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Making materials matter

THE AUSTRALIAN NATIONAL UNIVERSITY

Carbon of the ages

How measuring one atom in a trillion can reveal the age of a material

(Left) Dr Stewart Fallon looks at the high voltage deck of the new Single Stage Accelerator Mass Spectrometer (SSAMS) at RSES. The tube surrounded by silver rings next to him is where charged carbon ions receive a massive boost in accelerating voltage. SSAMS will become Australia's foremost facility for measuring carbon 14.

The Research School of Earth Sciences and the Research School of Physical Sciences and Engineering have recently established a state-of-the-art particle accelerator for measuring radiocarbon in materials. The facility is a Single Stage Accelerator Mass Spectrometer (or SSAMS for short) and its establishment means ANU is now a one-stop dating shop. In other words, if you have a sample containing a radioactive isotope that might enable its age to be determined, ANU has the technology to carry out that analysis.

Inside this MM

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Carbon 14, also known as radiocarbon, is a radioactive form of carbon found in all living things. Simply being alive means you'll have some in you. And that's great news for scientists wanting to find out how old biological materials are because by measuring the amount of radiocarbon present in a sample it's possible to estimate how long that material has been around.

It works like this. Cosmic rays are constantly bombarding our atmosphere. Often a cosmic ray collides with an atom creating an energetic neutron which may then collide with a nitrogen atom. This collision turns a nitrogen atom (with seven protons and seven neutrons) into a carbon 14 atom (with six protons and eight neutrons) and a hydrogen atom (with one proton and zero neutrons). The carbon 14 (or ^{14}C) quickly combines with oxygen to form carbon dioxide (CO_2).

Most of the carbon around us is not radioactive, and exists as carbon 12 or carbon 13. For every trillion atoms of normal carbon there's around 1 atom of carbon 14 so there's not much of the stuff around. And because carbon 14 is radioactive it's always slowly breaking down (back into nitrogen). Carbon 14 has a half life of 5730 years meaning it takes 5730 years for half of a group of carbon 14 atoms to decay. However, while carbon 14 atoms are always decaying, they are also always being replaced through the generation of new carbon 14 atoms in the atmosphere. Consequently there's a fairly constant ratio of carbon 14 to carbon 12 and carbon 13 in the environment around us.

The stuff of life

Living animals depend on carbon. Plants absorb it when they photosynthesise. Animals take it in when they eat the plants. Shell fish absorb it from the surrounding water and secrete it in their shells, and corals use it to build their skeletons. Throughout an animal or a plant's life it takes in carbon and stores it in its tissues. This stored carbon exists at the same ratio as the carbon in their surrounding environment, that is roughly 1 atom of carbon 14 for every trillion atoms of normal carbon.

However, when the organism dies it stops metabolic activity and accrues no more carbon. And this is when the radiocarbon clock starts ticking because over time the ^{14}C atoms decay but the normal carbon atoms stay the same. So, over time the number of carbon 14 atoms decreases and the ratio of carbon 14 to normal carbon decreases in a predictable manner. When 5730 years has passed, there will only be around one radiocarbon atom to every two trillion normal carbon atoms. At 11,000 years it will be something like one radiocarbon atom to every four trillion normal carbon atoms, and so on.

Unfortunately, after about 50,000 years there are so few radiocarbon atoms left that it becomes nearly impossible to use them to obtain a useable age estimation. Anything older requires a different technique (that usually measures a different isotope) The good news is that radiocarbon dating is a robust and reliable method for determining the age of biological materials that are younger than 50,000 years. This has made it the cornerstone of many of the sciences dealing with our recent history (eg archaeology), prehistory (eg anthropology) and global environment (oceanography and climate change).

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Carbon of the ages
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Wood, shell and bone

"Carbon dating can often be the only way to date something like say a piece of wood," says Dr Stewart Fallon from the RSES. "It's also excellent for dating organic materials which are often found in human garbage heaps and middens, and in the charcoal left in fires.

"Human bones are a bit more complicated because the carbon deposited in your bones comes from what you eat. If that's land plants or animals it's fine but if it's fish you need to know a bit about the age of the water in which the fish lived as that can contain carbon significantly older than atmospheric carbon. On average, the surface oceans at the moment are around 400 years old in terms of the levels of radiocarbon they contain.

