GEOCHRONOLOGY AND ISOTOPE GEOCHEMISTRY

Research in the Geochronology and Isotope Geochemistry Group is focused on the study of the origin and evolution of the Earth using geochemical tracers and geochronological techniques, the latter to provide time scales for geological processes and events. Progress in our research is heavily dependent upon a range of sophisticated instrumentation, much of which has been developed within the School, including the SHRIMP ion microprobes, which, together with our gas source mass spectrometers, enable us to undertake a wide variety of relevant analyses on geological samples. Geochemical studies range from isotope analyses on meteorites and on the earliest rocks known on Earth, as well as on samples that have been derived from the mantle in the recent past, enabling a broad perspective to be obtained on the Earth’s origin and evolution. Our studies in geochronology principally utilize the U/Pb dating technique on zircon and other suitable minerals, and the $^{40}\text{Ar}/^{39}\text{Ar}$ isotopic dating method on minerals exhibiting a wide range of closure temperatures for argon. With these techniques we can obtain precise and accurate ages for individual events as well as reconstructing cooling histories, providing better understanding of the evolution of the continents, including their growth and their tectonic history, and also providing important input and constraints for geodynamic modelling.

During the year two graduate students, Corine Davids and Paul Hoskin, completed and submitted their PhD theses, and Eleanor Dixon has made progress in writing up her thesis.

The efforts of the SHRIMP subgroup have been directed three ways, towards 1) the development of new instrumentation, 2) experimentation with new analytical techniques and 3) application of established techniques to explore the behaviour of isotopic systems and to solve a wide range of geological problems.

After several years’ work by Dr J. Foster and the School’s engineering and electronic workshops, an experimental multiple collector for SHRIMP II this year was installed and testing begun. Many problems of multiple collection remain to be solved, but the lens system in the new collector is working well, making it possible to stage the implementation of multiple collector analysis in tandem with an active analytical program. Substantial progress also was made on the SHRIMP RG, which has yet to operate to its design expectations. During a three-month visit to the School, the instrument’s engineering designer, Dr S. Clement, in consultation with Emeritus Professor W. Compston, worked closely with technical officer Mr B. Jenkins comparing the design performance with that predicted by a ray-tracing program written independently by Jenkins. The ability of the SHRIMP RG design to achieve high mass resolution with high transmission was confirmed, but it also was discovered that such performance is particularly sensitive to the dimensions and potentials of the various lenses. Now that the lens fringing fields are better understood, electrical and mechanical solutions for improving the focus of SHRIMP RG are being sought.

Several advances were made in analytical techniques. Foremost amongst these were Dr V. Bennett’s successful measurements of Ni isotopic zoning in Fe-Ni metal grains from carbonaceous chondrites, showing unexpectedly a zoning pattern inconsistent with simple closed system condensation. Techniques developed by Mr C. Magee in his study of C isotopes from diamonds (see P&EP report) proved very useful in improving the reproducibility of isotopic analyses of other light elements (Li, B etc). An algorithm for matrix correcting Pb/U analyses of very high-U zircon, proposed by Dr I. Williams following work on the Tasmanian Dolerites, has much improved the accuracy of such measurements.

Amongst the many zircon studies carried out during the year, three are of particular note. Dr D. Rubatto showed by carefully targeted studies of zircon grown or recrystallised at high metamorphic grade that the Rare Earth Element (REE) composition of such zircon reflects other REE-bearing minerals that were growing at the same time, thereby recording the metamorphic grade at the time and providing a specific time point in the metamorphic P-T-t path. Professor W.R. Van Schmus, who visited the group for a 3-month sabbatical mid-year, made several important and unexpected discoveries regarding the tectonic history of NE Brazil by studying
the changing provenance of Proterozoic sediments from the region. Emeritus Professor W. Compston discovered a formerly neglected source of error in zircon isotope dilution analyses, and developed new approaches to the calibration of SHRIMP analyses, both of which assist in explaining supposed discrepancies between zircon ages measured by the isotope dilution and SHRIMP techniques.

Thermochronological studies on the Victoria Range, South Island, New Zealand, utilizing the $^{40}\text{Ar}/^{39}\text{Ar}$ isotope dating technique, have confirmed that the range is an exhumed lower plate of a Late Cretaceous core complex, with its formation linked to the opening of the Tasman Basin as New Zealand separated from Australia.

By means of $^{40}\text{Ar}/^{39}\text{Ar}$ dating of single feldspar crystals, and by step-heating experiments, a detailed time framework has been established for a sequence exposed at Lothagam, northern Kenya, in which a rich vertebrate fauna has been recovered, including some hominoid fossils. The history extends from about 14 to 2 Ma ago in the Miocene to latest Pliocene, and the new results help provide constraints on the evolution of this part of the Kenya Rift.

The second edition of the book “Geochronology and Thermochronology by the $^{40}\text{Ar}/^{39}\text{Ar}$ Method” by Ian McDougall and Mark Harrison was published mid year by Oxford University Press.

Notable achievements during the year in noble gas geochemistry include further consideration of the remarkably primitive neon isotope composition found in some young Icelandic basalts, the analysis of several very old zircons for their fission xenon signature, and the measurement of cosmogenic neon ages on quartz, demonstrating the youthful nature of exhumation of an old terrane in northern Australia.

We wish to particularly acknowledge the important role played by the technical staff in our research achievements. Mr R. Waterford and the staff of the mechanical workshop and Mr N. Schram and the staff of the electronics workshop were involved in the major developments during the year as well as in the maintenance and refurbishment of laboratory facilities as required. In the noble gas area, Mrs R. Maier effectively maintained the K-Ar dating laboratory and assisted with the $^{40}\text{Ar}/^{39}\text{Ar}$ dating operations. Dr X. Zhang brought the VG1200 and its extraction line to full automated operation, as well as developing new code for our major acquisition and data handling programs, Noble and KArDate, and supporting the operation of the $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology laboratory. Dr I. Iatsevitch has designed and is currently building an automated noble gas extraction system, and has maintained and assisted in the operation of the VG5400 mass spectrometer and associated facilities. Mr N. Gabbitas very ably took responsibility for the operation of SHRIMP 1 and its supporting facilities. Mr J. Mya and Mr S. Paxton continued to provide excellent service in rock crushing and mineral separation for the group as well as for the School as a whole.
An experimental high sensitivity multiple collector for SHRIMP II

J.J. Foster, S.W. Clement\(^1\), R. Waterford, N. Schram, P. Lanc\(^2\), W. Compston and I.S. Williams

The widespread use, in thermal ionization mass spectrometry, of multiple collection in place of a single collector with peak switching, has resulted in major improvements in the precision of isotope ratio measurements. Because of the high spatial resolution of the SHRIMP ion microprobes and their sensitivity to small scale changes in target composition during analysis, it is expected that even greater benefits would be obtained through developing a multiple collector for those instruments.

In 1985 an experimental multiple collector, with a fixed array of eight multiplier channels designed particularly for the study of Ti isotopic anomalies in meteorites, was fitted to SHRIMP I. It proved difficult to obtain reproducible isotope ratios, but there was a substantial improvement in short-term analytical precision, showing that it was worth persisting with development of the concept. Because the Ti anomalies subsequently discovered were large, and readily measured using single collection, experimentation with the fixed-array multiple collector was discontinued. When the decision was made to build a second generation ion microprobe, SHRIMP II, the secondary mass analyzer was redesigned with a multi-element, adjustable multiple collector in mind.

