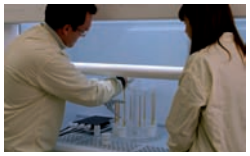
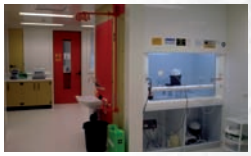


Technology development program

Background

GEMOC's research, training and Industry Interaction programs require a high level of geochemical analytical technology, which is provided by the state-of-the-art facilities available to the Key Centre. Continual development of both technology and innovative analytical and microanalytical approaches is required to meet our research aims and the needs of our industry collaborators. GEMOC develops new analytical strategies as required, to determine the chemical and isotopic composition of geological materials (both solid and fluid) in solution and *in situ*. Special emphasis is being placed on the development of advanced *in situ* microbeam methods. These developments are transmitted to industry via open and collaborative research, through technology exchange visits and workshops, and as an integral part of the training program.

THE ANALYTICAL INSTRUMENTATION and support facilities of the Macquarie University Geochemical Analysis Unit (GAU) represent a state-of-the-art geochemical facility. In 2005 this will be enhanced by installation of the Triton (TIMS) and the relocation of the stable-isotope operations of the former Centre for Isotope Studies, previously housed at CSIRO, North Ryde, to GEMOC.

- The GAU *contains:*
  - a Cameca SX-50 electron microprobe
  - a Cameca SX-100 electron microprobe (installed January 2003)
  - three Agilent 7500 ICPMS (industry collaboration (two installed October 2004))
  - a custom-built UV laser microprobe, usable on the Agilent ICPMS
  - five New Wave/Merchantek laser microprobes (two 266 nm, three 213 nm) for the MC-ICPMS and ICPMS laboratories (industry collaboration)
  - a New Wave/Merchantek excimer (193 nm) laser microprobe, based on a Lambda Physik OPTex laser
  - a Nu Plasma multi-collector ICPMS
  - a Nu Plasma high resolution multi-collector ICPMS (installed November 2003)
  - a Spectro XLAB2000 energy-dispersive XRF with rocker-furnace sample preparation equipment
  - a LECO RC412 H_2O-CO_2 analyser (delivered September 2003)
  - clean labs and sampling facilities provide infrastructure for ICPMS, XRF and isotopic analyses of small and/or low-level samples

"The analytical instrumentation and support facilities of the Macquarie University Geochemical Analysis Unit (GAU) represent a state-of-the-art geochemical facility."

One of the new clean-room laboratories.

- Experimental petrology laboratories in GEMOC include piston-cylinder presses (9, 15 and 40 kb), hydrothermal apparatus, and controlled atmosphere furnaces.
- The Centre for Isotope Studies has provided access to extraction lines and gas-source mass-spectrometers for stable-isotope analysis of fluids and minerals; these facilities will be moved to GEMOC during 2005.

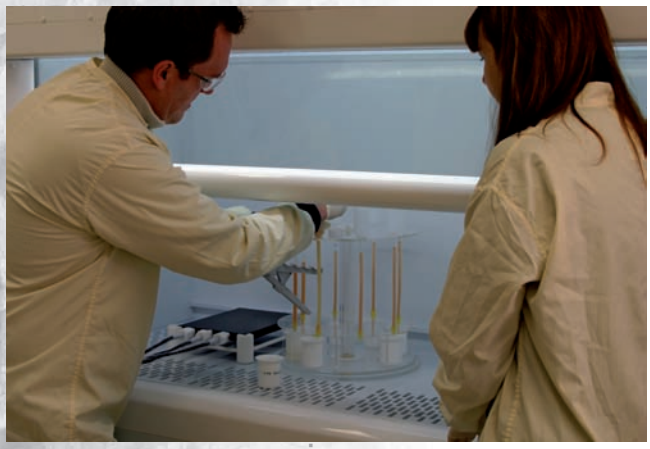
THE GEMOC FACILITY FOR INTEGRATED MICROANALYSIS (FIM) AND MICRO GIS DEVELOPMENT

GEMOC is continuing to develop a unique, world-class geochemical facility, based on *in situ* imaging and microanalysis of trace elements and isotopic ratios in minerals, rocks and fluids. The Facility for Integrated Microanalysis now consists of four different types of analytical instrument, linked by a single sample positioning and referencing system to combine spot analysis with images of spatial variations in composition ("micro-GIS"). All instruments in the FIM have been operating since mid-1999. Major instruments are being replaced or upgraded in 2002-2004 through the $5.125 million DEST Infrastructure grant awarded to Macquarie University with the Universities of Newcastle, Sydney, Western Sydney and Wollongong as partners.

