

GEOCHRONOLOGY AND ISOTOPE GEOCHEMISTRY

Research in the Geochronology and Isotope Geochemistry Group focuses on the application of geochronological and geochemical techniques to geological problems that address fundamental questions concerning the origin and evolution of the Earth. Geochronological studies provide age information on a wide range of geological processes and events, especially in the Earth's crust, helping us to understand how the Earth works. Geochemical studies likewise yield important insights into the history of the Earth and the Solar System.

The SHRIMP ion microprobes are a major analytical facility within the group, enabling precise and accurate elemental and isotopic analyses of small areas of samples (spot size commonly ~25 µm diameter). The ion microprobes are utilized principally for U-Pb isotopic dating of zircon and other suitable minerals and for analysis of major and trace elements. The other significant set of facilities within the group centre on gas source mass spectrometers and associated gas extraction systems; these are used for K-Ar and ^{40}Ar - ^{39}Ar isotopic dating measurements and for the isotopic analysis of noble gases extracted from suitable samples, mainly derived from the Earth's mantle.

Many of the analytical facilities of the Geochronology and Isotope Geochemistry Group are shared with the Australian Geological Survey Organization and our own organization Precise Radiogenic Isotope Services (PRISE) which provides analytical services to academia and industry; see elsewhere in this annual report for more details of their work.

Some of our group's research highlights this year, described in more detail in the following pages, were the discovery of Xe isotopic evidence for the former presence of now-extinct ^{244}Pu in early Archean zircon from Greenland; the discovery, also in Greenland, of Pb isotopically more primitive than any previously found on Earth; the first measurements of Pt abundances in eclogites; the first measurement, in an equilibrated natural system, of the partitioning of rare earth elements between garnet and zircon; the discovery that the effects of Carboniferous tectonism (the Alice Springs orogeny), previously thought to have been restricted to central Australia, actually extend south into the Adelaide Fold Belt; the demonstration, by direct age measurement, that subantarctic Marion Island was built up by at least eight distinct periods of volcanic activity; and the discovery, through age measurements on detrital zircon from Gondwana-margin sediments in the central Transantarctic Mountains, of evidence for Rodinian sedimentary connections between East Antarctica and Laurentia. These examples serve to demonstrate the diverse range of topics that are investigated within the group—most projects focus on a particular area or suite of samples, generally, however, aiming to answer questions relating to much broader global issues.

Instrument development continued to play a vital role in advancing our analytical capabilities, ensuring that we remain competitive in the microanalysis field. Considerable progress was made during the year in commissioning the prototype multiple collector on SHRIMP II. Also, the four electrostatic quadrupoles in the SHRIMP RG secondary mass analyser were redesigned and rebuilt, and their immediate structural environments modified, in order to achieve focal properties closer to those required by the ion optic model on which the instrument is based. This is expected to bring the instrument much closer to achieving design performance.

Academic staffing additions during the year expanded and strengthened the ion microprobe subgroup. Dr Vickie Bennett, formerly Research Fellow in the group, accepted a continuing appointment in April. She will undertake research into the chemical evolution of the Earth's mantle and crust, with a particular emphasis on the behaviour of the siderophile elements. Dr Trevor Ireland, formerly of Stanford University, took up his appointment within the group in September. Trevor brings to the group expertise in cosmochemistry and ion microprobe analytical techniques. Graduate student Eleanor Dixon successfully completed her PhD studies during the year and we wish her well in her postdoctoral appointment with NASA in Houston, Texas.

The success of our research effort owes much to the excellent support provided by the technical staff within the group, as well as by members of the School's mechanical and electronic workshops, and sample preparation laboratories. Without such support, much of our research simply would not be possible.

SHRIMP instrument development

S.W. Clement¹, J.J. Foster, T.R. Ireland, B. Jenkins, P. Lanc², N. Schram, R. Waterford and I.S. Williams

SHRIMP II: Over a period of three months in late 1999 the RSES SHRIMP II was fitted with a prototype multiple collector, the design and construction of which was described in the 1999 RSES Annual Report. Commissioning the collector has proved to be a difficult and protracted task, and although considerable progress has been made, much still remains to be done. One major difficulty is the fact that the SHRIMP II is the primary analytical instrument for the research of several RSES staff, PRISE and the AGSO geochronology group. Even short periods of down time for instrument development have a major impact on many research programs. We are grateful to these people for the understanding that they have shown as the development work has proceeded.

At intervals of approximately two months throughout this year, analytical work on SHRIMP II was suspended for periods of two to three weeks and a series of experiments carried out with a view to bringing the multiple collector into operation. It was important at an early stage to implement the single axial ion counter analysis mode, so that multiple collector experiments and single collector analysis could be interspersed with minimal interchange time. Initial multiple collector efforts focused on the mechanics and basic computer control of the drive mechanisms. Those achieved, questions of ion counting were addressed, including the performance of the newly-built pulse count system interface, counter control and data acquisition software, resolution, interferences, and the efficiency of the conversion electrodes and ion counters. Once all five ion counter assemblies were functional, it was possible to map the focal plane in both static and dynamic mode and to demonstrate that, over a distance of >100 mm either side of the central ray trajectory, the focal plane remained within range of the adjustment available in positioning the collector slits such that a resolution of >4000 could be maintained. It was also established that, in accord with the design objectives, it was possible to configure the multiple collector for the simultaneous detection of ¹⁶O, ¹⁷O and ¹⁸O on the one hand, and of ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁸Pb on the other.

Work has recently advanced to the stage where it has been possible to address the problems of isotope ratio measurement, including determining and setting multiple slit positions, measuring the relative gains of the various counters, synchronisation of counter-timers, measurement procedures and on-line data processing. Development and testing of the requisite protocols and software has been both the major task and the principal achievement of this round. The work has also identified a number of problems still to be solved, however, and we recognise that it will be several months before isotope ratios we measure by multiple ion counters will exceed in precision and accuracy those we measure by a single ion counter and peak switching. In the meantime, the emphasis in the multiple collection experiments will shift to implementing isotope ratio measurement by multiple Faraday cups.

SHRIMP RG: Detailed analysis of the overall SHRIMP RG ion optic model during 1999 had confirmed empirical observation that the focus of the instrument is considerably more sensitive to changes in ion optic parameters than is the focus of the forward geometry SHRIMP I or II. The analysis found no fundamental flaw in the model itself, however, so the task this year was to determine why SHRIMP RG nevertheless has so far failed to operate to its design specifications. The approach used was to try and identify which of the lens elements might have ion optic properties different from those which the Matsuda design requires.

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Close scrutiny of the four electrostatic quadrupole lenses, which involved comparing the focal properties of each lens in its particular local structural environment with the 'free space' properties assumed in the original Matsuda model, revealed that the design of the lenses and their supports, the location of some adjacent sub-assemblies, and the close proximity of some vacuum chamber walls were causing unintended clamping of the electrostatic fields. The effect of these perturbations was to reduce the effective lengths of the lenses, to shift the positions of the field boundaries, to increase the drift lengths before and after each lens, and to produce different fringing field distributions from those required. By modelling the mass analyser as a whole and adjusting the hypothetical strengths of the quadrupole lenses iteratively to maximise the quality of focus by minimising or cancelling the aberration coefficients responsible for image broadening and distortion, it was determined that it would not be possible to compensate for these effects simply by changing lens potentials. The lenses and their environments needed to be modified. All four quadrupole lenses and their housings therefore have now been redesigned and rebuilt, slit assemblies have been relocated, and the vacuum chambers have been selectively enlarged.

As this work proceeds, the focal properties of the magnetic sector of the mass analyser are being assessed. As with the electrostatic lenses, the principal difference between the theoretical and actual magnetic field distribution is in the fringing fields. Modelling suggests that the effect of these differences on ion focusing would be much less, however, than the effects of the discrepancies in the electrostatic lenses. Modelling is underway at both RSES and Danfysik, Denmark, to determine what modifications to the magnet and its field clamps might be required to achieve a field distribution which is better matched to that which the Matsuda ion optic design requires. To check the veracity of the modelling, however, the focal properties of the instrument will be tested immediately after the modifications to the electrostatic lenses, before any changes are made to the magnet.

Age and provenance of the Beardmore Group, Transantarctic Mountains, a Neoproterozoic-Paleozoic transition assemblage at the Gondwana margin

J.W. Goodge³ and I.S. Williams

Supracrustal assemblages of the Ross Orogen, eastern Antarctica, were deposited during the Neoproterozoic to early Paleozoic transition (~700–500 Ma), a critical period in Earth history marked by fragmentation of the supercontinent Rodinia, and the subsequent amalgamation of Gondwana. This fundamental rearrangement of the continents coincided with major mountain building, continental erosion, species diversification, sea level fluctuations, and changes in sea water composition on a global scale. Continental margin sedimentary sequences spanning this transition, such as those in the Transantarctic Mountains, contain detailed records of sedimentation patterns, sea level fluctuations, faunal distributions, and post-depositional tectonism.

