Earth Chemistry Introduction

The chemistry and isotope chemistry of natural materials is highly indicative of provenance and process throughout geological history. Our studies range in time from the earliest solar system through to processes that are actively taking place today, and in scope from planetary systems to individual molecules.

Most of our analytical work involves detailed analysis on the microscale, or concentrating trace elements from larger samples for high precision analysis. Isotopic systems can reveal both the nature of the processes involved (stable isotopes) as well as the timing of events (radiogenic isotopes), while chemical abundances can reflect protolith contributions and processes affecting various systems including biologic systems. As revealed in this year’s research contributions, analytical work can be applied to topics in tectonics, ore genesis, metamorphic petrology, paleoclimate, paleoecology and regolith dating.

Geobiology

A new direction in Earth Chemistry is the study of organic matter and biomarker molecules extracted from sedimentary rocks by Dr Jochen Brocks. Biomarkers give information about ancient microbial ecosystems and their environments. Earth Chemistry and RSES have committed to a new laboratory facility for biomarker research including a new mass spectrometer. We were able to secure central support for the construction of a new laboratory and construction started on 21 November and will be completed by end-February 2007.

SHRIMP

This year has seen systematic improvements in our abilities to measure stable isotope ratios with SHRIMP II in negative ion mode. A combination of terrestrial-magnetic-field suppression, mount redesign, and suppression of secondary ions induced by the electron gun, had all contributed to pulling analytical errors well into the subpermil range. SHRIMP I has had a computer refit, even though the 14-year-old Apple Mac II has performed flawlessly, and a stage drive upgrade such that stage positions can be computer controlled. This allows unattended computer-controlled analyses. SHRIMP SI progresses with the ordering of many of the major components and final designs for most assemblies being carried out or completed.

Personnel

This year we welcome APF Fellow Dr Ian Buick who has moved from Monash University to continue his studies in combinations of metamorphic petrology, conventional light isotope geochemistry of carbonates (O-C) and silicate (O) rocks, U-Pb geochronology and mineral-scale trace element geochemistry. Dr Yuri Amelin of the Canadian Geological Survey, Ottawa, has accepted a position funded by the Planetary Science Institute and is expected to arrive in early 2007. Dr Amelin’s specialty is high precision geochronology, focusing on the earliest chronology of the solar system.
ARC and MEC

This year saw one ARC Discovery awarded to Dr. Jochen Brocks for research into saline Lake Tyrrell mud. Further in this research, an ANU / U.C. Berkeley / Macquarie University collaboration in the Lake Tyrrell Metagenome/Biomarker project was successful with the award of US$1,920,911 from NSF to our collaborator Prof Jill Banfield (UC Berkeley) for the genome sequencing part of the project. Dr. Masahiko Honda and collaborators were successful in securing ARC and MEC funding for a multicollector noble gas mass spectrometer, and Dr Jochen Brocks received MEC funding for an automated solvent extraction system.

Research Highlights

Geochronology and Ti-thermometry of eastern Himalayan granitoids
Amos B. Aikman

Opening the possibility of more multiple analytical techniques on individual zircon grains: case study of U/Pb and (U+Th)/He dating, so called “double-dating”
C.M. Allen

Signatures of extinct nuclides preserved in Earth’s oldest (> 3600 Ma) rocks shed light on the “dark ages” of early planetary history
Vickie C. Bennett

Ancient steroids and the evolution of complex life
Jochen J. Brocks

Ar diffusion in muscovite
Julien Célérier

Some insights into the SHRIMP U–Pb analysis of xenotime
Andrew Cross

How chalcophile is Re? An experimental study of the solubility of Re in sulphide mattes.
Raúl O. C. Fonseca

Exploring the potential of allanite as a geochronometer of high-grade crustal processes
Courtney J. Gregory

Redesign of SHRIMP mounts to minimize geometric effects on isotopic and inter-elemental fractionation.
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Cosmogetic 21 Ne exposure dating of young basaltic lava flows from the Newer Volcanic Province, southwestern Victoria, Australia
M. Honda

Electron-Induced Secondary Ion Emission (EISIE): An important consideration in the analysis of light isotopes in insulators
Ryan Ickert

Solar Wind Oxygen in Lunar Metal Grains
Trevor Ireland

Complex histories of melt inclusions in archean komatiites
Antti Kallio

Extrasolar Planets and the Dry Brown Dwarf Desert
Charles H. Lineweaver

What happens to zircon during subduction?
Daniela Rubatto

Marginal Basin Development in the Svecofennian orogenic province 2.30 to 1.85 billion years ago
R.W. Roye Rutland

The Geology, Geochemistry and Geochronology of the El Abra Mine, Chile, and the adjacent Pajonal–El Abra suite of intrusions
Dianne L. Valente

Further advances in measuring the oxygen isotopic compositions of granite zircon using SHRIMP II
Ian Williams
Granitoids are frequently found in regions that have experienced prolonged crustal thickening. This spatial and temporal association places significant requirements on models of orogenesis. The distribution and timing of granitoid magmatism bears on the thermal budget and locus of tectonic activity within the orogen. Their geochemistry can provide insights into the sources and distribution of protolith materials and, in some cases, the structural architecture of the orogen. The nature of granitoid formation is such that magmas naturally concentrate many trace elements that may be characteristic of their source regions and melting processes. These elements are often conveniently incorporated into neoformed accessory phases, the age of which may in some cases be determined through the use of radioactive decay schemes. This has provided a valuable tool with which to understand the evolution of modern and ancient orogenic zones.

Zircon is a mineral that is particularly valuable in studies of granitoid petrogenesis. It is ubiquitous in granitic rocks and many other crustal rocks. It not only contains sufficient quantities of radioactive U and Th to be dated using a variety of analytical techniques, but it also hosts important isotopic tracers such as Hf and O. Furthermore, it is characterized by very low diffusivities of most elements such that their concentrations and/or isotopic ratios generally retain the characteristics of the zircon’s formative environment.

Recent studies have demonstrated the temperature dependency of Ti concentration in the zircon lattice (e.g. Watson and Harrison, 2005). We have developed a protocol for measuring Ti content ([Ti]) rapidly with high accuracy and precision, using the SHRIMP 2 Multi-collector (S2MC). This method also allows for high spatial resolution such that [Ti] measurements may be easily correlated with the results of conventional ion-probe U-Pb dating. This approach allows us to study the distribution of age, crystallization temperature, and trace elements (U+Th) within individual zircon grains.