"My research interest focuses on ocean circulation. Different parts of the ocean have different radiocarbon signatures, some parts are older due to upwelling or younger due to enhanced exchange of CO_2 with the atmosphere, we can use the ^{14}C trapped in coral skeletons to reconstruct past ocean circulation and currents."

And learning how to measure and read radiocarbon signatures has meant the Dr Fallon has acquired substantial experience in working with accelerator mass spectrometers, the technology that allows you to measure ^{14}C ratios. After gaining his PhD at RSES on climate records from coral archives he moved over to the US and worked on radiocarbon dating at the Center for Accelerator Mass Spectrometry (CAMS) at the Lawrence Livermore National Laboratory, one of the world's top centres for ^{14}C dating. Now he's returned to ANU to run the new SSAMS facility in his old stamping ground at RSES. And he's looking forward to the challenge.

Introducing SSAMS

"The SSAMS facility is state-of-the-art in the new smaller machines that are now available," says Dr Fallon. "This new generation of machines is much more affordable than the older traditional accelerator mass spectrometers that operate in the millions of electron volts range. The massive 14 UD Electrostatic Tandem Accelerator operated by Nuclear Physics at RSPSE, for example, operates at over 15 million Volts. Its one of the world's most powerful electrostatic accelerator mass spectrometers. In terms of radiocarbon dating it's more powerful than the new SSAMS facility but it takes a whole suite of technicians to run and fills up a six storey purpose-built tower and adjoining building. And radiocarbon dating is just one small application among many at this huge facility.

"The new SSAMS facility, on the other hand, only requires one person to operate. It's an ultra-compact AMS system operating at 250 thousand electron volts, and it fits into a normal size laboratory. It's dedicated to radiocarbon dating and we expect that by having this facility we'll be able to double the amount of radiocarbon measurements that are currently being made in Australia.."

So, what's actually involved in determining the age of a material using radiocarbon dating? First you need to extract some carbon from the sample in the form of elemental carbon (see box on extracting carbon). This is then loaded into the machine.

After being accelerated through the machine the different carbon atoms are collected and their ratio is estimated. Dr Fallon points at the carbon 14 detector.

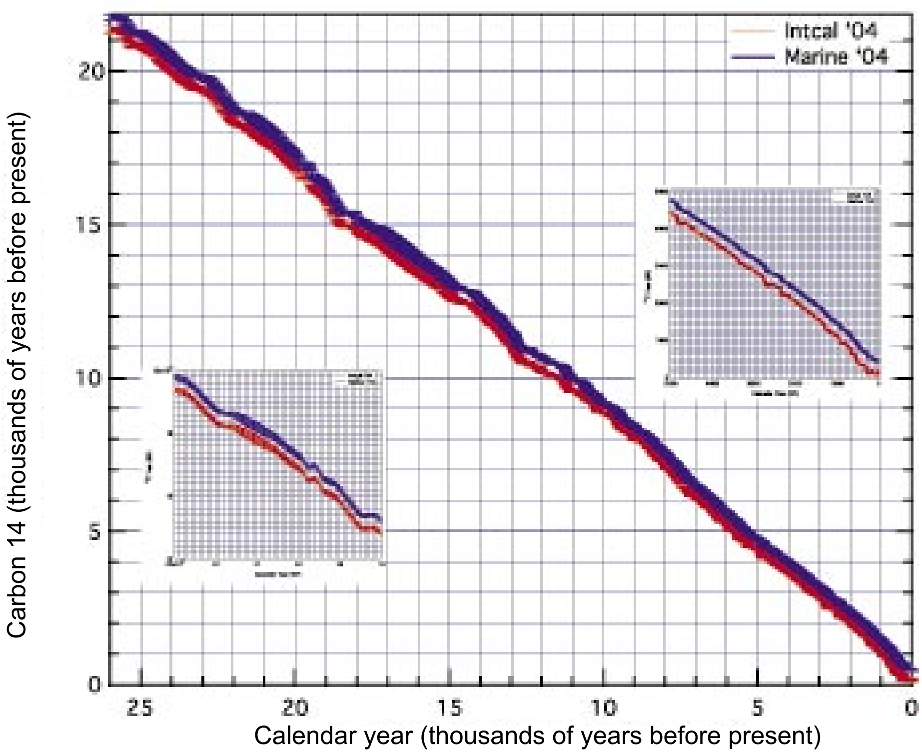
Inside SSAMS

"SSAMS has a caesium sputter source, it's the same sort of thing as they use on the SHRIMP ion microprobes at RSES" observes Dr Fallon. "Caesium is a metal but at slightly above room temperature it becomes molten. You heat up caesium and you get caesium vapour. The vapour hits an ioniser that ionises the caesium and these ions are then focused onto our carbon iron mixture. This causes negative carbon ions to be ejected.