As part of a project to determine the structure, stratigraphy, sedimentology, and chronology of these siliciclastic units, a comprehensive study is being undertaken of detrital zircon in sandstones of the Beardmore Group, the main Neoproterozoic to early Paleozoic clastic unit in the central Transantarctic Mountains. SHRIMP U-Pb ages for large populations of detrital zircon from Beardmore sandstones are providing the first reliable control on both the depositional ages of the various sediments and their diverse provenance. Work on four samples of sandstone from the Beardmore Group has been completed; work on eight more samples from the wider region is under way.

Initial results indicate that the Beardmore Group consists of at least two main assemblages — an inboard, proximal assemblage probably deposited in the late Neoproterozoic (<1.0 Ga), and a more voluminous outboard, distal assemblage that was deposited much later, probably in the Early to Middle Cambrian (<520 Ma). The inboard assemblage consists of mature, multi-

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cycle sediments derived from the Precambrian craton. It represents a rift- or passive margin succession derived from a wide variety of sources dominated by components with ages of 2.8 and 1.9–1.4 Ga. The ~1.4 Ga component is of particular interest because it is so very rare in the

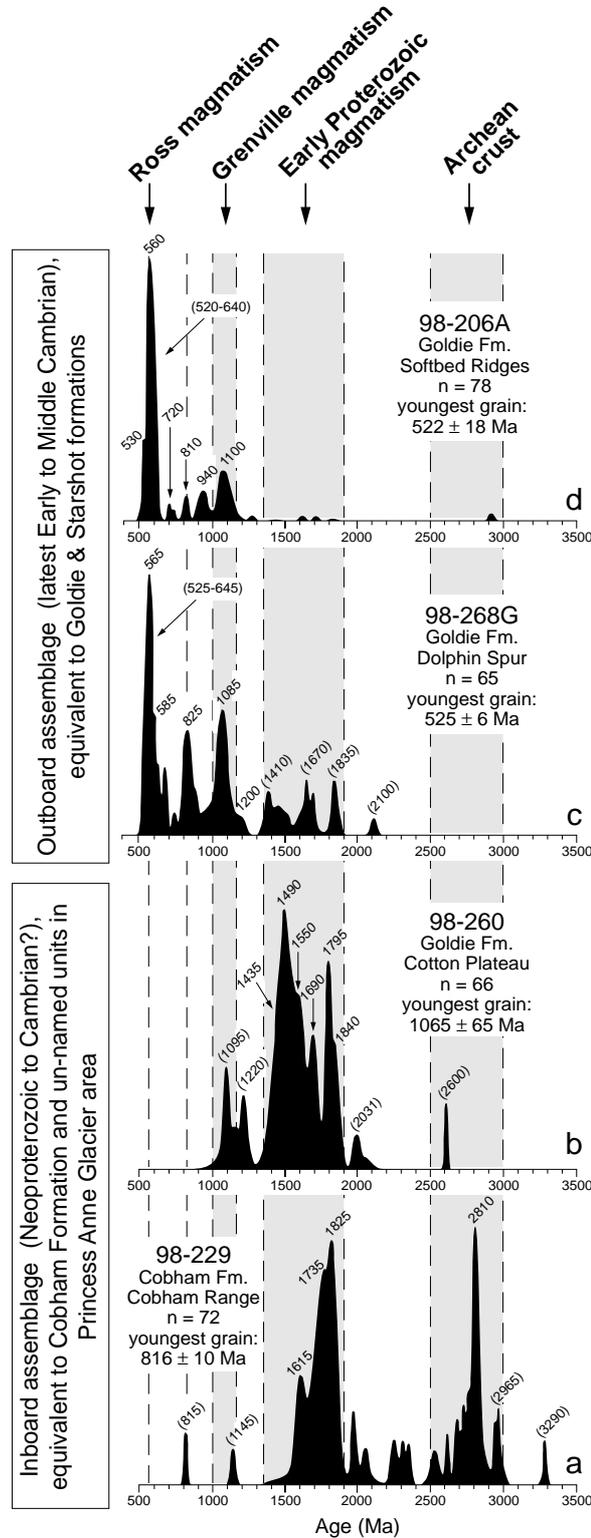


Figure 1: Relative probability plots of detrital zircon U-Pb ages from Beardmore Group samples (n = number of individual grains analyzed; ages in Ma). Ages have been assigned to peaks based on mixture modelling. Sedimentary rocks of the inboard assemblage (a, b) are characterized by a large proportion of Archean and Proterozoic components, whereas the outboard assemblage (c, d) is dominated by input from latest Neoproterozoic and Early Cambrian sources. The youngest grains in the latter (~520 Ma) indicate the deposition age of the outboard assemblage to be Early Cambrian or younger.

cratonic areas of East Antarctica and Australia. The outboard assemblage represents first-cycle sediments with a dramatically different provenance, including fresh, young (580–550 Ma), locally-derived material from an eroding volcanic arc, and contributions from Grenville-age basement (1100–940 Ma) and an ~825 Ma magmatic center. The youngest grains in the outboard assemblage are 526–518 Ma, consistent with the age of newly discovered Cambrian trace and body fossils in that sequence. The positions of these assemblages relative to the cratonic margin suggest a shift in time and space from inner margin sedimentation derived from the adjacent craton, to a younger outer margin succession that received most of its detritus from an active margin magmatic source. Contrary to earlier views regarding the deposition age of the Beardmore Group, the ages of the youngest detrital zircon in the outboard assemblage require that most of the Group is late Early Cambrian or younger. The presence of ~1.4 Ga components in both assemblages cannot be explained by currently known Antarctic or Australian sources, but possibly indicates a connection between elements of the Antarctic craton and Proterozoic granite provinces in Laurentia. Eastward paleocurrents in the outboard assemblage and input from a Cambrian continental margin magmatic arc indicate that the assemblage is autochthonous, not a terrane of exotic origin. The Beardmore Group therefore represents both rift- and active margin stages during Neoproterozoic-Cambrian time, and it may provide evidence for Rodinian sedimentary connections between East Antarctica and Laurentia.

SHRIMP dating of metamorphic titanite: precise pressure-temperature-time path and exhumation rate of deeply subducted crustal rocks

D. Rubatto and J. Hermann

The occurrence of high pressure rocks within orogenic belts provides evidence for dynamic subduction and exhumation of crustal material. The exhumation mechanism of deeply buried rocks remains unclear, and any exhumation model is dependent on the rate of this process. Although subduction rates are well known from plate tectonic reconstruction to be in the order of 1–10 cm/y, determination of exhumation rates can only be deduced from the pressure-time history of high-pressure rocks.

We tackled the problem of exhumation rate determination by marrying metamorphic petrology to geochronology to allow dating of titanite that formed at different pressure and temperature conditions. SHRIMP analysis was preceded by back scatter electron imaging of the titanite crystals in order to detect chemical zoning and mineral inclusions. The titanites were analysed *in-situ* in thin section using the SHRIMP ion microprobe, which allowed dating of crystals displaying textural equilibrium with major minerals. The growth zones of titanite contained mineral inclusions that could be linked to the paragenesis of the host rock and thus to metamorphic conditions.

We dated titanite from two calc-silicates of an ultra-high pressure unit (Dora Maira, Western Alps) that underwent Variscan high temperature metamorphism and Alpine ultra-high pressure metamorphism (~3.5 GPa and ~750°C) followed by retrogression to greenschist facies. The first sample contains a clear eclogite-facies paragenesis with garnet and omphacite (Jd₃₈) and only minor retrogression. Titanite is part of the ultra-high pressure paragenesis as indicated by equilibrium textures with omphacite and garnet and local occurrence of inclusions of omphacite and rutile (Figure 2a). SHRIMP analyses of the ultra-high pressure titanite yielded a Th/U ratio on the order of 1.5–2.2 and a mean age of 35.1 ± 0.9 Ma (Figure 2c). A few titanite cores with lower Al contents and higher Th/U ratios (2.1–8.1) had apparent U-Pb ages that scattered between 253 and 87 Ma. The presence of inherited radiogenic Pb components indicates that the rock never remained at high temperatures long enough to allow complete resetting of the U-Th-Pb isotopic system in the titanite cores. Therefore, the Alpine age dates the formation of the titanite and not the closure of the isotopic system during cooling.