The results of analyses of zircons from four granitoid sample suites yielded a spectrum of crystallization temperatures that are consistent with the processes of magma genesis inferred from bulk geochemistry. Offset temperature peaks in two anatetic samples correctly distinguish between vapor-present and vapor-absent melting, and a broad distribution skewed to higher temperatures, derived from a plutonic body, matches that predicted by fractional crystallization models.

Positive correlations of both [Th] and Th/U ratio with crystallization temperature were observed in data from all sample suites. These are attributed to co-crystallization with monazite, effectively starving the melt of Th. Similarly, core-to-rim transects through individual zircon grains, confirm the decreasing Th/U proportional to decreasing age and
temperature, and increasing degree of fractional crystallization. Furthermore, these factors are also correlated with Cathodoluminescence (CL) zonation. Analyses conducted parallel to CL-zones typically yielded similar ages, temperatures, Th/U and [Th+U]. However, analyses conducted across CL-zones frequently show large temperature and trace element excursions, which are interpreted to reflect thermal and compositional instability in the zircon's growth environment, possibly associated with convection and/or magma recharge. Anomalous areas that appear to cross-cut CL zonation yielded younger ages, lower temperatures and lower Th/U. They are attributed to localized re-crystallization associated with late/post magmatic fluids.

Opening the possibility of more multiple analytical techniques on individual zircon grains: case study of U/Pb and (U+Th)/He dating, so called “double-dating”

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The ability to U-Pb date zircon grains rough mounted on double-sticky tape opens up fields of research based on multiple geochemical analyses of individual grains, especially when the rim of the grain is of interest. In the LA-Q-ICP-MS facility, (Excimer laser plus Agilent 7500 ICP), we can ablate a small percentage of a grain, date it using the U-Pb system, and then have 99% of the grain left for other investigations such as (U+Th)/He dating, or Hf-Lu work (Figure CA-1). Thus far we have taken advantage of this analytical capability by U-Pb and (U-Th)/He dating zircons from active river sands from North America and from the Himalaya (Reiners et al., 2005; Campbell et al., 2005). Using this “double-dating method”, we can date when a zircon crystallized, and when it last cooled through 200°C, i.e. approached within a few kilometres of the Earth’s surface. This research has been going on for 4 years and we now have a substantial data set for North America. In this work about 20% of the U-Pb dated grains (~1100 for 6 river samples) are selected for (U+Th)/He dating. The selected grains have simple age and compositional structure.

This work, in part, has been to prove assumptions made in the first “double-dating” paper (Rahl et al., 2003) that double-dating can be used as a much more accurate provenance tool than either dating method individually. For instance, a Mississippi River zircon dated at 1100 Ma using U-Pb could have several potential sources: the Cordillera, the mid-continent rift, or the Grenville Province of Canada and the northeastern U.S. Grenville bedrock currently being eroded can be expected to have (U+Th)/He ages of about 1000-800 Ma based on region Ar-Ar work. Grains exposed in the Appalachian Mountains should have Appalachian orogenic ages, from about 430 to 220 Ma, if Triassic thermal disturbances are included in this grouping. Cordilleran rocks have 200 Ma and younger (U+Th)/He ages. What double dating signature the mid-continent rift would express is unknown. In a lower Mississippi River sand two distinct groupings of grains with U-Pb ages ranging from 1000-1200 Ma are encountered in the total age range of 3450 to 30 Ma: 1) (U+Th)/He ages of 1040 to 850 Ma, and 2) (U+Th)/He ages of 440 to 220 Ma. Although these zircons are indistinguishable from the traditional U/Pb dating method, clearly they have distinct sources, probably freshly eroded Grenville bedrock in the first case, and Appalachian sources (sediments uplifted during orogenic events, and now recycled into the modern river system) in the second. With such tools estimates of the amount of zircon recycling in modern sediments can be made.
Figure 1. Whole zircon from Kentucky River sand with laser ablation pit.


Signatures of extinct nuclides preserved in Earth’s oldest (> 3600 Ma) rocks shed light on the “dark ages” of early planetary history

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Revealing the mechanisms and timescales of planetary formation, including that of Earth, is a major quest of 21st century science. Owing to vigorous tectonic processing the earliest history of the Earth, during the 600 myr “dark ages” between the start of planetary accretion at about 4.567 Ga as dated by primitive meteorites and the beginning of the rock record at about 4.0 Ga is poorly understood. Yet, it is during this time period that the major chemical domains of the Earth formed, including the metallic core and silicate mantle, the growth of the first continents and the development of the oceans and atmosphere.

Here we are applying novel radiogenic isotopic approaches, the tracking of the signatures of “extinct” nuclides as preserved in the oldest rocks, to provide new types of information on Earth’s early history. Extinct nuclides are radioactive isotopes with short half-lives, on the order of 1 myr to 100 myr years, that were present at the time of solar system formation, but have now completely decayed into their daughter elements. Thus variations in the isotopic compositions of the daughter products of short half-life parents, if they can be found in the rock record, must record chemical events that occurred early in Earth’s history while the parent isotopes were still “alive”. Whilst various short half-life isotopic systems have applied to the study of meteorites, which formed and were chemical differentiated within a few 10’s of millions of years of solar system history, it has proved much more difficult to use this approach on Earth. A system with potential for early Earth studies is the decay of $^{146}\text{Sm}$-$^{142}\text{Nd}$ (half-life = 103 myr).