A prototype multiple collector for the ANU SHRIMP II has now been manufactured at RSES. Development of the multiple collector has been directed towards high precision simultaneous measurement of the relative intensities of ion beams over a wide dynamic range. The design therefore incorporates multiple electron multipliers in addition to multiple Faraday cups, the latter able to operate in either current or charge mode, providing the capability to measure the isotopic composition of both trace and major elements, and to measure very large isotopic ratios. Special design features include detector shielding, low input capacitance for the Faraday cups and the use of sapphire insulation, all of which should optimize the charge-mode performance of the three low-noise Keithley\(^\text{®} 642\) electrometer heads.

The multiple collector is designed to allow the simultaneous collection of five isotopic species in ion counting mode using continuous dynode electron multipliers (CDEMs) which will operate in particle counting mode in conjunction with an Ortec multichannel counting system controlled by an RSES-built pulse counting system interface (PCSI). Provision has been made for three of the CDEMs to be mechanically interchangeable with Faraday cups under computer control. The beam defining slits for the five channels can be nested together closely enough to enable simultaneous measurement of heavy isotopes such as Hf or Pb. The collectors immediately adjacent to the central collector are adjustable over a range of 1 mm. The two outer collector assemblies can be moved over a range of 10 cm. In the extended position they can be set for the measurement of light isotopes such as \(^{16}\text{O}\) and \(^{18}\text{O}\).

The entire multiple collector can be traversed parallel to the central ray trajectory to allow the beam defining slits to be placed on the focal plane for any chosen mass range. In addition, the outermost collector assemblies can be moved independently to compensate for any minor curvature in that plane. A choice of four beam defining slits of different widths has been provided for each collector.

The central multiple collector assembly can be withdrawn completely to pass the beam to an ETP electron multiplier for single collection using magnet field switching. A transfer lens refocuses the central beam to the entrance of an optional retardation lens that enhances abundance sensitivity. All slits, multiplier positioning motors and electrometers are under computer control.

\(^1\) Ion Optical Consulting, Crapaud, Prince Edward Island, Canada

\(^2\) Echidna Technologies, Canberra
The multiple collector has recently been fitted to the RSES SHRIMP II, replacing its single collector, and is currently undergoing testing and evaluation. Very satisfactory focus and sensitivity have been achieved in single collector, ion counting mode, enabling analytical work and multiple collector experimentation to be interspersed as required.

![SHRIMP II Multiple Collector Diagram](image)

*Figure 1:* Sketch of the main functional elements of the SHRIMP II experimental multiple collector.

**SHRIMP RG**

S.W.J. Clement¹, W. Compston, J.J. Foster and B. Jenkins

The RSES SHRIMP RG so far has not operated to its design expectations. It achieves high mass-resolution only when the angular divergence of the secondary ion beam is greatly restricted, contrary to the ion optic design. The last year was spent exploring whether the effect could be lessened by (i) adjustment of the mass-analyser alignment and its various quadrupole lenses and (ii) using a low-divergence but wide cross-section beam through a wide source slit. The latter gave enough sensitivity for zircon U-Pb analyses but it does not solve the basic focusing problem. Further empirical experiments with the instrument were suspended until a better theoretical understanding of the observed effects could be obtained.

1999 was spent mainly on an in-house review of the ion optical theory for the SHRIMP RG mass analyser. Using the LabView platform, Jenkins extended his first order ray-tracing treatment to second order, producing a program (SOIO) which incorporates the second order equations included in Matsuda and Matsuo’s third order program (TRIO) on which the SHRIMP RG design is based. Clement visited RSES for three months from July to implement a new version of TRIO. Using beam transport theory and hand calculation, he checked each operation and term in TRIO up to second order (time did not permit checking all third order terms). One inconsistency in the TRIO formulation was found which, although it does not
appear to be serious, will need clarification by Matsuo and Matsuda. Clement also changed TRIO’s input program to make it easier to use, and wrote a new program that plots the output as the image shape at the collector slit. This supplements the original numerical listing of aberration coefficients. Clement and Jenkins compared the matrix outputs from TRIO and SOIO item by item to identify and eliminate small but important arithmetical errors. The two programs are now close to agreement at second order, and the effects of third-order terms on the image can be distinguished.

Using the TRIO program, Clement confirmed that the focus of the SHRIMP RG is much more sensitive to small changes in lens strengths than that of the SHRIMP FG. In addition, considerable shifts of the image were observed for small changes in the assumed magnet fringing field, making it clear that the latter must be known accurately before the position, and possibly the quality, of the focus can be predicted. There are other fringe fields, such as at the entrance and exit of the ESA, which also may shift the focus substantially. Both programs agreed in showing that the beam should be at least two millimetres wide in the energy focal plane due to second- and third-order aberrations. This had been observed earlier by experiment, but had been interpreted as allowing the possibility that the pole-edge curvatures on the magnet might not be correct. The TRIO program also answered a long-standing question concerning the behaviour of the projection lens that follows the ESA: it keeps the energy- and directional-focus superposed at all values of lens strength.

Both the SOIO and modified TRIO programs can now be applied to examine whether the quality of the focus and its position are strongly altered by the different shapes and strengths of the various fringe fields. In particular, the mass-analyser configuration produced by Matsuda, with its very high quality image, assumes effective lengths for the quadrupole lenses that are different from those that we have built. Is it possible to adjust the lens strengths and/or other parameters to achieve an image of comparable high quality, or must the lenses be modified physically to approach the original design? Using SOIO, Jenkins has begun to answer this question by searching systematically for a minimum sum of selected second-order aberration coefficients, varying input parameters such as quadrupole lens voltages and dimensions, drift lengths and magnet pole face curvatures. Using his modified TRIO program, Clement is now preparing to produce an independent, third-order answer.

As stated last year, the SHRIMP RG would benefit from an extended period of use for analysis to shake out any remaining electronic and computing bugs in its control, to test the long-term stability of its refocussing, and to determine any mass and elemental biases peculiar to the reverse-geometry design. Armstrong and Fanning of PRISE kindly undertook several zircon U-Pb and feldspar Pb isotope analysis sessions early in the year, but were discouraged by variations in measured isotope ratios attributed to short term changes in the secondary ion focusing. The matter could not be pursued because by then Foster’s priority was the SHRIMP II Multiple Collector, with which he has been occupied for most of the year. Experimental work using SHRIMP RG will not be resumed until he is again available.

**Ni isotope compositions in zoned metal grains within chondritic meteorites measured using SHRIMP II – a record of early solar system processes**

V.C. Bennett and A. Meibom³

Carbonaceous chondrites are the most primitive meteorite group known. It is certain that they have never been involved in planetary processes and as such they provide direct samples of the chemical composition of the solar nebula and record processes operative during the earliest history of our solar system. Most chondritic components, however, have undergone significant nebular and asteroidal processing, such as melting/ heating during chondrule formation and parent body metamorphism/aqueous alteration, that have erased or significantly modified the original chemical and isotope signatures imparted during condensation from the solar nebula.

