

## **PETROCHEMISTRY AND EXPERIMENTAL PETROLOGY**

The Petrochemistry and Experimental Petrology Group uses the experimental investigation of chemical and physical processes to study the Earth, its origin, evolution and mineral wealth. The group operates a wide range of experimental apparatuses to generate the high temperatures and pressures that are needed to reproduce the natural conditions within the Earth. (Note that a pressure of 10,000 atmospheres is equivalent to 1 GPa.) The equipment includes: high temperature furnaces capable of reaching 1800°C, several of which are equipped for precise control of oxygen and sulfur fugacities by gas mixing; ten solid-media piston-cylinder devices for generating pressures to 6 GPa and temperatures in excess of 2000°C, some of which are large-capacity devices capable of synthesising relatively large volumes of high pressure phases for detailed mineralogical studies; a multi-anvil apparatus, which can achieve pressures of 26 GPa; and, through collaboration with the Department of Geology, the Faculties, a well-equipped hydrothermal laboratory. These high-temperature, high-pressure apparatuses are complemented by an array of microbeam analytical techniques, including electron microprobe, ion microprobe, laser-ablation ICP-MS, FTIR spectroscopy and visible-UV spectroscopy. This year a new ICP-MS instrument (Agilent 7500) was installed, principally to promote laser-ablation work, including trace-element microanalysis of experimental run products. The group has also been most fortunate to win funding for a new electron microprobe, in collaboration with a consortium of other Canberra users. As well as providing better imaging capabilities and more stable operation (hence accuracy), the new instrument will enable quantitative element mapping. It will replace our ageing Cameca Camebax, which is now entering its eighteenth year of operation, having obtained over 300,000 quantitative analyses – an incontrovertible testament to the importance of the electron microprobe to the group's activities over the years.

Most of the group's activities are concentrated into five areas: 1) Origin of the Earth and core formation; 2) Phase equilibria, including melting relations, in mantle systems; 3) Phase equilibria related to crustal evolution and ore deposits; 4) Physics of melting and melt extraction; and 5) Spectroscopic and thermodynamic property measurements on minerals and silicate melts. The latter area of research is undertaken in the belief that better understanding of large-scale geological processes often requires detailed, fundamental knowledge of the behaviour of minerals at the atomic scale.

In the latter context, the group continues to develop its use of X-ray absorption spectroscopy to characterise the chemical environment and oxidation states of trace elements in minerals and silicate melts. Synchrotron radiation at the Australian National Beamline Facility at Tsukuba, Japan, has been used by Drs Berry and O'Neill with the help of several other group members, to quantify oxidation states of Cr, V, and W in silicate melts as a function of oxygen fugacity, temperature, pressure and melt composition. This work has now been extended to in-situ measurements at temperatures to 1500°C and controlled oxygen fugacity, using a furnace designed and built by Mr M. Shelley, allowing unquenchable oxidation states in silicate melts to be observed directly. Preliminary results on the nature of ore-forming metal complexes in supercritical fluids obtained by members of our group (Drs A. Berry and J. Mavrogenes and Mr A. Hack) are reported in the Centre for Ore Systems Studies (COSS) section.

This spectroscopic work on silicate melts compliments the thermodynamic and phase equilibrium studies carried out by the group. Dr H. O'Neill and co-workers have measured the solubilities of several siderophile elements in silicate melts as a function of melt composition. Although the immediate aim of these measurements is to constrain better models for core formation in the early Earth, these data are also being used to work out generalised models for the activity coefficients of different groups of trace elements in silicate melts.

During the year Dr Taylor suspended his Research Fellowship to join PRISE, and further develop the commercial application of trace-element fingerprinting of diamond indicator minerals. He has used the laser-ablation ICP-MS extensively for this purpose. His place in the group was taken until the end of the year by Dr S. Eggins, whose work has focussed on the

improvement of the laser-ablation ICP-MS system. In the field of melt extraction, Dr U. Faul has developed a model to account for the rates of melt extraction beneath mid-ocean ridges, and the implications this holds for trace-element abundances and U-Th series disequilibria.

Dr J. Hermann and Professor D. Green continue their investigation of phase relations applicable to ultra-high-pressure metamorphic terrains. Dr T. Morishita, a JSPS Visiting Fellow, and Professor D. Green are using experimental methods together with extensive field observations and analytical work, to investigate the origin and significance of mafic layers in ultramafic peridotite massifs. Drs J. Mavrogenes and H. O'Neill have extended their experimental work on the properties of sulfur in silicate melts by studying very oxidizing conditions, under which the sulfur dissolves as sulfate not sulfide. The effects of  $fO_2$ ,  $fSO_2$ , melt composition and temperature have been quantified in this regime, and experiments are under way on the geologically important variables of pressure and water activity. Dr S. Kesson continues to develop expertise for the group in the field of powder X-ray diffraction using the Rietveld method.

The group contains five PhD students, Messrs Magee, Hack, Xi and Sommacal, and Ms L. Hanley. Mr C. Magee is poised to complete his thesis on the origin of carbonado. Ms L. Hanley continues her study of the Antrim Plateau flood basalts of the Northern Territory, and has recently demonstrated an early Cambrian age ( $513 \pm 12$  Ma, 1 Ma = one million years), possibly, and intriguingly, coincident with the Botomian-Toyonian mass extinction. Mr Silvano has begun a project in conjunction with Dr M. Sambridge to apply geophysical inverse theory to the modelling of phase equilibria. Mr Xi Liu continues with his study of the importance of chromium in mantle melting.

Of the technical staff, Mr M. Shelley has constructed a high-temperature furnace for X-ray absorption spectroscopy in silicate melts under controlled CO/CO<sub>2</sub> atmosphere to 1500°C, and continues to development of laser-ablation ICP-MS technology, including design of a new sample stage. Mr W. Hibberson and Mr D. Scott have continued the development of the 6-7 GPa piston-cylinder apparatus, and have been extensively engaged in sample synthesis for many of the group's activities. After many years spent advancing diamond and cubic boron nitride technology for commercial exploitation by the University, Mr P. Willis retired during the year; his place in the group being filled by Mr J. Derlacki, who brings experience from RSPHysSE. Mr N. Ware maintains and operates the group's CAMECA electron microprobe and has been much engaged in evaluating requirements for the proposed new electron microprobe, visiting both the Cameca factory in Paris and JEOL in Tokyo.

### ***The oxidation state of transition metal ions in silicate melts at temperatures up to 1700 K***

*A.J. Berry, H.StC. O'Neill, J.M.G. Shelley and G.J. Foran<sup>1</sup>*

The oxidation state of transition metal ions is a sensitive indicator of the redox conditions under which a melt solidified and is important for understanding partitioning between melt and crystals. X-ray absorption near edge structure (XANES) spectroscopy can be used to determine and quantify oxidation states using the position and intensity of pre-edge features. Due to the possibility of redox reactions on quenching to a glass, oxidation states are best determined at elevated temperatures. An X-ray absorption spectroscopy furnace has been designed and constructed allowing the acquisition of in situ XANES spectra at temperatures up to 1700 K. The oxygen fugacity inside the furnace can be defined by a variable CO/CO<sub>2</sub> atmosphere using mass-flow controllers. Spectra were recorded in fluorescence mode at the Australian National Beamline Facility, Photon Factory, Japan.

