PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Tandem-Accelerator Mass-Spectrometry Measurements of ^{36}Cl, ^{129}I and Osmium Isotopes in Diverse Natural Samples [and Discussion]

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Phil. Trans. R. Soc. Lond. A 1987 **323**, 103-119
doi: 10.1098/rsta.1987.0076

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Printed in Great Britain

Tandem-accelerator mass-spectrometry measurements of ^{36}Cl, ^{129}I and osmium isotopes in diverse natural samples

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Tandem AMS measurements at Rochester in the past few years have mainly involved the radioisotopes ^{36}Cl and ^{129}I, and some work on ^{10}Be, in a variety of terrestrial and extraterrestrial samples. Some measurements have also been made on certain stable isotopes of osmium in meteorites and geological samples from impact craters. Measurements of ^{36}Cl have been made in groundwater and surface rocks for dating purposes, in ice and soil samples containing nuclear-weapon testing fallout for tracing water movement, and in meteorites and Antarctic ice for terrestrial and extraterrestrial meteoritic age determination. Also, ^{10}Be has been measured in a lake sediment, and ^{36}Cl in Greenland ice, through the period of the Maunder minimum; ^{129}I has been measured in hydrological systems, in petroleum and in hydrothermal convection cells in the oceanic crust. Other applications involving measurements of these two radioisotopes include hydrothermal fluids associated with gold mineralization and the determination of the integrity of possible sites for deep nuclear-waste disposal. Previously, the Rochester tandem was employed to measure ^{14}C and isotopes of platinum and iridium in natural samples.

Introduction

Nine years ago, the first tandem-accelerator mass-spectrometry (TAMS) measurements of ^{14}C in natural carbon samples were carried out at the University of Rochester (Bennett *et al.* 1977) and at McMaster University (Nelson *et al.* 1977). In a remarkably short time, the technique was applied to a number of other cosmogenic radionuclides including ^{10}Be, ^{26}Al, ^{32}Si, ^{36}Cl, ^{41}Ca, ^{129}I and stable isotopes of osmium, platinum and iridium. Equally remarkable is the fact that, at the latest count, 33 tandem-accelerator laboratories throughout the world are engaged in accelerator mass-spectrometry measurements either part time or full time. The seminal measurements at Rochester involved a collaboration with the University of Toronto represented by Professor A. E. Litherland who gave the opening paper at this meeting, and the General Ionex Corporation represented by Dr K. H. Purser. This company manufactures an accelerator called the Tandetron, presently used in several laboratories for TAMS measurements.

The field of accelerator mass spectrometry is characterized by its considerable diversity. In the nine years since its inception, it has had an impact on virtually every field of science. These include archaeology, oceanography, geology, cosmology, meteorology, anthropology and many others.

This paper describes some of the measurements made at Rochester of the radioisotopes ^{10}Be, ^{36}Cl and ^{129}I as well as stable isotopes of osmium in a variety of natural samples. The following sections describe briefly the method employed at Rochester, followed by short accounts of tests carried out to establish ^{36}Cl as a suitable isotope for measuring the age of the groundwater and its injection into the environment from nuclear weapons tests as a tracer of water movement; ^{10}Be and ^{36}Cl increases in lake sediments and Greenland ice during the Maunder minimum; ^{36}Cl measurements in Antarctic meteorites that, along with measurements on other radioisotopes, establishes their terrestrial and extraterrestrial ages; ^{129}I measurements in marine sediments, granite formations, oil, and as an environmental tracer. Finally, measurements of stable osmium isotopes in known and possible terrestrial-impact craters will be described.

AMS AT ROCHESTER

The AMS system used at Rochester has been extensively described in the published literature (Gove 1985, and references therein). Figure 1 is a schematic of the overall system now employed at Rochester.

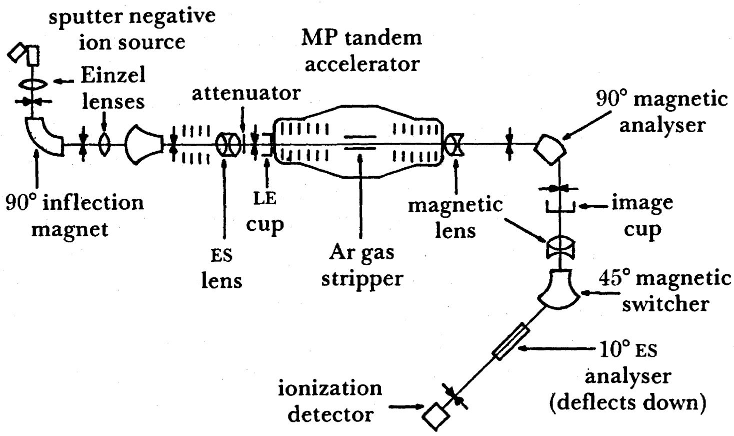

FIGURE 1. Schematic of the Rochester TAMS system.

Negative ions produced in the caesium sputter-ion source are mass analysed in the 90° inflection magnet and injected at an energy of about 150 keV into the first half of the tandem accelerator where they accelerate toward the terminal. A gas stripper in the terminal converts them to multiply charged positive ions. They are further accelerated through the second half of the tandem and then passed through two magnetic deflectors and one electrostatic deflector before reaching the final ionization detector. The combined magnetic and electric deflections define the ion velocity, and the final detector then defines their atomic number Z. The accelerator is principally employed for basic research in nuclear physics and only a relatively small fraction of its time is employed for the measurements described herein.

Table 1 lists the radioisotopes that have been measured at Rochester. They are all produced by cosmic rays although they may have other origins in addition. Their half-lives, shown in the second column, range from 6 ka to 16 Ma. Because AMS is not a high-resolution mass-spectrometry technique, the rare radioisopes of interest cannot be distinguished from their isobars (listed in the fourth column) on the basis of mass alone. In cases where Nature is kind, the possible interfering isobar (or in the case of atomic mass 36 – 1 of them) poses no problem because they do not form negative ions of sufficient stability to survive the journey to the stripper gas in the tandem terminal. Where they do form negative ions they must be reduced in concentration by careful chemistry and/or Z-identification. The final column lists the present detection limit for determining the ratio of the radioisotope to its stable isotopes. For ^{14}C and ^{36}Cl, this amounts to a few parts in 10^{16}. It is this sort of number that gives rise to the 'ultra-high sensitivity' part of the title of this symposium.

