Geochemical remote sensing of the deep Earth - 4D lithospheric mapping 2001





Figure 2. Density of SCLM sections as a function of thickness and geotherm, compared to the density of the asthenosphere. Stars show typical SCLM thicknesses.





G EOPHYSICAL DATASETS record the physical properties of Earth's interior at the present day. Translating this information into actualistic Earth models requires petrological and geochemical data on real samples of deep-earth materials. GEMOC has developed a range of tools, collectively termed 4-D Lithosphere Mapping (eg Publications 1, 234), to study the lithospheric mantle and its evolution, by defining its composition, architecture and the location of its important discontinuities (eg crust-mantle and lithosphere-asthenosphere boundaries). This methodology is based on the integration of geochemical and petrophysical analyses of mantle-derived materials with tectonic syntheses and geophysical datasets. It has

provided some important constraints on fundamental questions such as the compositional evolution of sub-continental lithospheric mantle (SCLM; see Fig. 1, p.20), the lateral variability of SCLM composition and its effects on tectonics, and the extent to which lithospheric mantle can be recycled into the convecting mantle, or is irreversibly differentiated from it. One of the most important results has been the demonstration that the composition of the SCLM varies in a systematic way that correlates with the age of the last major tectonothermal event in the overlying crust (Publications 90, 132, 234; Fig, 1).

The compositional variations within the SCLM result in differences in the density and elastic properties of lithospheric mantle of different age (Publication 228, Fig. 2). *Archean and Proterozoic* mantle roots are highly buoyant; they cannot be "delaminated" and recycled. This buoyancy, combined with the refractory nature and low heat production of Archean SCLM, may

explain the thickness and longevity of Archean lithospheric keels. However, 4-D Lithosphere Mapping (using mantle fragments sampled by magmas of different ages in regions such as eastern China) documents the dispersion of old, buoyant SCLM and the upwelling of fertile asthenospheric mantle, consistent with detailed tomographic imaging (Publications 64, 234; Fig. 3). Modelling of regional lithospheric strength (elastic thickness) in the eastern Siberian craton has shown a N-S lithosphere-scale weak zone within the lithospheric mantle that suggests lithosphere modification related to deformation (Publication 250; Fig. 4).

Typical *Phanerozoic SCLM sections* (about 100 km thick) are buoyant under conditions of high geothermal gradient (eg during their formation). However, they are at best neutrally buoyant after cooling to typical stable conductive geotherms; they become vulnerable to Rayleigh-Taylor instability and will tend to delaminate.

Asthenospheric material welling up into the resulting "space" will cool to form a new, little-depleted SCLM; this will raise geotherms and may cause crustal melting. As this new SCLM cools, it in turn will become unstable, and start the cycle again. This cyclic delamination may explain the ubiquitous presence of fertile xenolith suites in young basalts erupted through Paleozoic-Mesozoic orogenic belts.

Olivine is the most abundant mineral in all SCLM sections, and the Fe/Mg ratio of olivine is important in controlling the physical properties of the lithosphere (density, Vp, Vs). Decreasing Fe/Mg results in lower density but higher seismic velocity. Because olivine is rarely preserved (and contains little P or T information), we have inverted a garnet-olivine Fe-Mg exchange geothermometer to calculate the Fe/Mg of olivine coexisting with each xenocrystic garnet grain (Publication 222). This inversion has been used to track the compositional variation of olivine through well-characterised SCLM regions. It provides an independant confirmation that Archean SCLM is characterised by much more Mg-rich olivine than Phanerozoic SCLM. In many SCLM sections worldwide the Fe/Mg of olivine increases with depth (Fig. 5), paralleling an increase in Zr and Ti of garnet with depth. This pattern probably reflects the transformation (refertilisation) of SCLM over time by addition of asthenosphere-derived material.



Figure 4. Left: Elastic thickness map of the eastern Siberian Craton; kimberlite fields (black diamonds) lie on flanks of weak zones. Right: Bouguer anomaly map shows highs over Proterozoic areas, lows over Archean areas.

Paleozoic kimberlites

Shandong Province

50 - E

100

150

200

250

Depth

CMB

Graphite

I AB

50

-Ca harz. 🔳

Ca harz.

Lherzolite

Low Cr

Low

Diamond

Archean-~450 Ma

Harzburgites

Depleted Iherzolites

T °C

1000 1200

"Archean" Lithosphere CMB

Figure 3. Evolution of SCLM under the eastern Sino-Korean Craton, from thick, depleted Archean SCLM in Ordovician time to thin, hot and fertile SCLM now.

Mesozoic- Now

"Oceanic" lithosphere

1000 1200

"Archear

fertile

50

100

150

200

СМЕ

LAB

50

100

200

150

Figure 5. Variation of olivine composition with depth in SCLM sections, as mapped from garnet data.

The contrasting properties of different mantle domains require lateral contrasts in composition, density, thickness and seismic response in the present-day SCLM. They also suggest a secular evolution in Earth's geodynamics from Archean to Proterozoic time, and an increased importance for lithosphere-delamination processes in Phanerozoic orogens. The intrinsic buoyancy of Archean SCLM places major constraints on the tectonic behaviour of old continents; some dynamic models indicate that without this buoyancy in their cratonic cores, continents would not have survived on the convecting Earth.

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Mapping the Mantle with garnet variables – order from complexity **G** EMOC'S DATABASE on mantle-derived garnets, built up during 15 years of work with the diamond exploration industry, long since grew to over 30,000 analyses. Up to 1995, trace-element data were acquired with the CSIRO proton microprobe, in collaboration with Dr. Chris Ryan. Since 1995, we have exploited the greater sensitivity of GEMOC's laser-ablation ICPMS microprobes to gather data on a wider range of trace elements. This database has provided fertile ground for collaborating with statisticians Nick Fisher (formerly CSIRO) and Jerry Friedman (Stanford University). They have used the large array of variables in the dataset to develop new ways to recognise populations and anomalies within large data sets, with an emphasis on techniques that give simple and easily interpreted rules. The



distribution of these populations can then be combined with temperature (depth) estimates for each grain to map spatial occurrence and thus to analyse mantle structure.

Three of these novel statistical approaches (CARP, PRIM and ModeMap) were used to define compositional populations within a database (n > 13.000)of Cr-pyrope garnets from the subcontinental lithospheric mantle (SCLM). The variables used are the major oxides, and proton-probe data for Zn, Ga, Sr, Y and Zr. Because the rules defining these populations (classes) are expressed in simple compositional variables, they are easily applied to new samples and other databases. The classes defined by the three methods show strong similarities and crosscorrelations, suggesting that they are statistically meaningful.

The geological significance of the classes has been tested by classifying the garnets from 184 mantle-derived peridotite xenoliths, and from a smaller database (n >5000) of garnets analysed by LAM-ICPMS. Several classes reflect different degrees of depletion (melt extraction) of mantle peridotites, others reflect different styles of metasomatism, and several show the metasomatic

Figure 1. Chemical tomography sections for the lithosphere beneath the Siberian craton (Daldyn kimberlite field), Slave Craton and Kaapvaal Craton (in two time slices), showing the distribution with depth of garnet classes defined by classical Ca-Cr relationships (top) and three statistical tools described here, grouped according to their geological interpretation. "metas." = metasomatised.



