CSEM's
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SHRIMP story

Dr Trevor Ireland with the SHRIMP prototype (now known as SHRIMP I. The researchers who built it weren't sure if they were going to be able to make it work.

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THE AUSTRALIAN NATIONAL UNIVERSITY

It began as a bit of a gamble, but this SHRIMP is now huge on the world stage.

Here's a riddle: what's the link between the Moon rocks collected by Neil Armstrong, the discovery of the oldest crystals on Earth and one of the Australian National University's biggest technology success stories? The answer is the SHRIMP.

SHRIMP stands for Sensitive High Resolution Ion Micro Probe, and it was conceived, designed and developed in the Research School of Earth Sciences (RSES) during the 1970s.

The SHRIMP allows you to determine the age of microscopic samples of rock material by counting the atoms of specific elements found in that sample. The SHRIMP does this so well that it has become a pillar of geochronology, and today there are Australian-made SHRIMPs in several countries around the world. And yet, when it was first being developed it was seen as a bit of a high risk enterprise.

It's all about time and age.

Geochronology is the field of earth sciences engaged in determining the age of rocks and rock strata. A large part of this is done using radioactive elements. These elements, for example uranium and rubidium, decay over time into daughter isotopes, for example lead and strontium. The rate of this decay is known so if you can determine the amount of a radioactive element in a rock with the amount of its decay products then it's possible to calculate the age of that rock.

Of course, to make this analysis you need to know if there was any of the decay product already present in the rock when if was formed. Geochronologists look for certain minerals where these decay products don't naturally fit in the crystal lattice. Zircon, for example, is a mineral in which lead doesn't naturally sit, however it readily accepts uranium. If you find a zircon crystal it's likely the lead it contains resulted from radioactive decay of uranium rather then it being there when the zircon originally formed.

The early days of this type of analysis involved vast amounts of 'wet' chemistry as the elements you were interested in needed to be chemically separated from the minerals that contained them, and then mass-analysed for the isotopes in which you were interested. It was an exacting and time consuming process that involved many steps. It could only be done in the cleanest of labs using the purest of reagents, and errors could, and frequently did, enter into the process.

Dating Moon rocks

At the end of the 1960s humans landed on the Moon and returned with rock samples. The burning question of the time was: how old were they? NASA provided a handful of labs around the planet with lunar rocks and gave them three months to come up with an answer. One of those labs was the Geochronology Lab at ANU, headed up by Professor William Compston.

Professor Compston's team set about the task with enormous energy. They rebuilt their laboratory to guarantee minimum external contamination and made up the cleanest reagents they could. They handled and stored the Moon rocks with extreme care, processing them chemically, and then mass-analysing them at the highest

continued on next page

sensitivity and stability. From all this work they came up with an age of 3.8 billion years, which proved to be as good a determination as any of the other labs working on the project, though their overseas competitors had bigger, better resourced facilities.

However, there proved to be a greater legacy from this effort than just working out the age of a bunch of rocks from the Moon. Professor Compston later wrote:

"I hated having to operate a clean chemical lab, hated having to constantly check our chemical blanks, and hated the chanciness of thermal ionisation mass analysis which sometimes failed without warning." Consequently, he started looking for some technique that would allow an isotopic analysis to be made directly from the sample, without requiring chemical separation under ultra clean conditions.

The need for a SHRIMP

At that time electron microprobes had been developed that allowed chemical compositions to be determined in minerals through the measurement of the intensity of X-rays (emitted when the sample was hit with a beam of electrons). The electron probe performs well for major elements, but the background radiation restricted the measurement of trace elements, and geochronology is very much about trace levels of elements.

Zircon crystals, for example, are usually extremely small, often only tens to hundreds of microns in diameter. They may also have growth zones formed at different times over their geological history. For meaningful age determinations geochronologists need to sample spots of zircon less than 20 microns wide (and preferably not more than 5 microns deep) in order to stay within the same growth zone (see box on dating zircons). This adds up to only a few nanograms of zircon, which might contain amounts of uranium and lead for microanalysis that are a thousand times smaller again. No existing technology at the time could accurately assess such tiny amounts of material.