As part of our on-going studies of early Earth history we have undertaken high precision $^{142}\text{Nd}$ isotopic measurements of samples of the two most extensive early Archaean terranes, the Itsaq complex, southwest Greenland and the Narrayer gneiss complex, western Australia. Itsaq complex samples range in age from 3.63-3.87 Ga and include both felsic and mafic lithologies. The 3.73 Ga gneisses from the Narrayer gneiss complex are the oldest rocks in the Yilgarn craton. The Itsaq samples have $^{142}\text{Nd}/^{144}\text{Nd}$ compositions that are 8-17 ppm higher than modern terrestrial compositions (Fig. 1); five of the oldest (ca. 3.85 Ga) gneisses yield similar values of +15 ppm. The new results confirm (Bennett et al, 2006) and extend the high precision (< +/-5 ppm) data of Caro et al. (2006) and further document the existence of terrestrial $^{142}\text{Nd}$ variations arising from the decay of now extinct $^{146}\text{Sm}$. The 3.73 Ga gneisses from the Narrayer gneisses complex overlap in age with the Itsaq samples, but have distinctly lower $^{142}\text{Nd}/^{144}\text{Nd}$ compositions of ca. +4 ppm. The relative isotopic differences preserved in contemporaneous samples from two widely separated terranes points to the existence of early formed, chemically diverse mantle sources at 3.7 Ga. The Narrayer gneisses either formed from a mantle source with a lower
average Sm/Nd than the Itsaq source, or the Narryer mantle was partially remixed with a more LREE enriched source prior to 3.7 Ga, but after $^{146}$Sm was largely decayed. The Sm-Nd system also contains the commonly used long half-life isotopic scheme of $^{147}$Sm decaying to $^{143}$Nd (106 byr half-life). Using the information from the coupled long and very short half-life Sm-Nd systems in the same rocks provides additional age controls. The combined $^{143}$Nd- $^{142}$Nd data from the oldest (ca. 3.85 Ga) measured terrestrial samples require formation of differentiated silicate reservoirs in the first 60 myr of Earth history, that is shortly after core formation and points to very rapid timescales for the formation and chemical differentiation of terrestrial planets including Earth.

![Graph showing Nd isotopic compositions](image)

**Figure 1.** High precision $^{142}$Nd isotopic compositions expressed as parts per million deviations from modern terrestrial samples. The crystallization ages in Ga (billions of years) are indicated on the right axis. Early Archaean samples from West Greenland show anomalous isotopic compositions; contemporaneous Narryer gneisses have smaller isotopic effects pointing to an early formed, but chemically heterogeneous mantle source. Error bars indicate +/- 3ppm measurement precision.


Ancient steroids and the evolution of complex life

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Charles Darwin cited the apparent absence of fossils from rocks of Precambrian age (now dated at >0.542 billion years, Ga) as a valid argument against his concepts on the origin of species. One hundred years after Darwin, these concerns were resolved and petrified remains of prokaryotes (bacteria and archaea) were detected in all periods that preceded the Cambrian, dating as far back as 3.5 Ga. The oldest fossils of eukaryotes, the group of nucleated organisms that includes all animals, fungi, protists and plants, date back to at least 1.5 Ga. However, eukaryotic diversity and abundance remained low well into the Neoproterozoic (1.0 – 0.542 Ga) and the evolutionary pace to new eukaryotic forms and shapes remained more than ten times slower than in the following Phanerozoic. The first convincing evidence for animals, at this stage still mere clusters of cells, was detected in Chinese phosphorites, 600 Ma old. However, early eukaryotes were microscopic and generally lacked skeletons that are easily preserved. How do we know that the scarcity, low complexity and slow evolution of eukaryotes in the Precambrian are not an artefact of fossil preservation?

Biomarkers, or molecular fossils, provide an independent record of life in the Precambrian that can be used to test our understanding of early eukaryote evolution. Biomarkers are the hydrocarbon fossils of biological molecules such as lipids. A variety of steroid lipids are exclusively found in the cell membranes of eukaryotes, and the fossils of these steroids can be preserved in sedimentary rocks that are hundreds of millions of years old. Unfortunately, the study of minute traces of genuine Precambrian steroids is extremely difficult because of ubiquitous contamination with biomarkers from younger sources. As a consequence, published distributions of steroids in Precambrian rocks look curiously similar to steroids found in the Phanerozoic. To see a genuine Precambrian biomarker distribution, we devised a new technique (microsonication) that distinguishes between traces of Precambrian steroids and younger additions. Using the new technology, we discovered a distribution of eukaryotic biomarkers in 1.6 to 0.6 Ga old rocks from Australia, North America and China that are distinct from anything observed later in Earth history. The oldest steroids that we found are biosynthetically simple and could reflect evolutionary precursors to modern membrane lipids. The new results show that steroids remain generally rare throughout most of the Precambrian and the full range of known structures only becomes prevalent after 0.7 Ga ago. The simplicity and scarcity of steroids appears to be analogous to the rarity of eukaryotic body fossils in the Precambrian and suggests that the unusual microfossil distribution uncovered by Palaeontologists reflects ecological reality and is not simply preservational artifact.
Figure 1. An extant eukaryote growing on 1.65 Ga old braided river deposits of the Kombolgie Formation at Bardedjilidji in Kakadu National Park, Northern Territory, Australia. The early ancestors of this tree already existed when the rocks were deposited, but biomarker evidence from contemporaneous sea sediments suggests that they were still rare and probably ecologically unimportant.

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Ar diffusion in muscovite

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Muscovite is one of the most utilised minerals in ⁴₀Ar/³⁹Ar geochronology and thermochronology. Despite its importance, no experimental study of the diffusion behavior of Ar in muscovite – key to assigning closure temperature – has yet been published. This is largely attributable to the narrow experimental range between temperatures high enough to effect measureable (>5%) diffusive loss whilst not exceeding the phase stability field. Instead, the thermochronological community has tended to adopt a nominal value for closure temperature (e.g. Hodges, 1991) based on empirical calibrations. In the past year of research I have been able to produce preliminary results from diffusion experiments which have enabled determination of Arrhenius parameters for Ar diffusion in muscovite; activation energy (E) ≈ 60 kcal/mol and a frequency factor (D₀) ≈ 10 cm²/s [similar to that of phlogopite; Giletti (1974)]. These values correspond to a closure temperature (T_c) of 370°C for a grain with a 100 µm radius cooling at 10°C Ma⁻¹.

As starting material, we use a large muscovite crystal from a pegmatite in the Harts Range, Central Australia. This sample has been analysed by the ⁴₀Ar/³⁹Ar step-heating method revealing a uniform release pattern over >90% of the gas release (Fig. 1). We thus infer that it has been closed to loss of ⁴₀Ar since 325.8±2.5 Ma. Size fractions of the starting material of 38-45 µm were loaded in gold capsules together with AlOH₃ to buffer Al₂O₃ and H₂O activity during the experiments. The capsules were run in a piston cylinder apparatus for 1-6 weeks at temperatures ranging from 660°C to 730°C at 10 kbar pressure, ensuring that run conditions were well within the phase stability of muscovite. Treated samples were subsequently analysed by the ⁴₀Ar/³⁹Ar method to determine f (fractional loss), in turn allowing calculation of D (diffusion coefficient).