the facility provides:

- The capability to image both major- and trace-element distribution in a sample, as an interpretive tool and as the basis for higher precision spot analysis of trace-element concentrations and isotopic ratios
- Co-registration of images and spot data from different instruments, and use of digitised images to locate spots with a precision of better than 5 µm
- Analytical capability for most elements of the periodic table at ppm to sub-ppb levels
- *In situ* isotopic-ratio measurement for a range of elements, at the precision required for geologically useful results
- New approaches to data interpretation through application of micro-GIS principles

Ion exchange in action in the new clean laboratories for isotope separation.



Electron Microprobe: for imaging and point analysis of major and minor elements

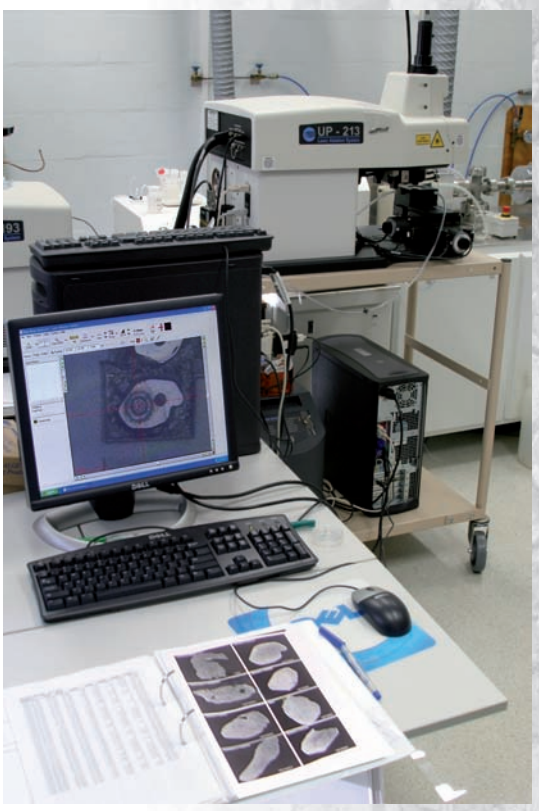
Scanning Nuclear Microprobe: for imaging and point analysis of trace elements at ppm levels

Laser-ablation ICPMS Microprobes: for point analysis of a wide range of trace elements at low ppb levels

Multi-collector Sector ICPMS with laser microprobe: for high-precision *in situ* analysis of isotopic ratios

Micro-GIS system: A key aspect of the Facility is the co-registration of images and point analyses collected on all instruments. All data for a sample, from any of the instruments or from a bench microscope, are in the same coordinate system and can be overlaid in the computer to enhance interpretation.

When fully developed, images from one instrument will be read into the computer of another instrument and used to guide the analysis. Major-element maps from EMP, or trace-element maps from the nuclear microprobe, can be linked directly to images from petrographic or cathodoluminescence microscopes, BSE or SEM, or to spot analyses.



Zircon analysis for TerraneChron™ using the LAM-ICPMS.

CURRENT STATUS

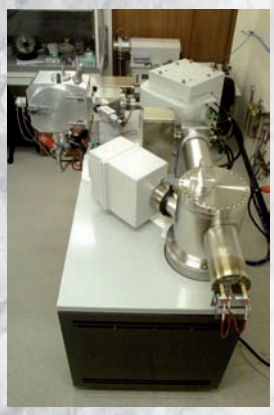
Electron microprobe (EMP): The original GEMOC EMP is a CAMECA SX50, installed in 1993; it routinely produces high-precision analyses of major and minor elements with a spatial resolution of one micron, as well as high-quality images of major-element (> 0.1 wt%) distribution over areas up to 45 x 45 mm, by stage-scanning with five fixed wavelength-dispersive spectrometers. In early 1999 the EMP was upgraded with an energy-dispersive X-ray detector to allow rapid and simultaneous mapping of all major elements. In early 2003 a new CAMECA SX100, with a similar configuration of spectrometers, was installed and the SX50 is now used mainly for the imaging and analysis of zircons, in connection with *TerraneChron*™ applications and basic research.