"Inside the machine we have a series of electric fields to accelerate the carbon 12, 13 and carbon 14 atoms. We use magnetic fields to sort the atoms by mass. .

"There are two sections to SSAMS, a low

Atmospheric and marine radiocarbon and calendar age through time



By combining a large number of datasets such as sampling from tree rings and sedimentary dating studies it's possible to create a calibration curve to correct carbon 14 age estimates to a calendar year. (Reimer, P et al 2004. IntCal04 Terrestrial radiocarbon age calibration, 26 - 0 ka BP. Radiocarbon *46, 1029-1058)* energy area and a high energy area. The carbon atoms come out of the ion source around the first magnet and experience sequential injection which boosts the energy of the ions. On the low energy side of the machine the ions are energised to about 40,000 volts.

"The ions then enter the high voltage deck, which is surrounded by a wire Faraday cage to prevent arcing and protect people from getting too close. This area operates at 250,000 volts. The carbon ions now go into a stripper where argon gas interacts with the carbon beam stripping off two electrons, changing their polarity from negative to positive.

"Individual carbon atoms are separated by another magnet to spread them out according to their atomic mass and they are then collected and numbers are compared.

"One of the reasons you can't use a traditional mass spectrometers for this work is that the ratio between carbon 12 and carbon 14 is so large. Most spectrometers are good for detecting 1 atom in a million or even on in 10 million (10^7). But with carbon 14 you're searching for one atom in a trillion (10^{12}) and more. It's like counting needles in haystack, and even with SSAMS sophisticated sensitivity the process is still only about 40% efficient. That's enough for most determinations because to increase that sensitivity you need to spend big money and construct massive instruments like the 14 UD particle accelerator."

Will you take sugar with that?

So, now you've measured a carbon 14 ratio but because you're counting such a small number of atoms there are any number of factors that could throw out your result. Consequently, whenever you're doing an analysis you need to also run in the same batch of tests a standard by which you can calibrate the unknown result. These standards use carbon sources for which the exact ratio of carbon 14 to normal carbon has been very carefully measured.

"We have internationally accepted standards that we compare each measurement we make with," says Dr Fallon. "The first international standard was made in 1955 from sugar beet and was prepared in the form of oxalic acid. Though some 1000 lbs of oxalic acid was made, it's all been used up. The second standard was created in 1977 and also came from sugar beet but it's also hard to get these days.

"ANU has also produced it's own international standard which is known as ANU sucrose. Basically it's just sugar, but this sugar all came from one place and one growing season in 1971, so it all has the same C14 to C12 ratio. ANU sucrose is now used around the world in radiocarbon dating to help calibrate ^{14}C measurements.

"Mention ANU sucrose to most people and they'll think your talking fancy about sugar. Mention it to someone working with radiocarbon and they'll know exactly what you're on about.

"It's part of the legends surrounding this school that in times gone by certain researchers would use ANU sucrose to sweeten their tea. When I told this to my colleagues at Lawrence Livermore they were horrified that such an important standard was being used as a sweetener. I hasten to add that to the best of my knowledge this practice no longer takes place, besides we have ample supplies available."

Now can we estimate the age?

So, having extracted the best possible estimate of the carbon 14 ratio in your unknown material, and referenced this against an international standard, you'd think you could now calculate the age of the object. However, there's something else you need to take into consideration – carbon 14 ratios in the environment have not been constant through time. Yes, as suggested in the beginning of this article, they've stayed somewhat similar, but the actual level has fluctuated back and forth for a variety of reasons. One reason is that cosmic ray levels have changed over time meaning the amount of ^{14}C being generated has varied.