So, Professor Compston looked at whether secondary ion mass spectrometry (or SIMS) might be adapted to allow the measurement of low abundance elements. In SIMS a beam of ions is focussed onto the target material. The ion bombardment erodes (sputters) atoms and molecules from the target, some of which are themselves ionised. These secondary ions are gathered using electrostatic lenses and transferred to a mass spectrometer, which separates them according to their atomic mass.

However, this process had its own set of problems. The beam of primary ions striking the target knocks out a wide variety of molecular fragments, and the ion microprobes available at that time were unable to deal with the complex molecular interferences produced in the sputtering process. They could not resolve the specific atomic masses they were searching for.

Building the SHRIMP

Professor Compston saw the solution to this problem in the design of a large ion microprobe capable of high mass resolution while maintaining high sensitivity. In theory such an ion microprobe was possible and Professor H Matsuda of Osaka University had designed the parameters of the ion optics that should make it work. However, whether it was possible to turn the theory into a working machine was far from certain. It would require the use of a double-focussing mass spectrometer (simultaneous energy and mass refocussing) with a very large turning radius (magnet radius 1 m, electrostatic analyser radius 1.27 m). The machine would be large and weigh several tonnes.

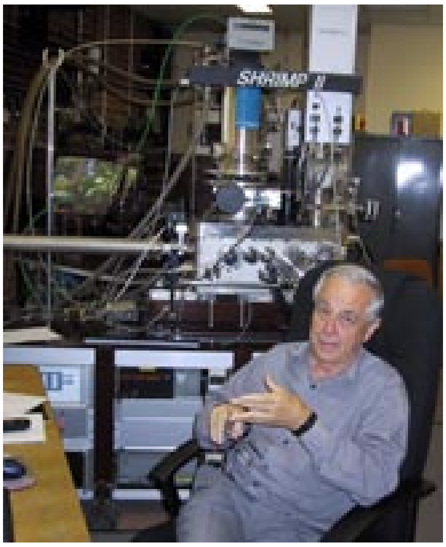
After extensive consultations and discussions Professor Compston was given permission to develop the ion probe, and so the first SHRIMP was constructed at RSES as an experiment over the period 1974-1980. Dr Steve Clement, an RSES graduate student who had designed his own mass spectrometer for his PhD, was engaged to design and help develop the new machine.

That it was called the SHRIMP was only natural given it was an **I**on **M**icro **P**robe with defining features of **S**ensitivity and **H**igh **R**esolution (coupled with a dash of Aussie humour because this machine was never going to be small). Building it, however, was no small feat as there were many challenges and frustrations to overcome. Professor Compston later wrote: "Practice can never be quite as good as theory. Matsuda envisioned perfectly uniform magnetic and electric fields and perfect geometry, but it is hard to achieve perfection with real materials and real engineering". There were problems with the magnets, which weighed some 6 tonnes, the field it was producing and the controls, but one by one each problem was conquered. The resulting instrument had a beam line over 7 m long and weighed more than 12 tonnes

By 1980 the SHRIMP was operating and the world had an ion microprobe capable of high accuracy isotopic analyses of trace elements in geological materials. And it wasn't long before its value was being demonstrated and it was establishing some major records. In 1983 it dated the oldest-known remnants of the Earth's crust (zircons from Mt Narryer, Western Australia, see box); by 1984 it was being used to study the anomalous isotopic compositions of titanium and magnesium in meteorites; by 1985 it was measuring hafnium isotopic compositions and by 1987 it was measuring sulfur isotopic compositions.

The evolving SHRIMP

By 1989 it was recognised that the performance of this prototype SHRIMP (now known as SHRIMP I) was limited by some of the basic features of its design, so over the next three years a greatly modified second generation instrument (SHRIMP II) was designed and built. At high mass resolution, SHRIMP II achieved four times the sensitivity of SHRIMP I. In



Professor Compston still keeps in contact with the SHRIMP project and, occasionally, can even be seen at its controls.

addition, it was capable of analysing areas down to 10 µm in diameter, was equipped for isotopic mapping, and included provision for fitting both a multiple collector and dual primary ion sources.

SHRIMP II was also developed as a commercial prototype with a computer-controlled, user-friendly interface installed for all operational components. Though each SHRIMP cost several million dollars, sales were made to institutions all around the world.