³ Hawaii Institute of Geophysics and Planetology, University of Hawaii
The exceptions are a few chondrites which contain compositionally zoned Fe-Ni metal grains. These grains are up to 150 µm in diameter and are unique in having well preserved core-rim zonation patterns, for example in Ni, Co, Cr and Si, with the Ni concentrations varying from 10% in the cores to 4% in the rims. The most straightforward interpretation of these variations is that they represent a condensation sequence from the cooling nebular gas with the zoning patterns consistent with predicted alloy compositions. These rare, well preserved grains provide a means of exploring and constraining the history of solar nebula regions where the metal grains formed.

![Ni isotopic ratios from compositionally zoned metal grains within a chondritic meteorite.](image)

*Figure 2:* Ni isotopic ratios from compositionally zoned metal grains within a chondritic meteorite. The high Ni cores of the zoned grains have low isotopic ratios compared with the standard (Henbury). This may reflect complex fractionation processes within the solar nebula.

We are investigating the origin of these metal grains using the high spatial resolution and high isotopic precision measurement capabilities of the SHRIMP II. If the zoning represents a condensation sequence then it could be expected to be accompanied by isotopic fractionation as well as compositional variability. All of the isotopes of Ni are stable and any variations in composition will likely result from thermal fractionation effects. Using SHRIMP II we have determined Ni isotopic ($^{60}$Ni, $^{61}$Ni, $^{62}$Ni, $^{64}$Ni) profiles in meteorite thin sections across the zoned grains. The data were referenced to a standard (Henbury iron meteorite) as well as to synthetic Fe-Ni mixtures. Ni isotopic compositions were constant between standards with external reproducibility from a 40-minute analysis being ± 1‰. The results for the zoned metal grains (Figure 2) show that significant and reproducible variations were present between the cores and rims in some cases with, for example, the cores being up to 4 ‰ isotopically light (low $^{61}$Ni/$^{60}$Ni), and the rim compositions within error of the standards. No isotopic effects were found in the unzoned grains.

The observed fractionation effects are opposite to those calculated for a simple closed system. Predictions from condensation models are that the first condensed material would be isotopically heavy, in this case having a high $^{61}$Ni/$^{60}$Ni, becoming isotopically lighter as condensation proceeds. We are currently conducting additional experiments to confirm these data as validation of these results will demonstrate that this approach can have a significant impact on the level of our understanding of nebular processes. One possible explanation is that the observed isotopic effects represent the mixing between distinct chemical reservoirs in the solar nebula during the formation of these grains, reservoirs that require separate early histories. These types of isotopic observations combined with textural and other chemical data provide a window onto the earliest events in our solar system more than 4.5 billion year ago.
Further evidence for matrix effects in SHRIMP measurements of Pb/U on high-U zircon

I.S. Williams and J.M. Hergt

Recent work by several research groups on high-precision dating of African and Antarctic segments of the Jurassic Karoo-Ferrar continental flood basalt province, which once extended over 5000 km along the proto-Pacific margin of Gondwana, has made it timely to look afresh at the age of another segment of that province, the Tasmanian Dolerites. Previous K-Ar studies of the dolerites have yielded a range of apparent ages, suggesting problems with argon mobility, so the present study utilized zircon U-Pb instead.

Most of the Karoo-Ferrar dolerites are not zircon bearing, but differentiation in rare layered intrusions and some of the thicker sills has produced granophyres in which there is a sufficient concentration of Zr and SiO₂ for trace zircon to have crystallized. One such granophyre, in the upper part of a large dyke rising from a thick dolerite sheet, is exposed at Red Hill near Hobart, Tasmania. This unit, one of the most strongly fractionated compositions known in Tasmania, contains both zircon and baddeleyite.

Zircon occurs in the granophyre as highly elongate grains characterized by very simple parallel growth zoning, such as is common in the zircon from relatively rapidly cooled mafic igneous rocks. Initial SHRIMP analyses, however, revealed a very wide range of Pb/U ages. Although it could be argued that the range is a consequence of Pb or U mobility, or that some of the zircon is inherited from older rocks, a strong correlation between measured Pb/U and U content suggests instead that these samples are displaying U-dependent bias in SHRIMP Pb/U measurements similar to that reported in an earlier study of high-U zircon from Sri Lanka. The large range in zircon U content (~400–10,000 ppm) and relative youthfulness of the granophyre provide an opportunity to quantify this bias.

Figure 3 shows the Pb/U apparent ages for zircon from one of the granophyre samples plotted against U. Below about 2500 ppm U the measurements of Pb/U are internally consistent, the weighted mean radiogenic ²⁰⁶Pb/²³⁸U yielding an age of ~186 Ma, which is similar to U-Pb zircon and baddeleyite ages measured by others elsewhere in the Karoo-Ferrar province. Above 2500 ppm U, the measured Pb/U increases as a function of U content at a rate of between 1.5 and 2.0% per thousand ppm U. The pattern is similar in two other granophyre samples, and a brief survey of the RSES data base suggests that both the cut-off point, and the magnitude of the effect, are similar for a wide range of zircon ages. There is no evidence that high U biases the measurement of Pb isotopic composition, so that it has no effect on the measurement of ²⁰⁷Pb/²⁰⁶Pb ages.

Recognition of this analytical bias has a number of wider implications for SHRIMP zircon geochronology. First it helps to explain several published data sets in which the higher U zircons in a population were found to be consistently reverse discordant. This in turn weakens the evidence that zircon losing U in preference to Pb is other than a very rare phenomenon. Secondly, it offers a means of, albeit crudely, correcting SHRIMP analyses of high-U zircon, providing a more reliable test for concordance and increasing the range of zircon types that can be dated accurately by SHRIMP U-Pb. Thirdly, and most importantly, it emphasises that the most accurate SHRIMP Pb/U measurements are those made on zircon with relatively low U contents. This is particularly relevant to the strategy adopted in choosing the zircon to analyse for calibration of the numerical time scale, and to the interpretation of Pb/U ages measured on relatively young, high-U metamorphic zircon overgrowths.

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⁴ School of Earth Sciences, The University of Melbourne, Parkville
Zircon trace element geochemistry: the link between U-Pb ages and metamorphism

D. Rubatto and I.S. Williams

Zircon geochronology has long had difficulty in linking U-Pb ages to specific segments of metamorphic P-T paths. Unlike other minerals used in geochronology, such as micas or garnet, the metamorphic reactions leading to zircon (re)crystallisation are largely unknown. This makes the correct interpretation of zircon U-Pb dating of metamorphic rocks extremely difficult. We have approached the problem by marrying in-situ U-Pb dating of zircon with in-situ trace element analyses of the different zircon domains. From the trace element composition of zircon that grew or recrystallised during metamorphism it is possible to obtain information on the metamorphic conditions at the time of zircon formation.

Zircon formed in different metamorphic settings has been analysed for U-Th-Pb using the SHRIMP ion microprobes, and for trace elements (Y, Hf, U, Th and REE) using both SHRIMP (RSES) and LA-ICPMS (RSES and ETH, Zurich).