"So, SSAMS gives you a radiocarbon age based solely the calculation of how much ^{14}C has decayed," explains Dr Fallon. "But then there's a thing called a calendar age in which you convert the radiocarbon age to a specific calendar year. This involves

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Extracting carbon

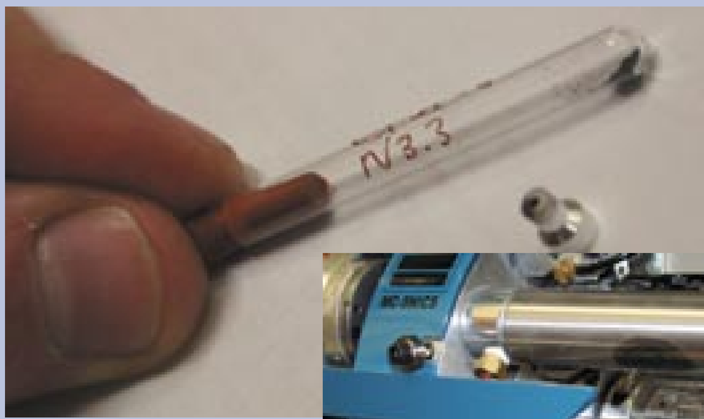
Extracting carbon from a piece of sample is a lot easier than squeezing blood from a stone but, as Dr Fallon explains, different types of samples require different techniques.

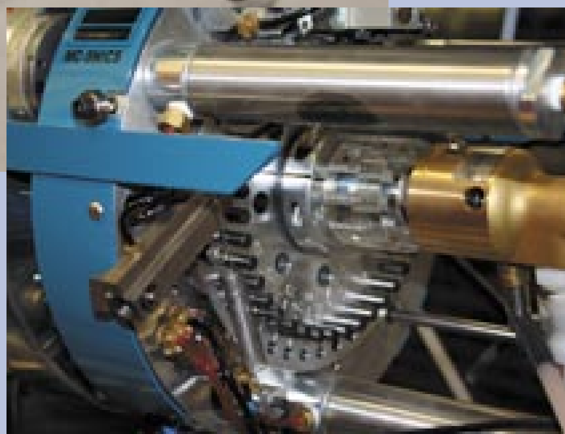
"For an organic sample, like wood, extracting carbon involves baking the sample at around 900 degrees to turn the carbon into carbon dioxide," explains Dr Fallon. "And you do that with an oxidiser, we use copper oxide. For something like a coral which is made of calcium carbonate, we simply dissolve a sub-sample in acid and collect the CO_2.

"From this CO_2 we then make 'graphite', as we call it. We put the CO_2 into a tube with some iron powder. The powder is simply a catalyst for the carbon to attach to.

"Then we mix this with hydrogen and you heat that at 570 degrees centigrade. This produces water and elemental carbon. The elemental carbon on the iron is then put into a sample holder and pressed into a tight little pellet. The sample is then loaded into the machine."

To perform an analysis you need about a milligram of carbon. Wood is around 40% carbon so you need around 3mg of wood to extract enough carbon, corals are 10% carbon meaning you need about 10mg of coral.





The powder in the test tube is elemental carbon extracted from a sample. It's packed into a sample holder (below the test tube) and then loaded into SSAMS (right) along with many other samples. The sample wheel holds 39 samples.

Home grown superconductors

Smart engineering adds a zip to heavy ions

Everyone's heard of superconductors but can you name the largest scale application of superconductors in Australia? It happens to be right here at ANU in the LINAC booster of the Heavy Ion Accelerator Facility at RSPSE (LINAC stands for Linear Accelerator). At the heart of the LINAC booster are 12 lead coated split loop resonators that boost the speed of heavy ions passing along the beam line. The lead coating is kept at just above absolute zero using liquid helium. At this temperature the thin layer becomes superconducting allowing electricity to flow without any resistance. In so doing it provides a highly efficient boost to the ion beam.

While the physics is impressive, so to is the fact that much of the engineering that has gone into making the system work has been developed in-house. Engineers and technicians in the Department of Nuclear Physics, the group that operate the Heavy Ion Accelerator Facility, developed all the essential expertise including the invention of innovative accelerating structures, the perfection of effective superconducting coating techniques as well as perfecting the cryogenic system that keeps it all at the right temperature. There are only of handful of such accelerator facilities in the world and all are funded and staffed at much higher levels than the one here.