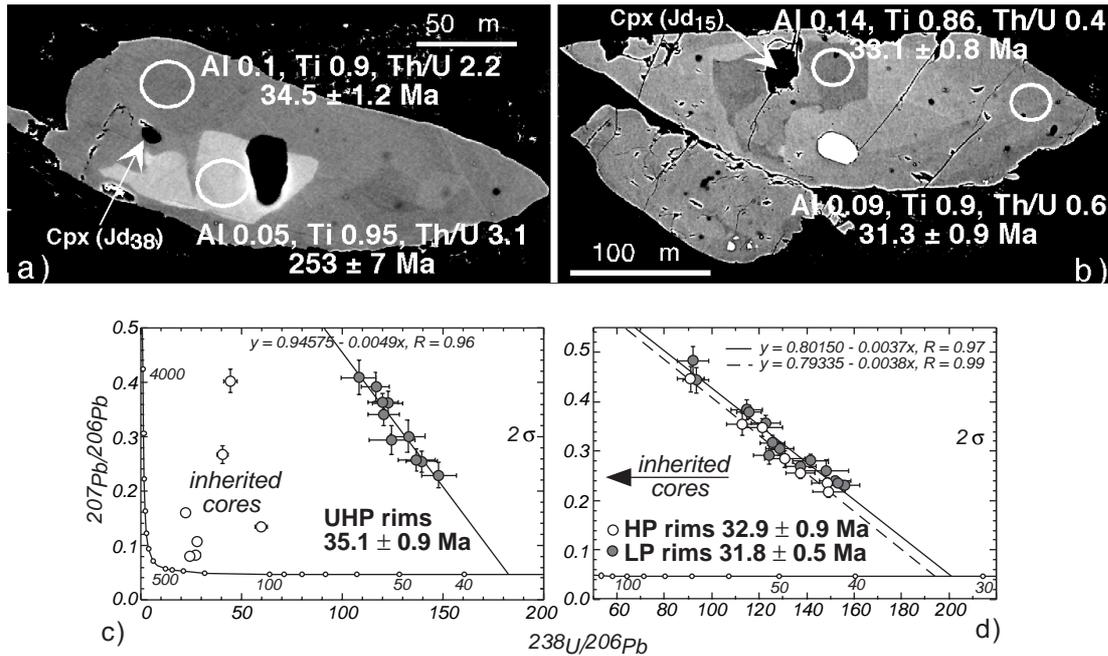


Figure 2: Backscattered-electron images of titanite crystals from (a) ultra-high pressure and (b) low-pressure calc-silicate rock. Circles correspond to SHRIMP analysis pits for which single ages ($\pm 1\sigma$) and Al-Ti contents (per formula unit) are given. Tera-Wasserburg diagrams plotting uncorrected U-Pb data for titanite from (c) ultra-high pressure calc-silicate rock and (d) low-pressure calc-silicate rock.

Widespread symplectites of pyroxene and/or amphibole + plagioclase after omphacite demonstrate that the second sample dated was strongly recrystallized during decompression at 1 ± 0.15 GPa (35 ± 5 km) and $\sim 550^\circ\text{C}$. A first symplectite stage involves omphacite (Jd_{20}) coexisting with oligoclase. The fact that Na-poor diopside (Jd_6) and albite were stable during a second symplectite stage indicates metamorphism at epidote-amphibolite facies, i.e., ~ 0.4 – 0.5 GPa (~ 17 km) and $\sim 550^\circ\text{C}$. There are three titanite generations in the second sample, and they have distinct textural and chemical features (Figure 2b). Rare cores with Al-Th-U compositions and ages similar to those of the pre-Alpine titanite cores in the ultra-high pressure sample are present. Domains with higher Al contents and low Th/U ratios (0.8–0.5) locally contain inclusions of omphacite (Jd_{10-20} , Figure 2b) and, thus, formed during the decompressional stage at 32.9 ± 0.9 Ma (Figure 2d). A third titanite generation has lower Al contents and forms the rims that are in textural equilibrium with the epidote-amphibolite facies paragenesis. For this titanite, a mean age of 31.8 ± 0.5 Ma was obtained.

The link between the high-precision U-Pb data on titanite and the metamorphic stages permits us to define a pressure-temperature-time path that describes the history of the Dora Maira from subduction to exhumation. The ultra-high pressure rocks of the Dora Maira unit were exhumed very quickly from 110 ± 10 (35.1 ± 0.9 Ma) to 35 ± 5 km depth (32.9 ± 0.9 Ma) with a mean exhumation rate of 3.4 cm/y. A minimum estimate, which considers the errors bars on ages and pressures, would still give an exhumation rate of 1.5 cm/y. Subsequently, the exhumation of the Dora Maira slowed down and proceeded at mean rates of 1.6 cm/y up to ~ 17 km depth. The late exhumation of the Dora Maira proceeded at an even slower rate of 0.5 cm/y.

At that time, erosion in the Alpine area was on the order of 0.25–0.5 mm/y and even the fastest erosion documented on Earth (1.5 cm/y) could not alone account for the exhumation of the Dora Maira to the base of the crust at 3.4 cm/y. Therefore, the fast exhumation may have resulted from the interplay of tectonic processes including buoyancy of continental rocks at mantle depth and slab break-off.

The early Archaean Itsaq Gneiss Complex in West Greenland – new areas of old rocks*A.P. Nutman and C.R.L. Friend*

The early Archaean rocks of the Godthåbsfjord region of West Greenland (the Itsaq Gneiss Complex) contain a sequence known as the Isua supracrustal belt. These rocks have been studied extensively because they include amongst their number, some of the oldest crustal material up (to ca 3.86 Ga). However the Isua superacrustal belt comprises only a few percent of the Gneiss Complex. We have accordingly directed our attention to the remainder of the complex, with rewarding results. Field work in some low strain zones has established extremely rare, undeformed 3.8 Ga meta-tonalites and ≥ 3.8 Ga abyssal peridotite enclaves which are locally neither hydrated nor metasomatised. Such samples are providing a unique geochemical resource for RSES researchers. For example, Xe isotope studies of 3.8 Ga magmatic zircons in the tonalites has revealed first evidence of incorporation of ^{244}Pu into the juvenile Earth (Honda et al., this report) and ancient abyssal peridotites are providing constraints on the early evolution of the mantle via Os isotope studies.

Two weeks of field work and detailed mapping were undertaken in July between the mouths of Ameralik and Godthåbsfjord rivers. This reconnaissance showed that unlike much of the southern part of the Itsaq Gneiss Complex, the rocks here had escaped early Archaean granulite facies metamorphism, and consist only of ~ 3.6 Ga (and younger) orthogneisses. These contain enclaves of early Archaean detrital sediments, which are extremely rare in other parts of the complex.

Tracts of ~ 3.6 Ga detrital sediments were examined in detail, and were found to be more extensive than expected. They consist of garnetiferous meta-quartzites and biotite schists, some of which are rich in graphite. Samples of these will provide information on early Archaean crustal composition and atmosphere, via zircon dating and radiogenic and stable isotope studies. The 3.6 Ga graphite-rich schists are currently the only known materials from that particular time with biogenic potential. Mapping showed that the gneisses divide into tracts containing only detrital sediment enclaves and tracts containing only enclaves of (metavolcanic) amphibolite, BIF and meta-chert. Some of these amphibolite + meta-chemical sediment enclaves are >1 km long, and were previously unknown. Samples of invasive orthogneisses have accordingly been collected to establish their age and tectonothermal history via SHRIMP zircon dating.

The short field season on a generally overlooked part of the Itsaq Gneiss Complex shows the value of studying the parts of the complex other researchers failed to explore. This strategy will continue in an expanded field programme next year, with investigation of additional areas from which reconnaissance studies suggest ≥ 3.85 Ga rocks are present, combined with further work in the district first visited in 2000.

Equilibrium trace element distribution coefficients between garnet and metamorphic zircon*D. Rubatto*

Garnet is the most important mineral for thermobarometry, whereas zircon is one of the best geochronometers. As a consequence, if coexistence between these two minerals can be proved it would be possible to link U-Pb ages to metamorphic conditions and thus obtain detailed pressure-temperature-time paths. Garnet and zircon are uniquely suited for this exercise because both minerals are enriched in Y and heavy rare earth elements and, therefore, when coexisting, zircon and garnet will influence each other's compositions.

Metamorphic zircons and garnets from granulite-facies rocks of the Reynolds Range were analysed for trace elements using laser ablation ICP-MS with the aim of obtaining trace element partitioning between these two minerals. In these granulitic migmatites garnet formed as a solid phase during melting. Metamorphic zircon overgrowths also formed in the presence of melt and therefore coexisted with garnet, which has a uniform Ca and Fe/Mg composition as well as

constant rare earth element contents. The equilibrium between garnet-melt and zircon-melt in leucosome and restite allows the calculation of zircon/garnet trace element partition coefficients ($^{TE}D_{zircon/garnet}$; Figure 3). The $^{TE}D_{zircon/garnet}$ in both rock types show that Y, Nb and particularly Hf are preferentially hosted in zircon. Among the REE (rare earth elements), Ce, Sm, Nd and Eu are enriched in zircon with the midrange REE being almost equally distributed between both minerals. The slight difference in $^{TE}D_{zircon/garnet}$ between the two samples is mainly due to a small variation in garnet composition. This variation is insignificant, however, when compared to the wide range of $^{REE}D_{zircon/garnet}$ obtained through the $^{REE}D_{zircon/melt}$ and the $^{REE}D_{garnet/melt}$ found in the literature. The variation in $^{REE}D_{zircon/garnet}$ obtained from the literature would be even bigger if different $^{REE}D_{zircon/melt}$ are used, which vary over an order of magnitude.