High temperature Cr K-edge spectra for a MORB composition indicate that over 50% of the Cr exists as Cr<sup>2+</sup> in the melt although only Cr<sup>3+</sup> can be detected in a quenched glass. This is evidence for the oxidation of Cr<sup>2+</sup> to Cr<sup>3+</sup> in the presence of Fe<sup>3+</sup> on cooling according to the

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<sup>1</sup> ANSTO

reaction  $\text{Cr}^{2+} + \text{Fe}^{3+} \rightarrow \text{Cr}^{3+} + \text{Fe}^{2+}$ . This Cr/Fe redox interaction may explain why all Cr occurs as  $\text{Cr}^{3+}$  in terrestrial basalts (which contain  $\text{Fe}^{3+}/\text{Fe}^{2+}$ ) even though  $\text{Cr}^{2+}$  occurs in synthetic Fe-free systems at typical terrestrial oxygen fugacities.

Work is also underway to determine the oxidation state of W and V in silicate melts as a function of oxygen fugacity.

### ***The mechanism and site of water incorporation in nominally anhydrous mantle minerals***

*A.J. Berry, H.St.C. O'Neill, J. Hermann, S.E. Ashbrook<sup>2</sup>, S. Wimperis<sup>2</sup> and M. James<sup>1</sup>*

The amount of structurally bound water identified in nominally anhydrous minerals of mantle origin is thought to be sufficient to accommodate the entire mantle water budget. The values obtained from natural samples assume that the water content does not change during exhumation to the surface, or at least represents a lower limit. Samples of olivine grown or equilibrated in piston cylinder experiments under enstatite-buffered conditions at upper mantle pressures and temperatures are characterised by infrared spectra of a type which are rarely observed in nature. Instead the spectra for most natural samples closely resemble those produced experimentally under magnesiowüstite buffering. This suggests that water occupies a Si vacancy in mantle olivine despite forming under conditions of high silica activity.

It is possible to create a Si vacancy under mantle conditions if the Si site was initially occupied by a different cation that exsolves at a later time. Ti is expected to occupy a Mg site in olivine, similar to the substitution in clinohumite. However, we have demonstrated by Ti K-edge X-ray absorption spectroscopy (XANES) that Ti is tetrahedrally coordinated.  $\text{TiO}_2$  has significant solubility in olivine at 1400°C and there is evidence of exsolved ilmenite in some mantle samples. Ti exsolution to produce a vacancy on a Si site probably develops much later, in the lower-temperature environment of the earth's crust. Therefore, water occupying a Si vacancy does not necessarily correspond to the water incorporated in the sample during formation in the mantle. Estimates of the mantle water content based on the analysis of natural samples should be viewed with caution.

A clinohumite-like defect may be viewed as a linear array of Si vacancies and is a possible model for the site of water incorporation in the olivine structure. To determine the position of hydrogen atoms in hydroxyl-clinohumite the structure was refined using powder neutron diffraction data. The H atoms of the hydroxyl groups were found to be disordered over two positions with an occupancy of approximately 0.5. This removes the possibility of a strong H-H interaction that was thought to destabilise the structure and also favours the presence of this defect in nature since coupled incorporation of Ti or F is not required. The limited occurrence of natural hydroxyl-clinohumite is the result of compositional rather than crystal chemical constraints.

Hydroxyl-clinohumite and hydroxyl-chondrodite have also been studied by  $^{17}\text{O}$  multiple-quantum (MQ) magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy. Complete assignments of the five crystallographically inequivalent oxygen sites in chondrodite and of the nine such sites in clinohumite have been made. The  $^{17}\text{O}$  resonances of the protonated sites were recorded and assigned with the aid of  $^{17}\text{O}$ - $^1\text{H}$  cross-polarisation experiments and comparison with the spectrum of  $^{17}\text{O}$  enriched brucite. It is hoped that the present work will serve as a model for future NMR studies of nominally anhydrous minerals.

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***The 1994 - 2000 Rabaul Caldera eruption: tracking the evolution of a basaltic injection within a shallow dacitic magma reservoir***

*S. Eggins, H. Patia<sup>3</sup> and C. Mckee<sup>3</sup>*

The current eruption at Rabaul Caldera, Papua New Guinea, commenced in September 1994 with eruption from both Vulcan and Tavurvur volcanoes on opposing sides of the caldera. Compositionally and mineralogically identical dacite magmas (~1.8wt% MgO, 63–64wt% SiO<sub>2</sub>) were erupted from both vents during the initial eruptive activity, as well as more primitive andesites from Tavurvur which show evidence of dacite hybridisation with a more primitive and mineralogically distinct (calcic plagioclase, magnesian olivine and clinopyroxene-bearing) basaltic magma. The initial activity waned and ceased by April 1995, but recommenced after a 6 month repose at Tavurvur in late 1995 and has continued intermittently until the present. Magma erupted in this second phase of activity extends the observed compositional trend along a tight linear compositional array from Phase 1 dacite to mafic andesite (4.6wt% MgO, 55wt% SiO<sub>2</sub>), projecting toward a mafic phenocryst-rich basalt composition with ~10wt% MgO. The end-member dacite magma is similar to that erupted at Rabaul in 1878 but less evolved than that erupted in 1937–43.

The eruption of identical dacite magma from opposite sides of the caldera in the current and in previous historic eruptions indicates these dacites likely derive from a single voluminous, caldera-wide magma reservoir. This is consistent with the results of recent seismic tomographic imaging (RELACS experiment; O. Gudmussun, pers comm, 2000), which point to the existence of a shallow (2.5–5 km depth) magma sheet with lateral dimensions similar to the seismically active caldera structure (ie 6–8 km diameter). Water contents (~2wt%) in dacitic melt inclusions measured by others show the dacite magma was probably volatile-saturated at 50MPa which is in agreement with the shallow depth to the low velocity anomaly identified in the RELACS experiment.

The combined observations of hybridisation with basaltic magma and the moderately large SO<sub>2</sub> flux at Tavurvur (~500 ktons during Phase 1; TOMS and COSPEC data reported by Roggensack) but not Vulcan, indicate the probable confinement of a mafic magma injection to the northeastern sector of the active caldera. The volume of injected mafic magma is estimated at 0.05 and 0.1 km<sup>3</sup> based on the uniformly high S concentrations (1800 ppm) present in basaltic glass melt inclusions and the SO<sub>2</sub> yield to the atmosphere measured during Phase 1 activity. The interspersed eruption of end-member dacite and hybridised magma during the Phase 2 activity points to the prevalence of two separate yet proximal magmas over a period of 6 years. These observations appear to provide important constraints on the progress of cooling and evolution (crystallisation, volatile exsolution from, and hybridisation) of basaltic magma layer ponded beneath a large silicic magma reservoir.

