

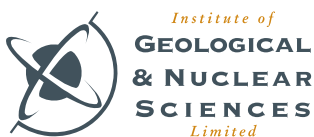
New Zealand Science Review

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Athol Rafter 1913–1996

Pioneer of carbon dating



Institute of
**GEOLOGICAL
& NUCLEAR
SCIENCES**
Limited

**Geochronological
techniques**



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A forum for the exchange of views on science and science policy.

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Cover photo: Athol Rafter at his office desk in Lower Hutt in the early 1970s when he was Director of the Institute of Nuclear Sciences in the Department of Scientific and Industrial Research.

Instructions to Authors

NZ Science Review provides a forum for the discussion of science policy. It covers science and technology in their broadest sense and their impacts on society and the environment, both favourable and adverse. It also covers science education, science planning, and freedom of information. It is aimed at all scientists and decision makers, and the interested public. Readability and absence of jargon are essential.

Manuscripts on the above topics are welcome, two copies of which should be sent to:

The Editor
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As well as full papers, short contributions, reports on new developments and conferences, and reviews of books, all in the general areas of interest of the journal, are invited. The journal also accepts reviews of a general nature and research reports.

Full manuscripts (with author's name removed) will be evaluated and authors will be sent copies of the reviewer's comments and a decision on publication. Manuscripts should not normally have appeared in print elsewhere but already published results discussed in the different, special context of the journal will be considered. They should preferably not exceed 2500 words.

To facilitate anonymous review, author's names on manuscripts and any acknowledgement of assistance should be on a detachable

cover page. Manuscripts should be accompanied by biographies of not more than 100 words on each author's personal history and current interests. Authors are also expected to supply a suitable passport-size photograph of themselves.

Manuscripts should be typed double-spaced with wide margins on one side of the page. Articles may be submitted in Word for PC, rich text format, or plain text, by e-mail, or on floppy disk or CD-R, but a hardcopy should also be sent so that fidelity may be confirmed. Diagrams and photographs should be on separate files (preferably eps, tif, jpg, all at 300 dpi), not embedded in the text.

All tables and illustrations should be numbered separately – Tables 1, 2, 3, 4, etc., and Figures 1, 2, 3, 4, etc. – and be referred to in the text. Footnotes should be eliminated as far as possible. Diagrams and photographs will be printed in black and white, so symbols should be readily distinguishable without colour, and hatching should be used rather than block shading.

References should preferably be cited by the author–date (Harvard) system as described in the Lincoln University Press *Write Edit Print: Style Manual for Aotearoa New Zealand* (1997), which is also used as the standard for other editorial conventions. This system entails citing each author's surname and the year of publication in the text and an alphabetical listing of all author's cited at the end. Alternative systems may be acceptable provided that they are used accurately and consistently.

As an earth science communicator within the public arena, one of the most common questions I am asked is this: 'How is the age of rock or a rock formation determined?' Most people have heard of radiocarbon dating and assume earth scientists use this method. In fact, the earth science world has been concerned primarily with questions and problems that relate to rocks and formations that are much much older than the range of the radiocarbon method. This method is only applicable to carbon-bearing materials that are less than 50 000 years old. Human prehistory, archaeology, cultural materials, and antiquities are of great fascination to us all, and it is through these lines of enquiry that radiocarbon dating has become prominent in the public mind.

This issue of *New Zealand Science Review* is all about dating, and specifically the dating of rocks and fluids currently undertaken in laboratories within the Institute of Geological and Nuclear Sciences (GNS).

GNS, earth science, and time

GNS is one of the nine New Zealand Crown Research Institutes and is based in Lower Hutt with two small subsidiary offices in Dunedin and Wairakei (near Taupo). It is one of the smaller CRIs and supports about 270 staff, of which about 150 are research scientists: mainly geologists, geophysicists, geochemists, palaeontologists and nuclear scientists. Within GNS there are three major research groupings: (1) hazards: earthquakes, volcanism, geothermal, landslides, tsunami; (2) resources: maps, minerals, rocks, fossils, fluids, energy, databases, and (3) isotopes: dating, tracing, nanotechnology, multi-beam analysis. Modern earth science is all about applied physics, applied chemistry, applied biology, and applied mathematics. Common to all earth science, and indeed almost all research effort at GNS, are three entities: rocks, fluids, and time.

In order to better understand the natural world we live in, we need to know how old things are, when did an event or process happen, what was the sequence of events involved, and how fast did it or they happen. The 'time' entity in an earth science context is all about dates, rates and determining the order or sequence of events and processes.

A celebration – of Rutherford and Rafter

There are two extremely worthy celebratory reasons for presenting this thematic issue of the *Review* at this point in time.

They relate to the extraordinary contribution of two New Zealanders to science and specifically to the determination and measurement of time using isotopic methods. As New Zealanders, we can all be immensely proud of the role that Ernest Rutherford and Athol Rafter have played in the history and philosophy of science.

Firstly, the 100th anniversary of a publication by Ernest Rutherford (1871–1937) and Frederick Soddy (1877–1956) in 1902 entitled: 'The cause and nature of radioactivity' (*Philosophical Magazine* 4: 370–396). In this paper, Rutherford & Soddy suggest the possibility of determining the age of crystalline minerals and hence rocks, using the common radioactive elements (potassium and uranium).

Secondly, the 50th anniversary of radiocarbon dating in New Zealand and the establishment of the Rafter Laboratory. This was begun in the mid-1950s by Athol Rafter (1913–1996) within the Institute of Nuclear Sciences, Department of Scientific and Industrial Research (INS, DSIR). The Rafter Laboratory can claim to be one of the oldest radiocarbon laboratories in the world and certainly the longest serving.

How does isotopic dating work?

Isotopes are atoms of an element with all the characteristics and properties of that element but different mass. All isotopes of a particular element have the same number of protons but different numbers of neutrons. Radiogenic elements such as uranium and potassium decay in a systematic way and at a known rate. Radioactive decay involves the loss of protons and neutrons, in the form of alpha-particles, or the conversion of a proton into a neutron (or vice versa). The isotopes produced by these processes are called daughter products. Dating of minerals involves the measurement of relative amounts of the parent element and the daughter isotope.

Measurement is done in a mass spectrometer. By analogy, this instrument is like a high-tech sheep race. Atoms (sheep) are led down a tube (race), and a powerful magnetic field (the gate) is used to separate out atoms of different mass (ewes from lambs), and the atoms are counted as they go out. Simple! From the count tallies and knowledge of the rate of production of daughter isotope, it is easy to calculate how long the radioactive decay process has been operating within that particular sample and hence how old it is.



Hamish Campbell is a Wellington-based earth scientist with the Institute of Geological and Nuclear Sciences (GNS). A New Zealander, he was educated at Otago, Auckland, and Cambridge Universities. He has been a professional research geologist since 1978. His specialist interests are concerned with the older Permian–Jurassic rocks and fossils of New Zealand, and the antiquity of endemism in New Zealand. Under a sponsorship arrangement between GNS and the Museum of New Zealand Te Papa Tongarewa, Dr Campbell is also resident geologist at Te Papa two days per week and has been since it opened in early 1998. Through his Te Papa work he has established a public profile as a science communicator. He is current Vice President of NZAS and may be contacted at h.campbell@gns.cri.nz

Minerals are ideal for dating because all minerals are crystalline and, as a general rule, all elements, including radiogenic elements and their daughter isotopes, are securely trapped and retained within the crystal structure. It is relatively easy to extract appropriate minerals from rock and then analyse them.

How old is the Earth – and the oldest rock in New Zealand?

We have come a long way from the calculations of the age of the Earth based on the Bible. For instance, in 1658 Vice Chancellor Lightfoot of Cambridge University pronounced that the Earth originated at 9:00 am on Friday 17 September in the year 4004BC. This was a refinement of an earlier calculation by Bishop Ussher in 1654.

Using standard radiogenic dating methods, the oldest rock materials in the Solar System are now dated at 4.53 billion years old (pers. comm. Carsten Münker, Münster University, Germany). It follows that this must also be how old the Earth is. The oldest rocks in New Zealand are considered to be of Middle Cambrian age, about 508 million years old. These rocks include fossil-bearing limestone and associated volcanic rocks in the Cobb Valley area of northwest Nelson. The oldest dated minerals (zircons) known from New Zealand are much older – in excess of three billion years old. These zircons represent sand grains within old sedimentary rocks, sandstone, of Ordovician age (490–443 million years) from near Greymouth, on the West Coast.

Contents of this issue

There are seven contributions in this thematic issue. They have been carefully chosen to exemplify some of the present range of dating methods that are available at GNS. They are not exhaustive, however, and do not embrace environmentally sensitive temperature-dependent stable isotope methods that are widely used as a proxy for determining age based on calibrated carbon, oxygen, and strontium curves for seawater through geological time. Nor does this thematic issue purport to represent all dating methods available in New Zealand. Palaeomagnetism is available at Otago and Victoria universities; thermoluminescence dating is available at Victoria University and stable isotope and carbon dating are available at Waikato University.

Five isotopic methods used at GNS are described herein in terms of topical research problems: (1) the dating of water and ice, using tritium, by Uwe Morgenstern; (2) the dating of lake sediments and their rate of accumulation, using lead–caesium, by Ian Graham, Bob Ditchburn, and Bernard Barry; (3) the dating and growth rate of submarine geothermal minerals associated with ‘black smoker’ chimneys, using uranium series, by Bob Ditchburn, Ian Graham, Bernard Barry, and Cornel de Ronde; (4) the dating of submarine manganese nodules and their rates of growth, using beryllium, by Ian Graham, Bob Ditchburn, and Albert Zondervan; and (5) the dating of surface exposure of exhumed rock surfaces, using beryllium, by Ian Graham and Albert Zondervan.

Some readers may be dismayed by overt expressions of enthusiasm and excitement of the research scientists herein who

are chasing submarine mineral resources. Please note, however, that GNS is not involved in mining per se, and is only interested in establishing the whereabouts and origins of potential resources. GNS completely endorses environmentally sustainable management of all mining operations.

The remaining two papers include a fascinating personal and historical insight into the development of radiocarbon dating in New Zealand, by Rodger Sparks; and a consideration of ‘relative dating’ of rocks using ‘the fossil record’, by Roger Cooper.

Diagrams for all time

Also presented in this issue are two diagrams that should prove popular amongst all who are interested in New Zealand geology. The first is a neat summary of the many different dating or geochronological methods that are available at GNS, or are used by GNS, showing the relevant age range for which they are applicable. Note that routine dating methods using potassium–argon, argon–argon, rubidium–strontium, uranium–lead and neodymium–samarium are not available in New Zealand. Accordingly, New Zealand earth scientists routinely use overseas laboratories, mainly in Australia and the USA, for these methods.

The second diagram is the New Zealand Geological Timescale. This is the most up-to-date presentation of established New Zealand and international subdivision of geological time calibrated in terms of absolute age (millions of years). This represents the culmination of a major FRST-funded project that will be formally published in the very near future, and it is with great pleasure that we are able to present this herein in advance. By far the quickest and cheapest way of determining age of sedimentary rocks is to use fossils, and the most common fossils, namely microfossils of single-celled planktonic animals and plants (foraminifera, radiolarians, nanofossils, and diatoms) and fossil palynomorphs (pollen, spores, and dinoflagellates), are especially useful. Macrofossils (graptolites, trilobites, brachiopods, molluscs) are just as useful and particularly so for older rocks of Palaeozoic and Mesozoic age.

Pure poetry

Lastly, we present a poem entitled ‘The Long Run’, from one of New Zealand’s foremost isotope geochemists, Peter Blattner. This is a tribute to Athol Rafter and a small reminder of the suppressed but ever present human and hence artistic quality of science.

Final thoughts

On behalf of Dr Alexander Malahoff (CEO, GNS) and all my colleagues at GNS, I trust you enjoy this thematic issue of *New Zealand Science Review*, with its insight into modern dating methods and applications that New Zealand-based scientists are using and researching here at GNS.

I put it to you that our ability to determine ages of crustal materials and processes over the past 100 years has completely revolutionised our perception of our natural environment, and with it, the significance and meaning of life itself. The earth sciences have played a huge role in effecting this change. Such is the power of dating!

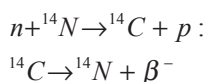
Radiocarbon dating – New Zealand beginnings

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It is possible that radiocarbon dating, sometimes known simply as carbon dating, is the scientific technique best known to the general public. Almost everyone knows ‘about’ carbon dating even if they have no idea of how it works. No doubt this is because it is concerned with basic questions that most people can relate to – ‘How old is this?’ or ‘When did that happen?’ But what may not be so well known is that, although carbon dating was invented in the United States by the chemist Willard Libby, New Zealand scientists played a significant part in its early development. Particularly Athol Rafter is internationally recognised as one of the pioneers of the technique, and his publications form part of the core of radiocarbon literature.

But what is carbon dating, really, and how did New Zealand get involved? Carbon dating is possible because carbon, the element on which all life on earth (and for all we know, the rest of the universe) is based, comes in the form of three isotopes, chemically identical atoms with different atomic weights. Two of these, ^{12}C and ^{13}C , are stable. The vast majority of the ^{12}C and ^{13}C atoms in our bodies and in the world around us have existed since before the solar system was formed, and possibly much longer than that. The third isotope, ^{14}C , is different. It is unstable and exists, on average, for just over 8000 years before it decays to the stable isotope of nitrogen, ^{14}N . The ^{14}C is constantly being replenished in the atmosphere by reactions caused by the impact of cosmic radiation: cosmic ray particles interact with atoms in the atmosphere to form, among other things, neutrons. The neutrons are slowed down by collision with surrounding atoms, and a slow neutron can be absorbed by a ^{14}N nucleus, resulting in the emission of a proton and leaving behind an atom of ^{14}C . The complete cycle can be written as follows:



Other reactions are possible, but this process is the dominant one. The ^{14}C is soon oxidised, first to carbon monoxide and then carbon dioxide, and some is eventually incorporated into the biosphere through photosynthesis. Since the cosmic ray flux is essentially constant (almost, but not exactly, true), an equilibrium has been established between formation and decay such that for every gram of carbon in organic material on the earth’s surface, 13.6 ^{14}C atoms decay every minute. Put another way, there is one ^{14}C atom for every 8.3×10^{11} stable carbon atoms in organic matter (e.g. us).



Rodger Sparks is the leader of the Rafter Radiocarbon Laboratory at the Institute of Geological and Nuclear Sciences (GNS), and has held this position for 14 years. Dr Sparks’ background is in experimental nuclear physics, and he helped establish the accelerator mass spectrometry (AMS) facility in the 1980s at what was later to become part of GNS. After heavy involvement with the technical aspects of AMS, his interests are now directed more to environmental radiocarbon and he is currently involved in studies on the movement of radiocarbon through the marine biosphere. Dr Sparks may be contacted at r.sparks@gns.cri.nz

In the period following World War II, Libby realised that radiocarbon could be used as a dating tool, acting as a kind of egg-timer to measure the time that had elapsed since an organism died and ceased ingesting carbon from its environment. By knowing the original amount of ^{14}C that was present when the organism was alive and the rate at which ^{14}C decays, a measurement of how much was still present would allow the elapsed time to be calculated. After some initial tests to confirm that the method would work, the technique was published in 1947 (Anderson et al. 1947). This was the first time that radiometric methods could be applied directly to archaeological problems, and its potential was immediately recognised.

New Zealand entered the picture soon after, when one day in 1950 Athol Rafter was asked by the Secretary of the DSIR to look into this new method of dating. The story is best told in Rafter’s own words (Rafter 1965):

...A few days later I was walking home quietly through the grounds of Parliament Buildings when coming in the opposite direction was the Head of our Department, a Mr Callaghan, who stopped me with the statement, “Rafter, I have just come from a meeting of geologists who tell me there is a method of dating by means of carbon that should be able to tell the age of our volcanic ash showers. Would you see if you could develop this method and stop the geologists arguing?” I said a confused goodnight and continued on my way home somewhat more puzzled than usual.

Libby’s original paper did not provide much useful information, so Rafter wrote to the man himself, who put him in touch with his colleague, Jim Arnold. With Arnold’s encouragement and advice, he set about building a radiocarbon counting system. The task had two broad components: preparing a sample to be dated by converting it into an appropriate physical form, and construction of a counting system to measure the very low level of radioactivity in the material. At first, Rafter and his team followed the approach taken by Libby. This involved converting the sample to solid carbon, in the form of lampblack, which was then coated in a thin film on the inside wall of a cylindrical Geiger counter. The counter was then connected to an electronic circuit that counted the electrical pulses resulting from the beta decay of the ^{14}C in the carbon. This method had a number of defects, including a lack of efficiency. The Geiger counter responded to the beta particles emitted into the gas that filled the counter volume. But if the carbon was

deposited on the walls, less than half the total emitted beta particles were available for counting, and the rest were directed uselessly into the walls. Another serious problem was contamination. Producing carbon involved reduction of carbon dioxide with magnesium, but finding a supply of magnesium that was not contaminated with radioactive impurities was a major difficulty.

But the worst feature was its fragility: the carbon was first mixed with water to form a slurry, which was then deposited on the counter wall by spinning it. The water evaporated, leaving a coating of carbon particles. But the carbon had little adhesion to the counter wall, and a slight shock could cause it to flake off and fall into a pile on the bottom. This was bad enough, but it was made worse by the fact that Rafter's laboratory, where the counter was prepared, was at the old Sydney Street site in Wellington, while the electronic counting system was at the DSIR laboratory in Gracefield. This meant that after the counter was prepared, Rafter and his assistant, Bill McCabe, had to make the 18 km road journey from Wellington to Gracefield, trying to protect it from the jolting caused by the Hutt road. Sometimes they succeeded, but more often they failed and arrived with a useless pile of soot in the counter chamber. It was after one of these frustrating journeys that, according to Bill McCabe, Rafter said, 'There has to be a better way to do this!'. This prompted them to look into making a counting system that incorporated the ^{14}C in the counter gas instead of a solid carbon lining.

