,995	3,605	970	21,140
1950-1959	14,960	6,465	7,710	2,400	31,535
1960-1969	21,620	9,420	15,530	6,950	53,520
Total	106,670	26,085	31,805	11,375	175,935

FIGURE 5.1

WORLD PRODUCTION OF FOSSIL FUELS

(1860–1969)

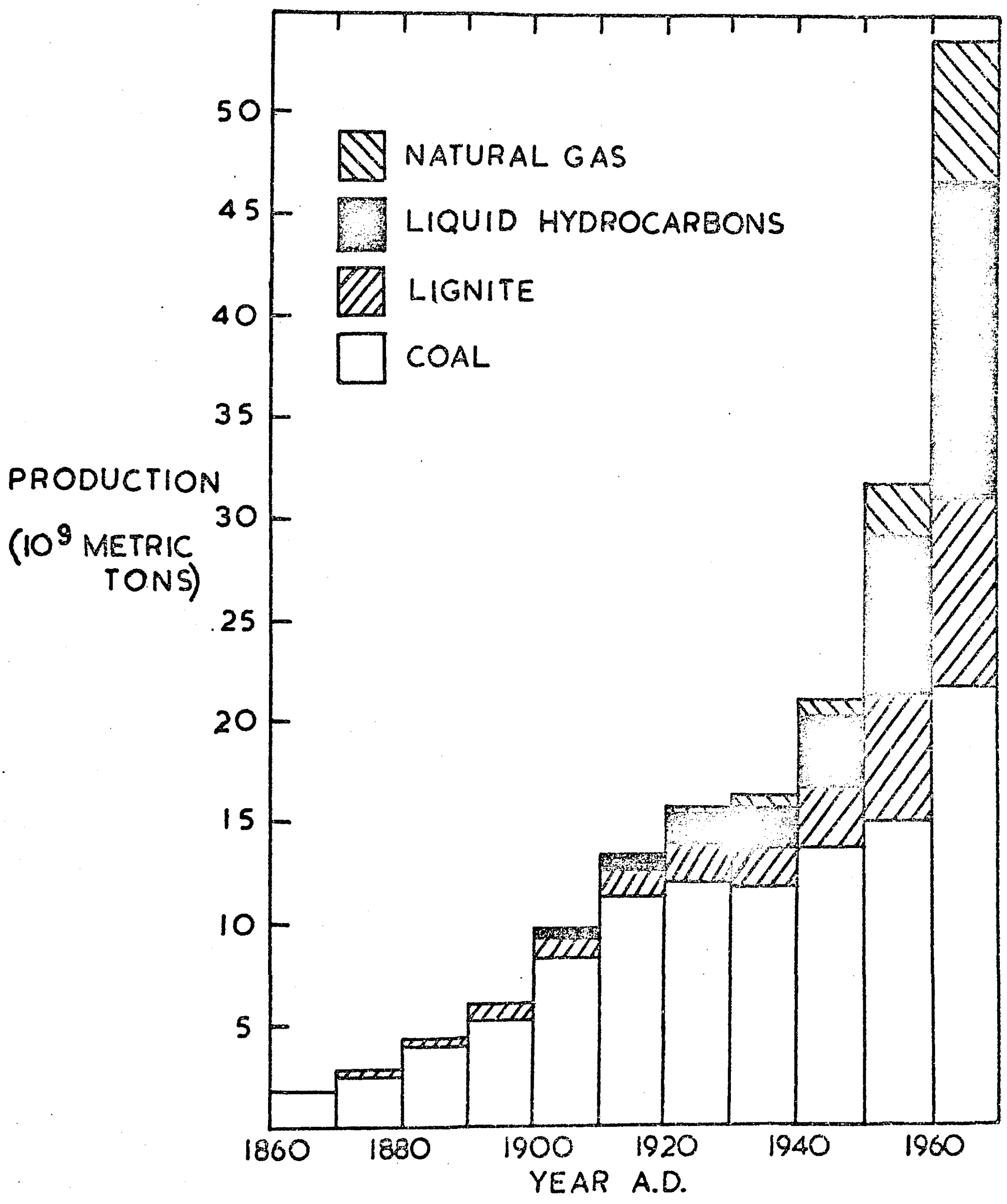


TABLE 5.2

CO_2 (10^{16}g.) PRODUCED BY FOSSIL FUEL COMBUSTION 1860 - 1969

Decade	Coal	Lignite	Liquid Hydrocarbons	Natural Gas	Total
1860-1869	0.46	0.01	-	-	0.47
1870-1879	0.70	0.03	-	-	0.73
1880-1889	1.06	0.05	0.02	-	1.13
1890-1899	1.49	0.08	0.04	0.01	1.62
1900-1909	2.33	0.15	0.10	0.02	2.60
1910-1919	3.10	0.21	0.19	0.04	3.54
1920-1929	3.26	0.31	0.48	0.07	4.12
1930-1939	3.16	0.35	0.74	0.12	4.37
1940-1949	3.74	0.49	1.14	0.25	5.62
1950-1959	4.11	1.07	2.44	0.62	8.24
1960-1969	5.94	1.55	4.90	1.78	14.17
Total	29.35	4.30	10.05	2.91	46.61

corresponds to an increase of only 10% over the natural level, it would appear that most of the added CO_2 has been transferred to other carbon reservoirs. Indeed, Bolin and Bischof (1970) have estimated that only 35 ± 7% of the excess CO_2 introduced to the atmosphere from combustion during the last decade has remained in the atmosphere.

5.2 Previous Estimates of the "Suess Effect"

The "Suess effect", as defined in Section 1.4(a), is the decrease in atmospheric ^{14}C concentrations due to the increase of ^{14}C-free CO_2 in the atmosphere as a result of the input of fossil fuel CO_2 to the atmosphere. The impact of this significant contribution of CO_2 on the dynamic carbon cycle has been assessed by several workers during the last 20 years, with particular emphasis on the resultant decrease of the atmospheric $^{14}C/^{12}C$ ratio this century. Suess, after whom the effect was named, found by direct measurement that the ^{14}C specific activity of wood has decreased since the turn of the century. Experimental observations of up to 4% depletion of the ^{14}C specific activity of modern (i.e. ~ 1950) wood were reported (Suess 1953, Hayes et al. 1955). Further measurements by Suess (1955), however, led him to conclude that some of the higher values were the result of local effects near industrial centres and that the world-wide ^{14}C depletion of the earth's atmosphere was probably about 1 - 3% at that time. Fergusson (1958) measured the effect for modern southern hemisphere wood at -2% by 1950. He added that the difference between the ^{14}C levels of modern wood from the northern hemisphere, into which most of the fossil CO_2 is initially injected, and the southern hemisphere was less than 0.5%. Broecker and Walton (1959) found a value of -2.9% for 1938 while De Vries (1958) quoted a similar figure for 1954. All these investigations were based on the assumption that deviations in atmospheric ^{14}C concentrations from the natural during the last 100 years were due solely to the "Suess effect". This approach is unrealistic in view of the fluctuations of natural ^{14}C levels which are known to occur over periods of the order of 50 years (Houtermans 1966). Indeed, although Fergusson purposely selected tree-ring segments covering a 10- or 20-year time period to avoid any perturbing factors in ^{14}C levels due to the 11-year solar cycle, several of Suess' measurements were performed on tree-ring sections of 5 years' growth or less. In view of the observed magnitude of annual ^{14}C fluctuations prior to times of significant industrial activity (Section 4.2) estimates of the "Suess effect" based on tree-ring sections corresponding to time periods of 5 years ($\frac{1}{2}$ a solar cycle) or less appear rather unreliable.

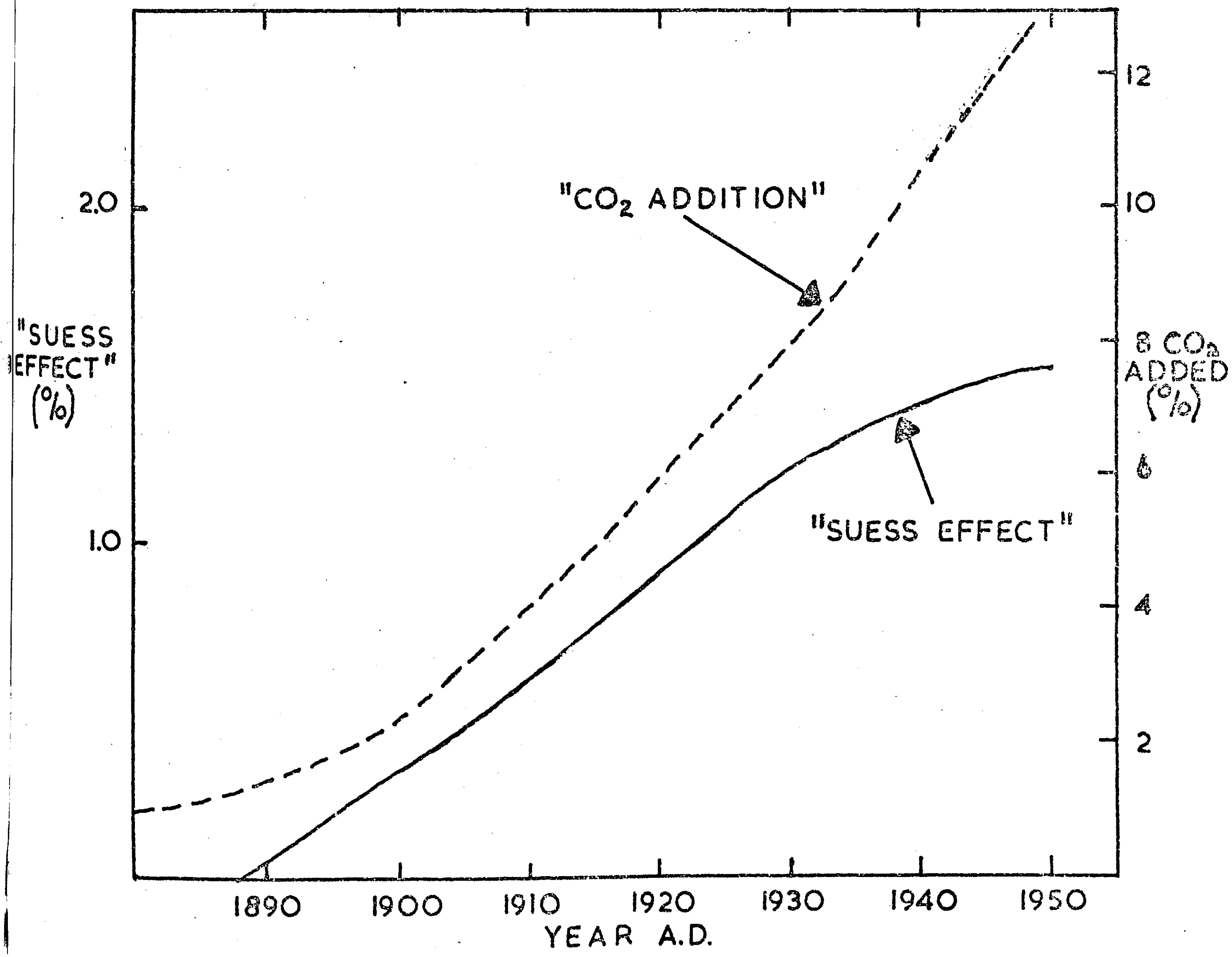
If it were possible to accurately predict natural ^{14}C levels since the turn of the century, then the difference between predicted and observed ^{14}C values until the advent of nuclear weapon testing would correspond to the "Suess effect". Grey (1969) has estimated natural ^{14}C levels from 1200 A.D. to the present using a model which is based on the modulation of the ^{14}C production rate by solar activity. From 1200 - 1900 reasonable agreement is observed between the calculated and observed ^{14}C values, which fluctuated typically by 2 - 3% over periods of 50 - 200 years. From 1900 - 1950 a discrepancy, which linearly increased to 2% by 1950, is evident between Grey's sunspot model ^{14}C levels and the observed ^{14}C data. Grey (1972) has since replaced the observed 20th Century ^{14}C data with the more recent data of Lerman et al. (1970). The resultant difference (the "Suess effect") is shown in Figure 5.2. The rate of increase of the "Suess effect" appears to have decreased since 1930 to a value of 1.4% by 1950. Houtermans et al. (1967), in a similar study, also used the correlation between sunspot numbers and atmospheric ^{14}C levels (over periods of 50 - 200 years) to estimate natural ^{14}C concentrations for the period 1880 - 1940. In spite of the "poor statistical quality of the prediction", Houtermans concluded that, as in no case did predicted Δ values fall below -0.5%, the decrease in atmospheric ^{14}C concentrations can be attributed to industrial fuel consumption. The size of the effect was estimated close to -3% by 1940.