Examination of experimental run products by transmitted light microscopy revealed that under hydrothermal run conditions, muscovite grains are undergoing grainsize reduction and/or recrystallisation. This bimodal grainsize distribution is reflected in the age spectra of the hydrothermally treated samples, which differ from that expected from outgassing of grains with a single diffusion size (blue curve, Figure 2). We have constructed a simple model which represents the effects of mixing a bimodal grainsize distribution under conditions of diffusive loss. Preliminary results indicate that the observed form of the age spectra for the experimental run products may be reproduced by varying 1) the loss parameter (Dt/r²), 2) the mass ratio of large to small grainsize domains, and 3) the enhanced diffusion parameter resulting from reduced grainsize. Together, these results indicate that incorporation of smaller diffusion domains leads to an overestimation of fractional loss. Calculations of closure temperature assuming loss from a single domain will therefore be underestimated.
Take for example the model in Figure 2. Best fit modelling indicates an $f$ substantially lower than the bulk loss resulting in a $D$ around an order of magnitude lower than that shown in Figure 1 b. This, in turn, results in a $T_c$ about 25°C higher.

Figure 1. Figure 3. a) $^{40}\text{Ar}/^{39}\text{Ar}$ age spectra of the Harts Range pegmatite before and after hydrothermal treatment in a piston cylinder apparatus over a range of experimental conditions. b) Arrhenius plot of diffusion coefficients calculated from experimental data using an infinite cylinder model, against reciprocal absolute temperature. Plot assumes a single diffusion domain size.

Figure 2. Observed and model age spectra for the experimental run products. Blue and green lines indicate the form of the age spectra that would be expected for the large and small grainsize domains respectively. Red lines indicates the combined age-spectra assuming a mass ratio of 17:1. Note that the model fit could be significantly improved through the incorporation of more than two grainsize domains.


Some insights into the SHRIMP U–Pb analysis of xenotime

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Introduction

Recent years have seen the mineral xenotime (YPO$_4$) proven as a valuable chronometer of mineralisation, metamorphism and sediment diagenesis. In these settings, xenotime is usually found as small (<20 μm) overgrowths and single grains, their small size restricting U–Pb isotopic studies to SIMS techniques. Xenotime preferentially incorporates the HREE (mainly Gd, Dy, Er, Yb) and also U, Th, Ca and Si into its structure. HREE contents typically range between ~15 and 25 wt % while U and Th can range up to ~7 wt %. Chemical contrasts between standard and unknown (especially in U) can result in SHRIMP U–Pb ages that are elevated by >20%. Correcting for this is a major challenge. Fletcher et al. (2000) recognised a correlation between increasing U contents and SHRIMP U–Pb ages and proposed a method of U abundance scaling to correct for this effect. More recently Fletcher et al. (2004) proposed matrix correction factors that consider the role of U, Th and REE in xenotime SHRIMP U–Pb analysis.

Present study

As a prelude to a number of proposed xenotime SHRIMP U–Pb studies, a series of experiments were carried out to determine optimal analytical conditions. The three xenotime standards used in these investigations (MG1, BS1 and Xeno1) vary in age and also have contrasting U, Th and REE contents. Initial experiments trialed energy filtering as a technique to eliminate the U–Pb matrix effects. This was tested as energy filtering increases the proportion of high energy ions collected, which Shimizu (1978) and Shimizu and Hart (1982) have shown to be less chemically fractionated relative to the low energy ion population. Although effective in reducing scattered ions observed at the $^{204}$Pb and background mass stations, energy filtering failed to reduce the U–Pb matrix effects. Experiments show that YbO/Y$_2$O ratios within a high U sample monitor the U–Pb fractionation. However, this effect is not consistent between samples and therefore cannot be used as a correction technique.

Xenotime U–Pb matrix correction protocols adopted for future experiments are similar to those used by Fletcher et al. (2004) and necessarily involve electron microprobe chemical determinations for U, Th and $\Sigma$REE for each spot prior to SHRIMP analysis. Corrected Pb/U ages are referenced to the primary standard MG1 which is used for the Pb/U–UO/U discrimination correction. BS1 and Xeno1 are used as secondary standards which monitor the effect of U, Th and REE on the raw Pb/U ratios. Matrix corrections are then derived from the chemical composition of each spot and the level of U–Pb fractionation relative to its reference age, via a simple least squares method. Interestingly, xenotime U–Pb matrix correction factors for U, Th and $\Sigma$REE can differ from session to session and
indicate that correction factors are sensitive to machine operational conditions, in particular the strength of the primary beam and therefore the resulting secondary ion transmission. For example, the matrix effect for U (expressed as the % U–Pb ratio change for a relative abundance difference of 1 %) was ~13 % when using an O₂ primary beam of ~2 nA and kohler aperture of 70 μm on SHRIMP II. In contrast to this, a session using SHRIMP RG employing an O₂ primary beam of ~0.9 nA and kohler aperture of 30 μm resulted in a matrix correction for U of ~10 %. Both of these results are quite different to those of Fletcher et al. (2004), who obtained a correction for U of ~7 % using different operating conditions. The matrix correction factors for U, Th and ΣREE for the above sessions indicate that the percentage effect that U has on the U–Pb ratios, increases with increasing secondary ion transmission. These results also indicate that the reproduceability of xenotime matrix correction factors for U, Th and ΣREE may need to be monitored on a session-by-session basis.


How chalcophile is Re? An experimental study of the solubility of Re in sulphide mattes.