***Nature and extent of compositional heterogeneity in NIST6010-617series glasses***

*S. Eggins and M. Shelley*

The NIST 610617 glasses fulfil an essential though originally unintended role as reference materials for trace element microanalysis, and their use in this capacity is set to grow further as new techniques, particularly laser ablation ICP-MS/AES (inductively coupled plasma-mass spectrometry/atomic emission spectroscopy) become more widely available. However, they are yet to be demonstrated fit for this purpose. Accordingly, we have undertaken an exhaustive compositional profiling and mapping study using a moderate resolution (30–50µm) laser ablation rastering technique. This has revealed the presence of extensive chemical heterogeneity within all (more than 30) NIST glass wafers examined to date. Each NIST glass wafer invariably contain domains with moderate to large depletions of Tl, Au, As and Se, that are associated with lesser but still significant depletions of B, Re, Te, W, Pb, Bi, Cd, Ag, Sb and

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Mo. These domains characteristically occur at the wafer margins but also extend into and can occur wholly within wafer interiors, and are readily observed using conventional microscopic techniques and by unaided visual inspection of polished wafers. They often form stretched planar structures as well as complex three dimensional folded structures that appear to be entrained from the wafer perimeters, most likely as a consequence of drawing a stiffer surface layer during cane production.

The chemical and optical properties of the depleted domains are consistent with the development of compositional cords, a common and usually unavoidable phenomenon in glass manufacture, that takes place due to volatilisation from and modification of the glass composition at the melt-atmosphere interface. The lack of accompanying depletion of refractory oxide forming elements indicates these depletions cannot be attributed to imperfect mixing of glass batch constituents, or with possible glass residues leftover from preparation of preceding glass batches. The association of element depletions with wafer perimeters, and observed antithetic enrichments of Pt and Cu in some cases, provide evidence of volatile element loss and Pt gain occurring from a boundary layer. Our findings diminish the consensus that has been formed by many previous studies that element distributions in the NIST glasses are reliably homogeneous apart from a handful of exceptions (ie F, B, Li and Br). Caution is necessary with the application of NIST glasses as reference materials for the analysis of siderophile and certain volatile elements, and the possibility of bulk compositional variation of wafers along the 200 m cane length formed from each NIST glass composition.

### ***Melt retention and segregation beneath mid-ocean ridges***

#### *U. Faul*

The amount of melt present (porosity) in partially molten regions of the upper mantle has wide ranging consequences for both the dynamics of mantle flow and the chemistry of erupted basalts. Geochemical models, in particular uranium decay series isotope models require very low porosities (of order of 0.1%) and in some cases also rapid ascent of these small amounts of melt. Seismic studies on the other hand indicate the presence of melt at the percent level. Figure 1 shows calculated maximum porosities at the top of a one-dimensional melting column for a range of permeability models and measurements on texturally equilibrated rocks. With measured permeabilities the porosity always exceeds 1%, near perfect fractional melting with porosities of order 0.1% is therefore not possible.

The contrasting constraints from seismology and geochemistry can be reconciled when the geometry of the melt inclusions in partially molten dunite and the changing character of the ascending melt are taken into account. Observation of ubiquitous H<sub>2</sub>O and CO<sub>2</sub> in mid-ocean ridge basalts points to the presence of a volatile-rich melt at depth below the onset of major element melting. This volatile-rich melt will have low viscosity and density and will therefore be mobile at porosities of order of 0.1%. Due to the two orders of magnitude higher viscosity of basaltic melt, rapid segregation can only continue after a threshold porosity of 1-2% is reached after the onset of major element melting. Uranium series disequilibria of isotopes with long half-lives (thorium, protactinium) can be preserved by fast melt transport above the anhydrous peridotite solidus, but Radium has such a short half-life (~1600 years) that excesses can not be generated by mantle melting. Association of the highest measured radium excesses with high chlorine contents, either in MORBs from the same ridge segment or the same sample (where data is available), suggests a possible role of brines from deep hydrothermal circulation in the shallowest parts of the mantle in generating the observed excesses.

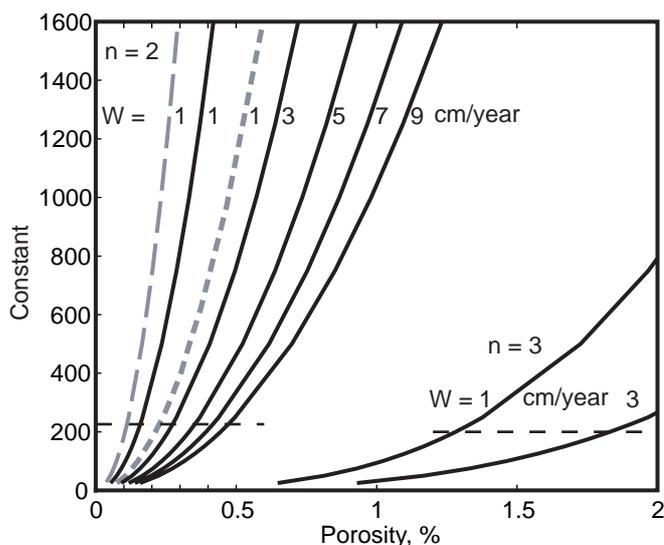


Figure 1: Porosity versus constant  $C$  in the permeability ( $k$ ) – porosity ( $\phi$ ) relationship  $k=d^2 \phi^n / C$  for  $n = 2$  and  $3$  and a range of solid upwelling velocities and a grain size  $d$  of  $1$  mm. Porosities are maximum porosities at the top of a melting column with a total extend of melting of  $15\%$  (solid lines)  $7.5\%$  (long dashes) and  $30\%$  (short dashes), melt viscosity of  $1$  Pas and a density difference between melt and matrix of  $500\text{kg/m}^3$ . The constants calculated for cylinders on a cubic grid ( $C = 226$ ) and obtained from permeability measurements ( $C = 200$ ) are indicated by horizontal dashed lines. The isotropic model of the melt distribution ( $C = 1600$ , upper limit of the Figure) yields porosities  $\geq 0.3\%$  even for slow upwelling and low total melt production.

### ***Nd and Sr Isotope Geochemistry of the Antrim Plateau continental flood basalts***

*L.M. Hanley and V.C. Bennett*

The Cambrian Antrim Plateau Volcanics and stratigraphic equivalents are exposed over an extensive area ( $\sim 1700$  km by  $>900$  km) of northern Australia. They dominantly comprise continental flood basalts which have trace element signatures similar to continental crust. Although their geographical extent is large, their major and trace element compositions are indistinguishable across the entire province. This requires either that the source of the tholeiites was enriched in crustal components as postulated for the Tasmanian dolerites (Hergt *et al.*, 1989, *Journal of Petrology*, **30**, 841–883), or the magmas were contaminated with continental crustal material en route to the surface. To investigate these possibilities, representative samples of Antrim basalts were selected for Rb-Sr and Sm-Nd isotopic analyses. Samples were chosen to explore isotopic variation across the geographical extent of the province and temporal variation through the use of multiple samples from a single stratigraphic sequence. To eliminate the effects of alteration, acid-washed clinopyroxene separates were prepared for all samples. The samples were analysed using isotope dilution methods, and measurements were performed on the Finnigan MAT-261 multiple collector mass spectrometer.

Isotopic data have been age-corrected to  $513$  Ma, the inferred eruption age of the basalts. Initial  $^{87}\text{Sr}/^{86}\text{Sr}$  values (Figure 2) have a restricted range between  $0.707$  to  $0.710$  with the exception of one slightly more radiogenic sample, which plots at  $0.711$ .

