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Atmospheric Radiocarbon Calibration to 45,000 yr B.P.: Late Glacial Fluctuations and Cosmogenic Isotope Production

H. Kitagawa* and J. van der Plicht

More than 250 carbon-14 accelerator mass spectrometry dates of terrestrial macrofossils from annually laminated sediments from Lake Suigetsu (Japan) provide a first atmospheric calibration for almost the total range of the radiocarbon method (45,000 years before the present). The results confirm the (recently revised) floating German pine chronology and are consistent with data from European and marine varved sediments, and combined uranium-thorium and carbon-14 dating of corals up to the Last Glacial Maximum. The data during the Glacial show large fluctuations in the atmospheric carbon-14 content, related to changes in global environment and in cosmogenic isotope production.

The atmospheric 14C content (expressed in Δ14C) (1) is sensitive to geomagnetic field strength and solar fluctuations (also through magnetic effects) as well as rearrangements in equilibrium between the major C reservoirs (atmosphere, ocean, and biosphere). Detailed calibration of the radiocarbon time scale into the glacial period is critical for accurate dating and a better understanding of changes in the Earth system. Radiocarbon calibration can be performed by 14C dating of samples that can also be dated by an independent, preferably absolute dating method. The ideal samples for this purpose are tree rings, which can be dated by dendrochronology. Dendro-calibrations with (for the most part) 20-year tree-ring resolution have been obtained for almost the complete Holocene, back to about 7900 B.C. for the absolute chronology and to about 9400 B.C. including a matched floating tree-ring curve (2).

Beyond the range of tree rings, calibration has been problematic. Radiocarbon dates of terrestrial macrofossils from annually laminated sediments can potentially provide a high-resolution record of atmospheric 14C changes. However, varve chronologies have been revised several times (3). At present, calibration data from glacial varves provide a consistent data set back to about 11,000 B.C. (4–6). In addition, a marine calibration curve for the Late Glacial period is obtained by combined 14C and U-series dates of corals (7, 8) and 14C measurements on foraminifera from varved marine sediments (9). Because these data are for marine materials, they have to be corrected for the apparent 14C age of the surface oceans, known as the reservoir effect.

Here we present a high-resolution atmospheric radiocarbon calibration from annually laminated sediments for the total range of the radiocarbon dating method [<45,000 cal yr B.P. (10)]. The sediments were taken from Lake Suigetsu (35°35′N, 135°53′E) near the coast of the Sea of Japan (11). The lake is 10 km around the perimeter and covers an area of 4.3 km². It is a typical kettle-type lake with a nearly constant depth at the center, ~34 m deep. A 75-m-long continuous core (Lab code, SG) and four short piston cores were taken from the center of the lake in 1991 and 1993. The sediments are laminated in nearly the entire core sections and are dominated by dark-colored clay with white layers resulting from spring-seas an diatom growth. The seasonal changes in the depositions are preserved in the clay as thin laminations or varves. The sedimentation or annual varve thickness is relatively uniform, typically 1.2 mm/year during the Holocene and 0.61 mm/year during the Glacial. The bottom age of the SG core is estimated to be older than 100,000 years, close to the beginning of the last interglacial period.

To reconstruct the calendar time scale, we counted varves, based on gray-scale image analyses of digital pictures, in a 10.43- to 30.45-m-deep section, producing a 29,100-year-long floating chronology. Because we estimated the varve chronology of older than ~20,000 yr B.P. (19-m depth of SG core) by counting in a single core section, the error of the varve counting increases with depth, and the accumulated error at 40,000 cal yr B.P. would be less than ~2000 years, assuming no break in the sediment (12).

The 14C/12C and 13C/12C ratios of more than 250 terrestrial macrofossils (leaves, twigs, and insect wings) in the sediments were measured by accelerator mass spectrometry (AMS) at the Groningen AMS facility (13), after proper sample pretreatment (14). The floating varve chronology was connected to the old part of the absolute tree-ring chronology (2, 15) by 14C wiggle matching (16), resulting in an absolute calendar age covering the time span from 8830 to 37,930 years before present (16).
The combined AMS $^{14}$C and varve ages provide an extension of dendro-calibration range (Fig. 1). The features in the data overlapping the absolute tree-ring record agree very well, and our varve chronology also supports the recent revision of the floating German pine chronology, and radiocarbon calibration during the deglaciation. Near (a few centuries after) the onset of the Younger Dryas (YD), the $^{14}$C value decreases by 80 per mil from 10,800 to 9800 yr B.P. (12,500 to 10,000 yr cal B.P.); the decrease thus extends into the Preboreal (the earliest Holocene). This radiocarbon plateau occurs in both marine (8) and terrestrial (5) records and is referred to as the YD plateau. Our calibration shows that the YD plateau consists of two subplateaus at 10,000 and about 10,400 yr B.P.; the older one is characterized by a time of slow increase of the radiocarbon age. A similar decrease in $^{14}$C of ~100 per mil (including magnetic effect) is observed from 12,600 to 12,100 yr B.P. (or 15,000 to 13,800 yr cal B.P.), which starts within the Oldest Dryas (OD) cold period and extends until nearly the end of the Allerød/Bølling warm period. This plateau can be related to the radiocarbon plateau recorded in (non-varved) sediment cores from Switzerland (21). Our data strongly indicate a plateau around the OD cold period. It appears that the two radiocarbon plateaus in the YD and OD cold periods started a few centuries after the warm-to-cold transition. Furthermore, we also observe the millennium-scale fluctuations of about 100 per mil in $^{14}$C before the OD; maxima at 16,000, 17,500, and 19,000 cal yr B.P.; and minima at 15,500, 17,000, 18,000, and 19,500 cal yr B.P.