Zircon grains from granulite grade metasediments of the Reynolds Range Group, central Australia, have metamorphic rims that have overgrown detrital cores mostly of magmatic origin. The zircon overgrowths are present only in samples that crossed the melting reaction biotite + sillimanite $\rightarrow$ cordierite $\pm$ K-feldspar + melt. This indicates that new zircon growth occurred at granulite facies and was triggered by partial melting, a conclusion that is confirmed by the zircon REE composition. Metamorphic zircon overgrowths from both the leucosome and metapelitic melanosome have steep REE patterns with strong enrichments in heavy REE, moderate negative Eu anomalies and strong positive Ce anomalies (Figure 4a). The cores have more variable REE patterns, are relatively flat in the heavy REE, and have a strong negative Eu anomaly and positive Ce anomaly. The metamorphic overgrowths differ from the detrital cores also in having systematically lower Th/U ratios ($\leq$ 0.1). Similar REE concentrations and patterns of the zircon overgrowths from the leucosomes and the melanosomes suggest that both reached equilibrium with the melt. The negative Eu anomaly reflects the presence of feldspar during zircon overgrowth.
formation, whereas the strong enrichment in HREE reflects the absence of garnet in the assemblage. Therefore, the zircon overgrowths crystallised after the breakdown of white mica to form K-feldspar + sillimanite. Garnet-bearing granulites that had the same metamorphic history also contain zircon with metamorphic overgrowths with low Th/U ratios. In that case, the presence of garnet in the paragenesis is reflected in the zircon REE patterns by a significant depletion in HREE (Figure 4a). Therefore, the metamorphic zircon grew after the breakdown reaction of biotite to form garnet ± cordierite + melt, which occurs at granulite-facies conditions.

An eclogite facies metasediment of the Sesia-Lanzo Zone, Western Alps, contains zircon with detrital magmatic cores surrounded by metamorphic rims with low Th/U ratios (<0.1). The detrital cores have higher U, Th and REE contents than the rims and steeper REE patterns with strong negative Eu anomalies (Figure 4b). On the other hand, the metamorphic zircon rims are characterised by extremely low contents of U, Th and REE. Their REE patterns show only a moderate enrichment in HREE, and no Eu anomaly. Flat REE patterns reflect the presence of garnet, which competes for the HREE. The absence of Eu anomalies indicates recrystallization of the zircon rims after the high pressure breakdown of plagioclase. These data demonstrate that the zircon rims formed during eclogite facies metamorphism at relatively low temperatures of 550–600°C.

Hydrothermal zircon from a metamorphic vein within the eclogitic micaschist of the Sesia-Lanzo Zone is rich in U and REE and poor in Th (Th/U <0.1). Its REE patterns (Figure 4b) indicate that the zircon grew in equilibrium with feldspar and in the absence of garnet. This implies that the zircon crystallised at low temperature, prior to the formation of the present eclogite-facies mineral assemblage, probably during prograde greenschist facies. This conclusion is supported by the U-Pb age of the zircon in the vein being 10 Ma older than that of the zircon rims in the eclogitic micaschist. The eclogite-facies metamorphism has not changed the chemical and isotopic composition of the pre-existing zircon. The formation of zircon in the low-grade vein and its resistance to higher metamorphic grade support the hypothesis that zircon crystallisation and isotopic resetting are not necessarily controlled by temperature alone, and can be driven by fluids or melts.

Zircon grains from a diamond-facies gneiss of the Kokchetav massif, northern Kazakhstan, have sector-zoned cores that contain inclusions of various metamorphic minerals. The mineral inclusions are stable at a range of P-T conditions from peak to retrogression, suggesting that zircon grew throughout that part of the P-T path. The ages of the zircon cores with different mineral inclusions, and of the zircon rims, could not be mutually distinguished by SHRIMP. However, the two zircon domains have different REE compositions. The zircon cores have flat REE patterns indicating growth in equilibrium with garnet. In contrast, the steep REE patterns and the marked negative Eu anomalies of the inclusion-free rims point to formation at amphibolite facies grade. From the trace element and isotopic analyses of the
Kokchetav zircon it is concluded that the host rock was exhumed from great depth to amphibolite facies conditions in less than 10 Ma.

Distinctive REE patterns and low Th/U ratios characterise metamorphic zircon and make it possible to link zircon formation with particular metamorphic stages. This correlation is the key to the precise dating of metamorphic events and particularly important because it is now evident that zircon formation can occur over a wide range of P-T conditions in different metamorphic settings.

**Detrital zircon studies of Neoproterozoic supracrystal sequences in the 600 Ma Borborema Province, NE Brazil: Implications for tectonic assembly of western Gondwana**

W.R. Van Schmus, I.S. Williams and B.B. de Brito Neves

The Borborema Province in NE Brazil comprises part of a major Pan-African / Brasiliano orogenic collage that formed as a consequence of the late Proterozoic (ca. 600 Ma) assembly of western Gondwana. The province consists of Palaeoproterozoic to Archean basement blocks with mid to late Proterozoic metasedimentary and metavolcanic sequences which form major fold belts within the central and southern part. Ten years of U-Pb, Sm-Nd and field studies by the senior authors, their students and colleagues have raised several questions that might be answered by SHRIMP analyses of detrital zircon populations. In particular:

1. Why do most of the metasedimentary sequences have Sm-Nd model ages ($T_{DM}$) of 1.2 to 1.6 Ga, even though there are no known igneous units in the Borborema Province with ages in this range?

2. Why does one of the younger metasedimentary sequences, the Seridó Group, have $T_{DM}$ ages of 1.2 to 1.6 Ga, but detrital zircons (measured by ID/TIMS) as young as 740 Ma? Was this unit really deposited about 2.0 Ga ago as some local geologists suggest?

3. Do the several metasedimentary sequences in basins flanking the Cariris Velhos magmatic belt, which also have ca. 1.3-1.6 Ga $T_{DM}$ ages and younger (ca. 1.0 Ga, ID/TIMS) zircons predate or postdate formation of that belt?

SHRIMP analyses of detrital zircon populations from twelve metasedimentary units within the Borborema Province both answered these questions and provided unanticipated insights into other aspects of the tectonic history of the Province. For example, a single ca. 970 Ma zircon population from a siliciclastic unit interbedded with 970 Ma metarhyolite in a basin flanking the Cariris Velhos magmatic belt suggests that the detritus was derived primarily from proximal Cariris Velhos volcanic rocks and that the $T_{DM}$ age of 1.51 Ga, which is similar to those found in the metavolcanic and metaplutonic units, is inherited from that source.

A low-grade member in the Seridó Group, with a $T_{DM}$ age of 1.39 Ga, yielded detrital zircon ranging in age from <700 Ma to >2500 Ma, indicating derivation from several sources. The $T_{DM}$ age is significantly greater than the ages of most of the zircons, consistent with most of the igneous units in the Borborema Province having had a prior crustal history. The presence of a detrital zircon population ca. 650 Ma old confirms that this rock was deposited at or after that time. As the collisional phase of this Pan African / Brasiliano orogen started about 620 Ma ago, the depositional age is now constrained to be within the interval 620-650 Ma, implying that the Seridó basin(s) developed on extended continental crust as pre-collisional flysch basins. This unexpected finding contributes significantly to regional tectonic interpretations.