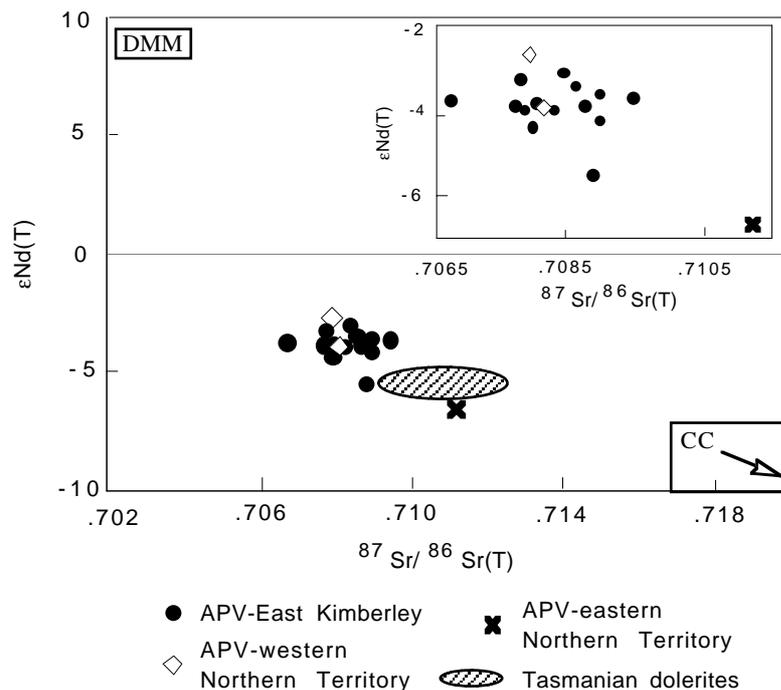


Figure 2: Initial Nd vs Sr isotopic variation diagram for the Antrim Plateau Volcanics (T=513 Ma). DMM = Cambrian Depleted MORB Mantle. CC = Proterozoic Continental Crust. The inset shows the data on an expanded scale. Data for the Tasmanian dolerites from Hergt *et al.* (1989).

Values of  $\epsilon_{Nd}(T=513 \text{ Ma})$  range from -2.5 to -6.5, but cluster in a narrow range between -2.5 and -4.5. As with the Tasmanian dolerites, this isotopic signature is considerably removed from depleted MORB mantle ( $\epsilon_{Nd}=+9$  age corrected for 513 Ma) and shows a strong crustal influence. The sample with the most extreme isotopic composition (from the eastern Northern Territory) is geographically the most removed from the others, which are ~1000 km to the west, and perhaps reflects contamination of crustal material of different isotopic composition.

Within the province, isotopic composition is not correlated with major element variability or with indices of fractionation as is shown in Figure 3 where the initial Sr isotopic composition is near constant over a range of molar[ $100 \cdot \text{Mg}/(\text{Mg}+\text{Fe}^{2+})$ ] for  $\text{Fe}_2\text{O}_3/\text{FeO}=0.15$ . This requires at least a two stage process to account for both the isotopic and geochemical characteristics of the Antrim basalts, with the isotopic compositions largely acquired before final magmatic differentiation.

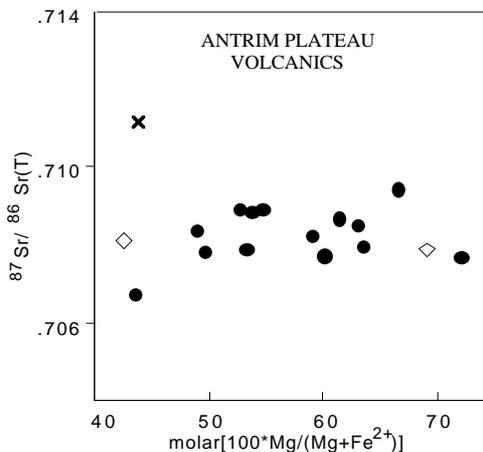


Figure 3: Initial  $^{87}\text{Sr}/^{86}\text{Sr}$  (T=513Ma) vs molar[ $100 \cdot \text{Mg}/(\text{Mg}+\text{Fe}^{2+})$ ]. Symbols as for Figure 2.

In addition, nine isotopic analyses obtained for a stratigraphic section through successive basalt flows in the Kimberley region (Figure 4) show no correlation with molar[ $100 \cdot \text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ ] or other geochemical indicators of crustal contamination, which would be expected if assimilation of crust was concurrent with fractional crystallization. For the major part of the sequence,  $\epsilon_{\text{Nd}}$  of the basalts lie within 1.5 epsilon units, although, the top-most sample is markedly less radiogenic with  $\epsilon_{\text{Nd}} = -5.5$ .

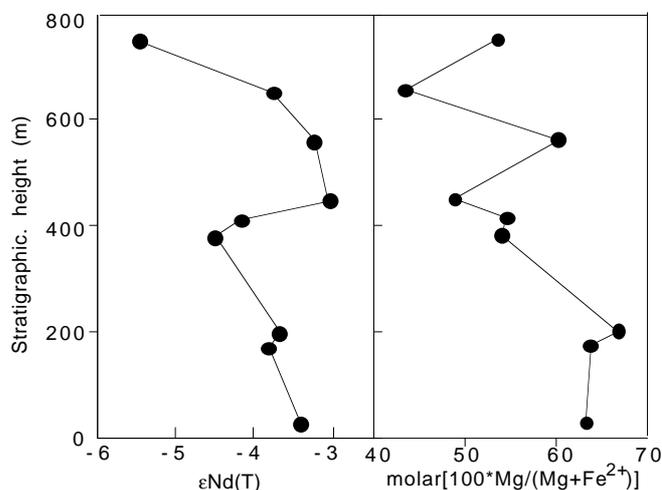


Figure 4: Stratigraphic height for an ~800 m section through the East Kimberley Antrim Sequence vs  $\epsilon_{\text{Nd}}$  and molar[ $100 \cdot \text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ ] demonstrating the lack of a simple relationship between isotopic and chemical composition.

It is possible, however, that assimilation of crustal material operated early in the genesis of the basalts, at a time when they possessed greater than 9wt% MgO. These processes could have taken place in deep-seated magma chambers where picritic magmas assimilated lower-crustal wall rocks. Subsequent fractionation in upper-crustal magma chambers would have been unaccompanied by significant bulk assimilation. However, a large degree of assimilation is required if a partial melt from a depleted mantle source is mixed with lower crustal material. The alternative is that the source region of the basalts was enriched with crustal material. Oxygen isotope studies are currently under way to distinguish these possibilities.

