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. Active areas of research centre on planetary studies, metamorphic and igneous geochemistry and geochronology, geochemistry of life processes, and chronology of all processes encompassed.

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.

Highlights

Commissioning of Dr Brock's paleobiogeochemistry laboratory has gradually taken place in 2007, with installation of mass spectrometers and operation of the chemistry laboratory. In early 2007, it was announced that an extension to the J5 (SHRIMP RG) Building was to be funded by the Chancelry. The project involves doubling the length of the extant building and adding a second floor to house offices, common room, and geochemistry laboratories. The ground floor allows an extension to the SHRIMP RG lab that will eventually house both SHRIMP SI and SHRIMP II. Building completion is expected in mid 2008. Construction of SHRIMP SI is now awaiting the completion of the building. In February 2007, Earth Chemistry ran an intensive course on Mass Spectrometry in Earth Sciences for RSES postgraduate students and staff. The course was well attended (~25 participants) and highlighted the need for continuing training.

In mid 2007, a stable isotope workshop was held to mark the achievement of subpermil reproducible stable isotope analyses on SHRIMP II. Guests at the workshop included Dr Marc Chaussidon and Dr Etienne Deloule of CRPG, Nancy, France, and Dr Doug Rumble of Carnegie Institution, Washington DC, USA. The meeting was attended by ANU researchers and other scientists from around Australia.

Personnel

Dr Marnie Forster was successful in her ARC request for an ARF and has joined Earth Chemistry for 2008. Dr Forster's research focuses on the interrelationships between microstructure development and geochronology. Following the successful installation of the C-14 accelerator-mass spectrometer, Dr Stewart Fallon will be joining Earth Chemistry in 2008. PhD studies were completed by Frances Jenner, Julien Celerier, Amos Aikman and Antti Kallio. Congratulations Doctors. Postgraduate studies were commenced by Tanya Ewing, Seann McKibbin, Rong Shi, and Richard Schinteie.

ARC

Professor Ian Campbell was successful is his ARC DP proposal for platinum-group elements in felsic rocks. A successful collaborative bid to ARC LIEF between ANU, University of Queensland (lead organization) and The University of Melbourne will see a new SEM especially configured for geological materials installed at RSES.

Probing *s*-process conditions in AGB stars: Constraints from Ba and Eu isotopes on presolar SiC grains

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The *s*-process occurs in red giant stars of low- to intermediate-mass (M ~ 0.8-8 M_o) during the asymptotic giant branch (AGB) phase of evolution [1], and operates in conditions of low neutron density (of the order of $10^7 - 10^8$ cm⁻³) with timescale for neutron capture much longer than that of any beta-decay.–Depending on neutron density and temperature, some unstable nuclei with long half-lives can capture neutrons rather than decay. In these cases, the *s*-process path splits into two branches, modifying the final abundances of nuclei affected by these branching points. In the helium intershell, neutrons are released by ¹³C(*a*,*n*) ¹⁶O and ²²Ne(*a*,*n*) ²⁵Mg reactions during interpulse and thermal pulse phases, respectively. Although the ²²Ne neutron source represents only a few percent of the total exposure, it suffices to modify the abundance patterns of several temperature– and neutron density–dependent branchings[2].

Since Eu isotopes are significantly affected by the branching at ¹⁵¹Sm, and Ba isotopes by the branching at ¹³⁴Cs, Eu and Ba isotopic ratios can be used to investigate temperature and neutron density of *s*-process sites. The B-decay rate of ¹⁵¹Sm and ¹³⁴Cs are highly susceptible to temperature, making the isotopes affected by these branching points good thermometers.

Eu and Ba isotopic ratios were measured, simultaneously, in presolar SiC grains from the Murchison meteorite using SHRIMP RG at RSES, ANU. The analyzed single grains are from mainstream population, which formed during mass loss from AGB carbon stars. As can be seen from fig. 1a, the $fr(^{151}Eu)$ is slightly sensitive to temperature and neutron density during the *s*-process[3]. The $fr(^{151}Eu)$ values obtained in this study for single SiC grains range from 0.593 to 0.643, except for one single grain, which has a $fr(^{151}Eu)$ value of 0.331 (fig. 1b). According to Arlandini et al.[2], the *s*-process signature in AGB stars yields $fr(^{151}Eu)$ values of 0.541 and 0.585 for the stellar and classical models, respectively. Our results are slightly higher than those values, but are notably different from the Solar System value of 0.478. Since ~95% of Eu in the Solar System is expected to originate from *r*-process[2], the value of 0.478 can be used as a *r*-process reference. The presolar SiC grains studied here are highly depleted in 134 Ba, except for one single grain (fig. 1b).

Both Eu and Ba isotopic data indicate high contribution from ${}^{22}Ne(a,n){}^{25}Mg$ neutron source in the final abundance patterns of presolar SiC, which can be explained by low neutron density and low temperature conditions.



Figure 1. a) The fr(¹⁵¹Eu) calculated for four temperatures (kT = 30 keV, 20 keV, 15 keV and 10 keV) as a function of neutron density (N_n) [3]. b) Plot of fr(¹⁵¹Eu) vs. $_{134}^{136}Ba$ on SiC aggregate and single presolar SiC grains.

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Molecular Fossils and Environmental Genomics

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Life in the Precambrian was dominated by bacteria and archaea, organisms that rarely leave diagnostic cellular remains in the fossil record. However, hydrocarbon biomarkers, the molecular fossils of natural products such as lipids and pigments, can yield a wealth of information about Precambrian ecosystems. Biomarkers often retain the diagnostic carbon skeleton of their biological precursors and may survive in sedimentary rocks for hundreds of millions of years. Many biomarkers are diagnostic for specific microbial groups such as methanogens, methanotrophs or phototrophic bacteria and, thus, may give information about ancient biodiversity. For instance, biomarkers discovered in mudstones that were deposited in a seaway in northern Australia 1,640 Ma ago describe a marine habitat that was fundamentally different from ecosystems observed later in Earth history. In this ancient sulfidic marine basin, eukaryotic algae were either insignificant or absent, and primary production was dominated by phototrophic green and purple sulfur bacteria. Generally, biomarkers can answer outstanding questions about Precambrian ecology and evolution, such as how ecosystems responded to the oxygenation of the atmosphere ~2.4 billion years ago, or how life responded to massive glaciations in the Neoproterozoic.

However, there is a major obstacle that hampers the application of biomarkers as palaeoenvironmental proxies: the incomplete knowledge of the lipid biosynthetic capacity of living organisms. According to some estimates, less than 1% of microorganisms can be isolated from the environment and grown in pure culture, and the biomarker content of these uncultivated microbes remains almost always unknown. Detecting and describing the lipids and pigments produced by the 99% of microorganisms that can not yet be cultured would boost the value of biomarkers extracted from ancient rocks.