Scanning nuclear microprobe (SNMP): This instrument was built by Dr C. G. Ryan (with GEMOC funding contribution) as a separate beam line on the HIAF particle accelerator at CSIRO, North Ryde. The design incorporates several complementary types of detector, a new high-resolution probe-forming system and an innovative optical system, and provides both images of trace-element distribution and spot analyses, with a lateral resolution of 1-3 µm. Current capabilities cover micro-PIXE, micro-PIGE and quantitative element imaging. Due to the closure of CSIRO's North Ryde site during 2004, the SNMP beam line has been relocated to the accelerator facility at the University of Melbourne.

Laser Ablation ICPMS microprobe (LAM-ICPMS): The original GEMOC LAM was installed in December 1994 using a Perkin-Elmer ELAN 5100 ICPMS (later replaced by an ELAN 6000), attached to a UV laser ablation microprobe built for GEMOC by Memorial University, Newfoundland. In 1999 the ICPMS was replaced by a Hewlett Packard 4500, and in 2000 an Agilent 7500S ICPMS was added. In 2004 two new Agilent 7500CS instruments were purchased (one primarily for solution work), and the 7500S replaced the HP4500 for zircon analysis at the end of 2004. The 7500S and one 7500CS now routinely provide quantitative analyses of > 30 elements at sub-ppm levels in minerals, glasses and metals, as well as precise U-Pb dating of zircons. The laboratory currently uses three Nd:YAG LAM systems: a Quantel Brilliant laser that can deliver beams of either 266nm or 213nm light, a Merchantek LUV 266nm system, and a Merchantek/New Wave LUV213 nm system. Spatial resolution varies with the application, but typically is on the order of 30-40 µm. Each LAM is fitted with a computer-driven sample stage to provide co-registration of X-Y coordinates with the other instruments. On-line data reduction with the GEMOC-developed "GLITTER" software enhances laboratory productivity and data interpretation; the software is marketed internationally by New Wave Research.

Multi-collector LAM-ICPMS microprobe (MC-LAM-ICPMS): A fully-equipped Nu Plasma MC-ICPMS is an integral part of the Facility. This instrument combines a laser ablation microsampler, an Ar-plasma ionisation source, and a multi-collector magnetic-sector mass spectrometer, to provide high-precision *in situ* analysis of isotope ratios in geological materials. The instrument uses either a New Wave 193 nm system based on an Lambda Physik OPTex excimer laser, a New Wave 266 nm Nd:YAG laser, or a New Wave 213 nm Nd:LAG laser. The MC-ICPMS also can be used in solution mode, with either a standard nebuliser or a desolvating nebuliser, to provide high-precision isotopic analysis of a wide range of elements, including many not accessible by standard thermal ionisation mass spectrometry. A second Nu Plasma instrument, with high-resolution capabilities and a retardation filter to enable U-series work, was installed late in 2003.

Above: Installation of the new TIMS, early 2005. Below: The assembled machine.



A Triton thermal ionization mass spectrometer (TIMS): was purchased in 2004 following a successful ARC LIEF application led by Professor Simon Turner and Dr Bruce Schaefer (Monash University), and was installed early in 2005.

Applications in use and under development include:

Laser Analysis (*in situ* point analysis)

- U-Pb geochronology of zircons from igneous and metamorphic rocks
- Hf isotope analysis in zircon for studies of crustal generation, mantle evolution and crust-mantle interaction
- Re-Os dating of sulfides in mantle-derived xenoliths
- Nd isotope analysis in apatites, titanites and other REE-rich minerals
- Sr isotope analysis of carbonates, feldspars, apatites, pyroxenes
- Pb isotope analysis of sulfides and silicates
- Stable isotope ratios of Fe, Mg, Zn, Cu and other cations in appropriate minerals from ore systems and mantle rocks
- Multi-element trace element analysis of silicates, sulfides, oxides and diamonds