Figure 2. Distribution of CARP groups (see Fig. 1) in "typical" Archean, Proterozoic and Phanerozoic SCLM sections.

re-enrichment of formerly depleted rocks. The distribution of these classes with depth has been mapped by measuring the temperature of each grain (from its nickel content) and deriving a depth by reference of the temperature to the local paleogeotherm (Fig. 1).

The relative abundances of these classes in the SCLM vary widely across different tectonic settings and define intrinsically distinct compositional mantle domains: some classes are completely absent in either Archean or Phanerozoic SCLM (Fig. 2). The distribution of classes can vary widely with depth within individual lithospheric sections. For instance, the SCLM section for the Daldyn kimberlite field in Siberia (Fig. 1) shows a thick layer of strongly depleted harzburgites and lherzolites, overlain by more fertile lherzolites, and the base of the section has been metasomatised by asthenosphere-derived silicate melts.

Phanerozoic garnet peridotites are uniformly fertile (Fig. 2). Archean SCLM sections generally show high degrees of depletion and varying degrees of metasomatism, and commonly are strongly layered. Proterozoic SCLM sections appear quite different (Fig. 2). Many show a concentration of more depleted material near their base, grading upward into more fertile lherzolites. The distribution of garnet classes reflecting low-T phlogopite-related metasomatism and high-T melt-related metasomatism suggests that some of these Proterozoic SCLM sections actually consist of strongly metasomatised Archean SCLM. If this proves to be true, at least part of the observed secular evolution of SCLM composition (Fig. 1, p.18) probably reflects reworking and refertilisation of SCLM that formed in Archean time, and has survived due to its buoyant and refractory nature.

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Chemical tomography beneath the Kalahari Craton **C** HROME-PYROPE GARNETS brought up from the mantle by kimberlites and basalts carry large amounts of information on the subcontinental lithospheric mantle (SCLM). The garnet-classification schemes developed by GEMOC (see *"Mapping the Mantle"*, *p.20*) now give us a powerful new tool for mapping the compositional structure of the SCLM, anywhere that enough volcanic rocks have sampled it. In 2001, GEMOC mapped the SCLM in space and time, beneath the Kalahari



Craton of southern Africa and its surrounding mobile belts (Fig. 1). The project used >3500 garnet xenocrysts from >60 kimberlites intruded over the period 520-80 Ma. Figure 2 shows the distribution of classes defined by the new classification scheme, CARP (developed by Nick Fisher and Jerry Friedman using the large garnet dataset and described on p.20-21), along a NE-SW traverse from the Limpopo Belt through the Kimberley area in the SW, and into the Proterozoic Namaqua-Natal Fold Belt. In order to image mantle composition laterally and vertically, we mapped the distribution of different classes at 150 km depth, along with the mean olivine composition, calculated from the garnet compositions and temperatures (Fig. 3).

The trace-element patterns of many garnets reflect the metasomatic refertilisation of originally highly depleted harzburgites and lherzolites, and much of the lateral and vertical heterogeneity in the SCLM observed within the craton is the product of this metasomatism. The SCLM beneath the Limpopo Belt is the most depleted section yet studied. It was sampled by early Paleozoic kimberlites, and the SCLM beneath other parts of the craton may

Figure 1. Tectonic map of southern Africa (by Lev Natapov) showing locations of sampled kimberlites (stars) and the traverse shown in Fig. 2 (dashed line).

Figure 2. Chemical tomography sections for areas along the traverse shown in Fig. 1, showing the distribution with depth of garnet groups defined by CARP. represent similar material modified by metasomatism during Phanerozoic time. The 1200 Ma Premier kimberlite intruded through the massive 2050 Ma



Bushveld complex (Fig. 1). The SCLM under Premier was strongly metasomatised and refertilised by the Bushveld event, to produce a much more iron-rich mantle than in the other sections. In the SW part of the craton, the SCLM sampled by "Group 2" kimberlites (>110 Ma) is thicker, cooler and less metasomatised than that sampled by "Group 1" kimberlites (mostly ≤95 Ma) in the same area (Fig. 1, p.20). That result affects our use of xenolith data in a wider perspective - it implies that the extensively studied xenolith suites from the "Group 1" kimberlites probably are not representative of primary Archean SCLM compositions.

The relatively fertile SCLM beneath the mobile belts surrounding the craton is interpreted as largely Archean SCLM, metasomatised and mixed with younger material during Proterozoic rifting and compression. There are strong correlations between mantle composition and the lateral variations in seismic velocity (Vp) shown by detailed tomographic studies (James et al., 2001, G.R.L. 28). Our study showed very small lateral temperature differences within the craton, so the seismic data can be used to map the lateral extent of different types of SCLM. Areas of relatively low Vp within the craton largely reflect the progressive refertilisation (resulting in Fe-enrichment) of the Archean root during episodes of intraplate magmatism, including the Bushveld (2 Ga) and Karroo (ca 180 Ma) events; areas of high Vp map out the distribution of less metasomatised Archean SCLM. The relatively low Vp of the SCLM beneath the mobile belts is consistent with its fertile composition.

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Figure 3. Chemical tomography map showing relative abundances of CARP groups in the 140-160 km depth slice, and the mean Fo content of olivine, calculated from the garnet data by the method of Gaul et al. (2000; Publication No. 222).

Sulfides – more evidence for plumes from the lower mantle?

"The distinct ultra-high pressure signature of sulfides included in concentrate minerals represents a new tool to recognise sublithospheric influences... " **R** e-OS DATING of sulfide inclusions in mantle minerals opens new perspectives on the origin of the mantle (see *Research Highlight "Green and gold - sulfides in olivine date the Siberian lithosphere"*, *p.30*). As part of this new research direction, we have recovered a suite of sulfide inclusions in concentrate minerals (mostly olivine) from the Lac de Gras kimberlites in the Slave craton, Canada (see *Research Highlights 2000 at www.es.mq.edu.au/GEMOC/*). A distinct population of these sulfides, with a non-stoichiometric structural formula of $[(Ni,Co,Fe)_{3x}S_2]$ has a high metal/sulfur ratio [(Fe+Co+Ni)/S], unusually high Ni/Fe and Co, and low Ni/Co relative to the common monosulfide solid solution (mss) that is more typical of mantle peridotites (Fig. 1). These Ni-Co sulfides also contain up to several percent of tungsten; this is unusual because W is not generally compatible in mantle minerals under common (lithospheric) conditions. These major and trace element

systematics imply an unusual origin for the sulfides from Lac de Gras.