Baxter and Walton (1970) have recently evaluated the "Suess effect" from a purely theoretical standpoint. They considered both the input of fossil CO_2 to the atmosphere and the distribution of excess CO_2 through the various carbon reservoirs as a function of time. A simple box-model was used, the calculations employing exchange rates obtained from studies of the distribution of "bomb" ^{14}C through the carbon cycle. The results showed a decrease in the atmospheric ^{14}C specific activity due solely to fossil fuel CO_2 of -3.2% in 1950. Similarly, they estimated a value of -5.9% for 1969. It is, of course, impossible to evaluate the "Suess effect" at the present time by methods involving direct measurement of atmospheric ^{14}C levels because of the excess ^{14}C in the atmosphere from the testing of nuclear weapons. Baxter and Walton pointed out that their estimate of -5.9% for 1969

FIGURE 5.2

THE "SUESS EFFECT"

(A comparison of the "Suess Effect", evaluated from the solar-wind model of Grey (1969), with the fossil-fuel CO_2 production)
(Grey 1972)



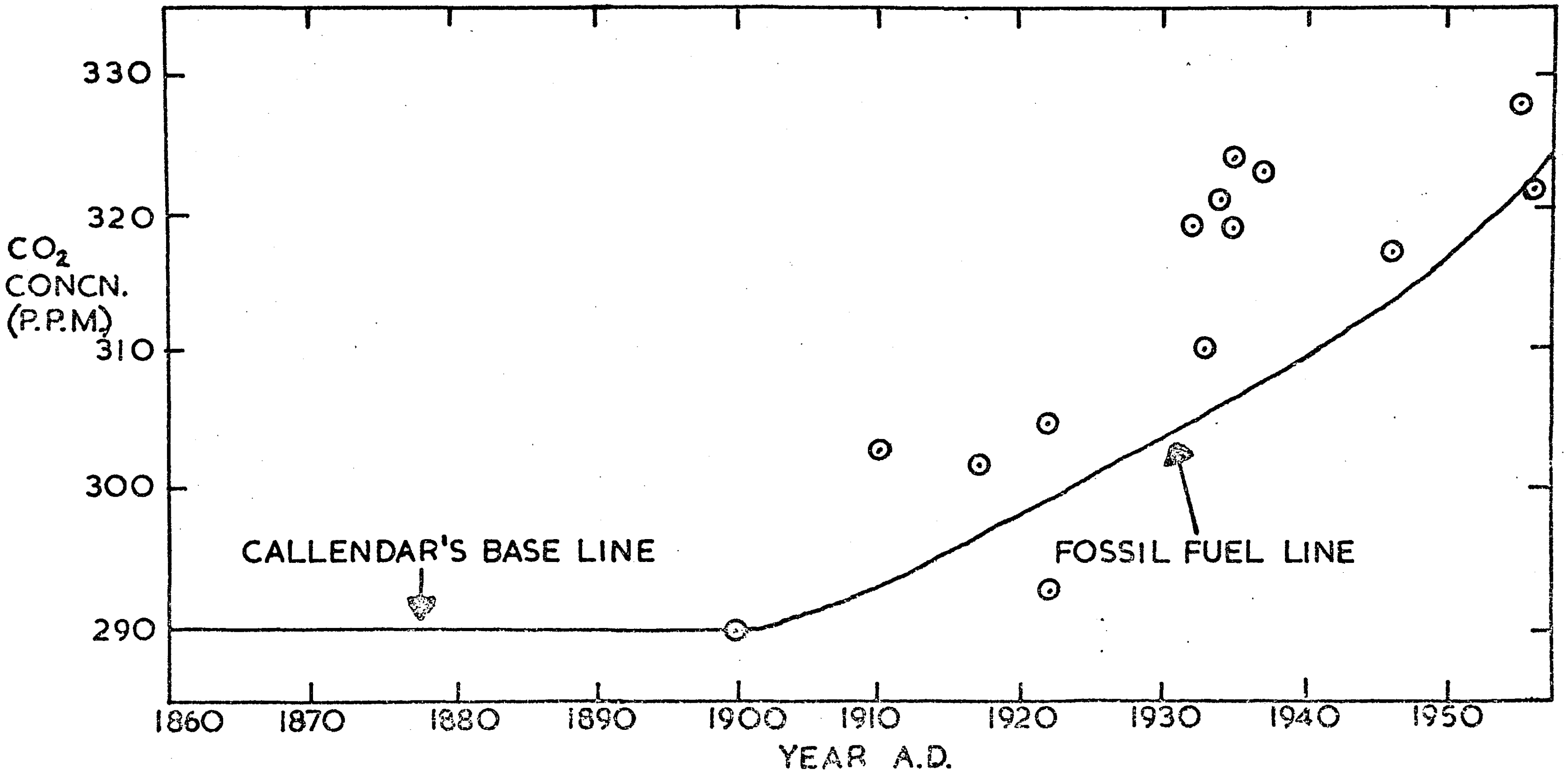
corresponded to an increase of 6.3% in atmospheric CO_2 concentrations, about 3.5% less than the measured increase in atmospheric CO_2 levels assuming a natural level of 290 p.p.m.

It is of interest to note here that Revelle and Suess (1957), using the observed decrease in ^{14}C levels due to fossil fuel combustion (Suess 1955), estimated an exchange time between atmosphere and ocean of only 5 years. Since, at the time of their study, the "Suess effect" was thought to be only 2 - 3% while the cumulative input of fossil fuel CO_2 to the atmosphere since 1860 amounted to 13 - 14% of the natural atmospheric CO_2 inventory, they concluded that most of the CO_2 due to combustion had been transferred into the ocean and that a net increase of CO_2 in the atmosphere of only a few per cent had occurred. Thus they disagreed with the findings of Callendar (1958) who, from a detailed survey of past measurements of CO_2 levels, considered that the increase amounted to 10% of the total amount of CO_2 present in the atmosphere in the latter years of the 19th Century. However, there must be some doubt as to the validity of some of the CO_2 determinations made both last century and in the first half of this century with respect to analytical precision and the time and geographical location of sampling in particular. Callendar, though, in his study, accepted only those measurements which satisfied several stringent criteria of careful, detailed and precise experimental work. Figure 5.3 includes the values which he considered to be most representative of the increase in atmospheric CO_2 content and the corresponding "fossil fuel line" based on the retention by the atmosphere of all the excess CO_2

FIGURE 5.3

MEASURED ATMOSPHERIC CO_2 CONCENTRATIONS (1860–1955)

(Callendar 1958)



produced by combustion.

Bolin and Eriksson (1959) were of the opinion that the above discrepancy between observed atmospheric CO_2 levels and the magnitude of the "Suess effect" may be explained by a consideration of the dissociation equilibrium of CO_2 in the oceans. The addition of CO_2 to the oceans could lower the pH and decrease the dissociation of H_2CO_3 to CO_3^{2-} and HCO_3^-. Since the pressure of CO_2 in the gas phase in equilibrium with CO_2 dissolved in water is proportional to the number of CO_2 and H_2CO_3 molecules in the water, an increase of the partial pressure occurs which is much greater (by a factor of ~12.5) than the increase of the total content of CO_2 in the water. Thus a 12.5% change in the atmospheric CO_2 would require only a 1% change in the total CO_2 concentration of the sea to maintain equilibrium. A theoretical model developed by Bolin and Eriksson confirmed a 10% increase of the CO_2 content of the atmosphere as a result of a total output due to combustion amounting by 1954 to 13% of the total natural CO_2 content. This evaluation of the increase was critically dependent on a residence time of water in the deep sea of around 500 years. Bolin and Eriksson considered that the change of the dissociation equilibrium in water resulting from a transfer of CO_2 to the sea would also shift the dissociation equilibrium for $^{14}CO_2$ in the sea, thus disturbing the ^{14}C equilibrium between the atmosphere and ocean. They believed that subsequent changes in the ^{14}C transfer and distribution among the carbon reservoirs would have a noticeable influence on the magnitude of the atmospheric "Suess effect". Using basically the same model as for the determination of the CO_2

levels, they calculated a "Suess effect" of -5% for 1954, a rather large value in comparison with the measured -3%. To account for the discrepancy they postulated that, because of the small buffering effect of the sea outlined above, the biosphere on land may play a more important role than had previously been believed in the changes actually occurring in the atmosphere due to the release of CO_2 by combustion.

There is obvious disagreement about the magnitude of the "Suess effect", values ranging from -1 to -5% by 1955. To a certain extent, this disagreement reflects inadequacies in the theoretical models employed. Doubt as to the size and role of the biosphere, for example, uncertainty as to the mechanisms involved in the control of carbon distribution (cf. Bolin and Eriksson (1959)) and to the precise values of exchange parameters impose limitations on the models employed (Revelle and Suess 1957, Bolin and Eriksson 1959, Baxter and Walton 1970). There are even significant variations in the published ^{14}C data for this century, necessitating revisions in estimates of the "Suess effect" from models such as the one employed by Grey (1969, 1972).

During the last decade, studies of carbon circulation in nature have placed major emphasis on the monitoring of "bomb" ^{14}C in the atmosphere, oceans and biosphere. The input of large quantities of ^{14}C (Table 1.1), although doubling atmospheric ^{14}C levels by 1963, had an insignificant effect on the total amount of carbon in the atmosphere. Thus exchange studies using "bomb" ^{14}C assume that the prevailing equilibrium in the carbon cycle is undisturbed and that the distribution of "bomb" ^{14}C reflects the general pattern of carbon circulation. It is of interest to note that "bomb" ^{14}C transport studies have neglected the increasing input of fossil CO_2 to the atmosphere, both with regard to the direct effect on atmospheric ^{14}C concentrations and to the possible disturbance of the assumed equilibrium conditions of the carbon cycle. Baxter and Walton (1970) have estimated that the resultant error due to the former effect in the assessment of the gradient of decrease in atmospheric ^{14}C concentrations amounts to a maximum of 5% and introduces an error of ~3.5% in calculations of the atmosphere/ocean exchange rate constant. They concluded that, since this error lies within the limits of accuracy of most determinations, the practice of neglecting the "Suess effect" seems justified.

The distribution of the excess CO_2 from fossil fuel combustion is nonetheless still of great interest. Extensive series of measurements of the increasing CO_2 content of the atmosphere have been reported in recent years (Keeling 1960, Bolin and Keeling 1963, Pales and Keeling 1965, Brown and Keeling 1965, Bischof and Bolin 1966, 1970). As mentioned previously, earlier measurements of CO_2 levels are regarded as extremely uncertain. However, knowledge of the extent and distribution of excess CO_2 in the past is of major importance for the following reasons:

(1) the precise detection of natural variations in 20th Century ^{14}C levels requires correction of the observed ^{14}C data for the "Suess effect" (cf. Baxter and Walton 1970),

(2) the prediction of future levels of atmospheric CO_2 and the possible climatological consequences (Section 5.4), as a result of the rapidly

increasing rate of fossil fuel combustion, is dependent on estimates of the partitioning of the excess CO_2 among the atmosphere, oceans and biosphere.

Thus information about the constancy, or otherwise, of the fraction of fossil fuel CO_2 remaining in the atmosphere throughout the past 100 years is extremely valuable. Section 5.3 describes a novel approach, based on the varying $^{13}C/^{12}C$ ratio of 20th Century wood, which may eventually provide reliable evidence of past atmospheric CO_2 levels and thus be of relevance to (1) and (2) above.

5.3 Changes in the Concentration and Isotopic Abundance of Atmospheric CO_2 in the 20th Century

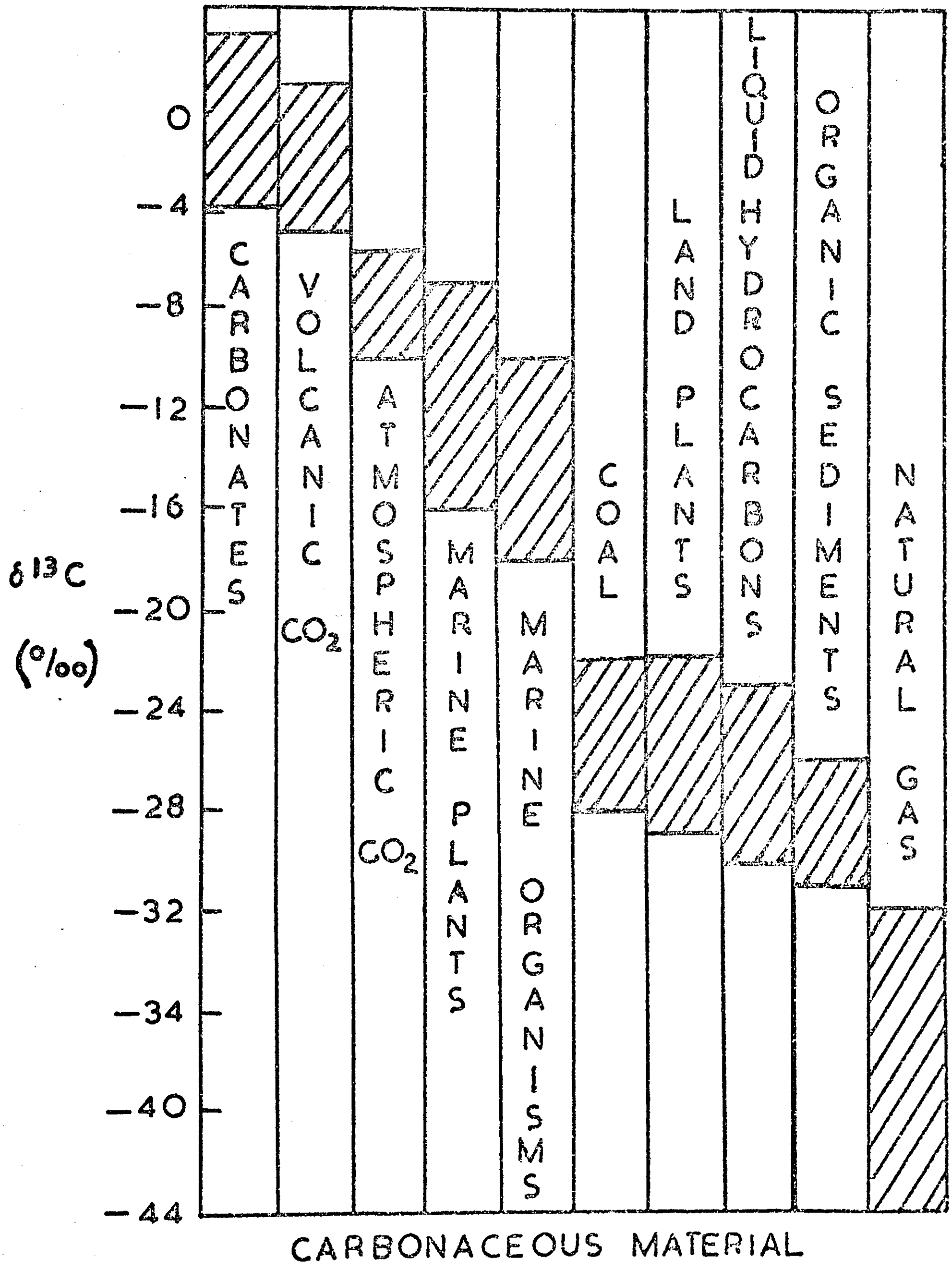
(a) Geochemistry of the stable carbon isotopes

As a result of chemical isotope effects the various natural carbon reservoirs have different and somewhat characteristic values of the $^{13}C/^{12}C$ ratio (Craig 1953). The carbon isotope ratios of various carbonaceous samples relative to the P.D.B. standard (Section 2.8) are presented in Figure 5.4. The range of variation in the ratio is 4.5%.

Terrestrial plants and their fossil remains (e.g. coal, petroleum) are depleted in ^{13}C by ~2% relative to atmospheric CO_2. Thus the burning of fossil fuels has released increasing amounts of ^{13}C-depleted CO_2 to the atmosphere. It seems reasonable to suppose that the $^{13}C/^{12}C$ ratio of atmospheric CO_2 will have decreased in sympathy with the addition of lighter CO_2 to the atmosphere. Consequently, if the isotopic fractionation factor during the photosynthetic assimilation of atmospheric CO_2 by the

FIGURE 5.4

CARBON ISOTOPE RATIOS OF VARIOUS CARBONACEOUS MATERIALS ($\delta^{13}C$ w.r.t. P.D.B.)



wood of trees has remained constant, tree rings should preserve a record of past changes in atmospheric $^{13}C/^{12}C$ ratios. Such variations, if they exist, should provide a measure of any secular variations of atmospheric CO_2 levels. The parameters involved in calculations based on this theoretical conception are discussed in (b).