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Although the Re/Os isotopic system has proved to be a valuable aid in understanding the evolution of the Earth’s mantle, interpretation of the data is currently hindered by limited knowledge of the high-temperature geochemical behaviour of Re. In particular, the extent to which Re in the mantle is hosted by sulphide or silicate phases is poorly known. We report the results of an experimental study of the solubility of Re in sulphide melts (called here “mattes”) coexisting with a Re-rich Re-Fe alloy in the system Fe-Re-S-O over a range of $f_{O_2}$, $f_{S_2}$ and temperatures, which allow extrapolation to conditions pertinent to the Earth’s mantle. The solubility of Re in mattes increases with increasing $f_{S_2}$, with Re$^{4+}$ dissolving as Re$^{4+}$ at high $f_{S_2}$ and Re$^0$ at low $f_{S_2}$. The effect of $f_{O_2}$ is negligible except at high $f_{O_2}$ where O in the matte becomes important. At constant $f_{S_2}$, an increase in temperature leads to an increase in the solubility of Re$^0$ in the matte, but a decrease in the solubility of Re$^{4+}$. These results, coupled with Re solubility in silicate melts from the literature, allow the calculation of Re matte/silicate-melt partition coefficients ($D_{Re{}^{ matte/sil}}$) according to:

Rhenium is shown to behave as a moderately chalcophile element during MORB petrogenesis, with $D_{Re{}^{ matte/sil}}$ ranging between 1 and 50, in agreement with the empirical observations of Roy-Barman et al. (1998). For slightly more oxidizing environments, such as the Lo’ihi OIBs, Re is predicted to behave as either a weakly lithophile or as a weakly chalcophile element, with $D_{Re{}^{ matte/sil}}$. This prediction is in agreement with the observed correlation between sulphide content, and therefore $f_{S_2}$, and Re concentrations in OIBs (Bennet et al., 2000). For more oxidizing environments, such as island-arcs, Re behaves as a strongly lithophile element, with an average $D_{Re{}^{ matte/sil}}$ for IABs of $\sim 10^{-4}$, which is consistent with the empirical observation of Re enrichment in volcanic glasses from undegassed island-arc lavas (Sun et al., 2003a,b, 2004).
Figure 1. Estimated average $D_{Re}$ matte/sil as a function of $f_{S_2}$ and $f_{O_2}$, for mid-ocean ridge basalts (MORB), Lo‘ihi ocean-island basalts (OIBs) and island arc basalts (IABs).

References


Exploring the potential of allanite as a geochronometer of high-grade crustal processes

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The focus of this study has been to explore whether we can date allanite successfully in situ using laser ablation ICP-MS techniques together with SHRIMP ion microprobe procedures. The accuracy of the calibration procedures has been demonstrated by analysing Phanerozoic allanite samples, previously dated by ID-TIMS, with different FeO, REE and Th contents. For U-Th-Pb analysis by LA-ICP-MS multigrain Th-Pb isochrons can be constructed with a precision of 1.5-2.5% (95% C.L.) at a resolution of 32µm×32µm×20µm. Accurate (+1-3%) and precise (1-2%, 95% C.L.), SHRIMP Th-Pb ages are achieved for allanite samples with REE+Th > 0.5 apfu, without additional matrix corrections.

The utility of the technique is now being explored through the analysis of samples from a range of geological environments. These include low-grade regional metamorphic rocks (central Lepontine Alps), subducted high-pressure metamorphic rocks (Lanzo massif, W. Alps), calc-alkaline plutons (Bergell, W. Alps; Tara, NSW), and amphibolite-grade migmatitic rocks (Petermann Ranges, C. Australia; central Lepontine Alps). Together with high-contrast imaging (BSE), trace element chemistry has been used to investigate the chemical response of allanite to different paragenesis in order to better interpret U-Th-Pb ages.

In situ study has revealed multiple ages and preservation of chemical signatures within single allanite-epidote crystals from migmatitic gneisses of the central Lepontine Alps (BSE image opposite, scale 200µm). The rocks experienced an episodic but extended period of partial melting of ~10 Ma at temperatures ~700°C. This has implications for the resistance of the allanite U-Th-Pb isotopic system with regard to radiogenic Pb retentivity.
Redesign of SHRIMP mounts to minimize geometric effects on isotopic and inter-elemental fractionation.

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Development of procedures for the analysis of oxygen isotopes on SHRIMP II at the ANU has been hindered by variable isotopic fractionation related to the geometry of conventional sample mounts. Temora zircons mounted as a 2 mm-spaced grid have revealed a >10‰ range in \(^{18}\)O/\(^{16}\)O fractionation across the mount surface. Such spot-to-spot differences are unacceptable for accurate and precise analysis of insulators. The same grid has been used to map correlations in geometric effects on Pb/UO\(_2\), U/UO\(_2\) and QT\(_{1,Y}\) which can be used to improve corrections for inter-element fractionation.

Possible causes of these fractionations include topography at the metal edge of the mount holder, and the transition from epoxy to metal at that edge. Two new mounts were designed to test these hypotheses. An epoxy mount was recessed into a modified conventional mount holder to remove topographic edge effects but retain the epoxy-metal transition. \(^{18}\)O/\(^{16}\)O fractionation was reduced (range ~5‰) and more systematic, but not eliminated, with progressively heavier compositions towards the edges of the mount.

A new "Mega mount" design was also tested to remove both effects. This design involved an epoxy disc 35 mm diameter screwed onto the face of the mount holder (Fig 1), increasing the area of the equi-potential surface and eliminating the epoxy-metal transition. Both standard insulating epoxy and conductive epoxy were tested. Conductive epoxy guaranteed conductivity, but at the expense of transmitted light imaging. It consisted of 1 part epoxy resin : 0.5 parts spectroscopic carbon powder : 0.12 parts epoxy hardener. Conductive epoxy proved unnecessary, however, provided that conductive adhesive tape was used to link the gold coat on the analytical face to the mount holder. Substantial improvements in the uniformity of U-Pb and \(^{18}\)O/\(^{16}\)O fractionation across the mount surface have been obtained during initial testing, the range in \(^{18}\)O/\(^{16}\)O fractionation approaching the detection limits of the experiment (±0.5‰).