One inclusion of Fe metal also has been recovered. This has negative Co- and Ni-anomalies S [20-60 wt%] relative to elements of similar siderophile (metal-seeking) **Pvrite** character (Fig. 2) and is Violarite Polydyr more enriched in W than the sulfides, suggesting a rrhotite entlandite related and Fe Ni+Co [0-80 wt%] [0-80 wt%] Fe-rich mss (Fe,Ni)1_vS Ni-Co-rich sulfide (Ni,Co,Fe)3-S

Figure 1. Reconstructed compositions of Fe rich and Ni-Co rich sulfides from Lac de Gras concentrate in the Fe-S-(Ni+Co) quadrilateral. Shaded field delimits mss compositions at 300° C. Highlighted area in small triangle indicates position of the quadrilateral in the ternary diagram. Stars show stoichiometric (with exception of pentlandite which has variable Ni/Fe) sulfide phases.

complementary origin for the Fe metal and the Ni-Co sulfides. Both phases may have formed under reducing conditions (corresponding to high metal/sulfur) where metal melts and sulfide melts are immiscible. After unmixing, Ni and Co will be concentrated in the sulfide melt, consistent with their chalcophile (sulfurseeking) nature, whereas the chalcophobic (sulfur-avoiding) W partitions into the S-poor metal. The presence of Fe metal and the W-enrichment in Ni-Co sulfides indicate very reducing conditions, at or below the iron-wüstite oxygen buffer, and suggests sources deeper than the subcontinental lithospheric mantle, such as the transition zone or lower mantle where metal saturation is thought to be reached.

However, reducing conditions alone are not sufficient to explain the major and trace element systematics of the Ni-Co sulfides. In particular the enrichment in Co and the resulting low Ni/Co (~8.5) of the Ni-Co sulfides relative to the primitive mantle (18.7; McDonough and Sun, 1995, Chem. Geol.) require conditions where more Co than Ni partitions into the sulfide. This is not the case for the simple

unmixing scenario described above, but may occur in equilibrium with a silicate melt at pressures corresponding to the lower mantle. The strong W-enrichment in the sulfides cannot be attained by simple equilibrium processes, such as partitioning between sulfide melt and silicate liquid, but may require an open system process, where W is continuously scavenged from surrounding silicates during percolation of a mobile sulfide melt. This enrichment mechanism would be far more effective at lower mantle depths because sulfide equilibrating with lower mantle phases can take up more W than sulfide equilibrating with silicate melt. Hence, both low Ni/Co and high W concentrations are consistent with formation of the sulfides at ultrahigh pressures.

The Ni-Co sulfides and Fe metal may have been emplaced in the upper mantle during upwelling of a plume originating at the coremantle boundary. A lower mantle component has previously been suggested for the Lac de Gras lithosphere based on the occurrence of lower mantle inclusions in diamond (Davies et al., see *Research Highlights 1998, 2000*). The distinct ultra-high pressure signature of sulfides included in concentrate minerals represents a new tool to recognise sublithospheric influences where diamonds and their inclusions are not (yet) available. Deep-seated mantle plumes may entrain diamond as they rise through the convecting mantle, including the transition zone. Thus, in 'cool' cratonic regions, which have low geotherms favourable to the preservation of diamonds, ultra-high pressure sulfides recovered from kimberlite concentrate may also be an indicator for the presence of abundant diamond in the mantle root.

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Sulfide inclusion in olivine grain (bottom) and after mounting and polishing in an aluminium tube (top)

Figure 2. Chondritenormalised trace element abundances of Fe metal and Ni-Co sulfides. Element order corresponds to increasing siderophile character.

Metal isotopes lead the way to riches Sotope GEOCHEMISTRY is a basic tool for understanding ore-forming processes. Data on variations in the stable isotopes of carbon, oxygen, sulfur and hydrogen have been used to identify the sources of hydrothermal fluids and to model the mechanisms that drive hydrothermal circulation systems. But not all fluids carry metals, and the sources of the fluids and the ore metals could be quite different. Many of the important commodity metals (Cu, Zn, Fe, etc.) have two or more stable isotopes, whose fractionation could carry more direct information on the sources, movements and precipitation of these elements.

Until recently, there have been few reliable data on the isotopic composition of



Figure 1. Distribution of copper-isotope ratios, expressed as E⁶⁵Cu, in chalcopyrite from worldwide sources. After Botfield (1999; Honours Thesis, Macquarie Univ.) these metals, because their high ionisation potentials made them very difficult to measure by conventional thermal ionisation mass spectrometry. Now the multi-collector ICPMS makes it possible to do high-precision analyses of the isotopic ratios of Cu, Fe and many other metals. With the addition of a laser-ablation microprobe, these analyses can be done *in situ*, adding information on the spatial context of isotopic variations.

In 1999, Andrew Botfield completed an Honours thesis on Cu isotopes in chalcopyrite from a wide variety of ore samples, that increased the world-wide database by a factor of five and showed that there were large and significant variations in Cu-isotope ratios within and between deposits (Fig. 1).

In 2001 GEMOC, supported by a consortium of five mineral exploration companies, has carried out a study of Cu and Fe isotopes in chalcopyrite, and Fe isotopes in pyrite, from several types of ore deposit. The results show large variations that can be correlated with parameters such as ore grade, temperature, and spatial position within the ore bodies.

The 1640 Ma McArthur River (also known as HYC) deposit is an unmetamorphosed stratiform Pb-Zn-Ag deposit in northern Australia (Fig. 2). The geological preservation and size of this deposit make it an ideal location to study the primary geological characteristics of a Proterozoic sedimentary-hosted Pb-Zn-Ag deposit. Sediment deposition and mineralisation occurred in a quiet marine environment below the wave base, as ore-bearing fluids percolated through the basin. Earlier studies of metal zoning, sulfur isotopes and organic chemistry have defined a temperature gradient, and suggest that bacterial reduction of sulfate was an important process in the cooler parts of the ore body, away from a main vent where the metal-bearing fluids entered the basin.

Chalcopyrite Cu-isotopes (115 analyses) and pyrite Fe-isotopes (140 analyses) were measured over a horizontal distance of approximately 1200 metres through the ore body and reflect changes in the chemistry of the brine as it passed through the basin. Chalcopyrite and pyrite in the hot Cu-rich section of the ore body have isotopically light Cu and Fe. As the brine moved and cooled, it became enriched in the heavy Cu and Fe isotopes (⁶⁵Cu and ⁵⁷Fe) as the light isotopes (⁶³Cu and ⁵⁴Fe) were preferentially removed from the solution by thermochemical sulfate reduction (TSR; Fig. 3). Beyond about 800 metres from the vent, a much greater range in

both ⁶⁵Cu/⁶³Cu and ⁵⁷Fe/⁵⁴Fe is observed, and this spread may indicate the beginning of bacterial sulfate reduction. Iron- and copperreducing bacteria are expected to preferentially remove the light isotopes from solution, with the result that the solution becomes isotopically heavy. The similar proportions of isotopically heavy and light pyrites and chalcopyrites above and below the TSR trend in Figure 3 suggest that up to 50% of the sulfides in this part of the deposit were formed as a direct result of bacterial reduction. This conclusion is supported by palaentological evidence in this region of the deposit.

The use of metal isotopes in ore-genesis studies is in its infancy, but it shows great promise. In deposits like HYC, the isotopic data also can be important in mineral exploration – they point toward the source regions of the ore metals.

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Figure 3. Variation in \mathcal{E}^{65} Cu and \mathcal{E}^{57} Fe in pyrite and chalcopyrite along the HYC ore deposit, showing trends possibly related to temperature (TSR) and scatter that may reflect bacterial sulfate reduction (BSR) in the cooler brines.





Figure 2. Map of the HYC Pb-Zn deposit, showing inferred flow direction of metalbearing basinal brines, Pb/Zn zoning pattern and the location of samples analysed for Cu and Fe isotopes.

How old are diamonds?