Solution Analysis

- Re-Os — determination of mantle depletion ages and isochron ages in whole rocks, ilmenites and chromites; dating of sulfide assemblages in ore bodies
- Lu-Hf — crustal genesis, mantle metasomatism; Lu-Hf dating of garnet peridotites, eclogites, granulites; basalt genesis
- Rb-Sr, Sm-Nd, U-Pb, Pb-Pb — faster than TIMS; simplified low-blank chemistry, no time-dependent mass fractionation, hence greater precision

- U, Th-series analysis – for dating of young processes, ranging from magma genesis to weathering and erosion
- Multi-element analysis of trace elements in whole-rock samples

PROGRESS IN 2004

1. Facility for Integrated Microanalysis

a. Electron Microprobe: A fully optioned Cameca SX-100 electron microprobe with five crystal spectrometers and an energy-dispersive spectrometer, to replace GEMOC's aging but still highly functional SX-50 instrument, arrived in late December 2002, and was installed in January 2003.

b. Laser-ablation ICPMS microprobe (LAM): During 2004, the LAM laboratory produced large volumes of data for eight Macquarie PhD thesis projects, several projects carried out by international visitors and Honours students, in-house funded research projects and industry collaboration. These projects included the analysis of trace elements in the minerals of mantle-derived rocks, in sulfide minerals and in a range of unusual matrices. *Over 5000 U-Pb analyses of zircons were carried out*, related to projects (including *TerraneChron*™ applications) in Scandinavia, China, Italy, southern Africa and Australia. The LAM laboratory also routinely provides data for projects related to mineral exploration (diamonds, base metals, Au) as a value-added service to the industry (see *Research Highlights*).

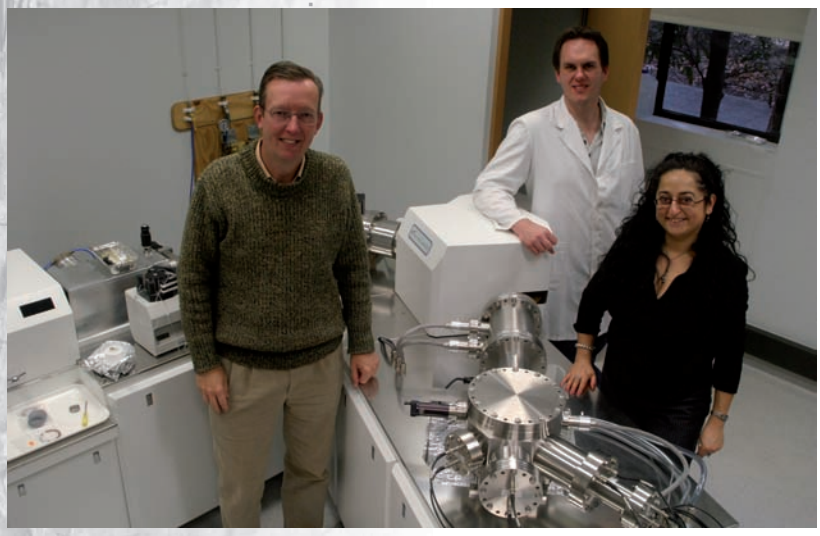
Three of the TerraneChron™ team: Ayesha Saeed, Elena Belousova and Eloise Beyer.

The HP 4500 instrument which has been dedicated primarily to U-Pb dating of zircons, was replaced late in 2004 with the existing Agilent 7500S, while two new Agilent 7500CS instruments were acquired to allow one instrument to be dedicated permanently to laser-probe applications, while the other is available for solution analysis.

c. MC-ICPMS: A multi-collector magnetic sector ICPMS for *in situ* (laser-ablation) and solution analysis of isotopic ratios was installed in November 1998. The instrument is the Nu Plasma (Nu05), designed and manufactured by Nu Instruments of Wrexham, UK. The instrument was producing good data only a few days after installation, and has continued to do so. Merchantek EO (now New Wave Research) provided a 266 nm UV laser microprobe (under a collaborative agreement; see below) for use with the MC-ICPMS and a 213 nm laser microprobe was purchased in 2000. During 2002 the MC-ICPMS was fitted with a New Wave/Merchantek excimer (193 nm) laser microprobe, based on a Lamba Physik OPTex laser. This has been used mainly for the analyis of Hf isotopes in zircon, where its different absorption characteristics have provided somewhat greater spatial resolution and beam intensity than were available using the 213 nm laser. In 2004, we purchased three new New Wave Nd:YAG lasers, two 213 nm and one 266 nm, and these also have been used on the MC-ICPMS for different applications.