TABLE 1

radio isotope	half-life / years	stable isotopes	stable isobars	10^{15} × detection limit
^{10}Be	1.6×10^6	^{9}Be	^{10}B	7
^{14}C	5730	^{12}C, ^{13}C	^{14}N†	0.3
^{26}Al	7.3×10^5	^{27}Al	^{26}Mg†	4
^{36}Cl	3.0×10^5	^{35}Cl, ^{37}Cl	^{36}Ar†, ^{36}S	0.2
^{41}Ca	1.0×10^5	^{40,42,43,44}Ca	^{41}K	500
^{129}I	15.9×10^6	^{127}I	^{129}Xe†	10

† Does not form negative ions.

At the beginning of this introduction it was mentioned that ^{14}C was the radioisotope that inspired the development of AMS. The first results (Bennett *et al.* 1977) of such measurements on natural samples are shown in figure 2. For comparison, the carbon spectrum from recent hardwood charcoal and graphite containing very little radiocarbon (less than about 50 ka, equivalent) is displayed. Relatively little work on ^{14}C has been carried out at Rochester because an MP tandem Van de Graaff is a far higher energy accelerator than is required for the job. Dedicated facilities based on the General Ionex Tandetron such as those at Arizona, Gif-sur-Yvette, Nagoya, Oxford and Toronto seem to be ideal accelerators for the lighter radioisotopes and so, at Rochester, the programme has concentrated on masses of 36 and higher.

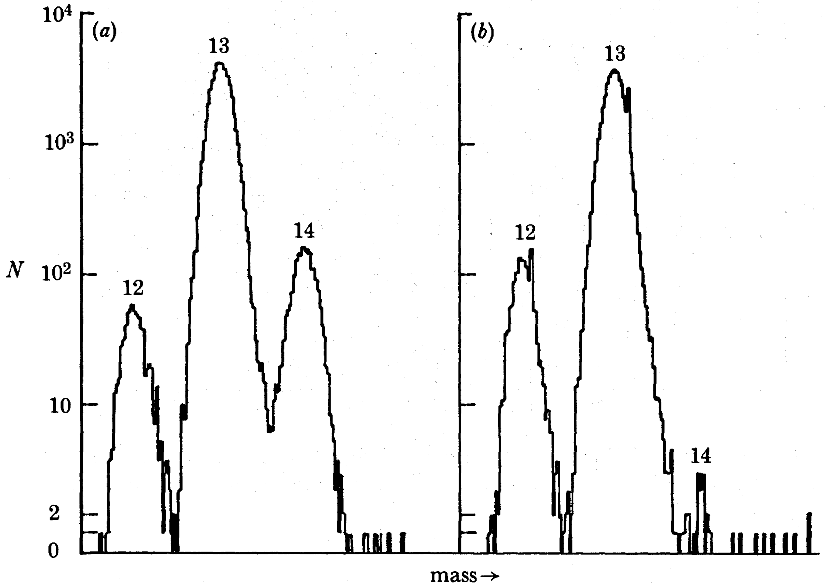

FIGURE 2. First results on detection of ^{14}C from natural samples (Bennett *et al.* 1977). The data from contemporary hard-wood charcoal is shown in (*a*) and that from petroleum-derived graphite in (*b*).

^{36}Cl AS A MEASURE OF GROUNDWATER AGE

Virtually all of the meteoric ^{36}Cl is derived from cosmic-ray spallation of ^{40}Ar and neutron activation of ^{36}Ar in the atmosphere. The neutrons are products of cosmic-ray interactions with the atmosphere. The ^{36}Cl so produced falls to Earth on a very short time scale and some of it enters the hydrological cycle. Once incorporated in groundwater it travels with the water.

It does not get removed as the water travels through an aquifer. Most rocks contain little chlorine in their solid matrix and thus do not constitute a chlorine source (Bentley *et al.* 1985).

Chlorine-36 thus has many advantages as a dating tool for very old groundwater. These advantages include a suitable half-life (0.301 Ma), simple geochemistry, conservation behaviour in groundwater, and a general absence of subsurface sources at levels comparable to the atmospheric input. Recent advances in TAMS have permitted the analysis of ^{36}Cl at the low abundance expected following residence in the subsurface for 10^6 years or more. To test the suitability of ^{36}Cl for dating very old groundwater, the ^{36}Cl:Cl ratios of 26 groundwater samples from the Great Artesian Basin of Australia have been measured and compared with ages computed independently from hydrodynamic simulations (Bentley *et al.* 1986). The hydrology of this basin is relatively simple and so the computed hydrologic ages are concomitantly credible.

Figure 3 is a map of the Great Artesian Basin area showing the location of the water sampling points. The solid curves are contour lines of isopleths of ^{36}Cl:Cl ratios that are converted to isochrons labelled in units of 1 Ma, based on the half-life of ^{36}Cl.

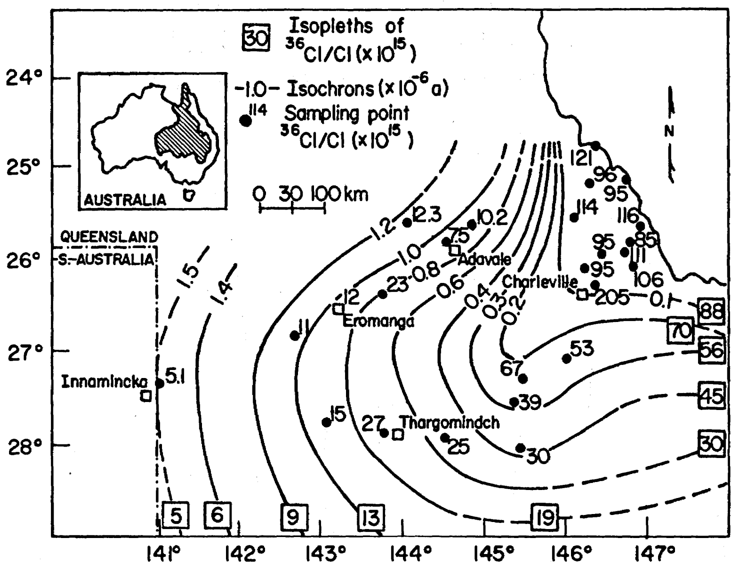

FIGURE 3. Map of the Great Artesian Basin area of Australia with solid lines of isopleths of the ^{36}Cl:Cl ratio converted to isochrons. The sampling points are shown. The inset shows the region of Australia in which the basin is located.