This great challenge might be solved in the coming years by combining lipid research with environmental genomics and microbial community proteomics. In a pilot study, we collected lake water from hypersaline Lake Tyrrell (Fig. 1) to reconstruct nearly complete genomes and lipid profiles of the dominant archaea and bacteria. We are currently sequencing the DNA of the collected samples at the J. Craig Venter Institute. The genomes will be screened for genes involved in lipid and pigment biosynthesis and matched with corresponding lipids detected in the same sample. This way we can assign individual lipids to microorganisms even if they evade isolation. Ultimately this technique will help us to understand the phylogenetic distribution of biomarkers in the tree of life, even from microorganisms that currently remain unknown. The intricate knowledge of the lipid biosynthetic machinery of present ecosystems will then serve to elucidate new biomarkers and biomarker patterns in ancient sedimentary rocks.

At Lake Tyrrell, we will then compare the lipids of living microorganisms with fossils lipids extracted from mud in the lake bed (Fig. 2). The lake bed of Lake Tyrrell is up to 6 meters thick and was deposited over a time span of about 120,000 years. We have found that even relatively complex lipids such as Archaeol from halophilic (salt-loving) Archaea are preserved in the lake sediments. These biomarkers may yield an important terrestrial record of Australia's past salinities and precipitation.



Figure 1. In winter, Lake Tyrrell in outback Victoria contains up to ~50 cm of water with salt concentrations at saturation level (~330 g/L). The brine is coloured pink from pigments of halophilic microorganisms.



Figure 2. Jill Banfield and Simon George search for biomarkers in the lake bed of Lake Tyrrell. The mud contains high concentrations of molecular fossils of salt-loving microorganisms. The lake bed is up to 6 meters deep, and the deepest layers were deposited ~120,000 years ago when the lake was probably 12 meters deep and contained fresh water.

Brocks, J. J. and Banfield, J. (2007) Molecular Fossils and Early Life. *Geochimica Cosmochimica et Acta*, **71**(15), A123.

Discovery of a new high-temperature borosilicate mineral: boromullite

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New research this year has focussed on the characterisation of a new borosilicate mineral, named boromullite. The sole occurrence of this mineral is in a sequence of unusually boron-rich, low-pressure (~3kbar) granulite-facies metapelites from Mt. Stafford, central Australia. Boromullite is a prismatic, colourless mineral that occurs as bundles of prisms up to 0.4 mm long, typically as fringes or overgrowths on aggregates of sillimanite or as narrow overgrowths around embayed prisms of werdingite, another rare borosilicate mineral (known from only 6 localities worldwide). Boromullite and sillimanite are locally intergrown on a fine (1-100mm) scale (Fig. 1). The boron-rich granulites additionally contain Fe-cordierite, potassium feldspar, biotite, hercynite and ilmenite, with other B-rich minerals (grandidierite and tourmaline) present locally.

Bormullite is compositionally heterogeneous on even a 1-5 micron scale (Fig. 1) and in the type specimen ranges in composition from $Mg_{0.00}Fe_{0.01}AI_{4.36}Si_{1.22}B_{0.40}O_{9.60}$ to Mg_{0.00}Fe_{0.02}Al_{4.60}Si_{0.68}B_{0.70}O_{9.47} (Fig. 1). Structural refinements of the holotype crystal shows that it corresponds to a 1:1 polysome of Al_2SiO_5 and Al_5BO_9 modules (Fig. 2). Module 1 has the topology and stoichiometry of sillimanite and carries all the Si, whereas module 2 is a type of mullite defect structure in which Si is replaced by B in triangular coordination and by Al in tetrahedral coordination, *i.e.*, Al₅BO₉. The holotype crystal has a measured composition of Mg_{0.01}Fe_{0.02}Al_{4.44}Si_{0.97}B_{0.57}O_{9.47}. Boromullite is the first recorded natural analogue of a group of B_2O_3 -Al₂O₃-SiO₂ phases ("boron-mullites") that have previously been synthesised experimentally and that are of relevance to the ceramics industry.

Boromullite at Mt. Stafford formed during anatexis of B-rich metapelitic rocks under granulite facies conditions ($T \ge ~790^{\circ}$ C, P ~ 3.6 kbar), mostly from the reaction of werdingite with siilimanite/andalusite, but possibly in some cases from the incongruent melting of werdingite. It also occurs as feathery intergrowths within coarse-grained blocky prismatic sillimanite (Fig.1), raising the possibility that it may also be a previously unrecognised prograde mineral in boron-rich rocks.



Figure 1: a) compositional variation in type sample 2006-MST22 (circles) and "boron-mullite" synthesized in the presence of melt (triangles); b) and c) BSE images of boromullite



Figure 2: The polysomatic structure of the bromullite holotype crystal.

SHRIMP U–Pb xenotime and Re–Os molybdenite dating of the Molyhil scheelite-molybdenite skarn, northeastern Arunta region, central Australia

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SHRIMP U–Pb xenotime and Re–Os molybdenite geochronology was undertaken on samples from the Molyhil scheelite-molybdenite skarn deposit in central Australia, with the aim of constraining the timing of mineralisation. In situ SHRIMP U–Pb xenotime analyses were carried out on xenotime within a thin section of endoskarn. The xenotime occur as overgrowths on euhedral zircon as well as single irregularly shaped crystals. Re–Os concentrations were determined by isotope dilution mass spectrometry undertaken by Dr Robert Creaser (University of Alberta) on a sample of ore-zone molybdenite.

New SHRIMP xenotime ²⁰⁶Pb/²³⁸U matrix correction procedures developed during this study build on those previously reported by Fletcher et al. (2000) and Fletcher et al. (2004) and provide for further confidence in SHRIMP xenotime ²⁰⁶Pb/²³⁸U age determinations. Similar to previous studies, contrasts in chemical composition especially U was found to be the cause of significant ²⁰⁶Pb/²³⁸U fractionation. The matrix correction procedures involve the concurrent SHRIMP analysis of three chemically distinct xenotime standards during each analytical session. Electron microprobe (WDS) analyses of the xenotime prior to SHRIMP analysis, allows for the ²⁰⁶Pb/²³⁸U fractionation of the standards to be measured and corrected according to their chemical composition. The derived correction factors are then applied to the 'unknown' xenotime samples.

Concordant to near-concordant SHRIMP (RG) analyses range from ~1710–450 Ma. The oldest xenotime has a 207 Pb/ 206 Pb age of ~1710 Ma. There is also 206 Pb/ 238 U age groupings at ~760 Ma and ~660 Ma, and individual 206 Pb/ 238 U xenotime ages at ~560 Ma, 500 Ma and 450 Ma. There is no apparent relationship between xenotime ages and their textural settings. Interestingly, all xenotime in the sample have a very similar chemical composition, Th/U ratio and chondrite normalised REE pattern. The Molybdenite Re–Os analysis gave a model age of 1720.7 \pm 8 Ma (95% confidence).