### ***Experimental constraints on high pressure melting in subducted crust***

*J. Hermann and D.H. Green*

Synthesis piston cylinder experiments were carried out from 2.0 to 4.5 GPa and 850 to 1150°C in a synthetic system consisting of  $\text{K}_2\text{O}-\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  (KCMASH) plus a selected set of trace elements to determine phase and melting relations in a model composition for subducted crust. As subduction zone magmas are enriched in water and large ion lithophile elements (LILE), the study has been concentrated on the stability of phases that host these elements. Biotite and phengite were found to be the stable phases able to transport water and LILE to mantle depth. At pressures below 3.0 GPa biotite is stable to higher temperatures than phengite and melting related to biotite breakdown occurs at about 900°C. At higher pressure, only phengite melting occurs along the reaction phengite + clinopyroxene + coesite  $\rightarrow$  garnet + kyanite + melt  $\pm$  K-feldspar, which has a positive slope to 1030°C, 4.5 GPa. Biotite reacts to phengite in subsolidus conditions with the preservation of LILE and water stored in the rock. The stability of phengite to high pressures and temperatures prevents liberation of LILE and water by “fluid absent” melting in subduction zones with a normal thermal gradient. It is suggested that these elements are probably released by melting in the presence of fluids, which derive from dehydration of the mafic or ultramafic layer of the slab. The experiments demonstrate that melts produced by mica melting or by addition of small amounts of water at

lower temperatures are granitic in composition and display an increase of K<sub>2</sub>O with increasing temperature. Determination of trace element partitioning between melt and residue indicates that the heavy rare earth elements (HREE) will be incorporated in garnet and strongly enriched in the residue in rocks having more than 10% garnet, whereas the LILE preferentially enter the melt even if there is phengite in the residue. The light rare earth elements (LREE) are not significantly enriched in the granitic melts because of small amounts of LREE-rich allanite in the residue.

The observed increase of K<sub>2</sub>O and decrease of water content in the melt with increasing temperature suggests that the extraction of K is more efficient at greater depth of subduction. The H<sub>2</sub>O/K<sub>2</sub>O ratio of hydrous granitic melts is significantly higher than the H<sub>2</sub>O/K<sub>2</sub>O of phlogopite and therefore it is unlikely that the entire granitic melt reacts and crystallizes with peridotites if conditions in the mantle wedge are outside the stability fields of talc, serpentine and chlorite. Consequently, it is possible that at least parts of the released water and trace elements from the subducted crust may remain mobile in the fluid phase and may reach the locus of subduction zone magma genesis.

***Age and exhumation rate of diamondiferous, deeply subducted continental crust (Kokchetav Massif, Kazakhstan)***

*J. Hermann, D. Rubatto, A. Korsakov<sup>4</sup> and V.S. Shatsky<sup>4</sup>*

Diamondiferous rocks from the Kokchetav Massif, Kazakhstan, represent deeply subducted continental crust. In order to constrain the age of ultra-high pressure (UHP) metamorphism and subsequent retrogression during exhumation, zircons from diamondiferous gneisses and metacarbonates have been investigated by a combined petrologic and isotopic study. Four different intracrystalline domains were identified within a population of zircon crystals, on the basis of transmitted light microscopy, cathodoluminescence, trace element contents and mineral inclusions. Mineral inclusions and trace element characteristics of the zircon domains relate zircon growth to metamorphic conditions. Domain 1 consists of rounded cores and lacks evidence of UHP metamorphism. Domain 2 contains diamond, coesite, omphacite and titanian phengite inclusions providing evidence that it formed at UHP metamorphic conditions (P>4.3 GPa; T~950°C). Domain 3 is characterized by low-pressure mineral inclusions such as garnet, biotite and plagioclase which are common minerals in the granulite-facies overprint of the gneisses (P~1 GPa; T~800°C). Domain 4 forms idiomorphic overgrowths and the rare earth element pattern indicates that it formed without coexisting garnet, most probably at amphibolite-facies conditions (P~0.5 GPa; T~600°C). The metamorphic zircon domains were dated by SHRIMP ion microprobe and yielded ages of 527±5 Ma, 528±8 Ma and 526±5 Ma for domains 2, 3 and 4 respectively. These indistinguishable ages provide evidence for a fast exhumation beyond the resolution of SHRIMP dating. The mean age of all zircons formed between UHP metamorphic conditions and granulite-facies metamorphism is 528±3 Ma indicating that decompression took place in less than 6 Ma. Hence, the deeply subducted continental crust was exhumed from mantle depth to the base of the crust at rates higher than 1.8 cm/year.

The recognition of multistage zircon growth during retrograde metamorphic evolution indicates that the often used assumption of zircon ages representing peak metamorphic conditions must be proven by petrology and/or trace element geochemistry. We suggest that two main processes are responsible for retrograde zircon growth: a) cooling of Zr-saturated partial melts from UHP to granulite/upper amphibolite facies and b) decomposition of Zr-bearing phases such as garnet at lower amphibolite-facies conditions.

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*The effect of Cr<sub>2</sub>O<sub>3</sub> on partial melting relations in the model mantle system CMAS-Cr<sub>2</sub>O<sub>3</sub>*

X. Liu and H.StC. O'Neill

The chromium (Cr) abundance in natural spinel lherzolites and garnet lherzolites from the Earth's mantle is on average about 2600 ppm, which is sufficient to exert considerable effect on both the melting relations and the subsolidus phase relations of the mantle. However, because chromium is a highly compatible element it mostly remains in the residue during partial melting and its importance to melting phase relations may not be obvious from the study of the melts themselves. While previous work in this laboratory and elsewhere has documented quantitatively the effect of Cr on subsolidus phase relations such as the spinel-to-garnet transition in the upper mantle and the solubility of alumina in orthopyroxene, no such systematic work has been done on the effect of Cr on melting equilibria. Therefore, in order to understand fully the effect of chromium on the partial melting process of the upper mantle, experiments have been carried out in system CMASCr (CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-Cr<sub>2</sub>O<sub>3</sub>) at a pressure of 1.1 GPa. The initial strategy is to characterise the composition of partial melts in equilibrium with the spinel lherzolite assemblage as a function of Cr/(Cr+Al) ratio.

Experiments were carried out using starting materials of synthetic olivine (ol), orthopyroxene (opx), clinopyroxene (cpx) and spinel (sp) of appropriate composition, synthesised from oxide mixes at subsolidus conditions. In an attempt to ensure that most Cr in the melt was Cr<sup>3+</sup> and not Cr<sup>2+</sup>, ReO<sub>2</sub> was added to try to buffer conditions at the Re-ReO<sub>2</sub> oxygen buffer. Unfortunately ReO<sub>2</sub> was completely reduced to Re in all experiments, indicating buffer exhaustion.

Experimental work so far has revealed a number of experimental problems, which have prevented accurate determination of melt compositions. In particular, the melt composition becomes increasingly picritic with increasing Cr/(Cr+Al) ratio, producing melts that do not quench to glasses but instead undergo much modification due to quench crystallization. Nevertheless, the following preliminary results have been obtained:

- 1) Cr in opx decreases the amount of Al<sub>2</sub>O<sub>3</sub> in both opx and cpx relative to the same pressure and temperature conditions in the system CMAS. Clinopyroxene contains not only more Cr<sub>2</sub>O<sub>3</sub> but also more Al<sub>2</sub>O<sub>3</sub> than opx. The pattern of Cr<sub>2</sub>O<sub>3</sub> distribution between cpx and opx (more Cr<sub>2</sub>O<sub>3</sub> in cpx than in opx) is not apparently related to pressure. However, pressure has a strong effect on the distribution of Al<sub>2</sub>O<sub>3</sub> between clinopyroxene and orthopyroxene: As the pressure increases, the amount of Al<sub>2</sub>O<sub>3</sub> in opx gradually approaches and finally overtakes that in cpx.
- 2) Surprisingly, the introduction of Cr<sub>2</sub>O<sub>3</sub> to the system CMAS only increases the solidus temperature slightly. For compositions with <12 wt% bulk Cr<sub>2</sub>O<sub>3</sub>, an increase in solidus temperature of 10 to 20°C is observed.
- 3) Although partial melting of spinel lherzolite in the system CMASCr at 1.1 GPa should be divariant, in practice the temperature interval over which five phases (ol+opx+cpx+sp+melt) co-exist in our compositions is so small that the melting reaction appears univariant and clinopyroxene ( $\pm$  opx) is lost immediately above the solidus. This property adds immensely to the difficulty of obtaining melt compositions in equilibrium with the four solid phases.
- 4) Partial melting along the solidus of the system CMAS takes place according to melting reaction cpx+opx+sp = ol+melt, but the melting reaction along the solidus of the system CMASCr becomes cpx+opx = ol+sp+melt. Thus spinel as well as olivine is in reaction relationship with the melt.
- 5) The compositions of the melt show a systematic variation with the bulk Cr<sub>2</sub>O<sub>3</sub> abundances. As the bulk Cr<sub>2</sub>O<sub>3</sub> abundance increases, Al<sub>2</sub>O<sub>3</sub> in melts decrease while SiO<sub>2</sub> and MgO increase.