(b) Parameters for the theoretical interpretation of $\delta^{13}C$ data

Consider the changing amounts of ^{12}C and ^{13}C in atmospheric CO_2 and the concurrent variations in $\delta^{13}C_{atm}$ within the following framework:

Let the number of ^{12}C atoms at time $t_0 = N$,

the total CO_2 concentration (p.p.m.) at time $t_0 = x$,

the total CO_2 concentration (p.p.m.) at time $t_1 = y$, $(y > x)$,

the isotopic ratio of the standard, $^{13}C/^{12}C_{PDB} = R$.

Then the number of ^{13}C atoms at time t_0 can be obtained from the relationship:

$$\delta^{13}C_{t_0} = \frac{(^{13}C/^{12}C)_{t_0}}{R} - 1 \qquad \text{(Section 2.4)}$$

where $\delta^{13}C_{t_0}$ is in fractional form i.e. unconverted to per millage.

It follows that $(^{13}C/^{12}C)_{t_0} = R(\delta^{13}C_{t_0} + 1)$

$$\therefore\ ^{13}C = R(\delta^{13}C_{t_0} + 1)\,^{12}C$$

$$\therefore \text{ Number of } ^{13}C \text{ atoms} = NR(\delta^{13}C_{t_0} + 1)$$

At time t_1, the number of ^{12}C atoms = yN/x (neglecting the small changes in isotopic ratio which have an insignificant effect, due to the low abundance of ^{13}C (1%), on the total concentration of atmospheric CO_2).

$$\delta^{13}C_{t_1} = \frac{(^{13}C/^{12}C)_{t_1}}{R} - 1$$

Similarly to before:

$$\text{Number of } ^{13}C \text{ atoms} = y\frac{N}{x}\,R(\delta^{13}C_{t_1} + 1)$$

Thus, in the time interval $t_1 - t_0$, the number of atoms in the atmosphere has increased by the following amounts:

$$\text{Increase in number of } ^{13}C \text{ atoms} = y\frac{N}{x}\,R(\delta^{13}C_{t_1} + 1) - NR(\delta^{13}C_{t_0} + 1)$$

$$= NR\left[\frac{y}{x}(\delta^{13}C_{t_1} + 1) - (\delta^{13}C_{t_0} + 1)\right]$$

$$\text{Increase in number of } ^{12}C \text{ atoms} = \frac{y}{x}\,N - N$$

$$= N\left(\frac{y}{x} - 1\right)$$

Consider the increased number of atoms as a "block addition" to the natural atmosphere.

Then $\delta^{13}C$ of the added amount is given by:

$$\delta^{13}C_{added} = \frac{\dfrac{NR\left[\frac{y}{x}(\delta^{13}C_{t_1} + 1) - (\delta^{13}C_{t_0} + 1)\right]}{N\left[\frac{y}{x} - 1\right]}}{R} - 1$$

$$= \frac{\frac{y}{x}(\delta^{13}C_{t_1} + 1) - (\delta^{13}C_{t_0} + 1)}{\left[\frac{y}{x} - 1\right]} - 1$$

$$= \frac{y(\delta^{13}C_{t_1} + 1) - x(\delta^{13}C_{t_0} + 1)}{y - x} - 1$$

$$\text{or } (\delta^{13}C_{added} + 1) = \frac{y(\delta^{13}C_{t_1} + 1) - x(\delta^{13}C_{t_0} + 1)}{y - x}$$

If t_1 corresponds to the present or some time in the last 10 years then the atmospheric CO_2 concentration, y, can be obtained from direct measurements. Also the difference between $\delta^{13}C_{t_1}$ and the $\delta^{13}C$ value of wood at time t_1 permits an evaluation of the fractionation factor between wood and atmospheric CO_2 during photosynthesis. This can be used to calculate $\delta^{13}C_{t_0}$ from the $\delta^{13}C$ value of tree-ring wood at time t_0, where t_0 may be any time in the past. Thus if $\delta^{13}C_{added}$ can be independently established, the equation can be solved for the atmospheric CO_2 concentration, x, at any time t_0 in the past. Conversely, if x is assumed from past CO_2 determinations (e.g. the estimate of 290 p.p.m. by Callendar (1958) for the turn of the century) then $\delta^{13}C_{added}$ can be calculated from the equation. Such calculations would provide a cross-check on the reliability of this treatment of the experimental data (Section 5.3(d)).

(c) $^{13}C/^{12}C$ ratios of tree-ring wood during the 20th Century

The approach described in (b) requires the determination of the $^{13}C/^{12}C$ ratios of 20th Century tree-ring wood. A small section of dendrochronologically-dated oak (planted 1848; felled November 1968) was obtained from Russell's Enclosure in the Forest of Dean (51°48'N, 2°37'W). Individual ring widths fell in the range 0.5 - 6 mm. Where possible, individual rings were separated from the section, but only groups of rings could be cut for the years 1898 - 99, 1915 - 17, 1923 - 24, 1933 - 35, 1940 - 42, 1954 - 56 and 1967 - 68 in the range 1894 - 1968. The whole-wood samples were not subjected to any chemical pretreatment prior to conversion to CO_2 (Section 2.8(a)) because of the risk of inducing isotopic fractionation effects. The isotopic ratios were measured (Section 2.8(b)) and the results expressed relative to P.D.B. to a precision of

± 0.2‰ (Table 5.3). To smooth out the distribution of results a 10-year running mean was calculated from the data (Table 5.4) and plotted as shown in Figure 5.5. The general trends of this curve are discussed in greater detail later but the basic features are a rapid decrease in $\delta^{13}C$ during the first 20 years of this century followed by a period of relative stability, the overall decrease in $\delta^{13}C$ amounting to ~2‰ by 1964.

(d) Atmospheric $^{13}C/^{12}C$ ratios and CO_2 concentrations (1899 - 1964)

Wood $^{13}C/^{12}C$ ratios can be converted to atmospheric $^{13}C/^{12}C$ ratios if the fractionation which occurs during the assimilation of CO_2 by trees is known. By comparing modern-wood carbon with atmospheric carbon, Grey (1971) has estimated the fractionation factor at -21‰. This factor is used here to assess $\delta^{13}C$ values for the atmosphere corresponding to those reported for wood in Table 5.4. Thus $\delta^{13}C$ for the atmosphere has decreased from -4.89‰ at the turn of the century to -6.88‰ in 1964. From Section 5.3(b),

$$(\delta^{13}C_{added} + 1) = \frac{y(\delta^{13}C_{t_1} + 1) - x(\delta^{13}C_{t_0} + 1)}{y - x}$$

Assuming that the 2‰ decrease in $\delta^{13}C$ of the atmosphere is due to excess CO_2 from the combustion of fossil fuels, a reasonable value for $\delta^{13}C_{added}$ is -26‰ (Figure 5.4). As the atmospheric CO_2 concentration in 1964, y, was ~316 p.p.m. (Keeling 1970), the equation can be solved for x, the atmospheric CO_2 concentration in 1899/1900 (t_0), viz.,

$$(-0.026 + 1) = \frac{(316 \times 0.99312) - 0.99511x}{316 - x}$$

TABLE 5.3

CARBON ISOTOPIC COMPOSITION ($\delta^{13}C$) OF OAK 1894 - 1968

($\delta^{13}C$ values expressed relative to P.D.B. and to a precision of ± 0.2‰)

Year	$\delta^{13}C$(‰)	Year	$\delta^{13}C$(‰)	Year	$\delta^{13}C$(‰)
1894	-26.12	1919	-27.18	1944	-27.37
1895	-25.55	1920	-26.33	1945	-27.82
1896	-26.01	1921	-26.57	1946	-27.25
1897	-26.39	1922	-27.28	1947	-28.58
1898	-25.88	1923	-27.49	1948	-27.69
1899		1924		1949	-26.90
1900	-25.89	1925	-27.12	1950	-26.74
1901	-25.25	1926	-27.35	1951	-26.88
1902	-26.17	1927	-26.77	1952	-27.05
1903	-25.74	1928	-26.59	1953	-27.22
1904	-26.18	1929	-26.89	1954	-27.37
1905	-25.91	1930	-27.18	1955	
1906	-26.13	1931	-27.62	1956	
1907	-26.08	1932	-26.82	1957	-27.49
1908	-27.18	1933	-26.73	1958	-27.01
1909	-26.80	1934		1959	-26.54
1910	-26.83	1935		1960	-26.60
1911	-25.68	1936	-27.62	1961	-26.37
1912	-26.96	1937	-27.32	1962	-26.82
1913	-26.86	1938	-27.22	1963	-28.36
1914	-27.29	1939	-27.01	1964	-27.95
1915	-27.78	1940	-27.37	1965	-30.28
1916		1941		1966	-27.77
1917		1942		1967	-28.94
1918	-27.92	1943	-27.79	1968	

TABLE 5.4

10-YEAR MEANS OF CARBON ISOTOPIC COMPOSITION ($\delta^{13}C$) OF OAK 1899 - 1964

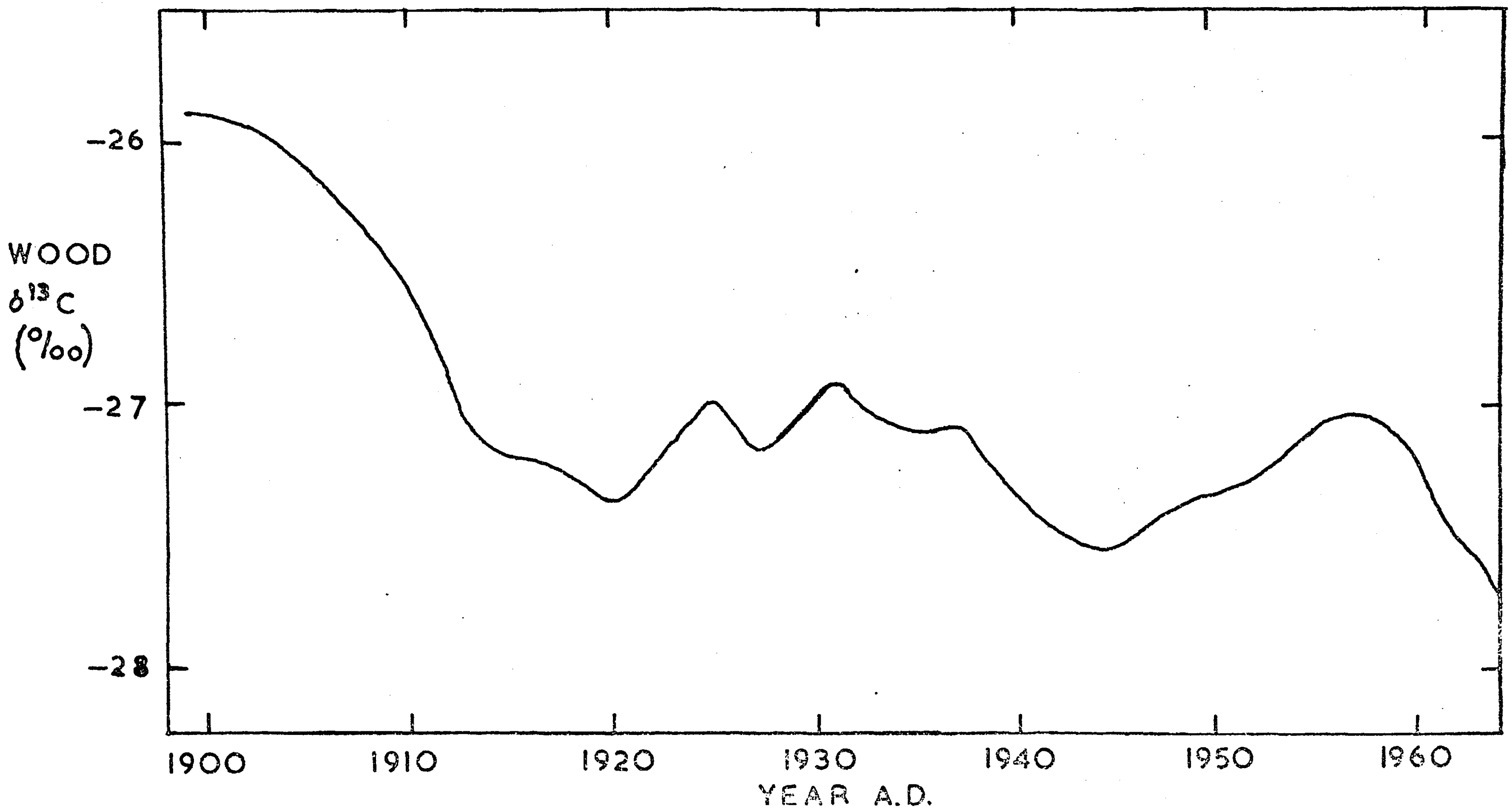
(Mean $\delta^{13}C$ values based on $\delta^{13}C$ from Table 5.3)

Mean year	Mean $\delta^{13}C$(‰)	Mean year	Mean $\delta^{13}C$(‰)	Mean year	Mean $\delta^{13}C$(‰)
1899	-25.89	1921	-27.29	1943	-27.52
1900	-25.89	1922	-27.25	1944	-27.56
1901	-25.93	1923	-27.15	1945	-27.55
1902	-25.94	1924	-27.02	1946	-27.49
1903	-25.91	1925	-26.99	1947	-27.44
1904	-26.04	1926	-27.07	1948	-27.41
1905	-26.13	1927	-27.18	1949	-27.35
1906	-26.23	1928	-27.13	1950	-27.35
1907	-26.27	1929	-27.06	1951	-27.31
1908	-26.35	1930	-26.98	1952	-27.32
1909	-26.46	1931	-26.94	1953	-27.21
1910	-26.57	1932	-26.97	1954	-27.14
1911	-26.76	1933	-27.02	1955	-27.10
1912	-26.92	1934	-27.09	1956	-27.09
1913	-27.09	1935	-27.10	1957	-27.06
1914	-27.17	1936	-27.12	1958	-27.04
1915	-27.21	1937	-27.09	1959	-27.15
1916	-27.16	1938	-27.15	1960	-27.21
1917	-27.25	1939	-27.25	1961	-27.50
1918	-27.28	1940	-27.32	1962	-27.54
1919	-27.34	1941	-27.43	1963	-27.69
1920	-27.36	1942	-27.39	1964	-27.88

FIGURE 5.5

TEMPORAL VARIATION OF $\delta^{13}C$ IN OAK (51°48′N, 2°37′W)

(The curve is smoothed by a 10-year running mean)



$$\therefore \quad x = 286.2$$

This value of x compares extremely favourably with Callendar's value of 290 p.p.m. for the turn of the century. Confirmatory evidence of the isotopic abundance of the excess CO_2 is provided in Table 5.5 which summarises solutions of the above equation for $\delta^{13}C_{added}$ corresponding to a range of values of x (280 - 300 p.p.m.), the atmospheric CO_2 concentration in 1900. Reasonable values of $\delta^{13}C_{added}$ (-24.54‰ → -30.04‰) are obtained for $284 \leqslant x \leqslant 291$. The extreme values of 280 p.p.m. and 300 p.p.m. correspond to -22.36‰ and -44.19‰ for $\delta^{13}C_{added}$, values outwith the likely range of fossil CO_2 (Figure 5.4).