Figure 2. 100µm sulfide inclusion in a zircon megacryst from Mir, showing negativecrystal form; the "wings" are expansion cracks lined with sulfide and formed during decompression. The sulfide gives a Re-Os age of 3 Ga. **D** IAMONDS often are described as mantle time capsules - mineral inclusions, once trapped inside a diamond, are protected from the environment, and give us one of our best windows into mantle conditions. But which conditions? When did the diamonds actually crystallise? The most direct way of finding out might be to date the inclusions, assuming that the diamond crystallisation process reset the isotopic clocks in the minerals that became included in the diamond. In the last few years, a

Figure 1. Aerial view of the Mir diamond mine in Siberia. High-rise apartment buildings near rim of pit give scale.



lot of time and technology has been spent on determining the Re-Os model ages of sulfide inclusions in diamonds. The results have been used to argue that most diamonds crystallised in Archean time.

This approach required rethinking after Slava Spetsius arrived at GEMOC during 2001 with a collection of large zircon crystals from the Mir kimberlite in Siberia. These zircons contain inclusions of peridotitic minerals —chromite, olivine, chromediopside, phlogopite — that tell us the zircons grew in the mantle wall-rocks, as part of a metasomatic process. Some of these zircons also contain inclusions of typical peridotitic sulfides, with negative-crystal forms (Fig. 2) showing that they underwent grain boundary adjustment during formation of the surrounding zircon. *In situ* LAM-ICPMS U-Pb dating and Hf-isotope analysis showed that the zircons probably crystallised 355 Ma ago, and in any case cannot be older than 600 Ma. But *in situ* Re-Os dating of three sulfide inclusions gave mean depletion ages of more than 3000 Ma! It appears that the growth of the zircon did *not* reset the Os isotope compositions of the sulfides; the metasomatic fluids probably carried little Os, while the sulfides contain 50-250 ppm Os.

This result implies that the ages of analogous sulfides in diamonds date the formation of the wall-rock in which the diamond crystallised, but would only date the formation of the diamond if the sulfide inclusion and diamond coincidentally formed at the same time. With our current knowledge and methodologies we



cannot unequivocally know when a diamond itself actually crystallised, and can only know that it is younger than its sulfide inclusions.

Contacts: Bill Griffin, Elena Belousova, Sue O'Reilly Funded by: Macquarie University visiting Fellow Research Grant, de Beers Australia, GEMOC Microdiamonds and microminerals -Slave Craton, Canada **M** INERAL INCLUSIONS within diamonds represent pristine mantle material trapped at the time of diamond growth – they have been protected from the processes that modify the mantle during its tectonic history. Mineral inclusions in microdiamonds from kimberlites at Lac de Gras in the Slave Craton, Canada have been studied to investigate unmodified compositions of the diamond bearing mantle, constrain the proportions of diamond bearing rock types and provide key

information that brings us closer to understanding the evolution of the Slave Craton in this region.

Microdiamonds, defined as less than 1 mm in cross section, were selected because they are more abundant and less valuable than macrodiamonds, and are used as indicators to evaluate the prospectivity of a kimberlite body in diamond exploration. Macrodiamonds from one pipe have been studied previously, and we wanted to find out if the two diamond types at Lac de Gras differed. Over two hundred mineral inclusions were extracted from 500 microdiamonds, representing eight kimberlite localities in the central Slave craton, and analysed for major and minor elements.

We found that although some diamond characteristics differ between macro- and microdiamond groups, inclusion compositions and the relative abundances of different paragenetic types of inclusions do not. Microdiamonds from Lac de Gras typically have low nitrogen aggregation states, suggesting that they formed at a late stage in the history of the mantle, possibly just prior to kimberlite emplacement. In contrast, the nitrogen contents and carbon-isotope compositions of micro- and macrodiamonds are similar.

At Lac de Gras a large proportion of microdiamonds contain inclusions from the eclogitic paragenesis (70%), followed by the peridotitic paragenesis (16%); diamonds containing unusual phases derived from the transition zone and lower mantle make up 14% of the microdiamond population. Inclusions in diamonds of lower mantle origin are the oxide ferropericlase, $MgSiO_3$ and $CaSiO_3$ - perovskite, SiO_2 and Mg_2SiO_4 ; the last is likely to have formed as a spinel-structured polymorph of olivine. The lower mantle phases, which occur in combination with one another in single diamonds, suggest a deep origin for these diamonds (~670 km). A small number of diamonds of both eclogitic and peridotitic paragenesis were identified as having possible transition zone origins.

The inclusion data suggest that mantle plumes transported diamonds from the transition zone and lower mantle to the base of the Slave Craton at Lac de Gras. Although lower mantle diamond inclusions typically reflect peridotitic bulk compositions, the abundance of eclogitic diamonds at Lac de Gras, also noted at other localities where transition zone/lower mantle diamonds occur, suggests the presence of eclogites is significant to the processes of mantle formation and dynamics in regions where deep mantle material has been transported to the Earth's surface.

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Figure 1. Cathodoluminescence image of a diamond, showing internal structure around a mineral inclusion



Figure 2. Ferropericlase inclusion in a microdiamond from Lac de Gras



Green and gold: sulfides in olivine date the Siberian lithosphere



Figure 1. Element distribution maps showing exsolution textures in a typical "enclosed" sulfide from Udachnaya.

Figure 2. Re-Os model ages of "undisturbed" sulfides from Udachnaya. **G** EMOC'S DEVELOPMENT of *in situ* Re-Os analysis of sulfide grains (using the LAM-MC-ICPMS) has provided new insights into the timing of stabilisation and modification of continental roots. As we analyse sulfide populations in more mantle xenoliths, it becomes obvious that most of these rocks have complex histories, with many generations of sulfides and mixtures of Re-Os components, that make whole-rock ages difficult to interpret. The *in situ* analysis of sulfides in single rocks can sort out this confusion, but it requires painstaking serial sectioning to locate and analyse the small and widely scattered individual sulfide grains.

In 2001, we took a new approach to surveying the age spectrum of a lithospheric section, by picking sulfide-bearing olivine grains (perhaps 1 in 10,000) out of concentrates prepared from kimberlites. Dr. Zdislav Spetsius, mineralogist/ petrologist with the Siberian diamond miner Alrosa (Mirny), scanned many litres of coarse olivine concentrate from the Udachnaya kimberlite. He arrived at GEMOC with over 100 grains, some containing up to 6 sulfide inclusions. Over 90 of these inclusions were successfully analysed for Re-Os and 26 could also be analysed (by LAM-ICPMS) for their contents of Platinum Group Elements and other trace elements.

The sulfides are mixtures of Ni-rich and Fe-rich monosulfide solid solutions (MSS), pentlandite and chalcopyrite, exsolved from MSS bulk compositions (Fig. 1). They can be divided into 5 populations (1, 2, 3A-3C) on the basis of Os content, Os/Pt and Re/Os. By comparison with published experimental data, Group 1 sulfides can be identified as MSS residual after low degrees of melting of a primitive mantle source, under sulfur-saturated conditions. Group 2 sulfides are best modelled as mixtures of MSS and alloy phases, formed under sulfur-undersaturated conditions. The other groups can be modelled as sulfide liquids, or as the products of reaction between these liquids and the MSS of Groups 1 and 2. Inclusions of different groups may occur within single olivine grains, suggesting repeated introduction of sulfide melts, followed by annealing and grain growth.

