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An International Journal of Cosmogenic Isotope Research

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# RADIOCARBON

An International Journal of Cosmogenic Isotope Research

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*Citations.* A number of radiocarbon dates appear in publications without laboratory citation or reference to published date lists. We ask that laboratories remind submitters and users of radiocarbon dates to include proper citation (laboratory number and date-list citation) in all publications in which radiocarbon dates appear.

Radiocarbon Measurements: Comprehensive Index, 1950–1965. This index covers all published <sup>14</sup>C measurements through Volume 7 of *RADIOCARBON*, and incorporates revisions made by all laboratories. It is available to all subscribers to *RADIOCARBON* at \$20.00 US per copy.

List of laboratories. Our comprehensive list of laboratories appears at the end of each volume. We ask all laboratory directors to provide their telephone, telex and fax numbers as well as their E-mail addresses. Changes in names or addresses, additions or deletions should also be reported to the Managing Editor.

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# FROM THE EDITOR

# SUMMARY OF THE INTERNATIONAL WORKSHOP ON INTERCOMPARISON OF <sup>14</sup>C LABORATORIES

[Editors' note: The full proceedings of this workshop, including transcriptions of general discussions, will appear in RADIOCARBON, vol 32 (3).]

On a bright September day in Scotland, 50 producers, consumers and analysts of <sup>14</sup>C dates began a workshop to ponder a darker topic: the results of a series of intercomparisons among radiocarbon laboratories. This was the "International Workshop on Intercomparison of <sup>14</sup>C Laboratories" held at the Scottish Universities Reactor Center, East Kilbride, near Glasgow, 12–15 Sept 1989, and hosted by E M Scott, T C Aitchison, D D Harkness, B F Miller, G T Cook, and M S Baxter. Beginning in 1982, Marian Scott and colleagues distributed a series of samples to willingly participating <sup>14</sup>C labs. The <sup>14</sup>C activities of these samples were unknown to the labs. The purpose of the study was to obtain a quantitative appraisal of how reliable <sup>14</sup>C dates are throughout the world, and if inaccuracies exist, what are the causes. Dr Scott and colleagues collected and summarized the results at intervals throughout the study and revealed the summaries to each participating lab without associating laboratories with specific results. Indeed the study did reveal significant discrepancies among labs, and it became apparent that some action was needed.

The recent workshop accomplished its three primary goals. The first was to assess the extent of the inaccuracy problem, the second was to agree on what, if any, remedial action should be taken, and the third was to decide on future similar intercomparison studies. It should be noted that only 50 of the 131 active <sup>14</sup>C labs participated. All classes of counting technologies (gas counting, liquid scintillation and accelerator ion counting) participated in the intercomparison, as did well-established and newer labs. Representatives of all of the above attended the workshop.

It is clear that an accuracy problem pervades all technological classes of <sup>14</sup>C labs. Many laboratories' data were in excellent agreement, but a few showed alarming divergences from the most likely values. Occasional inaccurate dates from a few laboratories can erode confidence in radiocarbon dating in general. Consumers of <sup>14</sup>C dates are anxious about value for their limited resources for dates; laboratory directors are worried about releasing bad data; and many of us are concerned about the image of the radiocarbon dating community. Workshop participants agreed that to help laboratories assure themselves they are producing accurate data, or to alert them when problems occur, we should establish a series of standard materials of "typical sample" composition and known <sup>14</sup>C activities. Samples of these materials would be available from the IAEA to laboratories wishing to make use of them for quality assurance. A recommended quality assurance protocol will be forthcoming, which will reflect the consensus of workshop participants.

To me, the most encouraging part of the meeting was the feeling of community spirit. The atmosphere at the meeting was not superciliously accusatory by some toward "a few bad apples in the barrel," rather one of colleagues recognizing a problem and together seeking the best solution. Some who have spent most of a career producing precise and accurate <sup>14</sup>C data talked about forming a Help Squad to advise labs who request it.

The workshop participants expect that by taking part in a rigorous quality assurance program, <sup>14</sup>C laboratory directors will quickly recognize if an accuracy problem arises, and take remedial action before incorrect data are released. Nevertheless, it was agreed that another round of intercomparisons with unknown samples, to be carried out in about 3 years, would yield quantitative data on the effectiveness of the quality assurance program. Those of us who attended this meeting hope that the same hosts will put on a repeat performance. Not only did we accomplish the technical goals, but we also enjoyed elegant meals and memorable excursions. The meeting closed in high "spirits," with bagpipes and the tasting of the haggis.

It may be yet a few years before the radiocarbon community can repolish its somewhat tarnished image. The important thing is that we have begun a process of self-healing.



Courtesy of the American Geographical Society

# SERGE ALEXANDER KORFF

#### 1906-1989

Serge Alexander Korff, Professor Emeritus of Physics at New York University and a pioneer in the study of cosmic rays, died in New York City on December 1, 1989 at the age of 83. His early research paved the way that led in 1949 to W F Libby's elaboration of the technique of <sup>14</sup>C dating, along with his collaborators, E C Anderson and J R Arnold, at the University of Chicago.

Beginning in the early 1930s, Dr Korff studied the streams of particles reaching the upper atmosphere from outer space, working with teams directed by the distinguished physicists, R A Millikan and A H Compton. This was before the days of high-altitude jet aircraft and satellites, when rocketry was in its infancy, and cosmic radiation was measured with instruments sent aloft by balloons or with heavy equipment placed at a few high-altitude stations in different parts of the earth.

From these studies, it was discovered that the charged particles of cosmic rays, arriving from far out in our galaxy and consisting mostly of protons, become sorted by the earth's magnetic field. Their intensity was found to vary with latitude and as a function of altitude, increasing at high altitude from the equator to about 60°N.

The impact of Dr Korff's work on Earth Sciences became apparent to Libby in 1940 when Korff, together with H A Bethe and G Placzek, realized that cosmic-ray-induced secondary neutrons react in the upper atmosphere with <sup>14</sup>N nuclei to produce <sup>14</sup>C. This discovery, acknowledged by W F Libby in his Nobel address in 1960, was critical in setting the stage for 1) tracing the pathway along which <sup>14</sup>C at equilibrium cycled in the biosphere by photosynthesis and respiration in living autotrophic plants, and 2) ascertaining from the half-life of <sup>14</sup>C and the specific activity of sample material, the ages of ancient plant and animal remains.

Serge Alexander Korff, born in 1906 in Helsingfors (now Helsinki), Finland, came from a family of Russian statesmen and academics. His formal university education, following the family's emigration to the United States, was at Princeton (A B 1927, A M 1929, Ph D 1931). Later, he held research positions at Mount Wilson Observatory, California Institute of Technology, Carnegie Institution of Washington and Bartol Research Foundation, before joining the faculty of New York University in 1940, advancing in rank to Professor of Physics in 1946, and remaining there until his retirement in 1973.

Dr Korff possessed the bearing of a statesman, diplomat and scholar, all of which developed naturally from his family background. His demeanor was one of polished authority and leadership, which qualities were to great advantage during times of service to the institutions he served as President, including the American Geographical Society (1967–1971), New York Academy of Sciences (1972), and the Explorers Club (1955–1958). At the same time, as a world traveler, he projected his zeal for research by the number of high-altitude stations he helped to establish, especially during the International Geophysical Year (1957–1958) at far-flung places exemplified by Chacaltaya (5220m) in Bolivia, Mt Wrangell (4269m) in Alaska and Norikura-dake (2840m) in Japan.

Dr Korff's career was in every sense a distinguished one, pursued with dedication to achieve in research, education and, above all, the understanding of earth phenomena.

C J Heusser

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# Radiocarbon

# 1990

# SUPERCONDUCTING MINI-CYCLOTRONS AS AMS INSTRUMENTS

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ABSTRACT. We have studied the limitations of conventional mass spectrometry and have examined accelerator based methods which could help circumvent these limitations. In particular, cyclotron-based accelerator mass spectrometric (AMS) techniques are discussed with an emphasis on evaluating performances of superconducting mini-cyclotrons designed for use as AMS instruments. We discussed the design of superconducting mini-cyclotrons dedicated to radioisotope dating research.

#### INTRODUCTION

Conventional carbon dating is based on the measurement of the beta-decay rate of the <sup>14</sup>C content of a biological sample, the age of which has to be determined. The <sup>12</sup>C to <sup>14</sup>C ratio is ca  $10^{12}$  so that 1g of organic matter will contain ca  $6 \ 10^{10} \ ^{14}$ C atoms. The half- life for the decay of <sup>14</sup>C is 5730 years, so that statistical accuracy of 1%, *ie*, 10,000 counts, could be achieved after 12 hours of measurement. Evidently, the efficiency of the use of <sup>14</sup>C content is only  $10^4/(6 \ 10^6) = 1.67 \ 10^{-7}$ .

An alternate approach in the measurement of <sup>14</sup>C content in samples of biological origin could be based on the use of mass spectrometers. If negative ions are employed, the only mass-14 ions interfering with <sup>14</sup>C will be <sup>12</sup>CH<sup>-</sup><sub>2</sub> and <sup>13</sup>CH<sup>-</sup> since <sup>14</sup>N cannot form the negative stable ion. The former differs by 1 part in 1000 and the latter by 1 part in 2000 in mass from <sup>14</sup>C. If both molecules form negative ions with the same efficiency, the <sup>14</sup>C current produced by the typical organic sample will be lower than <sup>13</sup>CH<sup>-</sup> current by a factor of 10<sup>10</sup>. If the current peak shapes are Gaussian, the required mass resolution should be >15,000 in order that the local yield ratio of <sup>14</sup>C<sup>-</sup> to <sup>13</sup>CH<sup>-</sup> at peak position of the former will be >10<sup>10</sup>. However, the unavoidable elastic scattering of <sup>12</sup>C ions from surfaces and residual gas further complicate the experimental situation making conventional mass spectrometry practically impossible for <sup>14</sup>C dating.

### ACCELERATOR MASS SPECTROMETRY

Accelerator mass spectrometric (AMS) techniques provide ultra-sensitive methods of <sup>14</sup>C ion counting. The efficiency of AMS is determined by the product of three factors: ion source efficiency  $\approx 1/20$ , accelerator transmission efficiency  $\approx 1/2$  and beam extraction efficiency  $\approx 1/10$  to 1. The typical efficiency value e = 1/400 - 1/40 evidently exceeds the efficiency of the technique based on beta decay measurements by a factor of  $10^4$  to  $10^5$ , allowing us to reduce the weight of the sample to the order of a few tens of micrograms. The sputter negative ion source which is most frequently used, produces negative ions with a cesium beam striking the surface of the sample. For AMS using a tandem accelerator, the produced beam is roughly analyzed, and after additional acceleration for increased transmission efficiency, the beam is injected and accelerated through the first half of the tandem. In the terminal the negative ions pass through a stripper canal using noble gases (Ar), where, after stripping, they become positive ions. The removal of the electrons greatly increases the molecule dissociation probability, eliminating the molecular ion inference. After acceleration in the second stage, the relevant ion species are analyzed, passing through a series of magnetic and electric deflection elements, and are finally identified and counted in appropriate detection systems.

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Cyclotron-based AMS precludes the need for a bulky system of magnetic and electric deflecting elements. Rather, cyclotrons inherently represent high mass resolution devices. When tuned for a given atomic mass, they are detuned for molecules of the same atomic mass number but different true masses, due to the acceleration phase slip. With a sufficiently high magnetic field, the cyclotron dimensions become considerably smaller (radius could be retained in the range of 10–20cm) than those of the bulky tandem machines (linear dimension of the order of tens of meters). Especially if built in the superconducting version in persistent mode, the cyclotron magnet does not need a power supply while operating. The only power consumption would be that used to operate the RF accelerating system and the ion source.

# CYCLOTRONS AS AMS INSTRUMENTS

The cyclotron resonance principle is the basis for the particle acceleration used in this type of machine. Ions produced in the ion source are extracted from the internal ion source using the puller configuration, or in the case of external ion source, they are axially or radially injected in the cyclotron median plane. The trajectories of the ions of mass m, charge q and impulse p in the homogeneous cyclotron magnetic field, the center of symmetry of which coincides with the machine center, are the stable circular equilibrium orbits of radius r = p/qB. The frequency of the particle motion along these orbits is  $\omega = qB/m$ , evidently constant, which does not depend on the particle energy  $E = p^2/2m$  but does depend on the particle q/m ratio. If electrodes (dees) are introduced into the cyclotron median plane and electrode RF voltage frequency equals multiple (h) of particle eigenfrequency ions of given q/m ratio could cross the electrode gap in phase with the peak of RF voltage. If we have the two-component beam and RF frequency is tuned for q/m ratio of one of the components, the other beam component will experience phase slip,  $\Phi$ , determined by:

$$\sin \Phi = 2\pi \ln n \frac{\mathrm{df}}{\mathrm{f}} \tag{1}$$

while energy gain per turn of both beam components is given by

$$dE = 2N qV \sin\left(\frac{hD}{2}\right) \cos\Phi$$
(2)

where h = harmonic number, n = number of achieved particle turns, f = eigenfrequency of the reference beam component, df = difference of the beam eigenfrequencies of beam components, V = maximum RF voltage, D = angular dee width, N = number of dees. The in-phase beam component will always experience a maximum energy gain at a gap crossings while the out-of-phase beam component, after executing a certain number of orbits at the given harmonic of RF field, will experience phase slip higher than 90°, *ie*,  $\cos \Phi$  will have negative value and this beam component will be decelerated and fall toward the machine center. The in-phase beam component which does not interfere with the out-of-phase component may be then accelerated up to the energies suitable for extraction and particle identification.

# THE SUPERCONDUCTING AMS MINI-CYCLOTRON

A superconducting mini cyclotron is proposed here for <sup>14</sup>C dating using AMS.

Design. The cyclotron dedicated to AMS should satisfy the high-resolution requirements, *ie*, those characterized by high-resolution value  $\mathbf{R} \approx \pi \mathrm{hn}$  numbers (Clark 1984). This requirement does not necessarily imply high energy needs, *ie*, the machine could be small, accelerating the ions in the range of the energy which allows easy detection and identification. The high bending power of superconducting cyclotrons could accelerate the particles up to 25–50 times higher energies than cyclotrons at room temperature with the same polar radii. AMS cyclotrons could have azimuthally constant fields with or without radial gradients since energy requirements are not too high and relativistic effects that eventually change the particle eigenfrequencies could be considered negligible. This dipole field could be produced in an air-core-type (Subotic 1984, 1988) superconducting version by two symmetrically positioned, relative to the median plane, superconducting coil sections. The zero-radial-gradient field design substantially improves the resolution of the device.

The demands for high particle turn number mean the very low RF power requirements. Typical dee voltage requirements are in the range of 100–500 V, so that relaxed design criteria for dee structure could be employed and cheap commercial components in power supply circuits may be used. The requirement of high RF harmonic number to obtain high resolution performances also works along the line of improving the machine focusing capability. Actually due to the absence of the radial field gradient and/or AVF (azimuthally varying field), the beam can suffer from a lack of focusing power which can be provided only by electrical focusing power of the acceleration electrodes. The electrical focusing power contributes to the  $v_r^2$  with phase focusing term (Gordon & Marti 1980):

$$h\frac{\sin\Phi}{4\pi n} \tag{3}$$

The effect of the mandatory present high turn number, n, which reduces the focusing power, thus may be compensated by the high value of harmonic number, h. This provides the frequency value of vertical oscillations high enough to produce sufficiently powerful particle focusing ( $F_z \approx v_z^2 z$ ). This feature is also relevant in determining the upper limit of intensity (in the first n turns necessarily) of the multi-component beam. The value of this limit which becomes extremely important when an intense contaminant beam component is accelerated to partial energy along with a low intensity measured beam component, reads (Blosser & Gordon 1961):

$$I = \epsilon_0 A \omega \nu_z^2 \frac{d\Phi dE}{2\pi q}$$
(4)

where  $\epsilon_0$  = permitivity, A = full beam aperture, d $\Phi$  = beam phase width, dE = energy gain per turn.

The chosen parameters of the proposed superconducting mini cyclotron provided for use as an AMS instrument are given in Table 1.

*Ion Source.* There are two possibilities for ion sources leading to the conclusion that 1) choice of internal source makes the machine simpler and less expensive and 2) the advantage of the external source is that there is more space for sample mounting and changing. This requires the construction of suitable injection lines, which makes machine hardware complex and more expensive.

However, it appears as desirable to use an external conventional sputter-type negative

	51
Resolution	$df/f = \pi n h = 25,000$
Extraction radius	10cm
Outer coil radius	14cm
RF frequency	35,566 Mhz
Outer machine radius	18cm
Cyclotron height	29cm
Dee voltage	100-500 V
SC current density	9-45kA/cm <sup>2</sup>
Re consumption	0.1L/hr
<sup>14</sup> C eigenfrequency	1.18433 Mhz

#### TABLE 1 Cyclotron design parameters

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carbon ion source to facilitate rapid sample changing and to produce the required current intensities  $\approx 5\mu$ A beam of <sup>12</sup>C (Bertsche *et al* 1987). The beam injection from the external ion source into the cyclotron median plane, in the case of the Berkeley cyclotron, was accomplished radially, due to problems with field non-uniformities when the axial injection scheme is applied to small iron core cyclotrons (Welch 1984). In our case, air-core design allows the use of the axial injection scheme. The study of an off-centered axial injection scheme based on the usage of electrostatic mirror to bend the beam, previously confined respectively by solenoid field and off-centered by an electrostatic deflector, gave satisfactory results.

Cyclotron Magnet and RF Structure. Figure 1 is a schematic representation of the cyclotron. The required cyclotron magnetic field is produced by two main coil sections at current density of  $9kA/cm^2$ . A cylindrical iron shield for effective screening of the magnetic field also provides part of the cyclotron magnetic field and mechanical support to the machine components. An axial hole 22cm in diameter provides axial access to the coil interior 22cm in diameter, and openings 5cm high are reserved for radial access to the median plane for beam extraction and RF feed.

Checking the cyclotron magnet thermal and magnetic stresses and coil net body forces, using standard procedures (Subotic 1988), shows that the design values could be retained inside the standard limits. Various protection schemes for coil quenching that retain the temperature and voltage drop inside safe boundaries are considered.

The design elements of RF configuration demands have shown that low power and dee voltage requirements permit the use of standard commercially available components and do not require using sine wave voltage (C Bieth, pers commun 1988).

Orbit Characteristics and Particle Identification. The resulting temporal change of the orbit radii for <sup>14</sup>C<sup>-</sup>, <sup>13</sup>CH<sup>-</sup> and <sup>12</sup>CH<sub>2</sub><sup>-</sup> species are given in Figure 2. The field parameters and harmonic numbers employed are approximately the parameters of the Berkeley AMS cyclotron (Clark 1984). This small room-temperature low-energy cyclotron has been designed and built at Berkeley for direct detection dating of <sup>14</sup>C (Bertsche *et al* 1987). The time is measured by counting executed particle turns, where each turn requires one period of closed-orbit particle motion lasting  $t = 1/f = 1/1.18433 \ \mu$ seconds. The particles are accelerated in a homogeneous magnetic field of 1.08 T using 180° wide dees. Peak dee voltage used was 125 V, while the RF system was operating at h = 29 multiple of <sup>14</sup>C ion eigenfrequency f = 1.18333 MHz. We can conclude that at the field level of 1.08 T and RF harmonic number h = 29, the <sup>12</sup>CH<sub>2</sub><sup>-</sup> beam component reaches a maximum radius r = 2.79



Fig 1. Schematic representation of the superconducting mini-cyclotron dedicated to AMS analysis



Fig 2. Changes of the orbit radii for interfering atomic and molecular species, as a function of the executed number of turns. The field parameters and harmonic numbers employed are the parameters of the Berkeley AMS cyclotron (Welch *et al* 1987; Clark 1984).

in after 121 turns, while the <sup>13</sup>CH<sup>-</sup> beam component will not experience deceleration before reaching radius r = 3.8 in after 230 turns, so that <sup>14</sup>C cannot be extracted before achieving r value of 10.16 cm, *ie*, after executing 163 turns. Maximum <sup>14</sup>C energy will then be 42keV, *ie*, 3keV/nucleon. Due to low particle energy, the problem of particle detection and identification is not trivial. Various schemes of ion identification, depending on ion energy achieved and extraction procedure assumed are needed for careful analysis.

Cyclotron-based techniques achieving the highest possible level of selectivity, should be able to solve the problems of 1) rare particle identification and counting, 2) attainment of the required accuracy in determining relevant isotopic ratio at <sup>14</sup>C dating with AMS.

It is important to note that, due to low ion energies, the standard techniques of ion identification and counting cannot be applied when a small cyclotron is used at a field level of 1 T. An inexpensive low-energy ion detector concept that we intend to use, was recently developed by the Berkeley group (Friedman *et al* 1988). At this successfully tested detection system, the 36keV C (3keV/nucleon) ion strikes a grazing-incidence  $AL_2O_3$  conversion dynode ejecting a few tens of secondary electrons which enter separate pores of a micro-channel plate and are independently multiplied. The output signal is proportional to the number of secondary electrons. The satisfactory background discrimination and counting efficiency at ion identification are observed. However, the operational field of the superconducting mini-cyclotron can be increased to the level of 5 T, allowing a corresponding increase of the C ion energies to the level of 1 MeV, where the standard detection methods can be applied.

The Berkeley group (Welch 1987, in press) also propose to obtain the ratio  ${}^{14}C/{}^{12}C$  by tuning the cyclotron to  ${}^{12}C$  and measuring the current at the detector position with a movable Faraday cup, replacing the Faraday cup with the ion detector and tuning the cyclotron to the  ${}^{14}C$  ions. The  ${}^{12}C$  current intensity may then be controlled, positioning the appropriate sensors along the axial injection line. The orbit off-centering techniques (Milinkovic *et al* 1988) can also be considered a possible solution in determining the  ${}^{14}C/{}^{12}C$  ratio.

Raising the magnetic field (up to a level of 5 T) gives the theoretical opportunity to increase the resolution to a factor equal to the field change ratio, to move the critical radii toward the machine center and to increase the ion energy to a level of easy detection and identification. The eventual use of a stripper canal beyond the highest critical radius can also substantially improve the beam extraction efficiency.

Cost Estimation. We estimate that hardware costs could be kept within a budget of 80,000. It is also important to note that such a dedicated type of the cyclotron also could allow us to enter the field of heavy ion decay (asymmetric fission).

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# FORMATION OF ${}^{13}C/{}^{12}C$ ISOTOPE RATIOS IN SPELEOTHEMS: A SEMI-DYNAMIC MODEL<sup>1</sup>

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ABSTRACT. A theoretical approach towards predicting the carbon isotope composition of carbonate cave deposits is presented. The proposed model simulates time variations of both the chemical and isotopic composition of the carbonate solution and deposited calcite in the course of CaCO<sub>3</sub> precipitation. Two phases of the precipitation process are distinguished and treated separately: initial outgassing of the solution until a certain degree of supersaturation of  $CO_3^{-2}$  ions is reached and subsequent precipitation of  $CaCO_3$  related to further outgassing. Precipitation rates of CaCO<sub>3</sub> predicted by the model agree fairly well with literature data. The model predicts  $\delta^{13}$ C values of deposited calcite within a range of ca -16 to  $+3\%_{00}$  depending on temperature, chemical and isotope parameters of the initial solution and actual degree of the precipitation process.

#### INTRODUCTION

Speleothems are deposits of calcium carbonate found in limestone caves (stalagmites, stalactites and flowstones). They are formed by precipitation from seepage water entering through the roof or walls of the cave which becomes supersaturated with  $CaCO_3$ . Several models describing the evolution of the carbon isotope composition of precipitated carbonates have been proposed (eg, Hendy 1971; Dreybrodt 1982; Salomons & Mook 1986).

The most comprehensive analysis of the CaCO<sub>3</sub> precipitation process was made by Hendy (1971). He describes mathematically CaCO<sub>3</sub> precipitation under equilibrium conditions for both open and closed systems. He also presents first attempts towards kinetic treatment of isotopic exchange in the reaction chain  $CO_{2g} \rightarrow CO_{2w} \rightarrow HCO_3$  and formulates physical and chemical conditions to be fulfilled for equilibrium fractionation of carbon and oxygen isotopes during speleothem formation processes.

Salomons and Mook's (1986) theoretical approach to the formation of <sup>13</sup>C content of precipitated carbonate is in fact, very similar to Hendy's model, with some simplifications.

Both these models assume that outgassing of the solution and precipitation of  $CaCO_3$  occur simultaneously from saturated solution. They also assume that isotopic equilibrium is maintained between gaseous and dissolved CO<sub>2</sub>.

Dreybrodt's model (1982) refers to specific conditions in caves situated under glaciers or in bare karst areas where precipitation of CaCO<sub>3</sub> may be due to geothermal effect. This model was proposed to explain very high  $\delta^{13}$ C values of speleothems (up to +10%) from the high mountain caves of the Alps (Geyh, Franke & Dreybrodt 1983).

Recent isotope investigations of streams precipitating  $CaCO_3$  revealed that deposition of  $CaCO_3$  starts, in fact, from supersaturated solutions, with activity of  $CO_3^{2^-}$  ions equal to ca  $2.2*10^{-5}$  mol/L (Usdowski, Hoefs & Menschel 1979); Dandurand *et al* 1982; Michaelis, Usdowski & Menschel 1985). Also, the assumption of full chemical and isotopic equilibrium in the solution cannot be strictly valid because the rate of removal of  $CO_2$  from the solution, especially at initial stages of the outgassing process, is much larger than its production rate of  $HCO_3^-$  ions. Consequently, kinetic isotope relationships rather than equilibrium should be used. Our model will hopefully eliminate many simplifying assumptions made in the above-mentioned models.

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#### THE H<sub>2</sub>O-CO<sub>2</sub>-CaCO<sub>3</sub> SYSTEM

The  $H_2O-CO_2$ -CaCO<sub>3</sub> system, under full chemical equilibrium conditions can be described by the following equations (Buhmann & Dreybrodt 1985)

$$(H^+)(OH^-) = K_W(H_2O)$$
 (1a)

$$(CO_2) = K_H P_{CO_2} \tag{1b}$$

$$(\mathrm{CO}_2) = \mathrm{K}_{\mathrm{O}}(\mathrm{H}_2\mathrm{CO}_3^{\mathrm{o}}) \tag{1c}$$

$$(H^+)(HCO_3^-) = K_1(H_2CO_3^*)$$
 (1d)

$$(H^+)(CO_3^{2^-}) = K_2(HCO_3^-)$$
 (1e)

$$(H^+)(HCO_3^-) = K_4(CO_2)(H_2O)$$
 (1f)

$$(H^{+})(HCO_{3}^{-}) = K_{3}(H_{2}CO_{3}^{0})$$
(1g)

$$(Ca^{2^+})(CO_3^{2^-}) = K_C(CaCO_3^o)$$
 (1h)

where  $(H_2CO_3^*) = (H_2CO_3^\circ) + (CO_2)$ ,  $K_H$  – solubility of  $CO_2$  in water and the expressions in brackets represent activity of individual ions in the solution. The presence of  $CaCO_3^\circ$  and  $CaHCO_3^+$  molecules can be ignored because of their low concentration in the solution, usually <1% of the total amount of all other carbonic components (Langmuir 1984). Also, the condition of electroneutrality of the solution should be fulfilled

$$c_{\rm H} + 2c_{\rm Ca} - c_{\rm OH} - c_{\rm HCO_4^-} - 2c_{\rm CO_4} = 0$$
<sup>(2)</sup>

where c represents the concentration of the given ion in the solution (in mol/L). The equilibrium constants quoted in Eqs (1a)–(1h) are temperature-dependent (see eg, Buhmann & Dreybrodt 1985).

In a natural environment, limestone dissolution occurs usually with participation of biogenic  $CO_2$  originating from plant respiration and decay of dead organic matter. The soil layer is the principal reservoir of biogenic  $CO_2$  where its partial pressure can be up to two orders of magnitude higher than in the bulk atmosphere.

Limestone dissolution may proceed along two extreme routes:

1) under open-system conditions where the solution is always in contact with the reservoir of  $CO_2$ ,

2) under closed-system conditions where the solution is isolated from the reservoir of gaseous  $CO_2$  before dissolution begins. In nature, the dissolution process mostly should be considered as a mixture of these extreme situations.

In an open system, with chemical and isotopic equilibrium between the  $CO_2$  reservoir and the solution, the chemical composition of the solution can be determined from Eqs (1a)–(1h) and (2). The carbon isotopic composition of individual ions in the solution can be calculated using the equilibrium isotopic enrichment constants listed in Table 1. It is evident that, under open-system conditions, the isotopic composition of all carbonic compounds present in the solution is controlled by the isotopic composition of the gaseous  $CO_2$ .

Under closed-system conditions, carbon atoms in the solution originate from two sources, the soil  $CO_2$  and dissolved limestone rock. Again, assuming full chemical and isotopic equilibrium in the solution, the carbon isotope composition of individual carbonate compounds in the solution can be calculated for each step of the dissolution process.

Figure 1 shows the evolution of the isotopic composition of  $HCO_3^-$  ions and total dissolved inorganic carbon (TDIC) in the solution during dissolution, for values of temperature and partial pressure of  $CO_2$  typical for cave environments. The calculations were based on the iterative method proposed by Hendy (1971). We assumed the  $\delta^{13}C$  of soil  $CO_2$  equal

TEMPERATURE 5°C					
B A	CO <sub>2g</sub>	CO <sub>2w</sub>	HCO <sub>3</sub>	CO3-	CaCO <sub>3</sub>
CO <sub>2g</sub>	+	+ 1.15	-10.20	- 9.61	-10.09
CO <sub>2w</sub>	- 1.15	+	-11.35	-10.74	-11.24
HCO3	+10.31	+11.48	+	+ 0.60	+ 0.11
CO32-	+ 9.70	+10.86	- 0.60	+	- 0.49
CaCO3	+10.19	+11.37	- 0.11	+ 0.49	+
TEMPERATURE 15°C					
B	CO <sub>2g</sub>	CO <sub>2w</sub>	нсо <sub>3</sub>	CO3 <sup>2-</sup>	CaCO3
CO <sub>20</sub>	+	+ 1.10	- 9.02	- 8.54	- 9.43
CO <sub>2w</sub>	- 1.10	+	-10.12	- 9.63	-10.53
HCO <sub>3</sub>	+ 9.10	+10.22	+	+ 0.49	- 0.41
CO32-	+ 8.61	+ 9.72	- 0.49	+	- 0.90
CaCO <sub>3</sub>	+ 9.52	+10.64	- 0.41	+ 0.90	+

Equilibrium isotope enrichment coefficients  $\epsilon_{A-B}$  (%)0) for the CO<sub>2</sub>-H<sub>2</sub>O-CaCO<sub>3</sub> system at 5° and 15°C. Data after Mook, Bommerson & Staverman (1974), Vogel, Grootes & Mook (1970), Thode, Shima, Rees & Kirshnamurthy (1965), Salomons & Mook (1986).

TABLE 1

to  $-25\%_{00}$  vs PDB which is the mean value occurring on areas covered by  $C_3$  plants. The  $\delta^{13}C$  of limestone carbonate was fixed at the level of  $+1\%_{00}$  vs PDB. As shown in Figure 1, the  $\delta^{13}C_{\text{TDIC}}$  values at the saturation point vary between  $-15\%_{00}$  and  $-19\%_{00}$  under open-system conditions, whereas the corresponding values for the closed system are in the range of  $-13\%_{00}$  to  $-15\%_{00}$ . The corresponding  $\delta^{13}C$  values for  $\text{HCO}_3^-$  ions in the solution lie in the range of  $-14.9\%_{00}$  to  $-16.1\%_{00}$  and  $-13\%_{00}$  to  $-14\%_{00}$ , for open- and closed-system conditions, respectively. There is only a slight dependence of  $\delta^{13}C_{\text{HCO}_3^-}$  on temperature because changes of equilibrium fractionation factors with temperature are compensated by parallel changes of the molar ratios of carbonic molecules in solution.

# FORMATION OF SPELEOTHEMS

Under natural conditions, calcite speleothems are formed when a thin film of carbonate solution depositing CaCO<sub>3</sub> flows down the given specimen. For a theoretical description of this process, a planar model has been proposed (Fig 2). The liquid film is assumed to be ca 0.01 cm thick, which is the value most frequently observed in nature. A constant pH value across the film was further assumed (Hoover & Berkshire 1969) which considerably simplifies numerical calculations. In view of the isotope and chemical data for carbonate precipitating springs (*cf* Introduction), the formation process of speleothems was divided into two parts: 1) outgassing of the solution without precipitation of CaCO<sub>3</sub> until a certain degree of supersaturation of the solution is reached, 2) simultaneous outgassing of the solution and precipitated as functions of the time elapsed since the beginning of the outgassing process.

# Outgassing of the Solution

During the release of  $CO_2$  from the solution, the conversion rate of  $HCO_3^-$  to  $CO_{2w}$  is usually much faster than the backward reaction. Thus, the reaction  $CO_{2w} \rightarrow HCO_3^-$  was omitted from the calculations. Further, we assumed that the solution preserves the initial



Fig 1. Dissolution of CaCO<sub>3</sub> in water under closed- (----) and open- (---) system conditions at +5° and +15°C. Numbers labeling the curves indicate  $\delta^{13}$ C values of the TDIC. Numbers in parentheses are  $\delta^{13}$ C values of HCO<sub>3</sub><sup>-</sup> in the saturated solution (S<sub>C</sub> = 1). The input  $\delta^{13}$ C values are -25 and +1%<sub>00</sub> vs PDB for soil CO<sub>2</sub> and limestone carbonate, respectively.

concentration of  $Ca^{2+}$  ions during removal of  $CO_2$ . Based on these assumptions, the outgassing of the solution can be described by

where the reaction  $CO_3^{2^-} + H^+ \Longrightarrow HCO_3^-$  is fast (Dreybrodt 1980). Conversion of  $HCO_3^-$  to  $CO_{2w}$  can be treated as a simultaneous, pseudo-first-order reaction. Consequently, temporal



Fig. 2. Schematic representation of processes on the surface of the growing speleothem

variations of concentration of  $HCO_3^-$  ions in the solution can be expressed by

$$c_{HCO_{3}^{-}}(t) = c_{HCO_{3}^{-}}^{atm} + \{c_{HCO_{3}^{-}}^{o} - c_{HCO_{3}^{-}}^{atm}\} EXP(-k_{HCO_{3}^{-}}t)$$
(4)

where  $c_{HCO_3^-}(t)$ ,  $c_{HCO_3^-}^{o}$ ,  $c_{HCO^-}^{atm}$  represent concentrations of  $HCO_3^-$  ions at the time instant t, t = 0 and in equilibrium with the atmospheric CO<sub>2</sub>, respectively. The rate constant  $k_{HCO_3^-}$  in Eq (4) depends on the pH of the solution and is equal

$$k_{HCO_{4}^{-}} = k_{-2} + k_{-1}c_{H^{+}}$$
(5)

where  $k_{-2}$  and  $k_{-1}$  are the rate constants of the reactions shown in Eq (3). Numerical values of  $k_{-2}$  and  $k_{-1}$  are listed in Table 2.

TABLE 2 Chemical rate constants for the reactions  $CO_{2} + H_{2}O \xrightarrow[k_{-1}]{k_{-1}} H^{+} + HCO_{3}^{-}$   $CO_{2} + OH^{-} \xrightarrow[k_{-2}]{k_{-2}} HCO_{3}^{-}$ (according to Buhmann & Dreybrodt 1985) k<sub>2</sub> [L/mol\*s] k<sub>-2</sub> [1/s] Temperature k<sub>-1</sub> [L/mol\*s]  $k_1$ [1/s] [°C] 6966 11096 17673 28136 4.4\*10<sup>-6</sup> 9.7\*10<sup>-6</sup> 2.1\*10<sup>-5</sup> 995 1574 2449 0 5 10 15 2.3\*10<sup>-3</sup> 4.2\*10<sup>-3</sup> 7.5\*10<sup>-3</sup> 1.3\*10-3 4.4\*10-5 3753

We further assumed that diffusion is a principal mechanism responsible for transport of  $CO_{2w}$  across the film thickness. The solution of a one-dimensional diffusion equation with a homogeneous source of  $CO_{2w}$  (reservoir of  $HCO_3^-$  ions), for the time intervals fulfilling the condition  $D_{CO_3}$  t/ $R^2 > 0.4$ , can be expressed by

$$c_{CO_{2w}}(t) = \frac{8}{\pi^2} \left( EXP \left( -t/T_D \right) \left\{ c_{CO_{2w}}^o - c_{CO_{2w}}^{atm} \right\} + \frac{\left\{ c_{HCO_3^-}^o - c_{HCO_3}^{atm} \right\} T_D k_{HCO_3^-}}{1 - T_D k_{HCO_3^-}} * \left\{ EXP \left\{ -k_{HCO_3^-} t \right\} - EXP \left\{ -t/T_D \right\} \right\} \right) + c_{CO_{2w}}^{atm}$$
(6)

where  $c_{CO_{2w}}(t)$ ,  $c_{CO_{2w}}^{o}$  and  $c_{CO_{2w}}^{atm}$  are the average concentrations of  $CO_{2w}$  in the liquid film at the time t, at t = 0 and in equilibrium with atmospheric  $CO_2$ , respectively.  $T_D$  stands for characteristic constant of  $CO_2$  decrease in the solution and is expressed as

$$\Gamma_{\rm D} = \frac{4R^2}{\pi^2 D_{\rm CO_2}} \tag{7}$$

where R is the film thickness (in cm) and  $D_{CO_2}$  is the diffusion coefficient of  $CO_2$  in water (in cm<sup>2</sup>/s). The temperature dependence of  $D_{CO_2}$  was adopted after Buhmann & Dreybrodt (1985).

The net mass and isotope fluxes of  $CO_2$  through the air-water interface can be expressed as a difference between corresponding fluxes "out" and "into" the solution (Siegenthaler & Munnich 1980)

$$F = F_{as} - F_{sa} = w * (K_H P_{CO_s} - c_s)$$
 (8)

$$F^{13} = w^{13} \alpha_{CO_{2g} - CO_{2w}} K_{H}^{13} R_{a} P_{CO_{2}} - w^{13} \alpha_{\Sigma - CO_{2w}}^{13} R_{\Sigma} c_{s}$$
(9)

where

F,  $F^{13}$  = net fluxes of <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub>, respectively w, <sup>13</sup>w = transport velocities of <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> molecules through the liquid film <sup>13</sup>R<sub>a</sub>, <sup>13</sup>R<sub>5</sub> = <sup>13</sup>C/<sup>12</sup>C isotope ratios of atmospheric CO<sub>2</sub> and TDIC in solution P<sub>CO<sub>2</sub></sub> = partial pressure of atmospheric CO<sub>2</sub>

 $K_{\rm H}$  = solubility of CO<sub>2</sub> in water

 $\alpha_{\rm CO_2-CO_{2w}}$  = equilibrium fractionation factor between gaseous and dissolved CO<sub>2</sub>

 $\alpha_{\Sigma-CO_{2w}} =$  effective equilibrium fractionation factor between TDIC and  $CO_{2w}$  in solution

 $c_s = \text{concentration of CO}_{2w}$  in bulk solution.

Dividing Eq (9) by Eq (8) and transforming the isotopic ratios R into corresponding  $\delta$  values we obtain

$$\delta^{13}C_{F} = \left(\frac{\alpha_{as}c_{CO_{2}}^{atm} \left\{\delta^{13}C_{CO_{2}}^{atm} 10^{-3} + 1\right\}}{K_{H}P_{CO_{2}} - c_{CO_{2w}}} - \frac{\alpha_{sa}c_{CO_{2w}} \left\{\delta^{13}C_{\Sigma} 10^{-3} + 1\right\}}{K_{H}P_{CO_{2}} - c_{CO_{2w}}} - 1\right) * 1000$$
(10)

where  $\alpha_{as} = \alpha_{CO_{2g}-CO_{2w}} * {}^{13}w/w$  and  $\alpha_{sa} = \alpha_{\Sigma-CO_{2w}} * {}^{13}w/w$ . The above formula represents the  $\delta^{13}C$  value of the net flux of CO<sub>2</sub> through the interface.

Calculations of the evolution of  $\delta^{13}C_{\text{TDIC}}$  during the outgassing process started from the parameters of the solution saturated with CaCO<sub>3</sub>. Based on Eqs (4) and (6), for the time step  $\Delta t$ , the actual concentrations of CO<sub>2w</sub> and HCO<sub>3</sub><sup>-</sup> ions were calculated. Assuming chemical activity coefficients of all carbonic molecules equal 1, we evaluated the concentration of hydrogen ions H<sup>+</sup> using conditions of electroneutrality and the assumption of chemical

equilibrium between  $\text{HCO}_3^-$  and  $\text{CO}_3^{2^-}$  ions. After computation of the concentrations of other ions in solution, the ionic strength was used (Garrels 1960) to calculate activity coefficients, which in turn, were applied to calculate the concentrations of carbonic compounds in solution more accurately. The iterative process was repeated until successive changes in activity coefficients were  $<10^{-4}$ . The values of  $\Delta c_{\text{TDIC}}$ ,  $\delta^{13}C_{\text{TDIC}}$ , and isotopic composition of all carbonic compounds remaining in the solution were then computed. Since the kinetic fractionation factor for the  $\text{HCO}_3^- \rightarrow \text{CO}_{2w}$  reaction is unknown, the equilibrium values have been adopted. The computation was performed for successive intervals  $\Delta t$ , until the activity of  $\text{CO}_3^{2^-}$  ions necessary for initiation of  $\text{CaCO}_3$  precipitation process was reached (~2.2\*10<sup>-5</sup> mol/L).

The degassing process was simulated for four carbonate solutions with different initial parameters. The results are summarized in Figure 3. The initial, fast increase of  $\delta^{13}C_{TDIC}$  is caused by release from the solution of large amounts of  $CO_{2w}$  with low <sup>13</sup>C content. A further increase of  $\delta^{13}C_{TDIC}$  proceeds slowly because the  $CO_{2w}$  reservoir is exhausted and the outgassing rate is controlled by the  $HCO_3^-$  ions. At 5°C, after the first 20 sec, the  $HCO_3^-$  ions entirely control the outgassing process. The influence of atmospheric  $CO_2$  on the isotope composition of the solution is negligible because the flux of  $CO_2$  "out" of the solution is much larger than the backward flux. In Figure 3 it becomes clear that solutions of similar origin (closed or open system), start to precipitate calcite earlier for higher partial pressures of  $CO_2$  at the time of their formation.

Temperature is an essential parameter accelerating the outgassing process. An increase in temperature slightly decreases the difference in  $\delta^{13}C_{TDIC}$  between saturated and outgassed solutions. As in Figure 3, this difference is in the range of 3-4%. It should be noted that final values of  $\delta^{13}C_{TDIC}$  may in reality be slightly lower because in the calculations we assumed isotopic equilibrium between carbonate compounds in solution. Escape of CO<sub>2</sub> to the atmosphere is a fast process and the HCO<sub>3</sub><sup>-</sup> ions probably are not able to reach equilibrium with CO<sub>2</sub> remaining in solution.

#### Precipitation of $CaCO_3$

When the activity of  $CO_3^{2^-}$  ions in solution reaches ca  $2.2*10^{-5}$ mol/L, both outgassing and precipitation of CaCO<sub>3</sub> proceed simultaneously. It is a well-known experimental fact that precipitation of 1 mole of CaCO<sub>3</sub> is accompanied by release of 1 mole of gaseous CO<sub>2</sub> to the atmosphere (Michaelis, Usdowski & Menschel 1985). We numerically simulated the precipitation process in a similar way to outgassing the solution, described above. The calculation started from outgassed, supersaturated solution with defined chemical and



Fig 3. Evolution of  $\delta^{13}$ C values of the TDIC in solution during initial outgassing without precipitation of CaCO<sub>3</sub>. The activity of CO<sub>3</sub><sup>2-</sup> ions in solution, corresponding to final points of the curves, equals ca 2.2\*10<sup>-5</sup> mol/L.

isotopic composition. The time evolution of  $\delta^{13}C_{TDIC}$  was computed by an iterative method, using the isotope mass balance formula

$$\delta^{13} C_{TDIC}^{i+1} = \delta^{13} C_{TDIC}^{i} \frac{c_{TDIC}^{i}}{c_{TDIC}^{i+1}} - \delta^{13} C_{F}^{i} \frac{\Delta c_{TDIC}}{2 c_{TDIC}^{i+1}} - \delta^{13} C_{CaCO_{3}}^{i} \frac{\Delta c_{TDIC}}{2 c_{TDIC}^{i+1}}$$
(11)

where  $\delta^{13}C_{TDIC}^{i+1}$  represents the carbon isotopic composition of the precipitated portion of CaCO<sub>3</sub>, corresponding to the change in the total carbon content of the solution  $c_{TDIC}^{i}$  by  $\Delta c_{TDIC}$ . Isotopic equilibrium between HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> ions in the solution was assumed (high rate of HCO<sub>3</sub><sup>-</sup>  $\rightarrow$  CO<sub>2</sub><sup>-</sup> + H<sup>+</sup> reaction). The isotopic composition of total precipitated calcite ( $\delta^{13}C_{CaCO_3}^{TOT}$ ) was calculated as a weighted mean of the  $\delta^{13}C_{CaCO_3}^{i}$  values. Results of the calculations are summarized in Figure 4, from which several interesting conclusions about the dynamics of the precipitation process can be drawn:

1) The <sup>13</sup>C content of individual portions of CaCO<sub>3</sub> increases strongly during the initial stages of precipitation. This is mainly due to an ongoing outgassing process accompanied by a relatively large isotope fractionation factor for the  $HCO_3^- \rightarrow CO_{2w}$  reaction which should be compared with the small value of  $\epsilon_{CaCO_3-HCO_3^-}$  (cf Table 1). This "two-sink," Rayleigh-type process results in values which, for a certain interval, may be even higher than equilibrium values with atmospheric CO<sub>2</sub>. Such an "inertia" effect can be seen especially well in the  $\delta^{13}C_{CaCO_3}^i$  curve calculated for 15°C. In later stages of precipitation, when the  $P_{CO_2}$  in solution is only 10–20% higher than in the bulk atmosphere, the influence of atmospheric CO<sub>2</sub> becomes noticeable, bending the  $\delta^{13}C_{CaCO_3}^i$  curve towards the equilibrium value.

2) Carbonate solutions formed under lower partial pressures of  $CO_2$  (open or closed system) precipitate  $CaCO_3$  more slowly and with higher  $\delta^{13}C_{CaCO_3}^i$  values than the solutions formed under higher  $P_{CO_2}$  values.



Fig 4A. Changes in  $\delta^{13}$ C values of individual portions ( $\delta^{13}$ C  $_{CaCO_3}^i$ ) and total precipitated ( $\delta^{13}C_{CaCO_3}^{TOT}$ ) calcite as a function of time elapsed since the beginning of the precipitation process, under different conditions of carbonate solution formation. Percentage of the CaCO<sub>3</sub> precipitated from the beginning of the process is also indicated. B. Temperature influence on  $\delta^{13}C_{CaCO_3}^i$  and  $\delta^{13}C_{CaCO_3}^{TOT}$  values during precipitation.

3) The influence of the temperature on the precipitation rate of  $CaCO_3$  is noticeable. The change from 5-15°C results in an increased precipitation rate by a factor of 2-3, depending on the actual stage of the precipitation process. This is due to the temperature dependence of the rate constants  $k_{1}$  and  $k_{2}$ .

# Influence of $\delta^{13}C$ of Soil $CO_2$

In order to examine the influence of different  $\delta^{13}C$  values of soil CO<sub>2</sub> on isotopic composition of precipitating calcite, the necessary numerical calculation was made according to the procedure described previously. The values of soil  $CO_2$  in the order of -30, -20and  $-16\%_{00}$  vs PDB was assumed.

In general, the time dependence of  $\delta^{13}C_{CaCO_3}^{TOT}$  and  $\delta^{13}C_{CaCO_3}^{i}$  of the precipitating calcite is similar to that presented on Figure 4. However, starting points of the  $\delta^{13}C^i_{CaCO_*}$  and  $\delta^{13}C_{CaCO_3}^{TOT}$  curves are shifted with respect to analogous points on Figure 4 calculated per  $\delta^{13}C_{CaCO_3}$ of the soil CO<sub>2</sub> equal to  $-25\%_{00}$ . For extreme values of  $\delta^{13}$ C of the soil CO<sub>2</sub>, *ie*, -30 and  $-16\%_{00}$ , the  $\delta^{13}C_{CaCO_{2}}^{i}$  in open-system conditions reaches the following values respectively:

> -22.0 and  $-6.3\%_{00}$  for  $P_{CO_2} = 0.05$  atm at 5°C -17.5 and  $-5.4\%_{00}$  for  $P_{\rm CO_\circ}=0.01$  atm at 5°C -21.1 and  $-7.1\%_{00}$  for  $P_{CO_0} = 0.05$  atm at 15°C

For the closed system with  $P_{CO_2} = 0.05$  atm at  $t = 5^{\circ}C$ , the corresponding values are  $-13.80_{00}$  and  $-6.60_{00}$ . Both  $\delta^{13}C_{CaCO_3}^{TOT}$  and  $\delta^{13}C_{CaCO_3}^{i}$  approach equilibrium with atm  $CO_2$  as the rate of precipitation approaches zero. The higher the  $\delta^{13}C$  of soil  $CO_2$ , the more rapidly  $\delta^{13}C_{CaCO_3}^{TOT}$  and  $\delta^{13}C_{CaCO_3}^{i}$  increase at the initial stages of the precipitation process.