On the assumption that the decrease in $\delta^{13}C$ of the atmosphere is due to the presence of excess fossil CO_2 of $\delta^{13}C \sim -26‰$, atmospheric CO_2 concentrations were calculated for the period 1899 - 1964 using atmospheric $\delta^{13}C$ values deduced from the mean $\delta^{13}C$ values of wood listed in Table 5.4. The resultant CO_2 concentrations (Table 5.6) are plotted in Figure 5.6 along with the "fossil fuel line" from Figure 5.3.

The calculated curve shows an increase of 21.4 p.p.m. in atmospheric CO_2 concentrations from 1900 - 1920, a reflection of the rapid decrease (~1.5‰) of $\delta^{13}C$ for that period. The magnitude of this increase is rather surprising because it is obvious from a comparison of the calculated curve and the "fossil fuel line" that atmospheric CO_2 concentrations up to 1930 could not have attained the levels indicated in Figure 5.6 even if all the excess CO_2 from fossil fuel combustion had remained in the atmosphere. However, Callendar's survey of 20th Century CO_2 levels included a reputedly reliable value of 305 p.p.m. for

TABLE 5.5

$\delta^{13}C$ VALUES OF EXCESS ATMOSPHERIC CO_2 AS A FUNCTION OF ATMOSPHERIC CO_2 CONCENTRATION IN 1900

Assumed value of CO_2 concentration (p.p.m.) in 1900	Calculated $\delta^{13}C$ (‰) for excess CO_2 1900 - 1964
280	-22.36
284	-24.54
285	-25.18
286	-25.86
287	-26.57
288	-27.35
289	-28.18
290	-29.08
291	-30.04
300	-44.19

TABLE 5.6

ATMOSPHERIC CO_2 CONCENTRATIONS 1899 - 1964

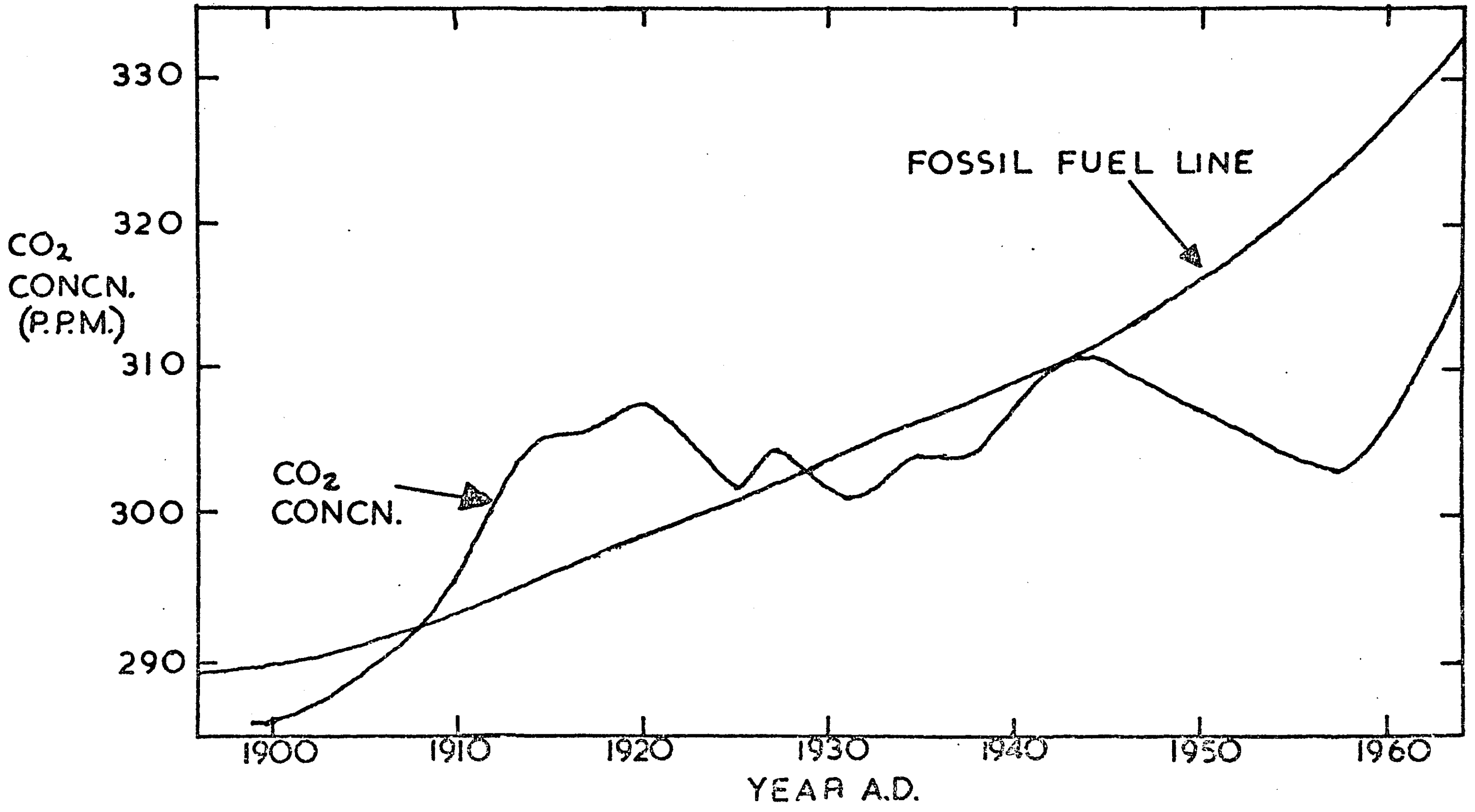
(Based on Table 5.4, assuming a fractionation factor of -21‰ between wood and atmospheric CO_2)

Year	CO_2 concn. (p.p.m.)	Year	CO_2 concn. (p.p.m.)	Year	CO_2 concn. (p.p.m.)
1899	286.2	1921	306.5	1943	310.2
1900	286.2	1922	305.9	1944	310.8
1901	286.8	1923	304.4	1945	310.6
1902	286.9	1924	302.4	1946	309.7
1903	286.5	1925	301.9	1947	308.9
1904	288.3	1926	303.2	1948	308.4
1905	289.5	1927	304.8	1949	307.5
1906	290.9	1928	304.1	1950	307.5
1907	291.5	1929	303.0	1951	306.9
1908	292.6	1930	301.8	1952	307.0
1909	294.2	1931	301.2	1953	305.3
1910	295.7	1932	301.6	1954	304.3
1911	298.5	1933	302.4	1955	303.6
1912	300.9	1934	303.5	1956	303.5
1913	303.5	1935	303.6	1957	303.0
1914	304.7	1936	303.9	1958	302.7
1915	305.3	1937	303.5	1959	304.4
1916	304.5	1938	304.4	1960	305.3
1917	305.9	1939	305.9	1961	309.8
1918	306.4	1940	307.0	1962	310.5
1919	307.3	1941	308.7	1963	312.9
1920	307.6	1942	308.1	1964	316.0

FIGURE 5.6

CALCULATED ATMOSPHERIC CO_2 CONCENTRATIONS
(1899–1964)

(Derived from wood $\delta^{13}C$ variations)



1920 (Figure 5.3) in close agreement with the value of 307.6 p.p.m. obtained here. Thus there is some independent confirmation of greatly increased levels of CO_2 during the first 20 years of the 20th Century.

The most obvious explanation of the discrepancy between the 2 curves (excluding the limitations of this approach which are discussed in Section 5.3(e)) is that an additional source contributed CO_2 to the atmosphere during the first 30 years of this century. The theoretical basis of this treatment implies that the additional CO_2 is of $\delta^{13}C \sim -26‰$. Thus the possible contribution of CO_2 from volcanic emission or from warming of the oceans ($0 \leqslant \delta^{13}C \leqslant -5‰$, Craig 1953, Grey 1971) is apparently excluded. Furthermore, it has been estimated that the present rate of influx of volcanic CO_2 is only 1% of that from fossil fuel combustion. However, it seems possible that the enlargement of the world's cultivated farmland since the middle of the 19th Century may have resulted in the addition of significant quantities of CO_2 to the atmosphere. Indeed Hutchinson (1954) considers this the most probable additional cause of the increasing CO_2 levels this century. Revelle (1965) has estimated an increase of arable land of $\sim 1.6 \times 10^6$ million square miles, corresponding to 2.7% of the land area of the earth and a consequent 5% decrease of forests and grasslands, in which is concentrated most of the soil humus. Assuming that the total humus is equal to twice the amount of carbon in the atmosphere and that half the carbon in the humus of the newly cultivated lands has been oxidised to CO_2, Revelle assessed the total injection into the atmosphere from this source as $\sim$5% of the "natural" CO_2 concentration.

This corresponds to ~10^{17} g. CO_2. The average excess CO_2 in the atmosphere as derived from Figure 5.6 for the period 1900 - 1930 is ~7 p.p.m. (~0.55×10^{17} g. CO_2) with a maximum of ~13 p.p.m. (~10^{17} g. CO_2). Although Revelle's estimate of 10^{17} g. represents the input of soil CO_2 up to recent years, the effect is clearly of an appropriate order of magnitude and may well account for part of the observed increase in CO_2 levels (Callendar 1957). The isotopic abundance of CO_2 from the oxidation of organic litter is related to that of land plants (Figure 5.4) and, at $\delta^{13}C \sim -25‰$, satisfies the imposed conditions of this treatment.

The CO_2 concentration of 307.6 p.p.m. for 1920 corresponds to a "Suess effect" of -6.96%, assuming that all the excess CO_2 in the atmosphere is derived directly from fossil fuels. A "Suess effect" of -6.96% for 1920 is obviously incompatible with measured ^{14}C data (Lerman et al. 1970, Baxter and Walton 1971). However, it has just been shown above that fossil CO_2 can only account in part for the increase in CO_2 levels by 1920. Assuming that the ^{14}C content of the postulated additional CO_2 is comparable to natural atmospheric levels, the "Suess effect" amounts to ~-2.9% by 1920. This value is still somewhat greater than Baxter and Walton's (1970) estimate of -1.69%, derived from a theoretical consideration of the distribution of fossil CO_2 among the various carbon reservoirs. The exchange of fossil CO_2 for CO_2 from the biosphere and oceans obviously decreases the depletion of atmospheric ^{14}C and thus -2.9% constitutes an upper limit for the "Suess effect", almost equivalent to a value based merely on the retention of the total input of fossil CO_2 from 1900 - 1920.

In a previous attempt to reconcile observed CO_2

levels and ^{14}C data for the earlier part of this century, Revelle and Suess (1957) postulated that a rapid exchange of CO_2 between the atmosphere and the biosphere would significantly decrease the change in ^{14}C activity resulting from industrial fuel combustion. In terms of the present treatment, this would result in a replacement of some inactive CO_2 by ^{14}C-containing CO_2 of similar stable-isotopic composition ($\delta^{13}C \sim -25‰$) from biogenic litter and soil carbon. However, as the turnover time of atmospheric CO_2 through the terrestrial biological cycle is of the order of 20 - 30 years (Harkness 1970, Bolin and Bischof 1970) it seems improbable that this mechanism, although maintaining the ^{13}C depletion of the atmosphere, could account for the observed discrepancies between atmospheric CO_2 levels and ^{14}C concentrations during the 30-year time period 1900 - 1930.

The rather erratic paths of the $\delta^{13}C$ curve (Figure 5.5) and the CO_2 curve (Figure 5.6) from 1930 - 1958 are surprising in view of the increased input of fossil CO_2 to the atmosphere during that period (Table 5.2). From 1930 - 1944, the calculated CO_2 curve is similar to the "fossil fuel line" but from 1944 - 1958 the CO_2 concentration decreased by 7.9 p.p.m. This latter trend corresponds to an increase of $\delta^{13}C$ of 1.28‰. A steady decrease of $\delta^{13}C$ might have been expected for 1944 - 1958, a period of rapidly increasing input of fossil CO_2 following the more stagnant years of the economic depression and World War 2.

An increase in the terrestrial biomass may have been responsible for this latter trend. As plant growth varies almost linearly with CO_2 concentration (Lundegardh 1957), enhanced atmospheric CO_2 levels could result in an increasing terrestrial biomass. Increased uptake of CO_2 by the biosphere would limit rises in atmospheric CO_2 concentrations and, at the same time, increase atmospheric $\delta^{13}C$ in view of the preferential assimilation of ^{12}C by plants. Bolin and Bischof (1970) estimate that an increase of ~7% in the size of the biosphere could have occurred since the onset of fossil fuel combustion. This idea is supported by surface photographic studies of forest areas over the last 50 years (Shantz and Turner 1958, Phillips 1963). Forest borders were shown to be advancing, but there is no real proof of a significantly increasing biomass, especially in view of the large-scale cultivation of land during the last 100 years (Hutchinson 1954).

It is also possible that a more rapid removal of CO_2 from the atmosphere to the oceans has occurred since 1940, as a result of temperature changes. The solubility of CO_2 in sea water is temperature dependent (Eriksson 1963) such that a 0.1 - 0.2°C decrease of average surface temperature of the world oceans would cause a decrease of ~1% in the atmospheric CO_2 level. Unfortunately, present ocean surface temperature data are not sufficiently adequate to assess the likelihood of such changes over time periods of a decade, but average land surface temperatures have decreased globally by 0.1 - 0.2°C since 1940.