The ~1720 Ma age of the ore-zone molybdenite is synchronous with the age of nearby granites and granulite facies metamorphism and is considered as the best estimate for the timing of mineralisation at Molyhil. However, only one of the xenotime analysed by SHRIMP has a similar age of ~1710 Ma, the remainder forming over 1000 million years latter. These dominantly Neoproterozic to early Palaeozoic xenotime probably formed in response to younger thermotectonic events. For example, the ~750 Ma xenotime age cluster is within error of the crystallisation age of the Mud Tank Carbonatite, located approximately 100 km SE of the Molyhil deposit. The near identical chemical features of these xenotime combined with their range in age, suggest that they formed during a number of cycles of local-scale dissolution and re-precipitation rather than the influx of distinct, successive Y– and HREE–bearing fluids.

The ability of xenotime to sometimes form at low temperatures, allows for the detection of low temperature and possibly far-field thermotectonic events to be recorded by this mineral. Indeed, the vast majority of xenotime analysed during this study, do not record the timing of mineralisation at Molyhil. Therefore, great care should be taken to the assignment of xenotime ages to specific geological events. Fletcher IR, McNaughton NJ, Aleinikoff JA, Rasmussen B, Kamo SL (2004). Improved calibration procedures and new standards for U–Pb and Th–Pb dating of Phanerozoic xenotime by ion microprobe. Chemical Geology 209: 295-314.

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U-Pb dating and Hf isotope systematics of rutile (preliminary work)

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Rutile (TiO_2) is a common metamorphic mineral which often contains measurable amounts of U, Pb and Hf. We are conducting a preliminary investigation with the ultimate aim of measuring U-Pb ages and Hf isotopic compositions of individual rutile grains in-situ. Little previous work has been done on hafnium isotopes in rutile, but Choukroun et al. (2005) reported a vast spread of ¹⁷⁶Hf/¹⁷⁷Hf values for rutile from mantle xenoliths (epsilon Hf values from -55 to +110). This large range is intriguing and suggests that an investigation into the controls on hafnium isotope ratios in rutile, and the effects of metamorphism thereupon, may be rewarding.

Initial results emphasise the suitability of rutile for the proposed study. Back Scattered Electron (BSE) imaging of 34 rutile-bearing samples from a wide variety of geological settings has shown that rutile is usually very simple structurally – compositional zoning occurs only rarely, and preservation of multiple generations of rutile growth has not been observed (Fig 1). However, needles of exolved ilmenite within rutile crystals are a common feature (Fig 1), and must be avoided during in-situ analysis. Laser Ablation ICPMS and electron microprobe analyses of rutile results for the 34 samples shows that rutile is also relatively simple chemically, consisting almost entirely of TiO_2 (usually >99%), with a limited range of elements with a similar ionic radius and, to a lesser extent, ionic charge substituting for titanium (Zack et al., 2002).

The simple structure and chemistry of rutile are favourable for the study of U-Pb and Hf isotopes in rutile. Th contents are always very low (usually below LA-ICPMS detection limits of ~0.01ppm, otherwise always <1ppm except for two samples of unusual composition), in keeping with theoretical considerations and mineral/melt partition coefficient experiments (eg Klemme et al., 2005; Brenan et al. 1994). This low Th content is advantageous for U-Pb dating because it allows for a very simple common lead correction: (virtually) all ²⁰⁸Pb present must be common lead, as little or no ²³²Th was present to form ²⁰⁸Pb through radioactive decay. Rutile also incorporates almost no Yb or Lu (predicted by mineral-melt partitioning studies, eg Klemme et al. 2005, and confirmed by our LA-ICPMS results). This is of great value for the measurement of Hf isotopes, as ¹⁷⁶Yb and ¹⁷⁶Lu cause isobaric interferences on the hafnium isotope of interest, ¹⁷⁶Hf.

Münker et al. (2001) reported a systematic error in solution MC-ICPMS measurements of hafnium isotope ratios where titanium was present with Ti/Hf>10, the exact cause of which was not well understood. We have demonstrated that this is unlikely to be a problem for measurements on our Neptune MC-ICPMS in laser ablation mode, in spite of the very high Ti/Hf ratio of all rutile. The ¹⁷⁶Hf/¹⁷⁷Hf ratios of synthetic rutiles doped with varying amounts of HfO₂ powder were measured and compared to the ¹⁷⁶Hf/¹⁷⁷Hf ratio obtained for the pure HfO₂. No systematic change in ¹⁷⁶Hf/¹⁷⁷Hf ratios was observed with changing Ti/Hf ratio, and all but one of the five mixtures agreed within error with the ¹⁷⁶Hf/¹⁷⁷Hf ratio measured for the pure HfO₂ sample (Fig 2). We are currently investigating the cause of the one discrepancy, but the lack of a systematic bias is an extremely positive result, and represents the first step towards demonstrating that ¹⁷⁶Hf/¹⁷⁷Hf ratios in rutile can be reliably measured by LA-MC-ICPMS.



Figure 1.



Figure 2.

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Unravelling prograde and anatectic histories: integration of petrography, trace element geochemistry and U-Th-Pb dating of zircon and allanite

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High-pressure amphibolite facies migmatites of the Cockburn Shear Zone (CSZ), northern Musgrave Block, formed during the 580-520 Ma intraplate Petermann Orogeny. They contain a number of new trace-element-rich accessory phases compared to their unmelted counterparts. As such, they provide an excellent case study with which to extend the approach of integrating *in situ* trace element geochemistry to understand the petrological significance of accessory mineral ages.

Of the four accessory phases present in the CSZ migmatites (zircon, titanite, apatite, allanite) only zircon and allanite contained sufficient concentrations of radiogenic elements for dating. A new SHRIMP U-Pb age of 555 ± 7 Ma was obtained for metamorphic zircon rims that formed during melting within the CSZ. Allanite grains that crystallised under prograde pressure-temperature conditions display compositional growth zoning. Relatively rare earth element-poor allanite cores were overgrown by REE-rich rims and the two domains give SHRIMP Th-Pb ages of 559 ± 6 Ma and 551 ± 6 Ma, respectively. The good agreement of allanite and zircon ages provide evidence that allanite with relatively high common Pb can be successfully dated by in situ methods.

Whereas the major element composition of minerals (with the exception of allanite) show little zoning or are unzoned, mineral trace element compositions reflect an internal redistribution during metamorphism and partial melting related to a changing mineral assemblage and thus provide a tool to decipher the relative timing of metamorphic mineral growth. Growth of porphyroclastic garnet and hornblende and some accessory phases was primarily controlled by subsolidus hydration reactions that consumed feldspar. This is supported by the notable and consistent lack of negative Eu anomalies in all metamorphic phases, despite the presence of relict igneous K-feldspar porphyroclasts. REE compositions of zircon and late-stage allanite growth also suggest disequilibrium with garnet. Thus, the major period of garnet and hornblende growth were not coeval with partial melting.