Future work will focus on using the sandwich experimental technique to enable more accurate determination of melt compositions by providing large areas of glass plus quench crystals for analysis. The problem of achieving the five-phase assemblage of ol+sp+opx+cpx+melt will be addressed by adding small amounts of K<sub>2</sub>O to the system to ensure true divariant behaviour, and extrapolating results as a function of K<sub>2</sub>O to zero K<sub>2</sub>O.

***Detrital zircon ages from the diamondiferous Tombador conglomerate***

*C.W. Magee, J.M. Palin and W.R. Taylor*

The Tombador conglomerate, a unit of the middle Proterozoic Espinhaço supergroup in Bahia state, Brazil, is believed to be the source for alluvial deposits of diamonds in the Chapada Diamantina region. These diamond deposits form one of the two regions where carbonado diamond is found. Detrital zircons from the Rio Cachorrinho, a small mountain stream, the drainage of which lies entirely within the Tombador conglomerate, were dated by laser ablation ICP-MS. Detrital grains were used because the large clast size (>25 cm) of the conglomerate makes processing a representative sample of the conglomerate difficult, and because transport in the Rio Cachorrinho should preferentially destroy metamict zircons. Previous studies of zircons extracted from the Tombador formation have shown that metamictization is a serious problem among detrital zircons found in these conglomerates and quartzites.

Forty-five of the 50 zircons dated had concordant U-Pb ages, and these ages correspond with the major tectonic events in the São Francisco craton. The oldest seven grains crystallized between 3250 and 3600 Ma. This is the age range of the oldest Archaean cratonic fragments found in the São Francisco craton. These cratonic fragments amalgamated to form the São Francisco craton at the end of the Archaean and 15 of the sedimentary zircons formed between 2400 and 2850 Ma, the age associated with this late Archaean continent-forming event. The youngest, and most prevalent zircon population crystallized between 2050 and 2250 Ma. The age of these 23 zircons corresponds with the Trans-Amazonian orogeny, a major tectonothermal event in the São Francisco and Amazonian cratons. Because all zircons were older than underlying 1.8 Ga metavolcanic and metasedimentary rocks, no additional age constraints can be made for the time of deposition.

A survey of diamond indicator minerals in heavy mineral separates from the Rio Cachorrinho revealed one rutile with >1% Cr<sub>2</sub>O<sub>3</sub> and 0.4% Nb. Because most rutile-bearing crustal rocks are low in chromium, and rutiles with >0.7% Cr<sub>2</sub>O<sub>3</sub> have not been reported from crustal rocks, this grain probably originated in the mantle. A tentative age of 2950 ±30 Ma has been obtained for this grain. If this age represents cooling below the rutile closure temperature caused by removal from the mantle, then mantle minerals, possibly including diamond, were emplaced as xenocrysts in mantle-derived magmas in the early Archaean core of the São Francisco craton during a time of apparent crustal magmatic quiescence. This is best explained by the anorogenic eruption of kimberlite or lamproite magma. These types of magmas have been erupting in cratonic settings throughout the last 1200 million years, and are responsible for most diamond deposits.

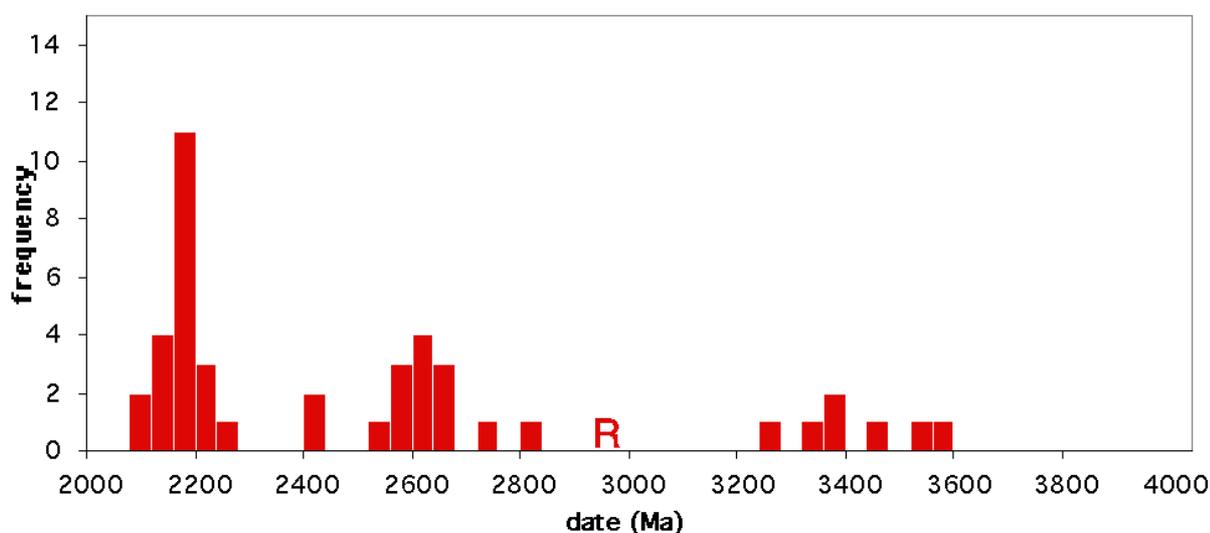


Figure 5: An age-frequency diagram for zircons from the Rio Cachorrinho, Bahia state, Brazil. R is the tentative age of a chromium-rich rutile that is probably derived from the mantle.

### ***Experimental and geochemical constraints on origin of corundum in aluminous mafic compositions: applications to evolution history of the Horoman Peridotite Complex, Japan***

*T. Morishita<sup>5</sup>, S. Arai<sup>6</sup> and D.H. Green*

High pressure experiments have been carried out at 1–4.5 GPa, 1100–1400°C, on an aluminous mafic composition, which has the same in major element composition as corundum-bearing mafic rocks in the Horoman Peridotite Complex, Japan. Trace elements (Rb, Sr, Ba, Y, Zr, La, Ce, Nd, Sm, Eu, Gd, and Yb) were added at about 200 ppm level. Corundum has been observed both in supersolidus and subsolidus conditions at pressure between 2 to 3 GPa. Kyanite has been observed at >2.4 GPa. Two possibilities can be considered for the genesis of corundum: 1) as a residue from partial melting; or 2) metamorphism of an aluminous mafic protolith. Experimental results suggest that corundum-bearing mafic rocks in the Horoman complex were derived from >2 GPa, eg upper mantle conditions, along with the surrounding peridotites.