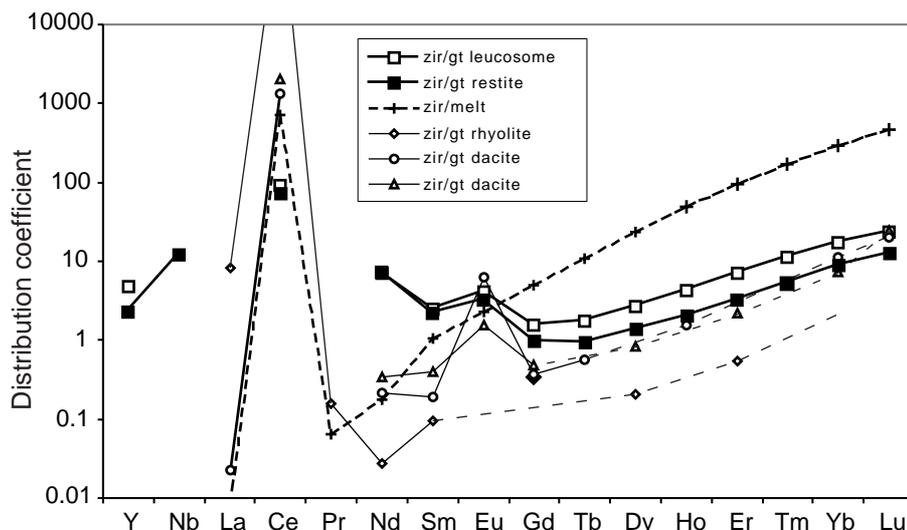


Figure 3: Trace element partition coefficients between zircon and coexisting garnet or melt. Values for leucosome and restite are calculated using an average composition for metamorphic zircon and garnet in each sample. Zircon/melt values and zircon/garnet partitioning has been derived from the literature.

This is the first report of zircon-garnet partitioning in metamorphic rocks where garnet and zircon can be proved to be in equilibrium. This partitioning is of great importance not only to establish that zircon and garnet are in equilibrium, but also to determine at what stage zircon formed in metamorphic rocks where garnet is zoned.

A more primitive Pb isotopic composition determined for the early Earth

V. Bennett and A. Nutman

The Pb isotopic composition of the silicate Earth through time is a fundamental geochemical parameter that has been used to constrain a range of large scale processes including the timescales of core formation and illumination of the mechanisms of crust formation and mantle differentiation. This can be accomplished because the fractionation of U and Th from their daughter Pb isotopes which originate in these processes, are recorded in the Pb isotopic compositions of modern and ancient rocks. The oldest terrestrial Pb isotopic compositions provide the most direct linkage between the Earth, and Solar System compositions as recorded in meteorites.

To provide information about early Earth processes, along with a basis of comparison between modern and ancient events, it is necessary to obtain accurate Pb isotopic compositions from the most ancient samples available. In practice this is complicated by the complex

metamorphic histories that characterize ancient terranes and the mobility of Pb in the geologic environment. The key reference point for early terrestrial Pb evolution for more than twenty years has been provided by Pb isotopic compositions measured from high-Pb, low-U sulphides, namely galenas, collected from near the Isua region of southwest Greenland. It is this data which, until now, has provided the starting point for all Pb models for Earth.

As part of our continuing investigations of early Earth evolution, centered on the early Archean terranes of southwest Greenland we have determined the Pb isotopic compositions of a “new” suite of galenas. This study benefits from RSES efforts in the area over the last ten years, which have established a detailed field, geochronological, and geochemical context for interpreting the new isotopic data. The Pb isotopic compositions of these galena samples were determined on 30 micron spots *in situ* on rock sections using SHRIMP II. In this way we could test for heterogeneity of composition within and between galenas, which comprise both massive and finely disseminated grains, as well as examine the relationship between Pb isotopic composition and Au and other sulphide mineralisation present in some samples. We obtained a range of compositions with seven of the nine samples measured having lower isotopic compositions for $^{207}\text{Pb}/^{204}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ than previously known and which are accordingly the most primitive terrestrial Pb isotopic compositions yet identified. In addition, the isotopic data are interpretable in terms of the range of ages present in the host rocks and in the geological context of these samples with the lowest isotopic compositions from galenas hosted by 3.81 Ga gneisses. We are currently using these new Pb isotopic compositions in conjunction with other types of data to address several questions, including providing refined estimates of the timing of core formation in the Earth and to better constrain the mechanisms of crust formation operating during the early Archean, both on the global and local scales.

Rhenium and platinum mobility during subduction zone processes

W. Sun, V. Bennett and S. Eggins

Rhenium and the platinum group elements (PGE) are providing significant new insights into mantle processes, both through their distribution patterns and from the rhenium-osmium (Re-Os) and platinum-osmium (Pt-Os) decay systems. Despite the rapidly increasing interest in employing these elements as petrologic tracers, there is still a surprisingly limited amount of high-quality data for non-economic systems, largely owing to analytical problems associated with their very low, part per trillion concentration levels. The lack of knowledge of the behavior of Re and the PGE in typical mantle environments, including the subduction cycle, is a major limitation to the fuller application of these tracers. For example Os isotopic anomalies measured in some ocean island basalts have been used to suggest the presence of outer core material within deep seated plume source materials, as this is one of the few environments where the necessary parent-daughter fractionation for the Pt/Os system might exist, yet it is not clear if other potential sites of fractionation exist within the mantle.

To provide a more detailed understanding of the behavior of Re and the PGE during mantle processes we have initiated investigations on samples from subduction zone environments where Re-PGE fractionation may be significant. Sample suites include eclogites representing basalts subducted to 100 km depth and back arc basin glasses representing deep slab influenced melts. Re and Pt were determined by isotope dilution ICP-MS for the eclogites. Re data from the eclogites show variable concentrations but with the range and average much lower than in mid-ocean ridge basalts. This supports previous suggestions that significant Re loss can occur during subduction. Pt data are the first obtained for eclogitic samples and show a range from near-MORB levels to extreme depletions, suggesting that Pt as well as Re can be mobile in this environment, with the potential for significant PGE fractionation. The Re contents of submarine basaltic glasses from the Lau back arc basin were determined *in situ* using laser ablation microprobe-inductively coupled plasma-mass spectrometry (ICP-MS). The selected samples were all from greater than 2000 m water depth to avoid problems of secondary Re mobility during shallow outgassing. Re concentrations are much higher than previously observed in arc lavas, supporting Re mobility in the mantle wedge, and show good linear

correlations with other trace and major elements including Yb, V, Zn, Cu as well as Ni and MgO contents.

Our on-going investigations are focussed on obtaining complete Re-PGE datasets from key subduction-related samples suites to identify the reactions and sites which result in significant Re and PGE fractionation. This will provide the basis for a refinement of Re-PGE budgets in crustal and mantle reservoirs.

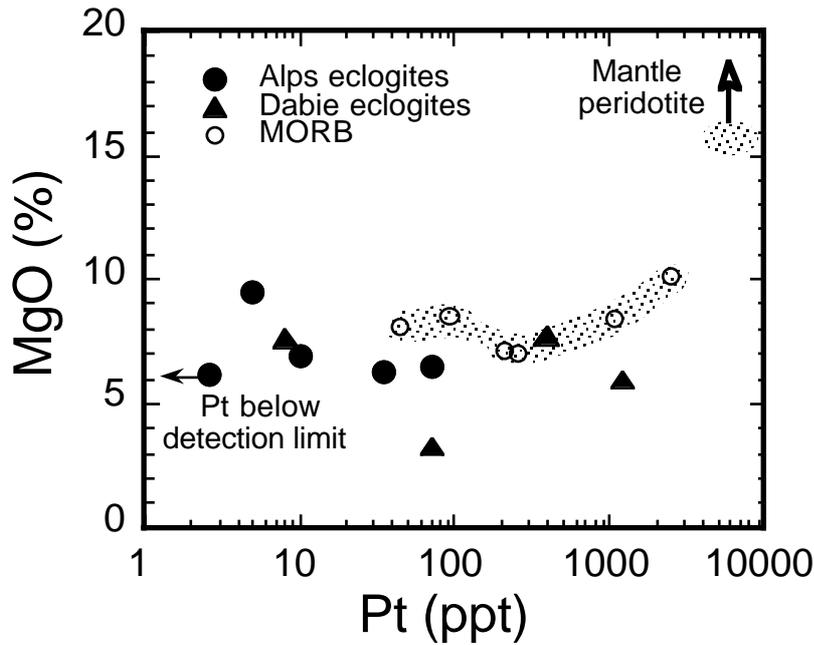


Figure 4: Pt concentrations for eclogites from the Alps and the Dabie Mts. China are shown in comparison with data for mid-ocean ridge basalts and peridotites. The very low concentrations seen in many of the eclogite samples suggest substantial amounts of Pt may be mobilized and removed from the slab during its descent into the upper mantle.

NOBLE GAS GEOCHEMISTRY AND GEOCHRONOLOGY

Noble gas geochemistry, and geochronology by the K-Ar and ^{40}Ar - ^{39}Ar methods, utilize similar techniques for measurement of small quantities of the noble gases. However, the two kinds of study rely for success upon very different initial conditions. Thus, for noble gas geochemical studies related to the Earth's origin and evolution we target samples such as mantle xenoliths or phenocrystic phases in mafic rocks that might reasonably be expected to retain noble gases from their source regions in the Earth's mantle. In the K-Ar dating system, the accumulation of radiogenic argon ($^{40}\text{Ar}^*$) from decay of naturally occurring radioactive ^{40}K gives a measure of time elapsed since crystallization and cooling of an igneous rock, provided that during eruption or emplacement any pre-existing radiogenic argon has been outgassed or equilibrated with atmospheric argon, setting the clock to zero. Knowledge and experience enables choice of appropriate samples to answer specific geochemical or geochronological problems.