Importantly, we were able to distinguish the dated allanite domains based on Lu, Eu and common Pb content and relate them to the major metamorphic minerals in the rock, such as garnet (a HREE-sink) and feldspar (a Eu- and Pb-sink). This provided constraints on the pressure-temperature conditions of allanite formation (Figure 1). For example, allanite cores show relative depletion in Lu (a HREE), which is generally consistent with the presence of garnet; in this case a subsolidus phase. On the other hand, allanite rims contain more Lu as well as less initial Pb; the latter is typical of allanite crystallising from a melt where it is involved in competitive partitioning of Pb and Eu with feldspar. In comparison, allanite cores are relatively Pb-rich, which is again supports a subsolidus origin and formation during the breakdown of feldspar and liberation of Eu and Pb.

The use of trace element partitioning shows that chemical equilibrium between co-existing minerals during prograde metamorphism cannot be assumed. This has implications for the calculation of P-T-time conditions on texturally complex assemblages and the construction of P-T-deformation-time paths.



Figure 1. Distinguishing Lu, Eu and initial Pb contents of different allanite domains determined from SHRIMP and complementary LA-ICP-MS analysis.

New Insights into Crustal Petrogenesis via *in situ* O and Hf Isotopic Compositions of Archean Zircon from Southwest Greenland

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The origin of the oldest continents and how the processes that generate continental crust have changed through time continue to be key questions in Earth Science. Applying a new, multiple isotopic approach to understand the petrogenesis of granitic rocks, we have obtained coupled U/Pb, O and Hf isotopic data from Archean tonalite-trondhjemite-granodiorite (TTG) suites of Southwest Greenland. The dataset consists of >250 analyses of zircon from 11 rocks ranging in age from 3.85 Ga to 2.55 Ga.

The advantage of analyzing zircon grains is that they are relict igneous minerals and as such avoid the potential compilations of secondary alteration which can affect metamorphosed bulk rock. Additionally, all the O and Hf isotopic analyses include age determinations on the same crystal domains. The samples include the most ancient tonalites of the Itsaq Gneiss Complex through to late Archean granitoids of the Qôrqut Granite Complex. All zircon grains were thoroughly characterized by cathodoluminesence (CL), secondary electron microscopy (SEM), reflected (RL) and transmitted (TL) light imaging. The U/Pb ages of the zircon were determined using SHRIMP RG; coinciding ¹⁸O/¹⁶O ratios were then measured on a freshly polished surface of the same zircon using SHRIMP II in multi-collector configuration; ¹⁷⁶Hf/¹⁷⁷Hf was subsequently measured by LA-MC-ICPMS with the RSES Neptune (Figure 1).

Zircon from the oldest, ca. 3.85 Ga, tonalites records $_{18}^{18}$ O compositions within 1‰ of mantle values ($_{18}^{18}$ O mantle = 5.3±0.3) and initial $_{Hf}$ values largely within ±1 epsilon unit of chondritic composition (calculated using $_{176}^{17}$ Lu = 1.867x10⁻¹¹yr⁻¹). These narrow, mantle-like, O-Hf fields contrast markedly with results from studies of Phanerozoic crustal suites [1, 2], which show diverse O-Hf isotopic arrays, and with $_{18}^{18}$ O generally displaced from mantle compositions towards higher values. Hf isotopic compositions of zircon from the youngest sample analysed, the 2.55 Ga Qôrqut Granite Complex (initial $_{Hf}$ -25), are in agreement with earlier Pb isotopic studies [3] suggesting the origin of the Complex by the remelting of >3.7 Ga crust. The O isotope data from this suite, however, lie 1-2‰ below mantle compositions, again in contrast with results for Phanerozoic suites.

A striking feature of the overall dataset is the absence of high (>7‰) $_{18}^{18}$ O values, highlighting the lack of recycled weathered supracrustal material in the genesis of the TTG. Of particular note is the prevalence of low $_{18}^{18}$ O values, with 4 out of 11 samples, with ages from 3.7 to 2.55 Ga, having compositions 1-3‰ below mantle values. Low $_{18}^{18}$ O values are a relatively rare feature in granitic suites [4] and typically result from hydrothermal alteration by surface waters, in some cases enhanced by glaciation. The presence of low $_{18}^{18}$ O in these mid-crustal level Archean granitoids is unexpected and may reflect different surface conditions and hence fluid compositions during the Archean. Taken together, these new results point to differing styles of Archean versus Phanerozoic crustal growth, with supracrustal rocks playing a less significant role in early crustal genesis.



Figure 1. Clockwise from top left: TL, RL, SEM and CL images for tonalite zircon 492120-10. CL image indicates location of coinciding ²⁰⁷Pb/²⁰⁶Pb age and _¹⁸O determinations (separated by mount polishing) with ~35µm diameter elliptical spots on oscillatory zoned zircon. ¹⁷⁶Hf/¹⁷⁷Hf analysis performed on larger 47µm diameter circular spots. SEM image following ¹⁸O/¹⁶O measurement indicates analysis was performed on pristine zircon, free of cracks or inclusions.

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Regional brecciation and alteration in the Wernecke Mountains, Canada: New constraints from He, Ne, Ar, Kr, Xe, Cl, Br and I

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The causes of regional brecciation in the Proterozoic Wernecke Mountains of Canada have implications for understanding the crustal evolution. Hydrothermal alteration associated with brecciation is characterized by variably saline fluid inclusions.

Two phase LV (liquid vapour) fluid inclusions (<26-30 wt % salt) in fluorite and barite plus most quartz samples are characterized by: greater than seawater Br/Cl values of up to 2.9_10⁻³; I/Cl of up to 54_10⁻³; and at four out of six localities they have elevated ³⁶Ar concentrations of 4 to >100 ppb and ⁴⁰Ar/³⁶Ar of <1000-2000. Sulphide fluid inclusions with similar ⁴⁰Ar/³⁶Ar values have near atmospheric ²⁰Ne/²²Ne and ²¹Ne/²²Ne values of ~9.8 and 0.029, respectively; and are enriched in radiogenic ⁴He* with ³He/⁴He of <0.02 Ra (Ra = atmospheric value of 1.4 x 10⁻⁶) and ⁴He*/radiogenic ⁴⁰Ar* and ⁴He*/nucleogenic ²¹Ne* values of greater than the crustal production ratios. All these characteristics are typical of sedimentary formation waters.

Halite saturated LVD (liquid-vapour-daughter) fluid inclusions, with salinities of up to 44 wt % salt, are present in all of the samples but dominate in only two quartz samples. One of these samples, from the Slab mega-breccia is situated close to a horizon of meta-evaporitic scapolite and it has the lowest measured Br/Cl and I/Cl values of $0.37_{-}10^{-3}$ and $0.32_{-}10^{-6}$, respectively. The range of Br/Cl and I/Cl is compatible with the involvement of magmatic fluids in addition to sedimentary formation water. However, interaction with halite is shown to have been an important mechanism for increasing fluid salinity.