Supporting evidence for the general CO_2 trend from 1930 - 1958 (Figure 5.6) and the carbon-reservoir effects postulated above is perhaps provided by Bolin and Bischof (1970) who estimate, from direct measurements of atmospheric CO_2 levels, that the proportion of fossil fuel CO_2 remaining in the atmosphere has probably decreased from a value in excess of 40% earlier this century to a current value of 35 ± 7%. Furthermore, Figure 5.2 (Grey 1972) shows an apparent slowing in the rate of increase of the "Suess effect" from 1930 - 1950, an effect in accord with increased rates of removal of fossil CO_2 from the atmosphere. However, Grey has indicated that the solar-modulated ^{14}C production-rate model (Section 5.2) involved in his "Suess effect" calculation neglected the possibility of increased ^{14}C production by solar protons during high solar-flare activity (Lingenfelter and Ramaty 1970). As the most recent solar maxima have been very strong, solar-proton effects may have partly offset Grey's calculated depression of ^{14}C production and thus decreased the apparent "Suess effect". Thus, while the above factors qualitatively support increased net transfer of CO_2 from the atmosphere to the biosphere and oceans, the assessment of the effect over 30 - 40 years is difficult in view of the uncertain changes in the terrestrial biomass and the unknown response time of the oceans to the accomodation of additional CO_2 from the atmosphere. In addition, the rapid depletion of ^{13}C (Figure 5.5) and the calculated increase of CO_2 for 1958 - 1964 (Figure 5.6) constitutes a trend opposite in direction to that of the period 1944 - 1958. Indeed, the calculated 13.3 p.p.m. increase of CO_2 for 1958 - 1964 represents an annual rate of increase approximately 3 times as great as that actually observed for the same period (Keeling 1970). It is possible that local effects (e.g. forest soil atmosphere, local industrial activity, climatic effects) may have contributed to the concentration and isotopic abundance of the atmospheric CO_2 in contact with the Forest of Dean oak and thus have been responsible for the irregular nature of the curves (Figures 5.5 and 5.6) in recent years. These effects and the general limitations and uncertainties of the method are discussed in (e).

(e) Limitations and conclusions of the method

(1) Calculations of atmospheric CO_2 concentrations were based on the assumption that $\delta^{13}C_{added} = -26‰$. In view of the trend in fuel consumption away from coal towards the liquid hydrocarbons and natural gases (Figure 5.1), changes may have occurred in the isotopic composition of the injected fossil CO_2. Natural gas, in particular, is significantly depleted (10 - 20‰) in ^{13}C relative to coal and the liquid hydrocarbons (Figure 5.4). However, it is only during the last decade that the input of CO_2 from the combustion of natural gas has amounted to even 10% of the total fossil CO_2 input to the atmosphere (Table 5.2). Although liquid hydrocarbon combustion now contributes ~35% of the total fossil CO_2 injection compared with ~17% for 1930 - 1939, any decrease in $\delta^{13}C$ of fossil CO_2 should be minimal considering the relative similarity of isotopic composition of coal and liquid hydrocarbon fuels (Figure 5.4). Thus, over the last 70 years, the $\delta^{13}C$ of fossil CO_2 has largely been controlled by the combustion of coal, which, with lignite, still contributes over 50% of the total fossil CO_2 input (Table 5.1). In view of the range of published $\delta^{13}C$ values for fossil fuels (Figure 5.4) a mean value of -26‰ appears satisfactory.

(2) The method further assumes a constant fractionation factor of -21‰ between atmospheric CO_2 and wood over the last 70 years. Measurements during the last 15 years suggest that the atmospheric $\delta^{13}C$ is ~ -7‰ (Keeling

1958) while recent tree-ring wood $\delta^{13}C$ values are of the order of -28‰ (Table 5.3, Grey 1971). However, detailed preliminary investigations of the concentration and isotopic composition of the atmospheric CO_2 in the environment of the tree under study would greatly aid the assessment of the fractionation factor. Such an investigation would be rather time-consuming in view of the known diurnal and seasonal variations of atmospheric CO_2 levels and isotopic composition in the region of forest eco-systems (Keeling 1958, 1960) and the atmosphere in general (Keeling 1970, Bolin and Bischof 1970). Such variations correspond to the diurnal and seasonal variations in the rate of photosynthetic assimilation and respiration of CO_2 by living material. The assumption of constancy of fractionation between atmospheric CO_2 and growing wood over the last 70 years is without proof. Craig (1954b) concluded that observed 1‰ differences in the long-term trend of wood $\delta^{13}C$ from 900 B.C. - 1600 A.D. were due to effects of varying external conditions on the assimilation and respiratory processes of the tree and not to variations of the atmospheric isotopic composition. However, a ~2‰ decrease in wood $\delta^{13}C$ since 1900 can hardly be attributed to variations in carbon isotope fractionation during photosynthesis, especially in view of the significant artificial disturbance of the dynamic carbon cycle by the injection of fossil CO_2. Despite this, it remains a possibility that gradual changes in fractionation during photosynthesis may have occurred this century. Suess (1965) has commented that young trees may show different fractionation from mature trees. This apparent effect is probably due to the fact that CO_2 close to the ground is of different isotopic composition to CO_2 of the free air because of sizeable contributions of CO_2 from the soil and the decay of organic litter. Strong CO_2 concentration gradients near the ground demonstrate the possibility of strong local influences on low plants such as young trees or grasses. Both the laboratory simulation of varying environmental conditions (e.g. temperature, humidity) on carbon isotope fractionation during photosynthesis (Park and Epstein 1960, 1961) and the study of atmosphere/forest/soil systems (Keeling 1958, 1960, Rafter and Stout 1970) may be of value in assessing the likely extent of possible past variations in fractionation.

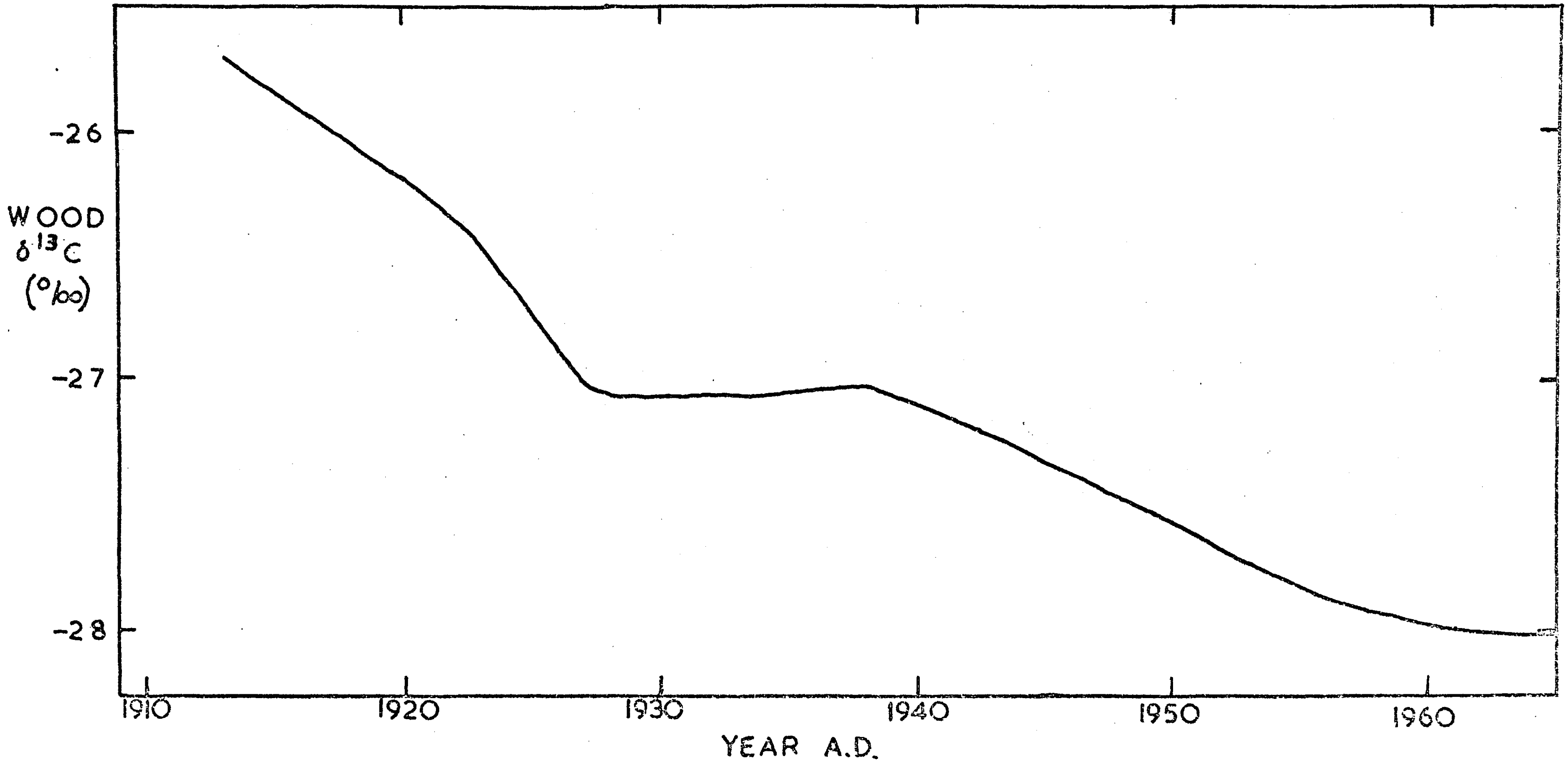
(3) The use of forest-tree wood for the detection of atmospheric $\delta^{13}C$ variations could be criticised on the grounds that the forest atmosphere is unrepresentative of the general isotopic composition and concentration of atmospheric CO_2. Keeling (1958), however, measured the concentration and isotopic abundance of atmospheric CO_2 in rural areas of the U.S.A. and found that the average minimum concentration (311 p.p.m.) and associated carbon isotope ratio ($\delta^{13}C = -6.96‰$) for forest and grassland areas agreed closely with corresponding values of 312 p.p.m. and -6.92‰ for atmospheric CO_2 over barren ground.

(4) It was mentioned in (d) that local effects might have been responsible for the irregular nature of the $\delta^{13}C$ curve (Figure 5.5) and CO_2 curve (Figure 5.6). The only comparable published $\delta^{13}C$ curve is that of Grey (1971) for poplar wood from the U.S.A. (Figure 5.7). Grey's data indicates a rapid 1.3‰ decrease in wood $\delta^{13}C$ for 1912 - 1927, an almost constant $\delta^{13}C$ of -27‰ for 1928 - 1938 and a gradual decline of 1‰ from 1938 - 1966.

FIGURE 5.7

TEMPORAL VARIATION OF $\delta^{13}C$ IN POPLAR WOOD (U.S.A.)

(The curve is smoothed by a 10-year running mean)
(Grey 1971)



The overall decrease is ~2.3‰. Figures 5.5 and 5.7 exhibit certain similarities, the most obvious being the rapid rate of decrease in $\delta^{13}C$ for both trees in the first 20 - 30 years of this century. Indeed, the initial decrease of 1.3‰ for poplar wood corresponds to a calculated increase of ~18 p.p.m. in atmospheric CO_2 concentration, almost twice the theoretical increase of 10 p.p.m. for 1910 - 1930 assuming complete retention by the atmosphere of excess CO_2 from fossil fuel combustion. Thus, although differing slightly in timing, both the oak and poplar wood $\delta^{13}C$ values imply a significant additional source of CO_2 for the first 30 years of this century.

The horizontal section of Grey's curve for 1928 - 1938 could reflect the lower rate of increase of fossil fuel CO_2 input due to the economic depression. Since 1938, $\delta^{13}C$ has decreased at a rate equivalent to only 40% of that for 1912 - 1927. As mentioned previously, the general trend during the last 30 - 40 years has been rather surprising, in view of the exponentially increasing rate of fossil CO_2 input to the atmosphere. Grey's data seem to support the theory that a much smaller percentage of fossil CO_2 is remaining in the atmosphere at present than in the past, possibly in line with an increased uptake of CO_2 by the terrestrial biosphere or by cooling oceans. Furthermore, it should be noted that the flattening of the "Suess effect" curve (Figure 5.2) corresponds to a reduced rate of decrease of $\delta^{13}C$ for 1930 - 1950 compared to 1912 - 1927 (Figure 5.7).

Although the general trends of Figures 5.5 and 5.7 are similar, differences do exist. This fact serves to emphasise the dangers of extrapolation from results which may reflect local effects to an interpretation of the global distribution of CO_2. The establishment of worldwide trends in $\delta^{13}C$ for the period of significant fossil fuel combustion obviously requires similar analyses of tree-ring wood from as many geographical locations as possible.

(5) It was stated previously (Section 5.2) that some estimates of the "Suess effect" neglected the possibility of significant variations in the natural ^{14}C content of the atmosphere. Similarly, the possibility of significant atmospheric $\delta^{13}C$ variations over periods of the order of a decade should not be overlooked. Consequently, the conclusion of (4) above should be extended to include the study of ^{13}C content of tree rings, preferably on an annual basis, from pre-industrial times. This should aid an understanding of such features as the rapid decrease of $\delta^{13}C$ from 1900 - 1930. Furthermore, analyses of tree rings from the mid-19th Century would provide further evidence as to the reliability of Callendar's estimate of 290 p.p.m. for the "base-line" of atmospheric CO_2 concentrations (Figure 5.3). A few additional measurements of oak $\delta^{13}C$ for the mid-19th Century gave a mean value of $\sim -25.4‰$, corresponding to a calculated CO_2 concentration of ~ 278 p.p.m., approximately 8 p.p.m. lower than 1900. If all the injected fossil CO_2 from 1860 - 1899 (Table 5.2) remained in the atmosphere, the 1900 CO_2 concentration of 286.2 p.p.m. ($\delta^{13}C = -4.89‰$) can be extrapolated to an 1860 concentration of 281 p.p.m. ($\delta^{13}C = -4.51‰$). This is in reasonable agreement with the experimental data above. However, extensive series of $\delta^{13}C$ measurements are required for both this period and

earlier centuries.

(6) The effect of tree physiological processes (e.g. movement of resin, sapwood to heartwood conversion) on wood $\delta^{13}C$ values can only be assessed through further analyses of tree rings from different species of tree.