The lead plated split loop resonators at the heart of the LINAC booster operate at a radio frequency of 150 MHz. Essentially what happens is that the charged particles that make up the ion beam (coming out of the big particle accelerator tower) are pulled towards the loops of the resonators. As they pass through each loop, the electrical polarity of loops is changed so the attractive force becomes a repulsive force pushing the ion away towards the next loop and so on.

Prior to plating the split loop resonators or polished and cleaned with high-pressure de-ionised water.

"The LINAC boosts the energy of the 14UD accelerator by up to 50% for a relatively modest financial investment," says Dr Nikolai Lobanov, the project engineer on the accelerator who invented multi-stub resonators jointly with project manager Dr David Weisser, and devised the process for applying the superconducting coating. "However, to achieve this we've had to be quite innovative in solving a number of engineering problems.

"The main incentive for developing a superconducting coating for the resonators is that they use substantially less electric power than resonators with normal conducting surfaces. The high electric field needed to accelerate the beam relies on high RF currents in the surface of the resonator. If the surface is a superconductor, then the power losses generated by the large currents are kept small – five orders of magnitude less than for a normal conductor."

(Above) Technical officer Justin Heighway in the Lead Plating Lab. (Right) A pneumatic arm moves the split loop resonators into the lead plating bath.

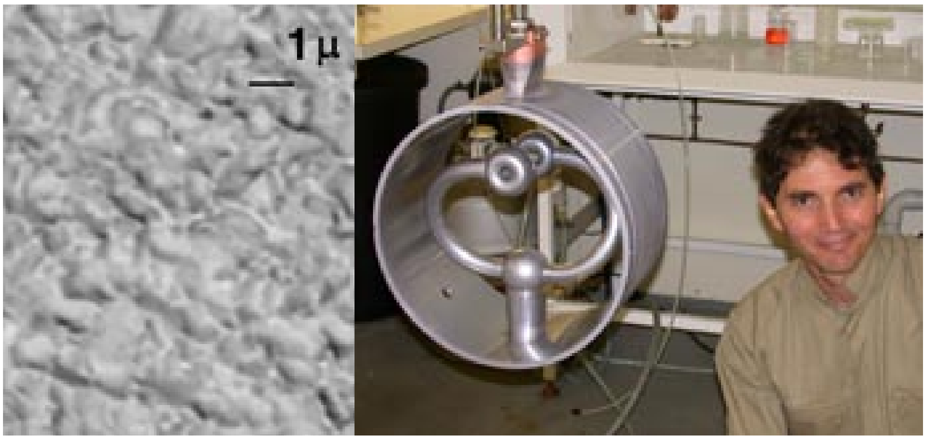
The resonators are made of pure copper and come in several configurations to accelerate different kinds of particles travelling at different speeds. To begin with, Dr Lobanov and his colleagues developed a system for coating the simpler quarter-wave resonators with niobium.

"We developed magnetron-sputtering system for the niobium," explains Dr Lobanov. "The magnetron-sputtering assembly was developed with the aid of a sophisticated computer simulation code called Superfish. This enabled us to tailor the magnetic field distribution in the magnetron to the shape of the resonator.

"While this coating technique worked well for the simple geometry of these resonators, unfortunately, it wasn't applicable for the more geometrically complex, split-loop and multi-stub resonators. For these we experimented with different approaches and eventually chose an electroplating process using a lead-tin alloy. As it turned out, this was an excellent solution, as it only required simple and relatively inexpensive equipment.

"Success didn't happen immediately because there were several problems that had to be overcome with the lead-tin plating approach. These included rough deposits with uneven finish, porosity co-deposition of organic additives and dendrite growth. Dendrites are microscopic worms of crystalline lead that grow out of the surface during plating. To work our way through these we developed a specialised lead-plating laboratory in which different combinations of plating procedures could be investigated.

