URANIUM–THORIUM DATING SETS THE CLOCK BACK ON CARBON-14 AGES

It's long been known that ages based on radiocarbon dating tend to be too young. The radiocarbon dates can be calibrated against tree-ring ages for the time period over which tree-ring samples are available—that is, over the last 8000–9000 years—but the corrections needed for earlier times have been unknown. Now a new chronometer is available that may permit some calibration back tens of thousands of years before the present era. The new benchmark is based on measurements of the decay of uranium into thorium. Researchers have dated materials using the uranium–thorium decay for many years, but the method they used was not very precise. Nor was there any set of samples systematic enough to use for C^{14} calibration. Two developments in the past few years have changed that: A Caltech team in 1987 adapted a mass spectrometry technique to obtain high-precision uranium–thorium results with small samples and established the validity of the uranium–thorium ages. This year a group from Columbia University's Lamont–Doherty Geological Observatory applied the new technique to samples of submerged corals collected off Barbados and was able to calibrate the C^{14} dates back at least 40 000 years.

The data recently reported[1] by the Lamont–Doherty team of Edouard Bard, Bruno Hamelin, Richard G. Fairbanks and Alan Zindler indicate that the discrepancy in radiocarbon ages tends to grow worse as one goes further back in time, with a maximum difference of about 3500 years at 20 000 years before the present (BP). The bias is most likely attributable to changes in the cosmogenic production rate of C^{14} caused by variations in the intensity of Earth's geomagnetic field. The Caltech team used the U–Th dating method to investigate possible links between Earth's climate and its orbit, and the method they developed has led many other investigators to focus renewed attention on this long-standing question.

Carbon-14 dating

The C^{14} method of dating organic materials that is so commonly used today is based on the measured ratio of the radioisotope C^{14} to the stable isotope C^{12}. Analysts assume that the initial concentration of C^{14} in a sample was equal to the concentration in the atmosphere at the time that the organism died. However, the atmospheric concentration has varied in the past, so these data are calibrated by dendrochronology, or tree-ring counting: The age of a particular ring is determined by counting how many rings (one for each year) precede it in moving out from the center. Then this ring age is compared with that found by C^{14} dating of a wood sample taken from that ring. Plots of the deviation between the C^{14} ages and tree-ring ages indicate that after about the first millennium BP the C^{14} dating yields ages that are too young.

The C^{14} abundance in a sample was once determined by counting the radioactive decay rate, but such counting is inherently slow and requires relatively large amounts of material, especially for an isotope such as C^{14}, whose halflife is about 5700 years. That difficulty was overcome in the late 1970s when accelerator mass spectrometers were adapted for radioisotope dating. The mass spectrometry method makes it possible to count all the atoms in a sample (or at least all that one can collect at the detector) rather than only those that decay in the allotted time. The sample is evaporated, ionized and accelerated through a magnetic field tuned to select isotopes with the correct ratio of charge to mass. Very often the isotope of interest may be in very small concentration, but it is isolated fairly effectively both by careful chemical separation during the sample preparation and by the highly resolved mass discrimination provided by the accelerator. (See the article by Richard Muller in PHYSICS TODAY, February 1979, page 23.) Similar methods can facilitate dating with other isotopes as well.

Uranium–thorium dating

C^{14} isn't the only isotope in town. Many others, each with their own particular strengths and weaknesses, can and are used for dating. The method of U–Th dating is based on measurements of U^{234} and U^{238} and their decay product Th^{230}. U^{238} undergoes several beta decays before emitting one alpha particle to become U^{234} and a second alpha to transform into Th^{230}, whose half life is 75 000 years. If one has a sample that initially contains no thorium and whose uranium content has not been altered since its deposition, one can compare the Th^{230}/U^{234} and U^{234}/U^{238} ratios to determine the age. Many researchers since the late 1950s have used this method of dating, especially to determine the sea level at various times in history by examining the uranium and thorium content of corals in uplifted reefs. The corals constitute a useful benchmark because they grow at the surface of the ocean.

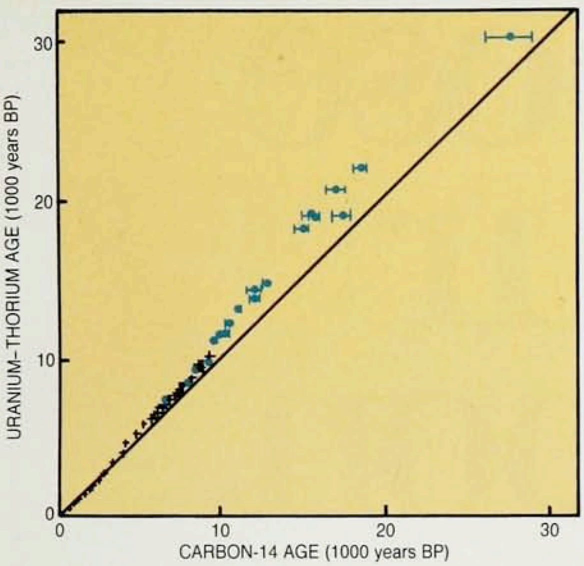
The precision of U–Th dating was strongly limited until the 1980s by the inherent imprecision of the alpha-counting method, especially in view of the low abundances of U^{234} and Th^{230}. In the 1980s U–Th dating benefited rather fortuitously by work being done to study astronomical rather than geophysical problems. At that time, Gerald Wasserburg and James Chen of Caltech needed to measure trace quantities of the rare uranium isotope U^{235} to check a theory that anomalous amounts of the isotope curium-247 (whose decay chain leads to U^{235}) had been deposited in the solar system by a supernova. They spent four years developing a chemically clean, high-sensitivity, high-precision method based on thermal ionization mass spectrometry. At the end of that time they had found virtually no variations in U^{235} abundance (and so had disproved the thesis), but in the process they had discovered a very useful tool.