Fluid inclusions with variable salinities (LV and LVD) in a sample from the Hoover locality have the highest measured ⁴⁰Ar/³⁶Ar values of ~40,000 and variable ³⁶Ar concentrations of 5 to 0.7 ppb. Fluid inclusions inferred to have similar ⁴⁰Ar/³⁶Ar values in sulphide have crustal ²⁰Ne/²²Ne and ²¹Ne/²²Ne values of 6.5 and 0.35; ³He/⁴He of ~0.002; and ⁴He*/⁴⁰Ar* and ⁴He*/²¹Ne* values only slightly above the crustal production ratios. Post-entrapment ingrowth of radiogenic ⁴⁰Ar* is minor and correctable, whereas ingrowth of radiogenic ⁴He* is difficult to preclude. However, we demonstrate that Ne isotopes together with He do not favour ingrowth and provide robust constraints on fluid origin in these Proterozoic samples. The combined noble gas data set is most easily explained by the involvement of a second fluid with magmatic origin from U-rich basement rocks. Therefore, these data provide evidence for a hitherto poorly constrained episode of magmatism in ancestral North America.

Correlated, In-Situ Analysis of U/Pb, _180 and _Hf in Zircon from Siluro-Devonian Granite in the Eastern Lachlan Orogen: Constraints on Juvenile Additions to the Continental Crust

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Introduction

The nature and origin of granite remains an outstanding scientific problem. Where does granite come from? Is granite derived entirely from partial melting of rocks with a long crustal residence time, or is there a significant juvenile (i.e. directly mantle derived) component? How do granites differentiate, and what is the relationship between granites with apparently linear correlations between elements on variation diagrams?

Even in some well-characterized granite terrains, there continues to be much debate on these questions. One such terrane is the eastern Lachlan Orogen. These granites have been the subjects of intense study for over 30 years, and have become a "textbook" locality for granite study (e.g., Winter, 2001) however there is little consensus in the literature as to the answers to most of the questions posed above. For example, Keay et al. (1997), Collins (1998), Healy et al. (2004), and Patino Douce (1999) have suggested that S-type granites contain appreciable quantities of directly mantle-derived material, and a number of workers, in particular Kemp et al. (2007) have suggested the same for I-type magmas. Other workers, in particular Chappell (1996) has suggested that they are derived entirely from the partial melting of crustal rocks. This problem has important implications for our understanding of crustal growth: if there is substantial input of juvenile magma into granitic magmas, then they may represent a hitherto unrecognized source of new crustal material, alternatively they simply represent a mechanism by which the crust differentiates.

Analytical Approach

Zircon is a highly refractory mineral that can remain both solid and closed to diffusion of U, Pb, O, and Hf during high-grade metamorphism, partial melting and in the presence of meteoric fluids. In addition, zircon is a common accessory mineral in granitic rocks and therefore can preserve evidence of magmatic processes with high fidelity. The approach in this study has been to take advantage of spatially resolved zircon isotopic analysis using high-resolution SIMS to measure U/Pb and _18O, and LA-MC-ICP-MS for _Hf in order to reconstruct magmatic processes and crustal evolution. Samples have been collected from S- and I- type granites and their enclaves in the Berridale, Wagga, and Kosciuszko Batholiths, where possible re-collecting from sites that have already been characterized for whole rock geochemistry as well as Sr, Nd and O isotopes.

Preliminary Results

We have determined the oxygen isotope composition of over 200 zircon grains from Siluro-Devonian granites of the Wagga, Berridale, and Kosciusko Batholiths. All zircon analyzed for oxygen were also analyzed for U-Pb. Rocks included in the dataset are ~433 Ma S- and ~416 Ma I-type granites of varying bulk compositions, one 414 Ma gabbro and a small dataset of zircon from the 433 Ma Cooma granite, a small pluton at the metamorphic culmination of a low-P high-T metamorphic complex. Analyses of Hf isotopes in these zircon grains are in progress. The $_^{18}$ O of zircon from the gabbro (~5.5‰) is indistinguishable from that of zircon in equilibrium with the mantle and provides a reference for the oxygen isotopic composition of zircon crystallized from uncontaminated, mantle-derived magma in the eastern Lachlan Orogen.

Zircon from the Cooma granite provides an estimate of the _¹⁸O expected in zircon crystallized from a magma derived entirely by partial melting of metasedimentary rocks and early measurements indicate a value of around 9.7‰. These values provide useful reference markers when interpreting results from granites.

A first order observation is that $_{18}^{18}$ O in zircon from granites previously identified as S- or Itype on petrographic, field, or bulk-chemical grounds (Chappell and White, 2001) have distinguishable $_{18}^{18}$ O enrichments. This can be plainly seen by the bimodal nature of the probability density diagram for all analyzed zircon. Zircon grains from S-type granites are fall under the high $_{18}^{18}$ O peak at ~ 9.7‰ and zircon from I-type granites fall on under the low $_{18}^{18}$ O peak at roughly 7.1‰, although there is a large amount of scatter in the median $_{18}^{18}$ O of populations of zircon from I-type granites.

Populations of zircon separated from hand-sample sized samples of granite behave differently in different rocks. S-type granites generally contain zircon that have $_{18}^{18}$ O values which scatter by ~2‰. All populations, however, seem to have identical median values near ~9.7‰. Work is underway to determine whether this scatter represents variation inherited from the source, via a viscous, poorly homogenized magma or whether it is due to true open system processes like magma mixing or contamination. I-type granites typically have a main population of zircon that have identical ¹⁸O enrichments, and some have outliers that have higher $_{18}^{18}$ O. Preliminary work on _Hf suggests that these ¹⁸O enrichments are correlated with ¹⁷⁶Hf/¹⁷⁷Hf suggesting that these granites contain zircon that has crystallized from magmas with very different isotopic characteristics.



Figure 1.

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Solar System Isotopic Heterogeneity from ⁵³Mn-⁵³Cr

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Introduction:

One of the requirements for the application of the short-lived nuclide chronometer ⁵³Mn (half-life of 3.7 My, anchored to angrite LEW86010) and short lived nuclides in general is that samples are derived from a common reservoir with a homogeneous distribution of the parent nuclide. Ideally, this should reflect the solar system abundances as a whole, but it requires that the solar nebula was well mixed after collapse of the molecular cloud. A more likely scenario is that the solar system is heterogeneous for many isotopes, but particular subsections (such as a specific parent body) will be homogeneous and suitable for short-lived nuclide chronometric studies. Short-lived radionuclide chronometry has been successfully applied and has produced useful information, but many assumptions about initial ratios and ages are involved because insufficient samples have had two or more chronometric systems applied to them. A few samples have been found to have isotope systematics that make them discordant in different systems, showing that a completely uniform distribution of short-lived nuclides in the solar system is not the case [1, 2].