From these data and the computed hydrologic age of the water at the various sampling sites one obtains the data plotted in figure 4. A one-to-one correspondence between ^{36}Cl age and hydrologic age would require the data to fit a line of 45° slope as shown. Although a better fit is to a line of slope about 51°, this is still considered reasonably convincing evidence that the ratio of ^{36}Cl:Cl in groundwater is a good measure of the length of time the water has been isolated from the atmosphere on a time scale of a million years.

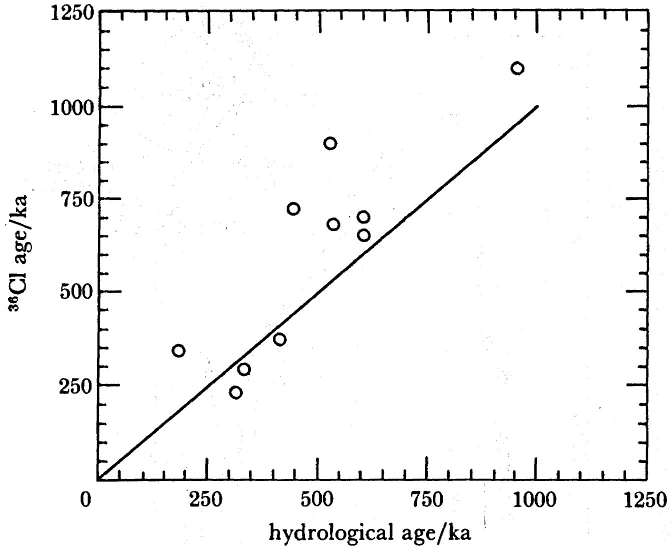

FIGURE 4. Plot of the ^{36}Cl age against hydrologic age for the water in the Great Artesian Basin in Australia.

^{36}Cl BOMB PULSE

Nuclear-weapons tests at oceanic sites during the 1950s produced a large amount of ^{36}Cl through neutron capture of ^{35}Cl in seawater. Part of this anthropogenic ^{36}Cl was injected into the stratosphere from where it was redistributed throughout the Earth. This pulse of ^{36}Cl was first detected in rainfall. The global deposition rates are several orders of magnitude larger than the natural pre-bomb and post-bomb ^{36}Cl production rate that reflects cosmic-ray spallation of atmospheric ^{40}Ar. Because ^{36}Cl is not a fission product, the anthropogenic ^{36}Cl is produced mainly in marine tests carried out on small islands and barges where a large amount of seawater chlorine is present to serve as a target. This target-element requirement leads to a temporal dependence from the other bomb-produced isotopes determined. The temporal dependence of ^{36}Cl fallout has been determined by measuring the depth profile of ^{36}Cl in an ice core from Dye 3 Greenland (65° 11′ N, 43° 50′ W) (Elmore *et al.* 1982) and in groundwater from the Borden Canadian Forces Base landfill site in Ontario Canada (Bentley *et al.* 1982).

The Greenland ice measurements were made on a 100 m core drilled in 1980. Each sample contained one year of precipition covering the years from 1950 to 1978. The age scale was determined by counting the seasonal variation in the ^{18}O:O ratio. Figure 5 shows a plot of the ^{36}Cl concentration (atoms per kg of ice) against the year. The inset map of Greenland shows the location of Dye 3. Plotted on this same figure are points representing the major nuclear-weapons tests carried out in the Pacific ocean between 1952 and 1958 with a vertical scale proportional to the explosive yield. These results show that ^{36}Cl concentrations at Dye 3 increased rapidly by a factor of more than 100 from the 1950 pre-bomb levels to 1955, held steady until 1960 and then declined up to 1970 exponentially with a half-life of about two years.

To test the possibility that the ^{36}Cl bomb pulse could be used as a tracer in natural water, samples were taken from groundwater at various depths in a landfill site at the Borden Canadian Forces Base in Ontario, Canada. The ^{36}Cl concentrations were measured by the TAMS method at Rochester and, in addition, the tritium concentration was measured by the standard decay counting technique. The results are shown in figure 6 plotted against the depths at which

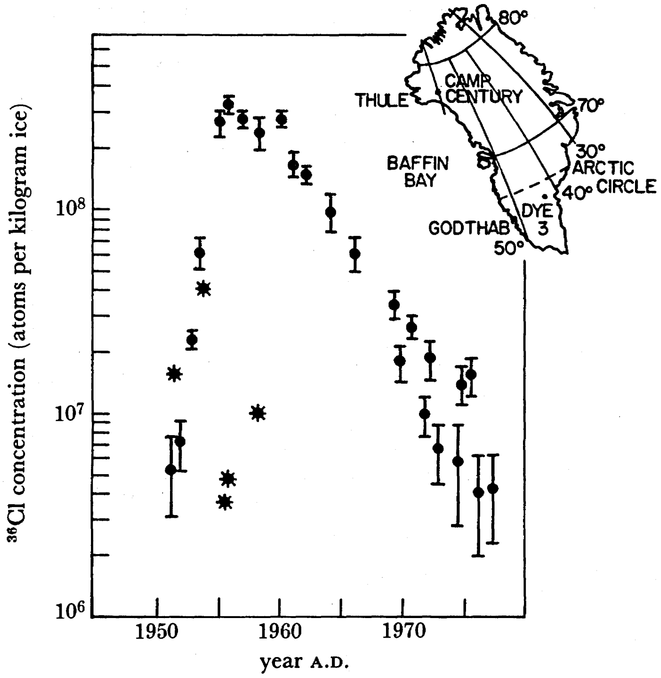

FIGURE 5. ^{36}Cl concentration plotted against year in the Dye 3 ice core. The relative explosive yields of nuclear-weapons tests in the Pacific Ocean are also shown. The inset map of Greenland shows the location of the Dye 3 site. Symbol: $*$, ocean nuclear tests.