With advances in the ion optics it was believed that the SHRIMP design could be improved even further with much higher mass resolution. This was achieved by reversing the geometry of the optics (consequently this version was dubbed SHRIMP RG for Reversed Geometry) with the electrostatic sector following, rather than preceding, the magnetic sector. This significantly reduced refocussing aberrations however operating the the SHRIMP RG proved trickier than was originally envisaged and this version is still considered a research model.

SHRIMPs around the world

Today, the SHRIMP is regarded as a major tool for research and the minerals industry.

"There are 11 SHRIMPs currently in existence around the world," says Dr Trevor Ireland, the man currently in charge of the SHRIMP group at RSES. "We have three here at ANU, there are two in Western Australia, two in Japan, and one in Russia, China, Canada and the US. When you consider that each SHRIMP costs in excess of $3 million, that's not a bad sales record.

"And the feedback we receive from the institutions that have purchased the machine is excellent. If there's one problem with the SHRIMP it's that the demand for its services usually outstrips its available capacity. Once its set up for a specific type of analysis it's often running 24 hours a day, seven days a week.

"With three SHRIMPs on campus – the original prototype, a commercial version and a research version – we have more capacity than any other institution in the world for this type of work and yet the demand for time on our machines still greatly outweighs what we can provide."

And the SHRIMP story is far from over with a new machine currently being developed to specialise in the analysis of stable isotopes such as carbon, nitrogen and oxygen. The SHRIMP SI (SI stands for stable isotope) is a joint project between the ANU, Wollongong University; University of Melbourne; University of Queensland; Curtin University; University of Tasmania; CSIRO Exploration and Mining; Geoscience Australia; Australian Scientific Instruments.

All of which is very pleasing to Professor Compston, who still maintains contact with the work of the SHRIMP team, and occasionally can even be seen at the controls of the SHRIMP itself.

When you consider that this device is one of the best available technologies for dating terrestrial and extra terrestrial materials (some older even than our Sun) then it would be fair to label the SHRIMP as one of the great time machines.

More info: Trevor.Ireland@anu.edu.au or http://shrimp.anu.edu.au/

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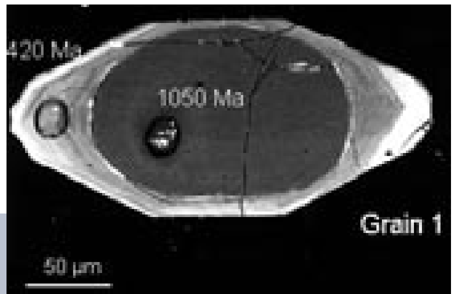


Dating zircons

The difficulty with dating rocks using zircon is that many rocks contain zircon crystals of many different ages. Zircon is so tough that when new rocks form from older rocks, zircon crystals from the older rocks survive. Even if a rock is melted, the old zircon crystals simply grow a new layer, like the toffee layer on a toffee apple (consider the image shown above of a zircon with an external layer with a different age to the core). Dating such mixed crystals by traditional methods, even one by one, gives meaningless average ages.

This is where the SHRIMP excels. It is able to measure the ages of layers within single zircon crystals as small as 10 micrometres (one hundredth of a millimetre) wide. The growth history of the crystal, which sometimes spans more than a thousand million years, is revealed.

SHRIMP works by firing a beam of oxygen ions (electrically charged oxygen atoms) at just one spot on the crystal. These ions are like tiny cannon balls. They hit the crystal and knock off atoms of all the elements in the crystal, including atoms of uranium and lead. These atoms are sucked away by electrical forces and then separated into their different types by magnetic forces (a process called mass spectrometry). The atoms of lead and uranium are counted and the age of the zircon at the target spot is calculated.

How important is it to determine the age of single crystals? Consider this example. Geologists were studying an ancient sedimentary rock from Mount Narryer, Western Australia. The rock was determined to be around 3 billion years old, which is amazingly old in itself. However, trapped in the rock were tiny zircon crystals, ancient sand grains less than half a millimetre long. The SHRIMP was used to measure the age of those crystals, finding just a few that came out at a staggering 4.2 billion years old. These were the oldest pieces of the Earth ever found, and an invaluable window on our planet's earliest formation. (The Earth is believed to be only 4.5 billion years old.)