Mn and Cr isotopic heterogeneity:

A widespread and systematic chromium isotopic heterogeneity in the inner solar system was recognised by Lugmair and Shukolyukov [1] who found an apparent linear relationship between heliocentric distance and initial 53 Cr/ 52 Cr expressed in samples from Earth, Mars and those inferred to originate in the Asteroid Belt. With a few exceptions, meteorites from the Main-Belt have a common 53 Cr/ 52 Cr, which suggests that 53 Mn/ 55 Mn is homogeneous within the Asteroid Belt and the chronometric interpretation of 53 Mn/ 55 Mn for samples from this region is justified. An anomalous case is that of the enstatite chondrites: Shukolyukov and Lugmair [3] showed that they have Mn/Cr ratios that are chondritic, coupled with 53 Cr/ 52 Cr ratios that are lower than those of all other meteorites believed to come from the Asteroid Belt. Chondritic Mn/Cr shows that elemental fractionation has not suppressed the evolution of 53 Cr/ 52 Cr in enstatite chondrites, so either 53 Mn/ 55 Mn or 53 Cr/ 52 Cr must be heterogeneous in the solar nebula.

Simple explanations of the radial trend could involve a stellar-derived nucleosynthetic heterogeneity in 53 Cr/ 52 Cr, or heterogeneity in 53 Mn/ 55 Mn, with either 53 Cr or 53 Mn increasing with heliocentric distance. Shukolyukov and Lugmair [4] noted that 54 Cr anomalies were not observed in meteorites other than carbonaceous chondrites, so anomalies of 53 Cr were probably absent as well. Recent 54 Cr data does show heterogeneity in the solar system for this isotope [5], but it is not correlated with radial heliocentric distance. Elemental volatility leading to a depletion in Mn (and hence 53 Mn) must also be considered. Mn and Cr are approximately in the middle of the volatility range, with Cr being referred to as a *common element* (50% T_c 1296 K) and Mn a *moderately volatile element* (50% T_c 1158 K) [6]. Difference in volatilities is not a favoured explanation because the bulk compositions of the planets are not well known and few constraints can be put on such models.

Comparison with ²⁶Al and Pb-Pb timescales:

Though CAIs are used as the reference point for 26 Al/ 27 Al, the 53 Mn/ 55 Mn ratios obtained from CAIs are inconsistent with the rest of the 53 Mn timescale [e.g. 7, 8] (Figure 1) and their generally anomalous isotopic composition suggests that they should not be used as anchors for short-lived nuclide chronometric systems. CAIs have average initial 53 Mn/ 55 Mn of 4.4 _ 10⁻⁵ [9] although values as high as 14.8 _ 10⁻⁵ have been reported [10]. As CAIs are known to have been isotopically disturbed, these values may represent a lower limit. Using the average 53 Mn/ 55 Mn value, this equates to a CAI age that is ~19 Ma older than LEW86010, implying a solar system timescale that is irreconcilably long. The Pb-Pb dates for Efremovka CAIs and LEW86010 [11, 12] give a much smaller age difference of 9.4 ±1.1 Ma, which is consistent with the 26 Al timescale, as well as theoretical models and astronomical observations of stellar system formation. The high initial 53 Mn/ 55 Mn may reflect an extreme early heterogeneity in the early solar system [1], which had been largely smoothed over by the time of chondrule formation.

Discrepancies between ²⁶Al and ⁵³Mn ages of some samples (D'Orbigny, Asuka 881394 and others; see [2]) are possibly expressions of solar system heterogeneity for these isotopes, or resolved differences in closure temperature. Placement of samples in the absolute timescale is also problematic, as Pb-Pb dates often have poor precision and different phases commonly return different ages. The most recent efforts at Pb-Pb dating of phases from D'Orbigny [13, 14] have yielded precise ages that are older than previously found, and make this meteorite discordant with the ²⁶Al-timescale. As such, a unique reconciliation of Pb-Pb, Al-Mg, and Mn-Cr isotope systematics is not possible with the data presently available.

Using SHRIMP to obtain ⁵³Mn/⁵⁵Mn:

Sensitive High-mass Resolution Ion Micro-Probe has the potential to obtain initial ⁵³Mn/⁵⁵Mn ratios for coexisting minerals. This is especially important for chondritic meteorites which are effectively sedimentary rocks or breccias; in these cases bulk-rock samples will not necessarily meet the requirements of internal isochrons and *in situ* analysis of individual chondrules is preferred. Success will hinge on the precision of ⁵³Cr/⁵²Cr ratios obtained by SHRIMP, and the range of ⁵⁵Mn/⁵²Cr in coexisting mineral phases (Figure 1).



Figure 1. X-ray map of Mn/Cr ratio (calculated from electron probe raw counts) for an unequilibrated olivine chondrule from the Allende carbonaceous chondrite. Coexisting high and low Mn/Cr domains allows determination of ⁵³Mn/⁵⁵Mn at the time of isotopic closure.

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Diachronous subduction to diamond- and coesite-facies conditions in the Kokchetav massif

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The study of crustal rocks that underwent ultra-high-pressure conditions (UHP), i.e. subduction to the coesite and diamond stability fields (> 90 Km depth) offers a unique insight into the deep Earth and the tectonic processes of subduction and exhumation.

It has been proposed that the first occurrence of UHP metamorphism defines the time of onset of modern cold subduction on Earth. The Kokchetav massif in Kazakhstan contains some of the oldest known UHP rocks, which reached diamond-facies conditions indicating subduction to at least 150 km depth, at ~530 Ma. These rocks therefore provide a rare opportunity to study fundamental processes at the onset of modern plate tectonics.

SHRIMP ion microprobe dating was performed on monazite from coesite-bearing micaschists of the Kulet unit. Based on texture, trace element composition and inclusions in monazite it is concluded that the pressures peak was reached at ~520-515 Ma. Decompression is dated by the formation of monazite symplectites (Figure 1) in a second sample at 508±6 Ma. This new data provides evidence that the Kulet unit underwent UHP metamorphism 10-15 Ma later than the diamond-facies rocks in the nearby Kumdy-Kol unit (Figure 2).

This new time constrain excludes models that argue for a simultaneous evolution of coesiteand diamond-facies rocks, it suggest that subduction continued well after continental crust was involved, and that exhumation was not initiated by a single event such as slab break-off. The dynamic of this UHP massif also indicates that Cambrian tectonic was similar to that of recent orogenic belts.



Molecular Palaeontology of the Neoproterozoic-Cambrian Interval: Lipid Biomarker Geochemistry and Ancient Microbial Ecosystems

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Lipid biomarker work began in the new biogeochemistry laboratories in Jaeger 1 in 2007. Work was conducted on a selection of Neoproterozoic and Cambrian samples from Australia and throughout the world. The aim is to reconstruct the microbial ecosystems during a time that has witnessed numerous changes: "Snowball Earth" glaciations; evolution and extinction of numerous microorganisms; the first occurrence of animals; and the oxygenation of the world's oceans. Thus far, the results look very promising and has let to the discovery of lipid biomarkers that are over 1 billion years old. I am also trying to investigate rock samples from that period that originated in shallow water facies. So far, most investigations concentrated on deep water facies. I have collected rock samples from drill cores held at Geoscience Australia (Canberra). These rocks are from shallow water facies and contain numerous evaporate (salt-bearing) sequences (Figure 1).