(7) It is quite apparent that more data are required for an accurate assessment of world-wide trends in atmospheric ^{13}C content. Also, various parameters ((2), (6)) have to be established before the theoretical treatment presented here can be considered valid. Nevertheless, both this and Grey's study suggest that:

(i) an additional source of CO_2 of $\delta^{13}C \sim -25‰$, in conjunction with fossil fuel combustion, contributed to rapidly increasing atmospheric CO_2 concentrations from 1900 - 1930,

(ii) variations in exchange and removal of CO_2 across the respective atmosphere/biosphere/ ocean interfaces have occurred during this century in view of the irregular and somewhat unexpected trends of $\delta^{13}C$ from 1930 to the present,

(iii) "Suess effect" calculations based on the exponentially increasing rate of fossil CO_2 input may not be strictly valid in view of (i) and (ii). However, until the effects of local factors on the isotopic composition of tree rings are eliminated and a global trend established, it is felt premature to extrapolate from ^{13}C to ^{14}C depletion.

Indeed, the accuracy of such a calculation (iii) may be partially dependent on related work aimed at the design of a conceptual mechanism for the removal of excess CO_2 from the atmosphere. For example, as mentioned in (d), it is possible that significant quantities of atmospheric CO_2 are being removed by an increasing terrestrial biomass. Future photographs from orbiting satellites should provide relevant information on the constancy, or otherwise, of the terrestrial biosphere. In addition, it is now suggested (Bolin and Bischof 1970) that some of the different water masses of the deep ocean are in more rapid exchange with the surface waters than is indicated by an average residence time of 1000 years. On the assumptions (1) that 50% of the industrial CO_2 has gone into the oceans and (2) that the effective CO_2 absorption capacity of the oceans is only 6 times that of the atmosphere (1/10 of 60, due to the buffering effect), Bolin and Bischof postulate that 20 - 25% of the oceans must have been accessible in a time less than or equal to the period of major industrial CO_2 output i.e. the last 30 - 50 years.

The quantitative assessment of potentially viable effects, such as an increasing terrestrial biomass or rapid turnover times of deep ocean water, may significantly affect our conceptual approach to the explanation of the distribution of fossil CO_2 through the carbon cycle. Thus, interpretation of atmospheric $\delta^{13}C$ variations could be considerably modified. Similarly, the identification of major $\delta^{13}C$ trends should assist in the isolation and evaluation of the controlling geophysical parameters.

5.4 Future Atmospheric CO_2 Concentrations and their Climatic Effects

(a) Future increases in atmospheric CO_2 content

Section 5.3 emphasises the limited nature of present knowledge concerning the rate of removal of fossil CO_2 from the atmosphere into the biosphere and oceans. Furthermore, both the results of Section 5.3 and recent direct measurements (Keeling 1970, Bolin and Bischof 1970) suggest that temporal variations will occur in the future distribution of fossil CO_2 among the carbon reservoirs. Thus, predictions of future atmospheric CO_2 levels must be regarded as uncertain, especially in view of the dangers of extrapolation based on the current rate of fossil CO_2 input to the atmosphere.

In 1956, the United Nations (1956) predicted an average compound rate of increase in fossil fuel utilisation of 3.5% per annum. As Baxter and Walton (1970) observed, however, annual fuel consumption increased by 4.5% per annum from 1955 - 1969. The Organisation for Economic Cooperation and Development (1966) has considerably revised the original estimates by the United Nations (1956) and forecasts a cumulative total input of fossil CO_2 to the atmosphere of 70 - 75% of the natural CO_2 content (290p.p.m.) by the year 2000, about 20% greater than the earlier U.N. estimate.

Bolin and Bischof (1970), on the assumption that 35% of the excess CO_2 (O.E.C.D. values) will remain in the atmosphere, have predicted an atmospheric CO_2 concentration of 371 - 378 p.p.m. by 2000. A corresponding range of 388 - 395 p.p.m. CO_2 is predicted for 45% retention by the atmosphere. These values may be further increased by secondary effects due to the influence of increasing CO_2 levels on climate as discussed below in (b).

(b) Effects of atmospheric CO_2 increases

(1) Climatic changes

The possibility of climatic change as a result of atmospheric CO_2 variations was first proposed by Chamberlain (1899). As mentioned in Section 1.4(a), increased levels of atmospheric CO_2 could lead to an increase in surface temperatures of the earth due to absorption and back-radiation of infra-red (12 - 18μ) radiation from the earth by CO_2. Indeed, Callendar (1938) suggested that the observed warming of northern Europe and North America after 1880 was attributable to an increase in atmospheric CO_2 of ~10% (Figure 5.3).

According to Plass (1961) a 100% increase in atmospheric CO_2 content would raise average world temperatures by at least 4°C. This estimate, however, is only valid for a dry atmosphere and thus neglects compensatory changes in humidity and cloud cover. Calculations based on Möller's (1963) model, which incorporates parameters for humidity and cloudiness, show that, for a 25% increase in atmospheric CO_2, the average temperature near the earth's surface could increase by 0.6 - 4.0°C depending on the response of the atmospheric humidity. However, Möller's model ignores the vertical transfer of heat by evaporation at the surface and condensation at high altitudes and thus probably over-estimates the effects of CO_2 increases on atmospheric temperature. More recent models (Manabe and Strickler 1964, Manabe and Wetherald 1967) have taken into account most major atmospheric factors-except circulation. Calculations based on these models show that a

2.8°C rise in temperature would result for a 100% increase in atmospheric CO_2, assuming a fixed relative humidity. However, due to the sensitivity of the models to changes in cloud cover, a 30 p.p.m. increase in CO_2 (1890 - 1970) would be compensated by a 0.3% increase in low clouds or a 0.6% increase in middle clouds.

The uncertainty attached to predictions of future temperature changes based primarily on increased CO_2 levels is further illustrated by world temperature trends during the last 100 years. Mean annual air temperatures rose by ~0.5°C from 1885 - 1940 but then fell by 0.1 - 0.2°C between 1940 and 1960 (Mitchell 1961, 1963), a period of rapidly expanding fossil fuel consumption. It thus appears that other climatic factors, including associated increases in atmospheric dust levels, have effectively masked any climatic changes due to increasing CO_2 levels in recent decades.

However, if future increases in atmospheric CO_2 concentrations are accompanied by rises in temperature, warming of the oceans could further enhance the CO_2 content of the atmosphere as a consequence of the inverse relationship between CO_2 solubility in sea water and temperature (Eriksson 1963). At the same time, though, in areas where there is sufficient sunlight and an abundant supply of plant nutrients, higher temperatures and the anticipated 30% increase in CO_2 by 2000 could significantly raise the level of photosynthesis, thus partially offsetting the effects of oceanic warming.

(2) Future ^{14}C levels

In the absence of further large-scale-nuclear tests, future atmospheric ^{14}C levels will become increasingly governed by the "Suess effect". Harkness (1970) has estimated that present excess atmospheric ^{14}C concentrations will return to "normal" by 2000, assuming a "Suess effect" of ~17% at that time (Baxter and Walton 1970). Thereafter, atmospheric ^{14}C concentrations will continue to decline at a rate determined by the extent of fossil fuel combustion and the subsequent distribution of fossil CO_2 within the carbon cycle.

CHAPTER 6

ATMOSPHERIC ^{14}C CONCENTRATIONS IN THE SOUTHERN HEMISPHERE (1910 - 1952)

6.1 Sample Selection and Pretreatment

(a) Sample selection

The investigation of past annual ^{14}C concentrations in the southern hemisphere required samples of similar validity (Section 4.1(a)) to those used in the northern hemisphere study (Chapter 4). The scope of the southern hemisphere programme was, however, restricted to 20th Century ^{14}C levels through the scarcity of short-lived biospheric samples (grains, wines, sheep's wool) and to the unavailability of accurately dated single tree rings from the pre-1900 period. This latter factor is a reflection of the limited dendrochronological-dating facilities in the southern hemisphere (Rafter 1970).

Australasia proved to be the most fruitful source of suitable samples. The types of samples obtained from intensive enquiries in both Australia and New Zealand were as follows:

(1) wines. An incomplete series of Australian wines for the period 1914 - 1944 was provided by the Australian Wine Research Institute. The grapes were picked in March of each year after 4 - 5 months of growth on the vine. Most of the soils on which the vines were grown were red brown earths and podzolic soils. Only table wines were analysed for ^{14}C content, dessert wines being rejected because of possible contamination through addition of non-

contemporaneous fortifying spirits.

(2) tree rings. A small section of radiata pine was obtained from the New Zealand Forest Service, Rotorua (38°9'S, 176°16'E). The tree had been planted around 1930 and the annual rings were clearly distinguishable from 1933 onwards. Although this particular species of tree can be inconsistent in the number of rings formed in any one year (which renders the precise dating of rings from older trees almost impossible), dendrochronological information accumulated by the Forest Service during the last 40 years enabled the assignment of a calendar year to each ring.

(3) seeds. Samples of wheat heads were supplied by the Department of Agriculture, Victoria. All the wheat samples were grown on red brown earths, usually between June and January, at the State Research Farm, Werribee, 20 miles west of Melbourne (37°52'S, 145°8'E). In addition, several wheat-seed samples from the earlier years of the century were provided by the Department of Agricultural Botany, University of Sydney.

(4) wool. Several samples of sheep's wool were obtained from the C.S.I.R.O. Division of Nutritional Biochemistry, South Australia. Each wool sample represented about 1 year's growth prior to shearing in the early months of the year.

All 4 sample types are reliable indicators of the atmospheric ^{14}C activity prevailing at their place of growth

(Chapter 3).

(b) Sample pretreatment

Individual rings were split from the section of radiata pine in the usual way (Sections 3.3(c) and 4.1(c)). The chemical pretreatment of the wood was identical to that employed for the Forest of Dean oak (Section 4.1(c)). The mean yields for the cellulose and charred cellulose fractions amounted to 50% and 15% of the total whole wood respectively.

All wines were distilled to remove colouring matter. The alcohol (~15 ml.) was then converted to CO_2 using the special alcohol combustion system (Figure 2.3). The ease of combustion control determined the pretreatment of the wool and seed samples. Thus, wool samples were charred at 500°C prior to combustion while seed samples were not treated in any way.

Gas preparation and counting techniques were as described in Sections 2.2 and 2.6.

6.2 Annual Atmospheric ^{14}C Concentrations in the Southern Hemisphere (1910 - 1952)

(a) ^{14}C analysis

The results of the ^{14}C measurements are classified according to sample types in Tables 6.1 - 6.4. All data are presented in Table 6.5 and plotted as shown in Figure 6.1. In general, there is good agreement between contemporaneous samples of both differing geographical location and type. For example, in only one (1938) of the 8 years for which ^{14}C data are available from both Australian wine samples and New Zealand wood is there disagreement (1.72 $\pm$ 0.8(1σ)%) outwith statistical uncertainty.

TABLE 6.1

^{14}C CONCENTRATIONS OF AUSTRALIAN WINES 1919 - 1944

Year*	$\delta^{14}C$(%) $\pm1\sigma$	$\delta^{13}C$(‰) ±0.1‰ (2σ)	Δ(%) $\pm1\sigma$
1919	-2.41 ± 0.50	-25.63	-2.29 ± 0.50
† 1928	-1.66 ± 0.59	-26.37	-1.39 ± 0.59
†† 1929	-1.49 ± 0.63	-30.74	-0.36 ± 0.63
1933	-0.72 ± 0.57	-29.63	$+0.20\pm0.57$
1934	-3.26 ± 0.59	-27.97	-2.68 ± 0.59
1934	-2.46 ± 0.56	-27.36	-2.00 ± 0.56
1936	-2.41 ± 0.50	-27.40	-1.94 ± 0.50
1938	-3.65 ± 0.56	-30.10	-2.67 ± 0.56
1939	-1.77 ± 0.59	-25.82	-1.61 ± 0.59
1940	-1.49 ± 0.59	-26.91	-1.11 ± 0.59
1941	-2.08 ± 0.57	-28.64	-1.37 ± 0.57
†† 1941	-1.03 ± 0.57	-25.28	-0.97 ± 0.57
1942	-2.23 ± 0.58	-26.95	-1.85 ± 0.58
1944	-1.89 ± 0.54	-25.48	-1.79 ± 0.54

* The calendar year refers to the time of grape-picking.

All wines were produced from grapes picked at vineyards in the Eden Valley, New South Wales (34°34'S, 139°E) with the exception of those designated by:

† grapes picked at Great Western, Victoria

and †† " " " Barossa Valley, South Australia,

within the Murray Region (33°20'S, 142°30'E).

TABLE 6.2

^{14}C CONCENTRATIONS OF RADIATA PINE TREE RINGS

(38°9'S, 176°16'E) 1934 - 1952

Year*	$\delta^{14}C$(%) ±1σ	$\delta^{13}C$(‰) ±0.1‰ (2σ)	Δ(%) ±1σ
1934	-2.17±0.78	-25.66	-2.04±0.78
1935	+0.57±0.63	-25.54	+0.68±0.63
1936	-1.37±0.57	-25.92	-1.19±0.57
1937	+0.06±0.60	-25.31	+0.12±0.60
1938	-0.92±0.59	-24.84	-0.95±0.59
1939	-1.20±0.60	-25.34	-1.13±0.60
1940	-0.63±0.57	-25.29	-0.57±0.57
1941	-0.86±0.59	-24.61	-0.94±0.59
1942	-2.29±0.57	-25.33	-2.22±0.57
1943	-1.71±0.57	-25.57	-1.60±0.57
1944	-1.97±0.57	-24.91	-2.05±0.57
1945	-1.61±0.58	-25.37	-1.54±0.58
1949	-1.69±0.58	-24.34	-1.82±0.58
1950	-2.44±0.57	-24.13	-2.61±0.57
1951	-2.72±0.57	-24.12	-2.89±0.57
1952	-3.49±0.78	-24.99	-3.49±0.78

* The calendar year refers to the time of completion of the ring.