(See the story on the next page for another example of zircons in geochronology.)

Travelling down a zircon time tunnel

Carl Spandler and a geological sample from north-eastern New Calendonia. By closely examining zircon crystals contained in the rock it's possible to reconstruct aspects of the tectonic history of the region.

Attempting to reconstruct the geological history of a region is not unlike a detective attempting to reconstruct an old crime scene. The detective scours the scene where the crime took place searching for clues knowing that what he or she finds will have been changed by time, the elements or people and animals interfering with the site.

For the geologists it's even tougher. The 'clues' they can see are the rocks that are at or near the surface, and these rocks have often gone through several cycles of alteration that completely change their chemical and physical nature.

Consider an igneous rock that gets weathered into sand. These sediments collect and may form sedimentary rock. These might become buried, experience extremes of heat and pressure and metamorphose into a different type of rock before being exposed at the surface. While this happens, over millennia, tectonic processes may have transported the rock vast distances. A geologist then examines these rocks and attempts reconstruct the processes by which they, and the surrounding landscape, formed. Considering that almost everything about the rock may have changed since it was originally formed, this is a big ask.

It's been known for many years that zircon crystals contained in rock can often serve as a valuable time capsule allowing the age of a rock to be determined. In recent years, however, it's been realised that by closely examining zircon crystals (often described simply as zircons) it's possible to gain a much better understanding of the life history of the surrounding rock. And this is exactly what Mr Carl Spandler, a PhD student at the Department of Earth and Marine Sciences, has demonstrated in his studies on the tectonic history of north-eastern New Caledonia.

Zircon or zirconium silicate ($ZrSiO4$) is a ubiquitous trace mineral found in most igneous rocks as small crystals or grains. It has long been used to date geological samples.

"When a zircon crystallises out of a magma forming part of an igneous rock it's like setting a geological clock," says Mr Spandler. "The crystal lattice of the zircon readily incorporates uranium atoms but excludes lead. Over geological time scales the uranium radioactively decays into lead. Because there was no lead in the zircon to begin with, the ratio of uranium to lead serves as an accurate measure of the age of the zircon and the rock that contains it."

Zircon crystals are usually microscopic, measuring less than a tenth of a millimetre in diameter – next to invisible to the human eye. Finding them requires thin rock sections to be prepared from rock samples (sections that are around 30 microns thick), and then detailed microscope studies need to be made to map where the zircons lie.

Once you've found the zircons it relatively easy for the SHRIMP to analyse spots on the crystal to determine their contents of uranium and lead (and thus the ratio of these two elements) and then provide an age of the crystal. (See the story on the SHRIMP for more details.)

"The SHRIMP has been used very effectively to age zircons in rocks for many years," says Mr Spandler. "More recently, geologists have realised that there is a lot more that zircons can tell us about the rocks they're found in. This is primarily because they are so tough. They can withstand enormous pressures and temperatures.

"The igneous rock in which they formed might weather down into sediments and these sediments might be metamorphosed into a new rock types. However, because they are so tough, zircon crystals retain some of their original character as they get carried along in this process. Parts of the crystal may carry evidence of what's been happening around the crystal, while the core of the crystal often preserves clues on its origins."

"The zircon crystals I have been studying came from metamorphic rocks I collected in New Caledonia. Our analysis has provided a fascinating key to what's been happening there.

"Close examination of the zircon crystals reveals they are made up of three different zones. There is the unmodified core of the crystal in which the crystal lattice is laid down in regular layers. Then their are core areas which contain tiny pockets or micro inclusions of minerals. We've labelled these regions as being altered core regions. Finally, around the unaltered and altered core is a metamorphic rim, a zone of zircon that could only have formed when the rock bearing the crystal was under intense pressure and temperature.

"In a sense, these three regions correspond to different 'life' stages of the rock. The unaltered core provides us with information on the formation of the original igneous rock. SHRIMP dating of these cores revealed the zircons, and the rocks that contained them, were originally formed around 55 million years ago.