Figure 1. New Mega mounts assembled with both insulating and conductive epoxy.
Cosmogenic $^{21}$Ne exposure dating of young basaltic lava flows from the Newer Volcanic Province, southwestern Victoria, Australia

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Cosmogenic $^{21}$Ne was utilised to determine exposure ages of young subaerial basaltic lava flows from the Newer Volcanic Province, southwestern Victoria, Australia. Within uncertainties, the ages (40 – 44 ka) determined from cosmogenic $^{21}$Ne analyses in olivines separated from basalts were consistent with extrusion ages previously determined by cosmogenic $^{36}$Cl exposure dating. In contrast to neon, cosmogenic $^3$He exposure ages appear to be hindered by coexisting mantle $^3$He in some of the samples in the present study. This paper clearly illustrates the potential utility of cosmogenic neon exposure ages in studying the eruption and surface morphology history of young volcanics, which are difficult to date using other conventional methods, such as K-Ar dating.
Electron-Induced Secondary Ion Emission (EISIE): An important consideration in the analysis of light isotopes in insulators

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Measurement of light stable isotopes on the SHRIMP is accomplished by sputtering a sample with a positive primary ion beam, Cs⁺, and extracting negatively charged secondary ions. During the analysis of electrically insulating materials, this configuration causes a charge build up on the sample surface and results in a reduction in the number of extracted secondary ions. Delivering electrons to the analysed insulator by an electron gun alleviates this problem. An unpleasant side effect of the use of an electron gun for charge neutralization is that the electrons alone (i.e., with the primary beam turned off) can produce measurable quantities of secondary ions which are both variable in abundance and have strongly fractionated isotopic ratios relative to the directly sputtered secondary ions. We report preliminary experiments, using ¹⁶O and ¹⁸O in zircon, designed to characterize and neutralize the electron-induced secondary ion emission (EISIE), and to characterize the electron gun itself and determine it's optimum operating conditions.

The experiments were conducted on the ANU SHRIMP II multicollector, equipped with a Kimball Physics ELG-5 electron gun mounted off the extraction lens housing and floated at primary column potential. It provides a focused electron beam directed at the target at an incidence angle of 45°. The electron energy can be adjusted over the range 0 to -3 kV, i.e. +0.75 to -2.25 kV relative to the target potential. All analyses were conducted on the modified grain mount design described by Heiss et al. (this volume) in conventional epoxy with a ~8 nm thick Au coat. Oxygen isotope measurements were made on both the TEMORA II standard zircon and zircon from the S-type 432 Ma Wantabadgery Pluton near Wagga Wagga, NSW.

Both the strength and time-dependant characteristics of the EISIE are dependant on a number of factors, including electron focus and energy, Cs⁺ current and flux, and particularly proximity to previously analyzed areas. EISIE occurs when electrons are directed at or near an analytical pit that either has been, or is being sputtered with Cs⁺. Material on a grain mount well away from a sputtered area does not exhibit EISIE. During the course of an analysis (of a pit well away from previously sputtered areas), the electron-induced contribution to the total secondary beam increases exponentially, although for long duration analyses the increase may abruptly shift to a linear form. The electron-induced secondary ions have a much lower average energy than ions directly sputtered by Cs⁺, and they are also isotopically much lighter, having an apparent ¹⁸O/¹⁶O over 150‰ lower than the Cs⁺sputtered oxygen ions.

These electron-induced secondary ions are a significant obstacle to making reproducible measurements of oxygen isotopes in insulators. For a typical 15-20 minute analysis, the effect is negligible at the beginning of the analysis, but can account for 1-2% of the total
secondary ions by the end of an analysis. Because the isotopic composition of the EISIE is highly fractionated it can reduce the measured $\delta^{18}O$ of a sample by 3‰.

Current work focuses on minimization or elimination of EISIE, and developing reliable corrections for when it is present. Simple peak-stripping procedures are used to correct for the electron-induced ions, and can result in a within-spot precision of $<0.3$‰ (1SE, n=25) relative to VSMOW for a 0.1 nA total secondary ion beam. Additionally, electron energies are kept as low as possible in order to minimize the effect. Future work will include the exploration of energy filtering to exploit the extremely low relative energy of the electron-induced ions.

In experiments to determine the behaviour of the electron gun, it was found that the efficiency of charge compensation (as measured by the total secondary ion current) is consistent over a wide range of high electron energies but drops rapidly to zero over a narrow range of low electron energies. In addition, it was confirmed that the electron gun settings (i.e., focus and deflection) that provide the strongest secondary beam also focused the beam at the sputtering pit and not somewhere else on the mount.
Solar Wind Oxygen in Lunar Metal Grains
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We have extended our studies on solar wind implanted oxygen in lunar soils. Previously we reported analyses of metal grains from lunar soil 10084 from the Apollo 11 landing site. Two grains have oxygen concentration profiles consistent with solar wind implantation. The oxygen concentration quickly decays over 10-20 nm and then stabilizes at a few wt % and decays slowly for a few hundred nanometers. The oxygen isotopic composition is enriched in the heavy isotopes of oxygen, $^{17}$O and $^{18}$O, by 5% relative to terrestrial oxygen. We have analyzed metal spherules from two further soils 61141 and 78481 from Apollo 16 and 17 respectively. The Apollo 17 soil has metal spherules that appear tarnished suggesting a surface oxidized layer. The oxygen signal is consistent with this interpretation with high and stable oxygen count rates, and the isotopic composition of the oxygen is normal. Some of the Apollo 16 spherules appear fresh and have low surface contributions of oxygen. However, the oxygen concentration falls monotonically with no suggestion of an implanted component. The oxygen isotope composition remains normal throughout the analysis. These new results do not provide us with another instance of solar wind oxygen, but they do provide additional information on the nature of exposure of lunar soils to solar wind. The gardening of lunar soil appears to be a stochastic process with variable exposure time to solar wind and variable oxidation of metal surfaces. The Apollo 16 spherules are particularly important because either they have never been exposed to solar wind, or the solar wind oxygen has diffused from them. At the temperatures expected for solar wind implantation O diffusion may be quite rapid and the oxygen lost on timescales of weeks to months.

A solar composition enriched in $^{17}$O and $^{18}$O is inconsistent with previous proposals suggesting either oxygen similar to terrestrial, or a composition enriched in $^{16}$O by 5% as found in refractory inclusions and some chondrules. It possibly reflects distinct gaseous (predominantly CO) and dust (predominantly silicate) O isotopic compositions, and the domination of the dust component alone in the planetary system.
Complex histories of melt inclusions in archean komatiites

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Silicate melt inclusions in komatiites are important for our understanding of archean volcanism and mantle processes. Current studies on the oldest (3.3 Ga) available olivine-hosted melt inclusions from the Barberton Greenstone Belt, South Africa, have uncovered unexpected complexities in trying to decide what inclusions are preserving pristine melt compositions. Inclusions from Barberton have various degrees of crystallinity and variable shapes and are difficult to understand petrographically. Visual heating experiments together with proper modelling of major element chemistry of inclusions and host olivines and analysis of Cl and S in inclusions are proving to be essential to see the preservation of primary features. Studies from other greenstone belts (Belingwe, Abitibi) highlight the problem that every sample behaves differently, so the details of every sample with melt inclusions have to be worked out separately. If uncompromised magmatic trends are identified, data for water and trace elements can be combined to form the beginning of a database on primary komatiitic melt compositions.