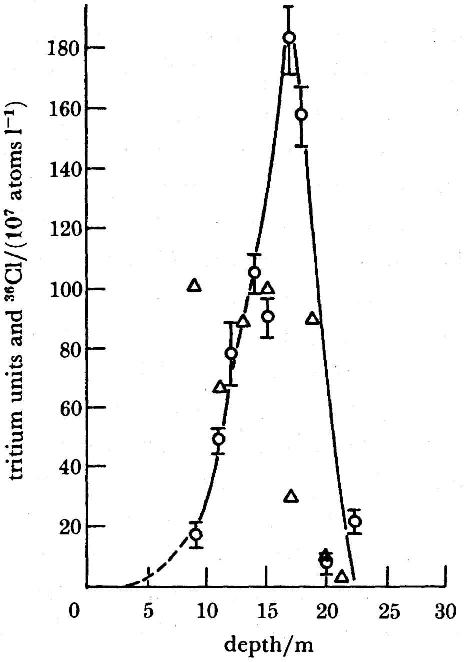

FIGURE 6. Tritium units, △, and ^{36}Cl concentration, ○, plotted against depth in groundwater at a Camp Borden landfill site.

the water samples were taken. Owing to uncertainties in flow patterns, the depths cannot be definitely correlated with the date of recharge. However, the shape is similar to that found in the Greenland ice core and also to that predicted by a fallout model (Bentley *et al.* 1982). The ^{36}Cl pulse characteristics appear to be well suited for use as an environmental tracer. The maximum fallout rate was large enough to be unequivocally distinguished from natural concentrations even after substantial dilution with stable chloride from natural systems. Chlorine-36 is one of the few hydrophilic anthropogenic tracers that has returned to natural levels since the time of the maximum input. This characteristic should be particularly valuable in the study of hydraulic flow and dispersive mixing. Decay of radionuclides and dispersive mixing of groundwater create decreases in concentration that are difficult to distinguish. The long half-life of ^{36}Cl should eliminate such ambiguities in interpretation of the bomb pulse. It is expected that, in the near future, bomb-produced ^{36}Cl will usefully supplement bomb tritium as an environmental tracer, and that, as the bomb-tritium pulse decays to background levels, ^{36}Cl may eventually replace it.

^{10}Be AND ^{36}Cl AND THE MAUNDER MINIMUM

From approximately 1650 to 1710, a period of about 60 years, the frequency of sunspots and auroras declined to virtually zero. During the same period, and perhaps for completely unrelated reasons, Europe went through what has been called a little ice age. A decline in sunspot activity, which in turn was responsible for fewer auroras, results in a lessening in the strength of the Sun's solar wind-derived magnetic field. This permits an increase in the cosmic-ray flux incident on the Earth's atmosphere, hence an increase in cosmogenic radioisotopes such as ^{10}Be, ^{14}C and ^{36}Cl. Figure 7 (Stuiver & Quay 1980) shows auroral and sunspot activity along with calculated changes in the ^{14}C production rate for the past nine centuries. In particular, the pronounced production increase of about 50% in ^{14}C during the

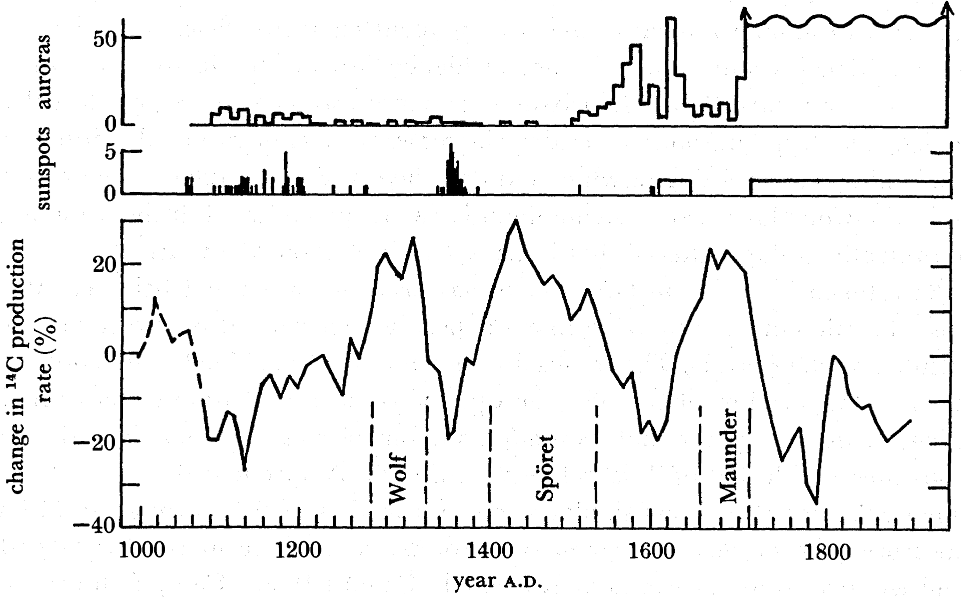

FIGURE 7. Sunspot frequency, aurora activity and changes in ^{14}C production from the 11th to 20th centuries.

Maunder minimum is evident. Because of reservoir effects, the actual increase in the ^{14}C:^{12}C ratio in tree rings is only about 2% (Stuiver & Quay 1980). The same reservoir effect does not apply to either ^{10}Be or ^{36}Cl, so the increase in these two cosmogenic radio isotopes in suitable terrestrial samples should approach 50% through the Maunder minimum.

The radionuclide ^{10}Be (half-life = 1.6 Ma) is produced in spallation reactions by galactic cosmic-ray particles interacting with nitrogen and oxygen nuclei, predominantly in the stratosphere. Because ^{10}Be has an affinity for aerosols and particulates, it is rapidly removed from the atmosphere by wet and dry precipitation and is incorporated into terrestrial reservoirs. The estimated atmospheric residence time is about one year. ^{10}Be is therefore ideal for investigating short-term and long-term variations in cosmogenic production and/or deposition rates. Of special interest are changes in the production rate due to modulation of galactic cosmic-ray intensity by variable solar activity and variable geomagnetic field strength. In an 'ideal' terrestrial reservoir and with no disturbance in the transfer mechanism, the ^{10}Be concentrations, unlike those for ^{14}C, should reveal production-rate variations with minimal attenuation and lag. The optimum reservoir is polar ice. Raisbeck *et al.* (1981) showed evidence for enhanced ^{10}Be production from measurements in Antarctic ice over the period of the Maunder minimum, when the solar activity was depressed, by using accelerator mass spectrometry.