Several metasediment samples collected from basins on the east and west flanks of the Cariris Velhos magmatic belt all contained detrital zircon from multiple sources. There was a

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5 Department of Geology, University of Kansas, Lawrence, Kansas
6 Instituto de Geociências, Universidade de São Paulo, São Paulo, Brazil
contrast between the ages of those zircons, however (Figure 5). Samples from east of a major fault (Serra do Caboclo Fault) all contained detrital zircon $\geq 970$ Ma old, consistent with those basins being syn- to post-depositional with respect to the $ca. 970$ Ma Cariris Velhos magmatism. Samples from west of the fault, on the other hand, all also contained younger zircons, down to $ca. 630$ Ma old, indicating sedimentation much younger than the magmatism. This conclusion that there are two major metasedimentary sequences separated by as much as 340 million years in depositional age was not anticipated, although it is consistent with limited ID/TIMS results for the region that had seemed anomalous prior to obtaining the SHRIMP data. Independent field and geochemical studies had indicated the duality of sequences, but not the large gap in age.

![Figure 5: Examples of detrital zircon populations from east (BR94–103) and west (94–98) of the Serra do Caboclo Fault, representing the two major metasedimentary sequences now recognised in the region.](image)

This study of detrital zircons from metasedimentary units in the Borborema Province has shown that the Sm-Nd $T_{DM}$ model ages could be the product of a variety of scenarios, ranging from a single source having older crustal residence ages to multiple sources ranging in age from 650 to 2500 Ma. Each case has its own depositional and tectonic implications, all of which contribute to a much better understanding of the pre-collisional (pre-600 Ma) history of Precambrian crust in this province. The SHRIMP has provided data on the depositional ages and provenance of Precambrian sedimentary sequences unobtainable in any reasonable time by more conventional means. The data do not solve all questions however; several of the age populations found in the detrital suites do not have recognized sources in NE Brazil, implying that much of the detritus may have been derived from distant, and presently unknown, sources.

**Problem-solving in defining the Palaeozoic Time Scale**

W. Compston

For the past ten years, SHRIMP time-scale work using zircon Pb/U dating has endured criticisms by practitioners of mass spectrometric isotope dilution (MSID) also working in this field. They are that the SHRIMP ages are ‘1–2%’ low owing to an analytical bias, and that SHRIMP errors are too large for useful time-resolution by present-day standards. These issues have been addressed now in several papers this year that review and compare SHRIMP and MSID dating from the early 1990s. Both of the above criticisms have been refuted and furthermore, several large errors in MSID dating have been discovered that arise from a neglected error-source.
The supposed bias has been attributed to our use of the SL13 zircon as an age-reference. Two known defects in SL13 as a standard, micron-sized excesses of radiogenic Pb and an internal variability in Pb/U on a larger spatial scale, are now known to be related to each other and interpretable as caused by metamorphic Pb redistribution some 10–20 Ma after original crystallization. However, the defects can be tolerated. Age systematics within SL13 combined with a one-off external calibration provide a parameter per analytical session that allows for the internal variability, and in practice, adjustment to the ages for samples based on this parameter is usually less than 0.5% and averages around zero. Use of this procedure replaces an otherwise unknown uncertainty in SL13-related ages by a known and quite acceptable level of uncertainty.

In the early 1990s, the errors we assigned to SHRIMP ages were too big. It was assumed that the precision per spot-age for any sample could never be better than that of the concurrent SL13 ages, and as a consequence the internal errors were deliberately augmented by the observed SL13 standard deviation. The latter dominated the errors in most cases, and this in turn lead to the masking of small age differences between zircons. The apparently single zircon age that resulted for many rocks suited the dogma of the times. The early 1990s was the era of belief in the perfectability of zircons as time-recorders, belief that cogenetic zircons in rocks could be recognized by eye (and others excluded), and belief that the zircons from an igneous rock were predominantly formed during its magmatic precipitation. Improved treatment of SHRIMP errors now shows that single-age zircon populations are the exception, and that inherited zircons just a little older than the latest magmatism are commonly present. This realization has occurred independently in MSID dating with the advent of single-grain analysis.

The original SHRIMP time-scale work on the Ordovician and Silurian British stratotypes has been revised and documented in detail using the above procedures and is now in press. Some of the original ages have gone up slightly and some down. There is agreement within error with $^{206}\text{Pb}/^{238}\text{U}$ ages by MSID for the same biostratigraphic stages, but generally the MSID $^{207}\text{Pb}/^{206}\text{Pb}$ ages are a little older. The latter reflects a newly realized potential for bias in the MSID ages caused by the common Pb correction, to which $^{207}\text{Pb}/^{206}\text{Pb}$ ages are especially sensitive. This was first understood by comparison between the SHRIMP age for the early Arenig and a surprisingly older MSID age for the adjacent late Tremadoc.

![Figure 6: Comparison of SHRIMP and reinterpreted MSID (open symbols) and published MSID (filled) ages for the Ordovician to the early Devonian. The line shown is interpolated between the SHRIMP points. The MSID ages either agree with or are older than the SHRIMP ages, and if older, it is due to the use of $^{207}\text{Pb}/^{206}\text{Pb}$ ages together with the choice of common Pb composition.](image-url)
The dependence of the derivative $^{207}\text{Pb}/^{206}\text{Pb}$ age on the amount and composition of the common Pb in the processed MSID sample became evident by reconstructing the raw observational data then applying slightly different values for the common Pb composition. If the latter was taken as 2% more radiogenic than that given by the global model traditionally used, the apparent single age population with variable Pb loss changed into two age groups, the younger of which agreed very well with expectations from the SHRIMP age. What first read as a conclusive age determination was transformed into an ambiguous one. Scrutiny of other MSID zircon ages that conflicted either with SHRIMP or well-documented ages by other radioactive decay schemes showed that the same ambiguity was present, and the conflict could be removed by adjusting the common Pb correction and allowing more than a single age population. This was especially so for recently published MSID ages for the Devonian that conflict with Rb-Sr and K-Ar determinations for the Frasnian in NE Victoria.

A large body of published and unpublished SHRIMP ages for biostratigraphically-defined volcanics within the Cambrian and late Proterozoic are now being reassessed and compared with recently published MSID ages. The main task is to make a correct and objective identification of age-groups as being inherited, cogenetic with the volcanics, or a post-extrusive Pb loss ‘group’.
NOBLE GAS GEOCHEMISTRY AND GEOCHRONOLOGY

The techniques of noble gas geochemistry and K-Ar and 40Ar-39Ar geochronology have close affinities. In all cases, measurements are made on very small amounts of noble gases extracted from geological samples, usually by heating in ultrahigh vacuum systems, with isotopic ratios and amounts of the noble gases determined in gas-source mass spectrometers operated in the static mode, that is isolated from the pumping systems. Particularly stringent requirements must be met in relation to cleanliness of the systems in order for the analyses to be made successfully.

Both the K-Ar and 40Ar-39Ar techniques for dating rocks are based upon the decay of the naturally occurring radioactive isotope of potassium, 40K, which produces 40Ar as one of its daughter products. Measurement of the accumulated argon and the amount of potassium in appropriate minerals and rocks, together with knowledge of the rate of decay of 40K, enables the time since the system became closed to argon diffusion to be determined. Rapidly cooled igneous rocks commonly yield precise ages, accurately recording the time since eruption. Such measurements are very helpful in stratigraphic geochronology and for determining numerical time scales for a wide range of geological events and processes. The 40Ar-39Ar dating technique is especially useful in relation to determining thermal histories of geological terranes, providing numerical cooling rates associated with the tectonic evolution of orogenic belts.