The rapid growth in the use of the *TerraneChron*™ application (see *Research Highlights*), coupled with the demand for *in situ* Re-Os analysis and stable isotope analysis, led to severe competition for instrument time on the MC-ICPMS. An order was placed early in 2003 for a second instrument, funded by the DEST infrastructure grant, and this instrument (Nu34) was installed in November 2003; it has operated satisfactorily throughout 2004. Nu34 is equipped with a retardation filter and high-resolution capability, specifically for U-series analysis. Methods for the analysis of other isotopic systems (Re-Os, Sm-Nd, Lu-Hf, Pb) have been transferred to Nu34 as well, and considerable time was spent in 2004 doing comparisons of the performance of Nu05 and Nu34 with respect to these isotopic systems.

Major applications during 2004 (see *Research Highlights*) included the high-precision analysis of Hf in zircons to trace lithosphere evolution and magma-mixing histories in granitic rocks, the analysis of copper and iron isotope compositions in minerals from ore bodies, the analysis of Sr isotopes in clinopyroxene phenocrysts from lavas, and Re-Os dating of single grains of Fe-Ni sulfides in mantle-derived rocks. We carried out Re-Os studies on xenoliths from the Kerguelen oceanic plateau, S. Africa, eastern China and Taiwan, north Africa and Sicily.



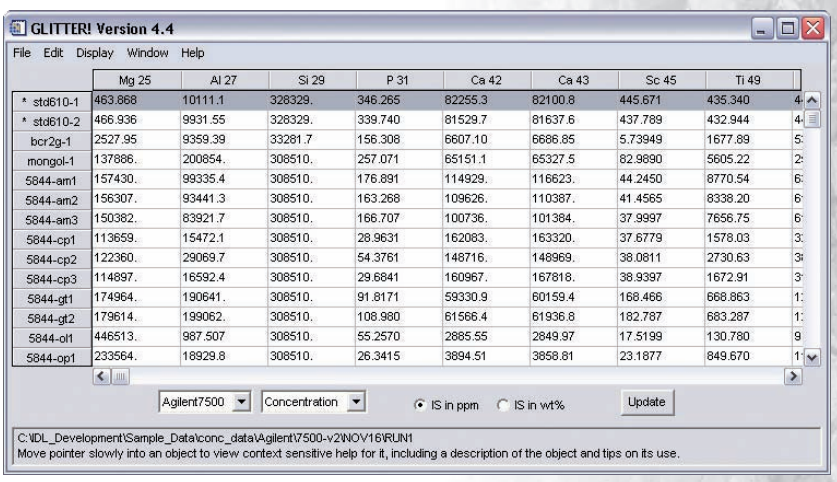
Norm Pearson (manager, GAU), Peter Wieland and Suzy Elhlou with the Nu34 MC-ICPMS.

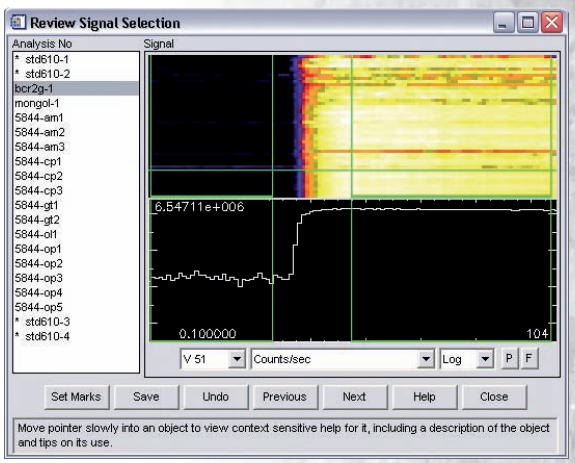
A major project was started on the isotopic composition of Fe, Cu and selected other elements in sulfides and whole rocks from major ore bodies, in a collaboration with Anglo American. Further developments were made in 2004 for the *in situ* analysis of Mg isotope compositions in mantle olivine and other phases in mantle peridotites. This involved the characterisation of potential standard materials and the investigation of the matrix effects on isotopic fractionation. Detailed studies were undertaken (both by laser and in solution) on olivine, pyroxene and amphibole in spinel peridotites from several localities, with the results providing further evidence of significant Mg isotopic fractionation during partial melting and metasomatism.