Sulfides of Groups 1 and 2 give geologically reasonable (0-4 Ga) Os model ages (T_{MA}). Most Group 3 sulfides contain unsupported ¹⁸⁷Os, implying a two-stage history. Our modelling shows that sulfides with ¹⁸⁷Re/¹⁸⁸Os <0.07 are unlikely to have been disturbed. 52 grains satisy this criterion; 45 of these give T_{MA} ages between 2.5 and 3.6 Ga (Fig. 2). These data suggest that most of the lithospheric mantle beneath the Daldyn kimberlite field formed during the period 3 - 3.5 Ga, and that lithosphere formation culminated in a major event at ca 2.9 Ga. There is little



evidence in the Re-Os data for significant further additions to the lithosphere after this time.

This analysis of sulfides from olivine concentrates gives us a (relatively) rapid way to assess the spectrum of depletion ages in a lithosphere section, and that will be a very valuable guide to interpretation of more detailed work on individual xenoliths. GEMOC has started a program of sampling worldwide, with the help of friends from the diamond exploration industry.

Contacts: Bill Griffin, Norm Pearson, Sue O'Reilly Funded by: Macquarie University, GEMOC, Industry Archean mantle hiding under Proterozoic crust in western Norway **O** ROGENIC PERIDOTITE MASSIFS occur in many mountain systems. Most are spinel-bearing peridotites, or their retrograded, hydrated equivalents (chlorite peridotites or serpentinites). Garnet-bearing peridotites are much less common, but many of these rocks bear a remarkable resemblance to some kimberliteborne mantle xenoliths and they appear to represent slices of lithospheric mantle tectonically emplaced into continental crust during subduction.

Coarse-grained garnet-bearing peridotites have been documented at several localities in the Western Gneiss Region (WGR) of southwest Norway (Fig. 1).

Figure 1. Garnet peridotite outcrop at Helgehornsvatn

Mantle sequences from the WGR mainly comprise minor garnet-bearing peridotites (including lherzolites, wehrlites and cpx-free harzburgites) and dominant, very depleted garnet-free dunites.

The recent development of high-precision *in situ* laser-ablation techniques enables us to rapidly obtain Re-Os isotopic ages from single sulfide grains in such peridotites. Where the sulfides contain significant amounts of Re, the calculation of Re-Os model ages ("Re-depletion ages" or $T_{\rm RD}$) requires back-calculation to the likely time of Re addition, to correct for any ingrowth of ¹⁸⁷Os. In xenoliths, this generally is taken as the time of eruption. In massif peridotites, the



correction is less straightforward, and must be based on the age of major magmatic or tectonic events that affected the peridotites.

Two main events may have affected the WGR peridotites. The first is the Gothian orogeny between 1600-1750 Ma, which saw widespread magmatic activity and crustbuilding in Norway. The second is the Caledonian ultra-high pressure metamorphic event at about 410 Ma, which marks continental subduction and probably the emplacement of the peridotites into the crust. The Sveconorwegian (Grenvillian) orogeny at ca 1000 Ma had a limited effect on the WGR.

Sulfides in the WGR garnet peridotites are predominantly pentlandite \pm heazelwoodite and occur both interstitially and as inclusions in silicate phases.

Re-Os model ages were measured for twenty-three sulfides from peridotites at Almklovdalen in the southern WGR. On a cumulative probability diagram the TRD ages (calculated at 400 Ma) define several peaks, some of which can be matched to major crust-building events in Norway. There are no obvious Caledonian sulfide ages. Sveconorwegian ages also are poorly represented in the sulfide population, which suggests that this crustal event was not very effective in resetting the ages in the sulfides. Ages greater than 1000 Ma are clearly resolved into distinct Proterozoic and Archean peaks with little overlap. The Proterozoic peak has a maximum at ~1700 Ma which falls within the age range for the Gothian orogeny Figure 2. Relativeprobability plot of T_{RD} model ages calculated assuming Re addition at 1600 Ma.





Garnet peridotites from the Western Gneiss region, SW Norway.

Ancient mantle beneath New England (1600-1750 Ma) and is close to the calculated Sm-Nd mineral age of 1703 ± 29 Ma for garnet peridotites from the Raudkleivane locality in Almklovdalen.

The greatest surprise, and perhaps the most exciting result of this study, is the significant number of Archean ages (peaks at 2900 - 3200 Ma). These ages are greater than known crustal ages in the region, and may suggest that the peridotites reflect a mantle depletion event that was not associated with crustal growth in this part of the Baltic Shield. Alternatively, the Archean crust corresponding to this mantle depletion event may have been reworked in Proterozoic time, to the point of being unrecognisable. In either case, it appears that mantle material that underwent depletion (melt extraction) in Archean time has survived in relatively shallow parts of the lithospheric mantle through a major episode of crustal generation in Proterozoic time. Its survival is almost certainly linked to the buoyancy of these highly depleted peridotites, relative to the underlying asthenosphere. This conclusion has major implications for our understanding of mantle evolution, and the linkages between crustal and mantle tectonics.

Contacts: Eloise Beyer, Sue O'Reilly, Bill Griffin Funded by: ARC, Macquarie University Postgradutae Grant, GEMOC

T HE NEW ENGLAND OROGEN, northern NSW (Fig. 1) was assembled during a convergent tectonic regime, active along the eastern margin of the Australian continent in Paleozoic time. It can be divided into two regions: the Tamworth Belt represents the sediments deposited at the continental margin inboard of the subduction zone, and the Tablelands Complex represents a collage of terranes accreted to and dispersed along the convergent margin. The two regions are separated by the Peel Fault and the Great Serpentinite Belt, which appear to be



relics of the suture along which oceanic crust was subducted.

Traditional methods of dating surface geology show that tectonic activity in the orogen ceased with the emplacement of the New England Batholith in Carboniferous and Permian time; in the Cretaceous the Tasman Sea was opened, and during Tertiary time abundant basaltic lavas were erupted. The oldest materials recognised thus far are 'exotic' blocks tectonically emplaced close to the Peel Fault. U-Pb dating (plagiogranites and eclogites) and fossils (limestones) give dates that stretch back as far as the Early Cambrian and late Neoproterozoic, but little is known about their affinities or position on the margin of eastern Gondwana.

Mantle xenoliths brought to the surface by erupting basalts represent samples of the upper mantle and lower crust. Xenoliths from several locations in the New Engand Orogen have been characterised as part of this study, and *in situ* Re-Os dating of sulfide grains found in the peridotites has been carried out using the GEMOC multi-collector ICPMS laser microprobe. The Re-Os data can be used to calculate model ages that correspond to periods of melt extraction from the peridotitic mantle.

Re-Os ages for the xenoliths in this study far exceed the ages determined for the surface rocks (Fig. 2). Xenoliths from Allyn River and Wallabadah Rocks, in the southern end of the Tamworth Belt, give ages in the range 0.8 to 1.8 Ga, and samples from Guyra, in the central part of the Tablelands Complex give ages in the range 0.6 to 1.8 Ga. Model ages for samples from Lawler's Creek, at the north western margin of the Tamworth Belt are significantly older, in the range 1.4 to 3.4 Ga.