"An analysis of the micro inclusions in the altered core reveals a range of minerals that provide strong evidence that the zircons were exposed to seawater, probably when the rock or sediment containing the crystals was on the ocean floor.

"SHRIMP dating of the metamorphosed rim of the crystal gives an age of around 44 million years. This suggests the rocks containing the zircon were drawn down into the Earth approximately 44 million years ago in a process of subduction in which one tectonic plate slides under an adjoining plate. This created the conditions of temperature and pressure sufficient to metamorphose the rock.

"Finally, this body of rock was brought back up when the subduction zone jammed tossing the rock to the surface where they now form part of north-eastern New Caledonia.

"Zircons can't tell us everything but when combined with what we know from other studies in the area they do provide us with a valuable window on how the region evolved. As it has turned out, our results fit neatly into what is already known about this region however our analysis has revealed several new pieces of information that simply couldn't have been uncovered by other means.

"We always knew that zircons were valuable time capsules. Now it seems that with a little care they might also prove to be microscopic rock diaries providing rich new detail on the life cycle of rocks."

More info:
Carl.Spandler@anu.edu.au

Dissecting a crystal

Pictured below is an example of one of the zircons Carl examined. The top image is a catholuminescence image while the bottom image was taken using back-scattered electrons.

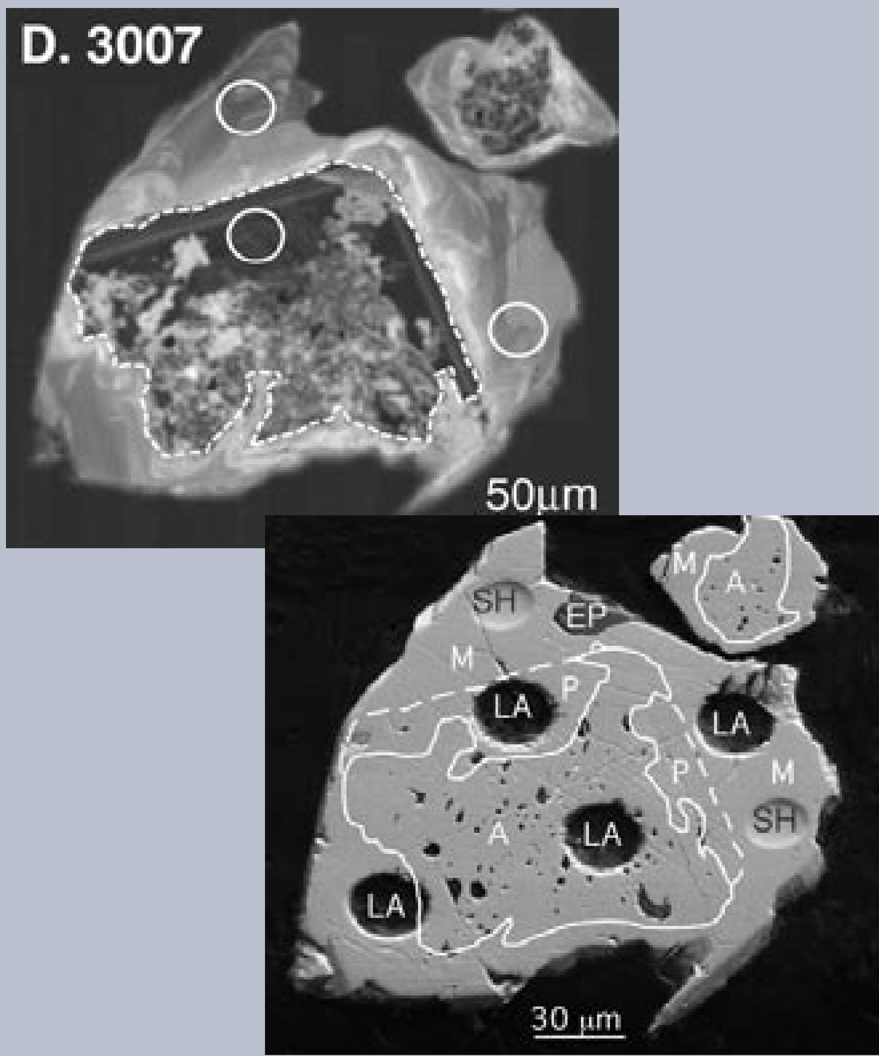
The dotted line in the top image separates the core of the zircon from its metamorphosed rim (marked M in the lower picture). This core is futher subdivided into a pristine (unaltered zone, marked P in the lower image) and an altered area (marked A) which carries micro inclusions of minerals.