Larry Edwards (University of Minnesota), then a graduate student at Caltech, adapted their method of thermal ionization mass spectroscopy to measurements of Th^{230}. The biggest challenges were to boost the ionization efficiency of the thermally excited thorium atoms and to measure small ion beams both accurately and precisely. The Caltech team succeeded in raising the precision of U–Th dating by a factor of 10 and lowering its measurement time by a factor of 30 compared with the counting method.[2] Edwards told us they were able to date 1000-year old corals to a precision of 3–5 years and to date 100 000-year samples with a 2-sigma error of 1000 years.

With the new measurement capabilities, the Caltech group, joined by Frederic Taylor (University of Texas), validated the U–Th chronometer by comparing U–Th ages both with radiocarbon ages and with ages determined by counting annual growth bands in coral skeletons.[3]

Coral samples

A comparative chronology of C^{14} and Th^{230} was provided by a set of 16 cores



Comparison of ages of corals dated by uranium–thorium abundances with the ages determined by carbon-14 dating (blue data points). The U-Th data agree with the calibration of C^{14} dates provided by tree rings (small black crosses) and varved sediments (large black crosses), and extend the scale they provide more than 30 000 years into the past. (Adapted from ref. 1.)

of Barbados coral that span a nearly continuous sequence between 7800 yr and 17 100 yr BP. Fairbanks of Lamont–Doherty obtained the island coral, which extends more than 150 meters below the present sea level, to study the sea level record during the last deglaciation. After successfully establishing a sea level record based on the C^{14} measurements of these cores, Fairbanks decided to improve the accuracy of the sea level record by determining the U–Th ages for the same samples. Thus he teamed up with Bard, Hamelin and Zindler. (Bard is now at CNRS–CEA in Gif-sur-Yvette, and Hamelin is at the University of Aix-Marseille III, both in France.) The C^{14} ages are plotted in the figure on this page against the ages determined by U–Th measurements on the same coral samples. The plot also compares C^{14} and U–Th ages determined from tree rings and varved sediments, the latter being lake-bed deposits whose alternating dark and light layers measure the passage of time. The C^{14} data have been corrected for the age difference between the reservoir of carbon in the atmosphere and that in the surface ocean. (The surface oceanic reservoir is assumed to have been 400 years older, as is the case today.) The U–Th dates are older than those determined by C^{14} dating by as much as 18%. Wally Broecker (Lamont–Doherty), who did considerable work with the U–Th counting method in the 1960s, was surprised that the discrepancy is so large.

The U–Th dating would be in error if the uranium content of the corals has been altered since the uranium was originally deposited. The Lamont–Doherty group tried to verify the constancy of the deposition by inferring from its measured data the U^{234}/U^{238} ratio that prevailed at the time the coral was formed: They found that it was equal to the value expected for modern seawater, evidence that the uranium had not shifted since its deposition. To gain even further confidence in their results, Fairbanks and Zindler plan to measure the coral ages with protactinium dating.

The young ages derived from C^{14} dating imply that the initial concentration of C^{14} in the atmosphere was larger than it is at present by as much as 40%. In the atmosphere C^{14} is produced by the reaction $n + N^{14} \rightarrow p + C^{14}$. (The neutrons are produced by cosmic-ray protons.) The C^{14} atmospheric concentration might have varied in time because of a number of effects but the only one large enough to have caused the observed variation is a change in the intensity of the geomagnetic dipole field. In fact, the available data indicate that 30 000 years ago, Earth's magnetic dipole was only about half its current strength. With the weaker field, more cosmic rays could penetrate at midlatitudes, creating higher abundances of C^{14}. The Lamont–Doherty team has tested the hypothesis that variations in the intensity of the geomagnetic field affected the C^{14} dates by comparing the discrepancies they calculate based on the dipole history with the measured discrepancies between C^{14} and Th^{230} dates.

Milankovitch theory

The new precision that thermal ionization mass spectroscopy brings to U–Th dating makes it a valuable tool in addressing many historic questions dealing with global climate. One issue still being debated is the Milankovitch theory, according to which the ice ages were precipitated by changes in the seasonal distribution of solar radiation reaching Earth as its orbit shifted. For example, as more summer sunlight reached the northern regions, ice caps would melt and lead the world into a relatively warm, interglacial period. Critical to that theory is the timing between the orbital shifts and the interglacial periods. Research on sea levels over the years has suggested that the last interglacial period was about 125 000 years BP, roughly in coincidence with the last period of maximum summer insolation in the Northern Hemisphere, at about 128 000 years BP.

In 1988 Isaac Winograd and his colleagues at the US Geological Survey challenged those data.[4] They had studied the variations in oxygen-18 concentrations in calcite deposits below the water table in a Nevada crevasse called Devil's Hole. In marine studies, O^{18} is taken to be a measure of the amount of glacial ice: Glacial ice is depleted in O^{18}, and hence seawater becomes enriched in that isotope at times of falling sea levels. The USGS team took the concentrations of this isotope in the groundwater of Devil's Hole as a measure of air temperatures. In defense of that assumption, Winograd points out that their records of O^{18} concentrations going back 300 000 years track the same trends as concentrations determined from marine data and from Vostok ice cores from the Antarctic, although the curves are offset from one another in time. The USGS group found that the interglacial period appeared to have ended 147 000 years ago to 20 000 years earlier than the oceanographers had believed. However, several groups have recently tried to date corals with U–Th mass spectrometry, and their results[5,6] are broadly consistent with the Milankovitch theory.

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