#### CONCLUDING REMARKS

Our model can be regarded as an up-to-date approach towards better understanding of the physical and chemical parameters controlling the isotopic composition of carbonate deposits formed in a cave environment. In numerical calculations, the most recent values of the equilibrium and kinetic chemical reaction constants were used together with the widely accepted values of carbon isotope fractionation factors. Supersaturation of the solution as a prerequisite for the initiation of precipitation was introduced in accordance with recent experimental data. The precipitation rates of CaCO<sub>3</sub> obtained in the model  $(10^{-7} - 10^{-8})$ mol/L s) are in satisfactory agreement with the values quoted in literature (Dreybrodt 1985).

For a temperature close to +5°C, which is typical for most mid-latitude caves, the model predicts values of  $\delta^{13}$ C of precipitated calcite in the range of ca -16 to +3%, depending on particular conditions of the precipitation process. The majority of  $\delta^{13}$ C values measured in speleothems are in the range of -11 to  $-5\%_{00}$ . This, with model predictions, suggests that only several percent of the total carbon in the solution is precipitated. It is worth noting that 100% yield of the precipitation would lead to yearly growth layers of speleothems up to two orders of magnitude larger than observed in nature.

Although the agreement between measured and calculated  $\delta^{13}$ C values of speleothems argues for the validity of the model, we should not forget the simplified assumptions on isotopic equilibrium between HCO3 and CO2w reservoirs in solution, the absence of backward reaction  $CO_{2w} \rightarrow HCO_3^-$  and of concentration gradients for H<sup>+</sup>,  $HCO_3^-$  and  $CO_3^{2-}$  ions in solution.

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# FURTHER INVESTIGATIONS ON <sup>14</sup>C DATING OF CALCAREOUS TUFA<sup>1</sup>

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ABSTRACT. Systematic studies on <sup>14</sup>C dating of tufa profiles in southern Poland have resulted in developing a simple phenomenological model which enables us to estimate the reservoir correction factor of <sup>14</sup>C dates of individual carbonate samples. We made further studies to test model assumptions and to verify relationships between the value of reservoir correction factor  $T_R$  and <sup>13</sup>C content of tufa carbonate. Two new study sites, Rudawa and Szklarka, are close to previously studied sites. Four tufa samples with associated organic fraction from ca 2000m asl in South America (Peruvian Andes) were measured to test the possible application of the developed model to tufas in different geochemical and climatic environments. Finally, a series of calcareous tufa samples from the Villers-devant-Orval profile (Belgium) were dated, although no direct comparison with organic matter dates is available for this profile.

#### INTRODUCTION

In earlier studies of tufa profiles from southern Poland (Pazdur, Pazdur & Szulc 1988; Pazdur 1988) we found highly different values of the reservoir correction factor  $T_R$  of the carbonate fraction of tufa samples, ranging from 900–11,000 yr. Observed values of  $T_R$  are related to the lithologic type of tufa. The highest values are observed for tufas deposited in highly turbulent water (oncoids, stromatolites, moss travertines), whereas the lowest values correspond to peloidal muds deposited in semilimnic environments. We observed constant values of  $T_R$  in most profiles (Racławka, Rzerzuśnia, Sieradowice).

The aim of this study is to extend the experimental base of the geochemical model developed for interpretation of <sup>14</sup>C ages of tufa profiles (Pazdur 1988) and to check its validity by dating tufa samples from other regions.

#### SITE DESCRIPTIONS

#### Rudawa and Szklarka, Southern Poland

These sites are in the Cracow-Wielún Upland, close to the Raclawka site studied previously (Pazdur, Pazdur & Szulc 1988). Tufa horizons are incorporated in a thick series of fluvial sediments of various origins, with variable admixtures of organic matter. A detailed description and discussion of sedimentology and stratigraphy of the profile in the Rudawa site was published elsewhere (Pazdur & Rutkowski 1987). The sequence of sediments in the Szklarka site, ca 5km from the Rudawa site in the valley of a small tributary to the Rudawa stream, is similar.

#### Checras, High Andes, Peru

This site is in the valley of the Checras River near Churin (10° 48' S, 76° 45' W), Prov Cajatambo, Dept Lima. Moss travertines occur in two series of gravels in Terraces I and III ca 2400m and 2100m asl, respectively, separated by a series of lacustrine sediments ca 300m thick (*cf* Pazdur 1989).

#### Villers-devant-Orval, Belgium

The profile of tufaceous sediments, >12m thick, consists of calcareous gyttja, fine- and coarse-grained tufas, fine calcareous detritus, and several layers of stromatolite in the upper part of the profile. Distinct sedimentologic changes in the lowermost part of the profile may suggest the presence of reworked carbonate. A detailed site description, including discussion of the results of pollen analysis, was published by Geurts (1976).

<sup>1</sup> This paper was presented at the 13th International Radiocarbon Conference, June 20-25, 1988, in Dubrovnik, Yugoslavia.

#### FIELD AND LABORATORY TECHNIQUES

Samples from profiles in Rudawa and Szklarka were collected in 1987 from natural exposures by J Rutkowski and S W Alexandrowicz, as part of systematic studies of the stratigraphy and sedimentology of Holocene fluvial deposits of the Vistula River and tributaries near Cracow (Rutkowski 1987) and malacologic studies of calcareous sediments in the Cracow-Wieluń Upland (Alexandrowicz 1983). Samples from the Checras site were collected in 1985 by P Libelt and members of the Polish Expedition to High Andes, Peru, from a natural outcropping. Samples from the Villers-devant-Orval profile were collected in 1975 by MA Geurts from natural exposures and submitted for dating in 1988.

All samples submitted for dating were first subjected to careful visual examination and lithological identification before further laboratory processing. A detailed description of laboratory methods was given elsewhere (Pazdur, Pazdur & Szulc 1988).

#### **RESULTS AND DISCUSSION**

#### Tufa profiles with Organic Matter

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Experimental data were obtained from two new sites in southern Poland, situated close to the Racławka site studied previously (Pazdur, Pazdur & Szulc 1988), and one site in High Andes, Peru. In each site, both carbonate and organic matter fractions were dated to determine experimentally the value of reservoir correction  $T_R$ . The results are given in Table 1.  $\delta^{13}$ C values of carbonate of four samples of moss travertine from the Checras site are shown in Figure 1 as functions of <sup>14</sup>C dates of organic and carbonate fractions. The clearly outlying result obtained on the organic fraction of sample I/O2 may be suspect because of very little organic matter (ca 60% dilution with inactive carbon) and possible contamination with recent organic dust. After rejecting this point, the remaining results show good regularity and can be approximated by least squares lines with equations:

$$\delta^{13}C = (3.0 \pm 0.93) - (0.21 \pm 0.03)T_c, \qquad (1a)$$

$$\delta^{13}C = (-0.36 \pm 0.27) - (0.16 \pm 0.02)T_{OBG}.$$
 (1b)

Experimentally determined values of  $T_R$ , listed in Table 1, are plotted as functions of  $\delta^{13}C$  in Figure 2, together with data previously obtained from tufa profiles in Racławka and Folkestone, UK (Pazdur 1988, Fig 2, p 12; see also Pazdur, Pazdur & Szulc 1988, Table 1). The new data points fit the previously obtained dependence very well (Pazdur 1988, line C, Fig 2). The least square line approximating the dependence of  $T_R$  (in ka) upon  $\delta^{13}C$  is described by equation

$$T_{\mathbf{R}} = (17.35 \pm 0.71) + (1.34 \pm 0.09) \,\delta^{13} \text{C.}$$
<sup>(2)</sup>

Comparison of C dates of organic and carbonate fractions of tura					
Sample	T <sub>org</sub> yr bp	Т <sub>с</sub> yr вр	T <sub>R</sub> yr	δ <sup>13</sup> C % wrt PDB	
Rudawa Rd-4	$6140 \pm 100$	$10.970 \pm 70$	4830	-9.20	
Szklarka Sk-121-C	$7600 \pm 130$	$10,240 \pm 100$	2640	-11.17	
Checras I/O1	$19,900 \pm 540$	$34,500 \pm 1300$	14.600	-3.71	
Í/O2	$24,500 \pm 2800$	$35,400 \pm 1700$	10.900*	-4.83	
ÍII/O3	$1000 \pm 100$	$17.100 \pm 200$	16.100	-0.65	
III/O4	$9500 \pm 1200$	$23,600 \pm 400$	14,100	-1.67	

 TABLE 1

 Comparison of <sup>14</sup>C dates of organic and carbonate fractions of tufa

\*Values estimated from Eq 2



Fig 1. Values of  $\delta^{13}$ C in carbonate fraction of tufa samples from Checras, High Andes, as functions of  $^{14}$ C ages of organic matter (A) and carbonate (B)



Fig 2. Dependence of experimentally determined values of the reservoir correction  $T_R$  on  $\delta^{13}$ C values of tufa carbonate for tufas deposited in high-energy water flow (line C, A) and in medium-energy water (line B, B). Dashed lines show  $1\sigma$  confidence limits (after Pazdur 1988, Fig 2, p 12, modified and completed with new data).

Belgium					_
Sample	Т <sub>с</sub> yr вр	δ <sup>13</sup> C % wrt PDB	T <sub>R</sub> yr	T <sub>corr</sub> yr BP	Palynologic age*
02/221	$9830 \pm 140$	-8.79	$2210 \pm 140$	$7620 \pm 200$	Early Atlantic
O2'/249	$11.230 \pm 180$	-8.78	$2220 \pm 140$	$9010 \pm 230$	Late Boreal
O2'/253	$9860 \pm 130$	-8.94	$2180 \pm 150$	$7680 \pm 200$	Middle Boreal
O2'/258	$10.300 \pm 80$	-10.08	$1890 \pm 260$	$8410 \pm 270$	Early Boreal
O2'/274	$27.200 \pm 700$	-0.83	$16,240 \pm 3640$	$10,960 \pm 3700$	Late Preboreal
O2'/286	$21,340 \pm 250$	-2.28	$14,290 \pm 3050$	$7050 \pm 3100$	Preboreal

 TABLE 2

 Radiocarbon and palynologic age estimates of tufa samples from the Villers-devant-Orval profile,

\*According to the subdivision of the Holocene, accepted by Geurts (1976, Fig 3, p 58), the Preboreal phase extends from 10,500 to 8500 BP, the Boreal phase from 8500-7500 BP, and the Atlantic phase from 7500-4500 BP.

This dependence can thus be used for estimating the real age of sample Checras I/O2. According to equation (2), the value of the apparent age is equal to  $10,900 \pm 2200$ , and the resulting age can be estimated as equal to  $24,500 \pm 2800$  BP.

#### Tufa Profiles Without Organic Matter

Six samples from the lower part of the Villers-devant-Orval profile were dated. The organic content in all the samples was too low for <sup>14</sup>C dating. The profile showed much differentiation of lithologic types of calcareous sediments, as well as distinct bipartition in  $\delta^{13}$ C values of carbonate. The two oldest samples, O2/286 and O2/274, show very high values of  $\delta^{13}$ C and <sup>14</sup>C age (Table 2). <sup>14</sup>C ages and  $\delta^{13}$ C values of four younger samples form a compact group and indicate different mechanisms of deposition of the younger series. Two distinct age inversions also occur in the profile. The  $\delta^{13}$ C values show a very high correlation with <sup>14</sup>C ages of carbonate (Fig 3). This dependence, described by

$$\delta^{13}C = (-14.4 \pm 0.8) + (0.52 \pm 0.05)T_c, \qquad (3)$$

is similar to that obtained for tufas from the Gliczarów and Folkestone sites (Pazdur 1988).

The presence of two significantly different groups of  $\delta^{13}$ C values and  ${}^{14}$ C ages in the profile suggests that they should be treated separately. High values of  $\delta^{13}$ C of samples O2/274 and O2/286 indicate that the reservoir correction factors of these samples should be estimated from the dependence of T<sub>R</sub> upon  $\delta^{13}$ C given by line C in Figure 2 (cf Pazdur 1988). The corrected ages (Table 2) are subjected to large errors (ca 30%), but indicate the beginning of sedimentation of tufas in the early Holocene. The mean value, equal to 9000 ± 2100 BP, is consistent with palynologic results by Geurts (1976:50) indicating a Preboreal age of the lowermost part of the profile (Fig 4).

Lithologic features and  $\delta^{13}$ C values of the second group of four samples suggest that corresponding reservoir corrections should be estimated from the dependence of T<sub>R</sub> on  $\delta^{13}$ C observed in profiles in Rzerzuśnia and Trzebienice (S Poland) and Thatcham Reedbeds



Fig 3. Values of  $\delta^{13}$ C of tufa samples from the Villers-devant-Orval profile, Belgium, as functions of  $^{14}$ C dates



Fig 4. Lower part of the tufa profile in Villers-devant-Orval, Belgium, with  ${}^{14}C$  and  ${}^{13}C$  data. Lithology and stratigraphy after Geurts (1976).

(S England), described by equation (Pazdur 1988:11)

$$T_{\mathbf{p}} = (4.41 \pm 0.98) + (0.25 \pm 0.11) \,\delta^{13} \text{C} \tag{4}$$

shown by line B in Figure 2. Estimated values of  $T_R$  and corrected ages are listed in Table 2. An inversion of dates of samples O2/249 and O2/253 also occurs after correction.

There is general agreement between the corrected ages of this set of tufa samples and the palynologic results (Geurts 1976) which indicate an early Boreal age for sample O2/258 and an early Atlantic age for the youngest dated sample, O2/221. However, the inversion of ages of samples O2/249 and O2/253 occurs after correction. Sample O2/249, with a corrected <sup>14</sup>C age equal to 9010  $\pm$  230 BP was collected from a thin layer of coarse-grained tufa, embedded in a series of fine-grained calcareous detritus, >1m thick. This distinct sedimentologic change in the profile may suggest the presence of reworked carbonate.

# CONCLUSIONS

The results obtained on paired organic and carbonate samples quoted in Table 1 seem to confirm that the validity of model considerations (Pazdur 1988) is not limited to local or

regional conditions of southern Poland. Application of this model to data obtained on samples from a profile in Villers-devant-Orval shows reasonable agreement of corrected <sup>14</sup>C ages of tufas with palynologic age estimates in the group of four younger samples. However, there are significant age inversions. A very rough lithologic description of the dated profile leads to conclusions that age inversions are associated with reworked sediments. It should be pointed out that very regular data from High Andes tufas were obtained on autogenic material with no evidence of redeposition or diagenetic changes. Therefore, it seems appropriate to repeat the conclusion from our previous study (Pazdur, Pazdur & Szulc 1988) that a detailed lithologic investigation of the dated profile and careful selection of tufa samples for <sup>14</sup>C dating is of crucial importance for reliable dating.

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# SURVEY OF THE DISPERSION OF <sup>14</sup>C IN THE VICINITY OF THE UK REPROCESSING SITE AT SELLAFIELD<sup>1</sup>

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ABSTRACT. We have been measuring <sup>14</sup>C in natural, biological materials growing in the vicinity of Sellafield, Cumbria as a continuing project with BNFL to understand the dispersion of releases from the site over several seasons. We have measured locally grown foodstuffs for monitoring purposes, individual tree rings to establish a chronology of releases, hawthorn berries for spatial investigations and are now carrying out controlled plot uptake experiments. We have been attempting to validate a current dispersion model (Clarke 1979) over a six-year period, and although we observe general agreement in most years, certain anomalies, which probably relate to topographical features, are leading to more detailed correlation with local meteorological data.

#### INTRODUCTION

The nuclear establishment at Sellafield, Cumbria, in northern England (54° 25′ 30″ N, 3°, 30′ W) was set up in the early 1950s and has, with continuing development, remained a major center for reactor research and development, power production and fuel reprocessing. The initial installations were two air-cooled graphite reactors specifically built to produce fissile material for the UK weapons program. In 1952, the first UK fuel reprocessing plant began work, in 1956 the Calder Hall power reactor—the first power reactor in the UK—came on line and in 1962 the first UK advanced gas-cooled reactor began operation.

Of these four nuclear installations, only the fuel reprocessing and the Calder Hall reactors are relevant to present-day emissions, and of these, the only radioisotope considered in these studies is <sup>14</sup>C. The mechanisms by which <sup>14</sup>C may be produced in reactor operations is given in Table 1, taken from Davis (1979). In practice, the dominant reaction in all the different types of reactor is <sup>14</sup>N(n,p)<sup>14</sup>C. The main source of the target material, nitrogen, is from impurities in the fuel and its cladding, the latter largely containing the <sup>14</sup>C during its time in the reactor. The main release of <sup>14</sup>C occurs during fuel reprocessing at Sellafield after which it is discharged either as liquid effluent to the sea or gaseous emissions to the atmosphere. Evidence of these <sup>14</sup>C emissions was first observed in this laboratory (Harwell) in 1977 through measurements on various foodstuffs, milk, grain and potatoes collected from farms in the vicinity of the Sellafield site (Otlet, Walker & Longley 1983). Finding localized values higher than the normal atmospheric levels prompted subsequent investigations with initial studies focusing on establishing a chronology of <sup>14</sup>C emissions over the earlier years of operation.

#### CHRONOLOGY OF <sup>14</sup>C EMISSIONS

Using the technique of measuring <sup>14</sup>C levels in individual tree rings to establish annual values, we began work on a 100-yr-old sycamore tree, found in Knocking Wood, 1.6km NE of the site. Maximum and minimum diameters of the trunk were 1m and 0.5m, respectively, and ring widths were 1-10mm. Wood of each ring was stripped off using a carpenter's mallet and chisel providing ca 15-25g for measurement.

The results for the Knocking Wood tree are shown in Figure 1 compared to the average Northern Hemisphere atmospheric levels for the same period. For 1952–1963, the levels are slightly above but generally follow the atmospheric line for the Northern Hemisphere. The small peak in 1957 may represent the Windscale incident when one of the graphite reactors caught fire. It occurred in October, when leaves would still have been on the tree, but how much photosynthesis would still have still been taking place is unclear.

<sup>1</sup> This paper was presented at the 13th International Radiocarbon Conference, June 20–25, 1988, in Dubrovnik, Yugoslavia.

TABLE 1
Activation cross-sections and reactions for <sup>14</sup> C production in nuclear reactions (after Davis 1979)
Cross-section (barns)

Reaction	2200 m/s neutrons	LWR neutron spectrum	Fast reactor neutron spectrum
<sup>13</sup> C(n,γ) <sup>14</sup> C	0.9 x 10 <sup>-3</sup>	1 x 10 <sup>-3</sup>	0.5 x 10 <sup>-6</sup>
<sup>14</sup> N(n,p) <sup>14</sup> C	1.81	1.48	12.6 x 10 <sup>-3</sup>
<sup>15</sup> N(n,d) <sup>14</sup> C	0	0	1 x 10 <sup>-3</sup>
<sup>16</sup> O(n, <sup>3</sup> He) <sup>14</sup> C	0	0	0.03 x 10 <sup>-6</sup>
<sup>17</sup> O(n,α) <sup>14</sup> C	0.235	0.183	0.12 x 10 <sup>-3</sup>

After 1963, as fuel reprocessing grew, the line shows major departures from the atmospheric level with clear peaks in 1973 and 1976 and minima in 1968–1969, 1974 and 1978. We first thought that these features might show a direct relationship to the plants' operations. Figure 2 compares some recently estimated <sup>14</sup>C discharge values (based on operational data) with the tree ring values. The estimated discharges and the tree-ring values are plotted on different scales chosen to demonstrate their similarities to best advantage.



Fig 1. <sup>14</sup>C in tree rings from Knocking Wood sycamore, 1950–1980, compared with Northern Hemisphere levels



Fig 2. Comparison of the tree-ring <sup>14</sup>C levels and estimated discharges of <sup>14</sup>C to atmosphere, 1953–1977

Although some agreement is visible, there are also some striking discrepancies, particularly the 1968–1969 trough in the tree-ring curve, matched with a strong increase in estimated discharges throughout, rising to a peak in 1972, one year ahead of the tree- ring profile. It is important, however, to realize the limitations of such a comparison. A tree only assimilates carbon during the daylight hours of the growing season and, possibly of more relevance, at only one location. Later work, described below clearly demonstrates that the average growing season concentrations in some directions are subject to large variations year to year due to the predominant wind fraction direction of that season.

An interesting spinoff result relevant to the techniques commonly used for wood pretreatment is the difference observed between samples pretreated using the standard AAA method (30 min boiling in 3M HCl + 30 min boiling in 1M NaOH + wash in 3M HCl) and those for cellulose extraction in clear verification of Olsson's (1980) earlier observations. Table 2 shows 6 samples measured by both techniques. The comparison was made after levels higher than the global average emerged from measurements made by the AAA technique for pre-1952 samples, *ie*, before the plants started working. In all cases, cellulose extraction samples gave lower results than those treated by the AAA technique, on average 2-3% lower, except one which was 8% lower. The greater efficiency of the cellulose technique is clearly demonstrated.

More trees were sought to observe spatial variations in the measured <sup>14</sup>C activities both at a distance and around more points of the compass. As there were not many that could be felled in the area, cores (ca 12mm in diameter) were taken from living trees; these were then split into yearly sections (ca 100mg wood per ring) and measured using small sample (mini-gas counter) measuring techniques (Otlet, Walker & Longley 1983). We were able to obtain results from a transect southward along the coast from Sellafield to ca 17km at Bootle. We later realized that this choice of line was unfortunate since later dispersion studies showed levels along the coastal boundaries are much lower than along inland transects and considerably more susceptible to perturbations caused by the meteorology of specific years.

	0.0000000000		mone wood, and en	racted condito
Ring no.	Year	Gross activity Cellulose	(Bq/kg carbon) Whole wood	Difference (%)
4	1975	674.5	694.5	2.9
10	1969	434.0	471.7	8.0
15	1964	458.4	472.9	3.1
19	1960	291.9	299.3	2.4
24	1955	239.4	246.8	3.0
30	1949	221.6	226.1	2.0

TABLE 2Comparison of  $^{14}$ C results of AAA pretreated (whole wood) and extracted cellulose

Thus, Figure 3 shows a general consistency but not an exact image in the main features of the Knocking Wood profile. Two groups of results that agree quite well within themselves appear to emerge (Fig 3), one for the sets of Knocking Wood, the Windscale AGR and Lady Wood (vii, iv, vi) and another for the distant sites of the coastal transect, Ravenglass and Bootle (ii, i) with those of Seascale (v) and Drigg (iii) showing less agreement to either in the more recent years.



Fig 3. Tree-ring <sup>14</sup>C profiles from trees taken along the coastal transect

The suggested controlling factor of these groupings is the distance inland. Thus, the Lady Wood and Knocking Hill results, which are both approximately NE to E of the site, agree well with each other and with the few values obtained from the AGR tree. The AGR results, however, were noteworthy in that they do not appear to have the highest values of the series which, in view of their proximity to the Sellafield Works (the tree closest to the Works on which any measurements were made), might have been expected.

The less obvious, or in some cases, apparent lack of synchrony in the profiles, of the more distant sites is explained by the stronger effects of the sea breezes during the growing season at these coastal sites and highlights the point that this transect was not the best for dispersion study.

#### DISPERSION OF <sup>14</sup>C

Although the tree-ring technique yielded good averages over past years, the sparsity of trees in certain areas made it difficult to obtain data in a current year by year study over a wide area. Thus, we decided to choose a sampling material with guaranteed single-year growth, available over the widest possible area. Although grass and leaves, if sampled carefully would be candidates, a fruit was considered more reliable. Apple is known to accumulate  $CO_2$  from neighboring leaves but, since apple is not common in the area, we chose hawthorn, *Crataegus*, a member of the apple family, which is prolific here. It grows from June to September, accumulating carbon, as determined experimentally both in southern England and in Cumbria, approximately exponentially with a halving time of about three weeks. Carbon uptake is similar to buildup in southern England (Walker, Otlet & Longley 1986) but about one week later in starting (this is relevant to the modeling assumptions mentioned below).

Initial studies on hawthorn looked at the variation with distance in samples collected along five transects radiating from the site (Fig 4). Although good agreement was found between the southward coastal transect and the tree-ring results, marked differences were observed between inland and coastal transects and these differences are the subject of continuing studies.

At first we thought that the differences were due to funneling, *ie*, concentration of air masses along valley lines, which, for convenience, were chosen for the transects. This idea was dispelled in 1982 when a sequence of points taken along a 4km arc to look for fine structure showed no particular correlation with the topography. We looked for an alternative explanation in annual meteorology, bearing in mind that, on the coast, pronounced sea



Fig 4. Hawthorn berry sampling sites along 5 transects, October 1981

breezes tend to occur during the daylight  $CO_2$  uptake period. Thus, we must examine the directional wind frequency for the specific uptake period since this may be very different from the annual average. We have collected hawthorn berries from the same 4km arc and collection points over the last 6 years. The predicted distribution for each year was calculated from the meteorological data, using the NRPB dispersion model R-91 (Clarke 1979). We average the values deduced from the dispersion categories recorded at intervals during daylight and weight them according to the wind fraction of the sector and the relevant uptake rate of carbon from the carbon uptake curve. Figure 5 shows the results of the 6-yr analyses compared to the model predictions.

For years 1982, 1985, 1986, the predicted distribution generally agrees with the hawthorn results, although the positions of the predicted peaks are not precisely the same as those measured. Agreement is especially good in 1984, both curves showing a pronounced peak at 120° which can be explained by wind pattern. During the growing period there was a high frequency of winds blowing towards the 120° sector, *ie*, compared with the whole year, the growing period in 1984 had predominantly on-shore winds. Figure 6 illustrates the wind rose analysis.

In 1981 and 1983 (Fig 5), a quite large difference of ca 50° occurs between the measured and predicted peaks. The wind patterns for 1981 and 1983 were similar to 1984



Fig 5. Net <sup>14</sup>C in hawthorn berries at 4km compared with predicted angular distribution, 1981–1986



Fig 6. Frequency of wind blowing into different sectors, 1984

with predominantly on-shore winds blowing into the 120° sector and, although initially considered a possibility, the discrepancy cannot be explained by a difference in growing period for the hawthorns in these 2 years compared with the other 4. It is therefore clear that the experimental results cannot be explained in all cases simply in terms of wind fraction and dispersion category. A possible hypothesis is that of the particular topography creating variable plume curvature. In some directions, the land rises to 170m asl at 3.5km from Sellafield. Should this be causing plume curvature, the plume direction derived from the anemometer close to the source may not be adequate for predicting its position at 4km. (Plume curvature has been observed in SF<sub>6</sub> experiments carried out in similar wind conditions.) This year meteorological data are being collected at three points on the 4km arc as well as the Sellafield coast in the hope that a logical explanation for the discrepancies can be found.

We are also paying closer attention to on-site air-sampler measurements, operating one sampler during daylight hours in comparison with a second one operating full time. Other crops (leaf and root vegetables) are also being grown at one of the collection points to provide comparative uptake data.

# CONCLUSION

Radiologically, the impact of <sup>14</sup>C from the Sellafield operations to the local environment is not significant and its presence can be detected only because of the sophistication of the <sup>14</sup>C measurement techniques. In the assessment of collective dose, however, with the big reductions of the earlier main contributors, eg <sup>137</sup>Cs, Webb et al (1986) predicted that <sup>14</sup>C would become the dominant isotope of the inventory. Studies directed to understanding the dispersion of <sup>14</sup>C and pathways to foodstuffs are, thus, likely to be of increasing importance in validating these prediction.

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## OPERATION OF THE HARWELL UK <sup>14</sup>C DATA BASE AND ITS EXPANSION THROUGH DATA EXCHANGE WITH OTHER LABORATORIES<sup>1</sup>

# A J WALKER<sup>2</sup>, R L OTLET<sup>3</sup>, R A HOUSLEY<sup>4</sup> and JOHANNES VAN DER PLICHT<sup>3</sup>

ABSTRACT. The use of computer data bases for storage and retrieval of <sup>14</sup>C data is a logical application for the rapidly expanding numbers of <sup>14</sup>C determinations. Harwell has established a data base for all samples originating from sites in the United Kingdom and Eire. The core of the data is the Council for British Archaeology's published Index of Radiocarbon Dates which we are expanding to include all Harwell UK dates released for publication by the submitters plus dates from other laboratories both within and outside the UK. As a demonstration of the feasibility of direct database-to-database communication, cooperation has been sought from Groningen and Oxford to transfer computer files containing <sup>14</sup>C results for UK sites. Neither of these laboratories use the same system as Harwell for their in-house data base and this exercise highlights the importance of a transfer language for both the national and international schemes as it is no longer practical to carry out such procedures through keyboard typing.

#### INTRODUCTION

Over the last five or more years, there has been continuing discussion regarding the use of database systems for storage of <sup>14</sup>C results and a considerable amount of effort has been devoted to their design and structure (Gulliksen 1983; Moffett & Webb 1983a, b; Gupta & Polach 1985; Engelsman, Taayke & Mook 1986; Engelsman, Mook & Taayke 1987). The data bases serve three different purposes (Fig 1).

First is the specific laboratory data base. This has probably been in existence the longest time and is designed primarily to serve the local needs of the measuring laboratory. All administration of the samples submitted, ie, their scheduling, movement through the measurement process, construction of measurement reports and preparation of laboratory date lists for publication in RADIOCARBON, is masterminded from this data base. A number of laboratories have already established such data bases, eg, ANU, Groningen, Harwell and Oxford, and many others are in the process of so doing.

Second is the worldwide data base. This seeks to enter all <sup>14</sup>C results, regardless of the discipline for which they are measured, into one data base for the benefit of any researcher who needs to use <sup>14</sup>C. This is particularly exemplified by the International Radiocarbon Data Base (IRDB) being established by Renee Kra (in press; 1989), who intends it to receive data from all the <sup>14</sup>C measuring laboratories in the world. There may also be national data bases, as proposed by Wilcock (1986) for the UK and by PACT (Mook, 1986) for Europe.

The third is a type that sets geographical boundaries on the origin of the samples, not on the laboratory producing the results. The Harwell data base is set up in this way and is devoted to archaeological <sup>14</sup>C results from sites in the UK and Eire (Walker et al, in press). At the Stavanger Museum, Norway, a similar data base is being set up to store geological samples originating from Norway, Sweden and Denmark (Selsing & Simonsen 1986). The laboratory at Lyon, France is establishing a data base system for archaeological <sup>14</sup>C results and will be making these available to French archaeologists through their national telephone network information retrieval system (Mintel).

With so many data bases now being established, it is becoming increasingly important that there should be a means of communication among them and it is the purpose of this paper to report an example demonstration of such exchange using the HLF transfer format.

#### PRESENT STATUS OF DATA BASES

The philosophy behind the establishment of data bases, for whatever discipline, is to make more information more easily available to more people than is currently possible. The

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Fig 1. Three types of radiocarbon data bases

number of <sup>14</sup>C laboratories now using databases for their data storage is growing. As the dated samples continue to increase and PCs and inexpensive data management packages become more widely available, the number of different bases can be expected to increase dramatically in the next few years. If these data are ever to be made available for future research, a structured search route must be established, entailing 1) an overall, or central, data storage system to which a researcher can refer for results and further reference, and 2) a means of communication among data bases, which will allow data to be collected in comprehensive, logical units through direct transmission (*ie*, using a suitable computer-readable medium) in common transfer format.

The IRDB is intended to answer the first need and considerable progress has been made in its establishment over the last three years. At a workshop held at the 2nd Symposium on Archaeology and <sup>14</sup>C in Groningen in 1987, it was decided that the IRDB would not attempt to hold *all* relevant information for each determination but would act as an index in which a minimum amount of data would be held for each result (Walker & Kra 1988). Within each file entry would be a reference field which would act as a signpost, telling the user where the full details on the result could be found (Kra 1989). This signpost field may refer the searcher to another data base, a publication, eg, date list, an archaeological site report or scientific paper, or simply to the measuring laboratory. The advantage of this index-type system is that it takes less space and, therefore, costs less and also makes it more feasible to consider loading a significant number of the many <sup>14</sup>C results published over the last 40 years.

It is now widely recognized that, with the ever-increasing numbers of dates produced each year, an efficient system for data exchange and communication has become extremely important.

#### THE INTERNATIONAL EXCHANGE FORMAT

Practical Demonstration of Data Exchange. We have made a feasibility study of transfers of data from other sources. So far, data have been successfully transferred from the laboratory data bases of Oxford and Groningen, which all use different database management systems. At the time of transfer, Oxford used dBase III on an Amstrad PCW microcomputer (the data have now been transferred to a different system on a VAX); Groningen used their own custom-made database system on an Apple computer and Harwell used STATUS on an IBM PC compatible.

Oxford and Groningen supplied Harwell with a floppy disk containing the most basic of output files, in ASCII format. Oxford's data came on the Amstrad 3" formatted disks and Groningen's in IBM-compatible format. We then wrote the necessary translation programs to convert the data into our version (HLF) of the proposed exchange format. We developed a general conversion program which will be readily adaptable for other format translations.

Translation of Oxford Data. The Oxford data consists of a single line for each entry, each line containing 12 fields. There was no coding of the fields but they were arranged in a set order and consistency of field numbering is maintained by including every stated field even if it is blank. The strict ordering made the conversion to the HLF format fairly simple. Look-up tables were required 1) to relate a given field number with a keyword heading, 2) to pick out the heading using the number and 3) to collect only dates from the UK and Eire.

The translation of 300 entries from the submitted file of ca 800 entries took only 3.5 minutes on our AT-type PC. The result was a reorganized file (Fig 2), which contains the same data coded according to the HLF fields. This was then transferred to the local STATUS format (Fig 2).

Translation of Groningen Data. The data supplied by Groningen consisted only of entries for the UK and Eire, so no sorting on country was required, and was similar to the Oxford data in that each entry consisted of a constant number of fields given in a set order. The Groningen data consisted of many more fields and required more involved assembly of items to bring them together for the HLF fields (Fig 3). Part of the Groningen information is laboratory treatment for which no provision has been made in the exchange format, except, perhaps in Laboratory Comment.

We feel that translation from almost any format to the exchange HLF format should not pose insurmountable problems. Ideally, translation should be done by the sending laboratory but, in order to complete our UK data base, we are prepared to receive data in

589, 'Gough's New Cave', 'BM-2183', 'bone', 'horse (E.ferus)', 'uPal', 'England', 'Jacobi', 12340, ' 150', -20, 'AM3'

Transfer Format (HLF)

*LABCODE	OxA-589 OXFORD	
*SERIES	Gough's New Cave	
*SUBSAMREF	BM-2183	
*SAMMATERIAL	bone	
*IDAS	horse (E.ferus)	
*PERIOD	uPal	
*COUNTRY	England	
*SUBM	by Jacobi	
*AGEC	12340 +/- 150	
*DC13	-20	
*MACHINE	AMS	
*REFERENCE 0:	Gowlett et al, 1986a	
*LABCOMMENT	Assumed delta C-13	
		•

Local Harwell Format (STATUS)

```
SST
0xA-589
ŚŚT
$$N LABDAT <
#MACHINE=AMS,#DC13=-20,#AGE=12340,#AGETYPE=+/-,#ERRORP=150,#ERRORM=150, 
SSN SAMDAT <
#LABCODE=OxA, #LABNAME=OXFORD, #LABNUM=589, <
Gough's New Cave
SSN SAMMTL <
#SAMMATERIAL=bone, <</pre>
horse (E.ferus)
$$N SITELOC <
#COUNTRY=England, <
$$N PERIOD <
uPal
$$E PUBLICATIONS <
Gowlett, J A J, Hall, E T, Hedges, R E M and Perry, C, 1986, Radiocarbon dates
from the Oxford AMS system: Archaeometry datelist 3: Archaeometry 28, 1, p 116-125
SSN LABCOMMENT <
Assumed delta C-13
ŜŜĂ
```

#### A J Walker et al

7400  3801 Ossom's C	ave  R.M.Jacobi	D.Bramwell  //56
7/11/75 Manifold	Valley  Staffor	dshire  Great Britain
	bone	Palaeolithic
excavation	settlement	archaeology acid Longin
collagen	-19.13	27.08/#0.22
26.76 #0.22   1	0000 - 11000	10590 # 70
	Cresswell	818  Jesus College
Camb	ridge CB5 8BL	United Kingdom

*LABCODE *LABCODE *SITENAME *SUBM *COL *TOWN *REGION *COUNTRY *SAMMATERIAL *PERIOD *DISCIPLINE *LABCOMENT *DC13 *PERMOD *AGEC *SITETYPE *SUBMADDR 0: *SUBMADDR 1:	GrN-7400 GRONINGEN Ossom's Cave //56 by R.M.Jacobi 7/11/75 by D.Bramwell Manifold Valley Staffordshire Great Britain bone, collagen Palaeolithic archaeology acid Longin -19.13 27.08 +/- 0.22 10590 +/- 70 Cresswell Jesus College, Cambridge, CB5 8BL United Kingdom
*SUBMADDR 1: *MACHINE	United Kingdom GC

Fig 3. Groningen data transfer

any computer-readable form. We are even working on the possibility of translating wordprocessed text in *RADIOCARBON* publication style format. The British Museum has been kind enough to supply us with a floppy disk containing their last *RADIOCARBON* date list, which, because of its well-defined format, may be a viable transfer process.

## RELATIONSHIP OF THE EXCHANGE FORMAT TO THE INTERNATIONAL RADIOCARBON DATA BASE

Our HLF exchange format is fully compatible with that of the IRDB (Fig 4). The main difference is in the field concerned with the <sup>14</sup>C determination, to which six fields are allocated in the HLF, to cover all possible forms, whereas the IRDB has one. Other differences are in the geographical coordinates, where the HLF has one field but the IRDB two, and in the comments section where HLF has two fields, one for the submitter and one for the laboratory, but the IRDB has one. It is the suggestion of this laboratory that data being provided for the IRDB should be provided in the full HLF format and that the extraction into the form required by the IRDB package should be made at the destination point, *ie*, Arizona. Data superfluous to the IRDB need not be removed from the HLF files supplied for IRDB entry.

#### THE WAY AHEAD AND CONCLUSIONS

The successful transfer of the Groningen and Oxford data to the Harwell data base was useful because 1) the data base was easily enlarged without any manual entry, which is not only time-consuming and labor-intensive but can also be a source of introduced errors and 2) it demonstrated that the exchange format is extremely versatile and might with modifications lend itself to a universally acceptable exchange system. Data from the HLF can be transferred directly to the form required for the IRDB, thus making the task of submitters easier.

In conclusion, the Harwell data base has been set up as a collection of all archaeological dates from samples taken at UK and Irish sites, and, if it is to fulfill this objective, it must be expanded from its original core, namely the dates published in the CBA Index (Lavell 1971).

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Fig 4. Exchange format (HLF) and IRDB format

Expansion through data exchange has been proved possible by the Oxford and Groningen examples and further data are actively sought from those laboratories which hold in their system UK and Irish dates. The key position held in this expansion by the exchange format reinforces the need to encourage others to accept it as the core of a universally accepted format which can then be used in any exchange situation. Unless data bases have the means to transfer data and thus to assemble single data sets for the researcher they will be of only limited long-term value.

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#### THE USE OF RADIOCARBON MEASUREMENTS IN ATMOSPHERIC STUDIES<sup>1</sup>

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ABSTRACT. <sup>14</sup>C measured in trace gases in clean air helps to determine the sources of such gases, their long-range transport in the atmosphere, and their exchange with other carbon cycle reservoirs. In order to separate sources, transport and exchange, it is necessary to interpret measurements using models of these processes. We present atmospheric <sup>14</sup>CO<sub>2</sub> measurements made in New Zealand since 1954 and at various Pacific Ocean sites for shorter periods. We analyze these for latitudinal and seasonal variation, the latter being consistent with a seasonally varying exchange rate between the stratosphere and troposphere. The observed seasonal cycle does not agree with that predicted by a zonally averaged global circulation model. We discuss recent accelerator mass spectrometry measurements of atmospheric <sup>14</sup>CH<sub>4</sub> and the problems involved in determining the fossil fuel methane source. Current data imply a fossil carbon contribution of ca 25%, and the major sources of uncertainty in this number are the uncertainty in the nuclear power source of <sup>14</sup>CH<sub>4</sub>, and in the measured value for  $\delta^{14}$ C in atmospheric methane.

#### INTRODUCTION

Trace gases in the atmosphere play a crucial role in determining our environment. Greenhouse gases in the troposphere determine the earth's temperature through selective absorption of infra-red radiation. Ozone in the stratosphere filters out ultra-violet radiation that would destroy complex organic molecules essential for life. Because the amounts of these gases are small and the balance of processes maintaining them complex, they are a potentially fragile part of our environment.

Many of the trace gases that must be studied in relation to changes in climate and atmospheric chemistry contain carbon. For these gases, isotopic measurements are directly relevant in determining sources and sinks, because sources will have different isotopic composition and sinks will involve fractionation. The importance of carbon isotope measurements in building global budgets for gases such as  $CO_2$  (Keeling, Mook & Tans 1979; Peng *et al* 1983),  $CH_4$  (Ehhalt 1973) and CO (Stevens *et al* 1972) has been recognized for some time.

The atmospheric concentration of gases with lifetimes of the order of minutes or less is determined by local atmospheric chemistry and the presence or absence of light. For gases with lifetimes of many years, concentrations are relatively homogeneous due to atmospheric mixing. Between these extremes there are atmospheric species with intermediate lifetimes, the concentration of which depends on both atmospheric transport and the distribution of sources and sinks. To understand the varying concentrations of such species, we must combine quantitative information on advection and diffusion in the atmosphere with information on the spatial distribution of sources and sinks. This is a difficult task, but holds the prospect that we may determine a consistent picture of all the processes involved.

Each of the gases  $CO_2$ ,  $CH_4$  and CO is a candidate for study using a detailed physical and chemical model of the atmosphere. Extensive modeling of the annual cycle of  $CO_2$ concentrations (Trabalka 1985; Heimann & Keeling 1986) has shown that even though this gas has a lifetime in the atmosphere of many years, the latitudinal and seasonal variation of its concentration yields information on long-range atmospheric transport.

 $CH_4$  has a lifetime similar to that of  $CO_2$ , but is a complementary tracer of atmospheric transport because the distribution of its sinks is quite different. While the sinks for  $CO_2$  are all at the surface, the dominant sink of  $CH_4$  is through reaction with the OH radical distributed throughout the atmosphere. The OH radical is produced photolytically in the troposphere and its maximum diurnal concentration, and therefore the sink strength for  $CH_4$ , varies considerably with latitude, altitude and season (Logan *et al* 1981).

Reaction with the OH radical is also the major sink for CO (Volz, Ehhalt & Derwent 1981), so CO has a sink structure similar to  $CH_4$ . As the lifetime of CO ( $\approx 4$  months) is shorter than the time required to mix throughout the troposphere, this gas does not become

<sup>&</sup>lt;sup>1</sup> This paper was presented at the 13th International Radiocarbon Conference, June 20-25, 1988 in Dubrovnik, Yugoslavia.

fully dispersed from its sources. In regions where the mean transit time for CO arrival from a source is of the order of its lifetime, we can expect significant variation in concentrations as a result of transient changes in atmospheric transport.

The natural cosmogenic formation of <sup>14</sup>C in the stratosphere (Lal & Peters 1962) leads to both <sup>14</sup>CO and <sup>14</sup>CO<sub>2</sub>. As this <sup>14</sup>C production is greatest in the stratosphere, we expect a natural vertical gradient in atmospheric <sup>14</sup>C. Human intervention through nuclear weapons testing, which put <sup>14</sup>C in the stratosphere, and release of fossil carbon from the surface has enhanced this natural gradient. Relatively rapid mixing in the troposphere can be expected to dissipate this gradient at lower altitudes, but across the tropopause and in the stratosphere it will persist.

Thus,  ${}^{14}C$  is a useful tracer of transport in the atmosphere, and particularly of vertical transport. The longer-lived species such as  ${}^{14}CO_2$  and  ${}^{14}CH_4$  provide information on the longer time scales associated with stratosphere to troposphere and interhemispheric exchange, whereas  ${}^{14}CO$  can provide information on the shorter time-scale movements associated with transport within a hemisphere.

We show here that the seasonal component of a 32-yr atmospheric  ${}^{14}\text{CO}_2$  record can be used to infer stratospheric residence times for  $\text{CO}_2$ . Our data are compared with a two-dimensional model of atmospheric transport and discrepancies are shown which imply either deficiencies in present modeling of vertical transport, or the presence of complex sources and sinks of  ${}^{14}\text{C}$  or both. We also show how measurements of  ${}^{14}\text{CH}_4$  can identify the relative strengths of fossil and modern sources of methane, and can set limits on the production of this species from nuclear power plants.

#### MEASUREMENTS OF ATMOSPHERIC <sup>14</sup>CO<sub>2</sub> IN THE SOUTH PACIFIC

Measurements of <sup>14</sup>C in atmospheric  $CO_2$  at Wellington, New Zealand and at other South Pacific sites ranging from the Antarctic to the Equator, were initiated by T A Rafter and G J Fergusson in the early 1950s. Early results and procedures are reported elsewhere (Rafter 1955; Rafter & Fergusson 1959; Rafter & O'Brien 1970). Our data report the results of this program up to May 1987.

The sampling procedures used to obtain nearly all the data are described by Rafter and Fergusson (1959). Trays containing ca 2L of 5 normal NaOH carbonate-free solution are exposed for intervals of 1–2 weeks, and the atmospheric CO<sub>2</sub> absorbed during that time is recovered by acid evolution. Considerable fractionation occurs during absorption into the NaOH solution, and the standard fractionation correction (Stuiver & Polach 1977) is used to determine a  $\Delta^{14}$ C value corrected to  $\delta^{13}$ C =  $-25^{0}/_{00}$ .

A few early measurements were made by bubbling air through columns of NaOH for several hours. These samples can be readily identified in the data as their  $\delta^{13}$ C value is much higher (*ie*, closer to the ambient air value). Also, some samples reported here were taken using BaOH solution or with extended tray exposure times. These variations in procedures do not appear to affect the results.

Table 1 lists the Wellington data for the period, Dec 1954–May 1987, and data for shorter periods at six other sites. Dates refer to the mid-point of the sampling interval, and an asterisk denotes a sample for which contamination is known or suspected. Figures 1A, B show the data after discarding these suspect cases.

Low latitudinal gradients are to be expected in the South Pacific, as the sources of  $^{14}CO_2$  are far from the sampling sites and  $CO_2$  has a mean lifetime in the atmosphere which is long compared to the time required for tropospheric mixing. This is borne out by our data which show only small variations between sites. Quantifying these differences is made difficult by the noise level, which appears to exceed the error due to counting statistics, and by the sparsity of data from different sites for common times.