These new data show that old mantle can persist beneath younger terrains, probably because of the inherent buoyancy of depleted peridotites (see *Research Highlight p.18*). The ages also raise questions about the early history of Eastern Australia, prior to the breakup of Gondwana. Why is the mantle beneath the orogen so much older than the rocks at the surface? Is it inherited from a precursor terrane that was broken up and dispersed prior to the onset of subduction along the eastern Gondwana margin? What is the association with other Proterozoic-age blocks now located in Antarctica and elsewhere?

Research is continuing on the subject

Contacts: Will Powell, Sue O'Reilly Funded by: Macquarie University postgraduate grant, GEMOC





Mt Kaputar, in the northwest of the New England Orogen. Numerous spectacular trachyte plugs remain as evidence of the volcanism here, which took place around 17-20 million years ago, bringing xenoliths to the surface at the nearby Lawler's Creek locality.

Figure 2. Re-Os model ages for sulfides from the New England xenolith localities. Coloured bars are centred on the calculated age, with the length covering the 2-sigma uncertainty.

Wandering poles in the Late Cambrian

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P ALAEOMAGNETIC STUDIES of rocks measure the direction of the magnetic pole at the time a rock crystallised or was deposited. The apparent movement of the magnetic pole between different time periods usually is interpreted in terms of the continental plates moving relative to the pole – but what if the pole itself, and not just the plates, really was wandering?

A palaeomagnetic investigation of Cambro-Ordovician limestones from Black

Mountain in western Queensland is being carried out to assess the possibility of a large-scale true polar wander event during the Late Cambrian. Inertial Interchange True Polar Wander (IITWP) is a special case of true polar wander; it describes the rapid rotation of the solid lithosphere of up to 90° by the physical crossing, or interchange, of the earth's intermediate and maximum moments of inertia.

For such a large-scale shift the earth must be modelled as a quasi-rigid spinning spheroid in which a concentration of mass at the poles would produce an inherent instability, leading to the realignment of mass towards the equator (Fig. 1).

Palaeomagnetic evidence to support an IITPW event in the Late Cambrian comes from selected groups of palaeopoles from Vendian to earliest Cambrian formations in Laurentia, Baltica, Siberia and Australia. These palaeopoles lie more than 90° away from similarly derived Late Cambrian-Early Ordovician poles.

Ambiguity with respect to the polarity of Early Palaeozoic and older palaeopoles presents a large degree of uncertainty when we attempt to define the directions of ancient apparent polar wander paths (APWPs). For the pole path presented in Figure 2, polarities of the ancient palaeopoles (>400 Ma) were invoked to minimise the length of the generated polepath, and IITPW is not supported.

However, a shorter path is not necessarily a better path. Before a more detailed APWP can be presented as a part of this study, identification of the age of magnetisations carried by limestones at and around Black Mountain will need to be ascertained. For example, GB1 in Figure 2 is the characteristic palaeomagnetic direction obtained from specimens at Black Mountain. Petrophysical tests will aid



in the distinction between an authigenic magnetite, supporting the Silurian remagnetisation age suggested by the presented APWP, and primary remanence, which will support IITPW. If the IITPW hypothesis is sustained by this investigation, it will require a radical restructuring of palaeogeodynamics and the Earth system as we know it.

Contacts: Kari Anderson, Mark Lackie Funded by: Macquarie University postgraduate grant, GEMOC

Figure 1. Visual representation of IITPW.

t_{max} Φω

 (\bigcirc)

Figure 2. Latest Proterozoic-Earliest Palaeozoic APWP for Australia. Selected Australian palaeopoles taken from the palaeomagnetic database maintained by M.R. McElhinny & J. Lock on-line at "http://dragon.ngu.no/ Palmag/paleomag.htm" Structure and chemistry of the Australian lithosphere **G** ARNET XENOCRYSTS from a series of localities in southern Australia have been used to construct a lithospheric transect across one of the major tectonic boundaries of the Australian continent, the Tasman Line. The localities, from Jugiong in central NSW to the Eyre

Peninsula in South Australia, cover a range of tectonic environments, from Phanerozoic fold belt to Proterozoic craton.

At each of these localities garnet data have been used to estimate the pressure-temperature regime within the lithosphere and the depth to the lithosphere/asthenosphere boundary (LAB).

These sections reveal thicker lithosphere and lower geothermal gradients with increasing tectonothermal age of the lithosphere domains. The paleogeotherm decreases from greater than 50 mW/m² at Jugiong to around 40 mW/m² in South Australia and the depth to the LAB changes from ca 100 km to 180 km. These physical changes are paralleled by higher MgO and lower CaO and Al_2O_3 contents in progressively older lithospheric mantle, consistent with the global secular variation in mantle composition (Publications 132, 234).

Comparison of the adjacent Springfield (Permian) and Orroroo (Jurassic) sections indicates lithosphere thinning by about 10-15 km over this time period, attributed to the effect of Pangean rifting.

A method of estimating olivine Mg content from garnet composition via an inversion of O'Neill and Wood's (1979) geothermometer has been developed (Publication 222). This method reproduces xenolith olivine compositions in the mantle to within ± 0.5 mol%.

Application of this inversion to the southern Australian transect shows high XMg_{ol} (Mg/(Mg+Fe)) in the shallow parts of the Proterozoic westerly sections and lower XMg_{ol} in the Phanerozoic eastern sections, reflecting greater degrees of melt extraction during formation of older lithosphere. There also is an overall trend to lower Mg# with increasing depth in each section, which may reflect infiltration by asthenospheric melts near the LAB. Olivine density varies inversely with Mg#, and the Proterozoic lithosphere in this traverse therefore is more buoyant relative to the asthenosphere than the Phanerozoic sections, despite the lower geotherm

beneath the craton. As Vp and Vs also vary with Mg# (the higher the Mg#, the higher the Vp and Vs) these compositional differences are important in the interpretation of seismic tomography.

Contacts: Oliver Gaul, Sue O'Reilly, Bill Griffin Funded by: GEMOC, ARC APA(I), Industry partners





Figure 1. Map of southern Australia showing sample localities relative to the Tasman line.

Figure 2. Contour plots of XMg_{ol} against depth for sections on the southern Australian transect.

Hafnium isotopes and the Baltic Margin jigsaw puzzle **T** HE INTEGRATED ANALYSIS of U-Pb ages and Hf-isotope composition in zircon is proving to be a valuable tool in sorting out tectonic relationships in complex terrains. A collaborative project between GEMOC and the Precambrian Geochemistry research group at the University of Oslo, Norway has used this approach to analyse the relationships between the different crustal blocks that now make up the Southwest Scandinavian Domain of the Baltic Shield.

Two contrasting tectonic models have dominated the recent debate about this



region. In one, the part of south Norway west of the Oslo Rift was an exotic microcontinent, accreted onto the Baltic Shield between 1.58 and 1.50 Ga along a suture, now conveniently masked by the Paleozoic rocks of the Oslo Rift. In the competing model, South Norway has been part of the Baltic Shield since the early Proterozoic, but the crustal terranes building up the area have been displaced southwards along the margin of the Baltic Shield during the Sveconorwegian (i.e. Grenvillian, ca 1000 Ma) orogeny.