Techniques aimed at removing potential contaminants from rock samples are under investigation. Thus far, the techniques have worked very well and helped to determine which biomarkers were likely derived from the Precambrian-Cambrian interval and which samples are contaminants (e.g. from the use of drilling fluids, fingerprints etc).

Field work was conducted at Hamlin Pool, Shark Bay Heritage Park, Western Australia (Figure 2). Microbial mat samples (smooth mats and tufted mats) were collected to study lipid biomarker diagenesis. Microbial mats at Hamelin Pool are significant in that they resemble fossilized microbial mats from the Precambrian (> 542 million years ago). Hamlin Pool mats flourish in saline conditions that preclude grazing animals, which would otherwise destroy them. Similar conditions were present in the Precambrian when animals had not yet evolved. Therefore Shark Bay mats are ideal candidates for understanding past biotas.



Figure 1. Rock sample from Geoscience Australia drill cores; brown colour = salt, grey colour = incorporated mud rock.



Figure 2. Hamlin Pool, Shark Bay Heritage Park, WA.

Systematics of noble gas, carbon and nitrogen isotope compositions in Australian diamonds from the Merlin and Argyle Mines

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Diamonds from Merlin and Argyle mines show different characteristics both on visual appearances and isotopic compositions, although the two mines are 1350 km apart from each other in opposite directions of south Darwin, Northern Territory. The Merlin diamonds (kimberlitic) are predominantly characterized by yellow colour, cube and dodecahedral form, whereas Argyle diamonds (lamproitic) are mainly octahedral in pale brown colour. Previous carbon isotopic studies on diamonds from both locations indicated the diamonds sharing _1³C range from -5‰ to -16.66‰ (Lee et al 1997; Hall & Smith 1984; Jaques et al 1989). Peridotitic diamonds from Argyle mine exhibit a restricted _1³C range of -4.4‰ to -9.1‰, compared to a wider _1³C from -5‰ to -16‰ for eclogitic Argyle diamonds (Jaques et al 1989). Limited noble gas studies on Argyle diamonds yielded a higher ³He/⁴He value $1.57\pm0.75X10^{-4}$ and solar Ne (²⁰Ne/²²Ne=12.6±1.8, ²¹Ne/²²Ne=0.0304±0.0048) for colourless diamonds, and a lower ³He/⁴He value (<4.5X10⁻⁸) for coloured composite diamonds (Honda et al 1987). A further systematically integrated study of noble gas, nitrogen and carbon isotopic compositions on Australian diamonds will help to understand regional time-integrated mantle history. Furthermore carbon and nitrogen isotopic compositions, combined with noble gases, in diamonds can elucidate the evolution and outgassing history of the subcontinental lithosphere.

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Relative oxidation determined by the Ce⁺⁴/Ce⁺³ ratio in zircon

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The Ce^{+4}/Ce^{+3} ratio in zircon as a measure of relative oxidation was developed by Ballard et al. (2002) and utilizes the observation that Ce^{+4} partitions more readily into the zircon mineral structure than Ce^{+3} and therefore the ratio between Ce^{+4} and Ce^{+3} can be used to estimate relative oxidation for a given population of zircons. However, the premise that the difference in the ratio is primarily a function of oxidation has been questioned. Rohrlach (2002) and Core (2004) have suggested that it is principally a function of temperature and the silica and phosphorus activities of the magmas.

An investigation was therefore undertaken on the suite of rocks originally studied by Ballard et al. (2002), the El Abra-Pajonal suite of granodiorites in Northern Chile, to determine if the observed increase in Ce^{+4}/Ce^{+3} ratio values in zircon in the evolving suite, was due to oxidation or was a function of the other factors discussed by Rohrlach (2002) and Core (2004).

Results

To confirm that Ce^{+3} is partitioned into zircon via the xenotime-type substitution for all intrusions of the El Abra-Pajonal suite, the P concentrations in the zircons were plotted against the sum of the REE⁺³ and Y⁺³ concentrations (Figure 1). The 1:1 correlation indicates that the xenotime-type substitution is the dominant mechanism by which Ce^{+3} is substituting into zircon in the El Abra-Pajonal suite. Whole-rock phosphorus concentrations in the intrusions are similar (Table 1) indicating that the phosphorus activities of the magmas was not a significant factor influencing the zircon Ce^{+4}/Ce^{+3} ratio values for the El Abra-Pajonal suite.

Comparing the spread in Ce^{+4}/Ce^{+3} ratio values against corresponding Ti-in-zircon (Watson and Harrison, 2005) measured temperatures for each of the El Abra-Pajonal suite intrusions (Table 1), the observed spread for a given population of zircons is broadly correlated to temperature, such that maximum Ce^{+4}/Ce^{+3} ratio values correspond with minimum temperatures. This is expected because as intrusions cool, the entropy of the magma decreases and crystallizing zircons become less elastic (Blundy and Wood, 1994). As a consequence, Ce^{+4} is preferentially partitioned into the zircon structure due to its similar sized radius to Zr^{+4} (Shannon, 1976) and the substitution requires less energy than the coupled Ce^{+3} substitution: $[ZrSi]^{+8} - [Ce^{+3}P]^{+8}$.

However, for intrusions with zircons of similar minimum temperature (broadly correlated to the solidus temperature of the magmas) and with similar silica and phosphorous whole-rock concentrations, there are significant differences in the maximum Ce^{+4}/Ce^{+3} zircon ratio values (Table 1), which have been interpreted to be due to oxidation effects.

For example, the Central granodiorite has a maximum zircon Ce^{+4}/Ce^{+3} ratio of 607.38 and $_Ce^{+4}/Ce^{+3}$ ratio value (i.e. the spread in the Ce^{+4}/Ce^{+3} ratio values) of 592.51. In comparison, the thermally and chemically similar Llareta quartz monzodiorite has a maximum zircon Ce^{+4}/Ce^{+3} ratio of 266.05 and $_Ce^{+4}/Ce^{+3}$ ratio value of 241.3 (Table 1).

If the zircon Ce^{+4}/Ce^{+3} ratio values were only a function of temperature and melt chemistry, then one would expect similar maximum Ce^{+4}/Ce^{+3} ratio $_Ce^{+4}/Ce^{+3}$ ratio values for all intrusions of the El Abra-Pajonal suite.

Therefore in suites where the whole-rock and zircon chemistry and thermal history of the intrusions is well constrained, it is possible to determine the relative oxidation state between intrusions using the Ce^{+4}/Ce^{+3} ratio in zircon method (Ballard et al., 2002).