Overseas, others had come to a similar conclusion. The favoured gas was methane, which seemed to give good results but required a difficult and rather dangerous procedure to make. Others had tried carbon dioxide, but it did not seem to work and gave erratic counting rates. Rafter decided to concentrate on a CO_2 counter, and was able to demonstrate that this gas gave excellent results provided it was meticulously purified. He achieved this success at about the same time that De Vries and Barendson announced a similar system in the USA. The CO_2 gas counters formed the heart of the DSIR (later, the Institute of Geological and Nuclear Sciences) radiocarbon facility until 1995, when they were finally phased out. Descriptions of how the solid and gas counting methods were developed are in Rafter (1953) and Rafter (1955a).

While Rafter and McCabe were working on the sample preparation methods at the Wellington laboratory, in Gracefield, Gordon Fergusson and Graham McCallum were designing the electronic systems to detect and count the ^{14}C decays. This was no trivial task. The amount of radioactivity they were trying to find was extremely low, and had to be distinguished from the background of natural activity in surrounding materials, including the materials the counting systems were made of, and background due to cosmic radiation (that, ironically, gave us the ^{14}C to start with).

Finally, a working system was put together, and in 1950 the first samples were measured. In 1953 the first list of dates obtained with the system was published in the *New Zealand Journal of Science* (Fergusson & Rafter 1953). Among those first published dates were two for charcoal taken from Taupo pumice. One of these, from near the Taupo-Rotorua road, showed an age of 1700 ± 150 years, the other, from the Desert Road, gave an age of 1800 ± 150 years. A third date, from a carbon-

ised log buried in Taupo pumice, gave 1850 ± 150 years. All were from contexts indicating that they were deposited during the last great Taupo eruption. At this stage, techniques to calibrate radiocarbon ages against tree-ring chronologies did not exist, so these results pointed to the Taupo eruption as taking place in about 170 AD. The current best estimate for the eruption places it near 230 AD (Sparks *et al.* 1995). In fact, if the mean of the three ages is calibrated with the modern calibration datasets, the eruption date falls in the range 56 AD – 434 AD with 95% confidence, with mid-point at 245 AD, so those first measurements were quite close to the mark, notwithstanding the (by modern standards) large uncertainties

Straight away, geologists and archaeologists wanted to use this new-fangled technique. Because ^{14}C has a half-life of 5700 years, carbon dating has limited applications in geology, where time scales are usually measured in millions of years. Nevertheless, there are many recent events for which it is suitable, such as fault movements, volcanic eruptions, or landslides, as well as sedimentation rates, all of which have played a role in forming the New Zealand landscape over the last few millennia. The Taupo event cited above is just one example. Archaeologists at last had a tool to unravel the chronology of human settlement in New Zealand, but Callaghan's wish to stop the arguments was (fortunately) not fulfilled.

Now that the method had been shown to work, attention shifted to the use of carbon dating as a scientific tool. Already by 1953 samples of wood, charcoal and shell were being sent to the DSIR laboratory for carbon dating. Rafter and Fergusson began investigating the ^{14}C levels in the environment, particularly in the atmosphere and surface ocean. This was of fundamental importance, since if carbon dating was to be reliable, the pathways by which the carbon got into the biosphere had to be properly understood. In 1954, samples of atmospheric CO_2 were being collected in trays of barium hydroxide exposed at Makara, near Wellington, primarily to check the observed degree of isotopic fractionation against the theoretical predictions of Harmon Craig in the United States. The first three of these measurements showed a significant upward trend from first to last that Rafter commented on in his 1955 paper on this work (Rafter 1955b). It was, in fact, the first observation of the increase in atmospheric ^{14}C due to the nuclear weapons testing programmes then in progress. The series of atmospheric measurements was continued, and in 1957 Rafter & Fergusson summarised the results to date in their paper on 'The atomic bomb effect' (Rafter & Fergusson 1957a). In the last paragraph of this paper the authors state:

If these ^{14}C increases in the main reservoirs of the carbon cycle can be adequately studied in both hemispheres, it would be possible to evaluate exchange constants across the stratospheric-tropospheric, tropospheric-surface ocean water, surface ocean water-deep ocean water, and inter-hemispheric interfaces. Such data would contribute to the study of meteorology and oceanography.

And so it proved to be. The observation of 'bomb carbon' and its implications were announced to the wider scientific community in a letter to *Science* (Rafter & Fergusson 1957b). It is probably safe to say that at that time no-one really anticipated how strongly the natural ^{14}C levels would be perturbed.

Figure 1 shows the behaviour of ^{14}C in the atmosphere from those first measurements to the present day.

From the 1950s onwards, carbon dating consolidated its position as a scientific tool in New Zealand and in the rest of the world. In 1965 Henry Polach left the DSIR to set up a radiocarbon laboratory at the Australian National University (rather to Rafter's chagrin, it must be said). In 1972 Lower Hutt hosted the 8th International Radiocarbon Conference; in 1974 a second radiocarbon laboratory was established in New Zealand, at Waikato University. That a country with New Zealand's population could support two world-class laboratories is a testament to the power and breadth of applicability of the technique, and currently the journal *Radiocarbon* lists over 170 laboratories worldwide.

Athol Rafter retired as Director of the DSIR Institute of Nuclear Sciences in 1978, but the laboratory he had established carried on. His departure coincided with a major change in the technique he had helped develop. If carbon dating was a revolution in determining chronologies, it underwent its own revolution in 1977 with the beginnings of accelerator mass spectrometry (AMS). Almost overnight the sensitivity of the technique, in terms of sample size needed to make a measurement, increased by a factor of over a thousand. Measurements could now be made with milligrams of material instead of many grams, and this has led to an explosion in the sorts of samples that can be analysed and in the sorts of problems that can be attacked.

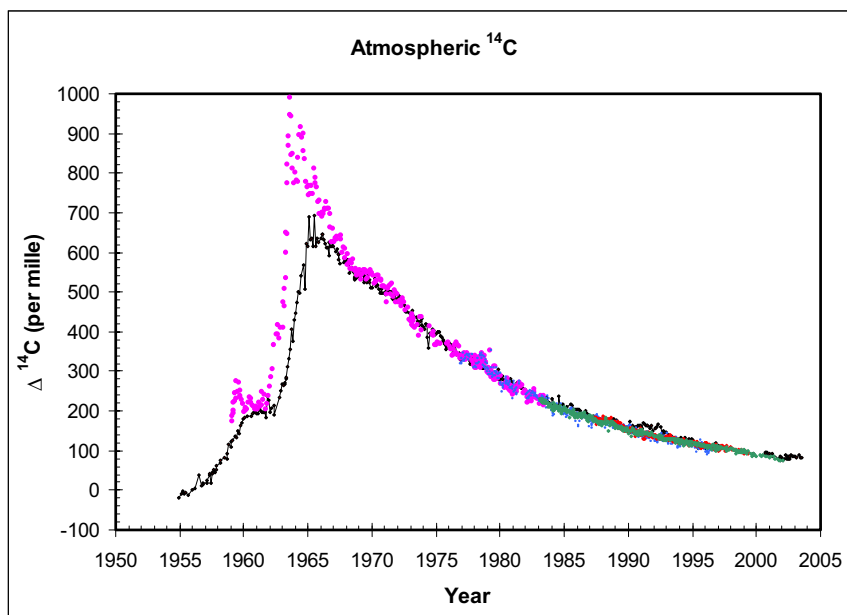
Fittingly, Graham McCallum, who had helped design and build the original counting system, was instrumental in arranging the purchase of a second-hand tandem Van de Graaff accelerator from the Australian National University, to bring the AMS technique to New Zealand. McCallum died in a mountaineering accident in 1981, but the accelerator he had worked so hard to obtain commenced work in 1986 as the first AMS facility in the Southern Hemisphere. In the years since, much has changed in New Zealand science. The DSIR has disappeared to be replaced by a number of independent Crown Research Institutes competing for funds in a commercial environment, and the demands on the scientific staff in those institutes

call for skills as much business as scientific. But the influence of the past can still be found. Rafter's radiocarbon laboratory now exists as the Rafter Radiocarbon Laboratory, part of the Institute of Geological and Nuclear Sciences, and it can trace its direct line of descent right back to that meeting in the grounds of Parliament Buildings in 1950.

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Figure 1. Trends of atmospheric ^{14}C since 1955. Continuous line is Wellington data, higher unconnected points are Northern Hemisphere. Data are expressed as parts per thousand above "normal" levels.



Tritium dating of water and ice

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The radioisotope tritium is a standard dating tool for groundwater. With its half-life of 12.3 years it can cover an age range from recent to 100 years. Tritium is naturally produced in the atmosphere by cosmic rays, but large amounts were additionally released into the atmosphere in the early 1960s due to nuclear bomb testing, giving rain and surface water a specific tritium concentration according to its recharge year (Fig. 1). When surface water infiltrates the ground, the water is separated from the atmospheric tritium source, and the tritium concentration decreases over time due to radiometric decay. The tritium concentration in the groundwater is therefore a function of the time (t) it has been separated from the atmosphere:

$$C_t = C_0 \cdot e^{-\lambda t}, \quad (\lambda = \ln 2 / T_{1/2}) \quad (1)$$

$$\text{and } t = \lambda \cdot \ln (C_0 / C_t) \quad (2)$$

where $T_{1/2}$ is the half-life of tritium, C_0 the initial tritium ratio, and C_t the tritium ratio in the sample at time t .

Most early applications involved tracing the global bomb tritium through the hydrological cycle. However, since the mid-1980s, atmospheric tritium has declined almost to the natural (cosmogenic) level in most parts of the world. This now allows tritium to be used for dating groundwaters more straightforwardly as a 'natural clock', using the decay equation (1, 2).

Sufficient sensitivity and accuracy for detection of tritium are necessary to make use of low-level natural tritium as a tracer for the hydrologic cycle. Because of the low tritium concentrations prevailing in the Southern Hemisphere, a tritium measurement system with extremely high detection sensitivity was established at the Institute of Nuclear Sciences, DSIR, in 1960. The current system at GNS uses Ultra Low-level Liquid Scintillation Spectrometry with 70-fold electrolytic tritium enrichment prior to detection. Reproducibility of standard enrichment is 2%, and accuracy of 1% can be achieved via deuterium calibrated enrichment (Taylor 1994). The tritium record of rain from Kaitoke (Fig. 1) is the longest, most complete, and most accurate record of the Southern Hemisphere. It is therefore used as the master record for the Southern Hemisphere.

Two examples will demonstrate recent achievements in tritium dating.

Stream water dating and future nutrient load to Lake Taupo

Lake Taupo in the central North Island of New Zealand is a national icon with its high water quality. However, this is declining due to increasing nutrient load (nitrogen). Large areas in the catchment were developed into pastoral agriculture 35 to 45 years ago (Vant & Smith 2002). Nitrogen concentrations in streams draining pasture have slowly risen since the 1970s, and are still increasing, despite little change in the intensity of farming since then. This delay between pasture development and the associated nitrogen increase in streams and groundwater draining the catchment suggests that water residence times in the aquifer are several decades.

To enable informed management of the lake, it is important to measure how long it takes for nutrient-enriched groundwater to travel from pastoral land to streams, and to the lake. This will allow prediction of future nitrogen mass loading to Lake Taupo, when all the old pristine groundwater has been displaced by N-bearing water. Nutrients from intensified land uses enter the lake predominantly from groundwater and groundwater-fed streams. Thus we started measuring the age of streamwater to determine the proportion of post-1965 water (the water that could be affected by the land use change).

The northern and western parts of the Lake Taupo catchment, with the largest impact of land-use, are large uniform areas of rhyolitic volcanics with similar hydrological characteristics. The northern part has relatively thick Taupo Ignimbrites overlying Rhyolite Pyroclastics. The western part has Whakamaru Group ignimbrites covered by thinner deposits of Oruanui and Taupo Ignimbrite.

Tritium from nuclear weapons testing in the early 1960s resulted in a peak-shaped tritium input to the whole hydrologic system on earth. Detecting how bomb tritium moves through the hydrologic system is the ideal way to study age distribution in groundwater systems. Tritium is the 'ideal tracer' because it is part of the water molecule (tritium is a hydrogen isotope), and it is inert to chemical alterations in the aquifer and therefore a conservative tracer for the study of groundwater flow.



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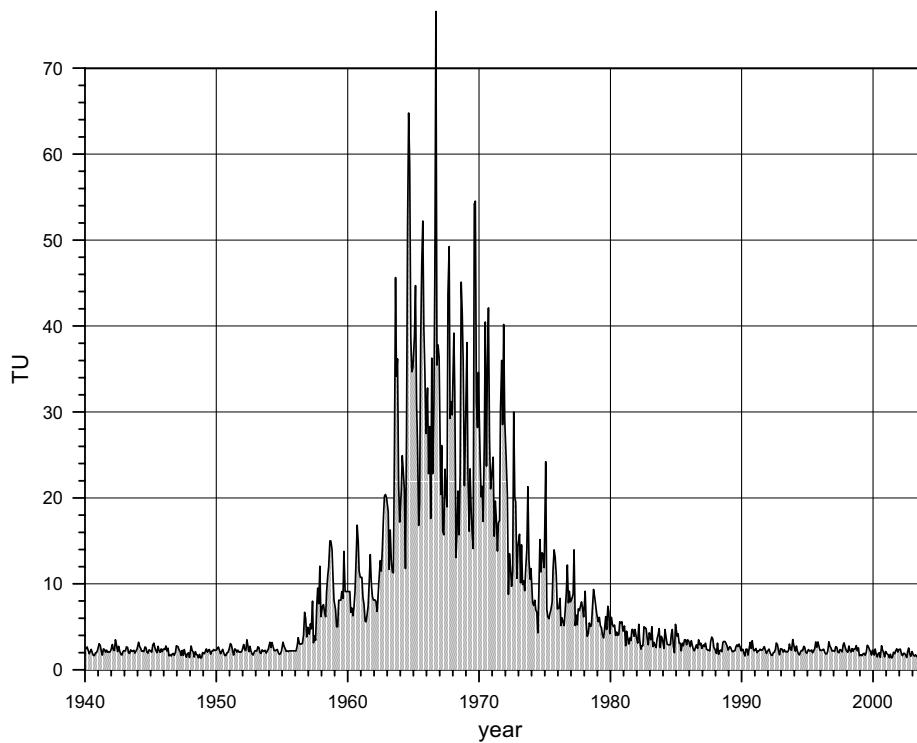


Figure 1. Tritium in rain from Kaitoke, 40 km North of Wellington. One TU is equal to a T/H ratio 10^{-18} . Tritium has been measured since July 1960 in rain samples from Kaitoke, collected monthly. Tritium data between 1955 and 1960 are deduced from tritium data of the Hutt River (Kaitoke is in the catchment of the Hutt River), of Wairakei rain, and of South Pole snow pits. Pre-bomb tritium data before 1955 are reproduced from the post-bomb period 1991–2002 according to solar cycles.

The exponential piston flow model (Maloszewski & Zuber 1982) was used to describe the groundwater flow situation for most of the streams. This model produces very good matches to the passage of bomb tritium through various New Zealand aquifers, and therefore describes sufficiently well the real flow situation. The model parameters were obtained by matching the model output to the measured tritium data. The fraction of water that had been recharged after land-use intensification began could then be calculated by integrating the age spectrum over the specified time range. The current contaminant levels in streams are still a result of dilution with old pristine water, and the contaminant concentration that will be reached in the future at steady state (when all water fractions have been affected by land-use change) was obtained by scaling the current contaminant concentrations to 100% of N-bearing water.

Exponential piston flow models with 40–60% exponential flow within the total flow were identified from matches to tritium data for the northern and western streams. The northern streams had pre-bomb tritium levels that gave unambiguous mean residence times (MRT) of 60–80 years (e.g. Mapara stream, Fig. 2). The western streams were mostly in the ambiguous tritium range and have ages between 35 and 60 years. Ambiguity could be resolved with hydrogeologic information. The older ages of the northern compared to the western streams can be explained by the overlying Taupo pumice, which has an extremely high porosity (80–90%) so that even thin layers can have an extremely high water storage capacity.

One stream (Kuratau) has a complicated hydrogeologic situation because it is at the boundary between andesitic and the rhyolitic volcanics. Hydrogeologic information was not sufficient to estimate the fraction between the two different aquifer systems. However, matching long-term tritium data enabled us to deduce the parameters of the age distribution (Fig. 2). The high tritium ratios in the early 1960s clearly show the contribution of very young water from the andesite. Two parallel models, 61% EM and 39% EPM, match the measured data extremely well. The young water of the EM (MRT = 1 year) represents the contribution from the andesite, and the old water of the EPM (MRT = 30 year) represents the contribution from the rhyolitic volcanics, with low and high water storage capacity, respectively.

An alternative model with MRT of 44 years (dotted line in Fig. 2) matches the recently measured Kuratau Stream tritium data, but conflicts strongly with the observed quick response to the bomb tritium. This clearly demonstrates the danger of wrong age interpretation if no means are available to distinguish between the different possible age solutions.

These results show that only 25–95% of the water fractions were recharged after land-use intensification in the 1960s. We predict that, when all fractions of the water reaching Lake Taupo have been recharged after land-use intensification, nitrogen loading of the lake from northern and western streams will increase by 20–40%.