The K-Ar and 40Ar-39Ar laboratories have been quite productive in the year under review with more than 2600 argon isotopic analyses having been made. Approximately 70 new K-Ar age measurements were produced, about 60 40Ar-39Ar age spectra, averaging some 28 steps per spectrum, were measured, and over 130 single crystal 40Ar-39Ar total fusion age measurements were made. A summary of some of the work accomplished follows. Technically, the major achievement during the year was the full commissioning of the automation on the VG1200 mass spectrometer and its associated extraction system, mainly through the efforts of Dr X. Zhang. Isotope ratio measurement of argon using the electron multiplier in the VG1200 was undertaken successfully, enabling samples about one fiftieth of the size previously measured to be utilized for age measurement on a routine basis.

We welcome Dr D. Phillips, who is employed by PRISE, as a user of the facilities in the K-Ar and 40Ar-39Ar dating laboratories. The automation of the extraction lines and mass spectrometers is making the laboratories more efficient and productive, and is particularly important in enabling a service to be offered to the wider geological community at a reasonable cost.

The noble gases, helium, neon, argon, krypton and xenon, are useful geochemical tracers. Studies of their abundances and isotopic compositions in geological samples provide important constraints on hypotheses concerned with the origin and evolution of the Earth’s atmosphere, crust, mantle and core. The identification of the primordial noble gas composition of the Earth is critically important for understanding how and when the Earth acquired its volatiles and how its atmosphere evolved. In recent years we have found a remarkable correlation between helium and neon isotope systematics in mantle-derived samples. These results have provided strong evidence for primordial helium and neon within the Earth of solar composition. It is clearly desirable to ascertain whether the primordial heavier noble gases, argon, krypton and xenon in the Earth were also solar in composition. Important insights also may be found by studying other volatiles in the mantle, including nitrogen and carbon dioxide. To better constrain the evolution of noble gas compositions in the mantle we plan to undertake noble gas studies on old mantle-derived materials, including Archaean komatiites and diamonds. Research projects related to cosmogenically-produced noble gases are being considered for the future. Research student Eleanor Dixon has completed her noble gas measurements on suites of basalts from Iceland and West Greenland, and she is currently writing her PhD thesis.

During the year we installed a Balzers secondary electron multiplier with a pulse counting system on the VG5400 mass spectrometer. The necessary source codes for operation of the pulse counting system and the data acquisition were written. The detection limit and precision of
measurement of small ion beams of krypton and xenon have been significantly improved using ion counting, compared with the existing Daly measurement system. Currently we are modifying the noble gas extraction system for the automation of gas handling procedures. When completed, we hope that there will be a considerable increase in both productivity and efficiency, allowing us to start some new projects.

In 1999 a total of 14 samples were analysed for noble gases. These included a number of very old magmatic zircons from Greenland, with the noble gases measured following step-wise heating from 400°C to 2000°C. Additional samples measured included quartz samples from central Australia and clinopyroxenes from the Alexandra Volcanic Province, New Zealand. The overall number of analyses on the VG5400 mass spectrometer was 177 during the year. About two-thirds of these analyses were related to measurement of blanks in the ultrahigh vacuum (UHV) system and calibrations of sensitivity and discrimination of the mass spectrometer. Summaries of some of the studies undertaken are given in the following sections.

**Stratigraphic geochronology at Lothagam, northern Kenya**

_I. McDougall and C.S. Feibel_7

Lothagam, located west of Lake Turkana in northern Kenya, is an uplifted fault block comprising a gently westward-dipping sequence of volcanic and sedimentary rocks, about 900 m thick, deposited in a half-graben basin within a zone of extension in the northern part of the Kenya Rift. A lower sequence of volcanic and volcaniclastic rocks (the Nabwal Arangan beds) is followed by a sedimentary sequence of sandstones, siltstones and mudstones of the Nawata Formation and the Nachukui Formation, deposited in fluvial, alluvial fan and lacustrine environments (Figure 8). An expedition led by Dr M.G. Leakey of the National Museums of Kenya has recovered a very rich and diverse fauna from this sequence, with a number of the vertebrates new to science. This fauna documents a turnover from Late Miocene forest communities to the early inhabitants of the Plio-Pleistocene in more open bush and woodland. Because of the remarkable faunal record, including the earlier discovery of a fragmentary hominoid mandible from the Apak Member of the Nachukui Formation, we have undertaken a detailed K-Ar and 40Ar-39Ar dating program on the sequence. The early volcanism recorded in the sequence extended from about 14 Ma to 9 Ma ago (Figure 8). A number of altered tuffaceous horizons in the lower member of the Nawata Formation contain small pumice clasts from which crystals of alkali feldspar were recovered, providing ideal material for single crystal 40Ar-39Ar age measurements. Highly precise, concordant results were found for feldspars from any one level, and excellent concordancy with the stratigraphic order also was found (Figure 8), demonstrating that the lower member was deposited over more than 1 Ma from >7.4 Ma to 6.5 Ma in the Late Miocene. In a mudstone just below the Lothagam Basalt in the Apak Member of the Nachakui Formation, small (~10 mm) altered pumice clasts were found; single crystal age measurements on feldspars from this horizon yielded a very precise age of 4.22 ± 0.03 Ma (Figure 8), presumed also to give a good estimate for the age of deposition. The overlying Lothagam Basalt proved very difficult to date because of the surprising presence of excess argon, but 40Ar-39Ar age spectra on whole rock samples and plagioclase separates yielded a best estimate age of 4.20 ± 0.03 Ma for the basalt, consistent with the other results. The hominoid mandible from the lower Apak Member could only be placed as older than 4.2 Ma and younger than 5.0 Ma on the basis of these results. Nevertheless, the new age control on the Lothagam sequence places the fossil faunas in a much better time framework than previously available, helpful also in relation to regional and global patterns of change in and around the Messinian Stage at the end of the Miocene. In addition, the sequence at Lothagam provides good documentation of some of the earlier history of rift valley evolution in this part of the Kenya Rift.

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7 Rutgers University, New Jersey, USA
Figure 8: Schematic composite stratigraphic column for Lothagam. Isotopic ages shown at the appropriate stratigraphic level. Magnetostratigraphy, together with the geomagnetic polarity time scale, shown on the right.

**Victoria Range, Cretaceous core complex confirmed**

*W.J. Dunlap, J. Braun and A. Tulloch*

Exploration of the Victoria Range, Westland, New Zealand, has confirmed suspicions that this portion of the Paleozoic-Mesozoic Karamea batholith is an exhumed lower plate of a Late Cretaceous core complex that formed at about the time of the initial opening of the Tasman Sea, and in a manner similar to that documented for the Paparoa Range to the west. The geometry,

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* Institute of Geological and Nuclear Sciences, Dunedin, New Zealand
fault kinematics and cooling history of the Victoria Range core complex have been explored through reconnaissance field study, detailed $^{40}$Ar-$^{39}$Ar step heating experiments on K-feldspars, and 3D numerical studies of block uplift, erosion and cooling. In studying the Late Cretaceous crustal evolution, however, we have been able to place constraints on subsequent Miocene tectonism, just prior to formation of the adjacent Alpine Fault.