For non-polar latitudes, lacustrine sediments might be used to search for production-related variations in the ^{10}Be concentrations over several hundreds or thousands of years. Lake sediments, however, are an inherently more complex reservoir than polar ice, and selection of a suitable lake is crucial. A further complication is the lack of information on geochemical behaviour of deposited ^{10}Be on watershed soils and in lake waters. Green Lake in Fayetteville, New York, is thought to have been formed as a plunge pool, carved into shales of the Upper Silurian Syracuse formation by falls from receding glaciers at the end of the last ice age. Its special chemical and physical properties leading to its meromictic character have been extensively investigated. Water entering the lake bottom waters is more saline than that entering the surface waters, and the resulting difference in water density leads to a permanent stratification. Lack of annual mixing causes a permanent oxygen deficiency in the bottom waters. This condition precludes the existence of higher forms of life in the top sediments, which thus remain undisturbed by bioturbation. Supersaturation with respect to calcite is temperature-dependent, and dissolution of calcite increases with temperature. Accordingly, the sediments are laminated, consisting of white and dark layers. Each couplet is regarded as an annual deposit, the white layer being predominantly calcite precipitated during summer, the dark layer representing other material that is deposited throughout the year.

The ^{10}Be:Be ratio in a core from Green Lake has been measured at Rochester (Wahlen *et al.* 1983) as a function of the date of sediment deposition determined by direct counting of the annual white and dark layers. The results are shown in figure 8. The ^{10}Be deposition rate for the sediment is enhanced by about 40% for a period coinciding (within the error limits of varve counting) with the Spörer and Maunder minima of solar activity. The data is in reasonable agreement with that of Raisbeck *et al.* (1981) for Antarctic ice.

To determine whether ^{36}Cl shows similar variations to that of ^{10}Be during the Maunder minimum, measurements on this cosmogenic radioisotope extracted from ice cores taken from the Greenland ice sheet were measured at Rochester (Conard 1986). Camp Century, where the ice core used in these measurements was drilled, is located in northern Greenland, east of Thule as shown in the inset map of figure 5.

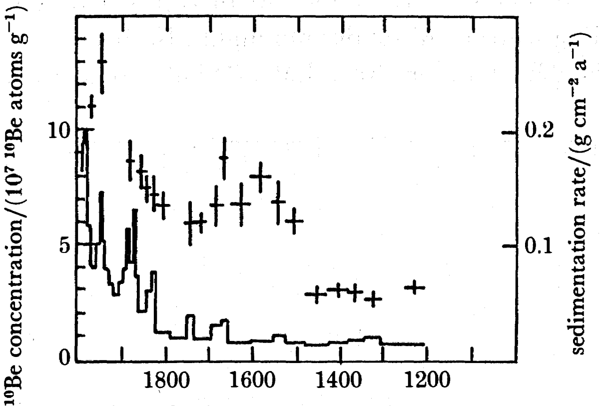

FIGURE 8. ^{10}Be concentrations (crosses) and sediment rates (histogram) in Green Lake as a function of time from the present to 1200 A.D.

The thirtyfive samples of ice taken from the upper portion of the Camp Century ice sheet ranged in mass from 270 to 2100 g. The latter corresponds to a cube of ice 5 inches† on a side and it contains only approximately 200 μg of chloride. Careful chemical procedures were followed (as in all the ^{36}Cl measurements at Rochester) to reduce the amount of sulphur (and thus of the stable interfering isobar ^{36}S). The annual variation of the ^{18}O:O ratio was used to obtain the actual age of the ice samples. This technique is limited to ages of 10 Ka or less.

The results are shown in figure 9, where the number of ^{36}Cl atoms per gram of ice is plotted against the time scale of years A.D. The short-term fluctuations (factors of 2 in about 8 years) are real but not understood. Similar fluctuations are found by Beer *et al.* (1984) who measured ^{10}Be in this same core. For comparison with the data of Stuiver & Quay (1980) shown in figure 7, the data of figure 9 were smoothed to give comparable peak widths.

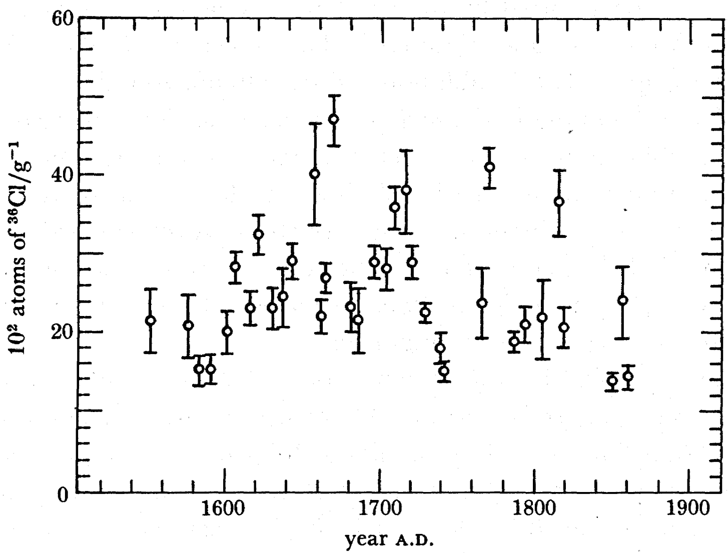

FIGURE 9. The number of atoms of ^{36}Cl per gram of ice against the age of the ice taken from the Camp Century core. The Camp Century location in northern Greenland is shown on the inset of figure 5.

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† 1 inch = 2.54 cm.

This is shown in figure 10. There is clearly a broad 40% peak over the period 1630–1720 A.D. approximately coinciding with the Maunder minimum. In this respect the data are somewhat more clear cut than the ^{10}Be data for Green Lake (Whalen *et al.* 1983).

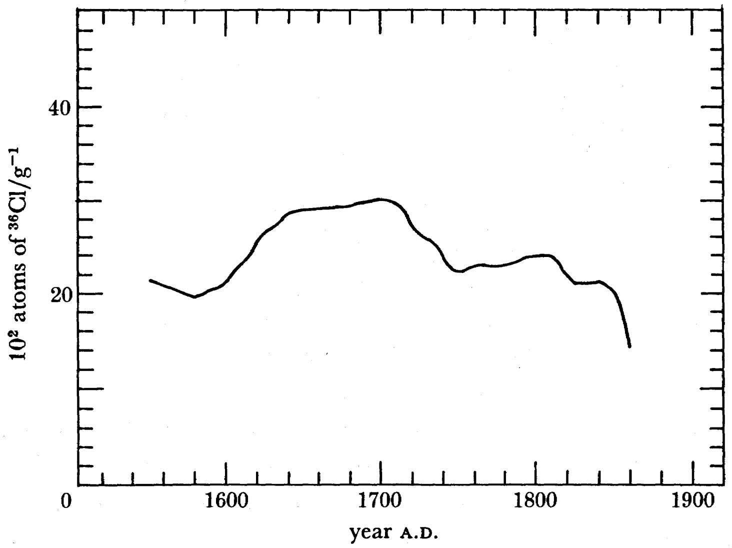

FIGURE 10. Plots of data shown in figure 9 suitably averaged to give peak widths comparable with those in figure 7.