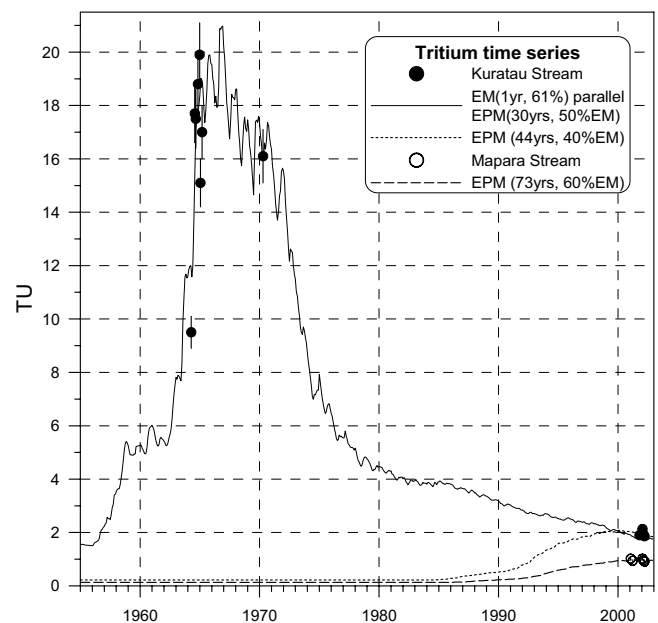


Figure 2. Model fit to time series of tritium data.

Dating of glacier ice in Mount Cook National Park

Tritium can also be used for glacier ice dating. We have dated the ice in the lower part of Tasman, Fox, and Franz Josef glaciers in this way to determine the age range of the ice contained in the glacier, and hence the maximum length of a climate record which could be derived from a deep ice core.

Ice samples from the surface of the glacier between the equilibrium line and the terminus cover the approximate time range of the glacier ice. We measured tritium in the ice to identify the position of the tritium bomb peak to accurately date the ice.

The ice at the terminus of Franz Josef and Fox Glaciers on the West Coast is 40 and 50 years, respectively. However, the Tasman Glacier on the east side of the Southern Alps contains older ice. At the end of the white ice, we measured an age of 90 years (Fig. 3). Though the oldest ice at the terminus is not accessible on the surface as it is covered by rock debris, the ice thickness at the end of the white ice is still several hundred metres, suggesting a total ice record of several hundred years.

The bomb tritium from the nuclear weapons testing period in the 1960s is well preserved in the Tasman Glacier ice, suggesting little or no inter-annual exchange processes during ice formation. The specific seasonal bomb tritium peaks allow for accurate ice dating back to 50 years with age resolution of several months. To calibrate annual layer dating farther back in time we use the natural pre-bomb tritium, and ^{32}Si (half-life 140 years).

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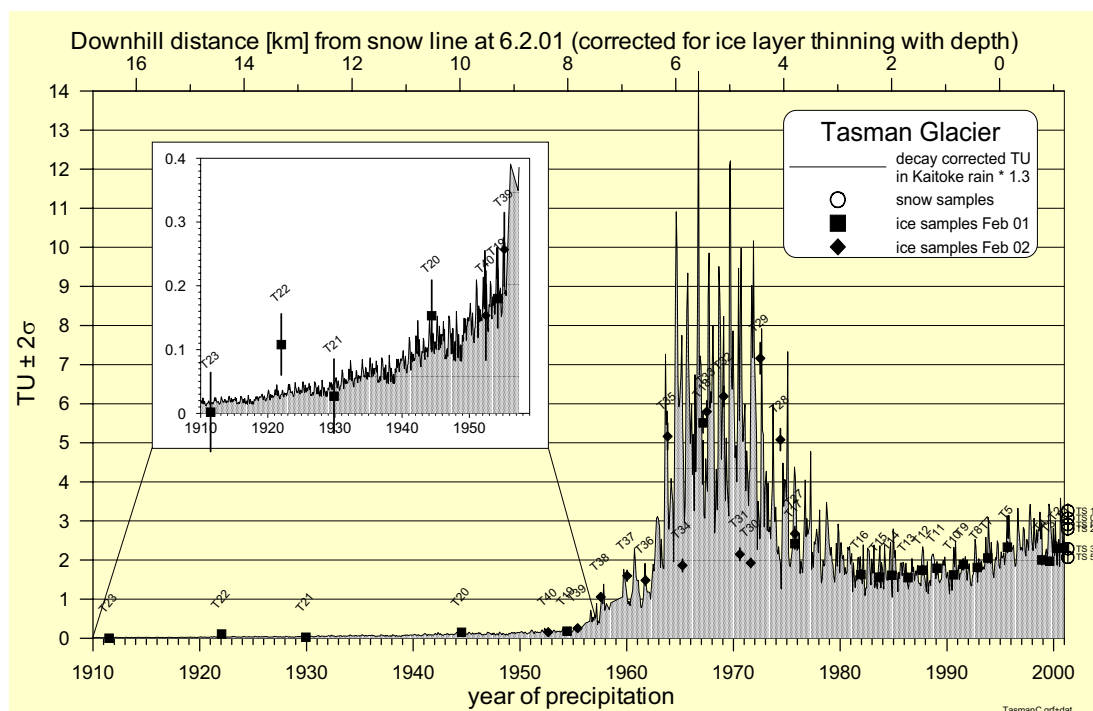


Figure 3. Tritium in surface ice from the ablation zone of Tasman Glacier, and the atmospheric tritium input function. All tritium data are decay-corrected to the date of first sampling (Feb. 2001). The data of the sampling campaign in Feb. 2002 are position-corrected for the ice flow (250 meters per year). Note the good agreement where data overlap from the two sampling campaigns. The downhill distance is corrected for ice layer thinning.

^{210}Pb – ^{137}Cs dating of glacial lake sediments

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Sediments deposited in New Zealand lakes in the recent past (see Fig. 1) provide excellent archives of local climate change via their trapped biodiversity, varve structure and sedimentological composition. To unlock the archived information, accurate and fine-scale dating of the deposits is essential. A combination of ^{210}Pb and ^{137}Cs dating provides the most reliable and robust approach. Under favorable conditions, ^{210}Pb dating can provide a detailed chronology to c. 120–140 y, and can be accurately calibrated by ^{137}Cs for the last 40 y or thereabouts.

^{210}Pb dating

Total ^{210}Pb activity in sediment comprises two different components, termed ‘supported’ and ‘unsupported’. The ‘unsupported’ component is continuously produced by radioactive decay of atmospheric ^{222}Rn (half life = 3.8 d) and is transported in rain to the Earth’s surface, where it becomes adsorbed onto silicate particles. Lake sediments which have been continuously deposited and have subsequently remained undisturbed should exhibit unsupported ^{210}Pb profiles which decrease systematically with depth due to radioactive decay (^{210}Pb half life = 22.3 y). Such decay profiles relate directly to sedimentation rates, assuming that the flux of ^{210}Pb from the atmosphere is constant (Appleby & Oldfield 1978). Unsupported ^{210}Pb values are obtained from the total measured ^{210}Pb by deducting a background of supported ^{210}Pb , the latter being generated in the sediment matrix from its grandparent ^{226}Ra via its short-lived daughter

^{222}Rn . A proportion of the supported ^{210}Pb is extracted during leaching of the sediment, and combined with the unsupported ^{210}Pb component. Assuming no diffusive loss of ^{222}Rn , the supported ^{210}Pb will be in equilibrium with ^{226}Ra throughout the sediment profile and, if the 6M HCl leaching is consistent, should be a constant value which can be deducted as a background from all samples.

For North Island volcanic lake sediments, Whitehead et al. (1998) derived sedimentation rates consistent with dated volcanic ash layers (e.g. Tarawera 1886). In these sedimentary systems, they suggested that the unsupported ^{210}Pb was entirely derived from rain, an assertion based on positive correlations between rainfall and unsupported ^{210}Pb activities, and zero activities at rainfall of less than 500 mm y^{-1} . Since rainfall over many decades for these inland lakes varies only by $\pm 20\%$ (Tomlinson & Sansom 1974), then the rate of supply of ^{210}Pb to the sediment must be also relatively constant. However, exclusive deposition from rain is not true for South Island glacial lakes that are fed from large complex catchments (Fig. 1). In 1965, when fallout from atmospheric nuclear bomb testing was at its maximum, the unsupported $^{137}\text{Cs}/^{210}\text{Pb}$ ratio in rain (c. 3.0) was much higher than that in Lake Tekapo sediment (c. 0.4), indicating that up to 85% of the unsupported ^{210}Pb represented deposition from previous years.

^{210}Pb activities in New Zealand sediments are unusually low, 5–10% of global continental sites (c. 50 v. 750 Bq kg^{-1} ; Benoit & Hemond 1991). This is because ^{222}Rn concentrations in New



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Robert Ditchburn joined the Institute of Nuclear Sciences (now part of GNS) in 1964 where he has developed chemical and radiochemical methods for uranium series dating of carbonates and for measuring lake sedimentation rates with ^{137}Cs and ^{210}Pb . He has set up uranium series procedures for alpha spectrometry at Florida State University (1984) and for thermal ionization mass spectrometry at the University of Queensland (1994). In recent years, he has refined the chemistry for ^{32}Si dating of groundwater and sediment, and for extracting ^{10}Be from water, sediment and ferromanganese deposits, and has produced models for dating Antarctic soils with ^{10}Be and hydrothermal deposits using ^{210}Pb and ^{226}Ra .



Bernard Barry is in the IsoScan Team at the Institute of Geological and Nuclear Sciences (GNS), Rafter Laboratory in Lower Hutt. There he has been using radioactivity counting systems and radio-isotopes for geological and industrial applications and for tracing work. As well he works with the proton microprobe on the 3MV van de Graaf accelerator to measure trace elements in both geological and biological samples.

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Figure 1. Head of Lake Tekapo showing extensive braided channels and associated levees supplying sediment to the lake floor. (Photo: Rayward Film Services, May 2003)

Zealand air are very low due to emissions from the sea being at least an order of magnitude less per unit area than those from land. New Zealand is an oceanic island with strong airflows; hence the ^{210}Pb fallout is also very low even though rainfall is relatively high. Supported ^{210}Pb concentrations in New Zealand sediments are low (40% of the global mean of $177 \text{ Bq m}^{-2} \text{ y}^{-1}$; Appleby & Oldfield 1978), which reflects a deficit of ^{226}Ra in New Zealand rocks and soils. However, the contrast between unsupported and supported ^{210}Pb is still relatively low, making ^{210}Pb dating rather more difficult here than elsewhere. Dating glacial lake sediments, in which a high proportion of the unsupported ^{210}Pb is derived from the catchment reservoir, is particularly problematical.

^{137}Cs dating

The radionuclide ^{137}Cs is anthropogenic, having been produced during atmospheric nuclear testing. The ^{137}Cs dating method depends on identifying variations in the concentration of the radionuclide through time. The concentration peak for ^{137}Cs in New Zealand rain occurred in 1965 (Fig. 2), just after the main period of atmospheric nuclear weapons testing. After correction for decay, a rain-like ^{137}Cs profile might be found in a sediment profile of appropriate age, allowing accurate identification of the initiation of testing (c. 1953) and the 1965 peak. In sediment dominated systems, however, the sediment profile departs from the 'rainfall' peak shape soon after 1953 due to reservoir effects in sediment catchments.

Age determination

Ideally, the total ^{210}Pb profile in a lacustrine sediment should decrease smoothly to a constant value at depth, which can be taken to be the supported ^{210}Pb background (this is best determined by weighted least squares regression analysis, using χ^2 as an assessment of fit). If the ^{210}Pb deposition rate (i.e. unsupported ^{210}Pb flux and sedimentation rate) is constant, a log-

¹ There is no evidence from National Radiation Laboratory data that it could be related to a recent drop in ^{210}Pb flux.

linear correlation of the unsupported ^{210}Pb should occur with respect to depth or cumulative weight of sediment (the latter taking care of any sediment compaction that might have taken place). Least squares regression can then be used to determine the slope of the decay curve, from which sedimentation rates can be calculated. Provided the sediment is aerobic, there should be no loss of ^{210}Pb through *in situ* leaching or diffusion. The first appearance of ^{137}Cs should indicate accurately where 1953 occurs in the profile (Fig. 2), providing a check on the ^{210}Pb -derived ages. In rain-dominated systems, the peak ^{137}Cs concentration at 1965 provides an additional calibration check.

Application of $^{210}\text{Pb} - ^{137}\text{Cs}$ dating to New Zealand lake sediments has been only partially successful (Whitehead et al. 1998). For most North Island volcanic lakes, e.g. Lake Taupo, the ^{210}Pb profiles are near-ideal, yielding single sedimentation rates backed up by ^{137}Cs . For most of the South Island glacial lakes, in contrast, the ^{210}Pb profiles show considerable scatter, making interpretation difficult (Fig. 3).

One feature of many ^{210}Pb profiles is a significant drop in activity near the sediment surface (Fig. 3). The most popular explanation for this is that it represents loss of ^{222}Rn from the sediment matrix (i.e. from the supported component) through diffusion.¹ However, the magnitude of the reductions (up to 85%) and the fact that it occurs only in 1 in 3 cases in New Zealand (Whitehead et al. 1998) rather suggests that it is related to delayed consolidation and isotopic equilibration of the top sediment layers prior to burial. If this is so, then the top point(s) of such profiles should be excluded from the ^{210}Pb age calculations. The scatter inherent in the remainder of each pro-

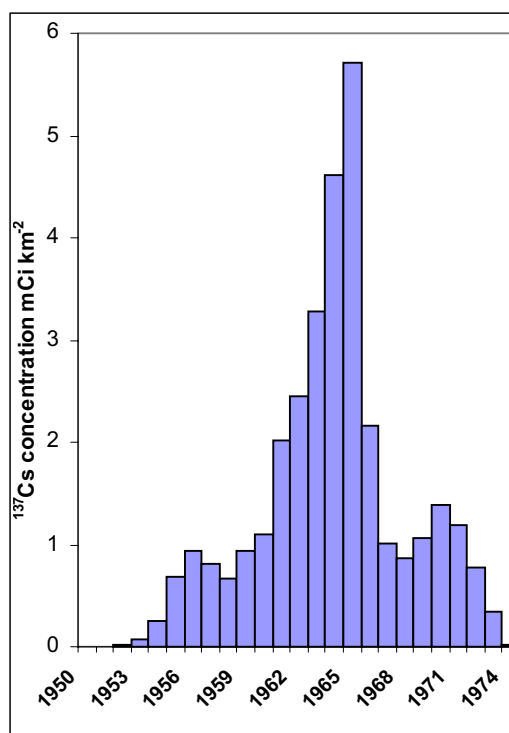


Figure 2. Distribution of ^{137}Cs in New Zealand rain, decay-corrected to 1974 (data sourced from observations at GNS, Lower Hutt, and UKAEA; Ditchburn & McCabe 1977).

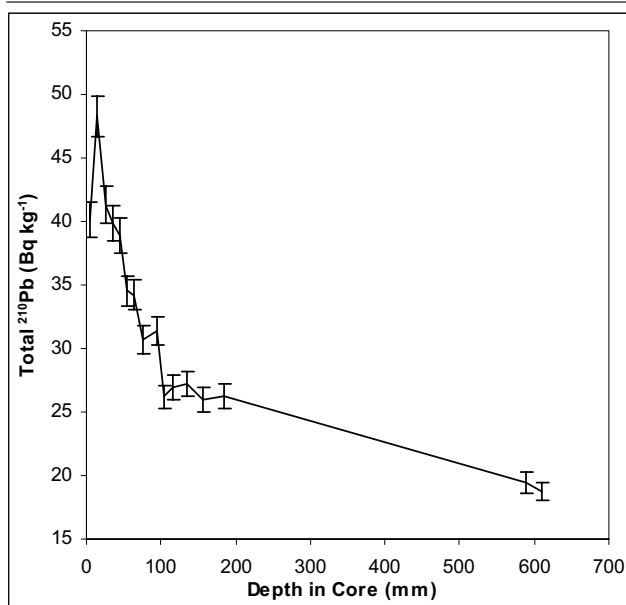


Figure 3. Total ^{210}Pb v. depth for Lake Tekapo sediment core L1401 (modified from Whitehead et al. 1998).

file makes estimation of the supported background component particularly difficult. The usual approach is to determine the total ^{210}Pb concentration at a depth in the core that represents sediment older than c. 134 y (i.e. 6 half-lives of ^{210}Pb). Minimum 'plateau' values are sought, sufficiently close to the main data sets that a constant supported ^{210}Pb value can be assumed for the sediment above. For the Lake Tekapo data set depicted in Fig. 3, a true plateau has not yet been found. If it is assumed that the supported ^{210}Pb background is equal to the mean of the lowest two total ^{210}Pb values, then a mean sedimentation rate of 3.5 mm y^{-1} is derived which is significantly slower than that predicted from the first appearance of ^{137}Cs (c. 5.5 mm y^{-1}). The ^{210}Pb - and ^{137}Cs -derived sedimentation rates agree, however, if a lower supported ^{210}Pb value, slightly less than the lowest values measured, is assumed.