In the field it is observed that the dominant Late Cretaceous extension direction was essentially strike-parallel. We believe that the complex was unroofed in a transtensional regime with a large component of strike slip. The strike slip motion was accommodated on steeply dipping faults in valleys at the margins of the complex whereas the cover rocks were removed from above the topographically high granitic core on low-angle detachments kinematically linked to the bounding strike slip faults. It is not yet clear if the dominant regional kinematics were right lateral or left lateral. Extensive sheets of granitic magma were emplaced during or shortly before the onset of extension and relatively rapid cooling of the lower plate granitic rocks ensued as the cover was removed.

Evidence for Cretaceous rapid cooling is preserved in both the fault zone microstructures and the age gradients of the K-feldspars. Fault zone microstructures in the core of the complex formed under lower amphibolite facies conditions whereas those in the bounding fault zones formed at sub-greenschist facies temperatures, as indicated by deformation mechanisms of quartz and feldspars, suggesting progressive unroofing during fault zone evolution. The age gradients preserved in the K-feldspars (Figure 9) have been used to track the lateral removal of the cover rocks through time. In addition, the vertical thermal gradients that prevailed at the end of Cretaceous tectonism are well resolved by the K-feldspar thermochronology.

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![Figure 9: Temperature – time history for the Victoria Range.](image-url)
Subsequent Miocene block uplift, possibly related to activation of the Alpine fault, or precursor transpression, is limited to a few kilometres. The geometry of this block uplift is relatively simple, which allowed us to use a straightforward 3D numerical code to model the uplift as a rigid block advecting vertically through a fixed topography, and track the thermal response to uplift and exhumation. Numerical results for the Cretaceous to Miocene exhumation show remarkable agreement with the thermochronological models from the K-feldspars, suggesting that the thermal gradient from mountain top to valley floor can only be preserved if the geotherm in the granitic core of the complex stabilized during tectonic quiescence from about 90 Ma to less than 20 Ma. Renewed exhumation later in the Miocene drove cooling to below the lower closure temperatures of the K-feldspars, as independently confirmed by published apatite fission track data. Moreover, we find no conflict between multidiffusion-domain models of argon diffusion in K-feldspars, the general geologic history of the region, the numerical model of exhumation and cooling, and the independent geochronologic data.

Preservation of solar neon isotopic ratios in Icelandic basalts

E.T. Dixon, M. Honda, I. McDougall and I. Campbell

Neon isotopic ratios measured in olivine and basaltic glass from Iceland are the most primitive ever observed in terrestrial mantle-derived samples. Ratios were measured in gas released from olivine and basaltic glass from a total of ten youthful samples from the Reykjanes Peninsula, Iceland, and include solar, mid-ocean ridge basalt (MORB)-like and atmospheric compositions. Neon isotopic ratios near the air-solar mixing line were obtained from the total gas released from olivine and glass separates from four samples. MORB-like neon isotopic compositions were measured in the total gas released from olivine and glass separates from six samples (Figure 10).

![Figure 10: Neon three isotope plot, showing total gas ratios from a total of 10 samples for 8 olivine and 10 glass separates. The air-solar mixing trend, the mass fractionation line from air (mfl), the Loihi trend and the MORB trend are shown for reference. Inset plot shows detail of samples that lie near the MORB trend and are distinct from the neon composition in air within two sigma uncertainty. One sigma uncertainties shown.](image)

Although there is clear evidence for a solar neon component in some of the Icelandic samples, there is no corresponding evidence for a solar helium ratio (320 Ra > ^3He/^4He > 100 Ra). Instead, ^3He/^4He ratios are between 12 ± 2 and 30 ± 2 Ra, similar to the range observed in other ocean island basalts, indicating that the He-Ne isotopic systematics are decoupled. Calculations show that such decoupling can be achieved by mixing between noble gases from
the Icelandic plume with those from a MORB-like component, provided that the two components have different $^3\text{He}/^{22}\text{Ne}$ ratios (Figure 11). The mantle source of Icelandic basalts is interpreted to be highly heterogeneous on a local scale to explain the range in observed helium and neon isotopic ratios.

Identification of primitive solar neon isotopic ratios in some Icelandic samples implies that solar neon trapped within the Earth has remained virtually unchanged over the past $\sim$4.5 Ga. Such preservation requires a source with a high $[\text{Ne}_{\text{sol}}]/[\text{U} + \text{Th}]$ ratio so that the concentration of solar neon overwhelms the nucleogenic $^{21}\text{Ne}^*$ produced as a result of decay of U and Th in the mantle over time. High $[\text{Ne}_{\text{sol}}]/[\text{U} + \text{Th}]$ ratios are unlikely to be preserved in the mantle if it has experienced substantial melting. A primitive, undegassed mantle component is postulated to be the host of the solar neon in the Icelandic plume source. Relatively small amounts of the primitive mantle component are likely to mix with more depleted and degassed mantle such that the primitive mantle composition is not evident in other isotopic systems (e.g., strontium and neodymium). The primitive, undegassed mantle in the Icelandic plume source can be compared with the MORB mantle source, which is known to have experienced substantial melting and degassing. The proportion of solar neon in the Iceland plume source is estimated to be at least 13 times greater than that in the MORB source. In comparison, the Hawaiian plume source, with a less primitive neon mantle endmember ratio than the solar neon end-member in Icelandic plume source, has a fraction of solar neon that is only about 6 times greater than in the MORB source. The lower mantle plume source is inferred to be relatively heterogeneous owing to being more viscous and less well stirred than the upper mantle. This discovery of near-solar Ne isotopic ratios is significant to our understanding mantle convection and degassing processes because it suggests that relatively primitive mantle may be preserved in the Icelandic plume source.

![Figure 11: Calculated mixing curves between solar noble gases in the Icelandic plume with MORB-like noble gases showing predicted variation in the $^3\text{He}/^\text{He}$ and $^{21}\text{Ne}/^{22}\text{Ne}$ ratios as a function of R. The box labelled “S” represents the results from this study with solar neon isotopic ratios and $^3\text{He}/^\text{He}$ ratios near 20–30 Ra. The box labelled “H” represents the results of an Icelandic noble gas study by Harrison et al. (1999, EPSL 171, 199–207) with comparatively less primitive mantle helium and neon ratios. Mixtures with an R value of 0.3 can explain the results from both the present study with solar neon ratios and those of Harrison et al. (1999). Mixtures with higher values of R near 6 can explain the results from this study with MORB-like neon ratios and $^3\text{He}/^\text{He}$ ratios near 12 Ra (box labelled “M”) that are higher than the expected MORB ratio of 8.5 Ra. The required differences in the R values can be explained by variable degrees of elemental fractionation of helium from neon in the plume or MORB-type magma prior to mixing.](image-url)
Xenon composition of magmatic zircons from 3.63 and 3.81 Ga granitoids from Greenland

M. Honda, A. Nutman and V. Bennett

Excesses of $^{129}$Xe relative to atmospheric xenon have been observed in mantle-derived samples, including MORB glasses and ultramafic xenoliths from Samoan ocean island basalts and from ancient diamonds. The excess $^{129}$Xe has been attributed to radioactive decay of the extinct nuclide $^{129}$I (half-life of 17 million years), present in the Earth at its formation. The difference between atmospheric xenon and that observed in mantle-derived samples generally is thought to be related to early degassing of volatiles from the solid Earth, implying that degassing must have occurred before all the $^{129}$I decayed, that is within about 100 million years after the formation of the Earth. The excess in $^{129}$Xe in mantle-derived samples appears to be correlated with excesses in $^{131-136}$Xe relative to atmospheric xenon. The majority of excesses in $^{131-136}$Xe are attributed to spontaneous fission of $^{238}$U (half-life of 4.468 million years), although an additional potential source is from another extinct nuclide, $^{244}$Pu (half-life of 82 million years). If the Earth had a chondritic $^{244}$Pu/$^{238}$U ratio of 0.007, as observed in meteorites, accumulation of fission $^{136}$Xe derived from $^{244}$Pu should be 30 times more than $^{238}$U-derived fission $^{136}$Xe. The apparent lack of Pu-derived fission xenon, in the presence of $^{129}$I-derived radiogenic $^{129}$Xe in samples from the mantle, is a paradox in relation to the early degassing of the Earth. This is because the half life of $^{244}$Pu is longer than that of $^{129}$I so that we would expect a significantly greater fraction of $^{244}$Pu-derived fission xenon to remain in the mantle in comparison with $^{129}$I-derived radiogenic $^{129}$Xe.