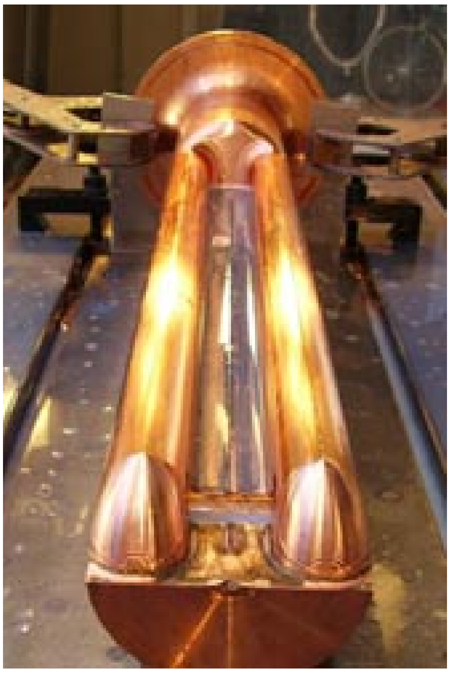
"As part of this process we came up



Dr Nikolai Lobanov with a lead-tin plated split loop resonator. When cooled down close to absolute zero this coating (seen under a microscope on the left) becomes superconducting.

with a new technique for mechanically polishing any unsatisfactory lead-tin surface and then re-plating it. This proved considerably easier and faster than the previous approach of chemically stripping the lead-tin and hand polishing the copper substrate. The new technique doesn't put at risk the integrity of electron beam welds used in the construction of the resonators and it only takes one week to re-plate three split-loop resonators. This is three times faster than the old process and more importantly, results in 100% better superconducting performance.

"We also developed a suite of materials and surface analysis procedures to characterise our deposited films. We undertook extensive microscopic and surface analyses to optimise the plating process and to determine the surface topography, surface structure and damage layer, grain boundaries and segregation of impurities and surface oxidation stages. These investigations were carried out with a range of tools including scanning electron and tunnelling microscopy, electron backscatter diffraction, transmission electron microscopy, energy dispersive X-ray spectroscopy, secondary ion mass spectroscopy, atomic force microscopy, Rutherford back scattering spectroscopy, elastic recoil detection analysis and Raman spectroscopy. You name it - we did it.



"These analyses were especially important in the suppression of dendrites produced by excessive plating currents.

"We also developed a new technique for in-situ investigation of the RF characteristics of full scale, superconducting resonators. We measured the intermodulation distortion conducted on the split-loop resonators, allowing more sensitive detection of non-linearity of the surface impedance as compared with conventional methods."

The successful development of the superconducting LINAC has proved that a small group of Australian engineers and scientists can successfully compete with major international major laboratories. In recognition of this achievement the work received the ANU Vice-Chancellor's Award for Excellence in 2006 is currently in the running for the Institution of Engineers excellence awards in 2007. (Note, this article focuses on the design of the superconducting coatings however their work is also in designing the resonators, RF control electronics, computer systems and cryogenic systems that allow the LINAC booster to work so effectively.)

More info:
Nikolai.Lobanov@anu.edu.au

A prototype two-stub resonator half way through the machining process (left) and after machining (above).

Launching SATOMGI

June saw the launch of a major new ANU educational initiative in managing government information. More than 50 senior public servants and business people involved in records management and personnel development gathered at the event which was jointly hosted by the National Archives of Australia.

The program, known as SATOMGI (short for a Systems Approach to the Management of Government Information) is a cross-campus initiative led by CSEM, with the Crawford School of Economics and Government, the Department of Computer Science and the ANU College of Business and Economics. The National Archives are a major partner in at least three of the courses on offer.

(From the right) Mr Ross Gibbs, Dr Zbigniew Stachurski and Professor Robin Stanton at the SATOMGI launch.

Mr Ross Gibbs, Director General of the National Archives of Australia, welcomed the launch of the program saying there had been a need for this type of course for some time and he is delighted to see that ANU is showing an active lead in this area. He thanked the Vice-Chancellor for his enthusiastic support of the program.

He observed that the National Archive is keenly aware of failures in document keeping processes and pointed out that the most common failure is the over-reliance by people of personal information storage systems, combined with people not participating in department-wide efforts to secure information.

As the lead academic in putting SATOMGI together, Dr Zbigniew Stachurski, Director of CSEM, also spoke at the launch pointing out that information management must be viewed as a systems challenge, an area in which engineers are well experienced.

SATOMGI is expected to be running in the next six months.

More info: www.anu.edu.au/CSEM/SATOMGI.php

Carbon of the ages

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incorporating information from a range of other age/radiocarbon studies. One of these involves studies on tree rings in which people have measured the ^{14}C in tree layers of a known calendar date. This gives you a curve and a database of ^{14}C values with which you can compare your ^{14}C samples.