The ^{137}Cs data, as discussed previously, become increasingly dominated by reservoir effects, showing a strong departure from the rain curve towards the cumulative rain curve by the mid 1960s (Fig. 4). The data profiles are also, like their ^{210}Pb counterparts, affected by variable sediment composition which relate to variations in the effective 'age' of the source sediment. Nevertheless, the first appearance of ^{137}Cs provides an unequivocal chronological tie point from which a reliable sedimentation rate can be deduced.²

The scatter in total ^{210}Pb (Fig. 3), while not proving fatal in the pursuit of age information in glacial lake sediments, results in poor precision and therefore uncertainty with regards the constancy or otherwise of the derived sedimentation rate. The fundamental cause of the scatter is variation in the composition of the sediment, which results in variation in the amount of leachable material as well as the radiogenic content of the leached sample. The varve structure of these type of sedimentary systems comprises light and dark layers which relate to variations in the relative amounts of key rock-forming minerals (principally quartz, feldspar, chlorite, muscovite), resulting from cyclical changes in the sedimentary regime (i.e. low rain-

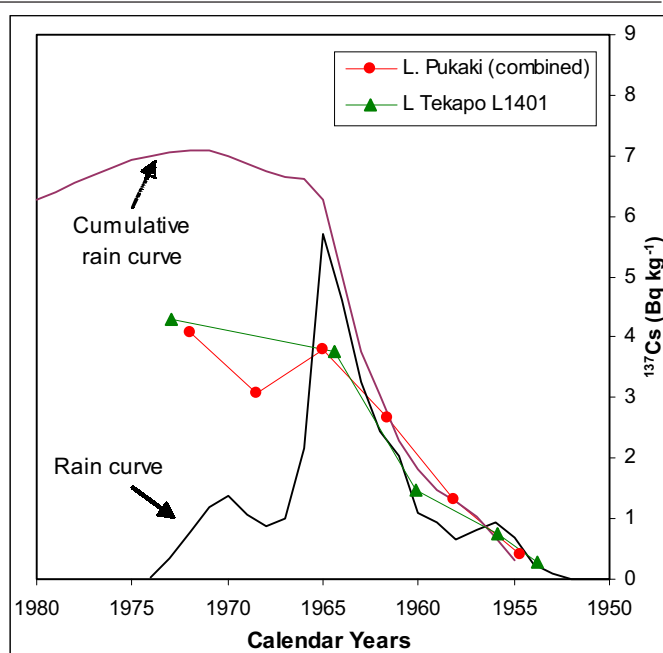


Figure 4. ^{137}Cs vs. age for combined Lake Pukaki cores (Ditchburn & McCabe, 1977) and Lake Tekapo sediment core L1401 (re-analysed after Whitehead et al. 1998). The data are compared with the standard ^{137}Cs in rain curve (Fig. 2) and a derived cumulative ^{137}Cs in rain curve. The ^{137}Cs data are scaled to match the rain curves, and are positioned relative to the rain curves by assigning appropriate sedimentation rates.

fall, dry spells with a high loess component, v. normal lake inflow v. occasional high rainfall, flood events). Broadly, the dark layers with less quartz and more chlorite are likely to have higher supported ^{210}Pb and a higher capacity for adsorbing unsupported ^{210}Pb . Spot sampling of one or more varve pairs, as is traditionally employed, will therefore produce compositional variations with a significant impact on the ^{210}Pb profile. One way of resolving this difficulty, is to sample a continuous suite of 'boxed' varves (say, 15–20 per sample), so smoothing out any cyclic or event-related compositional variations.

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² Assuming that diffusion of ^{137}Cs through the sediment profile is negligible (Comans et al. 1989).

Fossils and timescales

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Introduction

Fossils, the preserved organic and biogenic mineral remains of plants and animals, are the memory banks of life on Earth. Think of stratified sedimentary rocks as the pages of the book of Earth history, and fossils as the words. In the last few hundred years, humanity has mastered the art of unlocking a chronology for the last 550 million years of Earth history based on the succession of life as recorded by fossils. This is best exemplified by the names of the successive major geological time subdivisions: Paleozoic meaning ancient life; Mesozoic or middle life, and Cenozoic, modern life. More recently, with the advent of isotope science, we have also determined how to unravel complex environmental history of the oceans and the atmosphere from fossils.

In this article, we briefly explain how fossils are used in building timescales and dating rocks. This has been a major preoccupation of generations of palaeontologists at GNS and its predecessor, the New Zealand Geological Survey. Even now, fossils are still by far the easiest and quickest way to determine age and major environmental signatures of sedimentary rock. GNS maintains substantial palaeontological expertise and prides itself in housing the largest palaeontology skill and database in the Southern Hemisphere, and home to the National Palaeontology Collection. Lastly, we present the hot-off-the-press 2004 New Zealand Geological Timescale.

The beginning of a geological timescale

Robert Hooke (1635–1703) is credited with being the first person to suggest the possible use of fossils in establishing a chronology of rocks. William Smith (1769–1839) was the first to do so (see biography in Winchester 2002).

Smith began collecting fossils from successive rock formations that he had observed in his travels across England as an engineer and surveyor. He realised that each rock layer or stratum could be recognised by the fossils found in it, and furthermore, the same succession of strata could be observed wherever the rocks concerned were found. His first published geological work (1815) embraced this concept of a chronology of strata based on fossils (biostratigraphy)—it was a large map of England and Wales with an accompanying explanatory text. This was the world's earliest large-scale geological map of any extensive area or country. Over the next few years, Smith produced fuller accounts of his discoveries, particularly in his 'Strata Identified by Organised Fossils' (1816) and his 'Stratigraphical System of Organised Fossils' (1817). In so doing, he established stratigraphy and palaeontology as sciences in their own right, within the broader discipline of geology.

Note that the term 'geology' was first used as a proper term by J.A. De Luc in 1778 in his 'Lettres Physiques et Morales sur les Montagnes et sur l'Histoire de la Terre'. Prior to this it was commonly referred to as 'undergroundology'! The term 'palaeontology' was put forward independently in 1834 by Ducrotay de Blainville and Fischer von Waldheim. Until this point, the study of fossils was referred to as 'oryctology' or 'Petrefactenkunde'.

Biozonation and biocorrelation

Fossils are used in two main ways for building timescales and dating rocks. First, the evolutionary succession of species is used to build a succession of unique stratigraphic units – **biozonation**. The widely used geological timescale is a succession of stratigraphic units (e.g. Jurassic) that are defined by

(continued on page 49)



Roger Cooper retired as Chief Palaeontologist at the Institute of Geological and Nuclear Sciences (GNS) in 2002. Since then he has been contracted to complete the Geological Timescale Project at GNS. A New Zealander, Dr Cooper trained at Victoria University and commenced his career with the NZ Geological Survey (DSIR) in 1964, initially as a mapping geologist and then as a palaeontologist. His special interests relate to NZ's oldest sedimentary rocks of Early Palaeozoic age, and in particular Ordovician graptolite and trilobite successions. Laterly he has become a leading authority on quantitative stratigraphy. He is a Fellow of the RSNZ and counts as one of NZ's most distinguished earth scientists. Dr Cooper may be contacted at r.cooper@gns.cri.nz

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New Zealand Geological Timescale

This centrefold is copied at reduced size from 'New Zealand Geological Timescale 2004/2 wallchart' with permission of the Institute of Geological & Nuclear Sciences.

The correct reference is that given on the wallchart, namely:

Cooper, R.A. (Compiler) 2004. New Zealand Geological Timescale 2004/2 wallchart. *Institute of Geological & Nuclear Sciences information series 64.*

Copies of the wallchart may be obtained from the Publications Officer, Institute of Geological & Nuclear Sciences, PO Box 30-368, Lower Hutt, New Zealand.

fossils present within them, and subsequently calibrated in millions of years. Biozones are the fine subdivisions of these stratal units.

It is worth remembering that a detailed stratigraphic subdivision of geological time using fossils was achieved long before we were able to accurately date the divisions in millions of years. Calibration of the geological timescale divisions by methods such as radiometric dating is the field of geochronology and geochronometrists.

The second way in which fossils are used is **biocorrelation**, that is the correlation in geological time of events or rocks around the world. Biocorrelation of New Zealand strata with well-dated stratal sequences elsewhere and, in particular, with the Global Geochronological Scale, is the main method for calibrating the stages of the Early Cretaceous and older periods in New Zealand. Bioevents, such as the highest and lowest stratigraphic occurrences of species that are geographically widespread and found in a range of sedimentary facies, are those most useful for correlation. The more closely spaced the events are in time, and the more commonly they are encountered in stratigraphic sections, the more rigorously their invariance in stratigraphic order (homotaxy) can be tested.

Some of the most useful fossil groups for correlation are those that occupy the marine pelagic realm, in other words, marine organisms that live within the water mass and are widespread as a consequence of floating or swimming. They are global in distribution and are not constrained by sedimentary facies. In the Cenozoic, the most reliable groups are marine zooplankton such as planktic foraminifera and radiolarians, and phytoplankton such as coccolithophores, diatoms, and dinoflagellates. In the Paleozoic and Mesozoic, ammonoids, conodonts, and radiolarians enable fine biostratigraphic resolution and global correlation, as do the Paleozoic graptolites. Ammonites and graptolites are particularly useful, as many of their species have very short stratigraphic ranges. The presence of a single species in a sample sometimes is sufficient to correlate it with a single ammonite or graptolite zone.

The Geomagnetic Polarity Timescale (GPTS; see the New Zealand Geological Timescale diagram, page 50), is a well established global record of normal polarity (in black), and reverse polarity (when the N and S poles flip; in white), as preserved in iron-bearing magnetic minerals within rocks. Bioevents that are 'tied' to the GPTS, such as planktic microfossil events in deep-sea drill cores, are valuable for calibration. For example, the highest regional occurrence of *Globoquadrina dehiscens* is used for defining the base of the upper Tongaporutuan Stage and is a good correlation datum within southern middle latitudes.

Reversal in coiling direction in the trochospiral test of planktic foraminiferal lineages, such as in *Globoconella miotumida*—the "Kaiti Coiling Zone" (Scott 1995)—are particularly useful for correlation, and this event is used for the base of the Tongaporutuan Stage. Coiling reversals are likely to be related to regional and widespread environmental change in surrounding oceans.

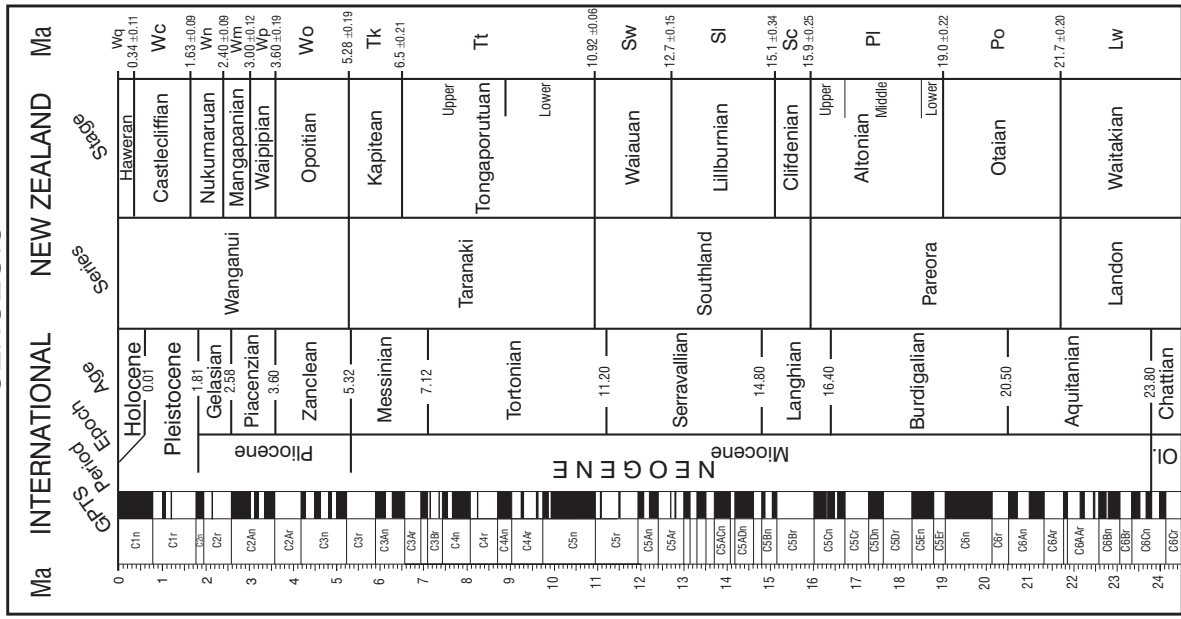
Progressive evolutionary transitions in a lineage are also extremely useful, and quantitative population studies of the lineage in dispersed areas can provide precise data for correlation. A New Zealand example is change in the foraminiferal *Orbulina* bioseries, from *Praeorbulina glomerosa circularis* to *Orbulina suturalis* (used to define the base of the Lillburnian Stage). Similarly, the four graptolite zones in the Castlemainian Stage (Ordovician) are defined on successive subspecies in the *Isograptus victoriae* bioseries (*lunatus*, *victoriae*, *maximus*, *maximodivergens*). Quantitative population analyses enable precise international correlation of this time interval (Cooper 1973; Williams & Stevens 1988). Subspecies of the lineage have been found in China, Siberia, Scandinavia, Spitsbergen, Newfoundland, Texas, Nevada, Alaska, and Argentina, as well as in New Zealand and Australia.

Precision in biocorrelation is greatly aided by quantitative analyses of fossil populations. In addition, regional changes of physical, chemical, and biotic parameters in the oceanic envi-

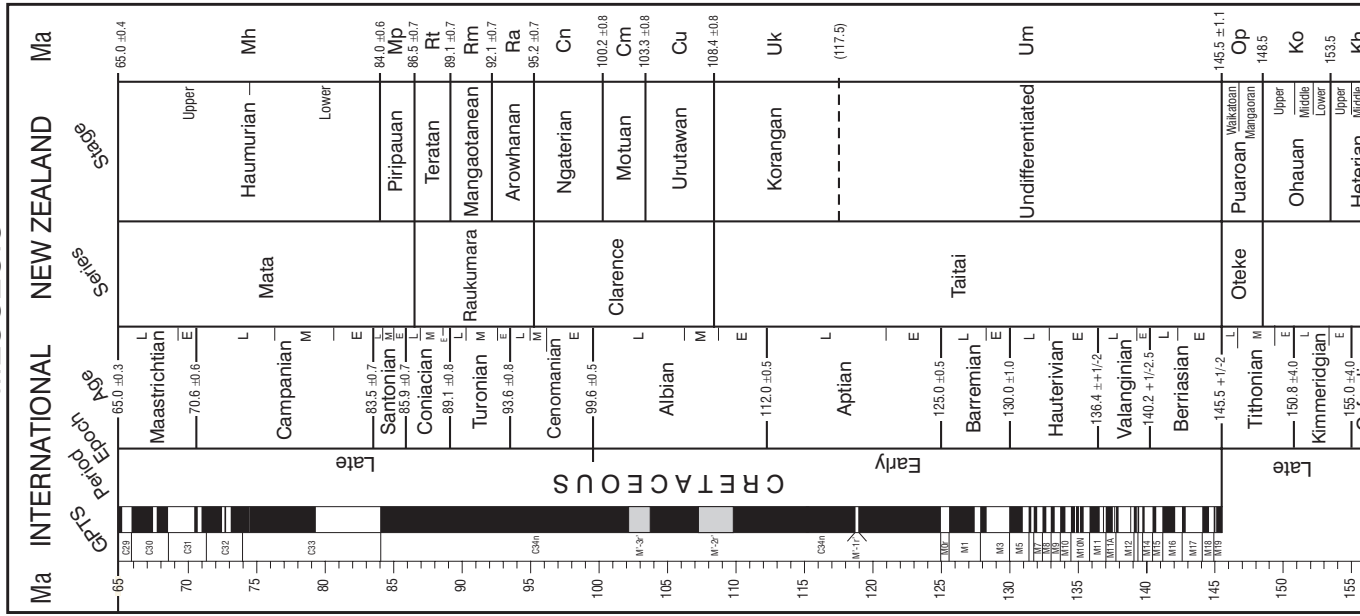
(continued on page 52)