Table 2 summarizes the station differences relative to the Wellington station, using months where data are common to both. This suggests that <sup>14</sup>C levels in atmospheric  $CO_2$  were slightly higher in the Equatorial Pacific than at mid-southern latitudes, and were

 TABLE 1

 Radiocarbon measurements of South Pacific air

ĺ		$\delta^{13}C$	$\Delta^{14}C$	Lab	
	Date	‰	%0	number	Date
					7501
and the second se	Tara	va, Kirib	ati, 1.5° N, 173	3.0° E	75020
	660805	-21.6	645.7±3.6	NZ2448	75060
	661004	-20.9	636.6±3.8	NZ2449	75070
	661205	-21.2	649.3±3.8	NZ2452	75082
	670205	-21.5	611.6±3.9	NZ2466	75090
	670605	-20.9	612.7±3.8	NZ2482	7510
	670805	-19.5	600.2±3.8	NZ2481	75110
	670905	-19.3	605.6±3.9	NZ2498	75120
	671005	-19.5	597.8±3.8	NZ2485	76010
	671205	-19.4	594.8±3.8	NZ2484	76020
	680305	-19.3	576.1±3.8	NZ2506	76030
	680405	-20.5	574.8±3.8	NZ2507	76040
	680505	-20.1	567.2±3.8	NZ2508	7605
	680605	-20.2	574.0±3.8	NZ2509	7606
	680705	-22.8	594.6±6.0	NZ2723	7607
	680805	-21.9	557.5±3.5	NZ2721	7608
	680830	-20.7	$593.8 \pm 6.0$	NZ2722	7708
	680906	-22.6	542.2±3.9	NZ3474	
	680927	-21.1	553.4±3.9	NZ3479	F
	681025	-21.0	564.1±5.9	NZ2724	6608
	681205	-19.4	554.9±3.8	NZ2557	6610
	690105	-20.3	548.8±3.8	NZ2558	6612
	690305	-21.5	559.1±3.8	NZ2559	6702
	690505	-20.6	545.2±3.8	NZ2563	6705
	690705	-18.9	536.7±4.0	NZ2569	6706
	690905	-18.7	519.4±3.6	NZ2568	6708
	691105	-20.6	$529.6 \pm 3.9$	NZ2579	6710
	700105	-22.4	533.0±3.8	NZ2578	6712
	700305	-21.5	513.6±3.9	NZ2596	6712
	700505	-19.9	510.3±3.9	NZ2597	6803
	700706	-21.8	507.4±3.9	NZ2608	6804
	700905	-21.5	514.0±3.9	NZ2609	6805
	701105	-23.1	507.4±3.9	NZ2626	6806
	710105	-23.3	507.6±3.9	NZ2627	6808
	710306	-22.8	502.7±3.9	NZ2628	6808
	710507	-22.7	486.5±3.9	NZ2630	6809
	710704	-21.5	486.3±3.7	NZ2655	6809
	710904	-21.2	492.0±3.5	NZ2654	6812
	711104	-23.5	506.2±3.9	NZ2656	6901
	721006	-21.3	460.5±3.6	NZ4095	6903
	721104	-21.9	463.6±3.3	NZ4096	6905
	721204	-20.5	455.9±3.6	NZ4097	6907
	730104	-22.8	442.8±3.3	NZ4098	6909
	730205	-22.9	444.8±3.7	NZ2685	6911
	730405	-22.7	438.1±3.3	NZ2686	7001
	730504	-22.3	452.7±3.7	NZ2687	7003
	740804	-21.3	401.8±3.3	NZ4080	7005
	740904	-22.5	405.4±3.7	NZ4081	7007
	741109	-21.5	394.2±3.6	NZ4099	7010
	741204	-21.8	393.9±3.6	NZ4100	7012

ļ		$\delta^{13} C$	$\Delta^{14}C$	Lab
	Date	%0	%0	number
	750105	-21.3	391.3±3.5	NZ4101
	750204	-18.6	376.4±3.3	NZ4102
	750605	-22.4	415.5±3.7	NZ4079
	750707	-20.8	401.3±3.3	NZ3829
	750826	-22.3	390.6±3.3	NZ4141
	750904	-23.2	$358.9 \pm 3.2$	NZ4142
	751014	-22.8	363.4±3.3	NZ4299
	751104	-23.1	$366.6 \pm 3.3$	NZ4300
	751204	-22.7	360.4±3.3	NZ5646
	760104	-22.6	371.7±3.3	NZ5647
	760204	-22.3	354.9±3.3	NZ5648
	760304	-22.2	353.4±3.3	NZ5649
	760404	-21.2	357.4±3.3	NZ5650
	760504	-21.7	$348.6 \pm 3.7$	NZ5651
	760612	-20.6	357.8±5.3	NZ5692
	760706	-20.6	353.3±3.3	NZ5693
	760813	-21.6	$352.0\pm3.7$	NZ5694
	770812	-16.9	348.4±3.3	NZ5695
	-	<del>.</del>		
	Funa	tuti, Tuva	alu, 8.5° S, 17	9.2°E
	660805	-21.6	$650.8 \pm 3.8$	NZ2446
	661005	-21.8	$638.5 \pm 3.8$	NZ2447
	661204	-21.9	$619.9 \pm 3.8$	NZ2450
	670205	-22.3	636.6±3.8	NZ2465
	670505	-20.5	$609.9 \pm 3.8$	NZ24/4
	670605	-21.1	$612.8 \pm 3.9$	NZ2475
	670805	-19.8	$596.9 \pm 4.5$	NZ2476
	6/1005	-20.7	$598.9 \pm 3.8$	NZ2483
	671205	-21.8	$582.7 \pm 4.5$	NZ2486
	6/1205	-21.8	$586.2\pm4.5$	NZ2489
	680305	-20.2	563.6±3.8	NZ2510
	680405	-21.0	$596.6 \pm 3.9$	NZ2511
	600505	-21.7	$501.1\pm3.0$	NZ2012
	680602	-19.5	$551.4 \pm 3.8$	NZ2013
	000004	-20.7	$549.0 \pm 3.9$	NZ2525
	680830	-22.3	$556.4 \pm 3.9$	NZ2520
	600900	-10.3	$544.0\pm4.0$	NZ2327
	691005	-21.1	570.2±3.1	NZ2725
	6001205	-21.0	$553.7 \pm 3.0$	NZ2000
	600205	-10.7	552.0 <u>+</u> 3.0	NZ2557
	600505	-20.7	$532.0\pm3.0$	NZ2554
	690505	-21.4	$535.9\pm3.9$	NZ2501
	600005	-20.0	$529.1\pm 3.9$ 518.6 $\pm 3.0$	NZ2505
	601105	-21.2	517 4 ± 2 0	N72575
	700105	-21.1	$5135 \pm 30$	N72577
	700304	-20.6	$527.0 \pm 3.9$	N72580
	700505	-20.0	523 5+3 0	N72594
	700705	-21.2	5045+30	N72595
	701005	-22.3	$516.8 \pm 3.9$	NZ2615
	701205	-21.9	517.1±3.9	NZ2616

TABLE 1 (continued)

	$\delta^{13}$ C	$\Lambda^{14}$ C	Lah	1		s130	A 14 C	l ch l
Date	%	<u>~</u>	number		Date	<i>%</i>		number
710205	-22.2	502.6+3.9	NZ2632		650813	-22.3	640 1+3.8	NZ2047
710305	-24.2	504.3±3.5	NZ2633		650924	-22.9	$654.6 \pm 3.9$	NZ2036
710505	-22.4	$512.8 \pm 4.0$	NZ2634		651105	-23.9	6532+38	NZ2041
710705	-22.7	$498.7 \pm 3.6$	NZ2637		660106	-22.0	$666.5 \pm 3.8$	NZ2039
710905	-23.0	496.2±3.9	NZ2648		660204	-23.4	$644.9 \pm 3.8$	N72042
711105	-22.5	487.4±3.5	NZ2649		660305	-21.8	$635.4 \pm 3.8$	NZ2040
720106	-22.2	$490.0 \pm 3.6$	NZ2674		660605	-23.2	$649.0 \pm 3.6$	NZ2044
720305	-20.8	487.9±3.6	NZ2083		660705	-23.3	$6225 \pm 38$	N72048
					660805	-24.3	626.4 + 3.9	NZ2043
Su	ıva, Fiji,	18.1°S, 178.4	۴°E		660905	-23.0	625.8±3.8	NZ2049
580402	-9.0	74.5±3.8	NZ2000		661205	-21.4	$636.3 \pm 3.8$	NZ2046
580407	-25.0	68.4±3.8	NZ2001		670220	-20.7	616.5+3.8	NZ2050
580510	-9.0	71.4±3.3	NZ2002		670714	-22.4	593.1+3.8	NZ2051
580510	-25.0	69.0±4.7	NZ2003		670804	-22.4	587.2+3.9	NZ2052
581104	-25.0	117.1±4.6	NZ2005		671006	-21.9	584.9+3.9	NZ2054
590228	-23.6	124.1±4.6	NZ2007		671205	-21.1	567.9 + 3.7	NZ2053
590703	-24.5	151.3±4.1	NZ2004		680205	-20.8	573.6+3.8	NZ2055
590922	-22.3	180.4±4.5	NZ2006		680415	-20.3	$5673 \pm 38$	NZ2056
600122	-22.1	$189.8 \pm 4.5$	NZ2009		680604	-19.6	$5537 \pm 39$	NZ2057
600414	-21.1	$185.1 \pm 4.5$	NZ2008		680805	-21.5	$549.3 \pm 3.6$	NZ2058
600902	-22.7	197.0+4.5	NZ2010		680906	-21 9	$545.4 \pm 3.6$	NZ2059
600929	-24.6	202.3+4.5	NZ2012		681005	-20.0	$549.4\pm5.0$	NZ2003
610120	-23.7	$196.5 \pm 4.5$	NZ2011		681105	-20.0	556 5±3 0	NZ2095
610301	-21.2	$196.8 \pm 4.2$	NZ2034		681205	-21.7	$530.3\pm 3.9$	NZ2061
610414	-22.9	$192.9 \pm 5.0$	B00945		690105	-20.7	$500.4 \pm 3.0$	NZ2001
610708	-22.1	$196.5 \pm 5.0$	NZ2013		690307	-20.7	$5460\pm38$	NZ2002
610818	-23.1	207.2+4.2	NZ2033		690505	-18.6	531 5±3 6	NZ2003
610929	-23.7	$180.8 \pm 5.0$	NZ2015		690706	-20.2	533 8±3 6	NZ2065
611110	-23.5	183.5+6.8	R00997		690905	-20.2	$505.0\pm 3.0$ 5/1 0±2 0	NZ2005
611219	-24.7	$198.2 \pm 4.9$	N72014		601107	-22.1	$541.9\pm 3.9$ 531.0 $\pm 3.0$	NZ2000
620119	-21.7	214.4+4.2	NZ2032		700109	-21.8	501.0 <u>+</u> 3.9	NZ2068
620301	-23.2	208.3+5.0	NZ2016		700306	-22.1	$525.8\pm3.9$	NZ2060
620301	-23.2	233.0 + 9.4	NZ2092		700509	-21.6	526.0±3.0	NZ2009
620412	-21.8	223.5+5.3	NZ2021		700705	-21.6	$51/3 \pm 30$	NZ2070
620412	-21.8	234.4 + 4.3	NZ2020		700905	-27.0	$5045\pm30$	NZ2073
620706	-26.5	238.9 + 5.9	NZ2091		701106	-22.3	$504.0 \pm 0.0$	NZ2072
620927	-24.5	259.3+3.9	NZ2019		710108	-21.6	$5121 \pm 39$	N72074
630117	-19.8	289.0 + 4.8	NZ2017		710305	-20.6	498 6+3 9	NZ2074
630705	-21.7	380.5+4.1	NZ2022		710509	-22.0	$492.3 \pm 3.9$	NZ2075
630917	-22.7	417.6+4.1	NZ2038		710710	-22 5	$432.0\pm0.3$ $486.9\pm4.0$	NZ2077
630927	-26.8	413.5±4.1	NZ2037		710905	-23.2	4946+36	NZ2078
631220	-21.6	497.0±3.4	NZ2024		711105	-21.5	$4984 \pm 39$	NZ2079
640116	-21.9	490.7±4.0	NZ2025		711205	-21.1	$4914 \pm 36$	NZ2087
640409	-21.9	545.6±3.5	NZ2026		720106	-21.4	488.6+3.3	NZ2088
640522	-23.2	548.7±3.5	NZ2027		720305	-28.8	501.5+3.6	NZ2080
640702	-26.1	580.4±4.0	NZ2028		720505	-21.1	474.3+3.6	NZ2081
640925	-22.6	630.1±3.9	NZ2029		720704	-24.5	496.5+6.7	NZ2094
641217	-22.7	644.4±3.7	NZ2030		720705	-24.6	473.9+3.3	NZ2082
650115	-19.6	654.5±3.8	NZ2045		720805	-20.2	473.4+5.1	NZ2096
650408	-20.2	643.0±3.9	NZ2031		721005	-24.1	468.8±3.3	NZ2084
650701	-22.9	647.8±3.9	NZ2035		730108	-18.4	$458.4 \pm 4.6$	NZ2095
			1	1				1

TABLE 1 (continued)

	$\delta^{13}$ C	$\Delta^{14}$ C	Lab			$\delta^{13}C$	$\Delta^{14}$ C	Lab
Date	%0	%0	number		Date	‰	<i>‰</i>	number
730205	-21.1	451.3±3.7	NZ2085		660905	-28.0	631.6±3.8	NZ2456
730406	-20.4	444.6±3.3	NZ2086		661005	-23.1	614.3±3.8	NZ2455
730605	-23.0	433.6±3.3	NZ2090		661205	-20.5	602.8±3.8	NZ2457
730805	-23.9	$456.2 \pm 3.7$	NZ2089		670205	-16.1	592.4±3.8	NZ2470
731005	-23.9	423,1+3,3	NZ4053		670606	-20.3	501.3±4.5	NZ2473
731126	-22.5	430.7±7.4	NZ3816		670705	-19.5	516.3±3.9	NZ2497
731207	-21.3	456.5+3.3	NZ4054		670805	-20.8	535.3±3.6	NZ2472
740106	-20.9	427.3+3.7	NZ4055		670905	-21.5	575.3±3.9	NZ2496
740319	-22.4	$409.8 \pm 3.7$	NZ4059		680205	-20.2	561.1±3.9	NZ2500
740405	-21.6	415.2+3.7	NZ4060		680405	-19.4	562.3±3.9	NZ2501
740505	-21.4	$416.1 \pm 4.4$	NZ3847		680605	-21.0	529.1±3.9	NZ2517
740607	-21.4	403.8 + 3.7	NZ4061		680704	-22.5	517.8±3.9	NZ3468
750307	-21.6	392.6+3.3	NZ4103		680804	-20.3	503.5±3.9	NZ2519
750404	-21.8	3841+33	NZ4104		680828	-20.2	533.1±3.9	NZ2518
750504	-19.7	379.0 + 3.3	NZ4105		680905	-25.0	531.7±3.9	NZ2533
750608	-22.0	3893+37	NZ4106		680926	-21.7	509.7+3.9	NZ2534
/30000	22.0	000.010.0	1121100		681003	-19.8	515.9 + 3.9	NZ3495
Melhou		tralia 37.8° S	144 9° F		681031	-22.8	521.8 + 3.9	NZ3480
581104	-23.6	76 5+4 0	N72311		681107	-22.3	535.0+3.9	NZ3482
500220	-24.6	$103.3 \pm 3.8$	NZ2312		681205	-19.7	512.7+3.9	NZ2532
500703	-24.0	$100.0\pm0.0$	N72318		690105	-19.5	534.8+3.8	NZ2555
500026	-25.1	$1366 \pm 45$	NZ2319		690305	-19.3	532.6+3.9	NZ2556
600122	-20.2	$161.5 \pm 4.5$	NZ2330		690505	-19.7	496.6+3.9	NZ2562
600/15	-22.7	$1821 \pm 4.5$	N72331		690705	-20.6	$496.3 \pm 3.4$	NZ2581
600709	-21.4	155 1 1 4 6	NZ2335		690906	-20.6	$488.3 \pm 3.9$	NZ2586
600030	-23.0	$173.0 \pm 4.5$	NZ2337		691104	-19.0	507.0+3.9	NZ2588
601112	-21.0	$170.0 \pm 4.5$ 181 7 $\pm 4.5$	N72342		700105	-18.0	515.8+3.9	NZ2587
610120	-20.0	$188.8 \pm 4.5$	N72343		700305	-19.4	509.0 + 3.9	NZ2620
610020	-22.5	$183.2 \pm 4.0$	NZ2357		700505	-20.0	486.7+3.9	NZ2621
611210	-20.7	$185.2 \pm 4.0$	NZ2358		700701	-20.3	475.6+3.9	NZ2622
620/13	-13.0	$103.2 \pm 4.0$ 198.6 \pm 4.0	NZ2359		700905	-19.7	486.5+3.9	NZ3547
620928	-22.5	$221.8 \pm 5.2$	NZ3580		701104	-20.3	480.3±3.5	NZ3548
620320	-18.2	$240.9\pm4.1$	NZ2366		710105	-19.2	484.6+3.9	NZ2625
630705	-21.0	$2823 \pm 39$	N72388		710604	-17.9	433.1+3.9	NZ2650
630026	-21.0	$3489 \pm 38$	NZ2385		710804	-18.8	463.6+3.5	NZ2651
621210	_10 /	$4115 \pm 38$	NZ2386		711004	-19.6	462.3+3.9	NZ2652
640116	216	411.0 10.0	NZ2387		711204	-18.4	$470.5 \pm 3.5$	NZ2653
640110	-21.0	430.0±3.0	N72397		720604	-18.8	$398.1 \pm 6.7$	NZ2733
640410	-19.7	400.0±4.0	NZ22007		120001	10.0		
640702	-20.3	512.0±4.0	NZ2390		Wellingt	n Now	Zealand 41.3°	S 174.8°F
640925	-20.2	500.3±3.9	NZ2400		541215	-94	-17 7+7 6	NZ2100
041210	-20.5	5/4.4±3.9	NZ2399		550222	-9.4	-101+77	NZ2099
650115	-20.6	609.3±3.0	NZ2439		550/14	-9.4	$-1.4 \pm 7.6$	NZ2098
650409	-20.1	500.0±3.9	NZ2422		550510	-24 9	$-10.3 \pm 7.8$	NZ2097
050520	-19.0	009.0±0.0	N70400		550615	0 A	-41+59	NZ2102
051001	-20.9	012.0±3.0	NZ2423		550013	9.9	-119+40	NZ2103
651105	-20.9	$520.7 \pm 3.8$	NZ2430		551215	-0.0	0.1+5.4	NZ2104
051205	-20.1	510.9±3.9	NZ2401		560210	-9.9	56+39	NZ2105
660107	-20.2	010.2±3.8	NZ2424		560615	-25.0	$37.9 \pm 4.8$	NZ2107
660305	-21.1	614.0±3.8	NZ2438		560025	-25.0	$10.1 \pm 4.8$	NZ2108
660505	-22.8	614.9±3.8	NZ2437		561021	0.0 0 ∩	$13.6 \pm 4.7$	NZ2110
660605	-20.5	507.3±3.9	INZ2440	I	1 301021	-9.0	10.014.7	,,,,0

TABLE 1 (continued)