d. Scanning Nuclear Microprobe: The pending closure of the CSIRO North Ryde site forced the shutdown of the SNMP in late 2003. The beam line was dismantled, and re-installed on the University of Melbourne accelerator during 2004. It is in operation for 2-3 days/week.

e. Laboratory development: Funding from the DEST infrastructure grant contributed toward the building of a new suite of clean-room laboratories on the second floor of building E5B, which include facilities for the work on U-series chemistry to be carried out by Dr Simon Turner and his group. Construction began in September 2003, and the facility was handed over in April 2004. The new facility, which is being used primarily for isotope separations, provides an ultra-clean environment within a 3-stage pressurized volume; it contains 6 Class 3500 work areas, three for radioactive isotopes and three for other activities.

f. Software: Chris Ryan further refined the GLITTER (GEMOC Laser ICPMS Total Trace Element Reduction) software, our on-line interactive program featuring linked graphics and analysis tables. This package provides the first real-time interactive data reduction for LAM-ICPMS analysis, allowing inspection and evaluation of each result before the next analysis spot is chosen. Its capabilities include the on-line reduction of U-Pb data. The use of GLITTER has greatly increased both the flexibility of analysis and the productivity of the laboratory. New Wave Research market the software together with their laser microprobe equipment; GEMOC provides customer service and backup through Macquarie Research Limited. Ten copies of GLITTER were sold worldwide in 2004, and the software appears to have achieved industry-standard status; more than 45 copies are in use worldwide, in forensics and materials science, as well as earth science applications. During 2005, Norm Pearson, Will Powell and Chris Ryan are further developing GLITTER, and Will Powell is the customer interface for the distribution of a new version (GLITTER 4.4).





The new GLITTER 4.4.

2. Laser development

GEMOC continues to benefit from an industry partnership with New Wave Research (formerly Merchantek EO), a major US manufacturer of laser ablation systems, which has made Macquarie its Alpha Test Site. New Wave donated their 266 nm Nd:YAG UV laser ablation sampling system to GEMOC and their new 213 nm system was delivered early in 2000. Both lasers can be coupled to the Nu Plasma MC-ICPMS, allowing high precision isotope ratio determinations to be performed on minerals *in situ*. The mobility of the probes has allowed them to be used on the quadrupole ICPMS instruments as well, in a range of applications. A Merchantek/New Wave Research 193 nm excimer system based on a Lambda Physik OPTex laser was delivered in March 2002 and was finally commissioned late in the year. Three more New Wave laser systems were acquired during 2004, a 266 nm and two 213 nm, representing a major upgrading of the instrument park and giving redundancy to limit downtime.

The 213 nm lasers are now used for most of the U-Pb work, especially where small grains are being analysed, while the excimer system is used mainly for Hf-isotope analysis. The 266 nm systems have proven most useful for analysis of sulfides, and for other stable-isotope applications.

"During 2005, Norm Pearson, Will Powell and Chris Ryan are... developing... GLITTER 4.4."