NEW ZEALAND GEOLOGICAL TIMESCALE 2004/2 WALLCHART

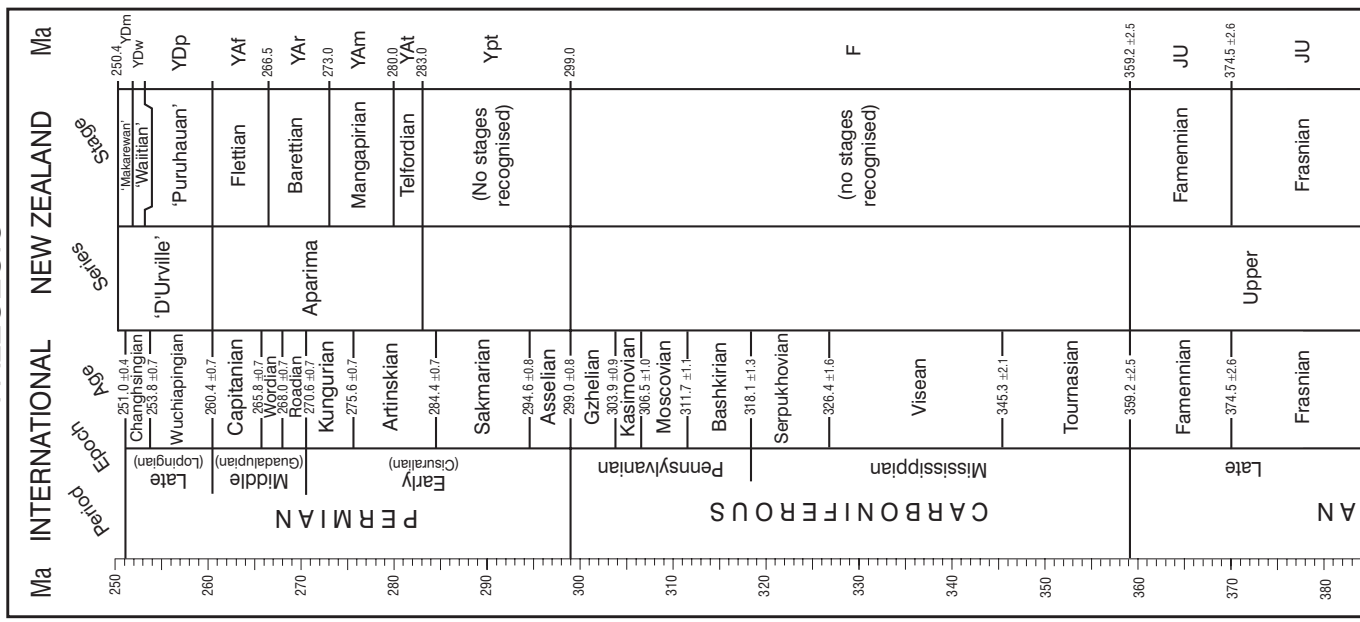
CENOZOIC

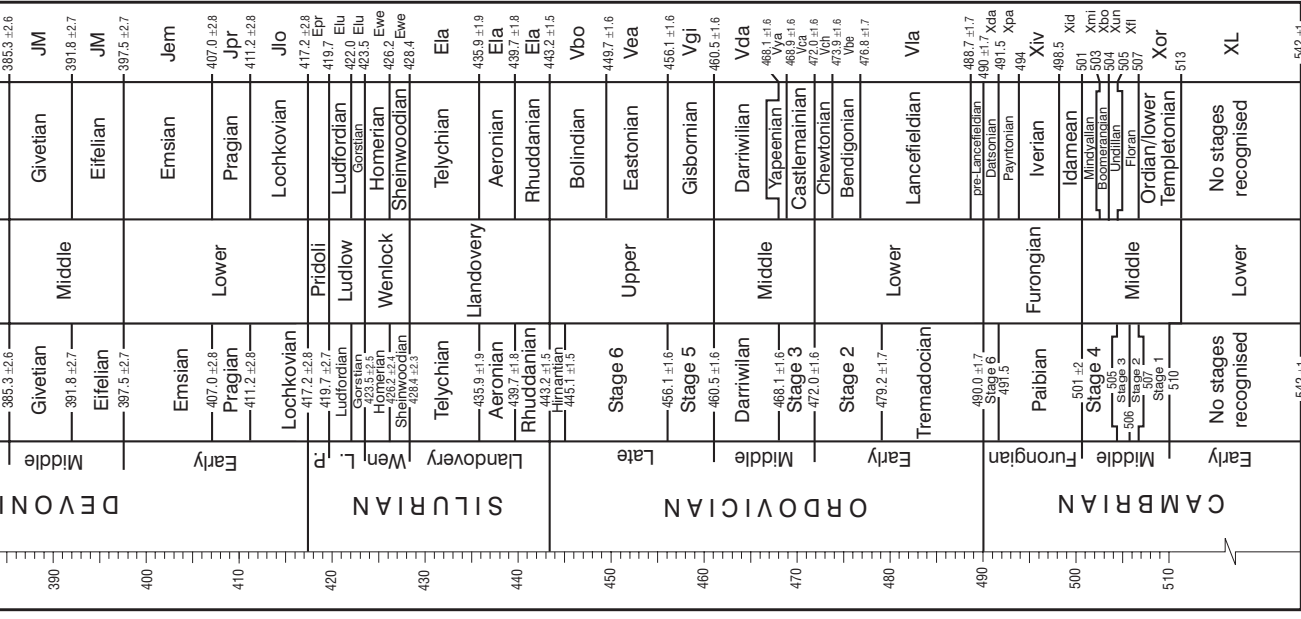
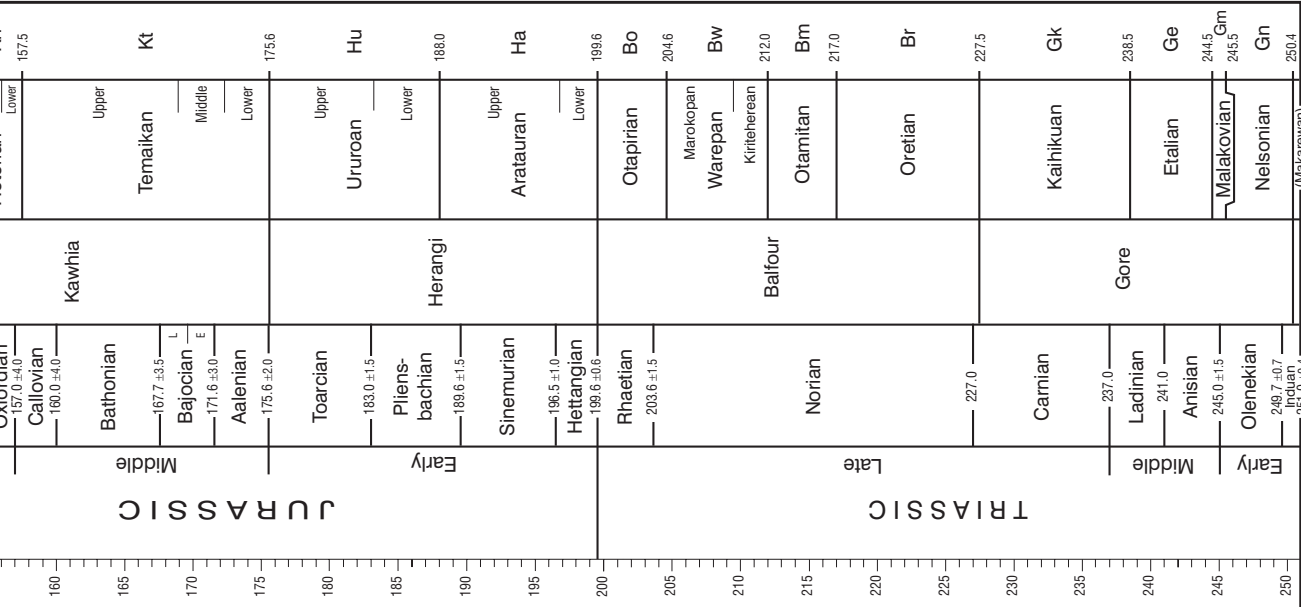
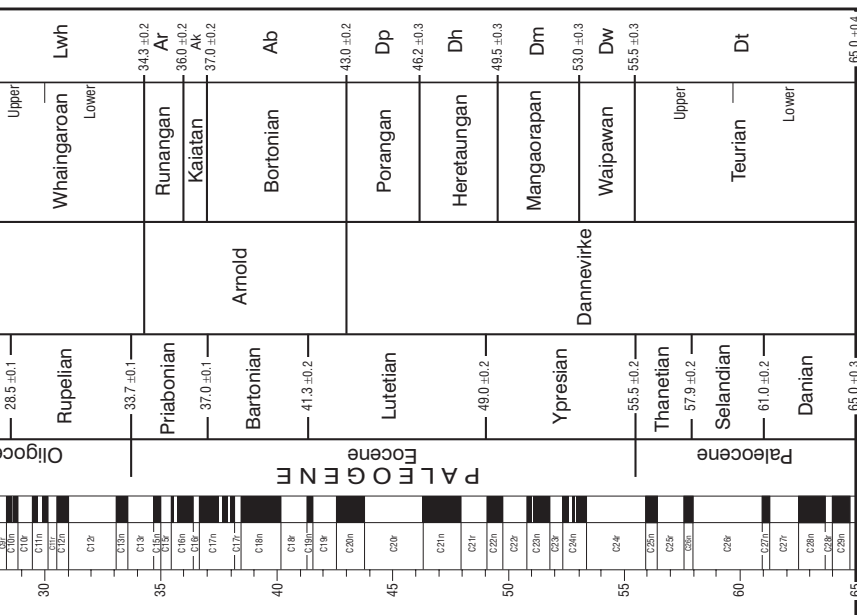


MESOZOIC



PALEOZOIC





NEW ZEALAND GEOLOGICAL TIMESCALE 2004/2 WALLCHART

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R.A. Cooper (Compiler), 2004.
 International divisions are those of the Global Geochronological Scale 2004 (Gradstein et al. 2004a, b). Ages of unit boundaries are from Cande & Kent (1995), Berggren et al. (1995), Gradstein et al. (2004a, b), Sadler & Cooper (2004, unpublished); other sources are quoted in Cooper (ed. 2004). Error ranges on boundary ages are from Gradstein et al. (2004a, b). Note that error ranges on Neogene stage boundaries are all less than 0.1 m.y. The Geomagnetic Polarity Time Scale (GPTS) is from Cande & Kent for Cenozoic and Gradstein et al. (2004a) for Cretaceous.
 New Zealand divisions, ages of unit boundaries and error ranges on ages are from Cooper (ed. 2004). "The New Zealand Geological Timescale", *Institute of Geological and Nuclear Sciences monograph 22* who gives a full description of the stratigraphic basis for the New Zealand scale and its calibration.

RECOMMENDED BIBLIOGRAPHIC REFERENCE
 Cooper, R.A. (Compiler), 2004. *New Zealand Geological Timescale 2004/2 wallchart. Institute of Geological & Nuclear Sciences information series 64.*

ronment can be detected by changes in the relative proportions of foraminiferal species abundance and diversity. These 'biologs' can be used for correlation, with good precision, throughout a basin or region.

Quantitative and semi-quantitative techniques, such as unitary associations (Savary & Geux 1999), graphic correlation (Shaw 1964), ranking and scaling (RASC) and correlation and standard-error calculation (CASC) programmes (Gradstein et al. 1985), and constrained optimisation (Sadler 2001), can provide highly precise correlations useful for timescale calibration. The new Global Geochronological Scale, to be published by Cambridge University Press this year, uses a constrained optimisation of graptolite successions from around the world (including New Zealand) to build a precise subdivision and calibration of Ordovician and Silurian time (some 70 million years).

These same techniques have been employed and utilised in construction of the New Zealand Geological Timescale (see page 50).

Origin of geological timescale terms

The jargon used in geological timescales can be bewildering to the uninitiated. Firstly, it is important to understand that there is such a thing as a Global Geochronological Scale. This has been established and refined over the years by a long-term, long-standing highly collaborative international science body known as the International Commission on Stratigraphy. Secondly, individual countries have historically established national geological timescales. Accordingly, there is a New Zealand timescale that is considered to be a regional timescale with a set of terms that have been satisfactorily developed for subdivision of strata that are peculiar to New Zealand.

The origins of the terms used in the subdivision of geological time are fascinating. Giovanni Arduino (1713–1795) subdivided all stratified rocks into three groups: Primary, Secondary and Tertiary. Only 'Tertiary' is still in common usage as a term. The terms Palaeozoic, Mesozoic, and Cenozoic were introduced by John Phillips in 1841. The race to establish and name the main geological time subdivisions, the periods and epochs, was an exciting phase in geology and took almost 60 years to accomplish, from 1822 to 1879.

First to be introduced, in 1822, were the terms Carboniferous, named by Conybeare for coal-bearing rocks, and Cretaceous by d'Halloy in Belgium for chalky rocks. Then the Jurassic was named in 1829 by Brongniart after the Jura Mountains in France. Charles Lyell named the Pliocene, Miocene, and Eocene in 1833, based on degrees of similarity of molluscan fossils in the Paris Basin with present day faunas; the older the faunas, the more different they are. Friedrich von Alberti named the Triassic in 1834 after three distinctive formations in Germany, and the Cambrian was named in 1835 by Adam Sedgwick after an ancient tribe in Wales. 1839 was a bumper year, with naming of: the Silurian by Roderick Murchison, after another Welsh tribe; the Devonian by Sedgwick and Murchison, after distinctive strata in Devon; and the Pleistocene by Lyell. The Permian was named by Murchison in 1841 after the Perm Basin to the west of the Urals in Russia. Neogene and Paleogene were introduced by Hoernes in 1853; Oligocene by Beyrich and Quaternary by Morlot in 1854; Palaeocene in 1874 by

Schimper, and finally Ordovician in 1879 by Lapworth, after yet another ancient Welsh tribe.

These names are now well established in our everyday language and are likely to remain fixed in the calendar of geological time, in the same way that more familiar time terms such as the days of the week and the months of the year are fixed.

Finer subdivisions of geological time such as 'ages, series, and stages' have had an equally chequered history of naming, recognition, introduction, and definition. Such terms are derived from many countries. For the Triassic, for instance, the age names are largely derived from places located in Italy and Austria within the European Alps (Anisian, Ladinian, Carnian, Norian, Rhaetian). For the Permian, the Wuchiapingian and Changhsingian are based on successions in China.

In New Zealand, series and stage names have been adopted largely from topographic place names associated with the best examples of the fossiliferous sedimentary rock successions in question. Hence, for instance, the Triassic stages are largely named from the Wairaki Hills, the Hokonui Hills, and Kaihiku Ranges in Southland: Malakovian after Malakoff Hill, Etalian after Etal Stream, Kaihikuan – Kaihiku Stream, Oretian – Oreti River, Otamitan – Otamita Stream, Warepan after Warepa, and Otapirian after Otapiri Stream.

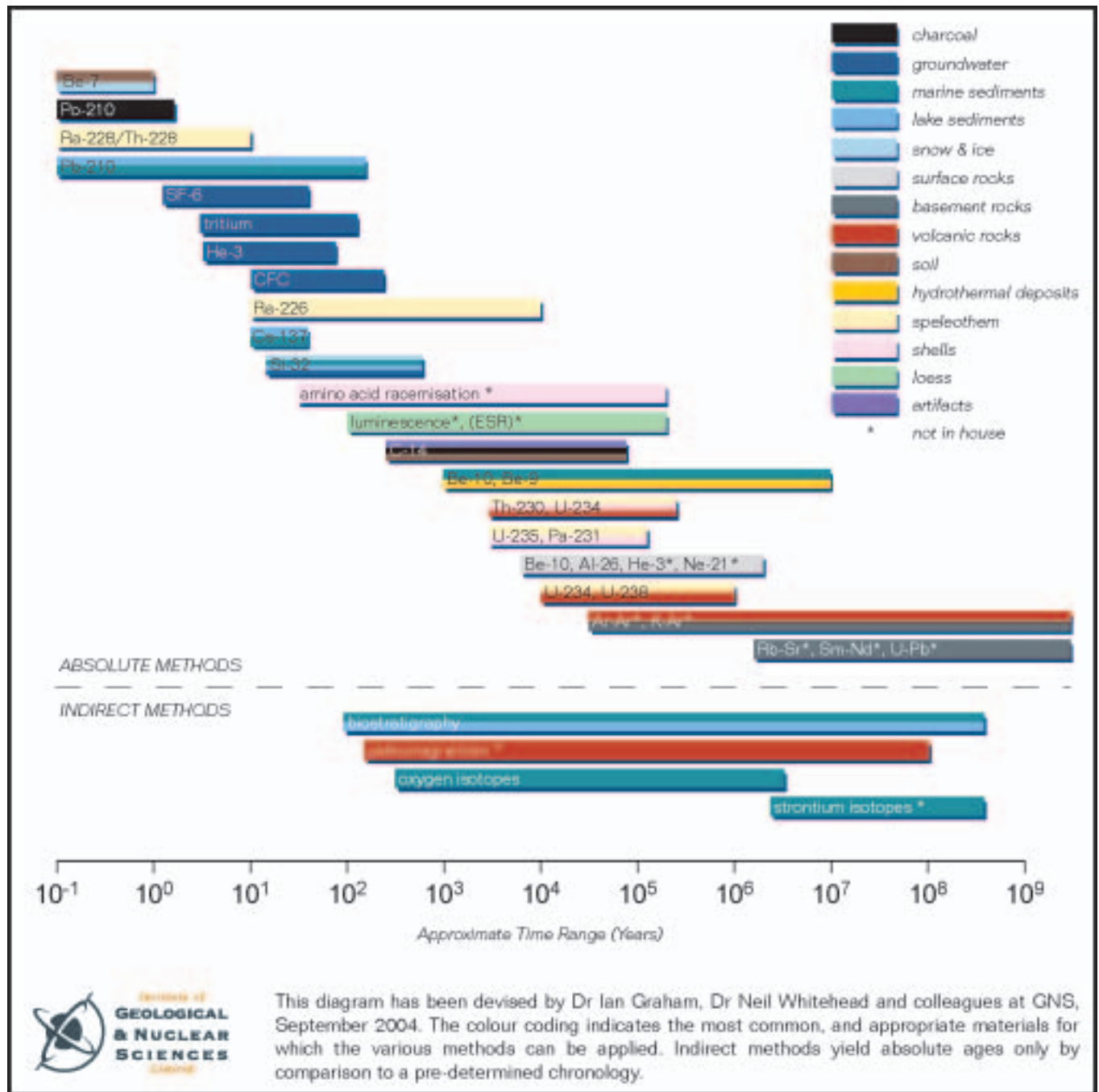
The New Zealand Geological Timescale

The New Zealand Geological Timescale 2004, presented herein, is the most accurate and most precise interpretation of calibrated geological time that has ever been produced for New Zealand. Furthermore, it is ground-breaking because all time boundaries (for periods, epochs, ages, and stages) are expressed in terms of an absolute time value complete with mathematically established error. This is the first time that this level of quantitative rigour has been brought to bear in the calibration of geological time for New Zealand sedimentary rock successions.