Whole-rock trace element compositions of a corundum-bearing mafic rock and related rocks in the Horoman complex were determined by laser-ablation ICP-MS. Variations of trace element compositions among these rocks can be explained by modal variations of plagioclase, clinopyroxene and olivine, indicating that they formed as gabbroic to peridotitic rocks at low-pressure conditions, and the corundum-bearing rock was derived from plagioclase-rich variety of them. These rocks show no evidence for partial melting after they formed as low-pressure cumulates. Mineral coronas around corundum show that corundum became unstable during the later P-T conditions experienced by the Horoman peridotite, which are those of high temperature diapirism. The geochemical evidence for low pressure protoliths combined with the petrological evidence for high pressure metamorphism at >2 GPa, but without partial melting, define the early history of the Horoman complex. Corundum was formed by metamorphism of a plagioclase-rich protolith probably due to subduction at low temperature, followed by re-heating in the upper mantle. The Horoman complex is an example of a large peridotite body containing possible remnants of subducted lithosphere which still retain their original compositions without major chemical modifications during subduction, reheating and exhumation.

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***High-pressure mafic rocks with low-pressure geochemical signature in the Ronda peridotite, Spain: “closed-system recycling of crustal materials”***

*T. Morishita<sup>5</sup>, S. Arai<sup>6</sup>, F. Gervilla<sup>7</sup> and D.H. Green*

Trace element compositions of aluminous mafic rocks ( $\pm$  corundum and/or sapphirine) alternating with peridotite from the Ronda peridotite massif, Southern Spain, were determined by laser ablation ICP-MS. On the basis of geochemistry, the rocks were originally crustal accumulates of plagioclase, clinopyroxene and olivine. On the other hand, their petrographical characteristics show a decompression history from high-pressure condition ( $P > 1.5$  GPa). This suggests a complex evolutionary history, including higher-pressure recrystallization after initial formation as gabbros at lower-pressure conditions. Furthermore, high contents of highly incompatible elements in the rocks suggest that they never experienced partial melting after their formation as low-pressure cumulates. The aluminous mafic rocks and their hosts are inferred to be recycled crustal materials now observed as cm-scale layered components in alpine-type peridotite. The rocks retain their original compositions without melting or other metasomatic modifications during subduction, intense deformation within the upper mantle and upwelling again to the surface.

***Trace element compositions of garnets and clinopyroxenes in corundum- and sapphirine-bearing aluminous mafic rocks from the Ronda massif, Spain***

*T. Morishita<sup>5</sup>, S. Arai<sup>6</sup>, F. Gervilla<sup>7</sup> and D.H. Green*

Trace element compositions of garnets and clinopyroxenes in aluminous mafic rocks alternating with peridotites from the Ronda massif, Spain, which sometimes contain corundum and/or sapphirine, were determined by laser ablation ICP-MS. In the sapphirine- and corundum-bearing rocks, primitive mantle-normalized pattern of garnets has positive anomaly of Eu, and that of clinopyroxene has positive anomalies of Sr, and Eu and negative anomaly of Zr. Trace element compositions both of garnet and clinopyroxene were inferred to be inherited from former plagioclase, reflecting the bulk composition of the rock, suggesting that the protolith formed as plagioclase-rich mafic rock at low pressure condition (lower crustal to the uppermost mantle conditions). Although plagioclase is now present in the rock as a low pressure alteration of the high pressure assemblage, garnet and clinopyroxene retain their high pressure compositions and cannot be considered as having equilibrated with minerals formed in the later exhumation or upwelling of the Ronda peridotite.

***The solubility of rhenium in silicate melts: implications for the geochemical properties of rhenium at high temperatures***

*H.St.C. O'Neill, W. Ertel<sup>8</sup>, D.B. Dingwell<sup>8</sup> and P.J. Sylvester<sup>9</sup>*

The chondritic ratios of the highly siderophile elements (HSE's) in the Earth's mantle are usually taken to imply that these elements were accreted to the primordial Earth in a late component after the Earth's core had formed — the “late veneer” hypothesis. Re is assumed to be one of the HSE's but existing experimental metal/silicate partitioning data appear to indicate that its siderophile tendencies may not be as great as the Platinum Group Elements. This raises the question of whether Re is really a HSE.

Accordingly, the solubility of rhenium (Re) in a simplified synthetic basalt melt (anorthite-

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diopside eutectic composition) has been experimentally determined using the mechanically assisted equilibration technique at 1400°C, as a function of oxygen fugacity ( $10^{-12} < fO_2 \leq 10^{-7}$  bar), imposed by CO-CO<sub>2</sub> gas mixtures. Samples were analysed by laser-ablation inductively coupled plasma mass-spectrometry (LA-ICP-MS). This is a true microanalytical technique, which allows small-scale sample heterogeneity to be detected, while providing a limit of detection of 2 ppb Re. Time-resolved LA-ICP-MS spectra revealed the presence of sub-optically sized micronuggets of Re in all samples, which, because they are present at the 0.5 to 10 ppm level, dominate the true solubilities of Re ( $< 1$  ppm at the conditions of the experiment) in bulk analyses of the samples. Nevertheless, the micronuggets could be filtered out from the time-resolved spectra to reveal accurate values of the true Re solubility. A number of time series of samples were taken at constant  $fO_2$ , to demonstrate that the solubilities converge to a constant value. In addition, solubilities were measured after both increasing and decreasing the imposed oxygen fugacity.

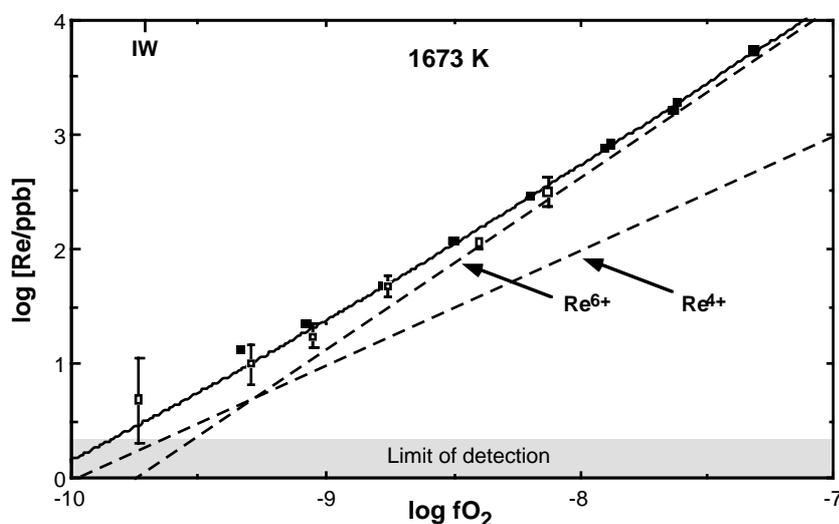


Figure 6: Re solubilities plotted versus  $\log fO_2$ . Closed squares are individual data, open squares are mean values from time series with observed standard deviations as error bars. The levels of  $Re^{4+}$  and  $Re^{6+}$  from the data fitting are plotted as dashed lines. The limit of detection (shaded area) is 2 ppb.