Figure 1. Evidence for the xenotime-type substitution mechanisms for the partitioning of Ce into the zircon lattice. Zircons off the 1:1 correlation line between REE + Y versus P (atomic) are inclusion rich and excluded from calculations of the Ce⁺⁴/Ce⁺³ ratios for the El Abra-Pajonal suite intrusions. As the determination of the Ce⁺⁴ and Ce⁺³ partition coefficients are determined by the concentrations of trivalent and tetravalent cations partitioned into zircon, enrichment in these elements due to inclusions will affect the veracity of the resultant

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Rate of growth of the preserved North American continental crust: evidence from Hf and O isotopes in Mississippi detrital zircons

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Detrital zircons from the Mississippi River have been analyzed for U-Th-Pb, Lu-Hf and O isotopes to constrain the rate of growth of the preserved North American continental crust. The zircon U/Pb dates, obtained by conventional Excimer laser ablation ICP-MS method, resolved six major periods of zircon crystallization: 0-0.25 Ga, 0.3-0.6 Ga, 0.95-1.25 Ga, 1.3-1.5 Ga, 1.65-1.95 Ga and 2.5-3.0 Ga. These age ranges match the ages of the recognized lithotectonic units of the North American continent in the hinterland of the Mississippi River. Ninety seven zircons, which show no age zonation and were within 7.5% of concordance, were selected from the six U/Pb age time intervals and analyzed for Hf and O isotope by laser ablation MC-ICP-MS and SHRIMP II, respectively. The δ^{18} O values of the zircons show a step increase in the maximum δ^{18} O values at the Archean-Proterozoic boundary from 7.5 ‰ in the Archean to 9.5 ‰, and rarely 13‰, in the Proterozoic and Phanerozoic. However, the average value of δ^{18} O in zircons changes little with time, suggesting that the change is as much due to an increase in diversity in the source regions of younger granitoids as to an increase in their sediment content.

 ϵ Hf_i values for the zircons range from 12.5 to -29.7. Zircons derived from juvenile crust, which we define as having mantle δ^{18} O (4.5 - 6.5 ‰) and lying within error of the Hf depleted mantle growth curve, are rare or absent in the Mississippi basin. The overwhelming majority of zircons crystallized from remelted pre-existing continental crust. The average time difference between primitive crust formation and remelting for each of the recognized lithotectonic time intervals, which is defined as crustal incubation time in this study, is 860 ± 360 Myr. There is also a suggestion that the crustal incubation time increases with decreasing age, which is consistent with the declining role of radioactive heat production in the lower crust with time. Average one-stage Hf model age (1.82 Ga), weighted by fraction of zircons in the river load, is in good agreement with the Nd model age (1.7 Ga) for the Mississippi River. One-stage model ages, however, are the minimum estimate for the average age of continental crust. The average, more realistic, two-stage Hf model age weighted by area, is 2.50 Ga, which is appreciably older than the one-stage model age.

Two-stage Hf model ages of zircons show two distinct periods of crust formation for the North American continent, 1.6 to 2.4 and 2.9 to 3.4 Ga. At least 45% of the preserved North American continental crust was extracted from the mantle by 2.9 Ga and 90% by 1.6 Ga, respectively. Similar two periods of growth are also recognized in Gondwana (Hawkesworth and Kemp, 2006), suggesting that these may be two major periods of global continental crustal growth. However, we stress that more data from other continents are required before the hypothesis of episodic global continental growth can be accepted with confidence.



Figure 1.

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Keyhole geochronology in north-eastern Poland

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In late 2003 RSES and the Polish Geological Institute (PGI) in Warsaw signed an agreement to collaborate in a study of the basement rocks of north-eastern Poland. The collaboration, in which petrographic and geochemical studies at the PGI are combined with SHRIMP U-Pb geochronology at RSES, is resulting in a much clearer understanding of the geological evolution of the western part of the East European Craton (EUC) and its tectonic relationships to adjacent terranes.

As with all the western EUC, the basement rocks of Poland are buried beneath an extensive cover of much younger sedimentary rocks. The thickness of the cover ranges from about 500 m in the east to over 5 km in the west. The main sources of information about the broad geological structure of the underlying basement are aeromagnetic and gravity surveys, supplemented by deep seismic investigations. The only samples of the basement rocks that can be studied directly are drill cores recovered from a limited number of boreholes, mostly drilled to investigate deep geophysical anomalies. The challenge is to piece together the geological evolution of the basement using the limited view provided by these irregularly-spaced 'keyholes' (Fig. 1).

The research project is being undertaken as a series of sub-projects, each focused on a particular geophysical anomaly, rock type or region. All the sites studied lie NE of the Trans European Suture Zone, a major basement boundary that cuts approximately NW-SE through central Poland. Completed sub-projects include studies of a late Paleoproterozoic mafic igneous suite at Lomza, about 150 km NE of Warsaw (Krzemi_ska et al., 2005), of the 'Archean' crystalline basement of the Mazowsze granitoid massif in far NE Poland (Krzemi_ska et al., 2006a) and of an Early Carboniferous alkaline complex in the Pisz region about 200 km NNE of Warsaw (Krzemi_ska et al., 2006b).

Work is nearing completion on a belt of rocks from the Warmia area about 50 km SE of Gda_sk. Once considered to be high grade metasediments, these gneisses instead contain zircon with very simple textures and uniform ages, consistent with an igneous origin. They are coeval with the Mesoproterozoic Mazury Complex to the east, and are probably part of the same system. Work is also well advanced on some of the metagreywackes that host the igneous complexes of NE Poland. The detritus in these little-studied rocks is proving to have an unexpectedly similar range of provenance ages to that in some of the better-known metasediments of Scandinavia.

One of the surprises to come out of the project is the discovery of the large regional extent and relatively narrow age range of Late Paleoproterozoic, possibly arc-related, granitic rocks and associated metavolcanics in NE Poland (Krzemi_ska et al., 2007). Even the granitic gneisses of the Mazowsze massif, long considered to be of Archean age, are now known to be products of Late Paleoproterozoic magmatism. This finding has led to a major reassessment of the tectonic setting of Paleoproterozoic Poland in relation to the Archean Ukrainian Shield to the east, and the Paleoproterozoic marginal basins to the north, as igneous rocks of very similar age are widespread in the countries to the north and west that border the Baltic Sea. The work in the Pisz region has helped to clear up some inconsistencies in earlier interpretations. The wide range of ages previously measured by Rb-Sr, K-Ar and fission track dating (265-350 Ma) does not appear to reflect differences in crystallisation age, but rather an extended post-crystallisation thermal history. Zircon ages measured at both Pisz and nearby Elk are ~345 Ma, consistent with zircon ages recently measured on alkaline rocks at Tajno, 40 km to the east.

The rocks at all three sites appear to be part of the same Early Carboniferous ultramaficalkaline complex, rather than the gabbro at Pisz being part of a dismembered Paleoproterozoic ophiolite complex, as previously thought.



Figure 1. Magnetic anomaly map of the south Baltic region (after Wybraniec, 1999), showing the ages measured during this project on Polish basement rocks recovered from drill holes. Black, Late Paleoproterozoic: Dark blue, Early Mesoproterozoic: Light blue, Early Carboniferous. MC – Mazury Complex, MD – Mazowsze Domain, BPG – Belarus-Podlasie Granulite Belt

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