LAM-ICPMS U-Pb dating of Mesoproterozoic intrusions from South Norway in the GEMOC laboratories showed that extensive calcalkaline magmatism occurred in the period *1500 -1600 Ma*, and this magmatism can be traced on both sides of the Oslo Rift (Fig. 1). The major and trace element characteristics of the 1500-1600 Ma

intrusive rocks indicate that they formed in a moderately evolved continental margin volcanic arc setting.

Zircons from these intrusions show a range of initial Hf isotopic compositions (Fig. 2). In the western part of the area, furthest from the Mesoproterozoic continent, the ¹⁷⁶Hf/¹⁷⁷Hf values are close to the depleted mantle at the time of intrusion. In the east, significantly lower values indicate that rising batches of magma may have interacted directly with Paleoproterozoic continental rocks. The



Figure 1. Tectonic map of the Baltic Shield and adjacent parts of the Caledonides, showing the hypothetical suture line through the Permian Oslo Rift in the study area

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distribution of Hf-isotope values is consistent with a Cordillieran-type model for the mid-Proterozoic evolution of the margin of the Baltic Shield.

Hf isotope data on other intrusions across southern Norway show that today, rocks with a crustal history extending back to early Proterozoic time and carrying a continental geochemical signature are present at depth west of the areas dominated by the Mesoproterozoic calkalkaline rocks. This supports suggestions that these western terranes originally lay farther north along the ancient Baltic continental margin, and were displaced southward along that margin during the Sveconorwegian orogeny (Fig. 3).

Contacts: Tom Andersen (Univ. of Oslo), Bill Griffin Funded by: GEMOC, Norwegian Research Council

a: Situation at 1.6 - 1.5 Ga



b: Situation after Sveconorwegian terrane displacement



Hf-isotope data. (a) The study area (in blue) was generated at a continental margin, with subduction offshore. (b) Older crust now occurring west of the study area was displaced southward during Sveconorwegian time (ca 1000 Ma).

Figure 3. Cartoon

showing tectonic model

implied by the U-Pb and

TerraneChron™ takes off

TerraneChron[™] is GEMOC's unique approach to terrane evaluation and the study of crustal evolution, based on the integrated *in situ* analysis of U-Pb age, Hf-isotope composition and trace-element patterns in single zircon grains. The zircons can come from modern drainages sampling a terrane of interest, from ancient sedimentary rocks, or from individual igneous rocks. Using GEMOC's EMP, LAM-ICPMS and

LAM-MC-ICPMS facilities (see *Technology Development*), this methodology gives the age, the host magma type, and the source of the magma (crustal or mantle), for each zircon grain analysed. Applied to zircon suites from ancient or modern sediments, it generates an 'event signature' that defines the evolution of the area in terms of the timing and nature of the magmatic events that have formed its crust (Publications 215, 251, 262).

In 2001, the interest in *TerraneChron*[™] as a tool in mineral exploration, basin analysis and crustal evolution studies took off to an exhilarating extent, with funded projects in Scandinavia, India, South America and Australia. More discussions about collaborative projects are in progress with exploration companies, and state and national geological surveys in Australia and overseas. The advocacy of Dr. Steve Walters from Advantage Geochemical Solutions has been a significant factor in generating this interest. The Geochemical Analysis Unit now reserves one of its laser-probe ICPMS instruments for the U-Pb work, and Ayesha Sayeed recently joined Elena Belousova to add increased capacity for the *TerraneChron*[™] work. The "brand name" is now going through the copyright process, and a series of papers on the results of projects will begin to appear in 2002.

Contact: Bill Griffin, Elena Belousova, Sue O'Reilly



Figure 2. Xenolith localities in Tasmania



M ANTLE XENOLITHS provide a basic but very powerful tool for investigating the nature of the lithosphere in space and time. A study of spinel peridotite xenoliths in Tasmanian basalts has revealed marked heterogeneity in the lithospheric mantle beneath the northern part of the island. Tasmania can be broadly divided into two terrains: a Proterozoic terrain in the west, and a Phanerozoic terrain in the east (Fig. 1). The Proterozoic terrain can be further divided into six regions or "Crustal Elements" based on geological and geophysical mapping (GSA Abstracts, 49, 1998). The Phanerozoic terrain is defined as the

Northeast Element. Each of the Elements has a distinct geological history and internal structure. An east-west traverse across northern Tasmania sampled xenoliths from the Rocky Cape (RC), Sheffield (SH) and Northeast (NE) Elements.

A correlation between mantle composition and the age of the overlying crust has been observed in numerous terrains around the world and has been interpreted as evidence that crustal volumes and their underlying lithospheric mantle formed at least quasi-contemporaneously, and can remain coupled for periods of eons. In Tasmania it was expected that the mantle xenoliths sampled in the Proterozoic Elements would resemble depleted Proterozoic lithosphere elsewhere in the world, while those erupted through Phanerozoic crust would be more fertile and representative of typical Phanerozoic lithosphere.

However, in Tasmania the majority of mantle peridotites are fertile, even in regions where they have been erupted through Proterozoic crust. In fact, the xenoliths with the most fertile compositions are found in the Rocky Cape Element, which has yielded some of the oldest crustal

ages in Tasmania. This suggests that the Proterozoic depleted lithosphere has been either removed and replaced by younger, chemically fertile lithosphere, or

refertilised by the infiltration of asthenospheric melts. Rare depleted xenoliths found at some localities may represent remnant Proterozoic lithospheric mantle that has persisted at least to the Tertiary, the time of xenolith entrainment. The seismic velocity of peridotite increases with its degree of depletion (see *Research Highlight p. 18*), and the overall fertile nature of the mantle beneath northern Tasmania is consistent with the relatively low mantle velocities recorded by recent Geoscience Australia seismic surveys.

The presence of unexpectedly fertile lithosphere in northern Tasmania may be related to rifting between Australia and Antarctica during Jurassic time. Crustal extension would thin and disrupt the old depleted lithosphere, providing space for upwelling asthenospheric material that would later cool to form new, little-



depleted lithospheric mantle. In this regard, northern Tasmania may be a good model for the generation of young lithospheric mantle beneath many terrains affected by Phanerozoic extensional tectonics.

Contacts: Eloise Beyer, Sue O'Reilly, Ming Zhang Funded by: ARC, Macquarie University Postgraduate Grant, GEMOC Plateaus, plumes and fluids in Kerguelen xenoliths CEANIC PLATEAUS are vast outpourings of lava on the ocean floor, and may be good analogues for the development of continents on the early Earth. The Kerguelen Archipelago (South Indian Ocean) lies on Earth's second largest oceanic plateau, and is being studied at

GEMOC in a joint research program with an international consortium, headed by the Université Jean Monnet (St. Etienne). The formation of the plateau is related to interaction between the South East Indian Ridge (SEIR) and the long-lived Kerguelen plume, and makes Kerguelen a unique laboratory for studying the generation of thickened lithospheric mantle in an oceanic setting.