^{36}Cl IN METEORITES

The recent discovery of large numbers of Antarctic meteorites has expanded the field of meteorite study. A systematic search over the last decade has yielded approximately 4700 meteorites from the Yamato Mountains by Japanese expeditions and about 1300 meteorites from the Allan Hills and nearby by U.S.–Japan and U.S. expeditions operating in the Antarctic. Meteorites are transported by the ice flow to ablation areas such as the blue-ice regions of the Yamato Mountains and Allan Hills. The movements of the meteorites and the surrounding ice sheet are upward at the ablation region, with horizontal flow inhibited because of bedrock topography and mountains. In such a region, surface ice is ablated by wind-blown snow combined with sublimation and the meteorites remain on the blue-ice surface. This hypothesis explains the abundance and variety of different classes of meteorites that have been found in some regions. It also explains how various terrestrial ages of meteorites can be obtained from the same region. To help understand the meteorite accumulation mechanism and the glaciology of Antarctic ice, a systematic survey of the terrestrial age of the Antarctic meteorites and the age of the surrounding ice is very important.

A programme to measure ^{36}Cl in Antarctic meteorites had been under way for a number of years (Nishiizumi *et al.* 1979, 1981, 1983*a*). These measurements, combined with those of other cosmogenic radionuclides as well as stable nuclides in the same objects, can provide information on their terrestrial age and their extraterrestrial cosmic-ray exposure history. Among the two dozen or so meteorites for which the ^{36}Cl content has been measured, the terrestrial ages range from about 10 ka to 0.7 Ma, and the cosmic-ray exposure age ranges from about 3 Ma to greater than 15 Ma. For example, one of the Allan Hills meteorites whose ^{36}Cl content was measured at Rochester had a terrestrial age of 0.37 ± 0.09 Ma and a cosmic-ray exposure age of 3.5 ± 0.8 Ma (Nishiizumi *et al.* 1981).

In addition to measurements of ^{36}Cl in Antarctic meteorites, a depth profile of ^{10}Be and ^{36}Cl has been made in an Apollo 15 drill core from the moon (Nishiizumi *et al.* 1984) to obtain information on galactic cosmic-ray production. The half-attenuation lengths for ^{10}Be and ^{36}Cl production were 120 and 132 g cm^{-2} respectively at depths below about 150 g cm^{-2}. It has also been shown that cosmogenic ^{129}I (Nishiizumi *et al.* 1983*b*) and ^{41}Ca (Kubik *et al.* 1986) can be readily detected by TAMS in meteorites and thus can also be used to determine their irradiation history.

^{129}I IN MARINE SEDIMENTS GRANITE FORMATIONS AND OIL

The rare radioisotope ^{129}I is produced in the atmosphere by cosmic rays and in the crust by spontaneous fission of ^{238}U. Because of its relatively long half-life (16 Ma) and the geochemical characteristics of iodine, this isotope has a number of promising applications in the marine environment such as dating of sediments, tracing of slow water movements and dating–tracing of hydrocarbons. The very low levels of the isotope in Nature have prevented its detection until the recent development of accelerator mass spectrometry. With this method, the detection limit for the ratio ^{129}I : ^{127}I is about 10^{-14}. Both in the case of the dating of the marine sediments and of crude oil one might expect to reach an upper limit of 100 Ma.

The first measurements (Fehn *et al.* 1986*a*, *b*) were made on a marine-sediment piston core taken on the continental slope east of Cape Hatteras, U.S.A., at a water depth of 1 km. The sediments in the ocean floor at the location are fine, silty sands and the annual sedimentation rate is about 0.02 g cm^{-2}. Figure 11 shows the ^{129}I : ^{127}I ratio as a function of depth below the ocean bed in that core.

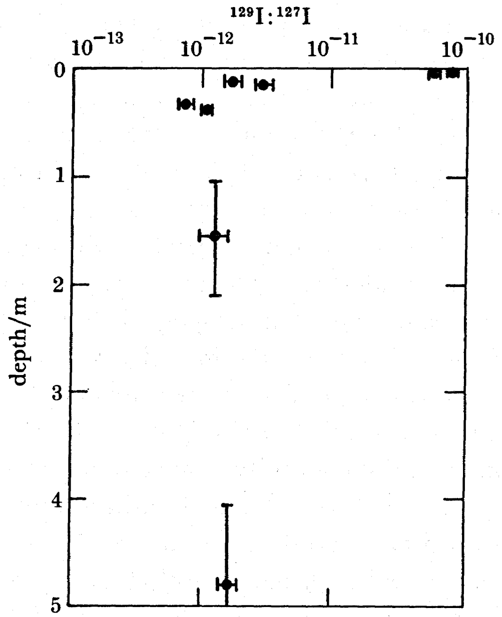

Figure 11. The ratio ^{129}I : ^{127}I as a function of depth in an ocean sediment piston core taken off Cape Hatteras. The 'pre-bomb' ratio of 10^{-12} is reached at a depth of 30 cm.

The profile in figure 11 has two important features with respect to the present distribution of ^{129}I in marine sediments: the strong enrichment of ^{129}I at the surface, and the relative stability of the ^{129}I : ^{127}I values in the deeper layers. The strong increase of ^{129}I concentration in the top 10 cm clearly reflects the recent input of anthropogenic ^{129}I. The ratio found for the surface sample is in good agreement with ratios measured in marine algae, collected in 1975–77 off the coast of California, but lower than that found for a whale thyroid from the Pacific.

The relatively smooth transition from the surface value to the constant values at depth reflects two processes, the incorporation of iodine into the sediments and bioturbation of the top layer. The concentration of iodine in marine sediments in general shows a strong correlation with the amount of organic matter present. As the organic matter decomposes under anaerobic conditions in the sediments, iodine is released into the pore water. The larger part of that iodine is transported back into the seawater, but a significant part reacts with the sediments close to the sediment–water interface and remains in the sediments. At the same time, the top layer undergoes extensive bioturbation, which probably is the main factor for the observed mixing profile between, and anthropogenic iodine at, the surface and the natural ratios at depth. The constant values in the deeper layers show that the influence of man-made ^{129}I is restricted to the top layers, in good agreement with the observation that almost all of the return flux of inorganic iodine originates in the top 10 cm of sediments.