The K-Ar and ^{40}Ar - ^{39}Ar isotopic dating techniques can provide very precise and accurate ages recording the time since eruption of rapidly cooled igneous rocks such as lava flows and shallow intrusives. Age measurements of these kinds, commonly to a precision of better than 1%, are particularly useful in stratigraphic geochronology and for determining numerical time scales for a wide range of geological events and processes. For slowly cooled rocks, the K-Ar system yields ages that generally reflect the time elapsed since cooling below the closure temperature for argon of the mineral being analyzed. Measurements on such rocks are utilized to obtain thermal histories of geological terranes and provide numerical constraints on cooling rates associated with the tectonic evolution of orogenic terranes.

Both the K-Ar and ^{40}Ar - ^{39}Ar dating methods have been applied to a number of geological projects during the year, and some of these studies are summarized below. Approximately 4840 argon isotopic analyses were made during the year, a significantly greater number than the previous best tally. About 110 new K-Ar ages were determined over the year, and 142 ^{40}Ar - ^{39}Ar age spectra were measured, averaging about twenty steps per experiment; in addition, 550 single crystal ^{40}Ar - ^{39}Ar total fusion ages were obtained. This high level of productivity reflects the value of full automation of the two ^{40}Ar - ^{39}Ar extraction and mass spectrometer systems, both of which have functioned well throughout the year. The high throughput was also in part owing to the effective use of the existing facilities by Dr D. Phillips of PRISE during the year.

The major technical achievements over the last year included the full implementation of the automation of the VG1200 mass spectrometer and its attached extraction system, and the upgrading of the automation on the VG3600 mass spectrometer and extraction system, principally through the efforts of Dr X. Zhang. A major setback was the failure of the plasma tube of the argon ion continuous wave laser early in the year. In due course a refurbished plasma tube was installed, and this has performed well.

The abundances and isotopic compositions of the noble gases, helium, neon, argon, krypton and xenon from mantle-derived samples provide useful and unique information concerning the origin and evolution of the Earth including its differentiation into core, mantle, crust and atmosphere. 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 of solar composition within the Earth. 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 are undertaking noble gas studies on old mantle-derived materials, including early Archaean materials from Greenland. We also plan to undertake noble gas studies on diamonds. Research projects related to cosmogenically-produced noble gases in rocks at the Earth's surface also are being considered for the future.

During the year the ultrahigh vacuum noble gas handling system on-line with the VG5400 mass spectrometer was refurbished principally through the efforts of Dr I. Iatsevitch. Programming for automating much of the operation of the extraction system and mass spectrometer is currently underway. We hope that this will result in a marked increase in both productivity and efficiency, and allow us to start some new projects.

Evidence of now-extinct ^{244}Pu in 3.8 Ga magmatic zircon from Greenland

M. Honda, A. Nutman and V. Bennett

The plutonium isotope, ^{244}Pu , is a relatively short-lived isotope with a half-life of 82 million years. As the spontaneous fission of ^{244}Pu generates xenon having a characteristic isotopic composition, it is, in principle, possible to use xenon studies to infer the past existence of now-extinct ^{244}Pu . Previous studies have identified ^{244}Pu -induced fission (plutogenic) xenon in meteoritic material, and successfully used this information to place strong constraints on the timing of the formation of meteorites. In contrast, the presence of plutogenic xenon in the Earth has not been demonstrated. However, if shown to exist, plutogenic xenon within the mantle would provide important constraints on models of accretion, differentiation, and outgassing of the early Earth. If the Earth indeed incorporated ^{244}Pu during accretion, then geological samples of sufficiently great age may record xenon isotopic compositions which are a mixture of xenon derived from ^{244}Pu plus xenon derived from ongoing spontaneous fission of extant ^{238}U (uranogenic Xe) and neutron-induced fission of ^{235}U . In order to investigate noble gas compositions during the initial stages of Earth history we have studied olivine, spinel, titanite, and zircon extracted from early Archaean rocks from Greenland.

Figure 5 presents three-isotope plots for $^{131}\text{Xe}^*/^{136}\text{Xe}^*$ versus $^{132}\text{Xe}^*/^{136}\text{Xe}^*$ and $^{131}\text{Xe}^*/^{136}\text{Xe}^*$ versus $^{134}\text{Xe}^*/^{136}\text{Xe}^*$ (the asterisks indicate that the isotope has been corrected for the presence of an atmosphere-derived xenon component). As shown in this figure, Xe extracted from a sample of 3.8 Ga old magmatic zircon (ANU# 97–518 from a well-preserved metatonalite) appears to lie on a mixing line between uranogenic and plutogenic Xe isotopic compositions. Thus, it appears that sample 97–518 incorporated a small amount of ^{244}Pu during its crystallization at 3.8 Ga. Another zircon sample (ANU# 97–611, granite, 3.6 Ga) may also have a small ^{244}Pu -derived fission xenon component. Importantly, these results are the first measurements consistent with ^{244}Pu in the early Earth.

Measurement of xenon isotopic composition released in stepwise heating of neutron-irradiated samples of St. Severin LL6 chondrite by earlier workers indicates that the atomic $^{244}\text{Pu}/^{238}\text{U}$ ratio in the solar system at 4.56 Ga was about 0.007. Assuming this value as a starting composition, and allowing the $^{244}\text{Pu}/^{238}\text{U}$ ratio to evolve over the period from 4.56 to 3.8 Ga, we predict that the $^{244}\text{Pu}/^{238}\text{U}$ ratio of chondritic material at 3.8 Ga to have been about 1×10^{-5} . In comparison, based on the ratio of ^{244}Pu -induced fission $^{136}\text{Xe}^*$ to ^{238}U -induced fission $^{136}\text{Xe}^*$ observed in sample 97–518, we estimate that the $^{244}\text{Pu}/^{238}\text{U}$ ratio in sample 97–518 at the time of crystallization (i.e., 3.8 Ga) was 5×10^{-6} . This value is within a factor of two of the ratio we estimated for chondritic material of the same age (note that uncertainties in the $^{244}\text{Pu}/^{238}\text{U}$ ratio in the solar system as a whole could be as high as 30%). Thus, allowing for the possibility of some elemental fractionation of plutonium and uranium during partial melting and zircon crystallization processes, the xenon results from Greenland zircons supports the view that the primitive Earth had a near-chondritic $^{244}\text{Pu}/^{238}\text{U}$ ratio. We are working to confirm and extend these important xenon results.