TABLE 6.3

^{14}C CONCENTRATIONS OF AUSTRALASIAN WHEAT SEEDS

1910 - 1936

Year*	$\delta^{14}C$(%) $\pm 1\sigma$	$\delta^{13}C$(‰) ± 0.1‰ (2σ)	Δ(%) $\pm 1\sigma$
† 1910	+1.14±0.78	-24.10	+0.96±0.78
† 1915	+1.26±0.53	-22.09	+0.67±0.53
† 1919	-1.03±0.58	-22.92	-1.44±0.58
‡ 1920	-1.54±0.80	-22.73	-1.99±0.80
‡ 1921	-1.66±0.77	-23.20	-2.01±0.77
† 1925	-1.60±0.56	-23.00	-1.99±0.56
Ø 1932	-0.74±0.60	-21.87	-1.37±0.60
‡ 1932	-0.17±0.60	-22.90	-0.59±0.60
‡ 1936	-0.91±0.78	-23.00	-1.31±0.78

* The calendar year refers to the time of harvest.

† Wheat grown in New South Wales, Australia

‡ " " at State Research Farm, Werribee, near Melbourne (37°52'S, 145°8'E).

Ø Wheat grown at Crop Research Division, D.S.I.R., Lincoln (43°38'S, 172°30'E), New Zealand.

TABLE 6.4

^{14}C CONCENTRATIONS OF AUSTRALIAN WOOL SAMPLES

1922 - 1947

Year*	δ^{14}C(%) $\pm 1\sigma$	δ^{13}C(‰) $\pm$0.1‰ (2σ)	Δ(%) $\pm 1\sigma$
† 1922	-0.69 ± 0.60	-23.39	-1.01 ± 0.60
†† 1923	-1.54 ± 0.57	-23.76	-1.79 ± 0.57
†† 1924	-1.42 ± 0.70	-27.64	-0.90 ± 0.70
∅ 1946	-1.89 ± 0.58	-21.04	-2.66 ± 0.58
∅ 1947	-2.24 ± 0.65	-21.45	-2.94 ± 0.65

* The calendar year refers to the time of shearing.

† Wool grown at Harrogate, South Australia (35°S, 139°E).

†† " " " Native Valley, Nairn, South Australia (35°S, 138°55'E).

∅ Wool grown at Robe, South Australia (37°10'S, 139°45'E).

TABLE 6.5

ATMOSPHERIC ^{14}C CONCENTRATIONS IN THE SOUTHERN HEMISPHERE 1910 - 1952

Year*	$\delta^{14}C$(%) ±1σ	$\delta^{13}C$(‰) ±0.1‰ (2σ)	Δ(%) ±1σ
1910	+1.14±0.78	-24.10	+0.96±0.78
1915	+1.26±0.53	-22.09	+0.67±0.53
1919	-1.03±0.58	-22.92	-1.44±0.58
1919	-2.41±0.50	-25.63	-2.29±0.50
1920	-1.54±0.80	-22.73	-1.99±0.80
1921	-1.66±0.77	-23.20	-2.01±0.77
1922	-0.69±0.60	-23.39	-1.01±0.60
1923	-1.54±0.57	-23.76	-1.79±0.57
1924	-1.42±0.70	-27.64	-0.90±0.70
1925	-1.60±0.56	-23.00	-1.99±0.56
1928	-1.66±0.59	-26.37	-1.39±0.59
1929	-1.49±0.63	-30.74	-0.36±0.63
1932	-0.74±0.60	-21.87	-1.37±0.60
1932	-0.17±0.60	-22.90	-0.59±0.60
1933	-0.72±0.57	-29.63	+0.20±0.57
1934	-3.26±0.59	-27.97	-2.68±0.59
1934	-2.46±0.56	-27.36	-2.00±0.56
1934	-2.17±0.78	-25.66	-2.04±0.78
1935	+0.57±0.63	-25.54	+0.68±0.63
1936	-1.37±0.57	-25.92	-1.19±0.57
1936	-0.91±0.78	-23.00	-1.31±0.78
1936	-2.41±0.50	-27.40	-1.94±0.50
1937	+0.06±0.60	-25.31	+0.12±0.60

TABLE 6.5 (CONTD.)

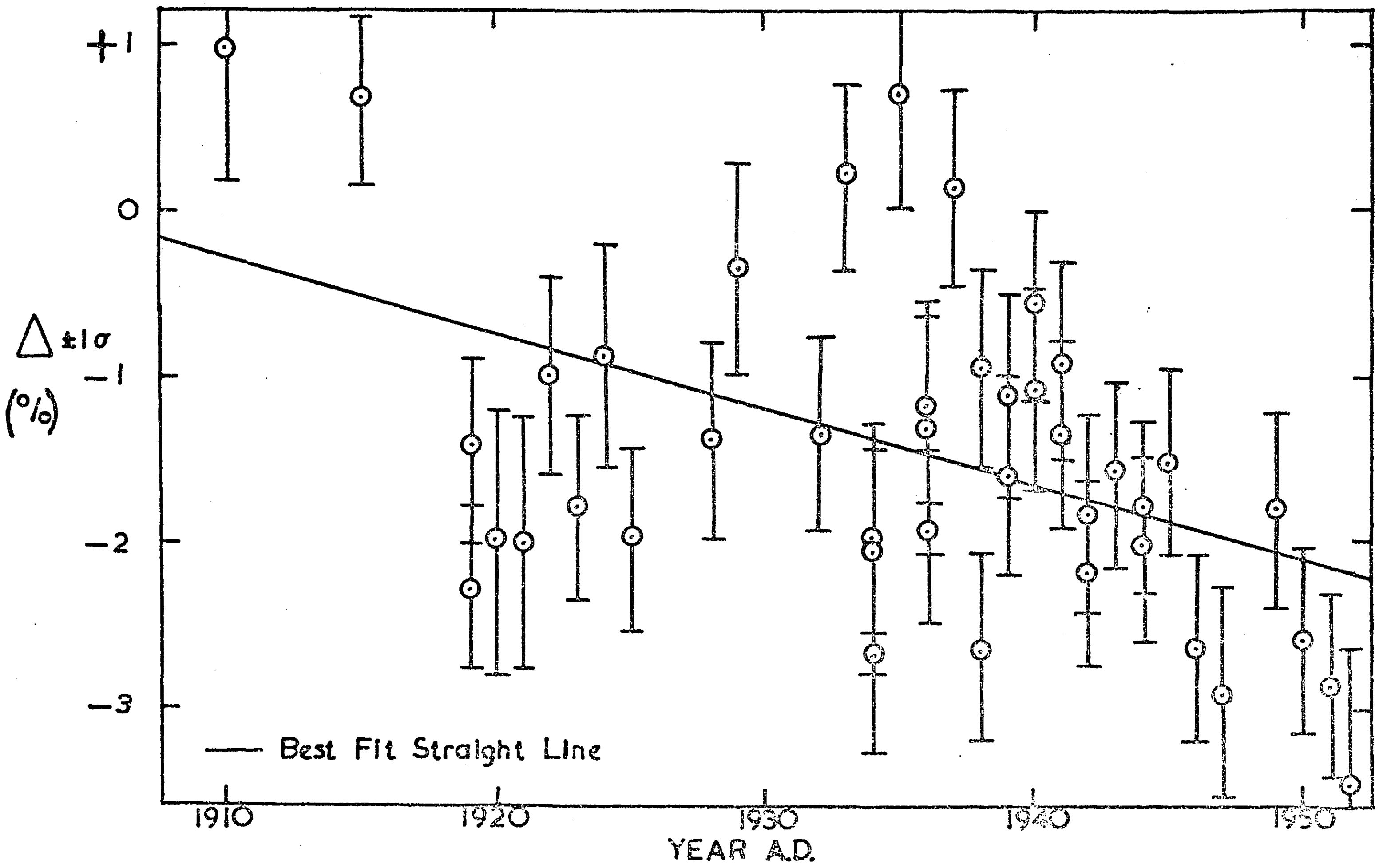
ATMOSPHERIC ^{14}C CONCENTRATIONS IN THE SOUTHERN HEMISPHERE 1910 - 1952

Year*	δ^{14}C(%) ±1σ	δ^{13}C(‰) ±0.1‰ (2σ)	Δ(%) ±1σ
1938	-0.92±0.59	-24.84	-0.95±0.59
1938	-3.65±0.56	-30.10	-2.67±0.56
1939	-1.20±0.60	-25.34	-1.13±0.60
1939	-1.77±0.59	-25.82	-1.61±0.59
1940	-0.63±0.57	-25.29	-0.57±0.57
1940	-1.49±0.59	-26.91	-1.11±0.59
1941	-0.86±0.59	-24.61	-0.94±0.59
1941	-2.08±0.57	-28.64	-1.37±0.57
1941	-1.03±0.57	-25.28	-0.97±0.57
1942	-2.29±0.57	-25.33	-2.22±0.57
1942	-2.23±0.58	-26.95	-1.85±0.58
1943	-1.71±0.57	-25.57	-1.60±0.57
1944	-1.97±0.57	-24.91	-2.05±0.57
1944	-1.89±0.54	-25.48	-1.79±0.54
1945	-1.61±0.58	-25.37	-1.54±0.58
1946	-1.89±0.58	-21.04	-2.66±0.58
1947	-2.24±0.65	-21.45	-2.94±0.65
1949	-1.69±0.58	-24.34	-1.82±0.58
1950	-2.44±0.57	-24.13	-2.61±0.57
1951	-2.72±0.57	-24.12	-2.89±0.57
1952	-3.49±0.78	-24.99	-3.49±0.78

* The calendar year refers to the end of the growth season i.e. 1910 represents $\leqslant$ 1 year's growth from 1909 - 1910.

FIGURE 6.1

ATMOSPHERIC ^{14}C CONCENTRATIONS IN
THE SOUTHERN HEMISPHERE (1910–52)



The best straight line fit through the data (Figure 6.1), defined by $\Delta_T = 86.19 - 0.045T$, where T is in calendar years, indicates a general decrease of gradient 0.045%/year from -0.3% (Δ) in 1910 to -2.2% (Δ) in 1952. These results are in excellent agreement with those of Fergusson (1958) (-2.04% in 1954) and Lerman et al. (1970) (-0.3% in 1902, -2.25% in 1951). The ^{14}C data of Baxter and Walton (1971) show a corresponding decrease in the northern hemisphere from -1.3% in 1910 to -3.8% in 1952, an average rate of -0.06%/year. Thus atmospheric ^{14}C concentrations in the northern hemisphere were apparently depleted by 1 - 1.6% relative to the southern hemisphere during the first half of this century. Indeed, a direct comparison of the measured annual ^{14}C concentrations, in years for which data are available from both hemispheres, indicates that the relative ^{14}C depletion of the northern hemisphere was -1.01 ± 0.36 (1σ)% for 1910 - 1930 and -1.26 ± 0.19 (1σ)% for 1930 - 1952. These values are greater than the maximum 0.5% reported by Fergusson(1958).

The comparatively lower ^{14}C activity of the northern hemisphere, where industrial activity is more intensive, is probably due to a correspondingly enhanced "Suess effect", despite fairly rapid interhemispheric mixing (1 year: Nydal 1968). Furthermore, the surface area of the oceans in the southern hemisphere is 40% greater than that of the northern hemisphere. As a result, increased absorption of fossil fuel CO_2 would be expected due to the larger surface area and also to the higher average wind speeds prevalent in the latitude belt 40^o - 50^oS. Since the effect of wind action is to promote mixing within the surface ocean layer, it thereby increases uptake of CO_2

by the sea (Kanwisher 1963). Confirmation of rapid transfer of atmospheric CO_2 into the southern oceans is provided by Rafter and O'Brien (1970) who found from ocean profiles that "bomb" ^{14}C is rapidly mixed to great depths at latitudes south of 40°S. Indeed, their calculations indicated a mean residence time for ^{14}C in the surface ocean of only 4.5 years prior to transfer to the deep ocean. As this corresponds to a turnover time for ^{14}C in the deep ocean of only 225 years, accelerated mixing must indeed be prevalent at specific sites in the southern oceans. Such an effect will naturally cause a more rapid oceanic uptake of fossil CO_2.

The disparity between observed atmospheric ^{14}C concentrations in the 2 hemispheres this century, as a result of the "Suess effect", underlines the inadequacies of "Suess effect" calculations based on simple "box-models" employing an undivided atmospheric unit. Similarly, the division of the ocean into a well-mixed layer (the surface ocean) and a single unit deep ocean is clearly unrealistic and further emphasises the limitations of box-model "Suess effect" calculations.

(b) Fluctuations of atmospheric ^{14}C concentrations (1910 - 1952)

Although the combustion of fossil fuels has been largely responsible for the observed decrease in atmospheric ^{14}C concentrations from 1910 - 1952, modulation of the cosmic-ray ^{14}C production rate by increasing sunspot activity has probably caused a simultaneous 0.5% reduction in natural ^{14}C levels (Baxter and Walton 1971). Apart from this general decrease, there is no obvious trend through the ^{14}C data (Figure 6.1) in contrast to the marked cycles of the northern hemisphere ^{14}C concentrations for 1829 - 1865 (Figures 4.1 and 4.4).

As the ^{14}C data are not corrected for the "Suess effect", any observed fluctuations are not strictly representative of natural ^{14}C fluctuations. However, it might be expected that cyclic trends, if they exist, would be superimposed on the general decreasing trend, assuming a steadily increasing "Suess effect". Thus, for example, the 11-year natural ^{14}C cycles in the northern hemisphere for the period 1890 - 1950 (Baxter and Walton 1971) were visually detectable prior to correction of the measured concentrations for the "Suess effect". Furthermore, when the dependence of the uncorrected 20th Century ^{14}C data (Δ) on sunspot number (R) was tested via the null hypothesis, b = 0, within the general expression:

$$\Delta_T = a + bR_T + cT + \text{error} \qquad \text{(cf. Section 4.2(b))},$$

a significant F value of 10.93 was obtained i.e. the null hypothesis, b = 0, was disproved. Thus the relationship between Δ and R was evident prior to "Suess effect" correction. However, a similar test for the southern hemisphere ^{14}C data proved insignificant (i.e. b = 0 was not disproved) with a correspondingly low correlation coefficient (r = -0.2). Indeed, subsequent correlation analysis of the 44 pairs of ^{14}C and sunspot data failed to show any significant variations of r with phase shift. Evaluation of the parameters yielded the following expression for Δ_T in terms of R_T and T:

$$\Delta_T = 83.73 - 0.0017R_T - 0.044T.$$

The coefficient of R_T is obviously insignificant. Thus 20th Century annual ^{14}C levels in the southern hemisphere appear unrelated to the 11-year solar cycle.