Although the exact sedimentation rate for these sediments is not known, a rate of 10 cm ka^{-1} is probably a good assumption for this area. With such a sedimentation rate, the age for the deepest sample is 50 ka. This age is, even allowing for sedimentation rates lower by an order of magnitude, much too young to show any sign of radioactive decay of the ^{129}I, given its long half-life of 16 Ma. The ^{129}I : ^{127}I ratios thus reflect directly the input signal from the oceans that must have been quite constant during this time period, in view of the relative stability in these ratios throughout most of the sediment column. This observation is in good agreement with the long residence time of iodine in the oceans (more than 40 ka) that suggests a well-mixed isotopic reservoir for iodine in the marine environment.

The most important finding of this study is that the level of ^{129}I in sediments before the input of anthropogenic ^{129}I is approximately two orders of magnitude higher than the current detection limit of TAMS. It suggests that the system can be used for dating purposes with an age range of about 80 Ma, a range of particular interest for questions concerning the formation of hydrocarbon in marine sediments. Because of the high mobility of iodine in its inorganic form, this system can probably also be used for the tracing of fluid movements in marine sediments, in particular of the slow movement of seawater through sediments in response to hydrothermal convection in the underlying oceanic crust. A number of other potential applications are related to the recent input of anthropogenic ^{129}I into the marine environment. Examples include the use of the ^{129}I pulse in the investigation of diagenetic processes in the sediments, and for the long-term tracing of deep-water currents in the oceans. Investigations of significantly older sediments than studied here might also be helpful concerning questions about the dating of old sediments and the stability of the cosmic-ray flux over extended periods of time, especially if they are combined with the use of other isotopic methods.

^{129}I : ^{127}I ratios were also measured in crude oil from the Monterey Formation, California, and were found to be about 5.5×10^{-12}, i.e. significantly higher than the ratios in the marine sediments, but still lower than the ratios measured in the associated source rock. The high levels of ^{129}I in the source reflect the *in situ* production of this isotope by the spontaneous decay of ^{238}U. These results are interpreted as indications of isotopic exchange between iodine from the source rock and iodine in organic matter with the original marine ratio that occurred during the maturation process of the hydrocarbons.

^{129}I AS AN ENVIRONMENTAL TRACER IN HYDROLOGY

To assess the use of ^{129}I as an environmental tracer several systems are under study. One of these is the Stripa mine in Sweden. The Stripa project is an international effort to develop and test methods for characterizing hydraulic parameters in fractured crystalline rock, including water age and origin, and sources of salinity. Fieldwork is conducted in the Stripa iron-ore mine, located in south-central Sweden. The mine is constructed in a granite intrusion. The granite is unusual in that its uranium concentration, 37 p.p.m. (by mass), is about 10 times greater than the average for granite.

Most of the sampling focused on packed-off intervals in two parallel boreholes, one extending to 822 m below the surface and the other to 1200 m. Figure 12 shows the results to date (Fabryka-Martin *et al.* 1985) for Stripa groundwater. The ^{129}I : I ratios in the deepest intervals are more than two orders of magnitude above meteoric background. Ratios and atomic concentrations both increase steadily with depth. A model is presently being developed (Fabryka-Martin *et al.* 1985) that will relate ^{129}I concentrations to residence time of the water in the granite. The model itself is rather simple, but the choice of parameter values is not.

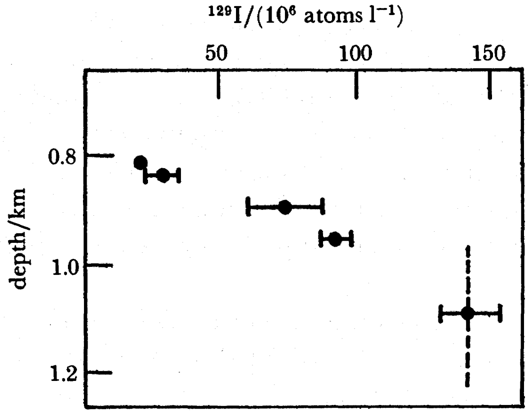

FIGURE 12. The concentration of ^{129}I as a function of depth in the Stripa iron-ore mine in Sweden.

OSMIUM ISOTOPE RATIOS IN TERRESTRIAL ROCKS

Osmium and rhenium are two elements that are significantly depleted in the Earth's crust by comparison with the mantle and the meteorites. One of the two rhenium isotopes, ^{187}Re, undergoes β-decay into ^{187}Os with a half-life of approximately 50 Ga. Because of this decay, and the fact that osmium is more depleted in the crust than rhenium, the isotopic ratio ^{187}Os : ^{186}Os in the crust is significantly higher than in the mantle and in meteorites. Thus, the ^{187}Os : ^{186}Os ratio is a very sensitive indicator for the presence of extraterrestrial material even in very low concentrations. The use of the Os system in this way was demonstrated recently by Luck & Turekian (1983) for sediments from the Cretaceous–Tertiary boundary.

A major obstacle for the application of this system is, however, the very low concentration of osmium in crustal rocks (typically around 0.01 p.p.b.† (by mass)). This extremely low level has prevented the measurement of osmium in conventional mass spectrometers, except for special cases such as meteorite samples, where it occurs at levels of the order of 10^{-6}. The

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† Parts per billion; in this paper, 1 billion is used to represent 10^9.

possibility of measuring the isotopic composition of osmium with TAMS has been previously investigated (Chew *et al.* 1984). The main potential advantages of this method are that significantly lower levels of osmium are needed for detection than with conventional mass spectrometry, and that no complete separation of osmium from its matrix is necessary for the measurement with TAMS.

At Rochester, the first measurements (Fehn *et al.* 1986*c*) of osmium isotopic ratios was made in unprocessed rocks from Meteor Crater, Arizona. This crater, also called Canyon Diablo Crater is a natural, hypervelocity impact crater 1220 m in diameter and 180 m deep. The osmium and rhenium concentrations in the iron meteorite that formed this crater are 2 p.p.m. (by mass) and 0.2 p.p.m. (by mass), respectively, and the ^{187}Os:^{186}Os ratio is 1.11 (Luck & Allègre 1983). Crushed meteoritic material was placed directly in the ion source of the Rochester TAMS system. The results were in excellent agreement with those quoted above.