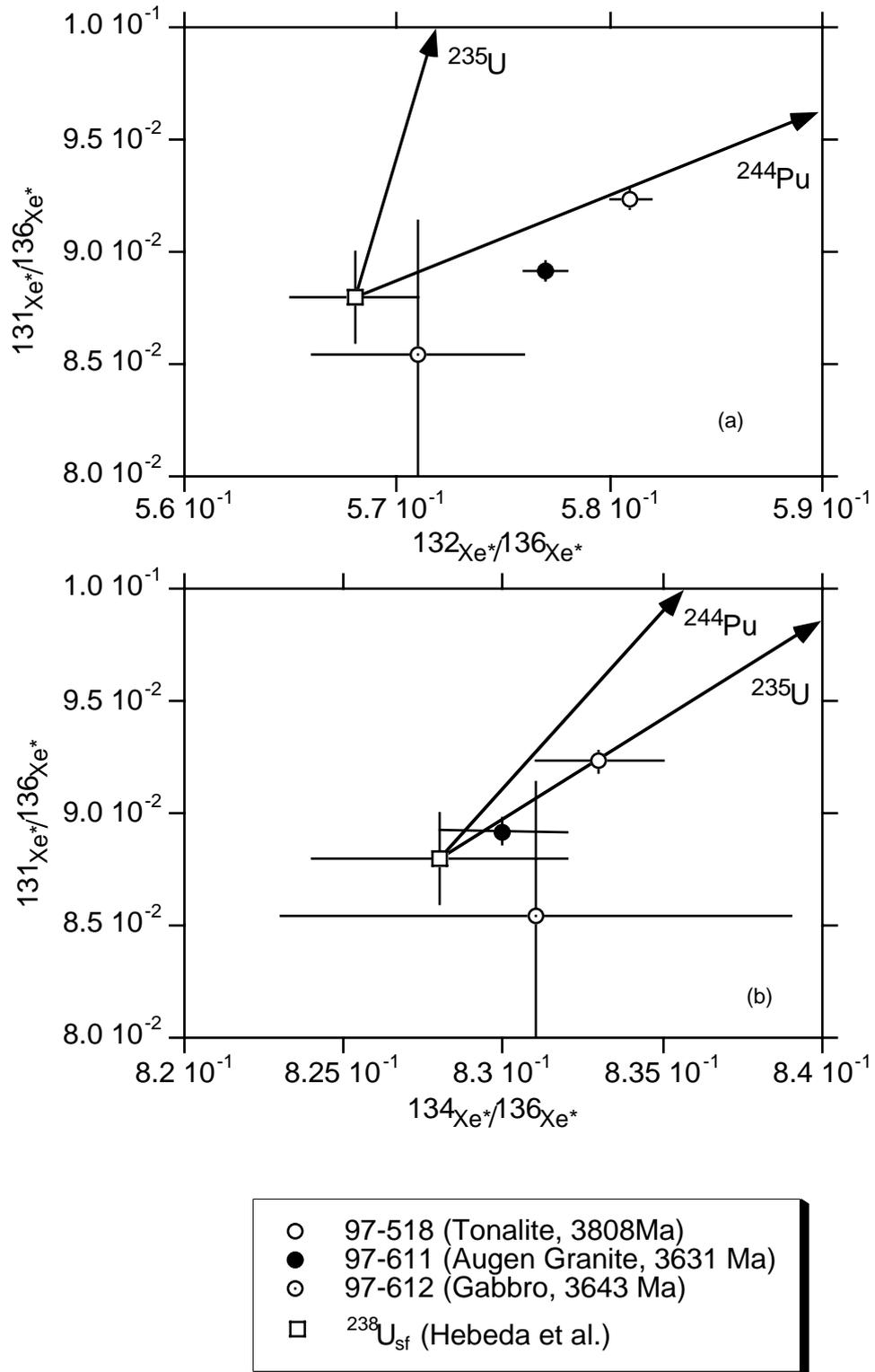


Figure 5: Plots of (a) fission $^{131}\text{Xe}^*/^{136}\text{Xe}^*$ versus $^{132}\text{Xe}^*/^{136}\text{Xe}^*$ and (b) $^{131}\text{Xe}^*/^{136}\text{Xe}^*$ versus $^{134}\text{Xe}^*/^{136}\text{Xe}^*$ observed in magmatic zircons from Greenland. Hypothetical mixing lines between spontaneous fission from ^{238}U and neutron-induced fission from ^{235}U , and spontaneous fission from ^{244}Pu are shown in the figure. The composition of spontaneous fission xenon from ^{238}U , as determined by Hebeda et al., *Earth Planet Science Letters*, 85, 79-90, 1987, is shown as open squares.

Noble gas geochemistry of Icelandic basalts

E.T. Dixon

The isotopic compositions of helium, neon, argon, krypton and xenon were determined on gases extracted from 26 young (<15 ka) mafic basalts from 13 sites in Iceland. The $^3\text{He}/^4\text{He}$ ratios of samples that were well-shielded from cosmic rays range from 12 ± 2 to 29 ± 3 Ra (where Ra = $(^3\text{He}/^4\text{He})_{\text{measured}} / (^3\text{He}/^4\text{He})_{\text{atmospheric}}$). In comparison, the average $^3\text{He}/^4\text{He}$ ratio in Mid Ocean Ridge Basalts (MORBs) is 8.5 Ra. Neon isotopic ratios from the well-shielded samples lie close to either the air-solar mixing line or the trend defined by MORB samples in a plot of $^{20}\text{Ne}/^{22}\text{Ne}$ versus $^{21}\text{Ne}/^{22}\text{Ne}$. The $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of all samples range from the atmospheric ratio to a maximum value of 1229 ± 150 . The krypton isotopic ratios are indistinguishable from the atmospheric ratio at the one sigma uncertainty level. The xenon isotopic ratios are also indistinguishable from the atmospheric ratios in all but one sample, which has $^{129}\text{Xe}/^{130}\text{Xe}$ and $^{136}\text{Xe}/^{130}\text{Xe}$ ratios of 6.67 ± 0.09 and 2.22 ± 0.03 , respectively. These ratios are about 2% higher than the corresponding atmospheric xenon ratios. Contrary to expectations, the helium and neon isotopic ratios in Icelandic basalts appear to be decoupled, and may reflect binary mixing between noble gases from the Icelandic plume and a MORB source.

The most important finding from this study is the discovery of near-solar neon isotopic ratios in a number of the Icelandic basalts. There are at least two possible means of preserving the near-solar neon isotopic ratios in the Icelandic plume source. The near-solar neon isotopic ratios may be derived from a plume source with a $[\text{Ne}_{\text{solar}}]/[\text{U}+\text{Th}]$ ratio that is about an order of magnitude higher than that in the MORB source. Owing to the highly incompatible nature of neon during mantle melting, a mantle source that has a high $[\text{Ne}_{\text{solar}}]/[\text{U}+\text{Th}]$ ratio is likely to be relatively unmelted and undegassed. Mantle of this kind would have a composition that is close to the postulated primitive mantle composition. The near-solar neon isotopic component in some Icelandic basalts may therefore originate from a primitive, undegassed mantle component in the Icelandic plume source. An alternative possibility is that the gases with near-solar neon isotopic ratios in the Icelandic plume source were derived from the Earth's core. This scenario is considered highly speculative owing to the lack of experimental evidence to show that noble gases could be stored in iron-nickel alloys under the pressure and temperature conditions that exist in the core.

Geochronology of Marion Island, Southern Ocean

I. McDougall, W. Verwoerd⁴ and L. Chevallier⁴

Marion Island is a subantarctic volcanic island situated at $46^{\circ}45'\text{S}$, $37^{\circ}45'\text{E}$, about 300 km south of the South West Indian Ocean Ridge. The island is about 20 km in diameter and rises to an altitude of 1240 m. It is an active oceanic intraplate shield volcano, built upon old oceanic crust that lies at a depth of about 3500 m. Marion Island is considered to be the surface manifestation of a mantle plume that can be back-tracked to Madagascar.

We have made many K-Ar age measurements on whole rock samples of lavas from Marion Island to elucidate its subaerial volcanic history. The lavas are mildly alkalic basalts and hawaiites, remarkably fresh and holocrystalline, appearing to be ideal for K-Ar dating.

In the Santa Rosa Valley on the southern flanks of the volcano, a section consisting of about 10 subaerial olivine basalt lava flows, totalling some 200 m in thickness, is exposed, part of the main shield building phase of the volcano. A schematic section is shown in Figure 6. Samples from 8 lavas in the main part of the sequence yield K-Ar ages between about 450 and 410 ka (ka = thousand years), generally consistent with the stratigraphy when the uncertainties are taken into account. Sample LC99 comes from a lava above a mapped disconformity; it yields an age of 343 ± 28 ka, indicating an hiatus or erosional break of about 80 ka across the

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disconformity. The highest lava in the section has flowed over a more profound erosional disconformity developed on the older flows (Figure 6); this lava yields an apparent age of 86 ± 8 ka, indicating an hiatus of ~ 250 ka. These results are fully consistent with the stratigraphic sequence, again demonstrating the usefulness of K-Ar dating in quite youthful volcanoes. The Santa Rosa lavas currently are the oldest known on Marion Island, suggesting that much of the subaerial volcanism is <500 ka old.

In contrast samples from a transect on the northeast flanks of the volcano yield somewhat conflicting apparent K-Ar ages. The transect extends from sea level over a distance of about 6 km toward the summit of the volcano, but comprising only about 100 m of stratigraphic thickness when seaward dips are allowed for. High in the sequence, at altitudes between 400 to 680 m, K-Ar measurements of several lavas yield ages of 50 ± 20 ka. But apparent K-Ar ages on seven lavas, exposed in the interval from sea level to about 350 m altitude, range from 110 to 280 ka, with many inconsistencies with the presumed stratigraphic order. Either there are complications related to unrecognized erosional cut and subsequent fill features or there are problems of excess argon in some of the lavas. This remains unresolved at present.

Overall this study has shown that the volcanism that has built Marion Island has been episodic; our results indicate up to 8 distinct periods of activity. This study has again demonstrated that the K-Ar dating system is of considerable utility in providing age constraints in youthful volcanoes, but that it is important to test the validity of the results by comparison with stratigraphic sequences.

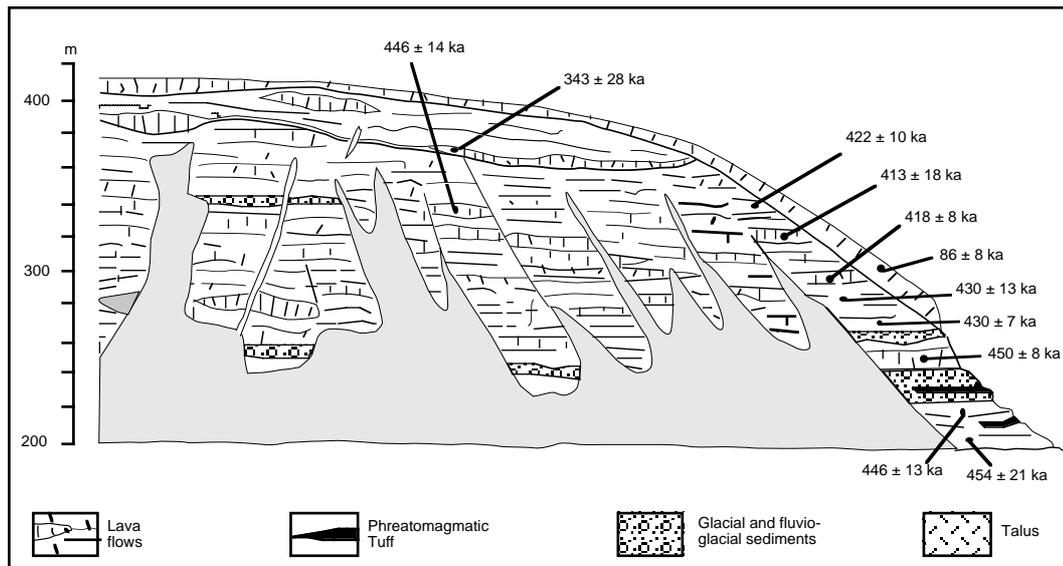


Figure 6: Stratigraphic profile of the eastern flank of Santa Rosa Valley, with sampling positions and K-Ar ages indicated.