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Geochronological methods available or applied at the Institute of Geological & Nuclear Sciences Limited



Uranium series disequilibrium dating of black smoker chimneys

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Within New Zealand's Exclusive Economic Zone there exists a vast submarine hydrothermal mineral resource associated with the Kermadec Ridge, an active intra-oceanic arc (Fig. 1). Along this ridge twenty six submarine volcanoes have been explored by GNS-lead researchers, and at least another nine await investigation. Of these, fifteen are known to be hydrothermally active, and each is almost certainly a site of active seafloor mineralisation. Determination of whether this mineralisation is economically viable in terms of grade and tonnage requires detailed seafloor exploration using manned submersibles and/or remotely operated vehicles (ROVs) capable of high-precision imagery and discrete rock and fluid sampling. A key aspect of these investigations is determining the age of the mineralisation, which will have a direct bearing on its mode of formation, time elapsed to amass an economic deposit and, ultimately, its capacity for sustainable extraction.

An intact barite-rich "black-smoker" chimney (Fig. 2) recovered from Brothers volcano (Fig. 1), along with other hydrothermal deposits provide evidence of active mineralisation

along the arc. The age range of such massive sulphide deposits can be determined from the disequilibrium between isotopes within the thorium or uranium decay chains (Ivanovich & Harmon, 1992) (Table 1).

The black-smoker depicted in Fig. 2 contained about 10 ppm uranium but negligible ingrown ^{230}Th , which indicates the deposit is very young (< c. 5000 years). Radiometric dating is possible via the ^{238}U to ^{210}Pb decay scheme. Black-smoker chimneys are produced by sub-seafloor hydrothermal reactions that extract barium and lead but not thorium from rock. Barium, which is chemically very similar to radium, is used as a proxy for radium concentration, which cannot be measured because no stable isotope of radium exists. The ^{230}Th , ^{226}Ra and ^{210}Pb within the rock are assumed to have been in secular equilibrium, i.e. their radio-activities were equal to each other prior to extraction. (There is no loss of ^{222}Rn gas from barite). However, barium is extracted twice as efficiently as lead, and barium and lead (including ^{210}Pb) are deposited in variable proportions within the rapidly forming chimney. Thus the ^{210}Pb will not be



Robert Ditchburn joined the Institute of Nuclear Sciences (now part of GNS) in 1964 where he has developed chemical and radiochemical methods for uranium series dating of carbonates and for measuring lake sedimentation rates with ^{137}Cs and ^{210}Pb . He has set up uranium series procedures for alpha spectrometry at Florida State University (1984) and for thermal ionization mass spectrometry at the University of Queensland (1994). In recent years, he has refined the chemistry for ^{32}Si dating of groundwater and sediment, and for extracting ^{10}Be from water, sediment and ferromanganese deposits, and has produced models for dating Antarctic soil with ^{10}Be and hydrothermal deposits using ^{210}Pb and ^{226}Ra .

Ian Graham is a Wellington-based Principal Scientist with the Institute of Geological & Nuclear Sciences (GNS). Originating from Oamaru in North Otago, he completed his undergraduate studies at Otago University in 1979 (BSc(Hons) and MMinTech). Since obtaining his PhD at Victoria University in 1985, he has pursued wide-ranging research projects in isotope geology and geochronology, specialising in applications of strontium and beryllium isotopes. As manager of the PGST programme at GNS on Mineral Wealth of New Zealand and its EEZ, Dr Graham is currently interested in the genesis of gold-bearing massive sulphide deposits in active subduction zones, and the origin and age of ferromanganese deposits.



Bernard Barry is in the IsoScan Team at the Institute of Geological and Nuclear Sciences (GNS), Rafter Laboratory in Lower Hutt. There he has been using radioactivity counting systems and radioisotopes for geological and industrial applications and for tracing work. As well he works with the proton microprobe on the 3MV van de Graaf accelerator to measure trace elements in both geological and biological samples.

Cornel de Ronde is a Principal Scientist at the Institute of Geological and Nuclear Sciences (GNS). He gained his undergraduate and Master's degrees at the University of Auckland, and a PhD from the University of Toronto. The next seven years saw him fill post-doctoral positions at the University of Cape Town, the Geological Survey of Japan, and Otago University, after which he joined GNS. Dr de Ronde's research has included studying a variety of hydrothermal ore deposits, Archean tectonics, evidence for early life on Earth, and crustal fluids in general. His current research focus is submarine hydrothermal vents associated with arc volcanoes offshore New Zealand and in the Western Pacific region.



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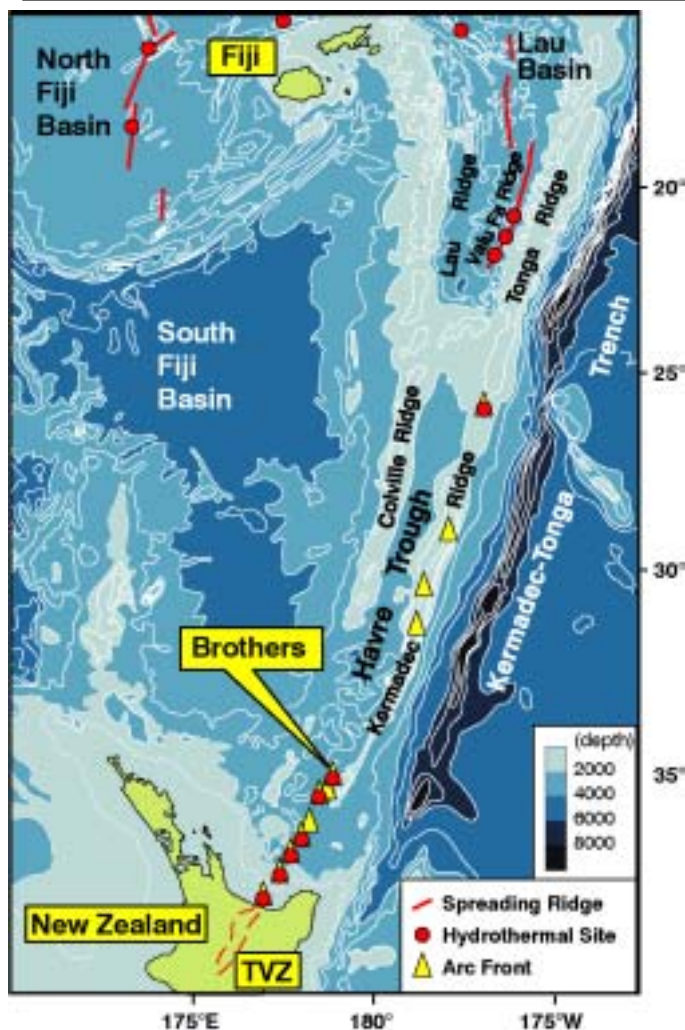


Figure 1. The Kermadec Arc, NE of New Zealand.

Table 1. Abbreviated decay schemes for parent isotopes ^{238}U and ^{232}Th .

Isotope	Half-life	Isotope	Half-life
^{238}U	4.49×10^9 years	^{232}Th	1.405×10^{10} years
	↓		↓
^{234}U	2.48×10^5 years	^{228}Ra	5.75 years
	↓		↓
^{230}Th	7.7×10^4 years	^{228}Ac	6.13 hours
	↓		↓
^{226}Ra	1600 years	^{228}Th	1.913 years
	↓		↓
^{222}Rn	3.824 days	^{224}Ra	3.64 days
	↓		↓
^{214}Pb	26.8 minutes	^{220}Rn	55.3 seconds
	↓		↓
^{214}Bi	19.8 minutes	^{212}Pb	10.6 hours
	↓		↓
^{210}Pb	22.3 years	^{208}Tl	3.07 minutes

in equilibrium with ^{226}Ra for c. 140 years and, by scaling the ^{226}Ra and ^{210}Pb activities¹ for constant lead concentration and plotting a ^{210}Pb - ^{226}Ra isochron, the chimney age can be calcu-

¹ The ^{210}Pb is measured by beta counting ^{210}Bi in precipitated PbCrO_4 . Direct measurement of the weak ^{210}Pb gamma is less reliable due to difficulty in correcting for absorption within the sample matrix.



Figure 2. Black smoker chimney containing metalliferous sulphides dated by the $^{210}\text{Pb}/^{226}\text{Ra}$ method. The length of the chimney is c. 86 cm.

lated from the gradient $(1 - e^{-\lambda t})$, i.e. the fraction of ^{210}Pb ingrown towards equilibrium with ^{226}Ra (Fig. 3):

$$\text{Measured } ^{210}\text{Pb} = (^{210}\text{Pb ingrown from } ^{226}\text{Ra} + \text{decayed original } ^{210}\text{Pb}) = (1 - e^{-\lambda t}) * ^{226}\text{Ra} + K * [\text{Pb}] * e^{-\lambda t}$$

$$K = ^{210}\text{Pb}/\text{Pb ratio at zero age.}$$

$$\lambda = ^{210}\text{Pb decay constant} = \ln 2 / ^{210}\text{Pb half-life.}$$

$$(1 - e^{-\lambda t}) = (1 - ^{210}\text{Pb}/^{226}\text{Ra})$$

As time elapses, the isochron pivots towards the equi-line (i.e. the equilibrium position). Errors limit the use of the method to c. 100 years. Because the hydrothermal reaction does not extract thorium from rock, the ^{226}Ra in the chimney is not supported by its relatively long half-life parent ^{230}Th . Provided that the barium and ^{226}Ra were deposited together from a common source and the initial $^{226}\text{Ra}/\text{Ba}$ is known, ages of c. 500–15 000 years can be calculated from the decrease in $^{226}\text{Ra}/\text{Ba}$ due to radioactive decay since the massive sulphides were deposited.² Having successfully dated a complete black-smoker by the ^{210}Pb - ^{226}Ra isochron method, the mean measured $^{226}\text{Ra}/\text{Ba}$ may be decay-corrected to zero age (a relatively minor adjustment) and taken as the initial ratio for calculating the ages of chimney fragments found in the same proximity.

Chimneys appear to break-up in less than 1000 years, and the isochron approach cannot be applied to isolated fragments. However, there are alternative dating methods involving the ^{232}Th decay scheme that can be used. While determining ^{226}Ra

² In one near-pure barite deposit from the Kermadec Arc, ^{226}Ra is very low but still measurable and the age is estimated to be c. 18 000 years.

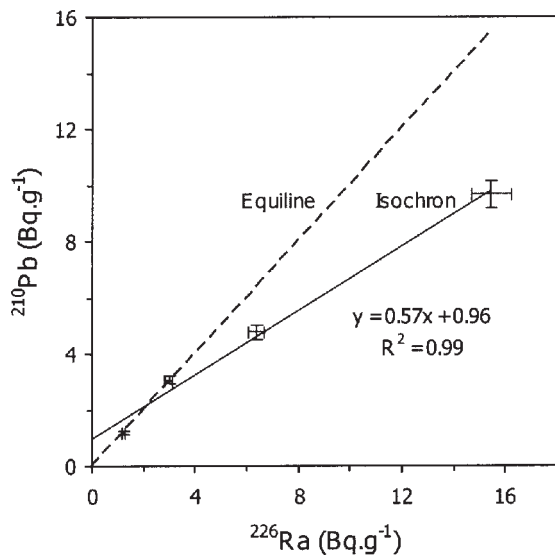


Figure 3. ^{210}Pb versus ^{226}Ra at constant Pb concentration for a black smoker chimney from Brothers volcano. Errors are 1σ . The calculated age is c. 25 years.

by gamma spectrometry ^{228}Ac (a proxy for ^{228}Ra deposited along with the other radium isotopes) and ingrown ^{228}Th may be measurable. From the fraction ingrown towards equilibrium with the decaying ^{228}Ra , deposits up to c. 15 years old can be dated (Fig. 4).

This age range can be extended by assuming the initial $^{228}\text{Ra}/^{226}\text{Ra}$ in the deposit is unity³. Once separated from their parent isotopes ^{230}Th and ^{232}Th , ^{226}Ra and ^{228}Ra decay, and the age can be determined from the decrease in $^{228}\text{Ra}/^{226}\text{Ra}$ (Fig. 5).

In all the dating methods described, any errors inherent in the short-term dating used to determine an initial $^{226}\text{Ra}/\text{Ba}$ value will be insignificant compared with the ^{226}Ra half-life, and therefore will have little effect on the accuracy of the derived ages. Note that, if ^{228}Ra (measured as ^{228}Ac) is present, the age must be <50 years.

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³ Thorium has typically three times the abundance of uranium, but ^{232}Th has a half-life three times longer than that of ^{238}U (i.e., three times less activity per unit mass) and, assuming ^{238}U , ^{234}U and ^{230}Th are in equilibrium, the activity ratios $^{232}\text{Th}/^{230}\text{Th}$ and $^{228}\text{Ra}/^{226}\text{Ra}$ should be near unity.

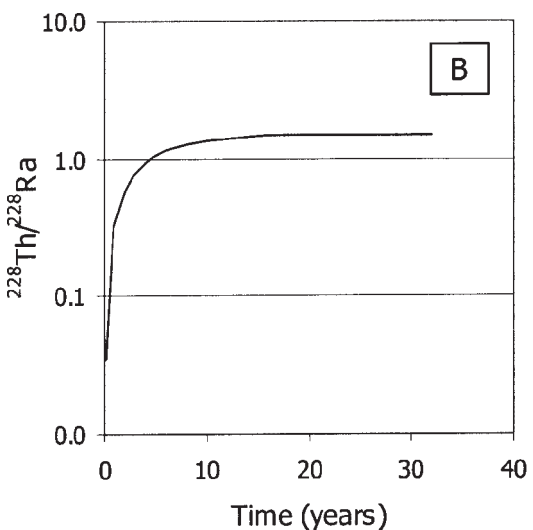
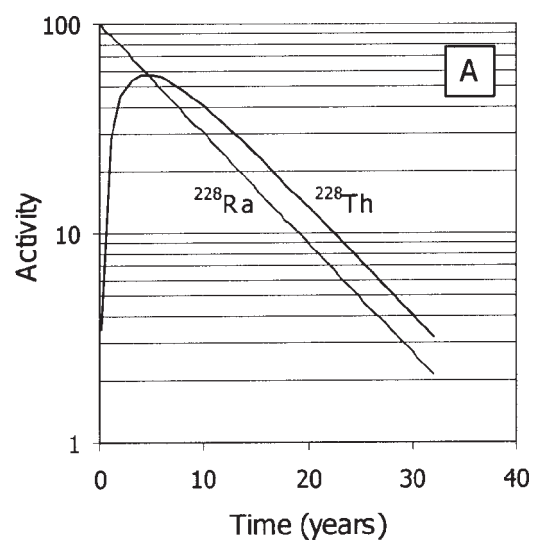


Figure 4. Theoretical curves using Bateman equations (cf., Ivanovich & Harmon, 1992). A. ^{228}Th ingrowing as ^{228}Ra decays; B. $^{228}\text{Th}/^{228}\text{Ra}$ versus time.

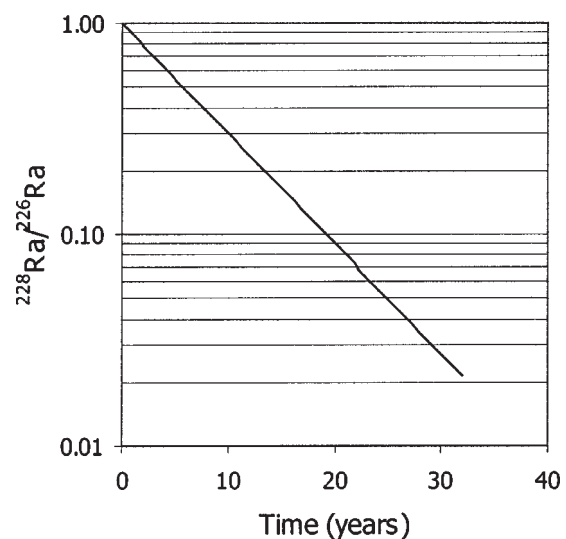


Figure 5. $^{228}\text{Ra}/^{226}\text{Ra}$ versus time.

Beryllium isotope dating of ferromanganese nodules and crusts

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Extensive deposits of ferromanganese nodules and crusts occur within the world's ocean basins. The Campbell Nodule Field (Fig. 1) extends south and SE of New Zealand beneath the flow path of the Antarctic Circumpolar Current (ACC) and the Deep Water Boundary Current (DWBC), and has been the subject of recent scientific investigation (Wright et al. 2004). Although the nodules have typically relatively low concentrations of Co and Ni, and the technology for extraction is presently under-developed, the nodule field represents an immense future resource for a wide range of strategic metals.

Knowledge of absolute age and growth rates is crucial for a proper understanding of the origin and mode of occurrence of ferromanganese deposits. While biostratigraphic and geochemical dating methods have been used with some success in the past (see Baturin & Savenko 1989), recent application of cosmogenic isotopes (i.e., ^{10}Be , ^{26}Al) and, for the last c. 500 ka, U-Th isotopes, has greatly increased precision and accuracy (e.g. Ku et al. 1979). Beyond c. 15 Ma, cosmogenic isotope dating becomes imprecise, and Co-based (Puteanus & Halbach 1988) or Sr isotope-based dating (Ingram et al. 1990) can be applied successfully.