It must be remembered though, that, besides lack of "Suess effect" treatment, the above lack of correlation was obtained via samples of different types from various geographical locations, so that local effects could have distorted general ^{14}C trends. However, since the same provisos applied to the previous study of Baxter and Walton (1971) without apparent error, it is unlikely that the southern hemisphere data are atypical of general trends. Therefore, there does not appear to be a significant relationship between sunspot numbers and southern hemisphere ^{14}C concentrations, although the possibility of low-amplitude cyclic fluctuations within ^{14}C analytical errors cannot be ruled out (Section 6.3(a)).

6.3 Implications of Southern Hemisphere ^{14}C Data (1910 - 1952)

(a) Factors influencing southern hemisphere ^{14}C concentrations

The apparent lack of correlation between 20th Century annual ^{14}C levels in the southern hemisphere and the 11-year sunspot cycle suggests that the solar-sensitive stratosphere/troposphere exchange mechanism discussed in Section 4.3(b) may be latitudinally variable. The possibility of latitudinal differences in atmospheric exchange processes is supported by "bomb" ^{14}C studies. For example, the existence of preferential sites for injection of stratospheric "bomb" ^{14}C into the troposphere is well known (Young and Fairhall 1968). Thus, "spring peaks" have been observed in northern tropospheric ^{14}C concentrations since 1963 (Figure 1.3) but not in the tropospheric ^{14}C concentrations of the higher southern latitudes

(30° - 90°S). However, the absence of "spring peaks" may be partially attributable to the greater extent of nuclear weapon testing in the northern hemisphere. Most "bomb" ^{14}C has been produced in the northern hemisphere stratosphere and since stratospheric mixing across the equator is comparatively slow (5 years: Nydal 1968), the introduction of "bomb" ^{14}C into the southern hemisphere may have been largely controlled by tropospheric mixing across the equator (1 year: Nydal 1968).

It is more likely that the absence of observable cyclic trends through the ^{14}C data is due to the increased rates of exchange in the southern atmosphere/ocean system. It has already been shown (Section 6.2(a)) that the southern oceans are capable of modifying the "Suess effect" in the southern hemisphere to the extent that a ~1% difference in ^{14}C content existed between the hemispheres in 1950. It might be expected that the oceans can similarly exert a "damping" influence on any natural ^{14}C fluctuations in the southern hemisphere. The influence of the southern oceans on ambient ^{14}C levels has been demonstrated by the tree-ring ^{14}C measurements of Jansen (1970) and Lerman et al. (1970). Depletions of 0.5 - 2% relative to the northern hemisphere were observed in the atmospheric ^{14}C content of the southern hemisphere during the last 600 years, presumably as a result of enhanced absorption of ^{14}C by the southern oceans. Furthermore, while the main trends were synchronous in both hemispheres, occasional variations were observed on a shorter time-scale. For example, Jansen (1970) commented that the minimum which occurred in the northern hemisphere around 350 years B.P. has not yet been detected in the New Zealand and Australian tree-ring

^{14}C data. It is thus evident that the asymmetric distribution of the oceans between the 2 hemispheres can significantly affect the respective atmospheric ^{14}C concentrations. However, the evaluation of oceanic effects (or indeed of latitudinal variations in stratosphere/troposphere exchange) on atmospheric ^{14}C concentrations in the southern hemisphere over 10-year periods must await annual ^{14}C measurements of increased precision (e.g. $\pm$ 0.2% (1σ)). Only then will a definite statement be possible on the occurrence of small ^{14}C variations and their relationship, if any, with the 11-year solar cycle.

(b) Tree-ring chronologies in the southern hemisphere

The precise investigation of past annual ^{14}C levels in the southern hemisphere is severely hindered by the lack of reliable tree-ring chronologies. The present study has been restricted to the 20th Century during which artificial effects have disturbed natural ^{14}C levels. Furthermore, it has relied on sample materials of differing location and type. As Jansen (1970) has observed, the development of a tree-ring chronology for the southern hemisphere (e.g. in Australia or New Zealand), similar to the Sequoia-gigantea, bristlecone-pine and oak chronologies of the northern hemisphere, is urgently required for the detection of past atmospheric ^{14}C fluctuations. There is evidence that the establishment of such a chronology may be possible (Ferguson 1970a). If so, then subsequent measurement of both short-term and long-term ^{14}C trends should aid the determination of the causes of natural ^{14}C fluctuations.

APPENDIX 1

REGRESSIONAL ANALYSIS - BACKGROUND COUNT RATE AS A FUNCTION OF BAROMETRIC PRESSURE

As mentioned in Section 2.6(c), an inverse relationship was observed between the background count rate and barometric pressure. The precise mathematical formulation of this relationship is obtained from linear regression of background count rate on barometric pressure.

i.e. $Y = a + bx$

where Y = mean count rate (c.p.m.)

x = mean measured barometric pressure during counting period

and b = regression coefficient.

The regression for a set of "n" data each comprising a measured count rate (y) and the corresponding barometric pressure (x), was calculated on a K.D.F.9 computer using the "least squares fit" programme overleaf. This programme was also used in the fitting of best straight lines through other experimental data.

```
begin  comment  This programme works out m and c for the
            equation y = mx + c by least squares from n
            pairs of x and y and gives the rms error
            (sqrt([v↑2]/(n - 2) ) plus the individual
            deviations in y ;

integer  n, i, p;
real  sx, sy, sxy, sx2, sy2, m, c, d;
open(20);  open(70);
start:  n:= read(20);
begin  array  x,y, e [1:n];
sx:=sy:=sxy:=sx2:=sy2:=0.0;
for i:=1 step 1 until n do
begin  x[i]:= read(20);
       y[i]:= read(20)
end;
for i:=1 step 1 until n do
begin sx:= sx + x[i];
      sy:= sy + y[i];
      sxy:=sxy + x[i]×y[i];
      sy2 := sy2 + y[i]↑2;
      sx2:=sx2 + x[i]↑2
end;
d:= n×sx2 -sx↑2;   m:= (n × sxy -sx × sy)/d;
c:= (sx2 × sy - sx × sxy)/d;
d:= sqrt((sy2 - sy × c - sxy × m)/(n - 2));
for i:= 1 step 1 until n do
  begin
  e[i] := y[i];
  y[i] :=  y[i] - m × x[i] - c
  end;
write text (70, [[4c] m*=*]);
write (70, format ([-d.ddddd₁₀-nd]), m);
write text (70, [[3s]c*=*]);
write (70, format([-d.ddddd₁₀-nd]), c);
write text (70, [[3s] rms*error*=*]);
write (70, format ([-d.ddddd₁₀-nd]), d);
write text (70, [[3c][6s]y*obs[8s]y*calc [7s]deviation[2c]]);
for i := 1 step 1 until n do
  begin
    write (70, format ([2s -d.dddd₁₀-nd]), e[i]);
    write (70, format ([3s -d.dddd₁₀-nd]), m × x[i] + c);
    write (70, format ([3s -d.dddd₁₀-ndc]), y[i])
end;
comment  if another set of data is to follow punch 1 otherwise 0;
p := read (20);
if p = 1 then goto start;
close (70);
close (20);
comment The data tape consists of n followed by n pairs of
    values of x and y.  A 1 is punched after each set of n
    pairs if another set follows, and a zero after the
    final set;
end  end  →
```

Confidence band

The best straight line describing the dependence of background count rate on barometric pressure (cf. Figure 2.12) is used in the correction of sample count rates for background. The error associated with the background, as determined from Figure 2.12, is less than that for any one experimentally determined background count rate, due to the averaging of individual observations in the process of fitting the line. The error is obtained using Natrella's (1969) procedure, which establishes the confidence band for a "calibration line", as described below.

(1) Choose desired confidence level, $1 - \alpha$.

(2) Calculate $S_Y = \left[\frac{\Sigma(y - \bar{y})^2 - b(\Sigma(x - \bar{x})\ (y - \bar{y})}{n - 2}\right]^{\frac{1}{2}}$

(3) Look up $F_{1-\alpha}$ for (2, n-2) degrees of freedom from mathematical tables.

(4) Choose a number of values of X (within the range of the data) at which to compute points for drawing the confidence band.

(5) At each selected value of X, compute

$$W_1 = (2F)^{\frac{1}{2}} S_Y \left[\frac{1}{n} + \frac{(X - \bar{x})^2}{\Sigma(x - \bar{x})^2}\right]^{\frac{1}{2}}$$

(6) A $(1-\alpha)$ confidence band for the whole line is determined by $\pm W_1$.

(7) At each selected value of X, plot $Y + W_1$ and $Y - W_1$. Connect the upper series of points, and the lower series of points, by smooth curves.

In Figure 2.12, $\alpha = 0.05$.

APPENDIX 2

COMPUTER PROGRAMME FOR THE CALCULATION OF $\delta^{13}C_{corr}$ AND $\delta^{18}O$

The following programme (Fortran language) was used in the calculation of $\delta^{13}C_{corr}$, $\delta^{18}O$ and associated statistical errors (cf. Section 2.8(c)).

```
C     DATA CARDS
C     FIRST CARD GIVES NUMRUN - NUMBER OF SETS OF DATA IN
C     RUN
C     THIS IS FOLLOWED BY NUMRUN SETS OF CARDS
C     FIRST CARD OF EACH SET IS TITLE OF RUN
C     SECOND CARD - POT VALUE,RATIO FACTOR,LEAKAGE X,
C     LEAKAGE Y
C     THIRD CARD - NUMBER OF SAMPLE READINGS
C     FOURTH AND SUBSEQUENT CARDS - N SAMPLE READINGS AND
C     N+1 REFERENCE READINGS(UP TO 30 REFERENCE READINGS)
C
C
      DIMENSION SAM(30),REF(30),DELTA1(30),DELTA2(30),
     /XSAM(30),XREF(30)
      DIMENSION TITLE(20)
      NIX=0
      READ(5,101)NUMRUN
 1111 NIX=NIX+1
      IF(NIX.GT.NUMRUN)GO TO 9999
      READ(5,103)(TITLE(J),J=1,20)
      WRITE(6,104)(TITLE(J),J=1,20)
      WRITE(6,218)
      READ(5,100)POTVAL,RFACT,XLEAK,YLEAK
      READ(5,101)N
      NN=N+1
      READ(5,100)(SAM(J),J=1,N)
      READ(5,100)(REF(J),J=1,NN)
      WRITE(6,210)
      WRITE(6,211)
      WRITE(6,200)POTVAL
      WRITE(6,201)RFACT
      WRITE(6,202)XLEAK
      WRITE(6,203)YLEAK
      WRITE(6,204)N
      WRITE(6,205)
      DO 99 J=1,NN
      WRITE(6,206)REF(J)
      IF(J.EQ.NN)GO TO 99
      WRITE(6,207)SAM(J)
   99 CONTINUE
      WRITE(6,212)
      WRITE(6,213)
      SUM1=0.0
      SUM2=0.0
      ASUM=0.0
      BSUM=0.0
      CSUM=0.0
```

```
      DO 1 J=1,N
      AA=SAM(J)*1.0E-06
      XSAM(J)=(POTVAL+AA)*RFACT
      SUM1=SUM1+XSAM(J)
    1 CONTINUE
      XRDSAM=SUM1/N
      DO 2 J=1,NN
      BB=REF(J)*1.0E-06
      XREF(J)=(POTVAL+BB)*RFACT
      SUM2=SUM2+XREF(J)
    2 CONTINUE
      XRDREF=SUM2/NN
      XRSAM=(1.0+XLEAK)*XRDSAM-XLEAK*XRDREF
      XRREF=(1.0+YLEAK)*XRDREF-YLEAK*XRSAM
      F=(XRSAM-XRREF)/(XRDSAM-XRDREF)
      WRITE(6,215)
      DO 3 J=1,N
      JJ=J+1
      SP=XREF(J)+XREF(JJ)
      SP=SP/2.0
      DELTA1(J)=((XSAM(J)-SP)*1000.0)/SP
      ASUM=ASUM+DELTA1(J)
      WRITE(6,207)DELTA1(J)
    3 CONTINUE
      NNN=N-1
      WRITE(6,216)
      DO 4 J=1,NNN
      JJ=J+1
      PQ=XSAM(J)+XSAM(JJ)
      PQ=PQ/2.0
      DELTA2(J)=((PQ-XREF(JJ))*1000.0)XREF(JJ)
      BSUM=BSUM+DELTA2(J)
      WRITE(6,207)DELTA2(J)
    4 CONTINUE
      DLMEAN=(ASUM+BSUM)/(2.0*N-1.0)
      DO 5 J=1,N
      IF(J.EQ.N)GO TO 6
      ST=DLMEAN-DELTA2(J)
      ST=ST*ST
      CSUM=CSUM+ST
    6 SS=DLMEAN-DELTA1(J)
      SS=SS*SS
      CSUM=CSUM+SS
    5 CONTINUE
      ABC=CSUM/(2.0*N-1.0)
      SIGMA=SQRT(ABC)
      DFMEAN=DLMEAN*F
      WRITE(6,214)F
      WRITE(6,208)DLMEAN,SIGMA
      WRITE(6,209)DFMEAN
C     FORMAT STATEMENTS
  100 FORMAT(8F10.4)
  101 FORMAT(I2)
  103 FORMAT(20A4)
  104 FORMAT(1H1,20A4)
  200 FORMAT(//1H ,'POT VALUE=',F10.4)
  201 FORMAT(1H ,'RATIO FACTOR=',F10.4)
  202 FORMAT(1H ,'LEAKAGE X=',F10.4)
  203 FORMAT(1H ,'LEAKAGE Y=',F10.4)
  204 FORMAT(1H ,'NUMBER OF SAMPLE READINGS=',I4)
```

```
  205 FORMAT(/////1H ,'SAMPLE READINGS          REFERENCE
     /READINGS')
  206 FORMAT(1H ,20X,F10.1)
  207 FORMAT(1H ,F10.4)
  208 FORMAT(1H0,'MEAN VALUE OF DELTA=',F10.4,'  AND
     / ERROR=',F10.4)
  209 FORMAT(1H0,'DELTA(M)=',F10.4)
  210 FORMAT(/////1H ,'INPUT DATA')
  211 FORMAT(1H ,15('*'))
  212 FORMAT(////////1H ,'RESULTS')
  213 FORMAT(1H ,10('*'))
  214 FORMAT(1H0,'F=',F10.4)
  215 FORMAT(1H0,'VALUES OF DELTA AVERAGING REFERENCE
     /READINGS')
  216 FORMAT(///1H ,'VALUES OF DELTA AVERAGING SAMPLE
     /READINGS')
  218 FORMAT(1H0,26('-'))
C
      GO TO 1111
 9999 STOP
      END
```

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