$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$		$\delta^{13}$ C	$\Delta^{14}$ C	Lab		1	$\delta^{13}{ m C}$	$\Delta^{14}$ C	Lab
661022 $9.2$ $18.1\pm4.7$ $N.22109$ $63011$ $-25.9$ $225.5\pm3.9$ $N.22154$ 570127 $-9.0$ $18.3\pm3.7$ $N.22112$ $630301$ $-23.6$ $269.7\pm3.9$ $N.22154$ 570428 $-10.6$ $39.0\pm4.7$ $N.22112$ $630301$ $-23.6$ $268.4\pm3.8$ $N.22165$ 570428 $-9.8$ $41.5\pm4.7$ $N.22114$ $630414$ $-23.5$ $280.9\pm3.8$ $N.22165$ 570522 $-24.8$ $16.6\pm4.8$ $N.22115$ $630562$ $-24.7$ $331.1\pm4.1$ $N.22163$ 570723 $-9.4$ $44.9\pm3.9$ $N.22120$ $630706$ $-24.7$ $331.1\pm4.1$ $N.22165$ 570727 $-9.6$ $43.4\pm3.9$ $N.22122$ $631100$ $-24.7$ $355.6\pm4.3$ $N.22165$ 571106 $-9.7$ $51.6\pm4.7$ $N.22122$ $641017$ $-23.1$ $445.7\pm3.8$ $N.22165$ 571106 $-9.7$ $51.6\pm4.7$ $N.22126$ $641031$ $-23.7$ $405.9\pm3.8$ $N.22166$ 580318 $-10.1$ $76.2\pm4.0$ $N.22126$ $640051$ $-24.6$ $67.4\pm0.0$ $N.22168$ 580318 $-10.1$ $76.2\pm4.0$ $N.22126$ $6400703$ $-24.7$ $542.4\pm3.7$ $N.22177$ 580282 $-25.0$ $77.8\pm3.8$ $N.22127$ $640733$ $-24.6$ $67.4\pm0.0$ $N.22175$ 590302 $-25.0$ $12.0\pm4.6$ $N.22130$ $641016$ $-24.6$ $67.4\pm0.0$ $N.22175$ 590411 $-25.1$ $13.2\pm4.8$ $N.22133$ $65027$ $-23.6$ $633.6\pm3.9$	Date	‰	‰	number		Date	‰	%0	number
	561022	-9.2	18.1±4.7	NZ2109	1	630118	-25.9	265.5+3.9	NZ2154
	570127	-9.0	18.3±3.7	NZ2111		630301	-23.6	269.7 + 3.9	NZ2156
	570127	-10.1	24.9±3.7	NZ2112		630301	-23.6	266.4+3.8	NZ2159
570428       -9.8       41.5±4.7       NZ2114       630414       -23.5       284.3±3.9       NZ2157         570522       -24.8       16.6±4.8       NZ2115       630526       -24.2       312.2±4.1       NZ2167         570723       -9.6       43.4±3.9       NZ2120       630706       -24.7       356.4±3       NZ2164         570007       -24.7       356.4±3       NZ2164       63029       -23.7       405.2±3.8       NZ2166         571106       -9.7       51.6±4.7       NZ2122       631110       -24.7       374.8±4.1       NZ2167         580318       -9.4       67.5±4.0       NZ2123       640117       -23.7       405.2±3.8       NZ2167         580028       -25.0       77.8±3.8       NZ2129       640301       -22.8       472.5±4.0       NZ2173         580029       -24.8       93.9±3.5       NZ2172       640703       -24.7       524.4±3.7       NZ2173         590021       -25.0       171.1±3.8       NZ2133       641103       -24.5       507.4±0.7       NZ2175         590032       -25.0       10.1±3.8       NZ2133       650115       -22.0       694.5±3.9       NZ2175         590031       -25.9 <td< td=""><td>570428</td><td>-10.6</td><td>39.0±4.7</td><td>NZ2113</td><td></td><td>630414</td><td>-23.5</td><td>280.9 + 3.8</td><td>NZ2160</td></td<>	570428	-10.6	39.0±4.7	NZ2113		630414	-23.5	280.9 + 3.8	NZ2160
	570428	-9.8	41.5±4.7	NZ2114		630414	-23.5	284.3 + 3.9	NZ2157
570723       -9.4       44.9±3.9       NZ2120       630706       -24.7       331.1±4.1       NZ2161         570723       -9.6       43.4±3.9       NZ2118       630706       -24.7       335.6±4.3       NZ2164         570027       -24.8       51.4±4.0       NZ2116       63029       -23.7       405.2±3.8       NZ2165         571126       -8.8       62.0±4.6       NZ2123       640117       -23.7       445.7±3.8       NZ2167         580318       -9.4       67.5±4.0       NZ2125       640301       -23.7       542.±4.0       NZ2167         580282       -25.0       77.8±3.8       NZ2129       640703       -24.7       542.±4.0       NZ2170         580282       -25.0       77.8±3.8       NZ2123       641003       -24.5       507.±4.0       NZ2173         581009       -24.6       116.9±4.6       NZ2130       641003       -24.5       507.±4.0       NZ2173         590101       -25.0       121.±3.8       NZ2132       64127       19.9       615.7±3.9       NZ2175         590202       -25.0       126.±4.6       NZ2133       650115       -22.0       689.±7.5       NZ2175         590213       -25.1       128	570522	-24.8	16.6±4.8	NZ2115		630526	-24.2	313.2+4.1	NZ2163
570723       -9.6       43.4±3.9       NZ2118       630817       -24.7       355.6±4.3       NZ2162         570827       -24.8       51.4±4.0       NZ2112       631110       -24.7       355.6±4.3       NZ2162         571106       -9.7       51.6±4.7       NZ2122       631110       -24.7       374.8±4.1       NZ2165         571126       -8.8       62.0±4.6       NZ2122       640117       -23.1       445.7±3.8       NZ2166         580318       -9.4       67.5±4.0       NZ2125       640411       -23.7       503.4±.0       NZ2170         580284       -25.0       77.8±3.8       NZ2127       640703       -24.7       542.4±3.7       NZ2177         580282       -25.0       77.8±3.8       NZ2129       640615       -24.6       567.4±4.0       NZ2172         581009       -24.6       116.9±4.6       NZ2130       641106       -24.7       52.9±30       NZ2172         590302       -25.0       121.1±3.8       NZ2133       650115       -22.0       683.6±3.9       NZ2172         590601       -25.9       132.8±3.8       NZ2135       650227       23.6       633.6±3.9       NZ2175         590601       -25.1       <	570723	-9.4	44.9±3.9	NZ2120		630706	-24.7	$331.1 \pm 4.1$	NZ2161
$570227$ $24.8$ $51.4\pm4.0$ NZ2116 $630292$ $22.7$ $405.2\pm3.8$ NZ2165 $571106$ $9.7$ $51.6\pm4.7$ NZ2122 $631110$ $22.7$ $749.5\pm3.8$ NZ2165 $571126$ $9.7$ $51.6\pm4.7$ NZ2123 $640117$ $22.7$ $749.5\pm3.8$ NZ2165 $580318$ $9.4$ $67.5\pm4.0$ NZ2125 $640117$ $22.8$ $472.5\pm4.0$ NZ2126 $580704$ $25.0$ $81.1\pm3.8$ NZ2125 $640411$ $22.8$ $472.5\pm4.0$ NZ2126 $580724$ $25.0$ $81.1\pm3.8$ NZ2129 $640703$ $24.7$ $542.4\pm3.7$ NZ2177 $580282$ $25.0$ $77.8\pm3.8$ NZ2129 $640703$ $24.7$ $542.4\pm3.7$ NZ2177 $581203$ $25.0$ $110.1\pm3.8$ NZ2130 $641003$ $25.4$ $507.0\pm3.9$ NZ2172 $590202$ $22.0$ $126.0\pm4.6$ NZ2132 $66115$ $22.0$ $694.47.5$ NZ2177 $590203$ $25.0$ $12.1\pm3.8$ NZ2136 $650227$ $23.6$ $633.6\pm3.9$ NZ2176 $590611$ $25.2$ $132.8\pm3.8$ NZ2136 $650621$ $21.4$ $615.2\pm3.8$ NZ2177 $590130$ $25.0$ $12.1\pm4.5$ NZ2137 $650702$ $25.7$ $694.5\pm3.9$ NZ2178 $590111$ $26.1$ $17.4\pm4.5$ NZ2138 $650613$ $23.9$ $614.1\pm3.9$ NZ2176 $590131$ $25.0$ $18.4\pm5.5$ NZ2143 $650227$ $23.6$ $633.6\pm3.9$ NZ2176 $590131$ $25.0$ $17.4\pm5.5$ <	570723	-9.6	43.4±3.9	NZ2118		630817	-24.7	$355.6 \pm 4.3$	N72162
	570827	-24.8	51.4±4.0	NZ2116		630929	-23.7	$405.2 \pm 3.8$	NZ2164
	571009	-12.5	46.3±5.1	NZ2122		631110	-24.7	$374.8 \pm 4.1$	NZ2165
	571106	-9.7	51.6±4.7	NZ2124		631220	-24.7	429.5+3.8	NZ2166
580318 $-9.4$ $67.5\pm4.0$ NZ2126 $640301$ $-22.8$ $472.5\pm4.0$ NZ2188580318 $-10.1$ $76.2\pm4.0$ NZ2125 $640411$ $-23.7$ $50.3\pm4.0$ NZ2170580828 $-25.0$ $81.1\pm3.8$ NZ2127 $640703$ $-24.7$ $542.4\pm3.7$ NZ2171580829 $-24.8$ $93.9\pm3.5$ NZ2129 $640703$ $-24.7$ $542.4\pm3.7$ NZ2171581009 $-24.6$ $116.9\pm4.6$ NZ2130 $641003$ $-24.7$ $542.4\pm3.7$ NZ2172581022 $-25.0$ $110.1\pm3.8$ NZ2131 $641103$ $-24.7$ $621.9\pm3.9$ NZ2174590117 $-25.0$ $126.0\pm4.6$ NZ2133 $65027$ $-23.6$ $633.6\pm3.9$ NZ2175590302 $-25.0$ $126.0\pm4.6$ NZ2137 $65027$ $-23.6$ $633.6\pm3.9$ NZ2176590611 $-25.0$ $12.5\pm3.8$ NZ2137 $650702$ $-25.7$ $694.5\pm3.9$ NZ2178590713 $-25.0$ $15.1\pm3.8$ NZ2137 $650702$ $-25.7$ $694.5\pm3.9$ NZ2180590101 $-26.4$ $164.6\pm4.5$ NZ2138 $650813$ $-23.9$ $634.1\pm3.9$ NZ2180591219 $-25.0$ $17.4\pm4.5$ NZ2140 $651126$ $-24.9$ $634.2\pm3.9$ NZ2180600121 $-25.2$ $18.8\pm4.5$ NZ2141 $651224$ $-24.9$ $634.2\pm3.9$ NZ2183600141 $-23.4$ $193.7\pm4.5$ NZ2143 $660206$ $-23.6$ $643.5\pm3.9$ NZ2186600292 $-25.2$ $195.9\pm4$	571126	-8.8	62.0±4.6	NZ2123		640117	-23.1	445.7+3.8	NZ2167
580318-10.176.2 $\pm$ 4.0NZ2125640411-23.7500.3 $\pm$ 4.0NZ2169580704-25.081.1 $\pm$ 3.8NZ2127640703-24.7542.4 $\pm$ 3.7NZ2171580282-25.077.8 $\pm$ 3.8NZ2127640703-24.6567.4 $\pm$ 4.0NZ2173581029-24.893.9 $\pm$ 3.5NZ21296410103-25.6567.4 $\pm$ 4.0NZ2173581203-25.0110.1 $\pm$ 3.8NZ2131641106-24.7621.9 $\pm$ 3.9NZ2175590302-25.0126.0 $\pm$ 4.6NZ2133650115-22.0693.4 $\pm$ 7.5NZ2175590311-25.1137.2 $\pm$ 3.8NZ2136650267-23.6633.6 $\pm$ 3.9NZ2176590713-25.0128.8 $\pm$ 3.8NZ2136650521-21.4615.2 $\pm$ 3.8NZ2177590813-25.0141.8 $\pm$ 4.5NZ2137650702-25.7644.2 $\pm$ 3.8NZ2179591101-26.4164.6 $\pm$ 4.5NZ2138650213-21.4615.2 $\pm$ 3.8NZ2179591119-24.5171.4 $\pm$ 4.5NZ214165122-24.6647.3 $\pm$ 3.9NZ2183600214-22.5195.9 $\pm$ 4.5NZ2142660204-24.6647.3 $\pm$ 3.9NZ2183600114-23.4187.9 $\pm$ 4.5NZ2145660204-24.6647.3 $\pm$ 3.9NZ2184600212-24.5195.9 $\pm$ 4.5NZ2145660204-24.6647.3 $\pm$ 3.9NZ218360113-26.4198.9 $\pm$ 4.5NZ2145660204-24.6647.3 $\pm$ 3.9NZ2	580318	-9.4	67.5±4.0	NZ2126		640301	-22.8	$472.5 \pm 4.0$	NZ2168
580704         -25.0         81.1±3.8         NZ2128         640523         -25.9         498.3±3.9         NZ2170           580828         -26.0         77.8±3.8         NZ2127         640703         -24.7         542.4±3.7         NZ2173           581009         -24.6         116.9±4.6         NZ2130         641103         -24.6         567.4±4.0         NZ2172           581223         -25.0         110.1±3.8         NZ2131         641106         -24.7         621.9±3.9         NZ2172           590302         -25.0         126.0±4.6         NZ2133         650115         -22.0         689.4±7.5         NZ2271           590411         -25.1         137.2±3.8         NZ2133         650227         -23.6         633.6±3.9         NZ2176           590713         -25.2         150.1±3.8         NZ2137         650702         -25.7         694.5±3.9         NZ2178           590713         -25.0         181.7±4.5         NZ2137         650702         -25.7         694.5±3.9         NZ2180           591119         -24.5         171.4±4.5         NZ2138         650813         -23.9         631.4±3.9         NZ2182           600121         -25.0         181.7±4.5         NZ2142	580318	-10.1	76.2±4.0	NZ2125		640411	-23.7	$500.3 \pm 4.0$	NZ2169
$580828$ $-25.0$ $77.8 \pm 3.8$ $NZ2127$ $640703$ $-24.7$ $542.4 \pm 3.7$ $NZ2171$ $581009$ $-24.6$ $116.9 \pm 4.6$ $NZ2130$ $641003$ $-24.7$ $521.4 \pm 3.0$ $NZ2172$ $581223$ $-25.0$ $110.1 \pm 3.8$ $NZ2131$ $6411003$ $-24.7$ $521.9 \pm 3.9$ $NZ2174$ $590117$ $-25.0$ $121.1 \pm 3.8$ $NZ2131$ $641103$ $-24.7$ $621.9 \pm 3.9$ $NZ2174$ $590302$ $-25.0$ $126.0 \pm 4.6$ $NZ2133$ $650115$ $-22.0$ $689.4 \pm 7.5$ $NZ2175$ $590301$ $-25.9$ $132.8 \pm 3.8$ $NZ2134$ $650227$ $23.6$ $633.6 \pm 3.9$ $NZ2178$ $590713$ $-25.2$ $150.1 \pm 3.8$ $NZ2137$ $650702$ $-25.7$ $694.5 \pm 3.9$ $NZ2179$ $591001$ $-26.4$ $146.4 \pm 4.5$ $NZ2137$ $650702$ $-25.7$ $694.5 \pm 3.9$ $NZ2179$ $591119$ $-24.5$ $171.4 \pm 5.5$ $NZ2143$ $650241$ $-23.9$ $634.1 \pm 3.9$ $NZ2179$ $591119$ $-24.5$ $171.4 \pm 5.5$ $NZ2143$ $650242$ $-22.6$ $634.2 \pm 4.0$ $NZ2183$ $600141$ $-23.4$ $187.9 \pm 4.5$ $NZ2143$ $650242$ $-22.6$ $634.2 \pm 4.0$ $NZ2183$ $600114$ $-23.4$ $187.9 \pm 4.5$ $NZ2143$ $660308$ $-26.4$ $646.5 \pm 3.9$ $NZ2184$ $600704$ $-22.5$ $193.7 \pm 4.5$ $NZ2145$ $660610$ $-25.0$ $612.4 \pm 4.2$ $NZ2189$ $601113$ $-26.4$ $198.4 \pm$	580704	-25.0	81.1±3.8	NZ2128		640523	-25.9	498.3 + 3.9	NZ2170
580929       -24.8       93.9±3.5       NZ2129       640815       -24.6       567.4±4.0       NZ2173         581009       -24.6       116.9±4.6       NZ2130       641003       -25.4       507.0±3.9       NZ2172         59123       -25.0       110.1±3.8       NZ2132       641106       -24.7       621.9±3.9       NZ2175         590302       -25.0       121.1±3.8       NZ2132       650115       -22.0       689.4±7.5       NZ2175         590411       -25.9       132.2±3.8       NZ2136       650408       -23.9       634.1±3.9       NZ2178         590601       -25.0       141.8±4.5       NZ2133       650521       -21.4       615.2±3.8       NZ2177         590713       -25.2       150.1±3.8       NZ2137       650702       -25.7       694.5±3.9       NZ2181         591001       -26.4       164.6±4.5       NZ2138       650813       -23.9       634.1±3.9       NZ2181         600121       -25.2       181.7±4.5       NZ2141       651106       -18.1       625.7±4.0       NZ2182         600141       -24.0       187.4±4.5       NZ2142       660308       -26.4       646.5±3.9       NZ2184         600121       -25.2	580828	-25.0	77.8±3.8	NZ2127		640703	-24.7	5424+37	NZ2171
581009       -24.6       116.9±4.6       NZ2130       641003       -25.4       507.0±3.9       NZ2172         59017       -25.0       126.0±4.6       NZ2132       641016       -24.7       621.9±3.9       NZ2175         590302       -25.0       126.0±4.6       NZ2133       650115       -22.0       689.4±7.5       NZ2175         590411       -25.1       137.2±3.8       NZ2134       650227       -23.6       633.6±3.9       NZ2176         590613       -25.0       16.0±4.6       NZ2133       650521       -21.4       615.2±3.8       NZ2177         590613       -25.0       141.8±4.5       NZ2133       650613       -23.9       634.1±3.9       NZ2179         5910101       -26.4       164.6±4.5       NZ2138       650613       -23.9       634.4±3.9       NZ2181         600121       -25.2       181.7±4.5       NZ2141       651106       -18.1       625.7±4.0       NZ2182         600121       -25.2       181.7±4.5       NZ2142       660204       -24.6       647.3±3.9       NZ2182         600901       -22.5       195.9±4.5       NZ2142       660204       -23.9       631.8±3.6       NZ2182         601219       -24.	580929	-24.8	93.9±3.5	NZ2129		640815	-24.6	5674+40	NZ2173
$581223$ $-25.0$ $110.1\pm 3.8$ $NZ2131$ $641106$ $-24.7$ $621.9\pm 3.9$ $NZ2174$ $590102$ $-25.0$ $126.0\pm 4.6$ $NZ2133$ $650115$ $-22.0$ $689.4\pm 7.5$ $NZ2175$ $590302$ $-25.0$ $126.0\pm 4.6$ $NZ2133$ $650115$ $-22.0$ $689.4\pm 7.5$ $NZ2176$ $590411$ $-25.1$ $137.2\pm 3.8$ $NZ2136$ $650227$ $-23.6$ $633.6\pm 3.9$ $NZ2176$ $590611$ $-25.9$ $132.8\pm 3.8$ $NZ2135$ $650227$ $-23.6$ $633.6\pm 3.9$ $NZ2177$ $590813$ $-25.0$ $141.8\pm 4.5$ $NZ2137$ $650702$ $-25.7$ $694.5\pm 3.9$ $NZ2179$ $59101$ $-26.4$ $164.6\pm 4.5$ $NZ2139$ $650813$ $-23.9$ $634.4\pm 3.9$ $NZ2180$ $591021$ $-26.4$ $164.6\pm 4.5$ $NZ2140$ $651106$ $-18.1$ $625.7\pm 4.0$ $NZ2182$ $600212$ $-25.2$ $181.7\pm 4.5$ $NZ2144$ $650204$ $-24.6$ $647.3\pm 3.9$ $NZ2183$ $60091$ $-22.8$ $193.7\pm 4.5$ $NZ2144$ $660204$ $-24.6$ $64.5\pm 3.9$ $NZ2184$ $600929$ $-22.5$ $193.7\pm 4.5$ $NZ2144$ $660202$ $-23.6$ $613.4\pm 2.8$ $NZ2186$ $601101$ $-24.5$ $193.7\pm 4.5$ $NZ2144$ $660260$ $-23.2$ $612.4\pm 2.8$ $NZ2186$ $60120$ $-25.5$ $194.9\pm 4.5$ $NZ2144$ $660260$ $-23.2$ $612.4\pm 4.2$ $NZ2186$ $610120$ $-25.5$ $194.9\pm 4.5$ $NZ2146$ <td< td=""><td>581009</td><td>-24.6</td><td><math>116.9 \pm 4.6</math></td><td>NZ2130</td><td></td><td>641003</td><td>-25.4</td><td>507.0+3.9</td><td>N72172</td></td<>	581009	-24.6	$116.9 \pm 4.6$	NZ2130		641003	-25.4	507.0+3.9	N72172
590117-25.0121.1 $\pm 3.8$ NZ2132641217-19.9615.7 $\pm 3.9$ NZ2175590302-25.0126.0 $\pm 4.6$ NZ2133650115-22.0689.4 $\pm 7.5$ NZ22175590411-25.1137.2 $\pm 3.8$ NZ2136650227-23.6633.6 $\pm 3.9$ NZ2176590713-25.2150.1 $\pm 3.8$ NZ2136650627-23.6633.6 $\pm 3.9$ NZ2176590813-25.0141.8 $\pm 4.5$ NZ2137650702-25.7694.5 $\pm 3.9$ NZ2180591011-24.4171.4 $\pm 4.5$ NZ2139650813-23.9644.1 $\pm 3.9$ NZ2182600121-25.2181.7 $\pm 4.5$ NZ2141651224-24.9634.4 $\pm 3.9$ NZ2182600141-24.0187.4 $\pm 4.5$ NZ2142660204-22.6634.2 $\pm 4.0$ NZ218260091-22.8193.7 $\pm 4.5$ NZ2143660308-26.4646.5 $\pm 3.9$ NZ2186600929-22.5195.9 $\pm 4.5$ NZ2144660520-26.1622.1 $\pm 3.8$ NZ2186601101-24.9207.1 $\pm 5.$ NZ2144660610-23.2613.8 $\pm 3.6$ NZ2186601219-24.5193.7 $\pm 4.5$ NZ2144660819-24.8621.2 $\pm 4.4$ NZ2187610120-25.5194.9 $\pm 4.5$ NZ2146660706-23.2614.8 $\pm 3.9$ NZ2190610310-24.9207.1 $\pm 5.1$ NZ2162670109-24.6616.4 $\pm 3.9$ NZ2193611031-25.1198.3 $\pm 9.5$ NZ2262670109-24.	581223	-25.0	110.1±3.8	NZ2131		641106	-24.7	$621.9 \pm 3.9$	NZ2174
$590302$ $-25.0$ $126.0\pm 4.6$ NZ2133 $650115$ $-22.0$ $669.4\pm 7.5$ NZ2171 $590411$ $-25.1$ $137.2\pm 3.8$ NZ2134 $650227$ $-23.6$ $633.6\pm 3.9$ NZ2176 $590601$ $-25.9$ $132.8\pm 3.8$ NZ2135 $650408$ $-23.9$ $634.1\pm 3.9$ NZ2177 $590813$ $-25.0$ $141.8\pm 4.5$ NZ2137 $650702$ $-25.7$ $694.5\pm 3.9$ NZ2180 $5910101$ $-26.4$ $164.6\pm 4.5$ NZ2139 $650702$ $-25.7$ $694.5\pm 3.9$ NZ2181 $591219$ $-25.0$ $181.7\pm 4.5$ NZ2140 $651166$ $-18.1$ $6577\pm 0.0$ NZ2182 $500112$ $-25.2$ $181.8\pm 4.5$ NZ2141 $651124$ $-24.9$ $634.4\pm 3.9$ NZ2183 $600114$ $-23.4$ $187.9\pm 4.5$ NZ2142 $660204$ $-24.6$ $647.3\pm 3.9$ NZ2183 $600011$ $-22.5$ $195.9\pm 4.5$ NZ2143 $660308$ $-26.4$ $646.5\pm 3.9$ NZ2184 $600714$ $-24.0$ $187.4\pm 4.5$ NZ2145 $660402$ $-23.6$ $631.8\pm 3.6$ NZ2186 $600120$ $-25.5$ $195.9\pm 4.5$ NZ2147 $660610$ $-25.0$ $612.4\pm 4.2$ NZ2188 $601120$ $-25.5$ $194.9\pm 5$ NZ2148 $660610$ $-25.6$ $612.2\pm 4.4$ NZ2188 $610120$ $-25.5$ $194.9\pm 5$ NZ2148 $660610$ $-25.1$ $614.8\pm 3.9$ NZ2192 $610526$ $-26.3$ $196.7\pm 4.5$ NZ2148 $660107$ $-23.8$ $614.8\pm 3.9$ <td< td=""><td>590117</td><td>-25.0</td><td>121.1±3.8</td><td>NZ2132</td><td></td><td>641217</td><td>-19.9</td><td>615.7 + 3.9</td><td>NZ2175</td></td<>	590117	-25.0	121.1±3.8	NZ2132		641217	-19.9	615.7 + 3.9	NZ2175
590411-25.1137.2 $\pm$ 3.8NZ2134650227-23.6633.6 $\pm$ 3.9NZ2176590601-25.9132.8 $\pm$ 3.8NZ2136650408-23.9634.1 $\pm$ 3.9NZ2178590713-25.2150.1 $\pm$ 3.8NZ2135650521-21.4615.2 $\pm$ 3.8NZ2179590813-25.0141.8 $\pm$ 4.5NZ2137650702-25.7694.5 $\pm$ 3.9NZ2180591001-26.4164.6 $\pm$ 4.5NZ2139650813-23.9614.1 $\pm$ 3.9NZ2179591119-24.5171.4 $\pm$ 4.5NZ2140651106-18.1625.7 $\pm$ 4.0NZ21816002121-25.2181.8 $\pm$ 4.5NZ2142660204-24.6647.3 $\pm$ 3.9NZ2186600714-24.0187.4 $\pm$ 4.5NZ2143660308-26.4646.5 $\pm$ 3.9NZ2186600929-22.5195.9 $\pm$ 4.5NZ2144660520-26.1622.1 $\pm$ 3.8NZ2189601113-26.4198.4 $\pm$ 4.5NZ2147660610-25.0612.4 $\pm$ 4.2NZ21866002929-22.5195.9 $\pm$ 4.5NZ2147660610-26.1622.1 $\pm$ 3.8NZ2191610113-26.4198.4 $\pm$ 5.NZ2147660610-26.6612.4 $\pm$ 4.2NZ2186610219-24.5194.9 $\pm$ 4.5NZ2147660610-26.1622.2 $\pm$ 4.4NZ218761020-25.5194.9 $\pm$ 4.5NZ2145660107-23.8614.8 $\pm$ 3.9NZ2190610310-24.9207.1 $\pm$ 5.1NZ2150661007-23.8614.8 $\pm$ 3.9 <t< td=""><td>590302</td><td>-25.0</td><td>126.0±4.6</td><td>NZ2133</td><td></td><td>650115</td><td>-22.0</td><td><math>689.4 \pm 7.5</math></td><td>N72271</td></t<>	590302	-25.0	126.0±4.6	NZ2133		650115	-22.0	$689.4 \pm 7.5$	N72271
590601-25.9132.8 $\pm$ 3.8NZ2136660408-23.9633.1 $\pm$ 3.9NZ2178590713-25.2150.1 $\pm$ 3.8NZ2135650521-21.4615.2 $\pm$ 3.8NZ2177590813-25.0141.8 $\pm$ 4.5NZ2137650702-25.7694.5 $\pm$ 3.9NZ2180591011-26.4164.6 $\pm$ 4.5NZ2139650813-23.9614.1 $\pm$ 3.9NZ2179591119-24.5171.4 $\pm$ 4.5NZ214065106-18.1625.7 $\pm$ 4.0NZ2181600121-25.2181.7 $\pm$ 4.5NZ2142661224-24.9634.4 $\pm$ 3.9NZ2182600121-22.6187.4 $\pm$ 5NZ2143660308-26.4646.5 $\pm$ 3.9NZ2185600901-22.8193.7 $\pm$ 4.5NZ2147660402-23.9631.8 $\pm$ 3.6NZ2186600929-22.5195.9 $\pm$ 4.5NZ2147660610-25.0612.4 $\pm$ 4.2NZ2188601113-26.4193.7 $\pm$ 4.5NZ2147660610-25.0612.4 $\pm$ 4.2NZ2187610120-25.5194.9 $\pm$ 4.5NZ2147660610-25.0612.4 $\pm$ 4.2NZ2187610121-24.5193.7 $\pm$ 4.5NZ2147660610-25.0612.4 $\pm$ 4.2NZ2187610120-25.5194.9 $\pm$ 5NZ2148660706-23.2612.2 $\pm$ 4.4NZ2187610120-25.5194.9 $\pm$ 5NZ2150661007-23.8614.8 $\pm$ 3.9NZ2192610526-26.3197.7 $\pm$ 5NZ2262670109-24.8627.8 $\pm$ 3.9NZ2192<	590411	-25.1	137.2±3.8	NZ2134		650227	-23.6	6336+39	NZ2176
590713 $-25.2$ $150.1\pm 3.8$ NZ2135 $650521$ $-21.4$ $615.2\pm 3.8$ NZ2177590813 $-25.0$ $141.8\pm 4.5$ NZ2137 $650702$ $-25.7$ $694.5\pm 3.9$ NZ2180 $5910101$ $-26.4$ $164.6\pm 4.5$ NZ2139 $650813$ $-23.9$ $614.1\pm 3.9$ NZ2179 $591119$ $-24.5$ $171.4\pm 4.5$ NZ2139 $650924$ $-25.2$ $634.2\pm 4.0$ NZ2181 $600121$ $-25.2$ $181.7\pm 4.5$ NZ2141 $651106$ $-18.1$ $625.7\pm 4.0$ NZ2182 $600121$ $-25.2$ $181.7\pm 4.5$ NZ2142 $660204$ $-24.6$ $647.3\pm 3.9$ NZ2183 $600714$ $-24.0$ $187.4\pm 5$ NZ2143 $660308$ $-26.4$ $646.5\pm 3.9$ NZ2186 $600929$ $-22.5$ $195.9\pm 4.5$ NZ2144 $660510$ $-23.0$ $631.8\pm 3.6$ NZ2186 $60120$ $-25.5$ $194.9\pm 4.5$ NZ2147 $660610$ $-23.2$ $612.2\pm 4.4$ NZ2186 $60120$ $-25.5$ $194.9\pm 4.5$ NZ2148 $660706$ $-23.2$ $612.2\pm 4.4$ NZ2187 $610120$ $-25.5$ $194.9\pm 4.5$ NZ2148 $660706$ $-23.2$ $612.2\pm 4.4$ NZ2188 $610120$ $-25.1$ $198.3\pm 9.5$ NZ2150 $661107$ $-23.8$ $614.8\pm 3.9$ NZ2190 $610262$ $-26.3$ $196.7\pm 4.5$ NZ2151 $661107$ $-23.8$ $614.8\pm 3.9$ NZ2191 $610264$ $-25.3$ $197.9\pm 6.3$ NZ2262 $670109$ $-24.6$ $614.3.9$ NZ219	590601	-25.9	132.8±3.8	NZ2136		650408	-23.9	$634.1 \pm 3.9$	NZ2178
590813 $-25.0$ $141.8\pm 4.5$ NZ2137 $650702$ $-25.7$ $694.5\pm 3.9$ NZ2180591001 $-26.4$ $164.6\pm 4.5$ NZ2138 $650702$ $-25.7$ $694.5\pm 3.9$ NZ2179591119 $-24.5$ $171.4\pm 4.5$ NZ2139 $650813$ $-23.9$ $614.1\pm 3.9$ NZ2179591219 $-25.0$ $181.7\pm 4.5$ NZ2140 $651106$ $-18.1$ $625.7\pm 4.0$ NZ2182 $600121$ $-25.2$ $81.8\pm 4.5$ NZ2141 $651224$ $-24.6$ $647.3\pm 3.9$ NZ2183 $600414$ $-23.4$ $187.9\pm 4.5$ NZ2142 $660204$ $-24.6$ $647.3\pm 3.9$ NZ2186 $600921$ $-22.8$ $193.7\pm 4.5$ NZ2144 $660308$ $-26.4$ $646.5\pm 3.9$ NZ2186 $600929$ $-22.5$ $195.9\pm 4.5$ NZ2144 $660706$ $-23.2$ $612.4\pm 4.2$ NZ2188 $601219$ $-24.5$ $193.7\pm 4.5$ NZ2146 $660706$ $-23.2$ $612.4\pm 4.4$ NZ2189 $610120$ $-25.5$ $194.9\pm 4.5$ NZ2150 $661077$ $-23.8$ $614.8\pm 3.9$ NZ2192 $610226$ $-26.3$ $196.7\pm 4.5$ NZ2150 $661107$ $-23.8$ $614.8\pm 3.9$ NZ2192 $61027$ $-25.1$ $198.3\pm 9.5$ NZ2262 $670109$ $-24.6$ $614.4\pm 3.9$ NZ2192 $61026$ $-25.1$ $198.3\pm 9.5$ NZ2262 $67010$ $-23.7$ $580.9\pm 5.4$ NZ2192 $611030$ $-24.7$ $182.8\pm 5.0$ NZ2152 $67024$ $-23.0$ $602.9\pm 4.4$ NZ2193 </td <td>590713</td> <td>-25.2</td> <td>150.1±3.8</td> <td>NZ2135</td> <td></td> <td>650521</td> <td>-21.4</td> <td><math>615.2 \pm 3.8</math></td> <td>N72177</td>	590713	-25.2	150.1±3.8	NZ2135		650521	-21.4	$615.2 \pm 3.8$	N72177
$591001$ $-26.4$ $164.6\pm4.5$ NZ2138 $650813$ $-23.9$ $614.1\pm3.9$ NZ2179 $591119$ $-24.5$ $171.4\pm4.5$ NZ2139 $650813$ $-23.9$ $614.1\pm3.9$ NZ2179 $591219$ $-25.0$ $181.7\pm4.5$ NZ2140 $651106$ $-18.1$ $625.7\pm4.0$ NZ2182 $600121$ $-25.2$ $181.8\pm4.5$ NZ2141 $651224$ $-24.9$ $634.4\pm3.9$ NZ2183 $600414$ $-23.4$ $187.9\pm4.5$ NZ2142 $660204$ $-24.6$ $647.3\pm3.9$ NZ2186 $600901$ $-22.8$ $193.7\pm4.5$ NZ2147 $660402$ $-23.9$ $631.8\pm3.6$ NZ2186 $600929$ $-22.5$ $195.9\pm4.5$ NZ2147 $660610$ $-25.0$ $612.4\pm4.2$ NZ2187 $610120$ $-25.5$ $194.9\pm4.5$ NZ2148 $660706$ $-23.2$ $612.2\pm4.4$ NZ2197 $610120$ $-25.5$ $194.9\pm4.5$ NZ2148 $660706$ $-23.2$ $612.2\pm4.4$ NZ2197 $610110$ $-24.9$ $207.1\pm5.1$ NZ2150 $661007$ $-23.8$ $614.8\pm3.9$ NZ2192 $610526$ $-26.3$ $196.7\pm4.5$ NZ2150 $661105$ $-25.1$ $614.8\pm3.9$ NZ2192 $610103$ $-24.7$ $183.8\pm5.0$ NZ2152 $670109$ $-24.6$ $616.4\pm3.9$ NZ2192 $611111$ $-23.8$ $612.11$ $-24.8$ $627.8\pm3.9$ NZ2192 $611103$ $-24.7$ $193.7\pm4.5$ NZ2262 $670109$ $-24.6$ $616.4\pm3.9$ NZ2192 $610319$ $-25.3$	590813	-25.0	141.8±4.5	NZ2137		650702	-25.7	6945+39	NZ2180
591119 $-24.5$ $171.4\pm 4.5$ NZ2139 $650924$ $-25.2$ $634.2\pm 4.0$ NZ2181591219 $-25.0$ $181.7\pm 4.5$ NZ2140 $651026$ $-25.2$ $634.2\pm 4.0$ NZ2181 $600121$ $-25.2$ $181.8\pm 4.5$ NZ2141 $651224$ $-24.9$ $634.4\pm 3.9$ NZ2183 $600714$ $-24.0$ $187.4\pm 5$ NZ2142 $660204$ $-24.6$ $647.3\pm 3.9$ NZ2185 $600901$ $-22.8$ $193.7\pm 4.5$ NZ2145 $660308$ $-26.4$ $646.5\pm 3.9$ NZ2185 $600929$ $-22.5$ $195.9\pm 4.5$ NZ2147 $660610$ $-25.0$ $612.4\pm 4.2$ NZ2187 $601113$ $-26.4$ $198.4\pm 4.5$ NZ2147 $660610$ $-25.0$ $612.4\pm 4.2$ NZ2187 $610120$ $-25.5$ $194.9\pm 4.5$ NZ2148 $660706$ $-23.2$ $612.2\pm 4.4$ NZ2187 $610120$ $-25.5$ $194.9\pm 4.5$ NZ2147 $660819$ $-24.8$ $590.8\pm 3.9$ NZ2187 $610120$ $-25.5$ $194.9\pm 4.5$ NZ2148 $660706$ $-23.2$ $612.4\pm 4.2$ NZ2187 $610262$ $-26.1$ $196.7\pm 4.5$ NZ2147 $660819$ $-24.8$ $590.8\pm 3.9$ NZ2187 $610310$ $-24.9$ $207.1\pm 5.1$ NZ2150 $661105$ $-25.1$ $614.9\pm 4.2$ NZ2193 $610766$ $-25.1$ $198.3\pm 9.5$ NZ2263 $661115$ $-25.1$ $614.9\pm 4.2$ NZ2193 $611031$ $-24.7$ $182.8\pm 5.0$ NZ2152 $670248$ $-23.0$ $602.9\pm 4.4$ N	591001	-26.4	164.6±4.5	NZ2138		650813	-23.9	$6141 \pm 39$	NZ2179
$591219$ $-25.0$ $181.7 \pm 4.5$ $NZ2140$ $651106$ $-18.1$ $625.7 \pm 4.0$ $NZ2182$ $600121$ $-25.2$ $181.8 \pm 4.5$ $NZ2141$ $651106$ $-18.1$ $625.7 \pm 4.0$ $NZ2182$ $600714$ $-24.0$ $187.4 \pm 4.5$ $NZ2142$ $660204$ $-24.6$ $647.3 \pm 3.9$ $NZ2183$ $600901$ $-22.8$ $193.7 \pm 4.5$ $NZ2145$ $660402$ $-23.9$ $631.8 \pm 3.6$ $NZ2186$ $600929$ $-22.5$ $195.9 \pm 4.5$ $NZ2147$ $660610$ $-25.0$ $612.4 \pm 4.2$ $NZ2188$ $601113$ $-26.4$ $198.4 \pm 4.5$ $NZ2147$ $660610$ $-25.0$ $612.4 \pm 4.2$ $NZ2188$ $601219$ $-24.5$ $193.7 \pm 4.5$ $NZ2147$ $660610$ $-25.0$ $612.4 \pm 4.2$ $NZ2189$ $610120$ $-25.5$ $194.9 \pm 4.5$ $NZ2147$ $660610$ $-25.0$ $612.4 \pm 4.2$ $NZ2189$ $610310$ $-24.9$ $207.1 \pm 5.1$ $NZ2148$ $660819$ $-24.8$ $590.8 \pm 3.9$ $NZ2190$ $610310$ $-24.9$ $207.1 \pm 5.1$ $NZ2150$ $661007$ $-23.8$ $614.8 \pm 3.9$ $NZ2192$ $610226$ $-26.3$ $196.7 \pm 4.5$ $NZ2262$ $670109$ $-24.6$ $614.9 \pm 4.2$ $NZ2193$ $611031$ $-25.1$ $198.3 \pm 5.0$ $NZ2262$ $670109$ $-24.6$ $614.4 \pm 3.9$ $NZ2192$ $611031$ $-25.1$ $198.3 \pm 5.0$ $NZ2262$ $67024$ $-23.6$ $614.8 \pm 3.9$ $NZ2193$ $611111$ $-23.8$ $23.7 \pm $	591119	-24.5	171.4±4.5	NZ2139		650924	-25.2	$6342 \pm 40$	N72181
$600121$ $-25.2$ $181.8\pm4.5$ $NZ2141$ $651224$ $-24.9$ $634.4\pm3.9$ $NZ2183$ $600414$ $-23.4$ $187.9\pm4.5$ $NZ2142$ $660204$ $-24.6$ $647.3\pm3.9$ $NZ2184$ $600714$ $-24.0$ $187.4\pm4.5$ $NZ2143$ $660204$ $-24.6$ $647.3\pm3.9$ $NZ2183$ $600901$ $-22.8$ $193.7\pm4.5$ $NZ2145$ $660204$ $-24.6$ $646.5\pm3.9$ $NZ2186$ $600929$ $-22.5$ $195.9\pm4.5$ $NZ2147$ $660610$ $-25.0$ $612.4\pm4.2$ $NZ2188$ $601113$ $-26.4$ $198.4\pm4.5$ $NZ2147$ $660610$ $-25.0$ $612.4\pm4.2$ $NZ2187$ $610120$ $-25.5$ $194.9\pm4.5$ $NZ2148$ $660706$ $-23.2$ $612.2\pm4.4$ $NZ2187$ $610310$ $-24.9$ $207.1\pm5.1$ $NZ2149$ $660909$ $-26.8$ $625.2\pm3.8$ $NZ2190$ $610310$ $-24.9$ $207.1\pm5.1$ $NZ2150$ $661107$ $-23.8$ $614.8\pm3.9$ $NZ2192$ $610526$ $-26.3$ $196.7\pm4.5$ $NZ2151$ $661107$ $-23.8$ $614.8\pm3.9$ $NZ2192$ $610310$ $-24.7$ $182.8\pm5.0$ $NZ2152$ $670109$ $-24.6$ $616.4\pm3.9$ $NZ2192$ $611031$ $-25.3$ $197.9\pm6.3$ $NZ2262$ $670109$ $-24.6$ $616.4\pm3.9$ $NZ2196$ $611111$ $-23.8$ $237.2\pm9.4$ $NZ2265$ $670610$ $-23.7$ $596.5\pm3.8$ $NZ2197$ $611219$ $-24.6$ $197.4\pm5.0$ $NZ2266$ $670610$ $-23.$	591219	-25.0	181.7±4.5	NZ2140		651106	-18.1	$6257 \pm 4.0$	N72182
$600414$ $-23.4$ $187.9\pm4.5$ $NZ2142$ $660204$ $-24.6$ $647.3\pm3.9$ $NZ2185$ $600901$ $-22.8$ $193.7\pm4.5$ $NZ2143$ $660308$ $-26.4$ $646.5\pm3.9$ $NZ2185$ $600929$ $-22.5$ $195.9\pm4.5$ $NZ2145$ $660402$ $-23.9$ $631.8\pm3.6$ $NZ2186$ $601113$ $-26.4$ $198.4\pm4.5$ $NZ2147$ $660610$ $-25.0$ $612.4\pm4.2$ $NZ2188$ $601219$ $-24.5$ $193.7\pm4.5$ $NZ2147$ $660610$ $-25.0$ $612.4\pm4.2$ $NZ2187$ $610120$ $-25.5$ $194.9\pm4.5$ $NZ2148$ $660706$ $-23.2$ $612.2\pm4.4$ $NZ2190$ $610310$ $-24.9$ $207.1\pm5.1$ $NZ2149$ $660909$ $-24.8$ $590.8\pm3.9$ $NZ2190$ $610526$ $-26.3$ $196.7\pm4.5$ $NZ2150$ $661107$ $-23.8$ $614.8\pm3.9$ $NZ2192$ $610526$ $-26.3$ $196.7\pm4.5$ $NZ2151$ $661105$ $-25.1$ $614.9\pm4.2$ $NZ2193$ $610706$ $-25.1$ $198.3\pm9.5$ $NZ2262$ $670109$ $-24.6$ $616.4\pm3.9$ $NZ2192$ $611031$ $-24.7$ $182.8\pm5.0$ $NZ2152$ $670224$ $-23.0$ $602.9\pm4.4$ $NZ2196$ $611111$ $-23.8$ $237.2\pm9.4$ $NZ2262$ $670610$ $-23.7$ $596.5\pm3.8$ $NZ2197$ $611219$ $-25.1$ $227.3\pm9.4$ $NZ2265$ $670610$ $-23.7$ $596.5\pm3.8$ $NZ2172$ $620192$ $-24.5$ $214.4$ $571.3\pm3.8$ $NZ2272$ $67022$	600121	-25.2	181.8±4.5	NZ2141		651224	-24.9	$634.4 \pm 3.9$	NZ2183
$600714$ $-24.0$ $187.4\pm4.5$ NZ2143 $660308$ $-26.4$ $646.5\pm3.9$ NZ2185 $600901$ $-22.8$ $193.7\pm4.5$ NZ2145 $660402$ $-23.9$ $631.8\pm3.6$ NZ2186 $600929$ $-22.5$ $195.9\pm4.5$ NZ2144 $660520$ $-26.1$ $622.1\pm3.8$ NZ2188 $601113$ $-26.4$ $198.4\pm4.5$ NZ2147 $660610$ $-25.0$ $612.4\pm4.2$ NZ2188 $60120$ $-25.5$ $194.9\pm4.5$ NZ2148 $660610$ $-25.0$ $612.4\pm4.2$ NZ2187 $610120$ $-25.5$ $194.9\pm4.5$ NZ2148 $660706$ $-23.2$ $612.2\pm4.4$ NZ2197 $610310$ $-24.9$ $207.1\pm5.1$ NZ2149 $660909$ $-26.8$ $625.2\pm3.8$ NZ2192 $610526$ $-26.3$ $196.7\pm4.5$ NZ2151 $661107$ $-23.8$ $614.8\pm3.9$ NZ2192 $610706$ $-25.1$ $198.3\pm9.5$ NZ2263 $661105$ $-25.1$ $614.9\pm4.2$ NZ2193 $610706$ $-25.3$ $197.9\pm6.3$ NZ2262 $670109$ $-24.6$ $616.4\pm3.9$ NZ2195 $611003$ $-24.7$ $182.8\pm5.0$ NZ2152 $670224$ $-23.0$ $602.9\pm4.4$ NZ2196 $611111$ $-23.8$ $237.2\pm9.4$ NZ2265 $670610$ $-23.7$ $596.5\pm3.8$ NZ2198 $620119$ $-24.6$ $197.4\pm5.0$ NZ2265 $670610$ $-23.7$ $596.5\pm3.8$ NZ2192 $620225$ $-24.5$ $214.3\pm5.1$ NZ2267 $670610$ $-23.7$ $595.9\pm5.4$ NZ2273	600414	-23.4	187.9±4.5	NZ2142		660204	-24.6	$647.3 \pm 3.9$	NZ2184
$600901$ $-22.8$ $193.7\pm4.5$ $NZ2145$ $660402$ $-23.9$ $631.8\pm3.6$ $NZ2186$ $600929$ $-22.5$ $195.9\pm4.5$ $NZ2144$ $660402$ $-23.9$ $631.8\pm3.6$ $NZ2188$ $601113$ $-26.4$ $198.4\pm4.5$ $NZ2147$ $660610$ $-25.0$ $612.4\pm4.2$ $NZ2188$ $601219$ $-24.5$ $193.7\pm4.5$ $NZ2146$ $660706$ $-23.2$ $612.2\pm4.4$ $NZ2187$ $610120$ $-25.5$ $194.9\pm4.5$ $NZ2148$ $660706$ $-23.2$ $612.2\pm4.4$ $NZ2190$ $610310$ $-24.9$ $207.1\pm5.1$ $NZ2150$ $661007$ $-23.8$ $614.8\pm3.9$ $NZ2192$ $610526$ $-26.3$ $196.7\pm4.5$ $NZ2151$ $661105$ $-25.1$ $614.9\pm4.2$ $NZ2193$ $610706$ $-25.1$ $198.3\pm9.5$ $NZ2262$ $670109$ $-24.6$ $616.4\pm3.9$ $NZ2195$ $611031$ $-24.7$ $182.8\pm5.0$ $NZ2152$ $670224$ $-23.0$ $602.9\pm4.4$ $NZ2195$ $611111$ $-23.8$ $237.2\pm9.4$ $NZ2265$ $670610$ $-23.7$ $596.5\pm3.8$ $NZ2197$ $611111$ $-23.8$ $237.2\pm9.4$ $NZ2265$ $670610$ $-23.7$ $596.5\pm3.8$ $NZ2192$ $620119$ $-24.6$ $197.4\pm5.0$ $NZ2266$ $670610$ $-23.7$ $596.5\pm3.8$ $NZ2272$ $620202$ $-24.5$ $214.3\pm5.1$ $NZ2267$ $670610$ $-23.7$ $596.5\pm3.8$ $NZ2272$ $620255$ $-24.5$ $189.4\pm9.5$ $NZ2269$ $670106$ $-23.$	600714	-24.0	187.4±4.5	NZ2143		660308	-26.4	$646.5 \pm 3.9$	N72185
$600929$ $-22.5$ $195.9\pm 4.5$ $NZ2144$ $660520$ $-26.1$ $622.1\pm 3.8$ $NZ2189$ $601113$ $-26.4$ $198.4\pm 4.5$ $NZ2147$ $660610$ $-25.0$ $612.4\pm 4.2$ $NZ2188$ $601219$ $-24.5$ $193.7\pm 4.5$ $NZ2146$ $660706$ $-23.2$ $612.2\pm 4.4$ $NZ2187$ $610120$ $-25.5$ $194.9\pm 4.5$ $NZ2148$ $660706$ $-23.2$ $612.2\pm 4.4$ $NZ2190$ $610310$ $-24.9$ $207.1\pm 5.1$ $NZ2149$ $660909$ $-26.8$ $625.2\pm 3.8$ $NZ2190$ $610310$ $-24.9$ $207.1\pm 5.1$ $NZ2150$ $661007$ $-23.8$ $614.8\pm 3.9$ $NZ2192$ $610526$ $-26.3$ $196.7\pm 4.5$ $NZ2151$ $661105$ $-25.1$ $614.9\pm 4.2$ $NZ2193$ $610706$ $-25.1$ $198.3\pm 9.5$ $NZ2262$ $670109$ $-24.6$ $616.4\pm 3.9$ $NZ2192$ $611003$ $-24.7$ $182.8\pm 5.0$ $NZ2152$ $670224$ $-23.0$ $602.9\pm 4.4$ $NZ2195$ $61111$ $-23.8$ $237.2\pm 9.4$ $NZ2265$ $670610$ $-23.7$ $590.\pm 3.8$ $NZ2197$ $61111$ $-23.8$ $237.2\pm 9.4$ $NZ2265$ $670610$ $-23.7$ $590.\pm 3.8$ $NZ2197$ $620302$ $-23.4$ $207.3\pm 7.5$ $NZ2266$ $670610$ $-23.7$ $590.\pm 5.4$ $NZ2272$ $620302$ $-24.5$ $214.3\pm 5.1$ $NZ2267$ $670610$ $-23.7$ $590.\pm 5.4$ $NZ2273$ $620525$ $-24.5$ $189.4\pm 9.5$ $NZ2267$	600901	-22.8	193.7±4.5	NZ2145		660402	-23.9	$631.8 \pm 3.6$	NZ2186
$601113$ $-26.4$ $198.4\pm4.5$ NZ2147 $660610$ $-25.0$ $612.4\pm4.2$ NZ2188 $601219$ $-24.5$ $193.7\pm4.5$ NZ2146 $660706$ $-23.2$ $612.2\pm4.4$ NZ2187 $610120$ $-25.5$ $194.9\pm4.5$ NZ2148 $660706$ $-23.2$ $612.2\pm4.4$ NZ2187 $610310$ $-24.9$ $207.1\pm5.1$ NZ2149 $660909$ $-26.8$ $652.2\pm3.8$ NZ2190 $610310$ $-24.9$ $207.1\pm5.1$ NZ2150 $661007$ $-23.8$ $614.8\pm3.9$ NZ2192 $610526$ $-26.3$ $196.7\pm4.5$ NZ2151 $661105$ $-25.1$ $614.9\pm4.2$ NZ2193 $61076$ $-25.1$ $198.3\pm9.5$ NZ2263 $661211$ $-24.8$ $627.8\pm3.9$ NZ2194 $610819$ $-25.3$ $197.9\pm6.3$ NZ2262 $670109$ $-24.6$ $616.4\pm3.9$ NZ2195 $611003$ $-24.7$ $182.8\pm5.0$ NZ2152 $670224$ $-23.0$ $602.9\pm4.4$ NZ2196 $611111$ $-23.8$ $237.2\pm9.4$ NZ2265 $670610$ $-23.7$ $596.5\pm3.8$ NZ2197 $611219$ $-25.1$ $227.3\pm9.4$ NZ2265 $670610$ $-23.7$ $596.5\pm3.8$ NZ2198 $620119$ $-24.6$ $197.4\pm5.0$ NZ2268 $670610$ $-23.7$ $596.5\pm3.8$ NZ2272 $620302$ $-23.4$ $207.3\pm7.5$ NZ2267 $670610$ $-23.7$ $595.9\pm5.4$ NZ2273 $620425$ $-24.5$ $214.3\pm5.1$ NZ2267 $670610$ $-23.1$ $575.1\pm3.8$ NZ2273	600929	-22.5	195.9±4.5	NZ2144		660520	-26.1	$622.1 \pm 3.8$	NZ2189
$601219$ $-24.5$ $193.7\pm4.5$ NZ2146 $660706$ $-23.2$ $612.2\pm4.4$ NZ2187 $610120$ $-25.5$ $194.9\pm4.5$ NZ2148 $660819$ $-24.8$ $590.8\pm3.9$ NZ2190 $610310$ $-24.9$ $207.1\pm5.1$ NZ2149 $660909$ $-26.8$ $625.2\pm3.8$ NZ2192 $610526$ $-26.3$ $196.7\pm4.5$ NZ2151 $661105$ $-25.1$ $614.9\pm4.2$ NZ2192 $610526$ $-26.3$ $196.7\pm4.5$ NZ2151 $661107$ $-23.8$ $614.8\pm3.9$ NZ2192 $610706$ $-25.1$ $198.3\pm9.5$ NZ2263 $661211$ $-24.8$ $627.8\pm3.9$ NZ2194 $610819$ $-25.3$ $197.9\pm6.3$ NZ2262 $670109$ $-24.6$ $616.4\pm3.9$ NZ2195 $611003$ $-24.7$ $182.8\pm5.0$ NZ2152 $670224$ $-23.0$ $602.9\pm4.4$ NZ2196 $611111$ $-23.8$ $237.2\pm9.4$ NZ2265 $670610$ $-23.7$ $596.5\pm3.8$ NZ2197 $611219$ $-25.1$ $227.3\pm9.4$ NZ2265 $670610$ $-23.7$ $596.5\pm3.8$ NZ2198 $620119$ $-24.6$ $197.4\pm5.0$ NZ2268 $670610$ $-23.7$ $596.5\pm3.8$ NZ2273 $620302$ $-23.4$ $207.3\pm7.5$ NZ2267 $670610$ $-23.7$ $595.9\pm5.4$ NZ2273 $620325$ $-24.5$ $214.3\pm5.1$ NZ2267 $670610$ $-23.1$ $575.1\pm3.8$ NZ2273 $620525$ $-24.5$ $189.4\pm9.5$ NZ2269 $671006$ $-23.1$ $575.1\pm3.8$ NZ2200 <td< td=""><td>601113</td><td>-26.4</td><td>198.4±4.5</td><td>NZ2147</td><td></td><td>660610</td><td>-25.0</td><td><math>6124 \pm 42</math></td><td>NZ2188</td></td<>	601113	-26.4	198.4±4.5	NZ2147		660610	-25.0	$6124 \pm 42$	NZ2188
$610120$ $-25.5$ $194.9\pm4.5$ NZ2148 $660819$ $-24.8$ $590.8\pm3.9$ NZ2190 $610310$ $-24.9$ $207.1\pm5.1$ NZ2149 $660909$ $-26.8$ $625.2\pm3.8$ NZ2191 $610414$ $-25.0$ $201.9\pm4.5$ NZ2150 $661007$ $-23.8$ $614.8\pm3.9$ NZ2192 $610526$ $-26.3$ $196.7\pm4.5$ NZ2151 $661105$ $-25.1$ $614.9\pm4.2$ NZ2193 $61076$ $-25.1$ $198.3\pm9.5$ NZ2263 $661211$ $-24.8$ $627.8\pm3.9$ NZ2194 $610819$ $-25.3$ $197.9\pm6.3$ NZ2262 $670109$ $-24.6$ $616.4\pm3.9$ NZ2195 $611003$ $-24.7$ $182.8\pm5.0$ NZ2152 $670224$ $-23.0$ $602.9\pm4.4$ NZ2196 $611111$ $-23.8$ $237.2\pm9.4$ NZ2265 $670408$ $-23.4$ $609.0\pm3.8$ NZ2197 $611219$ $-25.1$ $227.3\pm9.4$ NZ2265 $670610$ $-23.7$ $596.5\pm3.8$ NZ2198 $620119$ $-24.6$ $197.4\pm5.0$ NZ2268 $670610$ $-23.7$ $596.5\pm3.8$ NZ2272 $620302$ $-23.4$ $207.3\pm7.5$ NZ2267 $670610$ $-23.7$ $595.9\pm5.4$ NZ2273 $620425$ $-24.5$ $214.3\pm5.1$ NZ2267 $670610$ $-23.1$ $575.1\pm3.8$ NZ2200 $620928$ $-24.5$ $233.5\pm4.4$ NZ2155 $671110$ $-25.7$ $586.0\pm5.2$ NZ2274 $621109$ $-24.4$ $250.4\pm5.9$ NZ2270 $671209$ $-24.4$ $579.6\pm3.9$ NZ2201	601219	-24.5	193.7±4.5	NZ2146		660706	-23.2	612.2+4.4	NZ2187
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	610120	-25.5	194.9±4.5	NZ2148		660819	-24.8	$590.8 \pm 3.9$	NZ2190
$610414$ $-25.0$ $201.9\pm4.5$ NZ2150 $661007$ $-23.8$ $614.8\pm3.9$ NZ2192 $610526$ $-26.3$ $196.7\pm4.5$ NZ2151 $661007$ $-23.8$ $614.8\pm3.9$ NZ2192 $610706$ $-25.1$ $198.3\pm9.5$ NZ2263 $661105$ $-25.1$ $614.9\pm4.2$ NZ2193 $610819$ $-25.3$ $197.9\pm6.3$ NZ2262 $670109$ $-24.6$ $616.4\pm3.9$ NZ2195 $611003$ $-24.7$ $182.8\pm5.0$ NZ2152 $670224$ $-23.0$ $602.9\pm4.4$ NZ2195 $611111$ $-23.8$ $237.2\pm9.4$ NZ2264 $670408$ $-23.4$ $609.0\pm3.8$ NZ2197 $611219$ $-25.1$ $227.3\pm9.4$ NZ2265 $670506$ $-23.7$ $596.5\pm3.8$ NZ2198 $620119$ $-24.6$ $197.4\pm5.0$ NZ2268 $670610$ $-23.7$ $596.9\pm5.4$ NZ2273 $620302$ $-23.4$ $207.3\pm7.5$ NZ2266 $670610$ $-23.7$ $595.9\pm5.4$ NZ2273 $620325$ $-24.5$ $214.3\pm5.1$ NZ2267 $670610$ $-23.7$ $595.9\pm5.4$ NZ2273 $620525$ $-24.5$ $189.4\pm9.5$ NZ2269 $671006$ $-23.1$ $575.1\pm3.8$ NZ2200 $620928$ $-24.5$ $233.5\pm4.4$ NZ2155 $671110$ $-25.7$ $586.0\pm5.2$ NZ2274 $621109$ $-24.4$ $250.4\pm5.9$ NZ2270 $671209$ $-24.4$ $579.6\pm3.9$ NZ2201 $621220$ $-28.4$ $266.6\pm3.9$ NZ2153 $680113$ $-23.9$ $583.0\pm3.9$ NZ2201 <td>610310</td> <td>-24.9</td> <td>207.1±5.1</td> <td>NZ2149</td> <td></td> <td>660909</td> <td>-26.8</td> <td><math>625.2 \pm 3.8</math></td> <td>N72191</td>	610310	-24.9	207.1±5.1	NZ2149		660909	-26.8	$625.2 \pm 3.8$	N72191
$610526$ $-26.3$ $196.7\pm4.5$ NZ2151 $661105$ $-25.1$ $614.9\pm4.2$ NZ2193 $610706$ $-25.1$ $198.3\pm9.5$ NZ2263 $661211$ $-24.8$ $627.8\pm3.9$ NZ2194 $610819$ $-25.3$ $197.9\pm6.3$ NZ2262 $670109$ $-24.6$ $616.4\pm3.9$ NZ2195 $611015$ $-24.7$ $182.8\pm5.0$ NZ2152 $670224$ $-23.0$ $602.9\pm4.4$ NZ2196 $611111$ $-23.8$ $237.2\pm9.4$ NZ2265 $670408$ $-23.4$ $609.0\pm3.8$ NZ2197 $611219$ $-25.1$ $227.3\pm9.4$ NZ2265 $670506$ $-23.7$ $596.5\pm3.8$ NZ2197 $611219$ $-24.6$ $197.4\pm5.0$ NZ2268 $670610$ $-23.7$ $596.5\pm3.8$ NZ2172 $620302$ $-23.4$ $207.3\pm7.5$ NZ2266 $670610$ $-23.7$ $595.9\pm5.4$ NZ2273 $620425$ $-24.5$ $214.3\pm5.1$ NZ2267 $670610$ $-23.7$ $595.9\pm5.4$ NZ2273 $620525$ $-24.5$ $189.4\pm9.5$ NZ2269 $671006$ $-23.1$ $575.1\pm3.8$ NZ2200 $620928$ $-24.5$ $233.5\pm4.4$ NZ2155 $671110$ $-25.7$ $586.0\pm5.2$ NZ2274 $621109$ $-24.4$ $250.4\pm5.9$ NZ2270 $671209$ $-24.4$ $579.6\pm3.9$ NZ2201 $621220$ $-28.4$ $266.6\pm3.9$ NZ2153 $680113$ $-23.9$ $583.0\pm3.9$ NZ2201	610414	-25.0	$201.9 \pm 4.5$	NZ2150		661007	-23.8	$6148 \pm 39$	N72192
$610706$ $-25.1$ $198.3 \pm 9.5$ NZ2263 $661211$ $-24.8$ $627.8 \pm 3.9$ NZ2194 $610819$ $-25.3$ $197.9 \pm 6.3$ NZ2262 $670109$ $-24.6$ $616.4 \pm 3.9$ NZ2195 $611003$ $-24.7$ $182.8 \pm 5.0$ NZ2152 $670224$ $-23.0$ $602.9 \pm 4.4$ NZ2196 $611111$ $-23.8$ $237.2 \pm 9.4$ NZ2264 $670408$ $-23.4$ $609.0 \pm 3.8$ NZ2197 $611219$ $-25.1$ $227.3 \pm 9.4$ NZ2265 $670506$ $-23.7$ $596.5 \pm 3.8$ NZ2198 $620119$ $-24.6$ $197.4 \pm 5.0$ NZ2268 $670610$ $-23.7$ $596.5 \pm 3.8$ NZ2272 $620302$ $-23.4$ $207.3 \pm 7.5$ NZ2266 $670610$ $-23.7$ $595.9 \pm 5.4$ NZ2273 $620425$ $-24.5$ $214.3 \pm 5.1$ NZ2267 $670610$ $-23.7$ $595.9 \pm 5.4$ NZ2273 $620525$ $-24.5$ $189.4 \pm 9.5$ NZ2269 $671006$ $-23.1$ $575.1 \pm 3.8$ NZ2200 $620928$ $-24.5$ $233.5 \pm 4.4$ NZ2155 $671110$ $-25.7$ $586.0 \pm 5.2$ NZ2274 $621109$ $-24.0$ $250.4 \pm 5.9$ NZ2270 $671209$ $-24.4$ $579.6 \pm 3.9$ NZ2201 $621220$ $-28.4$ $266.6 \pm 3.9$ NZ2153 $680113$ $-23.9$ $583.0 \pm 3.9$ NZ2201	610526	-26.3	196.7±4.5	NZ2151		661105	-25.1	$6149 \pm 42$	NZ2193
$610819$ $-25.3$ $197.9\pm 6.3$ $NZ2262$ $670109$ $-24.6$ $616.4\pm 3.9$ $NZ2195$ $611003$ $-24.7$ $182.8\pm 5.0$ $NZ2152$ $670224$ $-23.0$ $602.9\pm 4.4$ $NZ2195$ $611111$ $-23.8$ $237.2\pm 9.4$ $NZ2264$ $670408$ $-23.4$ $609.0\pm 3.8$ $NZ2197$ $611219$ $-25.1$ $227.3\pm 9.4$ $NZ2265$ $670506$ $-23.7$ $596.5\pm 3.8$ $NZ2198$ $620119$ $-24.6$ $197.4\pm 5.0$ $NZ2268$ $670610$ $-23.7$ $580.0\pm 6.3$ $NZ2272$ $620302$ $-23.4$ $207.3\pm 7.5$ $NZ2266$ $670610$ $-23.7$ $595.9\pm 5.4$ $NZ2273$ $620425$ $-24.5$ $214.3\pm 5.1$ $NZ2267$ $670719$ $-24.4$ $571.3\pm 3.8$ $NZ2199$ $620525$ $-24.5$ $189.4\pm 9.5$ $NZ2269$ $671006$ $-23.1$ $575.1\pm 3.8$ $NZ2200$ $620928$ $-24.5$ $233.5\pm 4.4$ $NZ2155$ $671110$ $-25.7$ $586.0\pm 5.2$ $NZ2274$ $621109$ $-24.0$ $250.4\pm 5.9$ $NZ2270$ $671209$ $-24.4$ $579.6\pm 3.9$ $NZ2201$ $621220$ $-28.4$ $266.6\pm 3.9$ $NZ2153$ $680113$ $-32.9$ $583.0\pm 3.9$ $NZ2201$	610706	-25.1	198.3±9.5	NZ2263		661211	-24.8	$627.8 \pm 3.9$	NZ2194
	610819	-25.3	197.9±6.3	NZ2262		670109	-24.6	$616.4 \pm 3.9$	NZ2195
$611111$ $-23.8$ $237.2 \pm 9.4$ $NZ2264$ $670408$ $-23.4$ $609.0 \pm 3.8$ $NZ2197$ $611219$ $-25.1$ $227.3 \pm 9.4$ $NZ2265$ $670408$ $-23.4$ $609.0 \pm 3.8$ $NZ2197$ $620119$ $-24.6$ $197.4 \pm 5.0$ $NZ2268$ $670610$ $-23.7$ $596.5 \pm 3.8$ $NZ2172$ $620302$ $-23.4$ $207.3 \pm 7.5$ $NZ2266$ $670610$ $-23.7$ $595.9 \pm 5.4$ $NZ2273$ $620425$ $-24.5$ $214.3 \pm 5.1$ $NZ2267$ $670610$ $-23.7$ $595.9 \pm 5.4$ $NZ2273$ $620525$ $-24.5$ $214.3 \pm 5.1$ $NZ2269$ $670610$ $-23.1$ $575.1 \pm 3.8$ $NZ2200$ $620928$ $-24.5$ $233.5 \pm 4.4$ $NZ2155$ $671110$ $-25.7$ $586.0 \pm 5.2$ $NZ2274$ $621109$ $-24.0$ $250.4 \pm 5.9$ $NZ2270$ $671209$ $-24.4$ $579.6 \pm 3.9$ $NZ2201$ $621220$ $-28.4$ $266.6 \pm 3.9$ $NZ2153$ $680113$ $-23.9$ $583.0 \pm 3.9$ $NZ2202$	611003	-24.7	182.8±5.0	NZ2152		670224	-23.0	$6029 \pm 44$	NZ2196
	611111	-23.8	$237.2 \pm 9.4$	NZ2264		670408	-23.4	$609.0 \pm 3.8$	NZ2197
620119       -24.6       197.4±5.0       NZ2268       670610       -23.7       580.0±6.3       NZ2272         620302       -23.4       207.3±7.5       NZ2266       670610       -23.7       59.9±5.4       NZ2273         620425       -24.5       214.3±5.1       NZ2267       670610       -23.7       59.9±5.4       NZ2273         620525       -24.5       214.3±5.1       NZ2269       670719       -24.4       571.3±3.8       NZ2200         620928       -24.5       233.5±4.4       NZ2155       671110       -25.7       586.0±5.2       NZ2274         621109       -24.0       250.4±5.9       NZ2270       671209       -24.4       579.6±3.9       NZ2201         621220       -28.4       266.6±3.9       NZ2153       680113       -23.9       583.0±3.9       NZ2201	611219	-25.1	227.3±9.4	NZ2265		670506	-23.7	$596.5 \pm 3.8$	NZ2198
620302       -23.4       207.3±7.5       NZ2266       670610       -23.7       595.9±5.4       NZ2273         620425       -24.5       214.3±5.1       NZ2267       670719       -24.4       571.3±3.8       NZ2199         620525       -24.5       189.4±9.5       NZ2269       671006       -23.1       575.1±3.8       NZ2200         620928       -24.5       233.5±4.4       NZ2155       671110       -25.7       586.0±5.2       NZ2274         621109       -24.0       250.4±5.9       NZ2270       671209       -24.4       579.6±3.9       NZ2201         621220       -28.4       266.6±3.9       NZ2153       680113       -23.9       583.0±3.9       NZ2002	620119	-24.6	197.4±5.0	NZ2268		670610	-23.7	580.0+6.3	NZ2272
620425       -24.5       214.3±5.1       NZ2267       670719       -24.4       571.3±3.8       NZ2199         620525       -24.5       189.4±9.5       NZ2269       671006       -23.1       575.1±3.8       NZ2200         620928       -24.5       233.5±4.4       NZ2155       671110       -25.7       586.0±5.2       NZ2274         621109       -24.0       250.4±5.9       NZ2270       671209       -24.4       579.6±3.9       NZ2201         621220       -28.4       266.6±3.9       NZ2153       680113       -23.9       583.0±3.9       NZ2202	620302	-23.4	207.3±7.5	NZ2266		670610	-23 7	$595.9 \pm 5.4$	N72273
620525       -24.5       189.4±9.5       NZ2269       671006       -23.1       575.1±3.8       NZ2200         620928       -24.5       233.5±4.4       NZ2155       671110       -25.7       586.0±5.2       NZ2274         621109       -24.0       250.4±5.9       NZ2270       671209       -24.4       579.6±3.9       NZ2201         621220       -28.4       266.6±3.9       NZ2153       680113       -23.9       583.0±3.9       NZ2202	620425	-24.5	214.3±5.1	NZ2267		670719	-24 4	571.3+3.8	N72100
620928       -24.5       233.5±4.4       NZ2155       671110       -25.7       586.0±5.2       NZ2274         621109       -24.0       250.4±5.9       NZ2270       671209       -24.4       579.6±3.9       NZ2201         621220       -28.4       266.6±3.9       NZ2153       680113       -23.9       583.0±3.9       NZ2202	620525	-24.5	189.4±9.5	NZ2269		671006	-23.1	$5751 \pm 38$	N72200
621109       -24.0       250.4±5.9       NZ2270       67110       -23.7       500.0±5.2       NZ2274         621200       -28.4       266.6±3.9       NZ2153       680113       -23.9       583.0±3.9       NZ2201	620928	-24.5	233.5±4.4	NZ2155		671110	-25.7	$575.1\pm 5.5$ 586 0 $\pm 5.2$	N72274
621220 -28.4 266.6±3.9 NZ2153 680113 -23.0 583.0±3.0 NZ2201	621109	-24.0	250.4±5.9	NZ2270		671209	-24 4	$5796 \pm 39$	N72201
	621220	-28.4	266.6±3.9	NZ2153		680113	-23.9	583.0+3.9	N72202

TABLE 1 (	continued	)
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	$\delta^{13}$ C	$\Delta^{14}$ C	Lab		$\delta^{13} C$	$\Delta^{14}$ C	Lab
Date	%0	‰	number	Date	‰	‰	number
680211	-24.5	582.5±3.9	NZ2203	720317	-22.5	474.8±7.4	NZ2282
680311	-22.5	572.8±3.6	NZ2204	720331	-23.8	482.4±3.6	NZ2250
680406	-23.9	547.6±3.7	NZ2205	720420	-22.6	468.1±3.6	NZ2254
680531	-24.8	560.5±3.9	NZ2206	720504	-23.0	469.5±5.1	NZ2286
680607	-24.6	561.7±3.9	NZ2207	720610	-24.4	470.1±5.1	NZ2287
680705	-26.3	550.4±3.9	NZ2208	720707	-24.0	465.9±5.1	NZ2288
680809	-24.7	538.1±3.9	NZ2209	720901	-24.7	450.3±5.1	NZ2289
680830	-23.8	535.5±3.8	NZ2210	721007	-24.4	449.9±6.7	NZ2283
680906	-23.7	531.5±3.9	NZ2211	721208	-24.9	447.3±4.7	NZ2285
681004	-24.6	532.8±3.9	NZ2212	730210	-24.3	453.9±5.1	NZ2291
681018	-24.7	537.6±3.9	NZ2213	730309	-23.6	442.8±3.3	NZ2255
681102	-25.3	541.9±3.9	NZ3470	730706	-24.7	435.0±3.7	NZ2256
681108	-26.9	541.2±3.9	NZ2214	730811	-24.5	427.1±3.3	NZ2257
681206	-23.8	$539.6 \pm 3.9$	NZ2215	730907	-24.4	415.9±3.7	NZ2258
690110	-24.3	$539.1 \pm 3.9$	NZ2217	731006	-24.1	426.0±3.3	NZ2259
690207	-23.1	537.7±3.8	NZ2216	731109	-23.4	434.3±3.7	NZ2260
690308	-23.3	$550.4 \pm 3.8$	NZ2218	731207	-23.3	417.2±3.2	NZ2261
690413	-23.4	545.4±3.8	NZ2222	740111	-23.2	412.8±3.5	NZ3565
690502	-23.1	$530.4 \pm 4.0$	NZ2220	740201	-23.0	$405.1 \pm 3.3$	NZ3566
690509	-22.8	539.6±3.9	NZ2221	740308	-22.2	418.5±3.3	NZ3567
690607	-23.4	$525.2 \pm 4.2$	NZ2223	740404	-23.0	417.2±3.3	NZ3568
690711	-23.2	$526.3 \pm 3.9$	NZ2219	740510	-23.3	$386.8 \pm 3.3$	NZ3572
690809	-23.0	$522.8 \pm 3.9$	NZ2224	740607	-23.3	359.7±3.3	NZ4052
690905	-23.5	$544.9 \pm 3.8$	NZ2225	740706	-23.3	394.5±3.3	NZ4057
691010	-25.2	$531.2 \pm 3.9$	NZ2226	740807	-24.8	392.3±3.7	NZ4058
691103	-23.2	523.0±3.9	NZ2227	740906	-23.4	$405.0 \pm 3.3$	NZ4062
691205	-22.5	$510.2 \pm 3.9$	NZ2228	741005	-23.2	398.7±4.7	NZ3848
700109	-22.5	$510.2 \pm 3.9$	NZ2229	741108	-22.8	401.7±3.3	NZ4065
700306	-22.5	$535.3 \pm 3.9$	NZ2230	741208	-23.4	393.7±3.3	NZ4074
700410	-22.1	520.4±3.9	NZ2232	750110	-22.2	$396.3 \pm 3.3$	NZ4076
700509	-22.4	$513.5 \pm 3.9$	NZ2231	750207	-23.4	399.0±3.7	NZ4078
700606	-23.3	$516.2 \pm 3.9$	NZ2233	750307	-23.3	400.6±3.3	NZ4083
700710	-23.8	$505.9 \pm 3.9$	NZ2234	750405	-23.4	397.7±3.3	NZ4088
700807	-23.6	497.4±3.5	NZ2235	750510	-23.2	389.1±3.7	NZ4090
700911	-24.5	$508.0 \pm 3.9$	NZ2236	750620	-23.9	384.5±3.3	NZ4092
701010	-24.3	498.6±3.9	NZ2237	750709	-23.1	377.3±3.3	NZ4094
701106	-23.3	497.6±4.0	NZ2238	750810	-24.9	378.1±3.7	NZ4108
701223	-22.7	495.6±3.9	NZ2239	750912	-26.2	367.5±3.7	NZ4110
710110	-22.3	500.6±3.9	NZ2240	751003	-23.6	$354.0 \pm 8.8$	NZ4121
710205	-23.8	494.7±3.7	NZ2241	751010	-22.4	365.3±3.3	NZ4119
710305	-24.6	508.3±3.9	NZ2242	751115	-23.0	363.8±3.7	NZ4122
710409	-24.8	501.0±3.9	NZ2243	751205	-23.6	370.8±3.7	NZ4124
710507	-24.9	499.7±3.9	NZ2244	760113	-23.8	373.4±3.7	NZ4126
710611	-24.6	499.0±3.9	NZ2245	760206	-24.3	368.1±3.3	NZ4135
710709	-25.9	494.2±4.1	NZ2246	760306	-23.7	366.7±3.1	NZ4137
710808	-23.5	483.3±4.0	NZ2248	760410	-23.0	$346.1 \pm 3.3$	NZ4145
710910	-24.5	478.8±4.5	NZ2247	760510	-22.9	$359.6 \pm 3.3$	NZ4140
711010	-24.0	492.5±3.9	NZ2249	760606	-25.0	$360.9 \pm 3.4$	NZ4144
711203	-24.8	479.3±3.9	NZ2251	760704	-22.2	365.0±5.0	NZ4302
720109	-23.9	484.5±3.6	NZ2252	760815	-23.9	343.3±3.7	NZ5659
720206	-24.7	491.6±4.0	NZ2253	761011	-22.9	344.2±5.1	NZ5673

TABLE 1 (continued)