In order to solve the fundamental problem as to whether some $^{244}$Pu was included in the Earth when it formed, we have analysed magmatic zircons from three early Archaean granitoids from Greenland for xenon. Two samples, a granite and a ferrogabbro/ferrodiorite, are from the same intrusive body about 3.63 Ga old. The third sample is a well-preserved metatonalite with an age of ca 3.81 Ga. The U-Pb ages of these zircons were determined by SHRIMP. Xenon from the 3.63 Ga magmatic zircons is dominated by the products of spontaneous fission from $^{238}$U. In contrast, the 3.81 Ga magmatic zircons appear to have some excess fission xenon different from the $^{238}$U-derived fission xenon. This excess fission xenon is consistent with that expected from $^{244}$Pu fission, so that this may indicate that these zircons incorporated $^{244}$Pu when they crystallised at ca. 3.8 Ga; this would be expected if the primitive Earth had the chondritic $^{244}$Pu/$^{238}$U ratio at 4.55 Ga. Reaching this provisional conclusion required that all zircons in the 3.8 Ga sample were consumed. We plan to collect more of the sample in 2000 in order to authenticate these exciting xenon results.

Cosmogenic $^{21}$Ne in a central Australian quartzite

D. Patterson, M. Honda, D. Belton, R. Brown and B. Kohn

Cosmogenic $^{21}$Ne in near-surface quartz samples. Under favourable conditions (high altitude, high geomagnetic latitude, and surface exposure) production rates are sufficiently high to produce detectable amounts of cosmogenic $^{21}$Ne in less than 10 ka of exposure. Cosmogenic $^{21}$Ne in natural samples can be used to estimate exposure ages that constrain rates of uplift and erosion.

On the basis of stratigraphic and geomorphic evidence, Stewart et al. (Science, 233, 758, 1986) suggested that the present day land surface of parts of the Davenport Province of the Tennant Creek area in central Australia may be remnants of a Cambrian or Precambrian surface. If correct, this area is one of the oldest landscapes on Earth, and would be expected to have extraordinarily high cosmogenic exposure ages. This view, however, is being challenged by ongoing apatite fission track and cosmogenic $^{10}$Be studies by investigators at the School of Earth Sciences, University of Melbourne, who argue that this landscape is instead a relatively recently exhumed paleosurface. The Davenport Province therefore provides an excellent

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* School of Earth Sciences, University of Melbourne
opportunity to apply cosmogenic $^{21}\text{Ne}$ exposure dating to investigate whether the landscape might be an ancient one.

We analysed two quartz samples from quartzite at the surface from the Davenport Province (provided by University of Melbourne) for all five noble gases: DR98–6C (565 m altitude, 20°46.952' S, 134° 35.969' E) and DR98–16 (565 m altitude, 21° 21.934' S, 135° 18.564' E). Both samples were collected from within 5 cm of the present day surface. The samples are characterized by radiogenic $^{4}\text{He}/^{4}\text{He}$ ratios of $< 10^{-8}$ and non-atmospheric $^{21}\text{Ne}/^{22}\text{Ne}$, $^{40}\text{Ar}/^{36}\text{Ar}$ and $^{136}\text{Xe}/^{130}\text{Xe}$ ratios ($\sim 0.037$, $\sim 10,000$, and $\sim 2.3$, respectively). The high $^{40}\text{Ar}/^{36}\text{Ar}$ and $^{136}\text{Xe}/^{130}\text{Xe}$ ratios indicate unambiguous crustal-derived radiogenic and fissiogenic components, possibly trapped in fluid inclusions in the quartz. A significant fraction of the non-atmospheric $^{21}\text{Ne}$ is therefore nucleogenic $^{21}\text{Ne}$ ($^{21}\text{Ne}_{\text{Nuc}}$), produced by the $^{18}\text{O}($\text{\textalpha},\text{n}$)^{21}\text{Ne}$ reaction, where $\text{\textalpha}$ is generated from uranium and thorium decay in the crust. It is necessary to estimate the amount of $^{21}\text{Ne}_{\text{Nuc}}$ in the samples before attempting to calculate cosmogenic $^{21}\text{Ne}$ ($^{21}\text{Ne}_{\text{Cosmo}}$) exposure ages. For the following calculations, we assume that all $^{4}\text{He}$ and non-atmospheric $^{40}\text{Ar}$ ($^{40}\text{Ar}^*$) is radiogenic in origin. Combining observed $^{4}\text{He}$ and $^{40}\text{Ar}^*$ with known crustal $^{21}\text{Ne}_{\text{Nuc}}$/radiogenic $^{4}\text{He}$ and $^{21}\text{Ne}_{\text{Nuc}}$/$^{40}\text{Ar}^*$ production ratios provides an estimate of the $^{21}\text{Ne}_{\text{Nuc}}$ present. Subtracting $^{21}\text{Ne}_{\text{Nuc}}$ from the non-atmospheric $^{21}\text{Ne}$ yields the abundance of $^{21}\text{Ne}_{\text{Cosmo}}$. Based on this approach we estimate that only about 30% of the non-atmospheric $^{21}\text{Ne}$ in DR98–6C is cosmogenic. Similarly, for DR98–16, about 38% is cosmogenic. The amounts of estimated $^{21}\text{Ne}_{\text{Cosmo}}$ in DR98–6C and DR98–16 are approximately $4.6 \times 10^{-13}$ and $6.1 \times 10^{-13}$ cm$^3$STP g$^{-1}$, respectively.

To calculate cosmogenic $^{21}\text{Ne}$ exposure ages we have taken the production rate of cosmogenic $^{4}\text{He}$ in quartz of 21 atoms g$^{-1}$ a$^{-1}$ at high geomagnetic latitudes ($> 60^\circ$) and sealevel given by Niedermann et al. (EPSL, 125, 341, 1994). When scaled for latitude and altitude using the equations of Lal (EPSL, 104, 424, 1991), we estimate the local production rate in the Davenport Province to be 22 atoms g$^{-1}$ a$^{-1}$ or $8.2 \times 10^{-19}$ cm$^3$STP g$^{-1}$ a$^{-1}$. Using this production rate, we estimate quite young exposure ages of 560 ka and 750 ka for DR98–6C and DR98–16, respectively. These exposure ages are inconsistent with long-term subaerial survival of the Davenport landscape from Cambrian or Precambrian times, and support the suggestion of relatively recent exhumation.