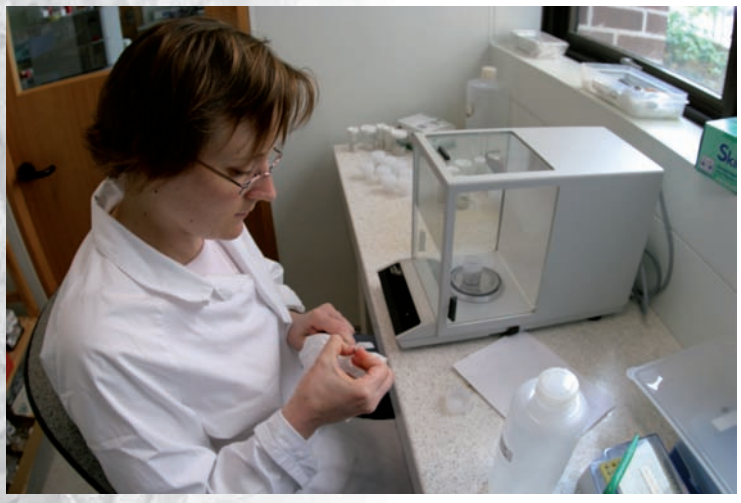
3. Energy Dispersive XRF

A Spectro XLAB2000 energy-dispersive X-ray spectrometer was installed in November 2000 in a joint venture with Tasman Resources. This instrument utilises the polarisation of scattered X-rays to substantially reduce backgrounds and enhance detection limits. The XLAB2000 uses a specially designed 300 W palladium X-ray tube that improves its performance for the lighter trace elements, and also for major elements, relative to the earlier instrument. In addition, this spectrometer is fitted with a silicon detector, of a type recently developed, that eliminates the low-energy "tail" from the lightest elements, and enables all major elements to be measured in a fused glass to levels below 0.01%. The capability of the instrument to provide major element analyses of a quality at least comparable to the more expensive conventional crystal spectrometers has been thoroughly evaluated and confirmed. This instrument provides highest-quality data for major elements and for most trace elements to sub-ppm levels. The operation of the equipment is enhanced by a 100 position sample loader, one of the first to be installed on a Spectro instrument, and the purchase of a rocker furnace for sample preparation. During 2003 over 5000 samples were analysed for major and trace elements, providing data to student theses, in-house research projects, and industry collaborators.

4. Solution analysis

An Agilent 7500 ICPMS is regularly used to provide trace-element analyses of dissolved rock samples for the projects of GEMOC researchers and students, and external users, supplementing the data from the XRF.

The *in situ* analysis of the Rb-Sr, Lu-Hf, Sm-Nd and Re-Os systems by laser ablation microprobe has required the development of corrections for isobaric overlaps (eg ^{87}Rb on ^{87}Sr), and has demonstrated that these corrections can be done with very high precision in the Nu Plasma MC-ICPMS. This has allowed us to simplify the ion-exchange chemistry traditionally used to obtain clean element separations for standard mass-spectrometry analysis. A new scheme for the dissolution of rocks, separation of Sr, Nd, Hf and Pb, and isotopic analysis using the MC-ICPMS in solution mode provides precise whole-rock isotopic analyses that are faster, simpler and ultimately cheaper than those obtained by traditional methods.



Stéphanie Touron preparing samples for isotopic analysis.

During 2004 improvements were made to the separation procedures for Cu and Fe, in support of the laser-probe studies, and the procedures for separation of Sr, Nd and Hf were modified.

A new LECO RC412 H_2O-CO_2 analyser (delivered September 2003) replaced an outdated unit, and is providing high-quality analyses to complete whole-rock analyses by XRF and solution-ICPMS.

5. Centre for Isotope Studies (CIS)

The Centre for Isotope Studies (CIS) was a consortium operated by the geoscience departments of the New South Wales Universities, CSIRO Exploration and Mining, and Petroleum Resources using jointly-purchased mass-spectrometers housed at the CSIRO in North Ryde. The facility allowed staff and students to obtain both radiogenic and stable isotopic analyses and used technical staff jointly funded by the University members; Dr Richard Flood of GEMOC has been University Consortium Convenor.

GEMOC has developed its own clean laboratories to prepare solutions for radiogenic isotope analysis by MC-ICPMS, but has used the stable isotope separation facilities at North Ryde. CIS was one of the rare laboratories where staff and students could obtain C, O, N, S and D analyses including the routine determination of O in silicates. Dr Anita Andrew developed techniques for C-isotope analysis of diamonds using very small sample sizes (0.1 mg), which allows analysis of microdiamonds or multiple fragments of different zones of small stones. This is now an essential part of GEMOC capabilities.

CSIRO's North Ryde site was closed in 2004, but the laboratories are still in operation. During 2005 Dr Andrew will move the stable isotope facilities to GEMOC, where they will form a self-funded entity, and GEMOC will continue to benefit from this collaboration.