	$\delta^{13}$ C	$\Delta^{14}$ C	Lab		1	$\delta^{13}$ C	$\Delta^{14}$ C	Lab
Date	‰	%0	number		Date	‰	‰	number
761104	-25.3	346.5±3.3	NZ5675	1	811203	-25.4	254.8±3.2	NZ6067
761210	-23.6	329.6±3.7	NZ5678		820402	-25.4	* 385.6±3.7	NZ6432
770103	-24.5	332.9±3.7	NZ5679		820509	-23.5	$245.2 \pm 3.2$	NZ6449
770211	-24.3	347.0±5.3	NZ5688		820605	-25.0	248.5±3.2	NZ6450
770311	-24.7	335.4±4.5	NZ5690		820708	-23.3	$249.2 \pm 3.8$	NZ6451
770506	-24.8	332.9±3.3	NZ5697		820902	-25.8	$241.3 \pm 3.2$	NZ6459
770612	-24.1	335.6±4.7	NZ5699		821206	-25.2	235.5 + 3.4	NZ6523
770715	-22.4	331.5±3.7	NZ5900		830117	-24.1	2336+37	NZ6527
770813	-24.1	323.6±3.3	NZ5702		830207	-24.9	2274+37	NZ6528
770909	-24.8	317.6±3.3	NZ5707		830306	-25.8	$2339 \pm 33$	NZ6529
771001	-28.1	$335.1 \pm 3.4$	NZ5730		830519	-22	$* 398 4 \pm 15 5$	NZ6623
771007	-24.2	322.0 + 3.7	NZ5731		830607	-25.2	$235.6 \pm 3.7$	NZ6530
771111	-23.4	325.0+3.7	NZ5732		830819	-25.0	$235.0\pm3.7$	NZ6538
780502	-24.6	314.6+3.7	NZ5866		831015	-24.0	200.0±0.7	NZ6520
780611	-25.8	3104+37	NZ5867		831020	-2-7-3	* 200 0+0 6	NZ6624
780630	-25.9	3148+37	NZ5868		840115	-25.0	230.0±3.0	NZ6540
780804	-25.2	$308.8 \pm 3.2$	NZ5869		840205	-23.0	$217.3\pm 3.3$	NZ6540
780908	-18.0	$309.0\pm5.1$	NZ5870		840509	-24.2	$230.3\pm3.0$	NZ0349
781007	-25.5	321 2 4 8 0	N75971		040500	-25.5	214.0±3.0	NZ0816
781110	-25 4	$3081 \pm 33$	N75972		040010	-25.9	244.0±4.5	NZ0815
790112	-24 0	$310.2 \pm 3.3$	NZ5010		040709	-25.5	$214.5 \pm 3.0$	NZ0017
700317	-24.3	$310.2\pm3.3$	NZ5011		040003	-20.4	$238.0 \pm 4.4$	NZ6807
700407	-24.7	$302.0\pm3.3$	NZ5911		040910	-25.4	$208.1 \pm 3.5$	NZ6820
700500	-20.0	$304.2\pm3.7$	NZ5912		041111	-25.4	$206.9\pm2.7$	NZ6821
700603	-24.5	290.2±3.2	NZ5913		841202	-26.4	$216.8 \pm 3.3$	NZ6831
790710	-24.5	292.3±3.3	NZ5914		850202	-26.5	$206.9 \pm 3.3$	NZ6847
700910	-24.9	290.0±3.0	NZ0915		850324	-25.4	$209.8 \pm 3.8$	NZ6858
790012	-25.4	$204.0 \pm 3.8$	NZ5916		850706	-27.2	$218.0\pm8.0$	NZ7257
791005	-20.0	202.9±3.7	NZ5950		850809	-25.7	$213.0\pm6.0$	NZ7277
701200	-20.2	$303.5\pm3.6$	NZ5957		850909	-25.8	$204.0\pm6.0$	NZ7272
000010	-24.3	$276.4\pm3.3$	NZ5958		851102	-26.0	$203.4 \pm 4.2$	NZ7408
000212	-25.3	$282.3\pm3.3$	NZ5959		851202	-26.6	$205.1 \pm 4.2$	NZ7409
000300	-25.1	209.0±3.8	NZ5960		860110	-23.7	$204.0 \pm 4.0$	NZ7264
000404	-24.0	$277.6 \pm 3.3$	NZ5961		860214	-26.0	$207.0\pm5.0$	NZ7286
800616	-23.7	279.4±3.3	NZ5969		860331	-26.0	$199.0\pm 5.0$	NZ7382
800706	-23.5	$239.1\pm7.9$	NZ5971		860502	-23.5	$184.0\pm7.0$	NZ7417
800801	-25.4	201.5±3.7	NZOUUO		860712	-25.8	$194.5 \pm 4.2$	NZ/410
800005	-25.0	274.3±3.7	NZ6009		860810	-26.5	$188.3 \pm 3.7$	NZ/412
801000	-24.0	2/0.1±3.3	NZCOIL		860907	-26.1	$200.8 \pm 3.7$	NZ/413
001009	-25.5	282.7±3.7	NZ6011		861005	-26.0	$194.0 \pm 4.0$	NZ7430
801204	-25.0	272.9±3.2	NZ6012		861108	-25.5	$191.0 \pm 4.0$	NZ7431
001204	-25.4	$268.6 \pm 3.4$	NZ6013		861207	-25.6	$189.0 \pm 4.0$	NZ7432
810000	-24.7	$266.0 \pm 3.7$	NZ6014		870103	-25.5	$185.0 \pm 4.0$	NZ7454
810206	-25.4	$260.9 \pm 3.7$	NZ6015		870405	-25.6	$189.0\pm 5.6$	NZ7395
810312	-24.0	$264.1 \pm 4.7$	NZ6016		870510	-25.5	$190.0 \pm 4.2$	NZ7455
010410	-20.2	270.9±3.3	NZ6017		870609	-25.8	$176.2 \pm 4.6$	NZ7456
810507	-24.5	$352.2\pm3.3$	NZ6421					
010000	-20.2	$263.3\pm3.7$	NZ6062		Campbel	i is, Neu	∠ealand, 52.5° €	5, 169.2° E
010809	-20.1	259.5±3.3	NZ6063		/00105	-25.2	501.6±3.9	NZ2600
010904	-25.1	258.0±5.1	NZ6064		/00305	-23.7	$511.0\pm3.9$	NZ2601
011002	-20.0	200.8±3.3	NZ6065		700504	-24.4	512.5±3.9	NZ2604
811101	-25.4	254.7±3.7	NZ6066	l I	700710	-25.2	496.7±3.9	NZ2607

TABLE 1 (continued)

1	$\delta^{13}C$	$\Delta^{14}$ C	Lab		$\delta^{13}C$	$\Delta^{14}$ C	Lab
Date	‰	%0	number	Date	‰	‰	number
700904	-25.6	486.7±3.6	NZ2662				
701104	-24.9	482.6±3.9	NZ2663	Scott Ba	se, Antai	rctica, 77.9° S,	166.7° E
710106	-24.3	494.0±3.9	NZ2664	611105	-26.1	195.7±6.4	NZ2695
710307	-23.3	504.6±3.9	NZ2665	611230	-25.6	196.7±9.6	NZ3577
710404	-18.3	506.1±3.9	NZ2666	620207	-27.7	180.3±9.9	NZ3575
710704	-25.2	489.9±3.7	NZ2667	620228	-27.4	203.2±6.3	NZ3573
710904	-26.1	483.7±5.2	NZ2742	621201	-32.3	251.5±3.9	NZ2373
730105	-26.2	453.9±5.2	NZ2743	630107	-29.1	255.8±4.1	NZ2374
731008	-22.7	409.8±3.7	NZ2690	660102	-26.1	622.0±3.8	NZ2426
731108	-25.2	406.4±3.3	NZ2691	660124	-23.1	635.2±3.9	NZ2417
731206	-26.1	403.3±3.3	NZ2692	660205	-23.8	622.5±3.8	NZ2427
740115	-24.8	404.8±3.3	NZ2693	660217	-14.9	633.3±3.6	NZ2418
740304	-25.4	411.5±3.7	NZ4066	671202	-23.4	573.8±3.9	NZ2493
740404	-25.1	403.2±3.3	NZ4067	671229	-24.6	577.6±3.9	NZ2494
740506	-26.1	412.2±3.7	NZ4068	680129	-21.3	$539.3 \pm 5.2$	NZ2715
740607	-25.9	408.4±3.3	NZ4069	680212	-17.6	573.6±3.9	NZ2495
740706	-25.9	401.1±3.7	NZ4070	681121	-23.2	539.1±3.8	NZ2547
740804	-24.8	402.8±3.7	NZ4071	681216	-25.0	542.3±3.9	NZ2548
740904	-25.4	397.2±3.7	NZ4072	690110	-24.6	545.1±3.8	NZ2549
740908	-26.6	400.4±3.7	NZ4084	690208	-26.3	542.4±3.9	NZ2550
741004	-25.2	420.2±3.2	NZ5644	691106	-19.4	556.6±8.8	NZ2729
741104	-24.1	402.2±3.3	NZ4086	691227	-19.2	476.1±7.3	NZ2730
741208	-22.9	393.5±7.4	NZ3835	700116	-16.4	492.4±7.3	NZ2731
750112	-23.3	393.7±5.1	NZ4127	710408	-22.9	496.2±3.5	NZ2658
750204	-24.4	374.5±4.6	NZ4128	710420	-24.5	497.3±3.9	NZ2657
750313	-24.3	389.3±3.7	NZ4111	710714	-24.5	479.5±3.6	NZ2659
750417	-25.7	395.3±5.1	NZ4112	711112	-27.8	477.7±4.0	NZ2661
750506	-25.2	385.1±5.5	NZ4113	711218	-26.5	477.5±4.0	NZ2660
750608	-25.4	400.4±5.8	NZ4114	730215	-20.5	447.3±3.7	NZ2682
750707	-26.1	368.4±3.3	NZ4115	730412	-23.6	433.7±5.2	NZ2747
750813	-25.1	359.7±3.7	NZ4116	730914	-25.0	432.4±4.5	NZ2750
750908	-22.7	$359.9 \pm 3.2$	NZ4117	731019	-20.3	438.0±6.8	NZ2738
751008	-26.8	373.2±3.3	NZ4129	740423	-22.6	406.7±5.2	NZ3849
751105	-25.1	368.9±3.7	NZ4130	740513	-18.2	400.1±6.9	NZ3825
751204	-25.9	364.0±3.3	NZ4131	740816	-19.0	340.8±8.7	NZ3826
760104	-24.7	370.4±3.3	NZ4132	751008	-16.6	403.8±5.2	NZ3850
760204	-25.4	363.8±3.7	NZ4133	751123	-26.1	361.7±3.3	NZ5660
760304	-25.3	353.6±3.7	NZ5666	751230	-25.6	361.6±3.3	NZ5661
760406	-25.3	$362.1 \pm 3.3$	NZ5667	760130	-25.5	$368.9 \pm 3.3$	NZ5662
760504	-24.3	352.5±3.2	NZ5668	760316	-22.4	374.0±5.1	NZ5663
760604	-25.5	350.2±3.5	NZ5669				
760704	-24.8	351.4±3.3	NZ5670				
760803	-25.2	344.0±3.3	NZ5671				
760904	-25.3	343.0±3.2	NZ5681				
761004	-24.9	330.4±3.2	NZ5682				
761104	-25.3	333.3±3.7	NZ5683				
761204	-25.2	342.0±3.3	NZ5684				
770104	-24.3	337.7±3.3	NZ5685				
770204	-23.5	334.3±3.7	NZ5686				



Fig 1.  $\Delta^{14}$ C values measured in atmospheric CO<sub>2</sub> at (A) Wellington, New Zealand and (B) other sites in the South Pacific, 1954–1987. Symbols used in (B) are: + Tarawa Is, 1.5°N; \* Funafuti, 8.5°S; O Suva, 18.1°S; × Melbourne, 37.8°S;  $\Box$  Campbell Is, 52.5°S; and  $\triangle$  Scott Base, 77.9°S.

slightly lower at higher latitudes during 1966–1976. The data from Melbourne are ca  $25\%_{00}$  lower than the Wellington data, and as pointed out by Rafter and O'Brien (1970), this is likely to be due to a local effect of fossil-fuel carbon at the monitoring site which was a rooftop in the center of Melbourne city.

The <sup>14</sup>C record for the South Pacific in Figures 1 A, B clearly shows a peak in 1965 occurring a little over one year later than that observed in the Northern Hemisphere (Nydal & Lovseth 1983; Levin *et al* 1985). Although Northern Hemisphere surface measurements of <sup>14</sup>CO<sub>2</sub> were higher than those reported here in the mid-1960s, this difference had disappeared by 1968. From 1980 onwards, the Southern Hemisphere  $\Delta^{14}$ C values appear slightly higher than those measured in Europe. This is consistent with a regional "Suess" effect influencing the European data. The continuing fall of excess <sup>14</sup>CO<sub>2</sub> has a 1/e time of ca 17 yr.

TABLE 2
$\Delta^{14}$ C for South Pacific sites relative to Wellington statistics of differences in data for the same month

	No of			Standard
	common	Median	Mean	deviation
Site	months	difference	difference	about mean
Tarawa, 1.5°N	58	8.7	7.3	16.2
Funafuti, 8.5°S	34	8.6	10.2	17.0
Suva, 18.1°S	86	8.7	8.7	20.3
Melbourne, 37.8°S	60	-22.3	-27.0	23.4
Campbell Is, 52.5°S	50	-6.4	-3.5	13.9
Scott Base, 77.9°S	29	-4.5	-6.6	21.1

The seasonal structure in the region of the peak Southern Hemisphere values is much less pronounced than for Northern Hemisphere data. This, together with the later arrival of the peak in the Southern Hemisphere, is consistent with the fact that most of the release of <sup>14</sup>C from nuclear weapons testing occurred in the Northern Hemisphere. Further, it is well established (Telegadas 1971) that most of the <sup>14</sup>C inventory produced by nuclear tests was located in the stratosphere by the mid-1960s. Figure 2 shows this stratification of the <sup>14</sup>C inventory between the stratosphere and troposphere by comparing surface data (Levin *et al* 1985; this work), with tropospheric and stratospheric data (Telegadas 1971).

#### ANALYSIS OF <sup>14</sup>CO<sub>2</sub> DATA

We average all the data (usually just one value) available for Wellington in each month in order to obtain a time series spanning 391 months with 104 missing values. The missing data are fairly evenly distributed through the record and so are unlikely to bias the following analysis.

In order to extract a seasonal component, we must determine a smooth trend in the data about which the seasonal variation occurs. There are many procedures for doing this (eg, Cleveland Freeny & Graedel 1983; Enting 1987). The methods used here are based on "loess" smoothing (Cleveland 1979) and the "STL" procedure for seasonal and trend decomposition (Cleveland & McRae 1989).

Loess smoothing determines a smoothed value at each point in the series from a window of a fixed number of nearest neighbors. The smoothed value is determined by fitting a straight line to the data window using weights that decrease with distance from the subject point. Both loess smoothing and the STL procedure are robust with respect to outliers, *ie*,



Fig 2.  $\Delta^{14}$ C values in the stratosphere and at the earth's surface shown as smooth spline curves fitted to available data; the upper two curves are for the stratosphere and the lower two for the surface; <u>a denotes</u> Northern Hemisphere and <u>a surface</u> data from Levin *et al* (1985) and Southern Hemisphere surface data from this work.

outlier points are identified by an initial calculation, their weights are reduced and the calculation repeated. The STL procedure determines the seasonal and trend components simultaneously with a consistent philosophy of the structure of each. The trend component is determined by loess smoothing of the data minus the seasonal component, the latter being determined for each calendar month by loess smoothing of the data minus the trend component. STL allows arbitrary variation of the seasonal component from month to month within the year (in contrast to band pass filtering methods) but ensures small variation in the seasonal cycle from year to year.

There are inherent difficulties in separating seasonal and trend components for both the rapid rise in  $\Delta^{14}$ C values during the early 1960s and the following decay. Further, the relative distribution of <sup>14</sup>C throughout the atmosphere may have been significantly altered by the very large tesss of the early 1960s. Thus, in order to determine a consistent and slowly varying seasonal component, we have limited the analysis to 1966 onwards.

The STL procedure does not allow for missing data, so missing values have been interpolated by fitting a Reinsch (1967) spline to the data, and adjusting the tension of the spline so that the number of sign changes in residuals agrees with that expected for a random sequence. We have tried alternative procedures for interpolating missing data which do not significantly affect the results. Figures 3A, B, C, show the trend, seasonal and remainder components. The seasonal component shows a cycle of decreasing amplitude with some evidence of a phase change in the latter part of the record.

Up to 1980, the cycle has a maximum in March and a minimum in August; a negative anomaly occurs in December. The amplitude of the cycle decreases steadily from a peak-to-peak range of 20‰ in 1966 to 3‰ in 1980. From 1966–1975, while the shape of the cycle is roughly constant, the amplitude decays exponentially with a 1/e time of 12 yr. From 1980 onwards, a different cycle emerges with an amplitude of ca 5‰, a maximum in July–August



Fig 3. The (A) smooth trend, (B) seasonal and (C) remainder components of the Wellington  $\Delta^{14}$ C data record determined by the STL procedure as discussed in the text.

and minimum in January. If present, this would have been masked in the earlier part of the record by the larger decaying cycle.

A direct indication of the change in the seasonal cycle can be seen by plotting the differences of the original data from a smooth trend, against a calendar month. Figures 4A, B show such "month-plots" of differences from the smooth trend, in the periods 1966–1977 and 1981–1987. Horizontal bars show the mid-mean (mean of values between the upper and lower quartiles) of all data for a given month. Individual data values are shown by a spike from the mid-mean for the corresponding month. The contrast in the annual cycle for these two periods confirms that the change in the seasonal cycle is not an artifact of the interpolation or outlier rejection techniques used with the STL procedure.

Finally, we note that the seasonal cycles at the other South Pacific sites are not well determined by our data, and for some months the differences between sites are large compared with errors due to counting statistics. These appear often enough to suggest that regional variations in <sup>14</sup>CO<sub>2</sub> may be as large as  $20^{0}/_{00}$ .

#### INTERPRETATION OF <sup>14</sup>CO<sub>2</sub> SEASONAL AND TREND VARIATION

The overall decline in atmospheric  ${}^{14}\text{CO}_2$  has been studied extensively in many analyses of the global carbon cycle (Oeschger *et al* 1975; Enting & Pearman 1983). This decline is predominantly determined by the rate of exchange of carbon between the atmosphere and the ocean, and is one of the best determinants of that exchange rate.

Although the seasonal cycle in atmospheric  ${}^{14}CO_2$  has not been well researched, seasonal cycles in other "bomb"-produced radionuclides, particularly  ${}^{90}Sr$  and  ${}^{3}H$ , are influenced by seasonal changes in transport of stratospheric air into the troposphere. The transport of gaseous tracers such as  ${}^{14}CO_2$  is by advection and diffusion, whereas for other radionuclides particulate deposition and rainout phenomena are dominant (Sarmiento & Gwinn 1986; Schell, Sauzay & Payne 1974). Thus, differences between the seasonal cycle of  ${}^{14}CO_2$  and other fallout species are expected.



Fig 4. Seasonal cycles of differences between  $\Delta^{14}$ C data and their smooth trend. Data are grouped by calendar month and shown as spikes from the mid-mean, (A) for period 1966–1977 and (B) for period 1981–1987.

Factors other than transport from the stratosphere also contribute to seasonal variation in  ${}^{14}CO_2$ . Levin (1985) reports variations at a European site due to seasonal changes in the release of fossil-fuel CO<sub>2</sub>, and at an Antarctic site due to seasonal changes in ocean-atmosphere exchange.

The seasonal cycle from 1966 to 1980 is consistent with a seasonal variation in the transfer of "bomb" <sup>14</sup>CO<sub>2</sub> from the stratosphere to the troposphere. The decay in the amplitude of this cycle is then explained by the depletion of the stratospheric inventory. Because mixing within the Southern Hemisphere troposphere occurs within a few months, we assume that the amplitude of the seasonal component seen at the surface is proportional to the amount of <sup>14</sup>CO<sub>2</sub> transferred from stratosphere to troposphere in the previous few months. If this is assumed to be proportional to the <sup>14</sup>CO<sub>2</sub> inventory in the stratosphere, modulated by the seasonally varying exchange rate, then the 12-yr decay time of the seasonal cycle is equal to the mean residence time for stratospheric CO<sub>2</sub>.

This estimate of stratospheric mean residence time is longer than the value of 7.0 yr (half-life of 58 months) derived by Telegadas (1971) from measurements of <sup>14</sup>C in the stratosphere up to 1969. This earlier data may reflect a residence time for just the lower part of the stratosphere. The value derived here is closer to an alternative estimate of 10 yr for the mean residence time of air in the stratosphere based on energy and mass flux (Walker 1977).

#### COMPARISON OF <sup>14</sup>CO<sub>2</sub> DATA WITH ATMOSPHERIC TRANSPORT MODELS

Modeling of tracer transport in the atmosphere due to advection and diffusion has progressed considerably in recent years (Mahlman, Levy & Moxim 1980; Golombek & Prinn 1986). Models that incorporate consistent global circulation and realistic (if approximate) climatology can now be used to predict tracer concentrations. This approach is preferable to inferring atmospheric transport from tracer data alone.

We now present some results using a two-dimensional model for atmospheric transport (Plumb & Mahlman 1987; Plumb & McConalogue 1988) which is a zonally averaged version of a larger three-dimensional global circulation model (GCM) (Mahlman & Moxim 1978). The zonally averaged version gives the same net tracer transport as the three-dimensional model, but requires much less computer time. A resolution of 2.4° in latitude and 10 vertical levels extending to the 10mBar level (33km) are used.

The vertical diffusion coefficients at the lowest two layers were increased to  $8m^2s^{-1}$  (bottom level) and  $6m^2s^{-1}$  (next lowest level), based on other work using this model for determining seasonal variation of atmospheric CO<sub>2</sub> concentrations (Plumb, pers commun). Otherwise the fields determining atmospheric transport are as determined from the three-dimensional GCM.

To relate our South Pacific <sup>14</sup>CO<sub>2</sub> data with this model, it was run from an initial condition where a tracer is injected instantaneously with uniform concentration throughout the lower three grid layers of the stratosphere representing pressure levels 110, 65 and 38mbar. The only sink for the tracer is at the surface, where there is a uniform sink strength set to give approximately the observed overall decay rate from 1966 onwards. Figure 5 shows the tracer concentration at 45°S predicted by the model. Note that results for the first two years are sensitive to the artificial initial conditions. Figure 6 shows a month plot, in the same format as Figure 4A, of the seasonal component of this predicted time series, extracted using the STL procedure after removal of the first two years of data.

There is a significant discrepancy in phase between the predicted seasonal cycle in Figure 6 and the observed one in Figure 4A. The model predicts that the concentration of a tracer injected into the stratosphere will peak in September and reach a minimum in January, almost totally out of phase with the observed result. This implies that either the seasonality of vertical transport in the model is incorrect or the observed seasonal cycle in  $^{14}CO_2$  is determined by effects other than seasonality in transport from the stratosphere.



Fig 5. Predicted concentration of tracer at 45°S after a stratospheric injection in the two-dimensional model discussed in the text. The units on the vertical axis are arbitrary.

The seasonal cycles for <sup>90</sup>Sr and <sup>3</sup>H in the Southern Hemisphere (Taylor 1968) are different from that given here for <sup>14</sup>CO<sub>2</sub>. As already mentioned, different transport effects determine the concentration of these isotopes observed at the surface. <sup>90</sup>Sr is deposited by aerosols with tropospheric lifetimes on the order of weeks, so its annual cycle at the surface closely follows variations in input from the stratosphere. In contrast, variations in the long-lived <sup>14</sup>CO<sub>2</sub> should lag behind, and in fact be almost completely out of phase with their input from the stratosphere. Comparing Taylor's results with ours shows the <sup>14</sup>CO<sub>2</sub> cycle lags by ca 5 months, much as expected. As the <sup>90</sup>Sr and <sup>14</sup>CO<sub>2</sub> data support one another, we believe that the annual cycle in transport between the stratosphere and the troposphere as used in the zonally averaged GFDL model is incorrect.

#### <sup>14</sup>CH<sub>4</sub> MEASUREMENTS IN THE SOUTH PACIFIC

There are many known sources of atmospheric methane (Khalil & Rasmussen 1983). The major sources appear to be biogenic, such as ruminant animals and rice paddies, in which methane is produced by anaerobic bacteria. Further, atmospheric methane concentra-



Fig 6. The seasonal cycle in the predicted concentration of tracer at 45°S after a stratospheric injection in the two-dimensional model discussed in the text. The format is as used in Figure 4 and the units on the vertical axis are arbitrary.

tions have been increasing at ca 1%/a over recent decades, suggesting an increasing source strength.

Measurement of <sup>14</sup>C in atmospheric methane provides a way to determine the relative amount of methane released from fossil fuel and primordial methane sources (Ehhalt 1973). Lowe *et al* (1988) recently reported Accelerator Mass Spectrometry (AMS) measurements from the South Pacific which showed lower ( ${}^{14}C/{}^{12}C$ ) ratios than anticipated, and indicated a significant (25–35%) component of recently released methane has been of fossil origin. Carbon isotope measurements of atmospheric methane from clean air, extending those given by Lowe *et al* and using the same sampling techniques, are shown in Table 3. We include 7 new measurements and omit 2 reported earlier which do not meet stricter consistency criteria now imposed on our AMS data to screen out unsatisfactory graphite targets.

All reported methane samples were taken at Baring Head (41°S, 175°E) near Wellington, New Zealand, under baseline conditions, *ie*, periods of strong onshore winds and while simultaneously measured CO<sub>2</sub> concentrations indicate well-mixed air. The sample mean and standard deviation for  $\delta^{14}$ C values in Table 3 is +78 ± 94%. The sample standard deviation is higher than the mean error associated with the AMS measurement, and this indicates some noise due to sampling and CH<sub>4</sub> extraction procedures.

An improved atmospheric methane sampling method is being developed in which sampled air is pumped through a molecular sieve into 67L stainless steel tanks to a pressure of ca 120 psi. Methane is subsequently extracted in the laboratory by oxidation to, and collection of  $CO_2$ , after use of a high-efficiency cryogenic trap to remove any residual  $CO_2$  and water vapor in the tanks.

In the next two sections, we indicate the nature of the constraints placed on methane sources by the isotope ratios of atmospheric methane. The analysis is based on a very simple model of methane sources, which classifies these as either "modern" or "fossil" and uses average values for the isotope ratios of each. Allowance is also made for <sup>14</sup>CH<sub>4</sub> from nuclear power plants. A more realistic model would incorporate sources of intermediate age, such as

 TABLE 3

 Carbon isotopic composition of atmospheric methane collected at Baring Head, New Zealand, under baseline conditions

Date	$\delta^{13}C$ (%)	pMC % mod	$\delta^{14}C$ (%)	Lab no.
870312	-47.24 + 0.05	102.7 + 5.4	-19 + 52	NZA-47
870316	$-47.03 \pm 0.05$	$106.8 \pm 3.3$	$+20 \pm 32$	NZA-62
870317	$-48.90 \pm 0.05$	102.3 ± 5.7	$-27 \pm 54$	NZA 46
870410	$-46.10 \pm 0.05$	$106.7 \pm 2.6$	$+21 \pm 25$	NZA 52
870616	$-45.68 \pm 0.05$	$105.4 \pm 5.2$	$+10\pm50$	NZA105
870619	$-45.57 \pm 0.05$	$104.0\pm4.5$	$-3\pm43$	NZA117
870626	$-45.96 \pm 0.05$	$109.5 \pm 3.6$	$+48 \pm 34$	NZA119
870626	$\textbf{-48.59} \pm \textbf{0.05}$	$129.1\pm6.5$	+229 $\pm$ 62	NZA135
870626	$-46.37 \pm 0.05$	$111.2 \pm 5.8$	$+64\pm55$	NZA142
870702	$\textbf{-45.80} \pm 0.05$	$131.3 \pm 5.4$	$+258\pm52$	NZA143
870715	$\textbf{-42.57} \pm 0.05$	$122.4\pm4.7$	$+180\pm45$	NZA201
870723	$\textbf{-46.62} \pm \textbf{0.05}$	$105.8\pm10.0$	$+12 \pm 96$	NZA128
870812	$\textbf{-45.05} \pm \textbf{0.05}$	$118.7\pm7.9$	$+138\pm76$	NZA150
870923	-40.	$122.7\pm4.4$	+189 $\pm$ 42	NZA225
871117	-46.9 ±0.05	$115.9\pm4.8$	+107 $\pm$ 46	NZA226
880317	-45.9 ± 0.05	$119.7\pm9.0$	$+146\pm87$	NZA273
880412	-43.9 ±0.05	$97.8\pm2.7$	$-60\pm26$	NZA297
880513	$\textbf{-43.79} \pm 0.05$	$113.6\pm4.8$	$+93\pm46$	NZA305

swamps, and use direct isotope measurements of a range of sources with appropriate source strengths. However, the simpler analysis gives an upper estimate for the proportion of methane derived from fossil fuel, and demonstrates the sensitivity of such estimates to some general parameters of atmospheric transport and chemistry.

#### A TWO BOX ATMOSPHERE MODEL FOR CH<sub>4</sub> ISOTOPES

To interpret the <sup>14</sup>CH<sub>4</sub> data above, we use a model treating the two hemispheres as well-mixed boxes with mass balanced exchange and consider the inventories of CH<sub>4</sub>, <sup>13</sup>CH<sub>4</sub> and <sup>14</sup>CH<sub>4</sub> separately. The changes in inventories are related to fluxes by

$$\frac{d}{dt}C_{h} = Q_{h} - k (C_{h} - C_{h'}) - \lambda C_{h}$$

$$\frac{d}{dt}{}^{13}C_{h} = {}^{13}Q_{h} - k ({}^{13}C_{h} - {}^{13}C_{h'}) - \epsilon \lambda {}^{13}C_{h}$$

$$\frac{d}{dt}{}^{14}C_{h} = {}^{14}Q_{h} - k ({}^{14}C_{h} - {}^{14}C_{h'}) - \epsilon^{2} \lambda {}^{14}C_{h}$$
(1)

where:

$$\begin{split} h & \mbox{labels the hemisphere S or N;} \\ h' & \mbox{labels the alternate hemisphere;} \\ C_h, {}^{13}C_h \mbox{and } {}^{14}C_h & \mbox{are the inventories of CH}_4, {}^{13}CH_4 \mbox{and } {}^{14}CH_4 \mbox{ in hemisphere h;} \\ a & \mbox{are the source fluxes of CH}_4, {}^{13}CH_4 \mbox{and } {}^{14}CH_4 \mbox{ into hemisphere h;} \\ a & \mbox{are the source fluxes of CH}_4, {}^{13}CH_4 \mbox{and } {}^{14}CH_4 \mbox{ into hemisphere h;} \\ b & \mbox{are the source fluxes of CH}_4, {}^{13}CH_4 \mbox{and } {}^{14}CH_4 \mbox{ into hemisphere h;} \\ b & \mbox{are the source fluxes of CH}_4, {}^{13}CH_4 \mbox{and } {}^{14}CH_4 \mbox{ into hemisphere h;} \\ b & \mbox{are the inter-hemispheric fractional exchange coefficient, taken to be (2 \mbox{yr})^{-1}; \\ \lambda & \mbox{is the inverse mean life of CH}_4, taken to be (9.6 \mbox{yr})^{-1} \mbox{ following Prinn et } \\ a & \mbox{al (1987). Note that the small difference between the mean life of } {}^{12}CH_4 \mbox{and CH}_4 \mbox{ is ignored here;} \\ \epsilon & \mbox{is the kinetic isotope effect coefficient, taken to be } 0.990 \pm 0.007 \mbox{ following Davidson et al (1987) ((k_{13}/k_{12}) \mbox{ in their notation).} \end{split}$$

The solution of these equations can be written as

$$C_{N}(t) + C_{S}(t) = \int_{-\infty}^{t} e^{\lambda(x-t)} \left( Q_{N}(x) + Q_{S}(x) \right) dx$$
  
$$C_{N}(t) - C_{S}(t) = \int_{-\infty}^{t} e^{(2k+\lambda)(x-t)} \left( Q_{N}(x) - Q_{S}(x) \right) dx$$
(2)

with similar equations for <sup>13</sup>C and <sup>14</sup>C.

The inventories are sensitive to the source flux terms Q only over the last few mean lifetimes of  $CH_4$ , *ie*, over the last few decades. For the recent past, we assume that the total  $CH_4$  source flux has increased exponentially at 1%/a and further that the regional distribution of fluxes has remained constant. Then

$$Q_N(x) + Q_S(x) = Q_{\text{tot}} e^{\mu(x-1987)}$$

$$Q_N(x) - Q_S(x) = \Delta Q_{\text{tot}} e^{\mu(x-1987)}$$
(3)

where:

 $Q_{\text{tot}}$  is the total CH<sub>4</sub> release/a in 1987;

 $\Delta Q_{\text{tot}}$  is the excess release in the Northern Hemisphere over the Southern Hemisphere;  $\mu$  is the exponential increase rate, taken as 0.01. Evaluating the appropriate integrals in equation (2) we have for the total  $CH_4$  inventories:

$$C_{N}(t) + C_{S}(t) = \frac{Q_{\text{tot}}}{\lambda + \mu} e^{\mu(t - 1987)}$$

$$C_{N}(t) - C_{S}(t) = \frac{\Delta Q_{\text{tot}}}{2k + \lambda + \mu} e^{\mu(t - 1987)}.$$
(4)

Assuming, in 1987, a mean atmospheric CH<sub>4</sub> concentration of 1670 ppb, and an interhemispheric difference of 90 ppb (Steele *et al* 1987; Fraser *et al* 1986), an atmospheric mass of  $1.82 \times 10^{20}$  moles, and values of  $\lambda$ ,  $\mu$  and *k* already quoted, we have

$$Q_{\text{tot}} = 3.47 \times 10^{13} \text{ moles/a}$$
  
 $\Delta Q_{\text{tot}} = 0.91 \times 10^{13} \text{ moles/a}.$ 

To determine the inventories of  ${}^{13}CH_4$  and  ${}^{14}CH_4$ , we assume that the  $CH_4$  source can be separated into fossil and modern carbon components each having different isotope ratios, which together with the relative proportions of the two sources, have not changed in recent decades. Then

$${}^{13}Q_h(t) = (1 + \alpha \,{}^{13}\delta_{\text{fos}} + (1 - \alpha) \,{}^{13}\delta_{\text{mod}}) \,{}^{13}R_0 Q_h(t) \tag{5}$$

where:

 $\begin{array}{ll} \alpha & \text{is the fossil carbon fraction of the total CH<sub>4</sub> source} \\ {}^{13}R_0 & \text{is the } ({}^{13}\text{C}/{}^{12}\text{C}) \text{ ratio of the PDB standard} \\ {}^{13}\delta_{\text{fos}} & \text{is the } \delta^{13}C_{\text{PDB}} \text{ of the fossil carbon CH}_4 \text{ source} \\ {}^{13}\delta_{\text{mod}} & \text{is the } \delta^{13}C_{\text{PDB}} \text{ of the modern carbon CH}_4 \text{ source}. \end{array}$ 

The inventories resulting from these fluxes are given by

$${}^{13}C_N(t) + {}^{13}C_S(t) = (1 + \alpha {}^{13}\delta_{\text{fos}} + (1 - \alpha) {}^{13}\delta_{\text{mod}}) {}^{13}R_0 \frac{Q_{\text{tot}}}{\epsilon \lambda + \mu} e^{\mu(t - 1987)}$$
$${}^{13}C_N(t) - {}^{13}C_S(t) = (1 + \alpha {}^{13}\delta_{\text{fos}} + (1 - \alpha) {}^{13}\delta_{\text{mod}}) {}^{13}R_0 \frac{\Delta Q_{\text{tot}}}{2k + \epsilon \lambda + \mu} e^{\mu(t - 1987)}.$$
(6)

Turning next to  ${}^{14}CH_4$ , note that the fossil carbon source has no contribution to  $Q_h$ , but that a nuclear power source (Povinec, Chudy & Sivo 1986) must be considered even though this is a negligible source of total CH<sub>4</sub>. Thus

$${}^{14}Q_N(t) = (1 - \alpha) \left(1 + {}^{14}\delta_{\text{mod}}(t)\right) {}^{14}R_0 Q_N(t) + {}^{14}Q_{\text{Nuc}}(t)$$
$${}^{14}Q_S(t) = (1 - \alpha) \left(1 + {}^{14}\delta_{\text{mod}}(t)\right) {}^{14}R_0 Q_S(t)$$
(7)

where:

<sup>14</sup> $\delta_{mod}(t)$  is the mean  $\delta^{14}$ C of the modern carbon source <sup>14</sup> $R_0$  is the  $({}^{14}C/{}^{12}C)$  ratio of the modern  ${}^{14}C$  standard (0.95 NBS oxalic acid), taken to be 1.176 × 10<sup>-12</sup> following Karleen *et al* (1964) and

 $^{14}Q_{\text{Nuc}}(t)$  is the nuclear power source term.

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This leads to

$${}^{14}C_{N}(t) + {}^{14}C_{S}(t) = \int_{-\infty}^{t} e^{\epsilon^{2}\lambda(x-t)} \left[ (1-\alpha) \left( 1 + {}^{14}\delta_{\mathrm{mod}} \right) {}^{14}R_{0}Q_{\mathrm{tot}} e^{\mu(x-1987)} + {}^{14}Q_{\mathrm{Nuc}}(x) \right] dx$$

$${}^{14}C_{N}(t) - {}^{14}C_{s}(t) = \int_{-\infty}^{t} e^{(2k+\epsilon^{2}\lambda)(x-t)} \left[ (1-\alpha) + (1+{}^{14}\delta_{\mathrm{mod}}) {}^{14}R^{0}\Delta Q_{\mathrm{tot}} e^{\mu(x-1987)} + {}^{14}Q_{\mathrm{Nuc}}(x) \right] dx. \quad (8)$$

The value of  ${}^{14}\delta_{mod}(t)$  has changed with time due to changes in the  $\delta^{14}C$  of atmospheric  $CO_2$  which provides the carbon from which the modern  $CH_4$  is derived. We assume a residence time of one year between carbon photosynthesis and methane production, and correct for fractionation to  $\delta^{13}C$  of  $-65\%_{00}$  (note this is the inferred value of  $\delta^{13}C$  for the modern carbon  $CH_4$  source—see below). Thus

$$(1 + {}^{14}\delta_{\rm mod}(t)) = \left(\frac{1 - 65\%_{00}}{1 - 25\%_{00}}\right)^2 (1 + \Delta^{14}C_{\rm atm}(t-1))$$
(9)

where  $\Delta^{14}C_{atm}(t)$  is the atmospheric  $\Delta^{14}C$  value for time t. In order to estimate this last term, we use an average of the atmospheric <sup>14</sup>C data of Levin *et al* (1985) representing the Northern Hemisphere, and the atmospheric <sup>14</sup>C data given here representing the Southern Hemisphere. Where the Northern Hemisphere data is missing we assume it is the same as the Southern Hemisphere, and prior to 1955 we assume a constant value of  $-200/_{00}$ . The lower limit of the integration range in equation (8) is taken as 1940, as the integrands become negligible prior to this. Numerical integration then produces

$$\int_{-\infty}^{1987} (1 + {}^{14}\delta_{\text{mod}}) e^{(\epsilon^2 \lambda + \mu)(x - 1987)} dx = 10.718$$
$$\int_{-\infty}^{1987} (1 + {}^{14}\delta_{\text{mod}}) e^{(2k + \epsilon^2 \lambda + \mu)(x - 1987)} dx = 1.0037.$$
(10)

Levin (pers commun) has estimated the nuclear power term  $Q_{Nuc}(t)$  and we use her estimates here. In 1987 the estimated release rate is 1100 Ci/a, corresponding to 17.6 moles of  ${}^{14}CH_4/a$ . This is more conveniently expressed as 0.43  ${}^{14}R_0Q_{tot}$ , based on the value of  $Q_{tot}$  given above. Using Levin's exponential growth rates, we have

$$Q_{\text{Nuc}}(t) = 0.43 \,{}^{14}R_0 Q_{\text{tot}} \, e^{0.16(t-1987)}, \text{ for } t = 1975 \text{ to } 1987,$$

$$Q_{\text{Nuc}}(t) = 0.063 \,{}^{14}R_0 Q_{\text{tot}} \, e^{0.26(t-1975)}, \text{ for } t = 1969 \text{ to } 1975 \text{ and}$$

$$Q_{\text{Nuc}}(t) = 0, \text{ for } t \le 1969. \tag{11}$$

The integrals in equation (8) involving  $Q_{\text{Nuc}}$  can now be evaluated as

$$\int_{-\infty}^{1987} e^{\epsilon^2 \lambda (x-1987)} Q_{\text{Nuc}}(x) \, dx = 1.6153^{-14} R_0 Q_{\text{tot}}$$

$$\int_{-\infty}^{1987} e^{(2k+\epsilon^2 \lambda)(x-1987)} Q_{\text{Nuc}}(x) \, dx = 0.3407^{-14} R_0 Q_{\text{tot}}.$$
(12)

#### INTERPRETATION OF <sup>14</sup>CH<sub>4</sub> DATA

We can now calculate  $\alpha$ , the fossil carbon fraction, from observed  $\delta^{14}$ C values for atmospheric CH<sub>4</sub>. To summarize, values of k,  $\lambda$ ,  $\mu$ , and mean hemispheric CH<sub>4</sub> concentrations are used to estimate  $Q_{tot}$  and  $\Delta Q_{tot}$ ; then estimates of  $\epsilon$ ,  ${}^{14}\delta_{mod}(t)$  and  ${}^{14}Q_{Nuc}(t)$  are used to calculate the hemispheric {}^{14}CH\_4 inventories relative to the total CH<sub>4</sub> inventory in terms of

an unknown  $\alpha$ . Finally, we relate the inventory ratio to the observed  $\delta^{14}$ C using

$$\frac{{}^{14}C_s}{C_s} = {}^{14}R_0 \left(1 + \delta^{14}C_{obs}\right)$$
(13)

giving an equation which is solved for  $\alpha$ . With the parameters values given above, this leads to

$$1.226 (1 - \alpha) + 0.150 = (1 + \delta^{14}C_{obs})$$

where 1.226 is the value of  $(1 + \delta^{14}C)$  that would arise if the only source was from modern carbon, and 0.150 is the shift due to the nuclear power source. From these values we have  $\alpha = 0.243$ .

Consistency of the <sup>13</sup>CH<sub>4</sub> and <sup>14</sup>CH<sub>4</sub> budgets is now considered. Equation 6 predicts a slight difference in the  $\delta^{13}$ C values of CH<sub>4</sub> for the two hemispheres. This arises because the larger source term in the Northern Hemisphere leads to a net export of aged (and, due to the kinetic oxidation effect, heavier) CH<sub>4</sub> to the Southern Hemisphere. Ignoring this very small effect, we have

$$1 + \delta^{13} C_{obs} \approx \frac{\lambda + \mu}{\epsilon \lambda + \mu} \left( 1 + \alpha^{13} \delta_{fos} + (1 - \alpha)^{13} \delta_{mod} \right)$$

or, to a good approximation

$$\delta^{13}C_{obs} \approx \alpha^{13}\delta_{fos} + (1-\alpha)^{13}\delta_{mod} + 9\%_{00}.$$
 (14)

If the fossil CH<sub>4</sub> source is assumed to be entirely from fossil fuels then the value of  ${}^{13}\delta_{\text{fos}}$  should be ca  $-30^{\circ}/_{00}$  and, in order to explain  $\delta^{13}C_{\text{obs}} = -47^{\circ}/_{00}$ , we must have  ${}^{13}\delta_{\text{mod}} \approx -65^{\circ}/_{00}$ . Although this inferred value is slightly lighter than that used in other CH<sub>4</sub> budgets (eg, Tyler, Blake & Rowland 1987; Stevens & Engelkemeir 1988), it is well within the range of  $\delta^{13}$ C values of the known sources of modern carbon CH<sub>4</sub>. Equation 13, based on observed  ${}^{14}$ C values, gives a more reliable estimate of  $\alpha$  than Equation 14, based on  ${}^{13}$ C values, because of the considerable uncertainty in  ${}^{13}\delta_{\text{mod}}$  in the latter. Thus, we have used equation 13 to determine  $\alpha$  and equation 14 to check consistency.

To estimate the sensitivity of  $\alpha$  to the parameters of this two-box model, we consider the effect of making variations in these parameters of the order of their uncertainties. This leads to

parameters as described above	$\alpha = 0.243$
k changed from $(2 \text{ yr})^{-1}$ to $(1 \text{ yr})^{-1}$	$\alpha = 0.255$
$\lambda$ changed from (9.6 yr) <sup>-1</sup> to (8.6 yr) <sup>-1</sup>	$\alpha = 0.252$
$\epsilon$ changed from 0.990 to 0.997	$\alpha = 0.233$
$Q_{\text{Nuc}}$ reduced to half equation (11)	$\alpha = 0.182$
$\delta^{14}C_{obs}$ changed from +78% to +172%	$\alpha = 0.166.$

This shows that  $\alpha$  is not very sensitive to the methane lifetime estimate, the kinetic isotope effect or the inter-hemispheric exchange time. Yet it is sensitive to the magnitude of the nuclear power source term, and to the value of  ${}^{14}\delta_{obs}$ . The estimated growth rate of 17%/a in the total nuclear power  ${}^{14}CH_4$  should cause a significant increase in the  $\delta^{14}C$  of atmospheric CH<sub>4</sub>. The figures used in the previous section imply an increase in the Southern Hemisphere of ca 25%/00/a and, provided the fossil carbon fraction  $\alpha$  is not also increasing, this should be clearly measurable after 2 to 3 years of measurements.

A more detailed calculation of the transport of methane between the hemispheres has been carried out using the zonally averaged atmospheric transport model already described. When the model is run with a northern mid-latitude tracer source and a uniformly distributed sink corresponding to a tracer lifetime of 10 yr, the difference between the predicted values of the tracer concentrations at 45°N and 45°S corresponds to a 2.5-yr inter-hemispheric exchange time. This supports the value of k used above.

#### CONCLUSION

Our 32-yr record of atmospheric  ${}^{14}CO_2$  measurements in the South Pacific covers nearly all the period in which atmospheric  ${}^{14}C$  has been influenced by nuclear weapons testing, and begins with  $\Delta^{14}$ C values below zero. Since 1966 the decrease of this "bomb" carbon in the atmosphere has roughly followed an exponential decay with a 1/e time of 17 yr. From 1966–1977, the <sup>14</sup>CO<sub>2</sub> data show a small latitudinal variation, and a definite seasonal cycle peaking in February. This seasonal cycle in <sup>14</sup>CO<sub>2</sub> is believed due to seasonal changes in the rate of transport of "bomb" carbon from the stratosphere and is consistent with the cycle of other fallout products. The cycle decayed in amplitude with a 1/e time of 12 yr, which is inferred to be the mean residence time for  $CO_2$  in the stratosphere.

A two-dimensional model of atmospheric transport based on a three dimensional general circulation model predicts a seasonal cycle in the arrival of a tracer injected into the stratosphere, but the phase of the predicted cycle disagrees with that observed for <sup>14</sup>CO<sub>2</sub>. It would seem that stratosphere-to-troposphere transport is not estimated correctly in the model.

An analysis of <sup>14</sup>CH<sub>4</sub> data has shown how these can be used to estimate the fraction of atmospheric methane derived from fossil carbon. A major uncertainty in this estimate appears to be the contribution of nuclear power plants to  ${}^{14}CH_4$  in the atmosphere. However, comparable measurements in both hemispheres over a number of years should enable the nuclear power source of CH<sub>4</sub> to be better determined.

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### RE-EVALUATION OF BRITISH MUSEUM RADIOCARBON DATES ISSUED BETWEEN 1980 AND 1984

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ABSTRACT. Dates issued by the British Museum radiocarbon laboratory between 1980 and 1984 are known to have been in error. This paper outlines the cause of the problem and the procedures adopted to revise the results affected. Where revision has been possible, on average this has given dates older by 200 to 300 radiocarbon years. The individual revised results are tabulated.

#### INTRODUCTION

The British Museum radiocarbon laboratory has employed liquid scintillation counting for some years. In the early 1980s, two counters were in operation with a scintillation cocktail comprising 5.5ml of sample benzene and 9.5ml of toluene containing PPO. Each counter was normally operated with only one modern (NBS oxalic) and two background samples. It is now known that from 1980 to 1984, BM <sup>14</sup>C results were in error, being too young by amounts that depend on the date of measurement and on the counter used (Tite *et al* 1987, 1988). This paper outlines how the problem was identified and the procedures adopted to try to provide revised results for some 470 archaeological samples; a more detailed report is available from the authors.

#### **IDENTIFICATION OF THE ERROR**

When the results of the intercomparison of radiocarbon measurements organized by the Glasgow group were published (International Study Group 1982), the BM results for samples measured in mid-1980 were on average ca 200 yr younger than the consensus data. This contrasted with the findings of an intercomparison organized by Harwell and the British Museum in 1979 in which the BM results were consistent with those of other laboratories (Otlet *et al* 1980).

During 1983 further samples of the wood provided for the Glasgow study were analyzed. The measurements were not conclusively different from the previous results, and the two counters were in agreement; however all data were still different from the Glasgow consensus results. This apparent self-consistency was taken as an indication that the counting system was not the cause of the problem and led to suspicion about the sample pretreatment, since cellulose extraction was not then a routine procedure at the BM. The situation was further clouded by measurements on archaeological samples which apparently gave the correct age or which were in broad agreement, within statistics, with those of other laboratories.

Subsequent more rigorous analysis of all the BM data for the 5-month period, July to November 1980, indicated a slight trend with time of measurement. Counting of the two moderns, one from each counter, in a single counter together with other modern samples, previously synthesized but not then in use for dating, showed an unacceptable range. Counting of archaeological samples ceased at the end of 1984.

Before 1984, the modern samples were kept in the counters for long periods (often several years) and had been infrequently weighed. When weight losses were observed, they were made up either by addition of dead benzene or scintillator solution. No reweighing of background samples or volume adjustments had been made. Given the long residency time of these reference samples in the counters, evaporation losses, particularly of the moderns, seemed the most likely cause of the error.

In addition, no correction was made for the differential loss of benzene relative to toluene in calculating the benzene weights. During the investigation it became apparent that this had a much larger effect than previously thought and hence reweighing of the moderns did not accurately adjust for evaporation losses. The net modern count rate per unit mass of benzene was therefore expected to be in error, even immediately after reweighing. This could not be re-evaluated due to the *ad hoc* addition of either dead benzene or scintillator

solution to make up volume, and moreover, since the screw caps of the vials absorb moisture and must be changed to facilitate reweighing, evaporation losses can be introduced during this process (Otlet & Slade 1974).

#### THE CURRENT COUNTING SYSTEM

To investigate the scale of the problem, the BM counting system was first upgraded. The measures adopted are summarized in Bowman and Ambers (1989) and were designed to remove biases, to ensure that they do not recur and to obtain a realistic measure of precision (now typically  $\pm$  40–50 yr for a full-sized sample equivalent to 5.5ml of benzene). In particular, a sample of accurately and precisely known <sup>14</sup>C age is counted quasi-simultaneously with all samples to be dated. The reference samples, kindly supplied by Mike Baillie and Jon Pilcher, are groups of 10 or 20 rings of bog oak dated by Gordon Pearson's high-precision radiocarbon laboratory in Belfast as part of their calibration study. The first four samples, representing three different ages, that were run by the BM differed on average by 14 years from the Belfast results (standard error  $\pm$  9).

#### THE DATA AVAILABLE TO RE-EVALUATE DATES IN ERROR

The problem period was 1980 to 1984, when some 470 archaeological samples were processed. The ideal solution to the problem would have been to redate from scratch all samples measured during this period. Apart from constraints on time available, this was not possible because few of the samples submitted had been sufficiently large for more than the initial measurement. Recounting of the stored sample cocktails was possible but would not have given accurate results because of additional problems due to evaporation and losses during transfer from counting vial to storage vial and back. The feasibility of evaluating correction factors was therefore investigated.