Mantle xenoliths provide key information on the geochemistry of the mantle, that can be used to understand the dynamics, physical properties and evolution through time of the lithosphere. On the Kerguelen Islands, mantle xenoliths usually are found in dikes or pipes of young alkaline basalts. However, harzburgite xenoliths recently were found in tholeiitic-transitional basalt dykes at Lac Michèle, on the Loranchet Peninsula (NW Kerguelen, Fig. 1). Their bulk-rock and mineral compositions (e.g Mg#₀₁ = 90.7-92.2, CaO_{WR}< 1wt %) indicate that these harzburgites are residues from an extensive partial melting event, possibly related to the early formation of the Kerguelen Islands when the plume hit the SEIR 40 Ma ago.

Secondary metasomatic processes that modify the original composition of the xenoliths are well documented in Kerguelen xenoliths and reflect metasomatism by alkaline melts and carbonated fluids. Some of the very depleted harzburgites contain an unusual metasomatic assemblage, composed of sodium-rich feldspar $(Ab_{78:83}An_{14:19}Or_{2:4})$, low Ca-spongy clinopyroxenes, olivine and apatite, that forms reaction rims on Cr-spinel grains (Fig. 2). To our knowledge, this is the first description of such Na-rich feldspars in mantle xenoliths. LAM-ICPMS analyses show that the clinopyroxene is extremely enriched in the light Rare Earth Elements, $Sr \pm Th \pm U$, and depleted in High Field Strength Elements (Nb, Ta, Zr, Hf, Ti). This geochemical signature strongly suggests that the metasomatic agent was a carbonated fluid. The crystallization of this unusual assemblage probably reflects the percolation of small volumes of volatile and Na-CO₂-rich fluids through the peridotitic matrix, reacting with the peridotite to

crystallise the metasomatic assemblage.

These observations have important implications for the diversity of geochemical signatures that can be generated in the oceanic mantle above a mantle plume. They show that the percolation of small volumes of fluids can lead to extreme trace element enrichment of previously very depleted oceanic mantle on a very small scale (i.e < mm scale). Further understanding of the processes will require evaluation of the petrogenesis of carbonatitic magmas in an Albite-Calcite (NaAlSi₃O₈-CaCO₃) system.

Contacts: Guillaume Delpech, Sue O'Reilly Funded by: ARC, Macquarie University, GEMOC



Figure 1. Lac Michèle, on the Loranchet Peninsula (NW Kerguelen).

Figure 2. Element distribution maps of a metasomatic "pocket" with Na-feldspar (Fs), clinopyroxene (Cpx), apatite (Ap) and olivine (OIII) in spinel (Sp).



Cooking mantle fluids - trace element mobility during subduction **S** UBDUCTION of oceanic crust is a crucial step in the generation of new continental crust, because it promotes magmatic processes in the mantle wedge above the subduction zone. The generation of these magmas is linked to water derived from dehydration and/or melting reactions in the subducted slab. This water is thought to enrich the magma source region with large ion lithophile elements (LILE), but not



Figure 2. Large chloritoid (with <0.1% ZnO) in fine grained matrix, inner capsule, 650 °C.



Figure 3. Crystal aggregate grown in fluid and quenched solute from fluid in outer capsule, 650 °C. Chloritoid contains 4% ZnO.



Figure 5. Talc aggregate and quench solute from fluid in outer capsule, 650 °C. N.B. This is actually Ni-talc (willemsite) with Ni coming from the outer capsule (see Fig. 1).



Figure 6. Upper zone of sample in inner capsule, 700 °C.





Figure 1. Crystal aggregate grown in fluid in outer capsule, 650 °C. The outer capsule contained 500 ppm Ni and 200 ppm Zn as impurities and these were very selectively taken up by silicate minerals grown in this capsule (eg pyroxene contains 0.6-1.7%, chloritoid 5-6%, phengite 3-4% NiO). No Ni and Zn were evident in the inner capsule, nor in minerals there.



Figure 4. As for Fig.3. Chloritoid contains 9-11% ZnO.



Figure 7. Crystal aggregate grown in fluid in outer capsule, 700 °C. Phengite contains 3% NiO.

Figure 8. Crystal aggregate grown in fluid in outer capsule, 700 °C. Talc contains 13% NiO, staurolite contains 3-5% ZnO, 3-4% NiO. with high field strength (HFSE) or rare earth elements (REE). Early experiments have confirmed this model on a bulk rock scale for a few trace elements, but did not discriminate the effects of different mineralogies.

We carried out new experiments on an oceanic tholeiite (MORB) enriched (10-100 ppm) in 25 trace elements; it was crystallized at 3.0 GPa, 650 and 700 °C for 2 weeks, with 30-50 wt.% added water. One set of experiments used a double capsule configuration, with fluid in the outer sealed Ag-Pd capsule and powdered MORB glass in the unsealed inner Ag-Pd capsule. These produced a clearcut separation of solid and fluid, with growth of some large crystals in the fluid, and the solute could be quenched for study. Experiments in a single sealed Ag-Pd capsule produced a remarkable separation of fluid and solid. The solid component in both capsule configurations showed a distinct mineralogical zoning. At 650 °C the fluid coexists with omphacite (Figs. 1, 2), lawsonite (Figs. 1, 2), chloritoid (Figs. 2-4), coesite (Figs. 5). At 700 °C garnet is conspicuous as a coarse layer at the top (Fig. 6), below which omphacite, coesite, phengite (Fig. 7), minor staurolite (Fig. 8), and rare lawsonite (Fig. 7), rutile (Fig. 8) and talc (Fig. 8) occur; chloritoid is absent.

The LAM-ICPMS microprobe lets us examine the trace element contents of individual minerals coexisting with fluid in these experimental charges, and the changes in trace element ratios for the fluid as the coexisting mineralogy changes. LAM-ICPMS spectra also indicate the presence of minute crystals of zircon and allanite, the latter commonly included in garnet or chloritoid crystals. Most importantly the LAM-ICPMS analyses establish *patterns* of trace element partitioning between minerals (data for omphacite, lawsonite, phengite, chloritoid and garnet) and fluid, if not absolute values.

The fluid shows strong enrichment of LILE relative to HFSE and REE. Rb/Sr, Cs/Sr and Ba/Sr decrease from 650 to 700 °C, apparently controlled by residual lawsonite; an increase in La/Lu is clearly controlled by garnet. Omphacite fractionates both Zr/Nb and La/Lu, so that Zr/Nb decreases and La/Lu increases in the fluid. Rutile strongly takes up Nb and Ta, but cannot explain an almost 4-fold increase in Nb/Ta observed in the fluid relative to the bulk sample.

These results indicate that the movement of a fluid derived by dehydration processes may increase LILE/HFSE, LILE/REE and decrease Zr/Nb in the mantle wedge, and thus in magmas derived from the wedge. The fluid may impart different Rb/Sr, Cs/Sr and Ba/Sr to the magmas, depending on the temperature at which dehydration took place. Residual rutile may explain Nb and Ta depletion without significantly affecting Nb/Ta ratios. The observed lack of fractionation in La/Lu restricts the role of garnet in the melting. Thus close examination of key trace element ratios in subduction zone magmas may point to a broad pressure/ temperature gradient in the dehydrating slab, giving rise to the fluids that ultimately drove the magma generation.

Contacts: Trevor Green, John Adam Funded by: Macquarie University Grants "....close examination of key trace element ratios in subduction zone magmas may point to a broad pressure/ temperature gradient in the dehydrating slab, giving rise to the fluids that ultimately drove the magma generation. "