The circles in the top image mark where SHRIMP sampling was done to determine the age of the rim and the core.

The lower picture shows where other forms of sampling was undertaken (LA stands for laser ablation; EP stands for electron probe.)

When the information is combined it turns the zircon into a window on time providing insights on the life of the rock in which it was found.

One interesting point to note in the lower image is the small amount of the zircon needed to perform a SHRIMP analysis as compared to the large hole when sampling is done via laser ablation.



A new materials network

ARNAM and ECRs

Starting out is never easy for an early career researcher. That applies to any field but possibly more so in materials where research is often multi disciplinary and involves labs and facilities spread over several institutions.

You're keen, you've got good ideas and you want to make a difference; but you still have to learn how to play the game. How do you form effective collaborations with other scientists from different institutions (including other early career researchers)? How do you produce effective ARC applications? Where do you find a mentor to help you learn the ropes? Where do you find support to attend conferences? How can you get recognition and acknowledgement in your field for your research?

If these are issues that affect you then you should sign up to ARNAM, a new ARC research network established to enhance communication, networking and collaboration in materials science around Australia. ARNAM is short for the Australian Research Network in Advanced Materials, and one of its specific aims is to assist early career researchers (ECRs) establish themselves.

"The network's charter is to basically add value to our science through meaningful interaction," says Professor Jim Williams, Director of the ANU Research School of Physical Science and Engineering and Convenor of the new network. "One area we're particularly focused on is helping early career researchers. Established career researchers have many advantages when it comes to building relationships. They know who's who, how to get money and build collaborations. It's a lot tougher for early career researchers and research students.

"ARNAM will be committing significant resources towards helping research students and ECRs in making contacts, gaining access to expertise, conferences and facilities around Australia and internationally, and finding mentors."

ARC's Research Networks are a recent addition to its Discovery and Linkage programs. The Networks aim to foster and catalyse highly creative, interdisciplinary research that is not averse to risk taking, and which aims to create exciting and novel research themes.

Professor Williams outlines plans for ARNAM at a recent planning meeting held at Monash University.

ARNAM, the network for advanced materials, has been awarded over $300,000 per year for five years to enhance the impact and outcomes of materials research in four broad themes: high-tech materials (IT and communications); functional materials; advanced manufacturing; and materials for a sustainable Australia.

~ARNAM will add value to our science through meaningful interaction~

"The hope is that we will not only enrich the research in these four chosen areas, but we'll also open up entirely new cross-disciplinary opportunities under the heading of emerging materials technologies," says Professor Williams.

"How ARNAM will operate is still being worked out. We have involved representatives from the materials research community from all over Australia, and we're currently engaged in a planning process to finalise the management committee and sub-committees. ARNAM will work with other institutions like Future Materials and Materials Australia to ensure it's engaged with industry and other materials related groups. We'll also be promoting international collaborations.

"Workshops, a website and a communications program are all currently being discussed. The first workshop supported by ARNAM was on the topic of nanoindentation. It was held at the ANU Kioloa campus in March, and more than 75% of the over 50 attendees were ECRs or research students. Over the next six months we'll be announcing a range of other activities and structure for the network.

"While we're still ironing out the details on how the network will function, one thing is clear; there is widespread enthusiasm from all quarters for the network to assist early career researchers and research students."

So, if you're just starting out in the world of materials research, ARNAM is one network that just might make your journey that little bit easier.

More info: http://www.materials.com.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

Administration:
Tiina Hatherall
Phone: (02) 6125 3525
Email: Tiina.Hatherall@anu.edu.au

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CSEM Office
Fax: (02) 6125 0506

Phone: (02) 6125 3525

Postal: CSEM
Dept of Engineering
Bld #32, ANU ACT 0200

Location: Room E212, Dept of Engineering, (Bld #32), cnr of North Road and University Ave, ANU

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