The data available to investigate the problem for each counter were the count rate for the background samples and the quench-corrected net modern count rate per unit weight, where the weight is not accurately known, as discussed above. Even had it been possible to evaluate the true net modern count rate, the counting efficiency of each counter at any given time was not independently known, and hence the error introduced by evaporation of the modern could not have been calculated directly.

There were a few other samples that had been in the counters over some or all of the problem period. For the data from these to be useful, however, they must be for flame-sealed samples. The results are limited and different for the two counters (referred to as PAC1 and PAC2):

PAC1—throughout the period 1980–1984, the <sup>14</sup>C age for a sample of unknown age (ref BM-477B);

PAC2—for the period from mid-1980 (earlier data could not be retrieved from the computer), the count rates for a hot sample of unknown activity (ref QS1).

Had these not been available, then no attempt could have been made to revise the results. To these data were added the results of redating ca 30 samples from scratch in the upgraded system. The samples were chosen primarily on the basis of sufficient material remaining, but also so that their initial times of measurement were at ca 4-month intervals through the problem period. These samples, together with those from Glasgow run in 1980 and 1983, give a measure of the discrepancy,  $\delta$ , in BM results at specific times. Each discrepancy obviously has an associated error term,  $\sigma$ , which is a combination of the error on the old and that on the new results (or, for the Glasgow samples, on the 1980 BM result and the consensus result).

Many of the redated samples were charcoal which, even for a single archaeological context, may represent a substantial age range. In choosing charcoal samples for redating, care was taken to ensure they were not likely to be dominated by material unrepresentative of the bulk sample as described on submission. To determine whether this assumption was justified, two samples were chosen that were sufficiently large to allow several <sup>14</sup>C measure-

ments. One was bone, the vertebrae of an ox from Badshot (original ref BM-2273). The other was charcoal from Down Farm (original ref BM-1852) (Table 1). The bone results indicate the variation for replicate samples (which is in line with the estimated errors). Four of the charcoal results were on non-selected material (*ie*, no regard was given to anatomy or species). The reasonable reproducibility for these samples is encouraging and necessary for the correction procedures adopted.

#### DATA ANALYSIS FOR THE TWO COUNTERS

Since the data available are different for the two counters, the approach was appropriately adapted.

#### PAC1

Four modern samples were used in PAC1 during the problem period, although only during the latter half of 1984 was there more than one in the counter at the same time. The sealed sample 477B was present throughout. For the period during which the original sample was dated (typically of 3 weeks duration), the correction to be applied has been estimated as the difference between the measured age (m) for the sealed sample (which varied in time) and an estimate of its true value, T, which is unknown, but was estimated from a plot of  $\delta$  vs m for the redated sample. The measured age, m, for a particular week was computed by averaging weekly values in the 3-week period centering on that week. This smoothing process, which was aimed at reflecting basic underlying trends rather than short-term variations, was restarted whenever a sample was reweighed, and after gaps in the record, in order to avoid averaging values obtained under very different conditions. Linear interpolation was applied to find the m value corresponding to the exact date at the mid-point of original measurement period. The correction applied was then given by T-m. Such corrections have a correlation of 0.7 with the discrepancies,  $\delta$ . This implies that ca 50% of the total variation in the discrepancies can be explained by trends in the measured age of the sealed sample, and that the correction is therefore worthwhile. The remaining 50% is obscure and is reflected in the uncertainty in the final corrections.

#### PAC2

One modern (ref M29) was in use in this counter during the whole of the problem period, though for part of 1984, a flame-sealed modern (M14) was also present. The usefulness of the data available from QS1 is limited in that QS1, a hot sample giving in the order of  $10^4$  cpm/g, is not sensitive to background evaporation. Thus it can therefore only be used as a monitor of the effect of gain changes on the modern count rate. Despite this major limitation, it was considered worthwhile to determine which trends in the modern count rate could be attributed to evaporation losses and which to gain changes.

Overall, five episodes of change in the quenched corrected count rate for M29 were observed. Surprisingly only one period of evaporation loss, from mid-1984, was identified within errors. On the basis of these data, the mean of 28  $\delta$  values was taken to provide a measure of the discrepancy in BM results from PAC2 for the period mid-1980 to mid-1984. Subsequently, two moderns were in use and the results were recalculated using only M14, which was flame-sealed and the count rate for which showed no time dependence. The mean  $\delta$  value, based on 3 values, was found for this period and used as the correction.

Prior to mid-1980, a time trend in M29 count rate is identifiable. However, since the data for QS1 are not available, there is no independent information on gain changes. A limited number of  $\delta$  values and the modern count-rate data are insufficient to provide a correction for the 44 dates from PAC2 issued in this period.

#### ERROR ANALYSIS

The final error term on a correction was a combination of factors: 1) error on the estimate of the true value adopted (T for PAC1 and the appropriate mean  $\delta$  value for PAC2),

2) residual uncertainty reflected in the variance of the  $\delta$  values (reduced by the analysis of time trends in the case of PAC1) and 3) underestimation of the original error. Factor 3 was necessary because following upgrading of the system to improve accuracy and evaluate precision more realistically, it became clear that the errors previously quoted would have been underestimates, even if the problem of inaccuracy had not existed. To allow for this,  $\pm$  60 yr has been added (in quadrature) to the original quoted error before any addition of the extra uncertainty introduced by the correction procedures. In a few cases, this may be an unduly pessimistic view of the likely errors, eg, when comparing groups of dates measured under the same conditions.

#### THE RESULTS

Following the analysis, two types of result have been issued: new dates where a sample has been reprocessed from scratch (these are the samples used to provide  $\delta$  values), and revised results, *ie*, results where a correction has been applied to the initial result and a new error term has been evaluated. These new and revised results are differentiated (from each other as well as from the initial result) by appending N and R, respectively, to the initial BM reference. Table 1 shows the new results and Table 2 the revised results, together with initial results and original *RADIOCARBON* references. Table 3 lists those samples measured in PAC2 for which no revisions have been issued.

#### DISCUSSION

Before discussing the revised results themselves, the period of the error will be considered. The end point is clear, being when dating ceased at the end of 1984 for investigation and upgrading. The beginning is less clear, but can be inferred. For PAC2, it is taken as the time when the counter began to be used for dating, *ie*, the beginning of 1980. For PAC1, the Harwell/BM intercomparison indicates that there was no problem in mid-1979 and the 3-weekly average dates for BM-477B indicate that there was little, if any, error on dates issued prior to 1980. Coincidentally, therefore, the start of the problem period is the same in the two counters. Prior to 1979, while there is no reason to doubt the results issued, there is no independent check on the data from PAC1.

On average, the revision has given results which are older by 200–300 <sup>14</sup>C yr. A few remain effectively unchanged, whereas a few others have changed by 300 yr. It is clearly not possible here to examine so many results from such a large number of varied sites; however, a small number of examples might help to illustrate the general effect of the revised data.

#### Cranborne Chase, British Isles

The Middle Bronze Age results in particular were problematic, suggesting a late occurrence of the Deverel-Rimbury culture in the Wessex area relative to the rest of the country. The revised results indicate a more unified picture for the country as a whole, and thus that the apparent temporal hiatus was an artifact of the <sup>14</sup>C results (Barrett, Bradley & Green, in press).

#### Peel Castle, British Isles

Two samples came from a cemetery allegedly of a pre-Viking, Celtic monastery of the 8th century AD (Burleigh, Ambers & Matthews 1984:63). One of the graves (BM-2305: 630  $\pm$  45 BP) was overlain by a hearth archaeomagnetically dated to ca AD 1150. Even allowing for the original underestimated error term and a  $2\sigma$  error range (*ie*, ca  $\pm$  150), after calibration (Stuiver & Pearson 1986), this result postdates the hearth. The revised result is 940  $\pm$  120 BP (BM-2305R) which calibrated indicates with 60% probability (Leese 1987) that this grave antedates the hearth.

#### Burghfield Quarry, British Isles

One sample from this site was counted in both PAC1 and PAC2. The results, BM-2096A and -2096, were  $1750 \pm 50$  BP AND  $1500 \pm 60$  BP, respectively (Burleigh, Ambers &

Matthews 1984:63). Applying the appropriate correction process to each result gives  $1840 \pm 100$  BP (BM-2096AR) and  $1720 \pm 120$  BP (BM-2096R). This sample was also dated from scratch giving  $1800 \pm 50$  BP (BM-2096N). The original results clearly indicate a different discrepancy in the two counters at the time of measurement whereas the revised dates are in reasonable agreement with each other and with the new result.

#### CONCLUDING REMARKS

Radiocarbon dating, while routine, nevertheless requires vigilance to avoid inclusion of substantial systematic errors. To many laboratories this is obvious, but the British Museum example is not an isolated one as demonstrated by Scott *et al* (in press) and Waterbolk and Lanting (in press) at the second Groningen Archaeology and <sup>14</sup>C meeting. Systematic errors can only be dealt with by the laboratory in question on the basis of the results it gains from participation in carefully designed intercomparison experiments such as those of Scott et al (in press) or from smaller scale self-checks, such as those described above in relation to the current counting system. Only the laboratory in question can provide the submitter with information on the likelihood of such an error at a given time since the situation is unlikely to be static.

Our recent experience has been a salutary lesson leading to a long overdue upgrading of the counting system and the introduction of continuous self-checking procedures. That this lesson was learned at the expense of loss of primary data from so many samples is, to say the least, highly regrettable. While it has been possible to salvage something for the majority of these samples, this does not wholly compensate, particularly given the loss of precision, and where appropriate, a selective program of dating new material is being considered.

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Site	Original BM no.	Original result (yr BP)	New BM no.	New result (yr BP)	Radiocarbon date list (nopg no.)
<i>British Isles</i> Petters Sports Field	1624	2450 ± 70	1624N	2630 ± 70	ХІІ-р 19
Handley Barrow	1648	2810 ± 60	1648N	3100 ± 50	XII-p 21
Welsh St Donats	1680	3190 ± 35	1680N	3510 ± 50	XII-p 22
Bigberry	1768	1920 ± 35	1768N	2060 ± 50	XIV-p 232
bown Farm*	1852	2740 ± 40	1852N1 1852N2 1852N3 1852N4	$3120 \pm 50$ $3270 \pm 50$ $3100 \pm 50$ $3150 \pm 60$	XV-p 271 """ """
			2577	2980 ± 50	
	1853	2790 ± 45	1853N	2980 ± 50	" "
Netherton	1899	920 ± 35	1899N	980 ± 70	XVI-p 41
Poundbury	1923	1500 ± 40	1923N	1620 ± 50	XVI-p 43
Street House Farm	1969 2007 2061	4720 ± 50 3220 ± 45 5070 ± 50	1969n 2007n 2061n	4940 ± 60 3470 ± 50 5080 ± 60	XVI-p 43 " " 9 44
Burghfield Quarry	2096 2096A	1500 ± 60 1750 ± 50	2096an	1800 ± 50	XVII-p 63 "
Dorchester	2268	3950 ± 70	4225N	4230 ± 50	XVIII-p 510
Badshot **	2273	4480 ± 100	2273N1 2273N2 2273N3	4780 ± 40 4710 ± 50 4730 ± 50	XIX-p 63 """
Oldbury	2291	1840 ± 40	2291N	2070 ± 50	XIX-p 65
Maumbury Rings	2282	3640 ± 70	2282N	3970 ± 50	XIX-p 64
<i>Egypt</i> Tell el-D'aba	1726	3410 ± 60	1726N	3490 ± 50	XV-p 275
<i>France</i> Choisy-au-Bac	2058 2050	2310 ± 50 2490 ± 50	2058N 2050N	2560 ± 60 2590 ± 80	XVII-р 67 "р66
India Zawar	2223	230 ± 60	2223N	530 ± 50	XVIII-p 519

 TABLE 1

 Published BM Radiocarbon dates for which new results have been measured

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\* EM-2577 is a new measurement on selected twiggy material from the same original material as was used for BM-1852. The other four new results on this charcoal sample were not selected in any particular way.

\*\* Three separate samples were prepared and dated from raw material. The mean date and standard error is BM-2273N: 4740 ± 20 BP.
Site	Original BM no.	Original result (yr BP)	New BM no.	New result (yr BP)	Radiocarbon date list (nopg no.)
<i>Jordan</i> Jericho	1780 1791	3890 ± 60 2040 ± 40	1780n 1791n	4320 ± 50 2360 ± 50	XV-P 279 " P 280
<i>Pakistan</i> Bhir Mound	1957	2000 ± 45	195 <b>7</b> N	2350 ± 50	XVI-p 52
<i>Spain</i> Ferrandell Oleza	1842	2430 ± 230	1842N	2850 ± 70	XV-p 282
<i>Syria</i> Tell Nebi Mend	2032	2925 ± 45	2032N	3160 ± 70	xvII-p 72
Tell Brak	*		2511	3960 ± 90 (Humic acida	5)
			2531	3840 ± 50 (Humins)	
<i>United States</i> Indian Fort Road	2121	200 ± 30	2121N	260 ± 50	XVII-p 73

TABLE 1 (Continued)

\* This sample was from the same context as BM-1971,-1972 and -1973 (XVI-p 57) but is not from exactly the same sample. As part of the pretreatment, it was separated into two component fractions before measurement. Statistically there is no difference in age between the two and therefore no apparent contamination had occurred during burial. The weighted mean of the two results is 3870 ± 50 BP.

Site	Original BM-no.	Original result (yr BP)	New BM-no.	Revised result (yr BP)	Radiocarbon datelist (nopg no.)
Algeria	1000	1700 + 120	10000	1000 + 170	W/T-m 20
Cherchel	1909	1/60 ± 130	1909R	1990 ± 170	xv1-p 39
	1910	1620 ± 70	1910R	1840 ± 120	50
	2129	1080 ± 130	2129R	$1310 \pm 160$	XVII-p 59
	2130	460 ± 50	2130R	690 ± 110	
	2132	65 ± 40	2132R	290 ± 110	
	2133	45 ± 35	2133R	270 ± 110	" "
	2134	modern	2134R	170 ± 110	" "
British Isles					
Holne Moor	1604	6760 ± 240	1604R	6900 ± 260	XII-p 18
	1605	1000 ± 60	1605R	$1080 \pm 110$	" "
	1606	$4730 \pm 360$	1606R	4840 ± 370	
	1607	3250 + 50	1607R	3390 + 100	
	1609	3060 + 60	16080	3190 + 100	
	1600	$3000 \pm 00$	16000	3400 + 110	
	1009	$3270 \pm 00$	16100	$3400 \pm 110$	
	1010	3150 ± 80	TOTOR	3290 ± 120	
	1611	$3150 \pm 80$	TOTIK	3300 ± 120	
	1612	2490 ± 110	1612R	2580 ± 140	

 TABLE 2a

 Published BM Radiocarbon dates for which revised results have been issued

Site	BM-no.	(yr BP)	New BM-no.	Revised result (yr BP)	Radiocarbon datelist (nopg no.)
Darent	1618	980 ± 80	1618R	1060 ± 120	XV-p 262
Gravels	1619	9770 ± 80	1619R	9840 ± 120	" "
	1672	115 ± 35	1672R	$360 \pm 100$	
	1673	780 ± 60	1673R	$1020 \pm 110$	" p 263
	1674	9760 ± 70	1674R	$10,080 \pm 120$	" "
	1675	150 ± 60	1675R	510 ± 110	" "
Thatcham	1634	8160 ± 560	1634R	8300 ± 570	XV-p 265
	1635	9560 ± 260	1635R	9700 ± 280	" p 266
	1636	9380 ± 80	1636R	9520 ± 120	" "
	1637	9170 ± 140	163 <b>7</b> R	9320 ± 170	
Dean Bottom	1668	3770 ± 35	1668R	3910 ± 100	XII-p 21
	1669	3580 ± 40	1669R	3750 ± 100	" "
Tolpits Lane	1676	5230 ± 60	1676R	5540 ± 110	XV-p 263
Southwark	1678	1740 ± 35	1678R	1990 ± 100	XV-р 267
Welsh 🖌	1679	2810 ± 35	1679R	3020 ± 100	XII-p 22
St Donats	1681	3250 ± 35	1681R	3470 ± 100	
Lingey Fen	1707	4630 ± 50	1707R	4860 ± 110	XV-p 267
	1708	6370 ± 70	1708R	6600 ± 120	" "
	1709	2050 ± 50	1709R	2280 ± 110	"p268
	1711A	$2620 \pm 40$	1711AR	2850 ± 110	
Lingey Fen	1711B	2560 ± 45	1711BR	2780 ± 110	XV-p 268
Kildale	1725	8270 ± 80	1725R	8490 ± 120	XVI-p 40
Feltwell	1735	11,560 ± 110	1735R	11,600 ± 140	XV-p 263
Caerwys	1736	7880 ± 160	1736R	8100 ± 180	XV-p 268
Binnel Point	1737	4480 ± 100	1737R	4700 ± 140	XV-p 268
Millpark	1738	3190 ± 170	1738R	3420 ± 200	XV-p 268
Ballybetagh	1794	15,170 ± 160	1794R	15,330 ± 180	XV-p 263
Castlethorpe	1795	3410 ± 80	1795R	3500 ± 120	XV-p 269
Freshwater	1798	860 ± 40	1798R	5130 ± 100	XV-p 269
Shells	1799	$4340 \pm 45$	1799R	$4490 \pm 100$	
	1800	$4140 \pm 50$	1800R	$4460 \pm 100$	
	2135	$1480 \pm 50$	2135R	$1780 \pm 100$	XVII-p 60
	2136	730 ± 180	2136R	$1040 \pm 200$	
Creswell Crags	1805	38,850 ± 2500	1805R	infinite	XV-p 264
Thor's Fissure	1807	20,100 ± 1900	180 <b>7</b> R	20,400 ± 1900	XVI-p 40

TABLE 2a (Continued)

 $\star$  Material from sites marked with an asterisk has also been redated from scratch. See Table 1 for new results.

Site	Original BM-no.	Original result (yr BP)	New BM-no.	Revised result (yr BP)	Radiocarbon datelist (nopg no.)
Swildon's Hole	1808	1730 ± 60	1808R	1960 ± 120	хv-р 270
Foel Fawr	1809	5240 ± 80	1809R	5470 ± 130	XV-p 270
	1810	5210 ± 130	1810R	5440 ± 160	" "
	1903	5100 ± 360	1903R	5330 ± 370	11 II
Peninsular	1824	$150 \pm 40$	182 <b>4</b> R	370 ± 110	XV-p 270
House	1825	230 ± 35	1825R	460 ± 110	" "
Lough Gur	1827	4020 ± 90	182 <b>7</b> R	4250 ± 140	XV-p 264
Rodney Stoke	1837	7940 ± 180	1837R	8170 ± 200	XV-p 269
Seamer Carr	1841	8620 ± 80	1841R	8740 ± 120	xv-p 264
Down Farm*	1850	2680 ± 130	1850R	2900 ± 160	XV-p 271
	1851	2730 ± 50	1851R	2950 ± 110	" "
	1854	2800 ± 45	1854R	3030 ± 110	11 TI
Vazon	1858	$3190 \pm 210$	1858R	3340 ± 230	XV-p 271
Valon	1859	4000 ± 50	1859R	4150 ± 100	
Ies	1891	3850 ± 50	1891R	4020 ± 100	XV-p 272
Fouaillages	1892	5590 ± 50	1892R	5850 ± 100	" "
<u>,</u>	1893	5510 ± 60	1893R	5900 ± 110	** **
	1894	5280 ± 140	1894R	5670 ± 170	" "
	1895	4000 ± 60	1895R	$4180 \pm 110$	
	1896	5090 ± 50	1896R	$5270 \pm 100$	
	1897	3820 ± 50	189 <b>7</b> R	$4000 \pm 100$	
Netherton*	1900	1000 ± 100	1900R	1080 ± 140	XVI-p 41
	1901	1000 ± 80	1901R	1330 ± 120	" "
	1902	720 ± 50	1902R	$1100 \pm 100$	" "
	2006	710 ± 80	2006R	$1000 \pm 120$	** **
Megaceros	1904	11,380 ± 280	1904R	11,720 ± 290	XV-p 264
Maldon	1905	150 ± 50	1905R	300 ± 100	XVI- p 41
South Lodge	1917	2790 ± 70	1917R	3010 ± 120	XVI-p 42
Camp	1918	2680 ± 110	1918R	2900 ± 150	" "
	1919	2910 ± 60	1919R	$3140 \pm 120$	
	1920	$2660 \pm 60$	1920R	$2890 \pm 120$	
	1921	$3020 \pm 60$	1921R	$3240 \pm 120$	
	1922	2890 ± 50	1922R	$3110 \pm 110$	
	2023 2024	$2680 \pm 50$ 2730 ± 70	2023R 2024R	$2900 \pm 110$ $2960 \pm 120$	н н
	1000	4700	10000	4040 + 110	NEXT 40
Street House	1965 1967	4/20 ± 60	1966K	$4940 \pm 110$ AQA0 + 110	xv1-p 43
raim	1968	4020 ± 60	19680	4940 ± 110 1970 + 110	11 11
	2008	2485 + 45	20088	2890 + 100	
	2009	3360 + 50	2009R	$3670 \pm 100$	" "
	2010	$3170 \pm 45$	2010R	$3460 \pm 100$	"p44
	2011	4630 ± 80	2011R	4960 ± 120	" "
	2012	4610 ± 80	2012R	4960 ± 120	" "
	2013	4510 ± 90	2013R	4840 ± 130	" "
	2014	4630 ± 70	2014R	4970 ± 120	" "
	2060	4500 ± 130	2060R	4480 ± 160	" "

TABLE 2a (Continued)

Site	Original BM-no.	Original result	New BM-no.	Revised result	Radiocarbon datelist
		(yr BP)		(yr BP)	(nopg no.)
Ascott-	1974	4430 ± 130	1974R	4680 ± 160	XVI-p 45
under-	1975	3480 + 50	1975R	3870 + 100	" "
Wychwood	1976	4535 ± 40	1976R	4930 ± 100	" "
Gugh	1980	modern	1980R	20 ± 100	XVI-p 40
		0.45	004.0-		
Vale Castle	2018	845 ± 40	2018R	$1110 \pm 100$	XVI-p 45
Jerbourg	2019	1300 ± 500	2019R	1620 ± 510	XVI-p 45
Northampton	2026	3400 ± 50	2026R	3780 ± 100	XVII-p 61
	2027	5230 ± 45	2027R	5630 ± 100	" "
	2074	23,880 ± 770	2074R	23,750 ± 780	" "
	2074C	25,500 ± 630	2074CR	25,810 ± 640	" "
Canterbury	2044	820 ± 150	2044R	1230 ± 180	XVI-p 45
Brixworth	2047	790 ± 70	2047R	680 ± 120	XVII-p 62
	2047A	740 ± 70	2047AR	670 ± 120	" "
	2048	950 + 50	2048R	860 ± 100	" "
	2040	710 + 220	2049R	700 + 240	TAS
Duimorth	2045	$1510 \pm 00$	20450	1/20 + 130	"
Drixworth	2000	$710 \pm 120$	20000	$690 \pm 150$	"
mortars	2078	$710 \pm 120$	2070R	$1000 \pm 100$	"
	2079	1180 ± 190	2079R	$1200 \pm 210$	
	2080	$770 \pm 100$	2080R	$830 \pm 140$	
	2141	660 ± 260	2141R	$980 \pm 280$	
	2151	910 ± 150	2151R	$1130 \pm 120$	
Brixworth	2152	1330 ± 50	2152R	1560 ± 110	JAS
Mortars	2153	1690 ± 150	2153R	1920 ± 180	"
	2154	900 + 150	2154R	$1130 \pm 180$	26 q-IIVX
	2155	890 ± 100	2155R	$1110 \pm 140$	" "
Harrow Hill	2071	4670 + 60	2071R	4900 + 120	XVII-p 62
and I OTT III I	2075	4790 + 50	2175R	5020 + 110	" "
	2073	4010 + 110	20070	5140 + 150	
	2097	$\frac{4910}{5120} \pm 120$	20071	5350 + 150	
	2098	5120 ± 120	2090R	$5350 \pm 130$	
	2099	4820 ± 70	2099K	5040 I 120	
	2124	4800 ± 170	2124R	5060 ± 190	
Unio	2072	1525 ± 30	2072R	$1470 \pm 100$	XVII-p 60
Tumidus	2073	750 ± 180	2073R	700 ± 200	
Witton	2088	3090 ± 60	2088R	3320 ± 120	XVII-p 63
Haddenham	2091	1760 ± 70	2091R	1990 ± 120	XVII-p 63
Bridged Pot	2102	8890 ± 340	2102R	9090 ± 350	XVII-p 65
Picken's Hole	2117	27,540 ±2440	211 <b>7</b> R	27,770 ±2440	XVII-p 65
	2118	12,400 ±1500	2118R	12,710 ±1500	
Flag Fen	2123	2610 ± 60	2123R	2830 ± 120	XVII-p 63
Ossom's Cave	2126	25,300 ±1500	2126R	25,610 ±1500	XVII-p 65
	2127	11,930 ± 310	2127R	12,220 ± 320	
	01.00	1010 + 120	21 20n	5120 + 130	

TABLE 2a (Continued)

Site	Original BM-no.	Original result (yr BP)	New BM-no.	Revised result (yr BP)	Radiocarbon datelist (nopg no.)
Devil's	2137	2315 + 35	2137P	2580 + 100	WIII-n 64
Dyke	2207	2010 2 00	21371	2300 1 100	WII-P 04
Devizes Castle	2150	525 ± 30	2150R	750 ± 100	XVII-p 64
Stonea	2157	1950 ± 50	2157R	2170 ± 110	XVIII-p 508
Ozengell	2158	modern	2158R	130 ± 100	XVIII-p 508
Dorchester	2161	3840 ± 40	2161R	4060 ± 110	XVIII-p 509
Cursus*	2162	3870 ± 60	2162R	4100 ± 120	** **
	2163	3780 ± 50	2163R	4070 ± 130	
	2164	3890 ± 60	2164R	4120 ± 120	** **
	2165	3330 ± 80	2165R	3550 ± 130	" р 510
	2166	3730 ± 45	2166R	4030 ± 130	17 17
	2167	3390 ± 70	2167R	3690 ± 130	" "
Kent's Cavern	2168	11,570 ± 410	2168R	11,800 ± 420	XVIII-p 510
Down Farm	2177	3050 + 70	21 <b>77</b> R	3270 + 120	XVIII-n 511
Ring Ditch	2178	3010 + 60	2178R	$3240 \pm 120$ $3240 \pm 120$	
<b>y</b>	2179	$2740 \pm 30$	2179R	2960 + 100	" "
	2180	2810 ± 50	2180R	$3030 \pm 110$	" "
Pitstone	2181	5520 ± 60	2181R	5750 ± 110	XVIII-p 511
Gough's	2183	12,120 ± 120	2183R	12,350 ± 160	XVIII-p 512
Cave	2184	12,020 ± 120	2184R	12,250 ± 160	
	2185	11,970 ± 230	2185R	12,200 ± 250	" "
	2186	$12,240 \pm 220$	2186R	12,470 ± 240	" "
	2187	$12,070 \pm 170$	218 <b>7</b> R	12,300 ± 200	
	2188	12,160 ± 210	2188R	12,380 ± 230	
Down Farm	2189	3390 ± 45	2189R	3620 ± 110	XIX-p 62
Pond Barrow	2190	3210 ± 45	2190R	3500 ± 130	
	2191	3670 ± 60	2191R	3900 ± 120	" "
	2192	3110 ± 100	2192R	3390 ± 150	** **
	2324	3190 ± 70	232 <b>4</b> R	3490 ± 130	" "
Whitton	2203	4820 ± 80	2203R	5040 ± 130	XVIII-p 513
H111	2204	$2860 \pm 90$	2204R	$3080 \pm 140$	
	2205	$3610 \pm 45$	2205R	$3830 \pm 110$	
	2206	3740 ± 50	2206R	3970 ± 110	
	2264	2880 ± 310	2264R	3190 ± 330	
	2265	3680 ± 80	2265R	$3980 \pm 130$	
	2266	3660 ± 50	2266R	$3960 \pm 130$	
	2267	$2770 \pm 170$	2267R	$3030 \pm 210$	
Roxby	2207A	1950 ± 150	2207AR	2180 ± 180	XIX-p 61
	2208A	7090 ± 120	2208AR	7310 ± 150	11 11
Rangoon Street	2214	$1050 \pm 45$	2214R	1270 ± 110	XVIII-p 514
-	2215	980 ± 50	2215R	1210 ± 110	
Asham	2216	2760 ± 120	2216R	2990 ± 150	xvIII-p 514
Quarry	2217	3460 ± 190	221 <b>7</b> R	3680 ± 210	" "
	2277	3580 ± 280	22 <b>77</b> R	3740 ± 290	" "
	2296	4590 ± 110	2296R	4720 ± 130	" p 515

TABLE 2a (Continued)

Site	Original BM-no.	Original result (yr BP)	New BM-no.	Revised result (yr BP)	Radiocarbon datelist (nopg no.)
S Heighton	2219	3450 ± 150	2219R	3620 ± 160	XVIII-p 515
Cow Gap	2220	4820 ± 350	2220R	5000 ± 360	XVIII-p 515
	2295	5860 ± 130	2295R	6080 ± 150	" "
Ferriters Cove	2227	5230 ± 200	2227R	5400 ± 220	XVIII-p 517
	2228	5580 ± 110	2228R	5750 ± 140	" "
	2229	5310 ± 130	2229R	5490 ± 160	" p 518
	2227A	5190 ± 110	2227ar	5420 ± 150	" p 517
	2228A	5620 ± 80	2228ar	5850 ± 130	
	2229A	5270 ± 90	2229ar	5500 ± 130	" p 518
Gallibury	2230	3560 ± 50	2230R	$3740 \pm 100$	XVIII-p 516
Down	2231	5150 ± 60	2231R	$5330 \pm 110$	" "
	2232	3380 ± 80	2232R	3560 ± 120	n n
	2233	3440 ± 150	2233R	3610 ± 180	
	2234	3520 ± 90	2234R	3700 ± 130	" "
Garden Hill	2236	1870 ± 80	2236R	2040 ± 100	to be
	2238	1590 ± 80	2238R	$1840 \pm 100$	
	2239	1940 ± 90	2239R	2090 ± 110	published
	2241	2370 ± 45	2241R	2520 ± 80	-
Soldier's Hole	2249	9930 ± 210	2249R	10,090 ± 230	XVIII-p 517
Mt Gabriel	2271	3200 ± 110	2271R	3410 ± 140	XIX-p 66
Badshot.*	2272	4420 + 90	22 <b>7</b> 28	4640 + 130	XIX-n 63
	2274	4600 ± 120	2274R	4860 ± 180	" "
Maumbury Rings*	2281	3650 ± 70	2281R	3940 ± 130	XIX-p 64
Wor Barrow	2283	4350 ± 70	2283R	4660 ± 130	XIX-p 64
	2284	4440 ± 70	2284R	4740 ± 130	" "
Oldbury*	2290	2310 ± 50	2290R	2610 + 130	XIX-n 64
-	2292	1910 ± 80	2292R	2210 ± 140	" p 65
Peel Castle	2303	170 ± 50	2303R	$480 \pm 140$	XIX-p 66
	2304	$150 \pm 40$	2304R	$440 \pm 140$	" "
	2305	630 ± 45	2305R	940 ± 120	" "
	2306	730 ± 50	2306R	1050 ± 120	** **
Springfield	2313	2780 ± 90	2313R	3090 + 150	XIX-p 65
	2314	2370 ± 80	2314R	$2670 \pm 140$	" "
		2150	22150	2460 + 130	VTV
Strichen	2315	2150 ± 60	20108	2400 1.10	
Strichen	2315 2316	$2150 \pm 60$ $3090 \pm 60$	2315R 2316R	$3390 \pm 130$	ліх-р бл
Strichen	2315 2316 2317	$2150 \pm 60$ $3090 \pm 60$ $2050 \pm 80$	2315R 2316R 2317R	$3390 \pm 130$ $2370 \pm 130$	" " " "

TABLE 2a (Continued)

TABLE 2a (Continued)

Site	Original BM-no.	Original result (yr BP)	New BM-no.	Revised result (yr BP)	Radiocarbon datelist (nopg no.)
Canada					
Canadian	1751	115 + 40	1751R	$210 \pm 100$	XV-p 273
Arctic	1753	360 + 25	1753R	$560 \pm 100$	" "
hictic	1754	1135 + 40	1754R	$1150 \pm 100$	•• ••
	1766	$155 \pm 40$	1766R	380 + 110	" "
	1767	85 + 40	1767R	310 + 110	•• ••
	1803	870 + 30	1803R	$1160 \pm 100$	" "
	1804	$800 \pm 30$	1804R	$1100 \pm 100$ $1100 \pm 100$	
Crete					
Platvvola	1813	4030 ± 50	1813R	4020 ± 100	XV-р 274
Cave	1814	3800 ± 50	1814R	4070 ± 100	" "
	1815	$1040 \pm 50$	1815R	1320 ± 100	17 11
	1816	$3800 \pm 40$	1816R	4090 ± 100	** **
	1826	4110 ± 50	1826R	4120 ± 100	
Cyprus					
Kalavasos-	1832	4810 ± 45	1832R	5040 ± 110	XV-p 274
Avious	1833	4780 ± 140	1833R	5000 ± 170	" "
-	1834	4800 ± 70	1834R	5030 ± 120	" "
	1835	10,790 ± 80	1835R	11,020 ± 130	
	1836	4480 ± 290	1836R	4700 ± 310	" p 275
Ayios	1906	5030 ± 80	1906R	5360 ± 120	XVI-p 46
Epiktitos	1907	5120 ± 45	1907R	5290 ± 100	
Vrysi	1908	5180 ± 60	1908R	5360 ± 110	" "
Lemba	2278	3930 ± 100	22 <b>7</b> 8R	4090 ± 120	XIX-p 67
Lakkous	2280	5710 ± 100	2280R	5890 ± 120	" "
Kissonerga Mosphilia	2279	4030 ± 110	22 <b>7</b> 9R	4180 ± 130	XIX-p 67
Greece					
Kvrenia	1639	2630 ± 45	1639R	2780 ± 100	XIV-p 239
Ship	2294	2090 ± 50	2294R	2390 ± 120	XIX-p 68
Servia	1885	6360 ± 190	1885R	6590 ± 210	XV-p 277
	1886	4040 ± 50	1886R	4270 ± 110	
	1887	6420 ± 120	1887R	6640 ± 150	"р278
	1888	3560 ± 70	1888R	3790 ± 120	
Agios	2020	6400 ± 80	2020R	6740 ± 120	XVI-p 48
Petros	2021	5510 ± 390	2021R	5860 ± 400	
Ecuador					
Hacienda	1682	1820 ± 70	1682R	2040 ± 120	XVIII-p 518
Guarumal	1684	1760 ± 70	1684R	2020 ± 130	
Egypt					
Deir-el	1796	3490 ± 40	1796R	3720 ± 110	х <b>V-</b> р 276
-Bahri	1796A	3520 ± 60	1796AR	3740 ± 120	
	1797	3310 ± 60	1797R	3540 ± 120	17 17
Manchester mummy no.1770	1839	1860 ± 120	1839R	2080 ± 160	хv-р 275

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Site	Original BM-no.	Original result	New BM-no.	Revised result	Radiocarbon datelist
		(yr BP)		(yr BP)	(nopg no.)
Gawasis	1844	3230 ± 45	1844R	3310 ± 100	XV-p 276
	1845	3555 ± 40	1845R	$3650 \pm 100$	" "
	1846	3180 ± 140	1846R	3080 ± 160	XVI-p 46
Bristol mummy	1872	2880 ± 140	1872R	3020 ± 170	xv-p 277
Tell el Ajjul	2114	8150 ± 300	2114R	8350 ± 310	XVII-p 69
France					
Arcy	1817	26,410 ± 440	181 <b>7</b> R	26,690 ± 450	XV-p 277
	1818	10,500 ± 190	1818R	$10,570 \pm 210$	
	1819	22,550 ± 350	1819R	22,600 ± 360	** **
Figure of	1977	440 ± 60	1977R	420 ± 120	XVI-p 48
Christ	1978	830 ± 100	1978R	840 ± 140	
	1979	$830 \pm 120$	19/9R 21.005	$840 \pm 150$	
	2100 2101	$490 \pm 100$ $340 \pm 100$	2100R 2101R	$400 \pm 140$ 540 ± 140	хvіі-р б/
Mant	1011	11 450 4 70	10110	11 600 ± 100	VI/I
montgaudier	1917	$11,450 \pm 70$ 12 180 + 120	1911K 1917D	$11,000 \pm 120$ 12 410 + 160	лvi-р 4/
	1913	$18.050 \pm 230$	1913R	$18,280 \pm 250$	
	1914	18,180 ±1070	1914R	18,410 ±1070	** **
	1916	13,320 ± 360	1916R	13,550 ± 370	** **
	2309	14,770 ± 270	2309R	14,940 ± 280	XIX-p 69
	2311	20,870 ± 370	2311R	21,050 ± 380	" "
Choisy-au-	2051	2480 ± 70	2051R	2710 ± 120	XVII-p 66
Bac*	2052	$2130 \pm 130$	2052R	$2360 \pm 160$	
	2053	$1/10 \pm 360$	2053R	$1930 \pm 380$	
	2054	2220 I 140 2370 + 60	2004K 2055₽	2440 ± 170 2590 + 120	
	2055	$2300 \pm 100$	2056R	$2530 \pm 120$ 2530 ± 150	
	2057	$2235 \pm 40$	2057R	2460 ± 110	11 17
Les Eyzies	2285	11,600 ± 380	2285R	11,780 ± 390	XIX-p 68
-	2286	12,590 ± 980	2286R	12,810 ± 990	" p 69
Hungary					
Hungary	1860	6080 ± 60	1860R	6220 ± 110	XVI-p 48
	1861	5630 ± 140	1861R	5760 ± 170	
	1862	$6580 \pm 60$	1862R	$6/10 \pm 110$	" n /9
	1864	6040 ± 110	1864R	$6180 \pm 140$	E <sup>7</sup> 47
	1865	$6190 \pm 140$	1865R	$6400 \pm 170$	" "
	1866	6620 ± 60	1866R	6780 ± 110	" "
	1867	5730 ± 90	1867R	5950 ± 130	
	1868	6830 ± 60	1868R	6970 ± 110	
	1870	6600 ± 80	1870R	$6950 \pm 120$ $6830 \pm 120$	
	10/1	04/0 I /0	TOLIK	0030 ± 120	
India Karan <b>t</b>	2017	modern	201 <b>7</b> D	110 + 260	WII-n 67
2dwar^	2017	modern	2017K 2065R	modern	и п илт-Б 01
	2005	2120 + 60	2148R	$2350 \pm 120$	" "
	2149	$1920 \pm 50$	2149R	$2140 \pm 110$	" p 68
	2222	$10 \pm 40$	2222R	240 ± 110	XVIII-p 519
	2243	80 ± 60	2243R	350 ± 130	" "

TABLE 2a (Continued)

TABLE 2a (Continued)

Site	Original BM-no.	Original result (yr BP)	New BM-no.	Revised result (yr BP)	Radiocarbon datelist (nopg no.)
Indian Ocean					
Tortoise	2125	750 ± 370	2125R	920 ± 380	XVII-p 68
<i>Iraq</i> Nimrud	1856	2300 ± 50	1856R	2530 ± 110	XV-p 278
Tell Taya	2109	3370 ± 45	2109R	3600 ± 110	XVII-p 68
	2110	$3650 \pm 40$	2110R	3870 ± 110	
	2112	$3640 \pm 40$	2112R 2112D	$38/0 \pm 110$	
	2115	3110 ± 200	2113R	3340 ± 220	
Khirbet Khatuniyeh	2293	2310 ± 80	2293R	2610 ± 140	XIX-p 70
Tell Abu Salabikh	2328	3700 ± 60	2328R	4010 ± 130	XIX-p 70
Israel					
Timna	2242	1210 ± 100	2242R	1400 ± 140	XVIII-p 519
Nahal Hemar	2298	8250 ± 70	2298R	8430 ± 100	XIX-p 71
	2299	9110 ± 300	2299R	9290 ± 310	" "
	2300	8690 ± 90	2300R	8830 ± 110	XIX-p 71
Italy					
Marcianese	2250	6290 ± 60	2250R	6590 ± 130	XIX-р 72
	2251	6250 ± 90	2251R	6570 ± 140	
	2252	6000 ± 110	2252R	6300 ± 170	** **
Cala Scizzo	2253	4880 ± 210	2253R	5200 ± 250	XIX-p 72
	2254	4230 ± 100	2254R	4540 ± 150	" "
	2255	3190 ± 80	2255R	3500 ± 130	" "
Santa Barbara	2256	5800 ± 120	2256R	6120 ± 170	XIX-p 73
	2257	5620 ± 130	225 <b>7</b> R	5920 ± 170	
	2258	5720 ± 120	2258R	6020 ± 160	" "
Cala Colombo	2259	4070 ± 60	2259R	4370 ± 130	XIX-p 73
	2260	4870 ± 90	2260R	5180 ± 140	" "
	2301	$1180 \pm 50$	2301R	1490 ± 130	"р74
	2302	4810 ± 180	2302R	5080 ± 250	<b>11</b> 11
Jordan					
Jericho*	1769	8700 ± 110	1769R	8930 ± 150	х <b>v-</b> р 279
	1770	8680 ± 70	1770R	8910 ± 120	17 11
	1//1	8660 ± 260	1771R	8890 ± 280	* *
	1773	$8730 \pm 100$	1//2R 1772D	$9040 \pm 140$	
	1774	4380 + 50	1774p	$4600 \pm 130$	
	1775	$4480 \pm 50$	1775R	$4710 \pm 110$	" "
	1778	4080 ± 70	1778R	4300 ± 120	" "
	1779	4160 ± 80	1779R	4390 ± 130	" "
	1781	$4120 \pm 40$	1781R	4350 ± 110	" p 280
	1783	$3360 \pm 40$ $3940 \pm 90$	1782R	$3/80 \pm 110$	
	1784	3620 + 40	1784R	4170 ± 130 3840 + 110	
	1787	9280 ± 100	1787R	9510 ± 140	" "
	1789	9200 ± 70	1789R	9420 ± 120	" "
	1790	3080 ± 40	1790R	3300 ± 110	
	1793	8660 ± 130	1793R	8890 ± 170	

Site	Original BM-no.	Original result	New BM-no.	Revised result	Radiocarbon datelist
	2.1.1.0.	(yr BP)		(yr BP)	(nopg no.)
Norway					
Grasvatn	1880	6460 ± 60	1880R	6680 ± 120	XV-p 280
Nigeria					
Igbo-Ukwu	2142	720 ± 360	2142R	940 ± 370	XVIII-p 520
	2143A	1030 ± 300	2143AR	1260 ± 310	" "
	21 <b>4</b> 3B	880 ± 240	2143BR	1100 ± 260	17 17
Pakistan					
Sarai Khola	1934	4250 ± 110	1934R	4470 ± 150	XVI-p 50
	1935	4140 ± 230	1935R	4370 ± 250	11 II
	1936	3890 ± 230	1936R	4120 ± 250	11 11
	1938	3810 ± 60	1938R	4030 ± 120	
	1939	4310 ± 120	1939R	4530 ± 160	" "
	1940	4380 ± 170	1940R	4600 ± 200	
	1942	3910 ± 70	1942R	4130 ± 120	** **
	1943	3700 ± 60	1943R	3920 ± 120	"р51
	1944	4040 ± 200	1944R	4270 ± 220	
	1945	3790 ± 60	1945R	4020 ± 120	XVI-p 51
	1946	3700 ± 80	1946R	3920 ± 130	" "
	1947	870 ± 50	194 <b>7</b> R	1090 ± 110	" "
Islam Chauki	1941	3690 ± 450	1941R	3910 ± 460	XVI-p 51
Hathial West	1948	3600 ± 60	1948R	3820 ± 120	XVI-p 51
	1949	3750 ± 100	1949R	3980 ± 140	11 H
	2196	1890 ± 60	2196R	2120 ± 120	XVIII-p 521
	2197	$1890 \pm 50$	219 <b>7</b> R	2120 ± 110	" "
	2198	2610 + 120	2198R	$2840 \pm 150$	11 11
	2199	$2210 \pm 70$	2199R	$2430 \pm 120$	** **
Hathial North	1950	1740 ± 40	1950R	1970 ± 110	XVI-p 51
Bhir Mound*	1951	1990 ± 60	1951R	2210 ± 120	XVI-p 52
	1952	1920 ± 170	1952R	2150 ± 200	
	1953	1930 ± 50	1953R	2160 ± 110	
	1954	1830 ± 40	1954R	2060 ± 110	" "
	1955	2050 ± 60	1955R	2280 ± 120	" "
	1956	1795 ± 35	1956R	2020 ± 110	
	1958	$2010 \pm 40$	1958R	2240 ± 110	
	1959	1950 ± 50	1959R	$2180 \pm 110$	" "
	1960	1805 ± 35	1960R	2030 ± 110	** **
	1961	2050 ± 80	1961R	2280 ± 130	" "
	1963	2120 ± 200	1963R	2340 ± 220	11 11
	1964	2080 ± 80	1964R	2310 ± 130	** **
	1965	2090 ± 90	1965R	2320 ± 130	XVI-p 52
	2195	2140 ± 130	2195R	2370 ± 160	XVIII-p 520
Rehman Dheri	2062	3730 ± 50	2062R	3960 ± 110	XVI p 53
	2063	3580 ± 110	2063R	3810 ± 150	** **
Jhang	2200	3780 ± 220	2200R	4010 ± 250	хVIII-р 521
5	2201	4030 ± 50	2201R	4260 ± 110	
	2202	940 ± 30	2202R	1170 ± 100	" p 522
Papua New Gui	nea				
Padad Kao	2093	modern	2093R	$30 \pm 150$	XVII-p 69
	2094	modern	2094R	modern	
	2138	modern	2138R	modern	

TABLE 2a (Continued)

TABLE 2a (Continued)

Site	Original BM-no.	Original result (yr BP)	New BM-no.	Revised result (yr BP)	Radiocarbon datelist (nopg no.)
Peru					
Cusichaca	1633	2380 ± 70	1633R	2530 ± 120	XVI-p 54
Poland					
Wierzbica	2103	2480 ± 100	2103R	$2720 \pm 140$	XVII-p 70
	2104	$2460 \pm 140$	2104R	2590 ± 170	" "
	2105	2230 ± 200	2105R	2470 ± 220	11 11
	2107	2380 ± 130	2107R	$2700 \pm 160$	11 11
Portuga l					
Segovia	2159	2280 ± 45	2159R	2510 ± 110	XIX-p 74
5	2160	2410 ± 50	2160R	2640 ± 110	" "
	2287	2140 ± 130	2287R	2460 ± 180	"p75
	2288	$1220 \pm 110$	2288R	1520 ± 170	" "
	2289	890 ± 60	2289R	1190 ± 130	17 II
Sardinia					
Grotta	2139	7530 ± 80	2139R	7760 ± 130	XVII-p 70
Filiestru					-
Spain					
La Riera	1739	20,880 ± 410	1739R	21,100 ± 420	XV-p 283
Formandall	1040	2050	10425	4020 . 110	
	1045	3930 ± 60	1043R	$4030 \pm 110$	XV-p 282
01224	1982	$3720 \pm 33$ 1710 + 60	1000R	$3040 \pm 100$	xv1-p 55
	1988	$3150 \pm 300$	1002R	$2030 \pm 110$ $2250 \pm 210$	W/TT n 70
	2297	2140 + 80	229 <b>7</b> 8	$2280 \pm 120$	$xy_{-p} 75$
	2312	$3210 \pm 80$	2312R	$3390 \pm 100$	ли-р /J
Cuevra de los	1075	$10,220 \pm 100$	10755	10 400 . 010	
$\Delta_{711}$	1876	$10,330 \pm 190$ $10,700 \pm 100$	1070R	$10,480 \pm 210$	xv-p 283
induics	1877	$10,700 \pm 190$ 11 100 + 350	1070R	$10,000 \pm 210$ $11,220 \pm 260$	
	1878	10.720 + 280	18788	$11,320 \pm 300$ 10,910 + 290	н н
	1879	$10,400 \pm 90$	1879R	$10,510 \pm 230$ $10,510 \pm 130$	" "
Hormon do la	1001	10 220 4 510	10015	10 450 . 500	
Deña	1992	$10,230 \pm 310$	1001K	$18,450 \pm 520$	xv-p 284
rena	1883	$19,950 \pm 300$ 20 700 + 250	1002R	$20,180 \pm 310$	
	1884	$24,120 \pm 460$	1884R	$20,930 \pm 370$ 24,340 ± 470	
	1001			·	
Moncin	1924	$2960 \pm 40$	1924R	$3210 \pm 100$	XVI-р 54
	1925	$3020 \pm 45$	1925R	$3290 \pm 100$	
	1920	2880 ± 35	1926R	$3260 \pm 100$	
	1927	$3040 \pm 45$	1927R	$3470 \pm 100$	
	2102	2910 ± 40	1928R	$3340 \pm 100$	MITTT 500
	2193	$2840 \pm 70$	2193R 2194R	$3080 \pm 120$ $3060 \pm 120$	xviii-p 522
<b>.</b> .					
Muertos	1993	855 ± 35	1993R	$1240 \pm 100$	XVI-p 55
Jailard	1994	4760 ± 50	1994R	5160 ± 100	
Son Matge	1995	3380 ± 50	1995R	3770 ± 100	XVI-p 55
Son Puig <del>-</del> Servera	1998	2645 ± 40	1998R	2990 ± 100	XVI-p 55
Dlive Wood	2001	175 ± 30	2001R	30 ± 100	XVII-p 71
	2002	modern	2002R	$230 \pm 110$	XVIII-p 522