This was followed by measurements (Teng *et al.* 1986) of two samples from the East Clearwater crater in Quebec, Canada, and four samples from the Ries crater in Germany. The Clearwater craters are generally agreed to be the result of a meteorite impact. The two samples from East Clearwater comes from the subsurface melt layer found in this crater. The high osmium concentration (55.5 p.p.b., by mass) measured for one of these samples has been part of the evidence for the extraterrestrial origin of this crater. Counting rates from untreated Clearwater samples were too low to allow reliable measurements, probably because of the silicate matrix of these samples, which, because of its low thermal conductivity and the resulting heat build-up, prevents the effective formation of negative ions. After preconcentration the counting rates found for these samples were about 5 times higher than those of the Canyon Diablo. The previously unmeasured isotopic ratios of the two Clearwater samples agree with those of Canyon Diablo, a result that strongly supports the extraterrestrial origin of the osmium in this melt layer.

The final set of samples come from the Ries crater in southern Germany. Although the formation of this crater is, in general, also attributed to the impact of a meteorite, a suite of samples from this crater investigated for traces of extraterrestrial material on the basis of element distributions displayed essentially crustal composition. At Rochester, two samples from this suite with known rhenium and osmium concentrations, together with two more samples from the Ries where concentrations were not known were measured.

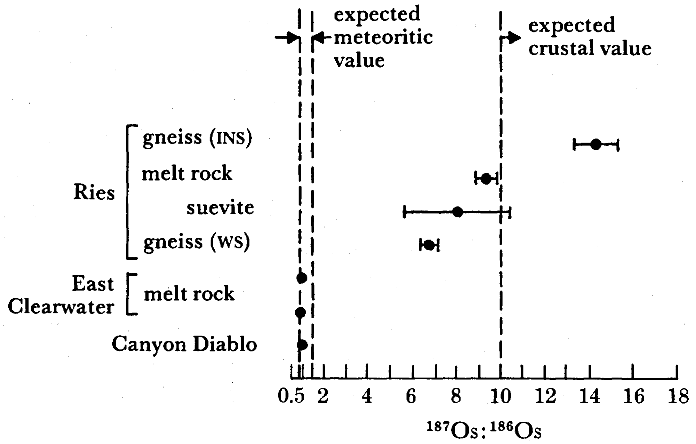

FIGURE 13. ^{187}Os:^{186}Os ratios measured for the Ries, East Clearwater and Canyon Diablo (Meteorite Crater, Arizona) craters.

The results are shown in figure 13. The agreement between Canyon Diablo and East Clearwater is heartening because both are generally believed to be meteoritic impact craters. The Ries samples have a distinctly different isotopic signature from that of the Canyon Diablo and the East Clearwater region. The ^{187}Os is significantly enriched in all of the Ries samples as compared to the meteoritic samples, demonstrating a predominantly crustal character. The isotopic ratios are, however, at the low end of the spectrum predicted for crustal values. Although there is a negative correlation between the concentration and the isotopic ratio that could be related to mixing between two osmium reservoirs, there are too few samples to draw any firm conclusions with regard to the presence of extraterrestrial material in Ries crater.

I acknowledge valuable discussions with N. J. Conard, D. Elmore, U. Fehn and R. Teng as well as contribution to the paper by H. W. Bentley, C. C. Langway, Jr and R. M. Phillips. The work was supported by grants from the National Science Foundation.

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Discussion

L. Brown. What level of reproducibility or accuracy does Professor Gove's group have for osmium if a standard is put in?

R. Teng (*University of Rochester, New York, U.S.A.*). We did seven measurements altogether, and they were all found to have an accuracy better than 5% for the ratios of the osmium isotopes.

M. Paul (*Hebrew University, Jerusalem, Israel*). Does Professor Gove's group have any numbers for the ^{129}I production in the atmosphere against the fission-produced ^{129}I?

U. Fehn (*University of Rochester, New York, U.S.A.*). We get about half of it from atmospheric production that flows into the ocean via vulcanism, and half of it from fission in uranium minerals.

W. Henning. What is the osmium isotope ratio for lunar material? The reason I am asking is because in Germany there have been speculations that some of the melt rock actually came from a splash from the Moon, and I am just wondering whether the osmium ratio is known.

U. Fehn. It has not been measured, but it is probably the same as for the mantle and meteorites.

G. Turner (*University of Sheffield, U.K.*). Does the extent of the osmium contamination, and the effect it has on the ratio, depend on whether the impacting body is an iron meteorite or a stone meteorite?

U. Fehn. The composition of stony and iron meteorites is the same, but the amount of osmium is different and the isotopic composition can then be used together with the concentration to find out which kind of meteorite, if any, was involved.

G. Turner. Is the concentration of osmium in a stone meteorite sufficient to give detectable contamination above the background osmium to demonstrate meteoritic material? It is sufficient with an iron meteorite, as I understand, because rhenium and osmium prefer to go into iron rather than stone, but I do not remember abundances.

U. Fehn. The abundances in iron meteorites are about 200 p.p.m. (by mass). In stony meteorites, abundances are in the high parts per billion range, i.e. about three orders of magnitude higher than in crustal material.

H. Margaritz (*Weitzmann Institute, Rehovot, Israel*). Does Dr Gove's group think that the possibility of dating groundwater by using ^{36}Cl is hampered by the production of ^{36}Cl in the aquifer itself, especially for a long period of time?

D. Elmore (*University of Rochester, New York, U.S.A.*). Yes; the ^{36}Cl is produced from neutrons from uranium in the Great Artesian Basin and it levelled off at about 2 Ma at about 6×10^{-15}, so we have a range of approximately 2 Ma that we can use.

W. Kutschera (*Argonne National Laboratory, Illinois, U.S.A.*). Professor Gove referred briefly in his talk to the Cretaceous–Tertiary boundary problem, and I know there were some measurements done at Rochester relating to heavy isotopes in that material. Are any more measurements planned?

H. E. Gove. We did make measurements in collaboration with the group at the University of Toronto. Platinum and iridium concentrations in the Cretaceous–Tertiary boundary layer from a Danish source were made, but we do not plan any further measurements at Rochester.