Since its discovery in the 1950s, ^{10}Be has been used increasingly to date ferromanganese nodules and crusts, initially by β counting (e.g. Bhat et al. 1973), and more recently with greater precision, by AMS (e.g. Sharma et al. 1983). The cosmogenic

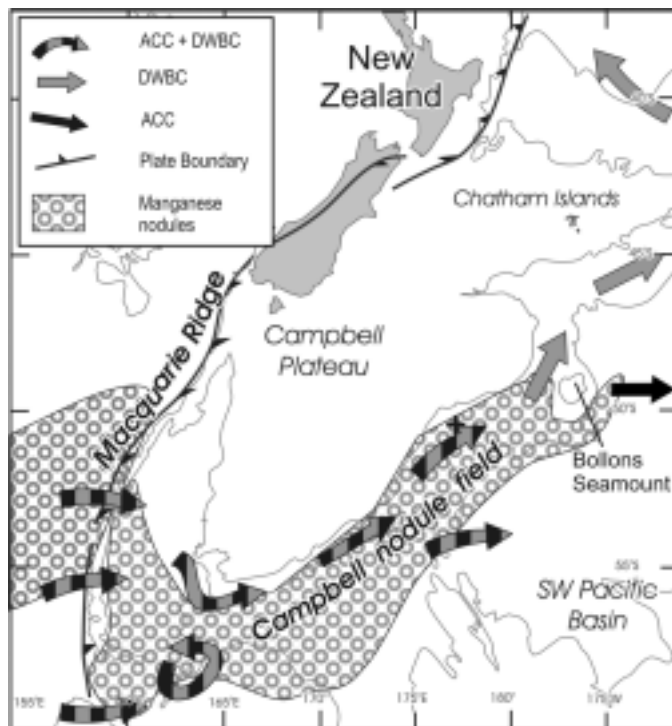


Figure 1. The Campbell Nodule Field showing flow-paths of major oceanic currents (after Graham et al. 2003).



Ian Graham is a Wellington-based Principal Scientist with the Institute of Geological & Nuclear Sciences (GNS). Originating from Oamaru in North Otago, he completed his undergraduate studies at Otago University in 1979 (BSc(Hons) and MMinTech). Since obtaining his PhD at Victoria University in 1985, he has pursued wide-ranging research projects in isotope geology and geochronology, specialising in applications of strontium and beryllium isotopes. As manager of the PGST programme at GNS on Mineral Wealth of New Zealand and its EEZ, Dr Graham is currently interested in the genesis of gold-bearing massive sulphide deposits in active subduction zones, and the origin and age of ferromanganese deposits.

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Albert Zondervan is a research scientist at National Isotope Centre of the Institute of Geological and Nuclear Sciences (GNS). He received his degrees in physics at the universities of Utrecht and Amsterdam. Since his PhD in nuclear physics, he has been involved with techniques for and applications of isotope ratio measurements. At the National Isotope Centre, Dr Zondervan leads the PGST programme that supports the accelerator and mass-spectrometry facilities, and is actively involved in applying surface exposure-age dating with cosmogenic isotopes.

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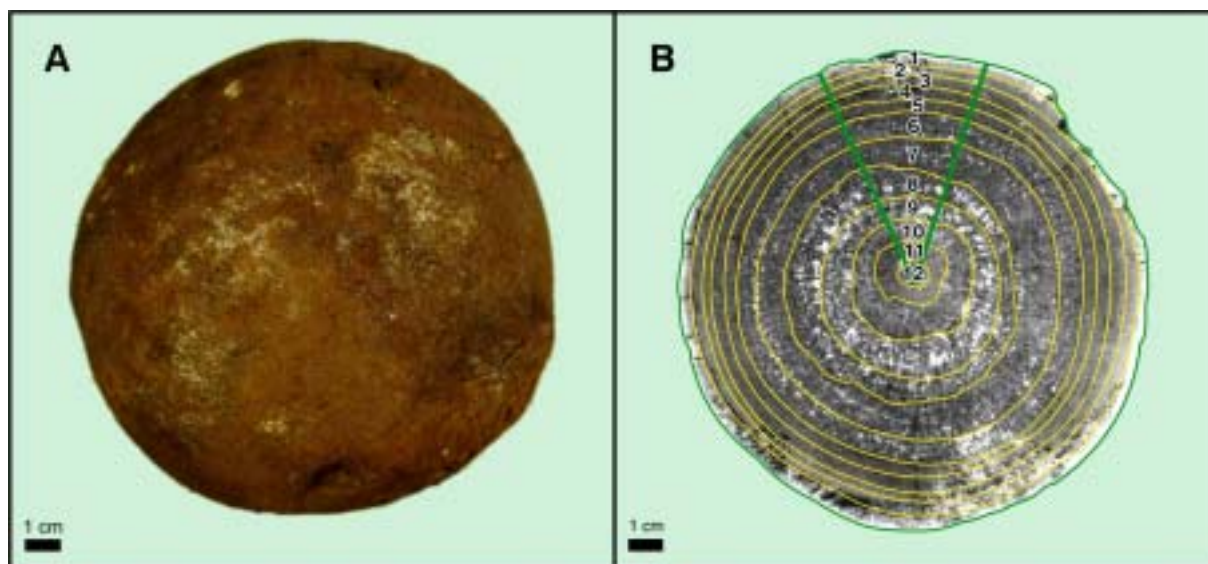


Figure 2. Ferromanganese nodule from the Campbell Nodule Field. A: Uncut nodule. B: cross-section with prominent growth layers outlined and numbered.

isotope ^{10}Be is produced mainly in the upper atmosphere by spallation of oxygen or nitrogen nuclei by cosmic rays. Shortly after formation, ^{10}Be is adsorbed onto aerosols and removed from the atmosphere by precipitation, then enters the oceans by fluvial and/or aeolian transport where it becomes incorporated in a variety of oceanic deposits (McHargue & Damon 1991). Ferromanganese nodules (Fig. 2) and crusts grow by accretion from seawater either just above the abyssal seafloor (i.e. hydrogenous growth) or just below the seafloor (i.e. diagenetic growth) and absorb ^{10}Be during growth, from which their ages can be determined.

The ^{10}Be dating method for ferromanganese deposits is based on the relative isotopic composition (i.e. decay difference) between growth layers:

$$\text{Age} = \frac{t_{1/2}}{\ln(2)} \ln(I/O) \quad (1)$$

where the radiometric half-life $t_{1/2} = 1.5 \pm 0.1$ m.y. (Bhat et al. 1973), and I and O are the measured isotopic ratios of the inner and outer layers, respectively. This equation, which is independent of the concentration of the daughter isotope ^{10}B , holds true only if both layers had the same initial isotopic ratio at the time of formation, and post-formational isotopic exchange is minimal. The traditional approach is to determine the beryllium isotopic composition in successive growth layers from the rim to the core of a nodule (Fig. 2B), and apply 'best-fit' line segments to log-normal plots to deduce absolute ages and growth rates. The exponential decrease in ^{10}Be activity with distance into the nodule may be interpreted in terms of a 'growth model' (Somayajulu 2000) which assumes that the nodule remains a closed system from the time it started growing, and that the change in ^{10}Be activity is due only to decay. This is represented by the differential equation:

$$S \frac{dC}{dz} + \lambda C = 0 \quad (2)$$

where C is the ^{10}Be concentration at depth z and S is the growth rate. Changes in the slope of the decay curve, $\ln(C)$ versus z , indicate changes in growth rate.**

In applying the growth model to ^{10}Be dating of ferromanganese nodules and crusts, two basic assumptions are made: (i) Be is incorporated at a constant isotopic ratio, and (ii) the growth rate is slow with respect to the ^{10}Be decay rate. In all recorded cases, analysis has shown assumption (ii) to be valid. Even in cases of relatively rapid growth (> 100 mm m.y. $^{-1}$) ^{10}Be decay is easily measured, yielding very precise ages. Available data on the marine chemistry of ^{10}Be and ferromanganese deposits indicate that assumption (i) also generally holds true. The atmospheric supply of ^{10}Be to the oceans in both time and space is relatively constant on, at least, a several hundred thousand year time scale (McHargue & Damon 1991). As a result, the isotopic ratio $^{10}\text{Be}/^9\text{Be}$ of deep oceanic water is relatively constant on a regional (von Blanckenburg & Igel 1999) and temporal (Ling et al. 1997) basis. It may also be assumed that ferromanganese nodules remain closed systems with respect to beryllium subsequent to formation, due to beryllium's low mobility under weakly acidic to alkaline conditions (i.e. $\text{pH} > 5$) (Mangini et al. 1986).

For each analysed nodule or crust, two sets of analytical data are available to derive its growth history (Fig. 3), (i) $^{10}\text{Be}/^9\text{Be}$ isotopic ratios and associated uncertainties, and (ii) the positions of the inner and outer boundaries of each sampling interval. Assuming that the sub-sampling has identified sections where the growth rate was relatively constant, exponential regression provides a way to interpolate or extrapolate the fitted exponential function to rim and core positions. A least-squares minimisation technique provides a goodness-of-fit

** The alternative *diffusion model*, which assumes that ^{10}Be diffuses into a pre-existing module through its surface (i.e., derived 'ages' are artefacts) can be ruled out as a plausible mechanism. Growth rates determined using radio-nuclides of widely differing half-lives are typically in good agreement (Baturin & Savenko, 1989), and calculated K values for Be in ferromanganese nodules ($< 1 \times 10^{-8}$ $\text{cm}^2 \text{y}^{-1}$; Mangini et al. 1986) are very low.

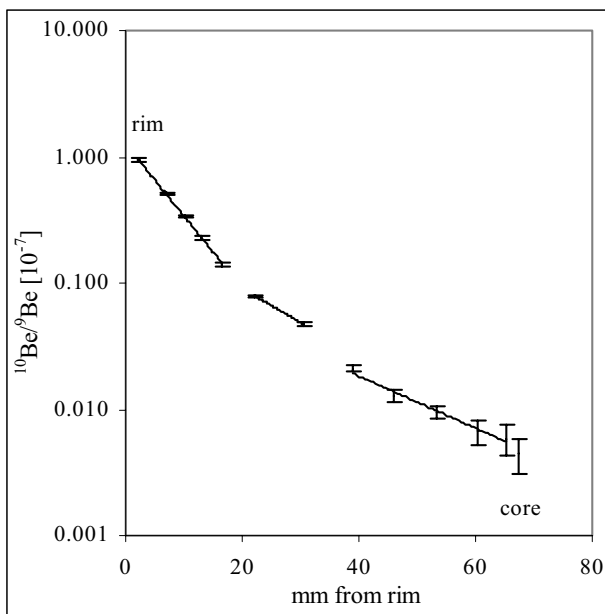


Figure 3. $^{10}\text{Be}/^9\text{Be}$ decay plot for the ferro-manganese nodule illustrated in Fig. 2. Three segments are defined, yielding growth rates of c. 11.0 (core) 5.0 (middle) and 3.5 (rim) mm m.y.^{-1} , and an overall age of 12.4 Ma.

parameter that is used to maximise the size of each data subset, i.e., the widest segment within a profile that is consistent with a single growth rate. To avoid ambiguity, each data point is allowed only to be part of a single segment (Fig. 3). For all nodules or crusts, that means that regressions on innermost and outermost (and often in-between) segments are performed separately. Obtaining a consistent description of growth between data points belonging to different regressions within the profile would require the addition of more model parameters, creating the risk of not finding a unique solution in a well-defined least-squares minimum.

There are two bias effects that invalidate the use of linear mid-positions of sampling intervals. The first is due to the exponential nature of radiometric decay, and the second is due to volumetric implications of sampling along the direction of growth perpendicular to surfaces with spherical symmetry.[†] Both effects displace the average $^{10}\text{Be}/^9\text{Be}$ ratio of each sample section slightly away from the linear mid-position towards the rim. This new position is referred to as the 'Centre of Interval' (COI) and the origin of the coordinate axis is placed at the rim. The magnitude of these two effects depends on the radial width of each sample so that, for samples with equal intervals, those closer to the core are more strongly biased. In order to incorporate these bias effects into the function fitted to the data, it is assumed that: (i) the curvature of equal-age surfaces is spherical around a centroid at a quantifiable distance from the rim, and (ii) the sampling volumes are defined by boundaries that are parallel and perpendicular to these equal-age surfaces (i.e., cone-shaped). Although shapes of actual sampled volumes are not always along orthogonal boundaries, taking this effect into account results in a more accurate regression particularly towards the core where sample intervals are usually wider. From

[†] The second effect disappears in the absence of radial curvature in crusts.

visual inspection, it can be concluded that most nodules and crusts started growing very close to their centre of curvature. Nevertheless, the fit function allows for situations where this is not the case. The inherent precision of calculated ages decreases with sub-sampling distance away from the rim, because: (i) closer to the AMS detection limit, measured $^{10}\text{Be}/^9\text{Be}$ ratios have progressively lower precision (Fig. 3), and (ii) inner samples of nodules are more difficult to extract accurately with respect to the growth lines.

Ages of nodules and crusts (i.e., total samples, or each growth segment represented by its COI) can be determined in several ways: (i) *Extrapolated Ages* are based on measured $^{10}\text{Be}/^9\text{Be}$ ratios and the extrapolated $^{10}\text{Be}/^9\text{Be}$ ratio of the rim. In this formulation, it is assumed that the rim value represents a constant initial $^{10}\text{Be}/^9\text{Be}$ ratio for that nodule or crust throughout its growth history, (ii) *Model Ages* are based on measured $^{10}\text{Be}/^9\text{Be}$ ratios and an assumed initial $^{10}\text{Be}/^9\text{Be}$ ratio. The latter ratio might be a mean value for several samples from the same field or oceanic region, depending on how well the data cluster, and (iii) *Growth Ages* (in m.y.) are based on the elapsed time from initiation of growth (i.e. core to rim).

Traditionally, ferromanganese deposits have been dated using ^{10}Be concentrations. However, such an approach is highly suspect, giving rise to erroneous results (cf. Segl et al. 1984, 1989). For the Campbell Nodule Field, calculated $^{10}\text{Be}/^9\text{Be}$ ages are consistently greater than the corresponding ^{10}Be atoms g^{-1} ages, with differences ranging from 4% to 58% (mean = $18 \pm 28\%$) (Graham et al. 2003). The reason for the age discrepancy and for the suspect nature of the ^{10}Be atoms g^{-1} ages in particular, is variable uptake of beryllium during growth resulting from changes in seawater chemistry, pH, temperature etc. (Mangini et al. 1990). This is illustrated by the ^9Be concentration profile (Fig. 4). The ^{10}Be and ^9Be concentration profiles track each other (i.e. with the decay component removed from the ^{10}Be data), resulting in a relatively constant and/or predictable $^{10}\text{Be}/^9\text{Be}$ trend (Fig. 3). There is a consistent (though of variable magnitude) reduction in ^9Be concentration from core to rim which, if translated into a corresponding reduced uptake

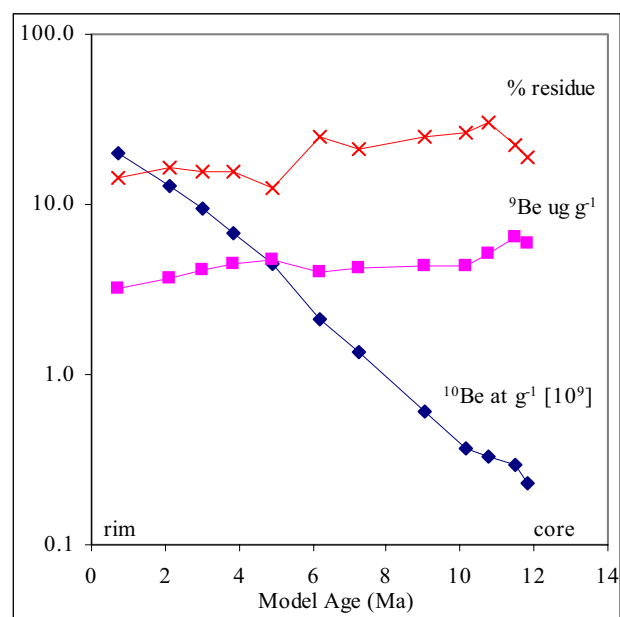


Figure 4. ^{10}Be , ^9Be and % residue vs. Model Age for the ferromanganese nodule in Fig. 2.

of ^{10}Be results in lower than expected ^{10}Be atoms g^{-1} ages. It is also important to note that the extrapolated rim $^{10}\text{Be}/^9\text{Be}$ ratios, particularly for the upper hemispheres, are much less variant than their ^{10}Be atoms g^{-1} counterparts, making the latter a less precise parameter by which ages can be calculated (Graham et al. 2003).

Growth rates, calculated from the age data, are determined by dividing the nodule radius (core-rim) or crust thickness (base-rim) by the *Extrapolated Ages* or the *Model Ages*. Growth rates of individual segments may be obtained by dividing the distance between successive COIs by the age difference of those segments, and *Cumulative Growth Rates* (from core to rim) may be obtained from the progressive distance between COIs and the core, divided by the corresponding *Growth Ages*.[‡] For nodules from the Campbell Nodule Field, mean growth rates are typically very slow, 4–10 mm m.y.^{-1} , and tend to decrease systematically from core to rim (Fig. 5). Even slower growth rates are recorded if ferromanganese growth only is considered (i.e. incorporated silicate is excluded from the calculations).