Site	Original BM-no.	Original result	New BM-no.	Revised result	Radiocarbon datelist
		(yr BP)		(yr BP)	(nopg no.)
Torralba d'en	2003	2090 ± 50	2003R	2360 ± 100	XVI-p 56
Salort	2004	1890 + 35	2004R	$2180 \pm 100$	
buible	2005	$1560 \pm 80$	2005R	$1960 \pm 120$	
_1 :	0000	0440 . 50	00645	00E0 · 100	NATT 71
Chinflon	2064	$2440 \pm 50$	2064R	$2350 \pm 100$	хv11-р /1
Son Matge Mortar	2140	2820 ± 40	2140R	3040 ± 110	XVII-p 71
Rio Tinto	2337	2330 ± 80	233 <b>7</b> R	2650 ± 140	XIX-p 75
Syria					
Tell Abu	1718	11,160 ± 110	1718R	11,140 ± 140	XV-p 284
Hureyra	1719	9120 ± 50	1719R	9100 ± 100	" "
1	1720	21.940 ± 180	1720R	$22.020 \pm 200$	11 11
	1721	8410 + 60	1721R	8490 + 110	" "
	1722	8610 + 50	17220	8640 + 100	" "
	1723	10700 + 500	17230	10.820 + 510	" "
	1724	7900 ± 50	1724R	8020 ± 100	" p 285
Tell Brak*	1758	3680 + 50	1758R	3720 + 100	XV-p 285
ICII DIAN	1759	3710 + 60	17500	3770 + 110	" "
	1760	4060 + 50	17600	4240 + 100	
	1761	4040 + 70	1761D	$4210 \pm 100$ 4210 + 120	
	1762	4040 ± /0	17620	4210 I 120 2720 ▲ 100	
	1764	3570 I 40	1764D	$3730 \pm 100$	
	1704	$3000 \pm 40$	1764R	3/10 ± 100	
	1/05	3540 ± 40	1070DR	3000 ± 100	WIT - 57
	TA\0	3440 ± 50	19/0R	$3820 \pm 100$	xv1-b 21
Tell Abada	1822	31,000 ±1250	1822R	31,250 ±1250	XV-р 278
	1823	5770 ± 45	1823R	5920 ± 100	17 H
Tell Nebi	2029	3310 ± 35	2029R	3540 ± 110	хVII-р 72
Mend*	2030	2700 ± 40	2030R	2930 ± 110	" "
	2033	2200 ± 50	2033R	2430 ± 110	
	2034	$2415 \pm 40$	2034R	2640 ± 110	
	2035	3000 ± 35	2035R	3230 ± 110	" "
	2036	4220 ± 120	2036R	4440 ± 160	
	2037	2720 + 230	2037R	2940 ± 250	" "
	2038	2390 + 45	2038R	2620 + 110	
	2030	4180 + 00	20300	4400 + 130	
	2040	$3140 \pm 60$	2040R	3370 ± 120	
Thailand					
Ban Don	2016	$1810 \pm 210$	2016R	2190 ± 230	XVI-p 57
Ta Phet					-
Turkev					
Can Hasan	1655	7660 + 70	1655R	7980 + 120	XV-n 286
imagdii	1656	7770 + 100	1656P	8090 + 170	" "
	1657	7760 + 00	1657p	8080 + 120	
	1658	7760 + 90	16590	8060 + 120	
	1660	700 ± 90	16600	8300 ± 140	
	1660	7350 ± 110	1660D	$0.370 \pm 140$ $0.460 \pm 110$	
	1662	$7040 \pm 100$	1662D	$0400 \pm 110$ $0250 \pm 210$	
	1003	7940 ± 190	1003R	$8330 \pm 210$	
	1004	8120 ± 110	1004K	8470 ± 140	
	1005	7990 ± 130	1665R	8270 ± 160	
	1666	$8160 \pm 110$	1666R	8460 ± 150	
	1667	8360 ± 60	1667R	8480 ± 110	., ,,

TABLE 2a (Continued)

Site	Original BM-no.	Original result (yr BP)	New BM-no.	Revised result (yr BP)	Radiocarbon datelist (nopg no.)
United States Indian Fort Road*	2120 2122	80 ± 35 125 ± 40	2120R 2122R	310 ± 110 350 ± 110	XVII-p 73 "
United Arab Em Ghanadha	i <i>rates</i> 2261	2 <b>47</b> 0 ± 100	2261R	2650 ± 120	хх-р 195
<i>Yugoslavia</i> Trnjane-Staro Groblje	1500 1501 1502	385 ± 50 950 ± 50 585 ± 40	1500R 1501R 1502R	610 ± 100 1070 ± 100 790 ± 100	XIV-p 254 """
Trgoviste	1503 1504	190 ± 45 285 ± 50	1503R 1504R	420 ± 100 510 ± 100	XIV-p 255 "
Doroslovo	1830 1831	2370 ± 40 2010 ± 70	1830R 1831R	2410 ± 100 2040 ± 120	XV-p 287
GEOLOGICAL SAM	PLES				
Material	Original BM-no.	Original result (yr BP)	New BM-no.	Revised result (yr BP)	Radiocarbon datelist (nopg no.)
Amber & Copal	2115 2116 2211 2235	10 ± 50 50 ± 50 140 ± 50 >36,000	2115R 2116R 2211R This figure	230 ± 110 280 ± 110 370 ± 110 is unchanged	XVII-p 73 " " XVIII-p 523 " "

TABLE 2a (Continued)

 TABLE 2b

 Unpublished BM results for which revised results have been issued

Site	Original BM-no.	Original result (yr BP)	New BM-no.	Revised result (yr BP)	
Portuguese	2275	6570 ± 120	2275R	6820 ± 140	
Shells	2276	8040 ± 100	2276R	8220 ± 120	
Collagen	2041	1270 ± 100	2041R	$1490 \pm 140$	
Amino Acids	2042	1220 ± 110	2042R	$1450 \pm 150$	
DUA Bos	2156	65 ± 35	2156R	290 ± 110	

Site	BM-no.	Radiocarbon date list (nopg no.)
British Isles		
Petters Sports Field Billingborough Fen Barling Braintree Nottington Barrow	1620 to 1623, 1625 <sup>*</sup> 1629 and 1630 1631 1632 1640	XII-p 19 XII-p 16 XII-p 19 XII-p 20 XII-p 20
Blackpatch Handley Barrow Milfield North Bishop's Cannings	1643 1644 to 1649 1650, 1652, 1653 1713 to 1717	XII-p 20 XII-p 20 XV-p 267 XII-p 22
<i>Ecuador</i> Hacienda Guarumel	1688,1689	XVI-p 46
<i>Egypt</i> Manchester Mummy Tomb of Horemheb Saqqara Tell el-D'aba	1602 1641 1727 and 1728*	xv-р 275 xIII-р 161 xv-р 275
<i>India</i> Snail shells	1670, 1671	xv-p 287
<i>Indian Ocean</i> Tortoise	1628	XIV-р 245
<i>Pakistan</i> Tarakai Kala Dherai	1690 to 1695	xv-p 281
<i>Spain</i> Ca Na Costa Son Oms Torralba d'en Salort Ferrandell Oleza	1677 1696 1697 1698	XV-р 282 XV-р 282 XV-р 282 XV-р 282 XV-р 282

TABLE 3

Published BM Radiocarbon results known to be in error but for which no correction can be issued

\* BM-1624 and BM-1726 have been remeasured: see Table 1.

## MEMORY EFFECTS IN AN AMS SYSTEM: CATASTROPHE AND RECOVERY

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ABSTRACT. A sample with a <sup>14</sup>C concentration estimated to be greater than 30,000 Modern was inadvertently graphitized and measured in an AMS system. No measurable contamination of the cesium sputter ion source was observed. Simple cleaning procedures removed the contamination from the sample preparation system, with the exception of the reaction vessel in which the sample was graphitized. Sample cross-contamination factors were estimated for all of the preparation and measurement procedures.

### MEASUREMENTS

We have begun a program of biochemical tracer experiments by making AMS <sup>14</sup>C measurements on synthesized compounds and stock reagents supplied by the biochemistry division of Lawrence Livermore National Laboratory. Cleaned separatory equipment used in previous tracer studies was also tested by processing unlabeled materials and tracer-free carriers. Despite our best efforts to alert our colleagues about the dangers of serious contamination, we unknowingly received a synthesized sample which proved to have an extremely high <sup>14</sup>C content. The measurement of this and subsequent samples provided measurements of process memory effects which would be difficult to estimate by other means.

These samples were prepared using our normal procedures (Vogel, Nelson & Southon 1987; Vogel, Southon & Nelson 1987). Samples were combusted in individual quartz tubes, with no possibility of cross-contamination. The  $CO_2$  was purified in a steel and glass transport line and then graphitized in 1 of 4 steel and quartz reactors. The graphite-on-cobalt powder from each sample was pressed into a sample holder using a drill stem. These holders were placed in the ion source together with Modern standards and background materials for measurement in our usual manner. The samples were processed and loaded in order of increasing expected <sup>14</sup>C concentration, based on estimates of the submitters, as shown in Table 1. In previous work, this protocol has prevented serious cross-contamination between disparate samples.

We expected maximum <sup>14</sup>C concentrations of a few times Modern, and we have measured such levels before without damage. However, one sample contained "catastrophic" levels of <sup>14</sup>C. The count rate from this sample grossly overloaded the data acquisition system (dead time was 65–75%), but enough data was obtained to estimate its <sup>14</sup>C concentration at greater than 30,000 Modern. It was immediately clear that the high <sup>14</sup>C concentrations found in other samples (2–40 Modern) were associated with the processing of this sample and that we could use the data to understand memory and cross-contamination levels in our system. The possible contamination paths were not unique, however, and only upper limits could be derived for some processes.

## CONTAMINATION LEVELS

The 30,000 Modern material had been expected to be low in <sup>14</sup>C and was the first of the series to be processed. The sample which immediately followed it through our gas transport (C3626 in Table 1) had a <sup>14</sup>C level that could not be fully understood. It may have been contaminated by remnants of the preceding "hot" sample in several steps of our preparation, or it may have had a high <sup>14</sup>C concentration from the biochemical preparation process. However, the CO<sub>2</sub> exchanged between these successively transported samples was less than  $1.4\%_{000}$ , assuming that all excess <sup>14</sup>C in this sample was due to the transport. Whenever it is not in use, the transport tubing is filled with water vapor to desorb CO<sub>2</sub> from the surfaces. This procedure reduced the "hot" CO<sub>2</sub> exchanged with the next set of samples to a maximum of 53ppm, as shown by the final <sup>14</sup>C concentration in sample C3656. The sample (C3657) subsequently graphitized in the same reactor as the "hot" sample may have been

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TABLE 1
Initial and final measured <sup>14</sup> C concentrations for samples processed after the graphitization of a
30,000 modern sample, listed in order of gas transport and graphite pressing

Sample	Material*	Reactor	Sample	<sup>14</sup> C cc	ncentration	(pMC)
no.		no.	size(µg)	Initial	Final	Expected
						10 100
C3627	Synth chem	2	565	>3x10°		10-100
C3626	HPLC solvent	1	190	4190	4190	10-?
		Water vapor	r cleaning of gas	transport		
C3656	Protein 1	1	780	1670	210	50-?
C3657	Protein 2	2	790	270	165	50-?
C3658	Protein 3	3	870	65	54	50-?
C3659	Protein 4	4	1260	76	58	50-?
		Gas transpo	rt and graphitizer	s cleaned		
C3662	Axel wood	1	1000		0.4	0.4
C3663	Axel wood	2**	1240		4.0	0.4
C3665	Axel wood	3	1250		0.4	0.4
C3664	Axel wood	4**	1400		1.0	0.4
		Original rea	actors #2 and #4	rebuilt		
C3666	Axel wood	2	1050		3.9	0.4
C3667	Axel wood	3	1030	0.7		0.4
C3668	Axel wood	4	840	0.7		0.4
*somple m	aterials: Synth ch	nem = svi	thesized phenyl i	midazo pyridi	ne (PhIP)	
sample in	HPLC s	olvent = hig	h-pressure liquid	chromatograp	h solvent	
	Protein	= ser	parated proteins in	a lauryl sulfa	ate carrier,	
	Axel wo	ad = 45	Myr old wood fro	m Axel Heib	erg island	
**Reactor	body and valve from	#4 was used	with #2 pressure	transducer an	d vice vers	a to determin

contamination in transducer.

primarily contaminated in transport or in pressing, but its final concentration indicated a maximum possible memory of 40ppm occurred in the graphitization of the CO<sub>2</sub>.

Pressing graphite into holders with a drill stem can leave a contaminant on the graphite surface from the preceding sample, even after cleaning the stem with emery paper. We normally sputter this away before final measurements are taken. The six biochemical samples were pressed with the same drill stem, which was then discarded. The measurements of the graphite surfaces ("Initial <sup>14</sup>C" in Table 1) showed that up to  $1.40/_{00}$  of the 30,000 Modern sample were transferred to the next sample surface. Moreover, nanogram quantities of the 30,000 Modern sample were transferred to the surfaces of the two succeeding samples despite the abrasion of the tip before pressing each sample.

The 30,000 Modern sample had been sputtered in the ion source for perhaps 10 seconds during positioning and measurement. A background sample was then immediately measured to check for cross-contamination in the ion source. The result was higher (by ca 0.1 pMC) than the previous measurements of this material (0.3-0.4 pMC), but other background samples showed no evidence of contamination. We also measured a machine background of 0.05 pMC using geological graphite only a few hours later. Assuming that the initial increase of 0.1 pMC was due to cross-contamination and that this contamination would scale as the sputtering time, the memory effect of our ion source from a typical sample (run for 100-300 seconds) is less than 1 ppm.

When we realized what had happened, we dismantled the entire graphitization apparatus and ultrasonically cleaned it with detergent for 12 hours. All parts were rinsed in water, dehydrated with a methanol rinse and baked in a vacuum oven at 200°C for 3 hours. The complete transport system, including the O-ring seals, was retained. The cold fingers, quartz tubes and all O-ring seals on the reactors were discarded. The pressure transducers were syringed with 0.1N HCl and deionized water. Several background samples were processed through each reactor and no excess <sup>14</sup>C was found, except from the reactor in which the 30,000 Modern material had been graphitized (Table 1). Approximately 1.5ppm (1.5ng) of the material appeared in two successive background samples. The transducer was identified as contributing most of the contamination, but the whole reactor was discarded. The reactor which processed the 40 Modern material was retained without detriment. Sixteen different coal samples were graphitized 12 days after this incident, and <sup>14</sup>C concentrations of 0.14-0.19 pMC were found in samples prepared in each of the 4 reactors (including a new reactor 2).

### CONCLUSION

This experience has provided some useful lessons about cross-contamination in AMS <sup>14</sup>C laboratories. A single purification and graphitization apparatus can be used for samples having <sup>14</sup>C concentrations from 50 Modern down to 0.2pMC, albeit with some care. However, it would be best to have separate systems for such disparate samples, or to use a sealed-tube graphitization (Slota & Taylor 1986) in which the "reactor" is disposable. Clearly, water vapor is a valuable means to minimize cross-contamination in the transport tubing. Reaction vessels can be cleaned effectively, except in an extreme case. New drill stems must be used for pressing especially old or small samples. Our experience with ion source cross-contamination is particularly heartening. However, most source contamination probably arises from re-evaporation or ionization of sputtered neutral atoms deposited on surfaces facing the sample, and the effect could be very different for other source geometries and sample materials. While these results show that a wide range of  $^{14}$ C activities can be accomodated in the same AMS system and that recovery from severe contamination is possible, we certainly do not advocate processing both natural and labeled samples in the same chemical laboratory. The long-term consequences are likely to be disastrous. However, it does seem possible to consider measuring both labeled and natural samples on the same accelerator. This will certainly require careful protocol. Pre-screening of some samples with liquid scintillation counters may be necessary until greater experience in AMS micro-tracing is available.

### ACKNOWLEDGMENTS

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### DISCUSSION

## RECOVERY FROM TRACER CONTAMINATION IN AMS SAMPLE PREPARATION

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Samples that contain high levels of tracer  ${}^{14}C$  are occasionally received at radiocarbon laboratories. Enriched samples of about 10 times modern can usually be handled without severe degradation of sample blanks, due to sample memory effects. It is not possible to identify such samples in advance, and one should be more wary of certain sources of  ${}^{14}C$  samples than others. We report here on a recent experience in our laboratory, similar to that reported by Vogel *et al* above.

In May 1989, we processed two samples of CO<sub>2</sub> gas through our normal gas-handling system, which uses a known volume and a capacitance manometer. The samples were then reduced to graphite as usual (Slota et al 1987). The first sample was measured to be ca 200 times modern, and the second was ca 5000 times modern. These samples were not run for more than two minutes on our accelerator. The samples were immediately removed from the accelerator, and blank samples, fabricated prior to receipt of the "hot" samples, were loaded. These samples confirmed that after some minutes of sputtering with Cs, that the accelerator blank was at its usual value. Subsequent to these "hot" samples, we processed a blank CaCO<sub>3</sub> sample through our sample preparation procedure. This sample was measured to contain  ${}^{14}C$  at a level of 82.6  $\pm$  0.6% that of modern carbon. After this result, the gas handling line was flushed with dead CO<sub>2</sub> and also degassed by heating the glassware. Two subsequent blanks measured one and three days later gave 7.6% and 1.4% modern, respectively. These samples were made into graphite on lines other than the one (no. 7) which had been used for the "hot" samples. After these measurements, we endeavored to identify and eliminate any potential source of "tracer" <sup>14</sup>C which was the cause of the elevated blank. The results of these measurements are given in Table 1. All the blank measurements listed were performed using commercial  $CO_2$ , which we normally find to have ca 0.4% modern carbon (Linick et al 1986). From the results presented in the table one can conclude the following:

1. Cross-contamination between a hot sample and a blank sample fabricated in the same glass vacuum system is of the order of 0.016%, so that processing a blank sample immediately after an oxalic-II sample would result in a blank of ca 0.02% modern.

2. Flushing of the system with "dead"  $CO_2$  reduces the contamination from the tracer levels to ca 1.4%. Subsequent re-equilibration of the sample handling system with "dead"  $CO_2$  did not improve this.

3. Subsequent tests of blanks showed variable <sup>14</sup>C, which we were eventually able to ascribe to contamination of some gas storage vessels. Test 4 involved replacement of the Kel-F plug in the Kontes high-vacuum valves in the gas storage vessels, and this did not eliminate the contamination.

4. The contaminated graphite line could not be cleaned up, as shown by test 5.

### CONCLUSIONS

After these investigations, we concluded that the only way to ensure low and repeatable blanks was to replace the entire gas-handling system, including an MKS Baratron gauge, the contaminated graphite line (no. 7), including the pressure transducer in the graphite line, and all gas sample vessels in the laboratory. When these materials were removed from the laboratory and replaced, normal blanks of 0.4% or better were again achieved. This experience can only serve to reinforce our belief that tracer <sup>14</sup>C should not be allowed in a

### Discussion

Results of blank and test measurements subsequent to processing of a tracer <sup>14</sup>C sample

Target	Date run	Description	Graphite line	Per cent modern
1. T	racer sample	25		
4607 4611	7 May 8 May	$CO_2$ gas sample $CO_2$ gas sample	7 7	20,000% 500,000%
2. B	lank tests su	bsequent to tracer samples.	Gas measured in co	ontaminated volume.
4613 4617 4625	9 May 11 May 14 May	blank 1 day after tracer blank 3 days after tracer blank 5 days after tracer	1 1 8	82.6% 7.6% 1.4%
3. T	est combusti	on line after equilibration with	$h CO_2$ for 3 days	
4627 A B	15 May 15 May		1 4	1.9% 4.7%
4. <i>T</i>	est of gas sa	mple storage vessels		
4629	16 May	Gas vessel stored in air for 5 days, then baked out, and pumped in vacuum oven. C on stopcock replaced.	l )-rings 4	1.3%
4630	16 May	Same as 4629, O-rings not replaced	5	1.3%
5. R	eplacement of	of stopcock plug and O-rings	on contaminated gr	aphite line
4632	16 May	Tank CO <sub>7</sub>	7	6.4%

radiocarbon laboratory. In fact, from the data presented in the table, we would expect that a sample containing 20 times the <sup>14</sup>C of a modern sample would temporarily double our contamination background.

As additional illustration of the dangers of tracer <sup>14</sup>C in a low-background laboratory, we note that in our laboratory we measured many blank targets prepared at the Carnegie Institution in Washington. The room in question at Carnegie was used as a tracer <sup>14</sup>C laboratory in the 1960s (Stafford, pers commun). Despite vigorous recent efforts to clean up the room, the "blanks" we measured all had <sup>14</sup>C contents equivalent to modern or even post-bomb levels. These cleaning efforts were eventually abandoned.

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## DISCUSSION

Ted Litheeland gave me the following account of a similar incident that appears in the 1984 Isotrace (University of Toronto) annual report:

"Last year an equivalent age of older than 70,000 years BP was reported for high purity aluminum. Since that time many samples have been analyzed and the source contamination has been re-examined several times. Up to wheel 10B, no evidence of cross-contamination had been observed. On October 18, the source was contaminated by an enriched sample, enriched to between 20,000 and 200,000 times modern. This sample was run for no more than 15 minutes, but immediately after, the system background was observed to be ten times greater. After the sample holder and the source aperture plate (behind which the sample is positioned) were replaced and the rest of the source thoroughly cleaned, the background was measured to be at the same level as it was before the enriched sample was analyzed."

> David Elmore Associate Editor

## DATING THE TURIN SHROUD—AN ASSESSMENT

## H E GOVE

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ABSTRACT. An assessment is made of the credibility of the radiocarbon dating of the shroud of Turin. The quoted final results produced a calibrated calendar age range of AD 1260–1390 for the linen of the Turin shroud at a 95% confidence level. The measurements were carried out independently in three accelerator mass spectrometry (AMS) laboratories located at the University of Arizona, Tucson, Arizona, USA, Oxford University, Oxford, England, and ETH-Hönggerberg, Zürich, Switzerland with assistance for certification and data analysis provided by the British Museum. The author concludes that, although the procedures followed differed substantially from those recommended at a workshop organized by the Pontifical Academy of Sciences, the results are credible. Although of negligible scientific value, they represent a major public triumph for the AMS method of carbon dating. However, many doubts have been raised, both real and fanciful, concerning the validity of the results and these are discussed. It is suggested that steps should be taken to conserve the shroud and that permission should be given for its examination by experts in medieval art.

In a paper presented at the 13th International Radiocarbon Conference held in Dubrovnik, Yugoslavia, June 20–25, 1988 (Gove 1989) the author reviewed the background and the status at that time of the project to radiocarbon date the Turin shroud. Of the three laboratories located in England, Switzerland and the USA only the latter at the University of Arizona had submitted its data at that time to the British Museum. Measurements were still in progress at the other two in Zurich, Switzerland and Oxford, England. In that paper concern was expressed about changes that had been made in the original dating protocol (Gove 1987) dictated by Turin ecclesiastical authorities but ultimately accepted by the three laboratories chosen by the Archbishop of Turin, Cardinal Ballestrero or, more accurately, by his science advisor, Professor Luigi Gonella, of the Turin Polytechnic.

Since then the final results have been published (Damon *et al* 1989). The reported result is that the flax from which the shroud's linen was woven was harvested between AD 1260 and 1390 at a confidence level of 95% (a mean of AD 1325 with a 33-year standard deviation). The agreement between the three laboratories for the shroud sample and the three control samples was within about one standard deviation. The possibility was raised by the author and many others that one of the laboratories might produce an outlier result, as was the case for an interlaboratory comparison carried out in 1986 (Burleigh, Leese & Tite 1986) involving these three laboratories and three others. One outlier among three cannot be statistically eliminated as it can among 6 or 7. Fortunately, this situation did not occur. Furthermore, the author is as sure as it is possible to be that there was absolutely no collusion between the three laboratories before they submitted their results to the British Museum. This belief must be widely shared since, among the many reasons advanced for disbelieving the results, no one has suggested such collusion as a possibility.

Turning now to the reasons that have been advanced for doubting the results, they are many and varied. Perhaps the most troublesome one is the fact that all three laboratories received a sample from essentially the same place on the shroud, and all likely would use essentially the same cloth cleaning procedures. This would mean that any contamination that is not removed by such cleaning procedures will equally affect all three measurements making them in agreement but wrong (Gove 1989). In the event, however, rather different cleaning procedures were employed by and within the three laboratories, ranging from ultrasonic cleaning to much more rigorous and thorough cleaning techniques (Damon *et al* 1989). Experts in the field do not know of any contamination that would not be removed by one or other of the cleaning procedures used. Even if it did exist in the form of contemporary organic carbon, which is one way the apparent age can be reduced, 64% of the shroud sample would have to be such contamination and only 36% of 2000-year-old carbon to change the measured date from the first century AD to the 14th century. Visible inspection by the author of the shroud sample received by Arizona before it was cleaned made it clear that no such gross amount of contamination was present.

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It has been argued (Maloney 1989) that a more subtle form of contemporary carbon contamination may have occurred during the fire the shroud was subjected to in 1532. To quote Maloney,

Worse yet, when the cloth was folded into 48 layers and stored in the silver reliquary in Chambery, France, this corner (from which the samples for radiocarbon dating were removed) lay precisely in the area where the super-heated water settled when the fire was doused to save the Shroud. Silver melts at 960 degrees centigrade so the Shroud must have been subjected to 'pressure-cooker conditions' which would have dissolved any contaminants and transport them into the very molecular structure of the flax fibers. In the words of retired British textile expert John Tyrer, the carbon 14 content of the Shroud would have been 'topped up' and make it appear younger than other evidence suggests it to be.

Exactly how Maloney knows the location of the sampled area when the shroud was lying folded in its silver chest in 1532 is not stated. In any case, if the contamination were carbon that was contemporary in 1532, the mixture would have to be 86% carbon dating from the year 1532 to only 14% dating to the year zero. One does not have to be a molecular biologist to recognize the absurdity of this "topping up" notion.

Despite this, at an International Conference on the Shroud and Iconography held in Bologna, Italy May 6–7, 1989, C Haberman reported in *The New York Times* of June 11, 1989 that a group of "specialists" concluded that contamination of the cloth over the years, including damage from a fire in 1532, could have undermined the tests. No details for the basis of this conclusion were given in the news report but one suspects that it was arguments like those outlined above that prevailed. Ockham's razor is increasingly frequently employed (Malone 1989) to argue the Turin shroud dates to well before the 14th century but surely the simplest, albeit the dullest, conclusion to reach is that the shroud's age is its historic age which is what the carbon date tells us.

The same New York Times article states that an unnamed French monk charged that the British Museum official who coordinated the radiocarbon measurements substituted snippets of 14th century cloth for the postage-size shroud samples. The only time the samples removed from the shroud in the Sacristy at Turin Cathedral on the morning of April 21, 1988 were out of the sight of representatives of the three laboratories was when they were taken to the adjacent Sala Capitolare to be divided and sealed inside numbered stainless steel containers (Donahue, pers commun June 1989). During this time only the representative of the British Museum and the Archbishop of Turin were present (Damon et al 1989). In addition to this charge by the unnamed French monk, serious questions have been raised by R Halisey (pers commun Aug 14, 1989) as to why the sampling of the shroud and the sealing of the samples took place in two separate locations since that opens the possibility that a substitution could have been made of the shroud samples. This sample sealing procedure was apparently not videotaped although all the other operations were (Damon et al 1989). Despite this inexplicable contretemps, it seems probable that the Archbishop would detect such a substitution except in the unlikely event the British Museum official was inclined to perpetrate such a fraud and was capable of the requisite legerdemain. Equally unlikely but at least more plausible would be the substitution of snippets of first century cloth for the shroud samples. In any case, the distinctive 3 to 1 herringbone twill weave of the shroud could not be matched as the British Museum officials discovered when they attempted to find such for control samples. It was actually fortunate that the shroud samples were, in fact, identifiable both to preclude the possibility of substitution and for other reasons discussed below.

Along these same lines is the claim that the 10mm x 70mm strip, cut from the edge of the shroud just above the place where a sample had been removed in 1973, contained stitching threads or possibly pieces of the backing cloth of much later than first century vintage. Not only would this have been spotted by the two textile experts present but subsequent examination by members of the dating laboratories would have instantly revealed such extraneous material. All the laboratories examined the textile samples microscopically and removed any foreign material. Another argument has been made (G Hoyas, pers commun May 2, 1989) that the part of the shroud from which the sample was cut had possibly become worn and threadbare from countless handlings and had been subjected to medieval textile restoration. If so, the restoration would have had to be done with such incredible virtuosity as to render it microscopically indistinguishable from the real thing. Even modern so-called invisible weaving can readily be detected under a microscope, so this possibility seems unlikely. It seems very convincing that what was measured in the laboratories was genuine cloth from the shroud after it had been subjected to rigorous cleaning procedures. Probably no sample for carbon dating has ever been subjected to such scrupulously careful examination and treatment, nor perhaps ever will again.

Although the original protocol (Gove 1987) specified the shroud and control samples were to be distributed to the laboratories in such a way as to ensure that the laboratories were not aware of the identities of the individual samples, the unique weave of the shroud made it instantly identifiable. The only way to have circumvented this would have been to unravel all four samples and to cut them into small pieces, too small, if possible, to identify which were warp and which weft threads. In the case of the shroud, these two classes of thread are of quite different denier. At the Turin workshop, this procedure was considered and wisely rejected since it would have risked the possibility that the cloth might be destroyed in the more rigorous cleaning procedures. In retrospect, it turned out to be important that the shroud samples were initially identifiable to the laboratory scientists so that the possibilities of contamination and reweaving of the kind discussed above could be shown to be out of the question. The arguments often raised, eg, by Maloney (1989) that radiocarbon measurements on the shroud should be performed blind seem to the author to be lacking in merit. It was never suggested that any other types of measurements on the shroud such as those carried out in 1978 be blind, so why should the only measurement that ever made any sense, ie, carbon dating, be subjected to this requirement? Since the three laboratories obtained the same date for the shroud without collusion and since the AD 1325 date could not have been the one hoped for by all the senior scientists at the three laboratories, lack of blindness in the measurements is a rather insubstantial reason for disbelieving the result.

One of the arguably more fanciful possibilities for the radiocarbon date of the shroud being in error has been advanced by T J Phillips (1989) of the High Energy Laboratory of Harvard University, Cambridge, Massachusetts (pers commun March 17, 1989). He has pointed out that the resurrection of Christ as described in the Bible was a unique physical event that was not accessible to direct scientific scrutiny. One cannot quarrel with that statement. He goes on to argue that since the image on the shroud appears to be a scorch, it suggests that the body on it radiated light and/or heat. From this he suggests the possibility that "it may also have radiated neutrons, which would have irradiated the shroud and changed some of the nuclei to different isotopes by neutron capture. In particular, some <sup>14</sup>C could have been generated from <sup>13</sup>C." This could have changed its apparent age from 1st century to 14th century AD. Phillips advances no theories as to how any biological process can produce intense heat or light, much less neutrons, even thermal ones. He does not remark on the astonishing coincidence between the date this ghostly neutron irradiation produced and the known historical date of the shroud ca AD 1353, nor does he note that, since the neutron intensity from such a hypothetical source must vary with distance from the source, the piece of cloth selected was at just the correct distance to produce the historical date. A piece closer to the image, on the Phillips' hypothesis, would have produced an even more recent date. Had such a result been obtained from the AMS radiocarbon measurement, it would certainly have strengthened Phillips' speculation but would have astonished most of the rest of the scientific community. An elegant answer to Phillips was provided by R E M Hedges (1989). One interesting suggestion that Phillips (1989) made is that this same burst of neutrons would have produced other long-lived radioisotopes such as <sup>36</sup>Cl through neutron capture on stable <sup>35</sup>Cl. The problem is that chlorine is not a natural component of flax and, if present, would probably arise from contamination through the centuries. The radioisotope  ${}^{36}$ Cl can also be produced by the interaction of high-energy neutrons from, eg.

cosmic rays with calcium. The AMS laboratory at the University of Rochester has the most experience with measuring <sup>36</sup>Cl in natural samples. Even in the unlikely event that Professor Gonella, in his capacity of science advisor to the Archbishop of Turin, were to request that Rochester undertake a <sup>36</sup>Cl measurement on the shroud, the offer would be declined.

When the author first read the report of the dating results (Damon *et al* 1989) he was struck by the fact that senior scientists at 2 of the 3 laboratories involved in the measurements, namely Oxford and Zurich, did not have direct control of the samples from cloth to ion source since, "after combustion to gas, the samples were recoded so the staff making the measurements did not know the identity of the samples." Hence, it appears that, at these two laboratories, no assurance can be given that no substitution occurred after the samples arrived in those two laboratories. Amazingly enough, it is implied in the report on the shroud dating (Damon *et al* 1989) that this added to the credibility of the result because, at least in these two laboratories, the measurements were carried out blind. On the contrary, this was an invitation to produce discordant results. Fortunately, however, the agreement in the measurements among the three laboratories precludes the possibility that any improprieties occurred.

The New York Times article (Haberman 1989) suggested that even the chief shroud scientist in Turin, Professor Luigi Gonella, found the shroud dating results credible. He is quoted as saying he "had no scientific reason to think the testing was inaccurate" but then went on to say "Even the law of gravity may turn out tomorrow to be in error." If he is implying that there is about as much chance that the shroud measurements are wrong as that law of gravity is in error, then he is very confident in the results indeed.

There are doubtless some whose religious beliefs have been profoundly affected by their exposure to the Turin shroud and choose not to believe the results. The writer, Ian Wilson, who has authored two books on the shroud (1978, 1986) as well as many articles, and who is presently President of the British Turin Shroud Society, is one such believer. He was apparently converted to Catholicism by his studies of the shroud. He was quoted in this same New York Times article as saying, "Until somebody can show me how the image was made-the carbon dating, for reasons we don't know, may be in error." This emphasizes the need to have real art experts, particularly those familiar with medieval art, examine the shroud as will be discussed below. Wilson is certainly not alone in continuing to believe, despite the radiocarbon results that the Turin shroud is Christ's shroud. The Rev Felice Cavaglia, pastor of the Turin Cathedral where the object is stored, is mentioned in the New York Times article as saying that after eight months since radiocarbon showed it to be inauthentic, the shroud retains its allure for believers that it is Christ's shroud. In that same article, even Pope John Paul II is quoted as still believing it is a relic and not merely an icon. The author's fear that if the shroud date was much more recent than the first century AD, it might affect some people's religious beliefs, was apparently unfounded. It is another remarkable example of "Plus ça change plus c'est la même chose."

W S A Dale (1987) of the Department of Visual Arts, University of Western Ontario, London, Ontario, Canada, in a study of Christian art concluded that, if the image on the shroud were an artistic representation of the crucified body of Christ, it was an icon dating from the 11th century. Comparing it with Christian art through the centuries, he asserts it was unlikely to have been created earlier than AD 969 or later than AD 1169. He remarks on the striking similarity between the frontal image on the Turin shroud and the Epitaphios of Milutin Ures in the Museum of Church Art in Belgrade, Yugoslavia. Although this dates from between 1282 and 1321 (the latter being amazingly close to the measured mean date for the shroud of AD 1325), he argues that similar *epitaphios sindons* go back to early in the 11th century. Dale (pers commun Aug 11, 1989), who published this study before the radiocarbon measurements had been made, considers the possibility that the artist who created the shroud of Turin may have used this Belgrade icon as a model, or for that matter, that the artist who created it may have been the shroud artificer himself to be exceedingly unlikely. In his view, both artists were influenced by depictions of the crucified body of Christ layed out for burial that date back to the 11th century. In any case, the radiocarbon date proves that the shroud image was almost certainly created by the hand of man most likely in the first half of the 14th century. Aside from the question of preservation of the shroud, discussed below, the most important question to be settled is how the image on the shroud was created and, if possible, by whom. A panel of medieval art experts selected by the Archbishop of Turin with advice from art experts in the Vatican should be given an opportunity to thoroughly examine the shroud using whatever scientific non-deleterious methods that are required to establish the nature of the image.

To the author, one of the most fascinating aspects of the radiocarbon date is the fact that the person who created the image must have been known to the person believed to be the shroud's original owner, Geoffry I de Charny, the French knight who allegedly first announced its existence ca 1353. He died in battle ca 1356 without revealing how and from whom he had obtained it. According to R W Kaeuper (pers commun Aug 29, 1989), de Charny was the exemplar of a medieval knight. He was a literate man and a rigid believer in chivalry. He is the author of the only book on chivalry up to that time ever written by a layman. A 15th century copy of the manuscript of this book exists in Brussels and copies of it can be found in a few libraries in the USA. A translation of the book from the medieval French is presently being undertaken by the noted British scholar, Elspeth Kennedy, of Oxford University, and when published, will contain an historical introduction by Kaeuper. Although the shroud is apparently nowhere mentioned in the book, one cannot but think that somewhere in the records of de Charny's time there must be some mention of the origin of the shroud.

It is also considered possible that the private papers of the former king of Italy, Umberto II, presently in the possession of his widow may contain information as to the origin of the Turin shroud. King Umberto II was the previous owner of the shroud, although it was confiscated from him by the Italian government after his banishment from Italy following the second World War. Upon his death on March 18, 1983, his will bequeathed the shroud to the Vatican and Pope John Paul II is its legal owner.

Finally, turning to the question of conservation, the Turin shroud is still a very valuable and precious artifact and is certainly worth preserving. It has been pointed out (Gove 1989) that its custodial treatment both in France and in Turin since its existence was first revealed in ca AD 1353 has been less than exemplary. It was involved in a serious fire in Chambery, France in 1532 and is presently stored in an environment lacking both temperature and humidity control. A sizeable piece of the main body of the shroud was removed in 1973 for examination by a Belgian textile expert and the whereabouts of this piece was so poorly monitored that, although it was allegedly returned to Turin, it was considered too suspect to be used for carbon dating. It was considered necessary to remove another piece very close to where this 1973 sample was taken for the recent radiocarbon measurements. In 1978 a group of scientists who were, almost without exception, convinced that the shroud was indeed Christ's burial cloth was permitted to bathe the shroud in potentially damaging electromagnetic radiation of various frequencies including ultra-violet and X-radiation all with the alleged purpose of performing scientific tests that might confirm its authenticity as Christ's shroud. On the whole, these tests turned out to be inconclusive. There is even serious talk of permitting this same group to perform similar tests at even higher electromagnetic power in addition to other measurements. One of these is determining the ratios of the 2 stable isotopes of carbon (which has already been carried out for another reason by two of the carbon dating laboratories) and the 3 stable isotopes of oxygen which it is claimed will reveal whether the flax from which the shroud's linen was woven grew in a warm, cold, wet or dry climate! Rather than permitting such questionable scientific forays on the shroud by self-appointed "experts," what is needed is dispassionate advice from real experts on how best to conserve the shroud and then from medieval art experts on how, and if possible, by whom the image was created. The latter can await the apparent gestation period of the Vatican which appears, at least on matters concerning the Turin shroud, to be of the order

of a decade or so but the former—the actions to be taken to ensure conservation—certainly cannot.

Accelerator mass spectrometry, first developed at the University of Rochester's Nuclear Structure Research Laboratory in 1977 (Purser et al 1977; Bennett et al 1977) and now widely practiced in many laboratories throughout the world, has achieved its greatest public success to date in establishing that the Turin shroud is of medieval origin and certainly not the burial cloth of Jesus Christ. Although few would rejoice in this particular result, it is an impressive example of the power of the accelerator-based carbon dating technique. Without it the measurement might never have been made. Whether that is a good thing or not only history can decide.

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## SOME RADIOCARBON DATES FOR TUFAS OF THE CRAVEN DISTRICT OF YORKSHIRE

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ABSTRACT. <sup>14</sup>C dates of relict tufa deposits at Gordale indicated a Subboreal age when the carbonate age was corrected with empirical bedrock dilution factors 'q' of 0.79 or 0.85. Estimates of 'apparent age,' based on extrapolated  $\delta^{13}$ C values were about twice those obtained with q, and the  $1\sigma$  error was large. The  $\delta^{13}$ C values of tufa samples were not correlated with carbonate age and were close to -10%. Application of q values in this district requires caution as they appear to be site-specific. We recommend that wherever possible, levels of <sup>13</sup>C and <sup>14</sup>C are measured in the associated tufa-depositing water, and an empirical dilution factor employed.

## INTRODUCTION

In this paper we report on some <sup>14</sup>C dates of tufas and associated organic material from the Craven district of Yorkshire. This region contains the widest range of tufas in the UK and tufa is still forming at many sites (Pentecost 1981; Pentecost & Lord 1988). Particular attention has been paid to Gordale Beck with its large cascade tufas. Carbon isotope studies of the stream waters, and some of the tufas, have been previously reported by Thorpe (1981) and Thorpe *et al* (1981). We have obtained further data from Gordale and report on some additional sites. At two of these, organic carbon was associated with the deposits.

#### METHODS

Tufa samples weighing ca 100g were collected from discrete areas at each site. Pretreatment of the raw sample materials to recover specific carbonaceous components and the subsequent determination of isotope enrichment values were carried out at the NERC radiocarbon laboratory.

Carbonates were hydrolyzed with 5M hydrochloric acid. Organic residues, acid-washed charcoals and the collagen fraction extracted from bones were oxidized by quantitative high-pressure combustion. In all instances, the product carbon dioxide was dried and collected by cryogenic trapping and then cleaned by vacuum distillation. Radiocarbon measurement was by liquid scintillation counting of benzene synthesized from the primary carbon dioxide produced (Harkness & Wilson 1973). Conventional age values were calculated at the  $\pm 1\sigma$  level for overall analytical confidence, in compliance with their definition by Stuiver & Polach (1977). The associated  $\delta^{13}$ C(PDB) values were recorded for carbon dioxide produced by quantitative burn-back of a small (5µl) aliquot of the benzene synthesized for radiometric counting. It is important to note, therefore, that the <sup>13</sup>C enrichment data in Table 1 may reflect a degree of isotopic fractionation induced during benzene synthesis.

### **RESULTS AND DISCUSSION**

## Gordale

Gordale contains some of the largest cascade tufas in the UK, and has been well studied (Thorpe, Otlet & Sweeting 1980; Thorpe *et al* 1981; Thorpe 1981; Pentecost 1981; Pentecost & Lord 1988). The stream rises in marshland and tufas are deposited over a 4km length beginning 1km downstream. In the upper gorge, a series of tufa terraces up to 4m thick have been partly cut through by the stream and form a prominent bench, 1km long (Fig 1). Sections of tufa were exposed for dating on both sides of the stream (National Grid Refs 34/91366444 and 34/91336449 for east and west banks, respectively) and samples taken for dating near the top and bottom of the profiles (Fig 1). The material consisted of a pale, soft crumb-like tufa. Narrow iron-rich layers—perhaps representing former piezomet-

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Fig 1. Diagram of Gordale Beck, looking north. Tufa terraces occur in the upper gorge and extend for ca 800m downstream. In lower Gordale there are three cascade tufas, two of which (relict upper mound, lower mound) are inactive. Arrows show location of samples collected near the top and bottom of the profiles.

ric surfaces, and beds of oncoids also occurred. There was insufficient organic matter for dating.

The carbonate dates were corrected for bedrock dilution using a factor 'q' (Vogel 1970). A value of q = 0.85 is commonly employed for tufa and appears to have general applicability (Geyh 1973; Srdoc *et al* 1980; Srdoc, Horvatincic & Obelic 1983) but a detailed study of the Gordale waters by Thorpe (1981) gave a value of  $0.82 \pm 0.022\sigma$  at the cascades.

Measurements of <sup>14</sup>C levels in the Gordale Beck springs and at the cascades demonstrated downstream enrichment of <sup>14</sup>C amounting to 3.4 pMC caused by atmospheric CO<sub>2</sub> exchange, and we estimate for the terraces, which lie above the cascades (Fig 1), a q value of  $0.79 \pm 0.03\sigma$ . Corrected dates using q values of 0.79 and 0.85 are given in Table 1. The corresponding  $1\sigma$  errors for these corrected dates are  $\pm 290$  yr for q = 0.85 and  $\pm 310$  yr for q = 0.79. Although the sections were separated laterally by 100m, both gave a q-corrected Subboreal age and showed stratigraphic concordance. The results suggest average deposition rates of 0.2 and 1cm yr<sup>-1</sup> for the east and west locations, respectively. Deposition rates for active tufas in the area range from 0.03-1 cm yr<sup>-1</sup> (unpub data). Thorpe (1981) analyzed 22 samples of tufa from profiles in the three cascade deposits of lower Gordale (Fig 1) and obtained a mean  $\delta^{13}$ C of -9.82, with 95% confidence limits -9.4 to -10.3. There was no correlation between the  $\delta^{13}$ C values and <sup>14</sup>C activity in these profiles. The terrace tufas were not formed on cascades but had a virtually constant  $\delta^{13}$ C of -10.0 (Table 1), not significantly different (p > 0.05) from those of lower Gordale.

Tufa forming the active upper mound of lower Gordale (Fig 1) has a well-documented history. After a catastrophic storm ca 1730, water burst through a rock wall to form a cave-like opening known as the "Hole in the Wall" (Phillips 1853). This left the former tufa

Site, depth	SRR* no.	Conventional age ( <sup>14</sup> C yr BP + 1σ)	q-corrected age ) (yr BP)	δ <sup>13</sup> C (PDB) ‰
Gordale terraces				
West, +2.6m	-3435	6150 + 60	4845 (4260) 4165**	-10.0
West, -0.6m	-3436	6480 + 60	5180 (4590) 4500	-10.0
East, +1.9m	-3433	5395 <del>+</del> 50	4090 (3500) 3410	-9 9
East, -0.26m	-3434	$6510 \pm 50$	5210 (4620) 4525	-10.2
Cave Ha 3				
Charcoal	-3442	3915 + 50		-24 5
Travertine. +5cm	-3444	$3030 \pm 50$	1730	-2.2
Travertine, -5cm	-3445	$4150 \pm 50$	2850	-2.5

TABLE 1 Conventional and q-corrected ages (q = 0.82) of tufas and associated organic material. Ages for q = 0.79 are shown in parentheses. For Gordale, heights are relative to the stream level

\* Scottish Universities Research and Reactor Centre

\*\* Corresponding  $1\sigma$  errors for these corrected dates are ±290 yr for q = 0.85 and ± 310 yr for q = 0.79.

mound to the west dry, and the active upper mound is assumed to have begun forming after 1730.

The bulk of the tufas composing the relict upper and lower mounds have been dated as 1910-4850 and 4000-4500 BP, respectively. The active upper mound age was underestimated when dated with q = 0.82 but a 'correct' age was obtained when q = 0.842 (Thorpe 1981).

Pazdur and Pazdur (1986) defined the 'apparent age' of tufa associated with datable organic matter as the difference between the carbonate age and the organic age. After a statistical analysis of several <sup>14</sup>C-dated profiles, Pazdur (1988) concluded that it was possible to estimate apparent age from empirical equations based on regression analysis. One equation related mean apparent age, defined as  $\langle T_{app} \rangle$ , to a  $\delta^{13}$ C value defined as  $a_{oc}$ . The latter was obtained as the intercept of the linear regression of tufa  $\delta^{13}$ C(PDB) on carbonate age. Pazdur considered that application of this equation was acceptable for profiles where  $\delta^{13}$ C is not correlated to the carbonate age, organic matter is absent, and the tufa deposited in turbulent water or as carbonate mud.

The deposits of lower Gordale are classic cascade tufas formed under highly turbulent conditions. Linear regression analysis of Thorpe's (1981) measurements on a profile through this material yielded a value of -9.56 (N = 11) for  $a_{oc}$ . Substitution of this value in Pazdur's (1988) equation 9 gave an 'apparent' age of  $3.04 \pm 3.5$ k yr. Plotting our  $a_{oc}$  value on Pazdur's accompanying Figure 4 (p 15) gave a similar apparent age but a smaller  $1\sigma$  error of 0.6k yr. The apparent age calculated by this method is considerably higher than that obtained with q. We have not applied Pazdur's equation to our upper Gordale sites because of the small number of sampling points. We suspect that here, most of the tufa was also deposited under turbulent conditions, as it contains oncoids and the remnants of tufa barrages. However, small impoundments may also have occurred behind the barrages leading to the deposition of tufa under quiescent conditions. Some of the tufa also shows evidence of comminution and may have been transported from further upstream. Application of Pazdur's equation 9 may not be strictly valid here, but given the similar  $\delta^{13}$ C values to lower Gordale, the apparent age estimation would have been close to that obtained for lower Gordale.