When compared with changes in the atmospheric $^{14}$C concentration measured directly in polar ice cores (22) and reconstructed from South American peat (23), minima at 13,500 and 15,500 cal yr B.P. seem to respond to sharp increases in atmospheric $^{14}$C concentration. These coupled signals suggest that $^{14}$C degassed from the ocean, especially from the intermediate-deep ocean, induced the change of atmospheric $^{14}$C because the ocean contains more than 90% of the global $^{14}$C inventory and the oceanic $^{14}$C is depleted in $^{14}$C. For a recent discussion concerning the connection of atmospheric $^{14}$C and paleo-oceanographic parameters, we refer to (24). Paleo-oceanographic observations suggest that millennium-scale oscillations of the ocean thermohaline circulation (THC) occurred during the deglaciation (25). The THC oscillation can be linked to atmospheric $^{14}$C as follows: $^{14}$C increases when formation of North Atlantic Deep Water (NADW) is reduced abruptly and THC decreases, after climatic cooling such as the OD and YD cold periods; in contrast, $^{14}$C decreases when THC northward heat ad-
vection and deep water production resume. Our atmospheric $\Delta^{14}C$ record implies that repeated cycles of such a process occurred, and a possibility that the NADW weakened for three or four periods during the last deglaciation is superimposed on the general trend of increasing ocean ventilation (26).

From the Last Glacial Maximum to 31,000 cal yr B.P., the long-term trend of $\Delta^{14}C$ agrees well with reconstruction of cosmogenic isotope production rate deduced by the $^{10}Be$ deposition reconstruction (19) and geomagnetic field intensity reconstruction (18) (Fig. 3). For this time span, we observe two pronounced peaks in $\Delta^{14}C$ at 23,000 and 31,000 cal yr B.P. The apparent $\Delta^{14}C$ increase correspond to an increase in the concentration of another cosmogenic isotope, $^{10}Be$, at 23,000 and about 35,000 cal yr B.P., respectively, observed in ice cores from the Antarctic (27) and Greenland (28) as well as in marine sediments (29, 30). Furthermore, a $^{14}C$ anomaly at these times has been observed previously in speleothems, dated by both $^{14}C$ and U series (31). The time gap between the $^{14}C$ and $^{10}Be$ enhancements can be explained by errors in both varve and ice-core chronologies, as well as by the different geochemical behavior of these isotopes; $^{14}C$ is present in gaseous form (CO$_2$) and gradually diffuses in the Earth system, whereas $^{10}Be$ is a solid attached to aerosol particles and deposited with precipitation (32).

The broad increase in cosmogenic isotopes (both $^{10}Be$ and $^{14}C$) at 23,000 yr B.P. can be explained as the increase in production rate by geomagnetic effects (28). The sharp $^{14}C$ peak we observed at ~31,000 yr B.P. is roughly 300 per mil in $\Delta^{14}C$ after removing the long-term trend. The $^{10}Be$ increase by a factor of 2 in ice cores during a period of ~2000 years (27). This factor of 2 increase corresponds to a $^{14}C$ increase by a factor of 1.3 or 300 per mil (33), which is exactly what we observe in our data. These sharp enhancements in $^{10}Be$ and $^{14}C$ at the same time are too large to be explained by rearrangements of the C reservoirs on the Earth.

Increased cosmogenic isotope production caused by a nearby supernova explosion has been suggested as a cause for the drastically increased $^{10}Be$ levels at this time (29, 34). Another possible explanation is a magnetic excursion with a sharp change in inclination of the geomagnetic field and the implied concomitant decrease in the geomagnetic field strength. Such events are observed in the Mono Lake and Laschamp excursions, dated at 28,000 and 33,000 yr B.P. (uncalibrated), respectively (35). The sharp $\Delta^{14}C$ increase from Lake Suigetsu corresponds chronologically to the Mono Lake excursion. However, all of these explanations remain hypothetical.