The $^{10}\text{Be}/^9\text{Be}$ dating method, as applied to ferromanganese nodules, relies on the beryllium having a constant $^{10}\text{Be}/^9\text{Be}$ when it is incorporated into the growing nodule. This assumption is supported by published agreement between different dating methods, but there is as yet no convincing direct evidence by which to verify it. Ling et al. (1997) provided some data to suggest that the $^{10}\text{Be}/^9\text{Be}$ ratio of North Pacific Ocean seawater is relatively constant at ca. $1.4 \pm 0.4 \times 10^{-7}$ over the past c. 12 m.y., but this has yet to be supported by similar data from elsewhere. Although the temporal constancy of the initial $^{10}\text{Be}/^9\text{Be}$ ratio for the Campbell Nodule Field cannot be easily verified, there are strong indications that measured nodule/crust ratios, after allowing for ^{10}Be decay, do correspond to a contemporary seawater value that has not changed significantly during nodule growth. Most $^{10}\text{Be}/^9\text{Be}$ decay curves are consistent and predictable, and show no sudden reversals. % residue after leaching, an approximate measure of the amount of aluminosilicate incorporated into the nodules during growth, shows no clear positive correlation with either ^{10}Be and ^9Be concentration (Fig. 4). Hence, it is unlikely that the nodules have undergone any significant isotopic exchange after formation.

Application of $^{10}\text{Be}/^9\text{Be}$ dating, following the methodology described here, has provided the opportunity to determine precise and detailed absolute chronologies for deep ocean ferromanganese deposits and in certain situations, pelagic sediments (e.g. Bourles et al. 1989) back to c. 15 Ma. This has allowed researchers to determine detailed isotopic profiles at key global locations, leading to an increased understanding of isotope geochemistry, and the evolution of major oceanic currents in relation to their associated continental catchments (e.g. Frank 2002).

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[‡] Growth Ages are weighted ages of the segment to which the growth rate applies.

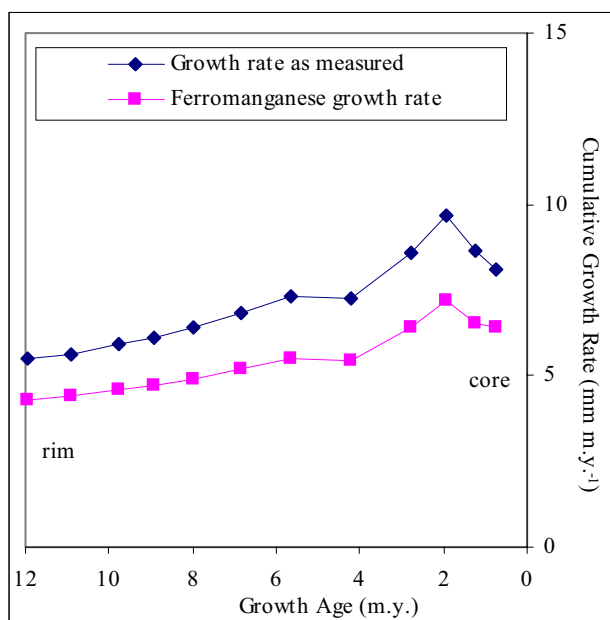
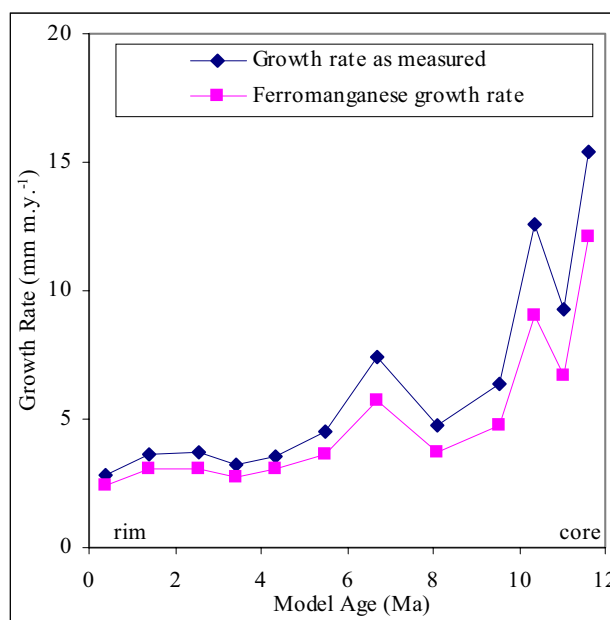


Figure 5. Growth rate v. model age (upper) and growth age v. cumulative growth rate (lower) for the Fe–Mn nodule illustrated in Fig. 2. Filled squares are rates for ferromanganese growth only.

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The Long Run

Peter Blattner*

We run the line each day, but now it was bewitched.
 arrived at dawn I walked in water, a hose had slipped,
 buckets to be mopped and carried out! And past that leak
 the seals had melted – to be renewed. That done, next day,
 the triode blew, of the induction – bang.
 Some persuasion’s needed to enthuse our sparky friends.
 Three days they measured, wired, tested. Replacement ordered,
 papers filled. At last it works somehow. Better to hurry:
 forget electronic perfection. Two standard points suffice.

The thing that tells the isotopic ratio, always productive
 hi-tech work horse, spectrometrying the masses, this time – alas –
 some devil poor fed nitric to its prisons. And what a tailing formed
 thereafter: exemplary a process, but no results, no data can be sold,
 however hard the work! The way back to the line: the corridor’s once
 grandly panelled rimu. Disfigured now with blobs of Prussian blue,
 like underpass graffiti, it feeds despair.

So, went on holiday, a course on *attitude*, in lecture halls!
 Then came back: reagent running low, this pentafluoride of bromine.
 With water it explodes in fireballs, a rocket fuel. Too hot to post by air,
 as deck cargo it comes a-sailing, across the sea to Aotearoa
 with thousand more restrictions. This takes a year.

Now poems I write. The fancy of science. Its cost in hours
 for man and child, in years, in centuries. Battles of engineers
 accounts, deliveries. Environmental impact. And yet! Just one result,
 although extract’ by force, with desperate effort among collapsing artefacts,
 if chosen well, might tell us how this land itself has sailed,
 and drifts ten-thousand miles, and is re-shaped even while demolished.

And the platinum-wound graphite? Its wondrous discharge glow,
 called up by dread impurities, signals the days’ other losses.

* With thanks to Athol Rafter and, obviously, many others.

¹⁰Be surface exposure dating of raised marine terraces and glacial moraines

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Geological processes at the Earth's surface have a profound effect on human activity. Interactions between various elements of the landscape influence the harshness of floods, the danger of earthquakes, the severity of landslides, the potential of soil erosion of croplands, and the reliability of water supplies. Landscape constantly evolves through the forces of tectonics, climate, weathering and hydrology, and analysis of its evolution provides insight into the controls on processes. Of prime importance is an understanding of the timing of events, allowing determination of cause and effect, and of rates of change.

The time period most relevant to this is the last two million years, the Quaternary Period. Geological surfaces and deposits are, however, difficult to date by conventional methods within this time period. Surface exposure-age dating (SED) using cosmogenic isotopes (i.e. nuclides produced by cosmic rays) can help resolve this problem. Geological materials, exposed to high-energy cosmic ray particles (principally neutrons and muons), build up small amounts of unstable and stable nuclides through nuclear reactions between these rays and target nuclei (e.g. O, Si, K, Ca, Cl, Al, Fe, Mg). Of the cosmogenic nuclides, particularly useful are the radio-nuclides ¹⁰Be, ¹⁴C, ²⁶Al and ³⁶Cl, and the stable nuclides ²¹Ne and ³He (Table 1), which can be measured precisely by accelerator and noble-gas mass spectrometry, respectively. Measurements of these isotopes, either singly or in combination, have been used successfully to determine the timing of glaciations, debris flows, lava flows, tectonic uplift, meteorite impacts, and erosion over the time period 0–10 Ma, but particularly 5–50 ka.

The principle underpinning the SED method is relatively simple, i.e. the age of the event during which a surface became exposed to cosmic rays is equal to the concentration of the target nuclide divided by its production rate at that location. However, production rates vary over space and time, and the

Table 1. Principle nuclides for surface exposure dating. Approximate production rates are given for sea level and > 60° latitude. (Data sourced from Gosse & Phillips 2001.)

Cosmogenic nuclide	Radiometric half-life (y)	Target material	Production rate (atom g ⁻¹ y ⁻¹)	
			Range	'Best'
¹⁰ Be	1.51 × 10 ⁶	Silica	4.7-6.5	5.2 ± 0.2
¹⁴ C	5,730	Silica	19-20	20 ± 4
²¹ Ne	-	Silica	8-21	18
		Olivine	32-45	39
²⁶ Al	0.71 × 10 ⁶	Silica	28-37	37.4 ± 1.9
³⁶ Cl	0.30 × 10 ⁶	Ca	44-99	66.8 ± 6.8
		K	74-321	137 ± 60
³ He	-	Olivine	47-116	115 ± 4

methodology needed to account for these variations is the subject of much on-going research and debate. At a particular locality (geometry) and point in time, cosmogenic nuclide production rates are proportional to the flux of cosmic-ray particles, weighted by their cross sections for nuclear reactions with their target atoms. For the above principle to properly apply, several temporal/spatial and global/site-specific factors have to be taken into account. These, in turn, are dependent on a number of factors, which can be difficult to define precisely, resulting in large errors in calculated SED ages.

1. *The primary galactic cosmic ray (GCR) flux:* The flux of primary GCRs entering the Earth's atmosphere is assumed to have been relatively constant over approximately the past 10 m.y., although there is some evidence from meteorite studies that it may have been significantly lower in the immediate past than at present. The GCR is modified by the 11- and 22-y solar cycles, which coincide with periods of high flux (solar minimum) and low flux (solar maximum),



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but this effect is smoothed out over long exposure periods of $10^3 - 10^4$ y.

2. *Position of the geomagnetic field:* The magnetic rigidity of a cosmic ray particle is defined as $r = pc/q$, where p and q are the momentum and charge of the particle, and c is the velocity of light. The Earth's magnetic field deflects incoming particles depending on their rigidity and angle of incidence. For each angle of incidence there is a critical rigidity below which the incident particle cannot interact with the Earth's atmosphere. As a result, there is a factor $c. 2$ difference in effective GCR flux (at sea level) between the equator, where the Earth's magnetic field stops cosmic ray particles with energies less than about 18 GeV, and the polar regions where particles can 'ride in' along magnetic field lines. The effect of this on the production rate at a particular site can be corrected for using plots and derived equations of Lal (1988) (Fig. 1) or Dunai (2000),¹ which take into account temporal changes in geomagnetic latitude due to shifts in the position of the pole (i.e. eccentricity of the dipole axis).
3. *Intensity of the geomagnetic field:* Archaeometric, volcanological and sedimentological data indicate that the Earth's magnetic field intensity has varied by up to 300% over the past 0.25 m.y. Given that the magnetic field inhibits cosmic rays, such variation has a significant effect on short-term production rates. Paleo-intensity curves for different regions of the Earth's crust can be used to adjust local, short-term production rates, but this becomes less important over longer time-spans.
4. *Altitude (overburden of atmospheric mass):* Attenuation of the GCR flux by air causes a decrease in production rate with decreasing altitude, the change being a factor $c. 2.7$ for every 1.4 km change in altitude (Fig. 1). The equations of Lal (1991) modified by Stone (2000), or Dunai (2000) can be used to correct for this effect. Because the production rate's altitude-dependences are so large, tectonic movement (up or down) and/or isostatic rebound can have a major effect on the accumulation of cosmogenic nuclides and thus on the dating of exposure events.

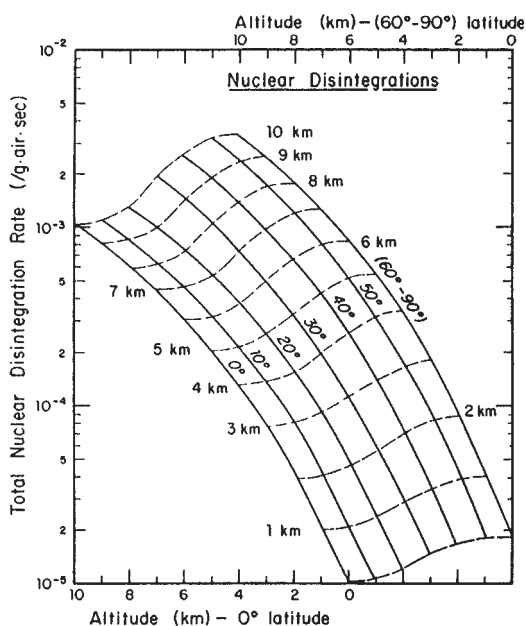


Figure 1. The total rate of nuclear disintegrations in the atmosphere (with energy release > 40 MeV) (after Lal 1988)

5. *Nature of the cosmic flux:* Neutrons account for 90+% of cosmogenic nuclide production at sea level, with muons accounting for the remainder. Neutrons and muons are affected differently by the Earth's magnetic field, atmosphere and lithosphere requiring different correction algorithms (see Stone 2000).
6. *Site geometry:* Cosmic rays approach the Earth's surface at various angles; oblique rays (and any surface-produced secondary particles) are attenuated by cliffs, mountains and/or large boulders near the target site. The effect is usually in the order of a few percent, and can be corrected for assuming that the geographic setting has remained constant through the time period of interest.
7. *Attenuation by rock mass:* The production rate of *in situ* cosmogenic isotopes within the top 5 cm of a rock surface is constant (Masarik & Reedy 1995), but decreases below this according to the following equation: $P_x = P_0 e^{-x/Le}$, where P_x = production rate at depth x ; P_0 = production rate at the rock surface; Le = absorption mean free path for nuclear interacting particles in the rock (for ^{10}Be , $Le = 157 \text{ g cm}^{-2}$).
8. *Other factors:* A number of other factors can be important in determining time-integrated production rates:
 - a. Overburden covering the target in the past (e.g. soil, snow, volcanic ash, vegetation) reduces the cosmic ray flux at the rock surface.
 - b. Erosion, which strips away the first irradiated rock layers, and exposes lower layers to a higher cosmic ray flux.²
 - c. In the case of moraines, tills or river gravels, prior exposure to cosmic rays or rolling (i.e. boulders changing position) can either increase or decrease the effective flux that the rocks receive.

Unfortunately, it is difficult to be certain to what degree these other factors have played a role at any particular site, and corrections can at best be guesses based on sound geological observation. Ignoring them can result in large bias in the calculated SED ages.

Because of its relative ease of measurement and its well established production rate (Table 1), the currently most frequently applied SED technique employs *in situ* produced ^{10}Be in quartz. This requires the extraction of very pure quartz from rock samples by eliminating all easily dissolved minerals (i.e. hydroxides, carbonates and clays) using $\text{HCl} + \text{H}_2\text{O}_2$, then eliminating all other silicates (particularly feldspar) using $\text{HF} + \text{HNO}_3$ (Graham et al., 1998). Reduction of the original rock sample to $c. 25-50\%$ of the original mass (depending on the quartz content of the rock) ensures that only the cores of quartz crystals remain. These are assumed to contain only *in situ* produced ^{10}Be , with negligible contamination by atmospherically-produced ^{10}Be carried in rain and groundwater. When the quartz is so purified, and its *in situ* produced ^{10}Be is extracted and precisely measured by AMS, an exposure age can be determined by dividing the measured ^{10}Be by the production rate (see Table 1), adjusted for the factors mentioned above.

¹ Dunai (2000) incorporates the influence of non-dipole components of the geomagnetic field on the cosmic ray flux.

² In principle, erosion rates can be determined using a combination of cosmogenic isotopes (e.g. 'banana plot' of Lal (1991)).

Two early applications the ^{10}Be SED technique to New Zealand rocks are detailed in Graham et al. (1998). The coastal section at Turakirae Head (Fig. 2) is a gazetted site of special scientific interest preserving a flight of Holocene marine terraces with sporadic outcrops of Mesozoic greywacke. The beach ridges are the crests of storm beaches and owe their origin to a very stormy coast, and episodic tectonic uplift. The most recent uplift (BR1) occurred as a result of the Wellington-Wairarapa earthquake of 1855, the next (BR2) formed prior to 1855, while the third (BR3) is AMS radiocarbon dated at c. 330 BC (Moore 1987).³ The higher terraces (BR4 & BR5) are both considered younger than c. 7000 BP, coinciding with the end of the post-glacial sea level rise when extensive beaches began to form globally. The beach ridges BR1–BR4 are tilted relative to sea level, at a mean rate of c. 4 m per 1000 y (Wellman 1967). ^{10}Be SED of



BR5, 26 m above present sea level, is consistent with this uplift rate. Correction of the sea level, $> 60^\circ$ latitude ^{10}Be production rate (taken to be $5.2 \text{ atoms g}^{-1} \text{ SiO}_2 \text{ y}^{-1}$; Table 1) was required for geomagnetic latitude (-7%), altitude ($+2\%$), site geometry⁴ and sampling depth. Exposed rock surfaces at the sampling site show little sign of erosion, and are covered with only sparse, thin layers of moss, so correction for these geological factors was not required. Calculated exposure ages of 5.5–6 ka are broadly consistent with, though slightly younger than the expected age of about 6.5–7.0 ka, marking post-glacial sea level rise.

^{10}Be SED has also provided a direct radiometric age for one of the younger (Otiran) glacial advances in the upper Clutha valley (Graham et al. 1998). Peat from the base of a now abandoned glacial melt water channel at Lake Hawea yielded a radiocarbon age of $15.1 \pm 0.2 \text{ ka}$ (McKellar 1960). Samples for SED were obtained upstream of this locality, from an outcrop of water worn biotite schist with abundant quartz veining. The ^{10}Be SED result, about 17.5 ka, though significantly higher than the radiocarbon age, is consistent with the accepted age for the last glacial maximum.

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Figure 2. Turakirae Head, near Wellington; view NE along the axis of the Rimutaka Range, showing Holocene beach ridges BR1–BR5.

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³ These dates were derived from micro-molluscs extracted from a mat of worm tubes beneath large boulders in stranded surge pools.

⁴ The sampling site (Fig. 2) is on the SE lee of a relatively steep cliff face, providing significant shielding of the cosmic ray flux.



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