Extrasolar Planets and the Dry Brown Dwarf Desert

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Sun-like stars have stellar, brown dwarf and planetary companions. Relatively few brown dwarfs (compared to the number of planets and stellar companions) have been found in close orbits around sun-like stars. Why this should be so is unknown. With PhD student Grether, Lineweaver compiled, analysed and interpreted the world’s data on exoplanet, brown dwarf and stellar companions. Our analysis i) confirmed that the brown dwarf desert was not a selection effect and ii) located the position of the driest part of the brown dwarf desert (the mass at which the fewest number of companions exist) at \( M = 31 ^{+25-18} \text{ M}_{\text{Jupiter}} \). We found that approximately 16% of Sun-like stars have close companions more massive than Jupiter: 11% +/- 3% are stellar, <1% are brown dwarf and 5% +/- 2% are giant planets. Our results are published in the paper,

What happens to zircon during subduction?

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Rocks that underwent high-pressure metamorphism and are now exhumed to the surface are the main geological record of subduction, the process by which continents are buried to depth by plate tectonic and mantle convection. The only way to constrain rates and duration of this process is to date accessory minerals in high-pressure rocks. An important step in this process is to understand what happens to datable minerals, like zircon, during high-pressure metamorphism. Metamorphic zircon that forms during subduction-exhumation is texturally distinctive. Two main features are observed: partial or complete replacement of a zircon crystal by a zircon of different composition (also called recrystallization) and new growth of zircon, often on a relict (inherited) grain. Generally replacement is common in sub-solidus conditions, whereas new growth is virtually ubiquitous when melt is present. The figure illustrates increasing degrees of structural modification of zircon in response to HP metamorphism. Zircon in equilibrated eclogite-facies rocks may be unaffected by metamorphism and represent the only magmatic relict in the mineral assemblage. The preservation of older zircon grains (inheritance) is the rule, particularly in HP rocks that experienced relatively low temperatures (<650°C). Metamorphic zircon first occurs along fractures, and likely formed in the presence of fluids (A). Commonly, inherited magmatic crystals have irregular domains where the original zoning is replaced by chaotic, patchy zircon (B and E). The altered zircon is often porous, rich in micro-inclusions, shows signs of corrosion (C), and is isotopically disturbed, i.e. ages measured in altered zones are geologically meaningless. An insight into zircon recrystallization is provided in D: a magmatic zircon has been replaced by an aggregate of small zircon crystals, intergrown with HP minerals. Common features in subducted rocks are discrete zircon rims or domains. These rims form on inherited magmatic (E) or detrital cores (F) and often provide reliable ages for the metamorphism. Occasionally, completely new zircon grains are found in HP metamorphic veins. This requires dissolution of Zr from other sources (most likely magmatic zircon in the country rock) and very high fluid/rock ratios. These hydrothermal zircon crystals lack inheritance, are euhedral and polygonally zoned, and may contain inclusions of HP minerals (G). In subducted rocks that reached partial melting (T > 650°C), inherited zircon can be completely lost to new metamorphic zircon (H and I), which tends to be euhedral and to exhibit regular zoning. Recent detailed studies reveal that zircon in HP rocks in fact forms over a wide range of conditions from subduction to exhumation. This is why zircon often preserves multiple growth zones formed at different stages of metamorphism (E, H and I).
Figure 1. Internal structure of zircon crystals from subducted rocks. Sources are own work and Tomascheck et al. 2003.

Marginal Basin Development in the Svecofennian orogenic province 2.30 to 1.85 billion years ago

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We continue to test the evidence for an alternative marginal basin accretion model for the development of the main part of the Svecofennian orogenic province in Sweden and Finland. From structural and aeromagnetic evidence in several districts we have concluded that, contrary to the prevailing arc-accretion model, the main episode of deformation in the underlying metamorphic complexes occurred before, not after, the overlying volcanic sequences were deposited (Rutland et al., 2001a, b). We have focused on dating this early tectonothermal episode and distinguishing it from a younger episode that affected the volcanic sequences. Structural field evidence has been used to select samples of metasediments (e.g. from the Robertsfors Grp., N. Sweden, Fig. 1) that might preserve evidence of the early episode as metamorphic overgrowths on detrital zircons. This episode has now been dated at ~1.92–1.91 Ga in the metamorphic complexes on both sides of the Gulf of Bothnia, and in the complex south of the Central Finland Granitoid Complex. Ages of ~1.94 Ga have also been obtained for granitic rocks that were deformed in the early deformation episode. The sedimentary protoliths of all these metamorphic complexes were deposited before ~1.94 Ga and detrital zircons indicate derivation from 2.10–1.98 Ga sources (Rutland et al., 2004; Skiöld & Rutland, 2006).

Crustal scale belts of high electrical conductivity in the Svecofennian province lie within the metamorphic complexes. The continuity of these belts provides further evidence for the continuity of the sedimentary basin in which the protolith sediments were deposited. We have interpreted this as a large back-arc marginal basin which developed after ~1.98 Ga, and which was accreted during a major tectonothermal episode at ~1.92–1.91 Ga.

We consider that the main episode of igneous activity in the Svecofennian province, between 1.90 and 1.87 Ga, was extensional, and was developed in and above the basement formed by the accreted marginal basin. This magmatism may still be regarded as arc-related magmatism in the sense that an active margin probably lay to the west or southwest, with the subducting slab dipping beneath the accreted marginal basin. We suggest, however, that the concept of crustal growth by accretion of a number of arcs within the province after 1.9 Ga can no longer be sustained.

Work in progress in collaboration with Swedish and Finnish colleagues is extending our studies to the Kiruna district in the boundary zone between the Svecofennian province and the Archaean basement of the Karelian province. The synthesis of these various studies will provide a new interpretation of the tectonic evolution of the Svecofennian province in northern Sweden and Finland, and a new framework for the setting of the numerous ore deposits.