The atmospheric radiocarbon calibration curve covering the past 45,000 years provides the basis for developing a better understanding of the past global C cycles and cosmogenic isotope production. Our high-resolution calibration curve is consistent with other proxies until 31,000 cal yr B.P. Beyond 31,000 cal yr B.P., much work is still needed to obtain a better understanding of the atmospheric $\Delta^{14}C$ signal. Here, our calibration deviates from paleomagnetic records (18, 20) and from recent combined U/Th and $^{14}C$ dating of speleothems (36). These data suggest that $^{14}C$ dates at this time are ~5000 years too young. This discrepancy can be caused either by speleothem dating problems (such as unknown initial $^{14}C$ age and possible detrital Th contamination) or missing varves in the older section of Lake Suigetsu. New $^{10}Be$ data from the Arctic GRIP and GISP2 cores show large spike at ~41,000 yr B.P. (37), which is inconsistent with both our $\Delta^{14}C$ maximum and the Antarctic $^{10}Be$ record (27). This finding would indicate instead a problem in one of chronologies, or that the $^{10}Be$ and $^{14}C$ peaks do not have the same cause. Future work on the Lake Suigetsu core can help to solve the remaining questions.

**REFERENCES AND NOTES**

1. $\Delta^{14}C$ denotes the atmospheric $^{14}CO_2$ content, expressed as the per mil deviation of the $^{14}C$ content defined by the international oxalic acid standard after decay and fractionation correction [M. Stuiver and H. A. Polach, Radiocarbon 19, 355 (1977)].


10. cal yr B.P expresses absolute years before the present, where the present is defined as 1950. Radiocarbon dates are expressed in yr B.P. (uncalibrated) with respect to 1950.


12. The SG core sediments from Lake Suigetsu were typically sampled per 90-cm-long section from one drilling hole, with the use of a so-called thin-wall sampler with piston. The recovered sediment is typically 80–90 cm long because of incomplete sampling or shrinking sediments. The sampling loss is typically less than 2 cm, corresponding to about 50 years during the glacial. Further details of the SG core are provided in (17). The accuracy is determined by sampling and counting errors. Based on the results of duplicate samplings of selected sections, we determined the counting error to be less than 1.5%, corresponding to 150 years for 10,000 varves.


14. To remove the possible contamination, we applied a strong acid–alkal–acid treatment [W. G. Mook and H. J. Steurman, PACBT 6, 31 (1983)] to both samples and reference blanks. The blanks consisted of more than 50 $^{14}C$-free plant materials, collected from the deep layer of the same SG core (corresponding to an age of about 90,000 to 100,000 years).


28. J. Beer et al., in The Last Deglaciation: Absolute and Radiocarbon Chronologies, E. Bard and W. S.
Probing Single Secretory Vesicles with Capillary Electrophoresis

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Secretory vesicles obtained from the atrial gland of the gastropod mollusk *Aplysia californica* were chemically analyzed individually with a combination of optical trapping, capillary electrophoresis separation, and a laser-induced fluorescence detection. With the use of optical trapping, a single vesicle that had attoliters (10^{-18} liters) of volume was introduced into the tapered inlet of a separation capillary. Once the vesicle was injected, it was lysed, and its components were fluorescently labeled with naphthalene-2,3-dicarboxaldehyde before separation. The resultant electropherograms indicated distinct variations in the contents of single vesicles.

Biological messengers are synthesized intracellularly and packaged into secretory vesicles, where they are stored until a physiological signal triggers fusion of the vesicle membrane with the plasma membrane, resulting in the extracellular release of a chemical messenger. This mode of cellular signaling is used by all eukaryotic organisms in biological processes ranging from sensory perception to the regulation of reproductive cycles. Analysis of secretory products has been done on populations of vesicles, but the technique of tapered capillaries (5) also addresses this challenge. For example, the on-column reaction volume for a normal capillary inlet with an inner diameter (i.d.) of 25 μm and a length of 1000 μm is 4.9 × 10^{-10} liters. The reaction volume for a tapered capillary inlet of 1-μm i.d. of the same length, however, is 7.8 × 10^{-13} liters. This reduction in volume by a factor of 625 leads to a faster and more efficient reaction with fewer unreacted dye molecules. With this manipulation capability and improved reaction conditions, the contents of single biological vesicles can be probed, one by one.

The vesicles studied in this experiment were obtained from the atrial gland of the gastropod mollusk *Aplysia californica* (7). These vesicles contain bioactive peptides that are packaged into secretory granules called dense core vesicles (DCVs) (8). These DCVs are large (average diameter ≈ 1 μm) and can be easily isolated from *Aplysia*. This advantageous attribute of the DCVs has motivated their use in the present study. The atrial gland was first dissected from the distal end of the hermaphroditic duct, and subsequent slicing of the gland with a sharp razor blade released DCVs into a solution of artificial seawater. Most research on the atrial gland of *Aplysia* has been directed at the bioactive peptides (9), which are involved in this animal’s reproductive behavior. Therefore, it is in interesting to find in the present study that the DCVs also contain large amounts of primary amine-containing compounds of...