Plate-scale tectonic events recorded as episodes of rapid exhumation in Victoria Range, New Zealand: Remarkable sensitivity of K-feldspars to tectonic forcing.

W. J. Dunlap, I. McDougall and A.J. Tulloch⁵

The Victoria Range, northwestern South Island (Figure 7), was proposed by other workers to be a Cretaceous core complex that formed about 100 Ma, about the time of formation of the adjacent Paparoa core complex. We have studied the structure and thermochronology of the

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Victoria Range, in detail, to clarify the temporal and tectonic connection between core complex formation and Tasman Sea opening.

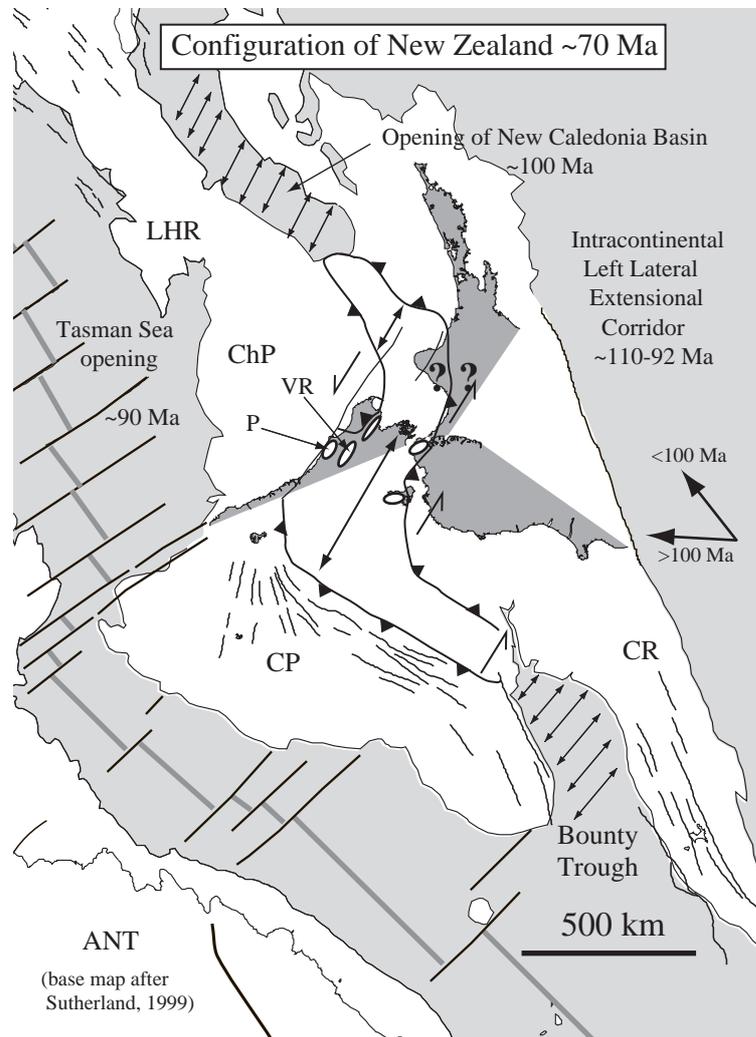


Figure 7: Configuration of the New Zealand continental crust at ~70 Ma, after initiation of spreading in Tasman Sea; presently exposed landmasses New Zealand darkly shaded, submerged continental crust as white, and ocean floor shaded. Plate convergence directions, right, for pre- and post-100 Ma periods are from hotspot tracks. Proposed intracontinental extensional corridor opened ~110–92 Ma; rimmed by teeth marking locus of crustal breakaway, with opening direction indicated by double-headed arrows. Core complexes shown as white ovals, with long dimension as local extension direction. Lineaments (faults) are from gravity, seismic and satellite data. ANT=Antarctica, CP=Campbell Plateau, CR=Chatham Rise, ChP=Challenger Plateau, LHR=Lord Howe Rise, VR=Victoria Range core complex, P=Paparoa core complex.

The thermochronology of the Victoria Range has been assessed with an extensive new ^{40}Ar - ^{39}Ar data set for micas, amphiboles and K-feldspars, a few Rb/Sr dates on micas, as well as numerous unpublished U-Pb dates on zircons. The thermochronological information has been integrated with field mapping and petrographic analysis. The Victoria Range is confirmed by the latest data set to be the lower plate of a Cretaceous core complex that formed during thinning of the continental crust at about 110 Ma to 92 Ma. Thermal modelling, particularly of K-feldspar data, indicates that the presently exposed levels of the lower plate granites and gneisses experienced rapid cooling during several episodes, three of which started about 110 Ma, 100 Ma and 95 Ma (Figure 8), lasting for only a couple of million years each. These cooling events are related to southward-directed transport of the upper plate of the core complex, and are the result

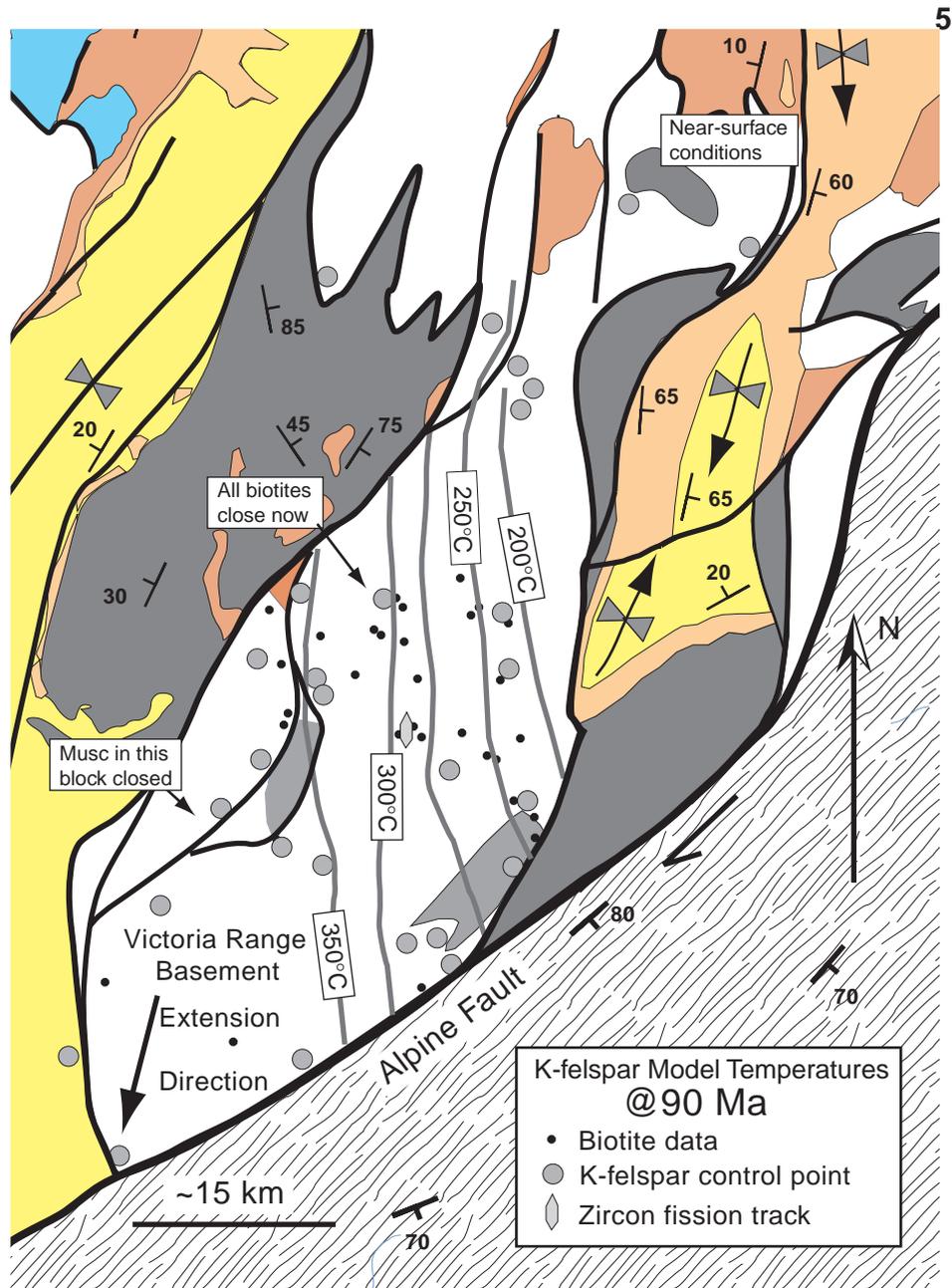


Figure 8: Inferred thermal state of the Victoria Range core complex, lower plate, at ~90 Ma after the third pulse of cooling associated with transport of upper plate rocks to the South. Core complex basement shown as white, adjacent basins shown as various shadings, the lighter three of which are sediments of Cenozoic age. Faults are thick black lines. Note that the younger sediments are strongly folded, including some Pleistocene sediments which are now dipping at ~65°. Rocks east of the Alpine Fault are Haast Schist, metamorphosed Paleozoic sediments. Isotherms are constrained by a large database of K-feldspar multidomain thermal models and biotite age spectra. The trend of isotherms is somewhat surprising, although this may be a function of the present-day topography cutting obliquely through the lower plate, with deeper levels exposed to the west.