### Cave Ha 3 and Kilnsey

Cave Ha 3 is a limestone rock shelter 12km west of Gordale. An excavated section revealed a 2m layer of travertine below a narrow, well-defined layer of charcoal. Above the

charcoal, another 30cm of travertine occurred. Chipped stone tools and animal bones were loosely associated with the charcoal (Pentecost & Lord 1988). The charcoal yielded a date of  $3915 \pm 50$  BP, consistent with the available archaeological evidence. However, the lower travertine showed age inversion when a q-correction of 0.85 was applied. Adjustment of q to give an age older than the charcoal, required values >0.98, suggesting negligible bedrock dilution. Another unusual feature of these travertines was their exceptionally high <sup>13</sup>C contents (Table 1). This might be explained by the admixture of limestone breccia with the deposit. The limestone  $\delta^{13}$ C averaged +0.63 (Thorpe 1981) and an admixture of limestone would raise  $\delta^{13}$ C but attenuate the <sup>14</sup>C level, giving a much older date than actually found.

If the percolating groundwater contacted the atmosphere for a period of several days prior to precipitation, almost complete equilibration with the atmospheric CO<sub>2</sub> ( $\delta^{13}$ C ca  $-9\%_{00}$ ) could occur and would raise the <sup>13</sup>C value of the travertine considerably and explain the high values observed. Complete equilibration of atmospheric CO<sub>2</sub> with the dissolved carbonates in open karst waters where HCO<sub>3</sub><sup>-</sup> is dominant will produce a  $\delta^{13}$ C of  $0 \pm 0.5\%_{00}$ and a <sup>14</sup>C content equal to atmospheric levels. The equilibrium fractionation between CO<sub>2</sub> gas and dissolved HCO<sub>3</sub><sup>-</sup> at 15°C ds +9.0\%\_{00} (Mook 1974) giving a small <sup>14</sup>C enrichment of ca 1.8 pMC in the dissolved bicarbonate. This indicates that the uncorrected <sup>14</sup>C age would give a better estimate of age than one corrected with q, which emphasizes the site-specific nature of these corrections.

Near Kilnsey, 7km NE of Gordale, is an active tufa-depositing site containing locally extensive tufa banks. In one of these, a horse jaw was recovered embedded in soft tufa, 75cm below ground level. Collagen extracted from the jaw gave a comparatively recent date of 310 BP (Table 1) although the associated tufa yielded a much earlier q-corrected date. If tufa and jaw were coeval, the 0.85 dilution factor is clearly inappropriate, and would need to be reduced to 0.73. Such low values have been reported elsewhere (Thorpe 1981; Srdoc *et al* 1982; Pazdur, Pazdur & Szulc 1988).

The  $\delta^{13}$ C value for this site is higher than Gordale by ca  $3\%_{00}$ . Discharge at Kilnsey is much less than at Gordale, and the feeder spring is only 200m above the tufa. Deposition occurs today on a moderate slope under turbulent conditions and probably did so in the past. The dilution factor q, for a site so close to the spring source, may well have been <0.85, but the  $\delta^{13}$ C value should then be  $< -10\%_{00}$ , given the similar hydrochemistry and bedrock characters. With these uncertainties, we cannot be sure that a low q value is appropriate at this site until more measurements have been made. Application of Pazdur's (1988) equation 7 to our data gives an apparent age of 2.65k yr for the deposit, which would indeed suggest that bone and tufa were deposited at the same time.

### CONCLUSIONS

During this investigation it soon became apparent that detailed sampling was necessary to provide sufficient information for dating purposes. Even where organic matter is present, it does not necessarily follow that the tufa and organic materials were formed at the same time. There are several sites in Craven where there is evidence of redeposition of tufa as comminuted and water-worn fragments, including upper Gordale. In such cases, organic materials are of little use for comparative dating, and could be misleading. Such situations are particularly likely where fine-grained or oncoidal material is deposited in lotic environments, eg, Gordale and Kilnsey. Pazdur, Pazdur & Szulc (1988) obtained some evidence for redeposition in Polish tufa profiles and recognized the potential problems of dating oncoids which are particularly prone to redeposition.

Where old deposits occur in areas of active deposition, and the stable isotopic composition is age-invariant, the reliable dating of tufas, even in the absence of organic matter, should be possible. This is apparent at Gordale, where the  $\delta^{13}$ C levels were always close to  $-10\%_{00}$ , indicating that the hydrochemical processes of limestone dissolution and tufa deposition have changed little over time.

Our studies have exposed three contrasting tufa-depositing environments and demon-

strate that q correction factors are site-specific. Considering the great potential for variation in the CO<sub>2</sub> sources, then bedrock dilution measurements from modern aqueous <sup>14</sup>CO<sub>2</sub>, corrected for bomb <sup>14</sup>C, ought to give us a reasonable estimate of age in the absence of organic matter. Active sites possess clear advantages, with the potential for comparisons between modern deposits and their associated waters. It is apparent that further progress will only be made in this area using large data sets (N > 10) taken from well-defined, preferably active sites.

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## TARTU RADIOCARBON DATES XI

## EVALD ILVES

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### INTRODUCTION

This list includes dates of geologic samples measured using a single-channel liquid scintillation <sup>14</sup>C counter at the Geochemical and Statistical Laboratory, Tartu, Estonian SSR. Our modern standard is made of benzene enriched in <sup>14</sup>C and its activity is checked with NBS oxalic acid standard sample. Dates are given in conventional radiocarbon years, based on the Libby half-life of 5570  $\pm$  30 yr. AD 1950 is the reference year. Errors refer only to 1 $\sigma$  standard deviation calculated from count rates involved.

## GEOLOGIC SAMPLES

Estonian SSR

### Haanja series

The Haanja upland in SE Estonian SSR belongs to an island deposit. Upper strata of basal Devonian deposits are at 100–160m asl. Glacial deposits 100–180m (40–50m on slopes) overlie the Devonian strata. The present upland was formed at the end of Valdai glaciation during the Haanja (Luuga) glacier retreat stage 13,500–13,200 BP. The Haanja upland consists of a variety of geologic and morphologic characteristics. Dates listed below are of sediments from center of upland, ca 300km<sup>2</sup>.

Samples coll 1976 by H Mäemets (Mäetilga) and by E Ilves and H Mäemets 1980 (Karuniidu), 1981 (Tuuljärv), 1983 (Vaskna).

TA-1081. Mäetilga	$3480 \pm 70$
Bryales peat from depth 370–380cm. Pollen Zone SB1.	
TA-1082. Mäetilga	$5670~\pm~100$
Sapropel with admixture of lime pelite from depth 550–560cm.	
TA-1359. Karuniidu	$870~\pm~60$
Fen peat with wood remains from depth 50–60cm. Pollen Zone SA3.	
TA-1396. Karuniidu	$1100~\pm~60$
Fen peat with wood remains from depth 100–110cm. Pollen Zone SA2	
TA-1397. Karuniidu	$1920~\pm~60$
Fen peat from depth 150–160cm. Pollen Zone SA1	
TA-1398. Karuniidu	$2180 \pm 60$
Fen peat from depth 200–210cm. Pollen Zone SA1.	
TA-1399. Karuniidu	$2080 \pm 60$
Fen peat from depth 250–260cm. Pollen Zone SA1.	
TA-1400. Karuniidu	$2500~\pm~60$
Fen peat from depth 300–310cm. Beginning of climatic period SA.	
TA-1401. Karuniidu	$3000~\pm~60$
Fen peat from depth 350–360cm. Pollen Zone SB2.	

100	Evald Ilves	
TA-1 Fen r	<b>402. Karuniidu</b> Deat from depth 400–410cm. Pollen Zone SB1	3510 ± 6
TA-1 Bryal	<b>403. Karuniidu</b> les peat from depth 450–460cm. Pollen Zone SB1.	3560 ± 6
<b>TA-1</b> Fore	<b>404. Karuniidu</b> st peat from depth 500–510cm. Beginning of climatic period SB.	4120 ± 7
<b>TA-1</b> Fore climatic p	<b>405. Karuniidu</b> st peat from depth 520–530cm. Boundary of Atlantic and Subboreal eriods.	<b>4300</b> ± <b>7</b> (AT and SI
TA-1	406. Karuniidu	6000 ± 8
Basal	layer of forest peat on sand from depth 530–550cm. Climatic period	AT.
TA-1	277. Karuniidu	1830 ± 6
Burie outer tre Estonian	ed oak trunk found overlying sediments (while digging pond). Date e rings. Sample subm 1979 by U Riispere, Inst Zoology and Bo SSR.	e is from 1 tany, Tart
TA-1	598. Tuuljärv	380 ± 10
Cares	x-Sphagnum peat from depth 100–105cm. Pollen Zone SA3.	
TA-1	599. Tuuljärv	1670 ± '
Fore	st-Phragmites peat from depth 140–150cm. Pollen Zone SA2.	
TA-1	610. Tuuljärv	<b>2600</b> ± 8
<i>Equis</i> Pollen Zo	setum-Bryales peat with remains of trees from depth $240-250$ cm. E one SA1.	Beginning
TA-1	613. Tuuljärv	3040 ± 1
Fore	st peat from depth 320–330cm. Pollen Zone SB2.	
TA-1	614. Tuuljärv	3560 ± 8
Fore	st peat from depth 360–370cm. Pollen Zone SB2.	
TA-1	617. Tuuljärv	<b>4070</b> ± 2
Fore	st-Phragmites peat from depth 450–460cm. Pollen Zone SB1.	
TA-1	615. Tuuljärv	6560 ± 9
Sapr	opel with remains <i>Equisetum</i> from depth 480–490cm. Pollen Zone AT	2.
TA-1	616. Tuuljärv	<b>7940</b> ± 8
Phra	gmites-Bryales peat from depth 490-500cm. End of climatic period BC	).
TA-1	515. Tuuljärv	8790 ± 8
Parti period BC	ally decomposed Bryales peat from depth 560–570cm. Beginning D.	of clima
TA-1	694. Vaskna	$830 \pm 6$
Cares	x peat with remains of trees from depth 25–30cm. Pollen Zone SA3.	

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TA-1693. Vaskna	$1510~\pm~70$
Forest-Carex peat from depth 30–35cm. Boundary of Pollen Zones SA2 and	SA3.
TA-1692. Vaskna	$2120~\pm~60$
Forest- <i>Carex</i> peat from depth 45–50cm. Pollen Zone SA2.	
TA-1691. Vaskna	$2300~\pm~60$
Forest-Phragmites peat from depth 50–55cm. Boundary of Pollen Zones SA	2 and SA1.
TA-1690. Vaskna	$2590~\pm~60$
Forest-Carex peat from depth 55–60cm. Boundary of climatic periods SB an	d SA.
TA-1698. Vaskna	$4210~\pm~60$
Forest- <i>Carex</i> peat from depth 70–75cm. Pollen Zone SB2.	
TA-1688. Vaskna	$5030~\pm~60$
Forest- <i>Carex</i> peat from depth 80–85cm. Pollen Zone SB1.	
TA-1687. Vaskna	$6850~\pm~60$
Forest-Bryales peat from depth 95–100cm. Climatic period AT.	
TA-1686. Vaskna	$7250~\pm~60$
Equisetum-Eriophorum peat from depth 110–115cm. End of climatic period I	302.
TA-1727. Vaskna	$8050~\pm~60$
Bryales peat from depth 115–120cm. Pollen Zone BO2.	
TA-1685. Vaskna	$8280~\pm~60$
Bryales- <i>Phragmites</i> peat from depth 125–130cm. Pollen Zone BO2.	
TA-1737. Vaskna	$8730~\pm~60$
Bryales peat from depth 145–150cm. End of climatic period PB.	
TA-1684. Vaskna	$9680~\pm~70$
Bryales-Phragmites peat from depth 160–165cm. Upper layer of climatic per	riod PB.
TA-1683. Vaskna	$9870~\pm~70$
Dy from depth 170–175cm. Climatic period PB.	
TA-1682. Vaskna	$9970 \pm 70$
Sapropel from depth 185–190cm. Climatic period PB.	
TA-1600. Vaskna	$9930~\pm~70$
Sapropel from depth 200–205cm. Beginning of climatic period PB.	

# Järvesoo series

Järvesoo bog, 90ha, lies in Saaremaa Island, 18km W of Kuressaare and is formed of fen and mesotrophic peat. Samples coll 1977 by E Ilves and A Sarv, Inst Zoology and Botany, Inst Geology, Tartu.

TA-771. Järvesoo	$1420 \pm 70$
Peat from depth 20–30cm.	
<b>TA-772. Järvesoo</b> Peat from depth 60–70cm.	$1460~\pm~70$
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<b>TA-773. Järvesoo</b> Peat from depth 70–80cm.	$1450 \pm 70$
<b>TA-774. Järvesoo</b> Peat from depth 80–90cm.	$1750 \pm 70$
<b>TA-775. Järvesoo</b> Peat from depth 100–110cm.	4090 ± 80
<b>TA-776. Järvesoo</b> Peat from depth 110–120cm.	$4570~\pm~80$
<b>TA-778. Järvesoo</b> Peat from depth 130–140cm.	$5440~\pm~70$
<b>TA-779A. Järvesoo</b> Peat from depth 160–170cm.	$6280~\pm~90$
<b>TA-779B. Järvesoo</b> Lake lime from depth 160–170cm.	$6510~\pm~70$
<b>TA-780. Järvesoo</b> Lake lime from depth 220–230cm.	$6770 \pm 90$
<b>TA-777. Järvesoo</b> Lake lime from depth 260–270cm.	$7610~\pm~80$
<b>TA-781. Järvesoo</b> Lake lime from depth 320–330cm.	8380 ± 80
TA-782. Järvesoo	8800 ± 90

Lake lime from depth 340–350cm.

#### Ukrainian SSR

#### **Stojanov series**

Stojanov bog lies in Malye Polesje near Stojanov village, Lvov oblast, Ukrainian SSR. Bog is drained and peat extracted. Peat stratum reaches thickness of 5.25m. Samples coll and subm 1978 by A T Artjushenko and L G Bezus'ko, N G Holodnyi Inst Botany, Kiev, Ukrainian SSR (Bezus'ko, Ilves & Kayutina 1980).

#### TA-1214. Stojanov

Carex peat with remains of Phragmites from depth 35-40cm. Pollen Zone SA2.

#### TA-1215. Stojanov

*Carex* peat with remains of *Phragmites* from depth 85–90cm. Boundary of Pollen Zones SA2 and SA1.

#### TA-1216. Stojanov

Carex peat with remains of Phragmites from depth 140-145cm. Pollen Zone SA1.

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#### Evald Ilves

# $600 \pm 70$

1130 ± 60

 $1900 \pm 70$ 

<b>TA-1321. Stojanov</b> <i>Carex-Phragmites</i> peat from depth 202–203cm. Climatic period SB.	$2680~\pm~70$
<b>TA-1322.</b> Stojanov <i>Carex-Phragmites</i> peat from depth 298–303cm. Pollen Zone AT2.	$3390~\pm~70$
<b>TA-1323. Stojanov</b> <i>Carex-Phragmites</i> peat from depth 348–353cm. Pollen Zone AT2.	$4850~\pm~70$
<b>TA-1217. Stojanov</b> <i>Carex-Phragmites</i> peat from depth 423–428cm. Pollen Zone AT1.	$6280~\pm~70$
<b>TA-1218. Stojanov</b> <i>Phragmites</i> peat from depth 498–503cm. Pollen Zone SB.	$7360~\pm~70$

#### **Byelorussian SSR**

#### **Sudoble series**

Samples from basal sediments, 300m from W shore of Sudoble Lake, 5km SE of Zhodino, Smolevitschki dist, Minsk Obl. Samples coll and subm 1979 by I I Bogdel, V I Lenin Byelorussian State Univ, Minsk (Bogdel *et al* 1983).

	<b>TA-1219. Sudoble</b> Dy from depth 140–160cm. End of climatic period SB.	$2360\pm80$
	<b>TA-1220. Sudoble</b> Dy from depth 280–300cm. Climatic period SB.	$3930~\pm~80$
	<b>TA-1221. Sudoble</b> Dy from depth 380–400cm. Beginning of climatic period SB.	$4960~\pm~70$
	<b>TA-1222. Sudoble</b> Dy from depth 485–500cm. Climatic period AT.	$5950~\pm~80$
	<b>TA-1223. Sudoble</b> Dy from depth 580–600cm. Boundary of climatic periods BO and AT.	$8510~\pm~70$
	TA-1224. Sudoble Sapropel from depth 680–700cm. Basal layers of climatic period BO.	9080 ± 90
AL.	<b>TA-1225. Sudoble</b> Sapropel with slight admixture of lake lime from depth 770–790cm. C	$11,160 \pm 100$ Slimatic period
Clim	<b>TA-1226. Sudoble</b> Peat with admixtures of lake lime and macroparticles of wood from dept atic period AL.	<b>11,550</b> ± <b>100</b> h 875–885cm.
Kob I Bog	<b>uzi series</b> Kobuzi bog lies in Vilei dist, 400 m N of Kobuzi village. Samples coll and s gdel.	ubm 1979 by I

TA-1369. Kobuzi	$730~\pm~60$

Peat with undecayed vegetal remains from depth 22-28cm.

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	<b>TA-1368. Kobuzi</b> Same type, from depth 28–35cm.	$1440 \pm 70$
	<b>TA-1367. Kobuzi</b> Same type, from depth 50–55cm.	2750 ± 70
	TA-1366. Kobuzi Same type, from depth 75–80cm.	$4320~\pm~70$
	<b>TA-1365. Kobuzi</b> Same type, from depth 100–105cm.	$6050~\pm~60$
	<b>TA-1364. Kobuzi</b> Peat from depth 125–130cm. Color of peat turns into light brown.	$7650~\pm~70$
	<b>TA-1331. Kobuzi</b> Peat from depth 150–155cm. Color of peat turns into yellowish brown.	8760 ± 70
	<b>TA-1330. Kobuzi</b> Peat from depth 175–180cm.	8730 ± 70
	<b>TA-1329. Kobuzi</b> Peat with slightly decayed woody remains from depth 225–230cm.	$9640 \pm 90$
	<b>TA-1326. Kobuzi</b> Wood "A" from depth 240cm.	9550 ± 80
roo	<b>TA-1327. Kobuzi</b> Wood "B" from depth 240cm, from layer where partly decayed wood ts and branches were collected.	<b>10,430</b> ± <b>90</b> from trunks,
	<b>TA-1328. Kobuzi</b> Forest peat from depth 250–255cm.	9530 ± 80
	<b>TA-1325. Kobuzi</b> Forest peat from depth 275–280cm.	10,430 ± 90
	<b>TA-1324. Kobuzi</b> Peat with sand from depth 295–300cm.	11,200 ± 90

Georgian SSR

## Anaklija series

Dates of lake and bog sediments reported below refer to complex study of Inguri River basin, W Georgia. Samples coll and subm 1981 by L R Serebryannyi, Inst Geography, Tartu (Serebryannyi et al 1984).

TA-1303. Anaklija	$3090 \pm 100$
Peat from depth 217–220cm. Base of Pollen Zone SB2.	
TA-1301. Anaklija	$4090 \pm 90$
Peat from depth 315–320cm. Pollen Zone SB1.	

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<b>TA-1300. Anaklija</b> Peat from depth 380–385cm. Pollen Zone SB1.	$4530 \pm 70$
<b>TA-1299. Anaklija</b> Peat from depth 530–535cm. Pollen Zone AT2.	$4570~\pm~70$
TA-1298. Anaklija	$5640~\pm~100$

Peat from depth 625–632cm. Pollen Zone AT2.

#### Hungarian PR

#### Lovaszberen

Sample from buried soil from Lovaszberen loess, Hungary, site with coordinates (47°18'N, 18°33'E). In 1977 while examining the section, numerous large charcoal fragments were observed (Ilves, Pecsi & Serebryannyi 1980). Sample subm 1977 by M Pecsi, Hungarian Acad Sciences.

#### TA-1196. Lovaszberen

 $20,220 \pm 300$ 

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AV 1984 Late- and postglacial history of phytolandscapes of Colchis. Proc Acad Sci Georgian SSR Biol Ser 10(5):306-312 (in Russian).

#### NOTES AND COMMENTS

## SPECIAL REPORT FROM THE GLASGOW INTERCOMPARISON WORKSHOP ON QUALITY CONTROL AND ASSURANCE

#### WILLEM G MOOK

The results of the Glasgow Intercomparison Project and discussions about ways to increase a laboratory's quality as well as an archaeologist's confidence led to a general agreement at the Workshop about the outline of a procedure for Quality Control and Assurance. The scheme is primarily based on proposals presented by Dr Austin Long, University of Arizona, Dr Roberto Gonfiantini of the International Atomic Energy Agency and our Glasgow hosts. It consists of three elements:

#### I. Quality Control/Assurance Protocol

This QC/QA protocol of internal laboratory procedures serves to alert laboratory personnel to existing problems (QC) and equally to convince outsiders/customers of the quality of the laboratory's data (QA).

Details about the recommended protocol follow this report. Each laboratory director may wish to adjust the procedures to his/her particular circumstances and to certain national rules or requirements.

An essential part of the QC/QA program is the analysis at regular intervals of certain standards. For these we have decided to choose:

#### **II. IAEA Reference Materials**

Presently, a set of <sup>14</sup>C reference materials is being prepared which consists of different types of material and different ages, but including modern cellulose, charcoal of a few thousand BP, wood of 11,000 BP and possibly 25,000 BP, travertine of 40% <sup>14</sup>C and background marble. Distribution of these materials will start in February 1990 to those laboratories who have applied to the IAEA. The deadline for submitting results is July 1, 1990. All data will be sent under name (*not anonymous*) to those laboratories which submitted results. During Fall 1990, all the results will be discussed in Vienna at the IAEA headquarters by everyone who wishes to attend. A few specialists will be invited. This meeting will result in a report stating the consensus ages obtained. Laboratories who wish to stay anonymous may order samples and should *not* send in their results but rather wait till the final report is published.

Naturally the quantity of reference material stored at the IAEA is large, but not unlimited. Laboratories may obtain sufficient material of certain standards to check their counter monthly. However, if laboratories with several counters in operation were to run a standard in each counter monthly or bimonthly (as the QC/QA protocol requires) the supply of reference material at the IAEA would become exhausted in a few years' time. These laboratories, therefore, have to choose their own laboratory standards which should have to be compared to international standards regularly.

#### III. International Intercomparison

The recent intercomparison study has highlighted some difficulties within the <sup>14</sup>C community relating to the comparability of results from different laboratories. As a result of these findings and as part of the proposals for Quality Assurance, regular intercomparisons will be organized by the Glasgow group. An important feature of the comparisons will be the use of natural sample materials, the results of which will not be known in advance.

The first such intercomparison is planned to begin in 1991, with sufficient time allowed for the IAEA reference samples to have been widely assayed within the <sup>14</sup>C community.

The new intercomparison will take place over a shorter time period, typically one year for the experimental work, and will involve a smaller number of samples, the majority of which will require full laboratory processing. At present, we envisage that each laboratory will receive a minimum number of samples, which can be supplemented by additional samples on request. Sample materials will, eg, include wood, grain, shell, peat, marine sediment and possibly bone.

A report on the results would be available to the participating laboratories within three months of completion of the experimental phase and will be discussed at the then next International Radiocarbon Conference.

A key component of the entire operation would be the "help" offered to participating laboratories and it would be hoped that participants would seek advice from relevant experts concerning any difficulties identified.

#### NOTES AND COMMENTS

## A QUALITY ASSURANCE PROTOCOL FOR RADIOCARBON DATING LABORATORIES<sup>1</sup>

#### Compiled by AUSTIN LONG, with advice and consent from many colleagues Department of Geosciences, The University of Arizona Tucson, Arizona 85721

The purpose of this Quality Assurance (QA) protocol is to summarize guidelines that have been accepted by the majority of directors of radiocarbon dating laboratories throughout the world, and by the International Atomic Energy Agency (IAEA). Laboratories that carefully adhere to this protocol will produce consistently reliable data which will be comparable in accuracy to all other laboratories following this or any other equally rigorous quality assurance program. This statement does not, however, pertain to samples with <sup>14</sup>C activities highly sensitive to method or degree of pretreatment, as pretreatment techniques vary among laboratories.

The newly-formed Association of Carbon-14 Laboratories (ACL) has authorized laboratories following this protocol to state in data reports that "These analyses were performed according to ACL-approved quality assurance protocol." Radiocarbon date consumers should understand that ACL cannot guarantee the accuracy of the date, as a variety of factors, many of which are beyond the laboratory's control, can affect accuracy.

BASIC ELEMENTS OF THE QUALITY ASSURANCE (QA) PROTOCOL

- I. Sample Documentation, Traceability
- II. Written Procedures
- III. Analysis of Primary Standards
- IV. Replication of Secondary Standards
- V. Recognition and Correction of Problems
- VI. Establishment of Total Analytical Precision
- I. Sample Documentation and Traceability
  - It should be possible for anyone who is unfamiliar with the laboratory, using the laboratory's written and computer records, to reconstruct what happened to any sample, and when it happened, and who did it, from the sample's arrival to the report of the data and the ultimate disposition of the remains of the sample.
    - 1. Log Book. All samples, upon arrival, must be logged-in with a sequential number. The log book will contain the sample lab number, an identification code the submitter gave it, a brief description of the physical or chemical nature of the sample, the name of the submitter, and the date of arrival in the lab. The lab number will follow the sample through the lab.
    - 2. Procedures. The lab personnel will keep up-to-date records of all operations performed on each sample (for example, type of pretreatment performed, comments on pretreatment,  $CO_2$  yields, benzene yields, counter performance, purity corrections, age calculation details and copies of relevant correspondence.)
    - 3. Sample Archival. Remaining sample material, if any, should either be kept in laboratory, returned to submitter or discarded after an established length of

<sup>&</sup>lt;sup>1</sup> The author welcomes suggestions from readers which will be incorporated into the final version of this protocol and published later this year as "A Suggested Quality Assurance Protocol for Radiocarbon Dating Laboratories" by Austin Long and RM Kalin in the Glasgow Proceedings.

#### Austin Long

time. Each laboratory must have a policy on sample archival and maintain records of the final disposition of each sample.

- B. A minimum of primary records should be kept in perpetuity. This minimum is the information required for publication in *RADIOCARBON* or the International Radiocarbon Data Base (IRDB), plus laboratory processing data and counting and calculation summary. Some laboratories even retain primary count-rate data.
- C. Laboratories should retain primary counting data for samples and the graphs of standards and backgrounds (or blanks, in the case of AMS) as long as the particular analysis equipment is in service, and for at least five years after the data appear in publication.
- II. Written Procedures
  - A. An up-to-date procedures notebook, containing detailed steps with diagrams of equipment, must be in the laboratory while the analysis is underway.
  - B. Records must indicate the nature and dates of all changes in procedures, replacement, repair, modification and adjustment of equipment.
- III. Analysis of Counting Background, Chemical Blanks and Primary Standards
  - A. Establish the count rates of background and NBS Oxalic Acid at regular intervals and immediately after replacement, repair, modification and adjustment of measurement equipment.
  - B. Time intervals between routine measurements of background and NBS primary standard will vary with general stability of equipment and frequency of measurement of secondary standards, but should not exceed one month.
  - C. Plots of these data  $(\pm 1\sigma)$  should be on calendric scales, with annotations explaining adjustments of equipment or procedures, that accompanied aberrations and discontinuities in the linearity of the plot. Annotations will also explain adjustments in data (for example, atmospheric pressure corrections, purity compensation). These graphs will be available to illustrate the system's reliability.
- IV. Replication of Secondary Standards
  - A. Three or four standard materials will soon be available from the IAEA. The results of several laboratories' analyses of these materials will also be available soon. For details, see Long and Kra (1990).
  - B. The purposes of repeat analysis of these known-age materials at regular intervals are:
    - 1. Continual monitor of analytical accuracy
    - 2. Recognition of analytical problems before they propagate to the release of erroneous data
    - 3. Establishment of analytical precision of procedures
  - C. Technicians will run each of these samples through each combustion/hydrolysis/ purification/catalysis/counting system in the laboratory at least twice a year. One of the younger secondary standards should be run more often, at least at first, in order to establish analytical precision and error multiplier (see below). New or modified equipment should be tested more frequently until steady operation is proven.
  - D. New personnel should run these test samples until they can "solo", and be tested more frequently than experienced personnel.
  - E. Under routine operation, 20 to 30% of counting time will be devoted to quality assurance activity (background, primary standard, secondary standards). Change in equipment, procedures or personnel will require a more intensive quality assurance effort.

- V. Recognition and Correction of Problems
  - A. All QA analyses should be plotted on calendric graphs and examined for deviations beyond statistical expectation.
  - B. Frequent analysis of background and primary and secondary standards should reveal problems before affected dates are released.
  - C. Trouble-shooting is beyond the scope of these guidelines. However, considerable expertise is available within the <sup>14</sup>C dating community, and several of our most experienced have expressed surprise at never having been consulted for advice.
- VI. Establishment of Total Analytical Precision
  - A. Radiocarbon dating convention (Stuiver & Polach 1977) requires dates to be reported with the ± figure reflecting only the counting statistics. In practice, only some laboratories adhere to this convention. Some laboratories arbitrarily increase this figure; AMS laboratories usually report an uncertainty based on replication of data.
  - B. The error figure most relevant to the consumer of <sup>14</sup>C dates is the Total Analytical Precision obtained by repeat analysis, through the entire chemical and physical system in the laboratory, of a homogeneous material similar to many samples of unknown age normally run through the lab.
  - C. For  $\beta$ -counting systems:
    - 1. Calculate the Total Analytical Precision from the standard deviation of repeat <sup>14</sup>C analyses of the known-age test samples available from the IAEA. Analyses included in this calculation should be all those analyzed within the past year with the following exception. Do not include analyses originally affected by some analytical problem now recognized and corrected before release of erroneous data. Analyses included in this calculation should have about the same standard deviation. Laboratories that produce data that, for the same age range, have significantly different counting statistics for whatever reason (longer or shorter counting times, different counters or pressures, dilution), should carry out separate standard deviation calculations for each set of data grouped by similar ( $\pm 20\%$ ) values of counting statistics errors.
    - 2. Calculate the error multiplier factor (Stuiver & Pearson 1986) for each data set characterized by size of the counting statistics error. The error multiplier for a particular data set is the ratio of the standard deviation of the ages within a data set ( $\sigma_i$ ) to the average counting error of the individual dates ( $\sigma_c$ ). This error multiplier, called "K" by Stuiver and Pearson, should be equal to or greater than 1.0. It will also depend on the value of  $\sigma_c$ . Laboratories should re-evaluate this factor annually, and after significant changes in equipment, procedures or personnel.
    - 3. Laboratories should either release the relevant K value along with dates in publications and with an explanation of its application, or publish the laboratory analytical error instead of the conventional  $\pm$  figure. In either case, the laboratory responsible for the date should clarify which error figure is presented.
  - D. For AMS systems:

It is not practical to use counting statistics as a 'conventional error' in AMS <sup>14</sup>C dating. We recommend that AMS laboratories report  $\pm$  values on their <sup>14</sup>C measurements based on reproducibility of test samples within a single loading of a batch of targets, and on repeat samples run over several months. This would be comparable to the Total Laboratory Precision in  $\geq$ b-counting laboratories. Laboratories should specify how the error is calculated (see Donahue *et al* 1990).

E. All  $\pm$  values reported should be based on  $1\sigma$  standard deviations.

#### Austin Long

#### References

Donahue, DJ, Linick, TW and Jull, AJT 1990 Isotope-ratio and background corrections for accelerator mass spectrometer radiocarbon measurements. *Radiocarbon*, this issue.
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 Stuiver, M and Pearson, GW 1986 High-precision calibration of the radiocarbon time scale, AD 1950–500 BC. *In* Stuiver, M and Kra, RS, eds, International <sup>14</sup>C Conf, 12th, Proc. *Radiocarbon* 28(2B):805–838.
 Stuiver, M, and Polach, HA 1977 Discussion: Reporting of <sup>14</sup>C data. *Radiocarbon* 19(3):355–363.

#### REVIEW

The Environmental Record in Glaciers and Ice Sheets. Edited by Hans Oeschger and C C Langway, Jr, Report of the Dahlem Workshop, Berlin, March 13–18, 1988. Chichester, 1989, John Wiley & Sons, 400 pages.

In recent years, the ice in polar ice sheets has become an increasingly important source of paleoenvironmental information. *The Environmental Record in Glaciers and Ice Sheets* offers the non-specialized reader an overview of the subject, which is difficult to find all in one place. This book has arrived to fill a need felt by many non-glaciologists who wish to gain an understanding of how ice sheets store such data and how they can be recovered.

This volume is a report of the Dahlem Workshop held in Berlin in March 1988, the general goal of which was to assess and interpret the environmental record in glaciers. The book consists of background papers and summary group reports. In the Introduction, Langway and Oeschger (p 6) outlined the four specific problems that the Workshop addressed:

- 1. How do glaciers record environmental processes and preserve information?
- 2. What anthropogenic impacts are recorded in glaciers?
- 3. How can an ice core chronology be established?
- 4. What does the long-term ice core record tell us about global changes in the environment?

The discussions and reports that follow make instructive reading for scientists and students who wish to review information on the environmental record of our planet over the last few hundred thousand years.

To my surprise, the volume also contains some novel ideas in this field and is not merely a review of results already published elsewhere. For example, in the paper, "The Transformation of Snow to Ice and the Occlusion of Gases," by Jakob Schwander, the idea that there might be a gravitational separation of atmospheric gases in the firn is presented, to my knowledge, for the first time. The polar ice sheets, and the information contained therein are no longer of interest only to glaciologists but also to those concerned with the human impact on the planet—acid rain, heavy metal pollution, the Greenhouse problem, etc. To illustrate the global and interdisciplinary nature of the field, Group 4 alluded to the fact that the carbon dioxide concentration of the atmosphere was much lower during glacial than during interglacial times (p 382), a result that was quite unexpected.

This volume is well structured and provides a general review of the subject as well as some thought-provoking *avante-garde* ideas.

Alex Wilson Geosciences Department The University of Arizona Tucson, Arizona 85721

#### **INSTRUCTIONS TO AUTHORS**

#### General Guidelines

*RADIOCARBON* is an international journal published three times a year in the United States. The editors therefore ask contributors to use simple, straightforward language. We prefer the active rather than the passive voice and encourage the use of "I" or "we" in manuscripts. We also prefer American spellings rather than British and encourage foreign contributors to consult with English language experts before submitting their manuscripts.

Manuscripts should generally follow recommendations in "Suggestions to Authors of the Reports of the U S Geological Survey," 6th edition, 1978, Superintendent of Documents, Government Printing Office, Washington, DC 20402. A new edition, which may be printed soon, will be the preferred reference.

For a guide to bibliographic citations and abbreviations used in references, see "Bibliographic Guide for Editors and Authors, 1974, The American Chemical Society, Washington, DC 20036. This is the latest edition of this useful manual. For general style guidelines, format and abbreviations often used in Radiocarbon Date Lists, see *RADIOCAR-BON* Style Guide (Radiocarbon 26(1):152–158, 1984). Reprints of both the 1984 and 1990 Style Guides are available upon request from the Managing Editor.

An excellent reference for writing and publishing is the latest edition of "The Chicago Manual of Style," The University of Chicago Press.

We accept manuscripts in triplicate with a cover letter which includes the author's telephone number, Fax number, E-mail address and/or Telex number. All copy, including the abstract and references, must be double spaced. Leave adequate margins (minimum size 1" or 2.5cm) on each side of the paper and at least 1.5" or 4cm on the top and bottom. Indent the first line of each new paragraph. Number all pages including the references, tables and figures. The editors greatly appreciate receiving the final revised version of a manuscript in digital form as well as on paper. We prefer WordPerfect 5.1, 5.0 or 4.2 in IBM format, but we also will accept Microsoft Word and Wordstar in IBM-compatible MS DOS. Please convert text written in other word-processing programs or on other formats (eg, Macintosh, CP/M) to ASCII, and designate format. We can accommodate either 3.5" (720 kb or 1.44 mb) or 5.25" (360 kb or 1.2 mb) diskettes. We can also download text from Bitnet.

#### **Conference** Proceedings

The length of a manuscript is unrestricted for regular issues, but may not exceed 12 pages for Special Issues, such as the Proceedings of Radiocarbon Conferences. All papers are reviewed by the Editor, Associate Editors and outside referees. Presentation of a paper at a conference, except for an invited paper, will not guarantee publication in the Proceedings issue. If we accept a paper but its publication is delayed, we will place it in the next available regular issue. The editors will consider for publication only those manuscripts submitted in proper format by the conference deadline.

#### **Regular Issues**

The organization of research articles or reports should include the following sections:

- 1. Title-boldface capitals, centered-avoid abbreviations
- 2. Author(s) and affiliations—centered capitals—full first name or two initials. Addresses should be complete, including zip or country code numbers.
- 3. Abstract—double spaced—200 words or less
- 4. Introduction
- 5. Methodology or descriptive background
- 6. Results or discussion
- 7. Conclusions
- 8. Acknowledgments—should be brief
- 9. References-see new style below

10. Tables—camera-ready copy is preferred, after editing

11. Figures—with separate captions

Headings—capitalize and center.

Sub-heading 1—in italics, initial capitals, at left margin.

**Sub-heading 2**—in italics, indent, with period (full stop) and text following.

Running heads—short titles that the author may supply (optional).

**Footnotes**—avoid if possible, but when necessary, cite with superscripts in Arabic numerals in the text and at the bottom of the same page. Footnote an author's address in the same manner, using consecutive numbers for more than two affiliations, eg: GT Cook<sup>1</sup>, DD Harkness<sup>2</sup>, BF Miller<sup>2</sup>, EM Scott<sup>3</sup>, MS Baxter<sup>1</sup> and TC Aitchison<sup>3</sup>. For footnotes to tables, see below.

**Equations**—center and leave ample space around them. Number equations, enclosing the number in parentheses to the right of the equation at the margin. Use punctuation with equations.

**Tables**—must show titles and numbers at the top. Clearly mark columnar headings. Place footnotes to a table at the bottom of the table and cite in order by  $*, **, +, \ddagger, \$, ||, #$ . We prefer to receive tables in camera-ready form after the editing process. All tables must be cited in the text.

**Figures**—original line drawings, glossies, laser prints or half-tones. The quality of the end-product depends directly on the illustration that the author provides. Figures should be reduced as much as possible, not exceeding 5.5" x 8.5" (14cm x 21.5cm) to conform to our new journal trim size. Figures must have captions, numbered consecutively with Arabic numerals (eg, Fig 1). Type captions on a separate sheet of paper. Explain all symbols that appear in the figure. Cite all figures in the text. Write out the word "Figure" when it is part of the sentence (eg, Figure 1 shows . . .) and abbreviate it when it is in parentheses (eg, (Fig 1)). Designate multiple parts of a figure by capital letters (eg, Fig 1A, 1B). Clearly identify illustrations (by taping a piece of paper to the bottom) with author's names and figure number. Use gloss-coated paper for laser prints.

**Measurements**—always use SI or metric units. Use English units in parentheses only in combination with metric units.

**Isotope numbers**—precede symbols (eg, <sup>14</sup>C). We prefer "<sup>14</sup>C" rather than "radiocarbon" in the text but the reverse for titles.

Symbols, abbreviations, acronyms and Greek letters—clearly define these at their first appearance in the text, eg, Accelerator Mass Spectrometry (AMS); one standard deviation  $(1\sigma)$ . Use signs and symbols such as >, <,  $\simeq$  with arabic numerals. We use the abbreviation "ca" with numerals. Other abbreviations that we often use are: *ie*, *vs* (italics) and eg (no italics).

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#### **Other Sections**

**Date Lists** should follow the style of a recent issue. For more details, see *RADIOCAR-BON* Style Guide 1984 *Radiocarbon* 26(1): 152–158. Free reprints are available upon request from the Managing Editor.

**Notes and Comments** should follow the same style as outlined above. Authors of reports and letters should place their names and addresses at the end.

**Discussions** may include comments on articles or reports published in recent issues of *RADIOCARBON*. They may also originate from audience participation at conferences. These comments undergo the usual review process and are sent to the author of the original manuscript for a reply.

Book Reviews should not exceed two pages and should bear headings as follows, eg:

Radiocarbon Dating Literature: The First 21 years 1947–1968. Annotated Bibliography. Compiled by Dilette Polach. San Diego, California, 1988. Academic Press, Inc. 370 pages, \$24.00.

**Laboratories** generally are listed at the end of each volume. We have extended our list to include Accelerator Facilities and are adding telephone, Telex, Fax and E-mail information wherever possible. Send changes of personnel, addresses or numbers to the Managing Editor.

**Announcements** should be sent to the Managing Editor in time to meet our Winter, Spring and Fall deadlines.

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Cite references in the text within parentheses: author's last name and date without a comma. If quoting a page number, it should follow a colon (eg, Kalin & Long 1989:6). We use the ampersand character (&) within parentheses. Cite the names of one to three authors and use *et al* for more than three authors. Cite *all* authors in the references, as described below.

When citing data from notes or observations, cite as (ms) in the text and use the proper citation in the references, below. Cite an unpublished manuscript (eg, a doctoral dissertation) as (ms) both in the text and in the references.

Refer to a personal communication in the text, *not* in the references (eg, Long, pers commun 1989). Include the date of the communication whenever possible.

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- Stuiver, M and Kra, RS, eds 1983 Internatl <sup>14</sup>C conf, 11th, Proc. *Radiocarbon* 25(2): 171–796.
- \_\_\_\_ 1986 Internatl <sup>14</sup>C conf, 12th, Proc. *Radiocarbon* 28(2A): 175–804.

List individual authors first followed by those with co-authors, eg:

- Stuiver, M 1982 A high-precision calibration of the AD radiocarbon time scale. *Radiocarbon* 24(1):1–26.
- Stuiver, M and Pearson, GW 1986 High-precision calibration of the radiocarbon time scale, AD 1950–500 BC. In Stuiver, M and Kra, RS, eds, Internatl <sup>14</sup>C conf, 12th, Proc. Radiocarbon 28(2B): 805–838.

Following is our new reference format for:

- 1) Article in a periodical:
- Author's surname, initials of given name, year of publication (no commas before or after), title. *Name of periodical* (in italics or underlined) volume(number): inclusive pages, eg:
- Vogel, JS, Nelson, DE and Southon, JR 1989 Accuracy and precision in dating microgram carbon samples. *Radiocarbon* 31(2): 145–149.

2) Book citation:

- Same as above for authors and year. Italicize title of book. Place of publication, publisher: number of pages, eg:
- Broecker, WS and Peng, T-H 1982 *Tracers in the sea*. Palisades, New York, Eldigio Press: 690 p.
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List all authors in the reference. If an author is not given, list the organization as author.

Works "in press" must actually be in press, *ie*, accepted by a journal. "In press" should follow the citation when the date of publication is known. When date of publication is not known, "in press" should replace the date:

Becker, B and Schmidt, B, in press, Extension of the European oak chronology to the past 9224 years. *In* Mook, WG and Waterbolk, HT, eds, Internatl symposium Archaeology and <sup>14</sup>C, 2nd, Proc. *PACT*.

If an author confidently expects to publish a manuscript before the galley proof is returned, he/she may use blank page numbers (000–000). Place (ms) after the authors and before the date (if known) for a manuscript that has been submitted but is not yet accepted. Cite an unpublished manuscript such as a doctoral dissertation or a manuscript in preparation in the same manner, eg:

Roeleveld, W (ms) 1974 The Groningen coastal area. PhD dissert, Amsterdam: 252 p. Kra, R (ms) Paleoenvironmental data retrieval from the International Radiocarbon Data Base (IRDB). In preparation.

For a paper presented at a conference that has not been published, give the author (ms) year and title followed by, eg:

Paper presented at Internatl <sup>14</sup>C conf, 13th, Dubrovnik, Yugoslavia, June 20–25.

# INTERNATIONAL WORKSHOP ON INTER-COMPARISON OF RADIOCARBON LABORATORIES

GLASGOW, 12-15 SEPTEMBER 1989

A workshop was held in Glasgow in September, 1989 on the topic of the Inter-Comparison of Radiocarbon Laboratories. The meeting was hosted by the University of Glasgow, Scottish Universities Research and Reactor Centre and the NERC <sup>14</sup>C laboratory at East Kilbride. The scientific program of the workshop covered previous and current intercomparison studies of radiocarbon laboratories, as well as future developments in this field.

The Proceedings will be published by *RADIOCARBON* as a Special Issue in Volume 32, No. 3, 1990.

For more information please contact:

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V MARKGRAF (USA), Palaeoclimates in Central and South America since 18,000 BP based on pollen and lake-level records.

K-E BEHRE (FRG), Biostratigraphy of the last glacial period in Europe. A-M LÉZINE (France) & J CASANOVA (Canada), Pollen and hydrological evidence for the interpretation of past climates in tropical West Africa during the Holocene. N EYLES, C H EYLES (Canada) & A M McCABE (UK), Sedimentation in an ice-contact subaqueous setting: the mid-Pleistocene North Sea Drifts' of Norfolk, UK. J P BRADBURY (USA), Late Quaternary lacustrine paleoenvironments in the Cuenca de México.

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#### **NOTICE TO READERS AND CONTRIBUTORS**

Since its inception, the basic purpose of *RADIOCARBON* has been the publication of compilations of <sup>14</sup>C dates produced by various laboratories. These lists are extremely useful for the dissemination of basic <sup>14</sup>C information.

In recent years, *RADIOCARBON* has also been publishing technical and interpretative articles on all aspects of <sup>14</sup>C. We would like to encourage this type of publication on a regular basis. In addition, we will be publishing compilations of published *and unpublished* dates along with interpretative text for these dates on a regional basis. Authors who would like to compose such an article for his/her area of interest should contact the Managing Editor for information.

Other sections recently added to our regular issues include NOTES AND COMMENTS, LETTERS TO THE EDITOR and ANNOUNCEMENTS. Authors are invited to extend discussions or raise pertinent questions to the results of scientific investigations that have appeared on our pages. These sections include short, technical notes to relay information concerning innovative sample preparation procedures. Laboratories may also seek assistance in technical aspects of radiocarbon dating. Book reviews are also encouraged as are advertisements.

*Manuscripts.* Papers may now be submitted on both floppy diskettes and hard copy. When submitting a manuscript on a diskette, *always* include *two* hard copies, double-spaced, or wait until the final copy is prepared, after review, before sending the edited diskette. We will accept, in order of preference, WordPerfect, 5.1 or 5.0, Microsoft Word, WordStar or any major Macintosh or IBM word-processing software program. ASCII files, MS DOS and CPM formatted diskettes are also acceptable. The diskettes should be either  $3\frac{1}{2}$ " (720K or 1.44 megabytes) or  $5\frac{1}{4}$ " (360K or 1.2 megabytes). Radiocarbon papers should follow the recommendations in *RADIOCARBON* Style Guide (R, 1984, v 26, no. 1, p 152–158). Our deadline schedule for submitting manuscripts is:

For	Date	
Vol 33, No. 1, 1991	Sept 1, 1990	
Vol 33, No. 2, 1991	Jan 1, 1991	

Half life of <sup>14</sup>C. In accordance with the decision of the Fifth Radiocarbon Dating Conference, Cambridge, 1962, all dates published in this volume (as in previous volumes) are based on the Libby value, 5568 yr, for the half-life. This decision was reaffirmed at the 11th International Radiocarbon Conference in Seattle, Washington, 1982. Because of various uncertainties, when <sup>14</sup>C measurements are expressed as dates in years BP the accuracy of the dates is limited, and refinements that take some but not all uncertainties into account may be misleading. The mean of three recent determinations of the half life, 5730  $\pm$  40 yr, (Nature, 1962, v 195, no. 4845, p 984), is regarded as the best value presently available. Published dates in years BP can be converted to this basis by multiplying them by 1.03.

AD/BC Dates. In accordance with the decision of the Ninth International Radiocarbon Conference, Los Angeles and San Diego, 1976, the designation of AD/BC, obtained by subtracting AD 1950 from conventional BP determinations is discontinued in Radiocarbon. Authors or submitters may include calendar estimates as a comment, and report these estimates as cal AD/BC, citing the specific calibration curve used to obtain the estimate. Calibrated dates will now be reported as "cal BP" or "cal AD/BC" according to the consensus of the Twelfth International Radiocarbon Conference, Trondheim, Norway, 1985.

Meaning of  $\delta^{14}C$ . In Volume 3, 1961, we endorsed the notation  $\Delta$  (Lamont VIII, 1961) for geochemical measurements of <sup>14</sup>C activity, corrected for isotopic fractionation in samples and in the NBS oxalic-acid standard. The value of  $\delta^{14}C$  that entered the calculation of  $\Delta$  was defined by reference to Lamont VI, 1959, and was corrected for age. This fact has been lost sight of, by editors as well as by authors, and recent papers have used  $\delta^{14}C$  as the observed deviation from the standard. At the New Zealand Radiocarbon Dating Conference it was recommended to use  $\delta^{14}C$  only for age-corrected samples. Without an age correction, the value should then be reported as percent of modern relative to 0.95 NBS oxalic acid (Proceedings 8th Conference on Radiocarbon Dating, Wellington, New Zealand, 1972). The Ninth International Radiocarbon Conference, Los Angeles and San Diego, 1976, recommended that the reference standard, 0.95 times NBS oxalic acid activity, be normalized to  $\delta^{13}C = -19\%_{00}$ .

In several fields, however, age corrections are not possible.  $\delta^{14}$ C and  $\Delta$ , uncorrected for age, have been used extensively in oceanography, and are an integral part of models and theories. For the present, therefore, we continue the editorial policy of using  $\Delta$  notations for samples not corrected for age.

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