The Geology, Geochemistry and Geochronology of the El Abra Mine, Chile, and the adjacent Pajonal-El Abra suite of intrusions

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El Abra is a classic, yet simple porphyry copper deposit. World-class exposure of the complete suite of weakly altered, plutonic rocks directly associated with the ore-body provides a unique opportunity to examine the accepted paradigm of the relationship between igneous activity and copper porphyry formation.

Results of work completed to date indicate that the El Abra-Pajonal suite represents upper crustal magma chambers underpinned by a mid to lower crustal chamber which evolved over an 11 Ma period, between 45.1 and 34.5 Ma. Periodic injection a new pulses of magma into the upper crust from the lower crustal chamber occurred approximately every one Myr. Interpreted magmatic processes including assimilation, fractional crystallisation and magma mixing took place in the mid to lower crustal chamber. Zircon inheritance and field work shows crustal assimilation occurred however, as emplacement-aged zircon $\delta^{18}O$ data plot within mantle values, it is likely to be a minor process. The likely assimilate is hydrothermally-altered meta-igneous rocks, rather than meta-sediments.

Ti-in-zircon thermometry (Watson and Harrison, 2005) shows that the Pajonal-El Abra suite lies on a clearly defined cooling trend (Fig. 1a), initiated and then truncated by at least two major thermal events interpreted to be injection of mafic magma into the lower crustal chamber. The overall cooling trend is consistent with the dating data, suggesting relatively slow cooling in the interpreted lower crustal magma chamber is ~15°C/Myr.

Interpretation of whole rock major element and trace element data, especially whole rock Sr/Y ratios (Fig. 1b), along with comparative emplacement-aged zircon Ce$^{4+}$/Ce$^{3+}$ ratios (Ballard et al., 2002), reveals the El Abra-Pajonal suite can be broadly divided into a dry magma series (plagioclase/pyroxene dominated fractionation) and a wet magma series (amphibole dominated fractionation). As the Ti-in-zircon thermal data only shows one cooling trend, this implies that the interpreted mid-to deep crustal chamber is chemically stratified.

Temperature corrected, zircon Ce$^{4+}$/Ce$^{3+}$ ratios clearly show that the wet magma series is more oxidised than the dry magma series, with the economic porphyries recording the highest Ce$^{4+}$/Ce$^{3+}$ ratios. Comparing the Ti-in-zircon temperatures against corresponding Ce$^{4+}$/Ce$^{3+}$ ratios for the same zircon (Fig. 1c), allows intrusions associated with mineralisation to be discriminated from barren intrusions. This observation indicates that with further development, a threshold value for temperature corrected, Ce$^{4+}$/Ce$^{3+}$ ratios in zircons could be used to define rocks which may be prospective for copper porphyry style mineralisation.
Figure 1. A): Age versus temperature plot for the El Abra-Pajonal suite based on emplacement-aged zircons. The suite clearly defines a single cooling trend, indicating the suite evolved from a single magma chamber at mid to lower crustal levels. B): Whole rock Sr/Y ratio which clearly discriminates the intrusions associated with mineralization from barren intrusions. C): Temperature versus Ce$^{4+}$/Ce$^{3+}$ ratios from emplacement-aged zircons which shows dry series (barren) intrusive rocks are more reducing than wet series rocks, for intrusions of similar age and temperature (e.g. Clara granodiorite c.f. Apolo granite). The El Abra porphyry associated with the main mineralization event at El Abra, is also the most oxidized intrusion relative to the rest of the El Abra-Pajonal suite.

Ballard, J.R., Palin, J.M., and Campbell, I.H., 2002, Relative oxidation states of magmas inferred from Ce(IV)/Ce(III) in zircon: application to porphyry copper deposits of northern Chile, Contributions To Mineralogy And Petrology, 144, 347-364.

Further advances in measuring the oxygen isotopic compositions of granite zircon using SHRIMP II

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Numerous international studies of zircon from granites around the world (e.g. Valley, 2003), including British studies of some Australian granites (e.g. Kemp et al., 2005) have demonstrated the ability of zircon to preserve a record of changes in the oxygen isotopic composition of magmas as they evolve. Such compositions provide valuable information on the nature of the magma source and the relative contributions of crust- and mantle-derived components that commonly cannot be obtained from whole-rock oxygen compositions because of late alteration or interaction with meteoric waters. Although not as precise as conventional analytical techniques, the preferred method of zircon oxygen analysis is SIMS, which provides sufficient spatial resolution (≤25 µm) to track changes in the isotopic composition within individual zircon crystals, and hence the magma, as they grew.

Until recently, the only SIMS instruments configured for oxygen isotopic analysis were Cameca ion microscopes in laboratories outside Australia. A program at RSES designed to provide Australian researchers with the same capabilities using SHRIMP II ion microprobes is now well advanced. Initial experiments in 2005 showed that the principal limitation on analytical accuracy was control of instrumental mass fractionation. Instrumental modifications led to a major improvement (see RSES Annual Report 2005), but were not the whole solution. Experiments in 2006 have focused on modifications to mount design (see Hiess et al., this Report), charge neutralisation (see Ickert et al., this Report), sample preparation and analytical protocols. As a result, data acquisition times have been reduced from 250 seconds to 100 seconds per spot and within-spot precision increased from ~0.25‰ to ~0.05‰ (s.e.m.). The oxygen isotopic composition of zircon populations expected to be isotopically uniform can now be measured with standard deviations of about 0.4‰ on multiple analyses over periods of several hours. Geometric effects related to the distribution of samples within the sample mount have been reduced to sub-permille levels. It is now possible, using SHRIMP II, to measure differences in the mean oxygen isotopic composition of granite zircons with uncertainties of less than 0.2‰ and to begin to resolve quite subtle differences in the initial oxygen isotopic compositions of closely related granites within a single batholith (Fig. 1). The principal limitation on measurement quality is now shifting from instrumental limitations to sample selection.


Figure 1. Oxygen isotopic compositions measured on individual 25 µm spots on zircon grains from three Bega Batholith granites, southeastern Australia. An internal precision of ~0.05‰ (1σ) is obtained in 100 seconds of data collection per spot using the SHRIMP II multiple collector. Error bars 2σ.