of structural exhumation. The first two episodes at 110 Ma and 100 Ma clearly predate any ocean floor in the Tasman Sea (oldest ocean floor ~84 Ma; oldest crustal lineament ~92 Ma). Subsequent episodes of rapid cooling indicated by K-feldspar modelling occurred at 86 Ma, 43 Ma and 20 Ma.

The rapid cooling events recorded in the K-feldspars are clearly tracking the response of the Victoria Range crust to plate-scale tectonic events, including addition of mantle-derived melts to the crust at ~86–80 Ma, rifting and passive margin formation at ~43 Ma, and inception of the Alpine Fault at ~20 Ma. The timing of the onset of the cooling events is derived from the results of the multi-domain modelling, and at present there is no other method sensitive enough to illuminate the subtle complexities of upper crustal thermal histories within the 150–350°C range. Regardless of the particular interpretation of K-feldspar data, it is clear that the Victoria Range K-feldspars are sensitive recorders that allow detailed thermal mapping and assessment of the thermal imprint of a series of plate tectonic events, as shown by our 28 detailed diffusion experiments, comprising more than 1200 analyses.

Carboniferous tectonism at Mount Painter, South Australia: the Alice Springs Orogeny moves south

S. McLaren⁶, M. Sandiford⁶, W. J. Dunlap, and I. McDougall

Deformation and metamorphism in the Northern Flinders Ranges, South Australia are ascribed to the ~500 Ma Cambro-Ordovician Delamerian Orogeny. The subsequent thermal history of these rocks, however, is largely unknown. We have assessed this history for the Mount Painter province through K-Ar age determinations on hornblendes, ⁴⁰Ar-³⁹Ar age measurements on micas and multiple-diffusion-domain thermal modelling of K-feldspar ⁴⁰Ar-³⁹Ar data. Results are consistent with a complex post-Delamerian exhumation history (Figure 9). Although the new data cannot constrain the timing of deformation and peak metamorphism, which are presumably Delamerian in age (~500 Ma), they do suggest that the hottest rocks were at temperatures of around 500°C until 400 Ma (middle/lower crust below MP on Figure 7). Between 400 and 390 Ma, the Mount Painter terrane underwent a period of very rapid cooling to temperatures between 350°C and 250°C, depending on stratigraphic position. Following this cooling episode the terrane entered a period of relative tectonic quiescence remaining essentially isothermal until ~330 Ma. This long residence near the closure temperature of biotite has resulted in significant argon loss in the interval between 400 Ma and 330 Ma. This period of relative tectonic and thermal stability was terminated by further rapid cooling (>8°C/Ma⁻¹) in the interval between 330 Ma and 320 Ma. The two cooling episodes at ~400 Ma and ~330 Ma are interpreted to be the result of uplift with a combined minimum of 8 km of denudation. We associate both with the Alice Springs Orogeny (ASO), a major intraplate tectonothermal event known throughout central Australia, but not previously recognized in the Adelaide Fold Belt.

In view of the SE trend of major tectonic lineaments reactivated in the Carboniferous in the southeastern Arunta Block, central Australia, and the presence of Carboniferous age granites intruding the Warburton Basin to the north of the Mount Painter area, the possibility of Alice Springs age tectonism in the Mount Painter region is not surprising. We speculate that tectonic reactivation in this area during the ASO is a consequence of two factors. First, the Mount Painter crust is likely to have been significantly weakened due to the presence of anomalous concentrations of heat producing elements at depth in the Mount Painter basement rocks. Second, we suggest that the Paralana Fault, which bounds the Mount Painter block to the east, is linked to a regional scale system of faults to the north that have controlled ASO age deformation not only in the Mount Painter area but also in the Warburton Basin and central Australia. We suspect that this fault system penetrates into the lithospheric mantle and that it is a persistent zone of weakness that is still active today (as indicated by the seismic activity and young topography of the region). The extent of ASO age exhumation to the south of the Mount Painter region needs to be assessed in further thermochronological studies, particularly of the crustal scale fault systems.

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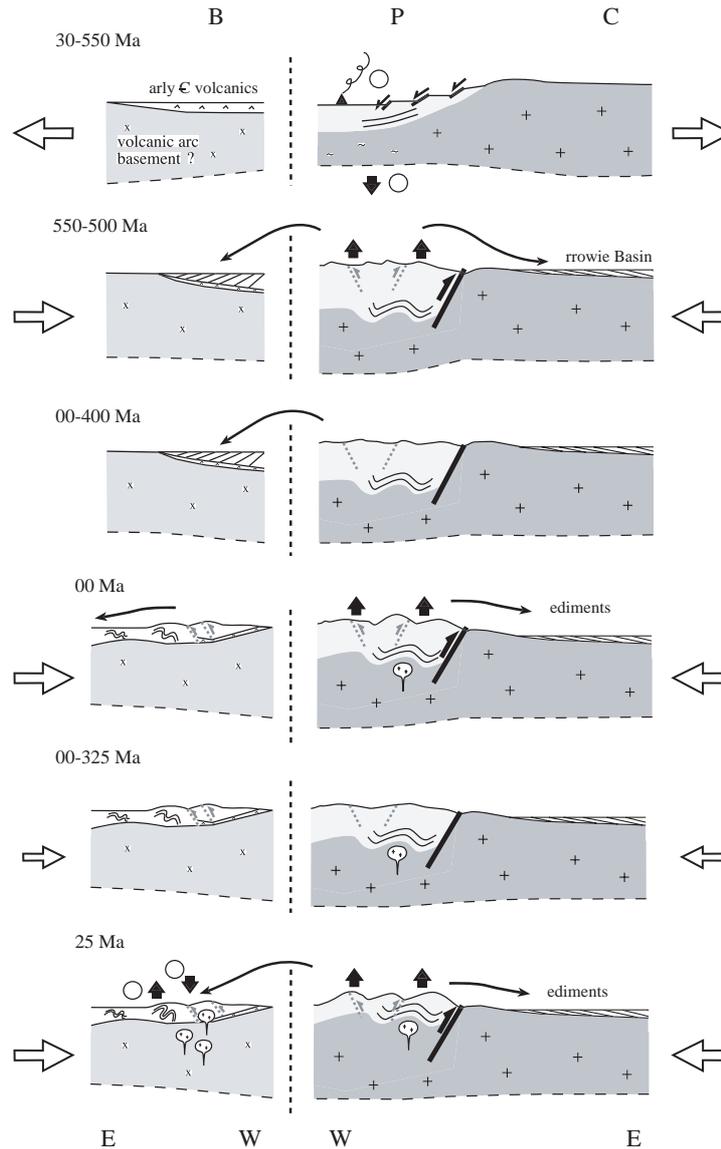


Figure 9: NE-SW and NW-SE schematic cross-sections showing the development of the Mount Painter province (MP) and adjacent crustal blocks (the Warburton Basin, WB, to the north, and the Curnamona Craton, CC, to the southeast). The approximate modern crustal thickness is ~38 km. Arrows represent inferred tectonic stresses, with size indicating relative magnitude. **(a)** The interval between 830 and 550 Ma represents deposition of the Adelaidean sedimentary cover during (1) dominantly rift and sag phase subsidence (830–690 Ma) followed by (2) dominantly sag phase subsidence. **(b)** Uplift of the MP during the Delamerian Orogeny was gradual and largely driven by isostatic rebound. **(c)** Interval from 500–400 Ma characterised by very slow post-Delamerian isostatic uplift, with continued sedimentation in the Warburton Basin. **(d)** Schematic initial uplift of the MP during the earliest Alice Springs Orogeny. **(e)** From 400–325 Ma, MP experienced little erosion or cooling. **(f)** Final exhumation of the MP by a further 3 km with emplacement of the Big Lake granite suite, followed by (1) rapid uplift, and (2) uplift and extension in the Warburton Basin.