"Of course tree rings don't give us a continuous 50,000 year history but they do go back to around 12,000 years ago, though this isn't based on one tree but many trees providing overlapping tree ring series.

"As you get further back in time you use other materials that can be independently dated like corals. These can be dated using uranium series dating, something in which RSES is also very skilled. We use the TIMS thermal ionisation mass spectrometer, and the new Neptune spectrometer. Then there's also areas where people find good sediment records, called varves, which can be independently dated in addition to radiocarbon dating.

"The calibration to calendar years is good going back to 26 thousand years. Beyond that it gets a bit patchier but there's an international research effort to add to the radiocarbon dating knowledge and the calibration curve gets better all the time."

Human interference

In addition to the background rate of ^{14}C varying, human activity has also complicated the process in recent centuries. Since the beginning of the industrial revolution atmospheric CO_2 levels have been rising. As most of this CO_2 was created by burning fossil fuel, which is much older than 50,000 years, it's not adding any additional carbon 14 to the atmosphere. Therefore it's effectively diluting the carbon 14 by adding to levels of normal carbon.

Then there's the effect of atomic weapons testing. This has generated increased levels of ^{14}C through the interaction of energetic neutrons with nitrogen atoms.

All these factors need to be considered and compensated for to produce a reliable estimate of age using radiocarbon dating, and the further you go back the larger the error.

"The further you go back the bigger the error bars," explains Dr Fallon. "And that's not necessarily just the reliability of the calendar calibration. It has a lot to do with just the measurement itself. The older the materials being tested, the fewer the radiocarbon atoms. As you get older you

An experimental rig for injecting the carbon samples as CO_2 gas directly into SSAMS. This by passes the need to use solid carbon and may transform radiocarbon research.

simply don't have that many ^{14}C atoms to count therefore you get into counting statistics being an error in the actual measurement.

"For instance, say something is 5000 years old, the error that comes off the machine is about 15 to 30 years, however when you add the calendar calibrations it might expand to plus or minus 100 years, which isn't too bad.

"For something 50,000 you're looking at errors of 500 years but with the calibration that might grow to 1,000 years. The machine error is fairly small though the calendar correction tends to blow this out a bit."

A one stop shop

Funding for the SSAMS facility came about through a ARC Linkage Infrastructure grant originally proposed by Professor Keith Fifield from RSPSE and Professor John Chappell from RSES.

"With the establishment of this SSAMS facility, ANU has become a one stop dating shop," comments Dr Fallon. "Basically any type of dating or analysis you'd like to do you now can at ANU.

"SSAMS provides us with state-of-the-art carbon 14 dating and I expect we'll be doing a lot of Australia's work in this area.

"We'll also be pushing the frontiers of what's possible with radiocarbon dating. One aspect of this is research into using CO_2 as the carbon source rather than converting the CO_2 into solid carbon.

"The idea of doing it this way is to be able to measure very small samples because very small samples don't always graphitise and that's our normal source. Also, whenever you do the graphitisation you can introduce a little contamination. For a normal size sample it doesn't really matter because the amounts are so small compared to the size of the sample. However, for a very small sample the proportion is larger and that can cause you some trouble. So, if you can eliminate that graphitisation step and just run things as CO_2 we believe you'll be able to achieve a better result."

"To give you some idea on this, you normally need about a milligram of carbon to work with. Wood for example is 40% carbon so you need around 4mg, corals are 10% carbon meaning you need about 10mg. However, what we're talking about for very small samples is things on the order of 10 micrograms. If we begin working at that level it'll open wide the field of carbon dating and allow some amazing things including dating of single compound extractions.

"At the moment there are only a few places in the world that are directly using CO_2 samples for radiocarbon dating so our research will be at the leading edge."

SSAMS arrived at RSES at the beginning of 2007. Setting it up and getting it operational has taken several months and it was officially launched at the end of June.

More info: Stewart.Fallon@anu.edu.au or Keith.Fifield@anu.edu.au

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Contacting CSEM

Director
Dr Zbigniew Stachurski
Phone: (02) 6125 5681
Email: Zbigniew.Stachurski@anu.edu.au

Editor, *Materials Monthly*
David Salt
Phone: (02) 6125 3525
Email: David.Salt@anu.edu.au

CSEM Office
CSEM
Department of Engineering
Bld #32, ANU ACT 0200

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