The results (Figure 6) show that Re dissolves in the silicate melt as  $ReO_2$  ( $Re^{4+}$ ) and  $ReO_3$  ( $Re^{6+}$ ) species, with the latter predominating at typical terrestrial upper-mantle oxygen fugacities. The total solubility of Re is described by the following expression ( $fO_2$  in bars):

$$[Re/ppb] = 9.7 (\pm 1.9) \times 10^9 (fO_2) + 4.2 (\pm 0.3) \times 10^{14} (fO_2)^{1.5}$$

Assuming an activity coefficient for Re in Fe-rich metal of 1, this gives a value of  $D_{Re}^{met/sil}$  of  $5 \times 10^{10}$  at  $\log fO_2 = IW-2$ , appropriate for metal-silicate partitioning in an homogeneously accreting Earth. Thus Re is indeed very highly siderophile, and the mantle's abundance cannot be explained by homogenous accretion.

### **Mathematical petrochemistry: two-pyroxene equilibria**

*S. Sommacal, M. Sambridge and H.StC. O'Neill*

A new thermodynamic model to describe phase equilibria between coexisting clinopyroxene and orthopyroxene as a function of composition, temperature and pressure has been developed. Initial application is to a simple four-component system (diopside, hedenbergite, ferrosilite, enstatite).

The Gibbs free energy principle states that a closed multi-phase system is at its equilibrium state if the temperature, pressure and chemical potential of each phase within the system are equal. Only under these conditions does the system's Gibbs free energy reach its minimum value. It follows, for the purpose of modelling, that it is essential to find appropriate expressions for the chemical potential of each system component. For complex solid solutions such as pyroxenes, we take the total free energy to be given by the sum of contributions from the Gibbs free energy of the end-members, ideal mixing on sites, the reciprocal solid solution effect, and excess site mixing terms. Hence the chemical potential ( $\mu_i$ ) of each component  $i$  is given by:

$$\mu_i = \left( \frac{\delta G(\text{tot})}{\delta n_i} \right) = \left( \frac{\delta G(\text{end - members})}{\delta n_i} \right) + \left( \frac{\delta G(\text{ideal})}{\delta n_i} \right) + \left( \frac{\delta G(\text{reciprocal})}{\delta n_i} \right) + \left( \frac{\delta G(\text{excess})}{\delta n_i} \right)$$

In order to solve the Gibbs free energy minimization problem a  $\chi^2$  measure method of data-fitting will be used. The need for this procedure, instead of a least-squares approach, comes from the non-linear nature of our data-fitting problem. This is a direct consequence of the error that systematically affects our input data resulting in  $\chi^2$  having a non-quadratic dependence on the unknowns. In order to find the best-fit values of these unknowns a conjugate gradient method (a non-linear optimization technique) will be used. In addition we also need to carry out an error propagation through to our calculated parameters. A program has now been written that enables the evaluation of all the expressions we need, with the next step being the solution to the data-fitting problem.

Future work will focus on applying the model to a more complex system with two coexisting pyroxenes (ie adding Mg, Ca, Fe-Tschermak components) and then extending it to more heterogeneous systems consisting of spinels, garnets, olivines, in addition to pyroxenes. This will provide the basis for a more comprehensive thermodynamic modelling tool for investigating phase/melting relationships in the Earth's mantle at high pressure and temperature.

### ***Geochemistry of mantle xenoliths and xenocrysts from the Skerring kimberlite pipe — evidence for lithosphere refertilization***

*W.R. Taylor and M. Richardson*

The Skerring kimberlite pipe is an elongate diatreme of ~800 Ma age located in the North Kimberley kimberlite province in far north Western Australia. The pipe lies at the north-east end of a lineament on which the diamondiferous Lower Bulgurri and Ashmore kimberlites also lie. The Skerring pipe, however, is non-diamondiferous and is one of a number of barren, picroilmenite-rich kimberlites that occur in a zone close to the north Kimberley coast. The Skerring pipe is noteworthy for its abundance of mantle-derived xenocrysts, principally picroilmenite and pyrope garnet. Other indicator minerals include Cr-spinel, Cr-diopside, zircon megacrysts, and megacrysts comprising graphic intergrowths of ilmenite + altered pyroxene.

During field-work in 1999, two large silicified peridotite xenoliths of ~25 x 50 cm size were collected from exploration pits. These are believed to be the largest mantle xenoliths ever recovered from a post-Tertiary age pipe in Australia. One of the xenoliths, SKX1, has an unusual corrosion-sculptured external surface texture that suggests the xenolith may have originally been carbonatized prior to silicification. Heavy mineral extraction of the xenoliths yielded Cr-spinel in one case (SKX1) and Cr-pyrope garnet, Cr-spinel  $\pm$  olivine inclusions in the other (SKX2). Secondary minerals include galena and chalcopyrite. In addition to the xenoliths, an array of xenocryst and megacryst minerals (garnet, diopside, picroilmenite) were sampled to constrain lithospheric composition.

Major element compositions were determined for over 200 garnet grains and laser-ablation ICPMS trace element analyses were undertaken on a sub-set of 40 grains. About 40% of the garnets are high-Ti, low-Cr (~3wt% Cr<sub>2</sub>O<sub>3</sub>) pyropes derived from fertile lherzolite. These garnets have 'normal' rare earth (REE) patterns with Dy ~20–30 chondritic levels, and Nd ~5,

and nickel geothermometer temperatures that fall within the range 1300 to 1500°C, suggesting deep mantle sampling. About 45% of garnets are low-Ti, high-Cr (~6–10 wt% Cr<sub>2</sub>O<sub>3</sub>) lherzolitic compositions with REE patterns showing variable Dy-depletion, Dy <10, and Nd enrichment, Nd ~2–30. The REE compositions define a trend between a strongly Dy-depleted harzburgitic garnet endmember (with pronounced “S-shaped” REE patterns) and the fertile high-Ti pyropes. Nickel temperatures fall within the range 900 to 1500°C indicating sampling along the full mantle stratigraphic column. There are smaller populations of harzburgitic garnets (>10% Cr<sub>2</sub>O<sub>3</sub>), high-Ti megacryst garnets and eclogitic garnets.

Chrome diopside recovered at Skerring is of restricted composition 100 Mg/(Mg+Fe<sup>2+</sup>) ~89, Ca/(Ca+Fe+Mg) ~0.32). Application of the Taylor and Nimis Cr-diopside thermobarometer yields P,T conditions of 50–55 kbar and ~1400°C compatible with the high-Ti lherzolitic pyrope. Chrome diopside associated with other lherzolitic garnets has not been recovered.

Garnet and Cr-spinel compositions from xenoliths SKX1 and SKX2 indicate that the rocks are garnet-spinel lherzolites. Thermobarometry yields P,T conditions of ~1230°C and ~38 kbar. Calculated redox conditions indicate relatively high fO<sub>2</sub>. Combined with P,T information from Cr-diopside, a ~48 mWm<sup>-2</sup> palaeogeotherm can be defined for the mantle beneath the Skerring pipe. Such a geotherm is greatly elevated over typical stable cratonic geotherms of near 40 mWm<sup>-2</sup> and indicates thermal disturbance of the lithosphere.

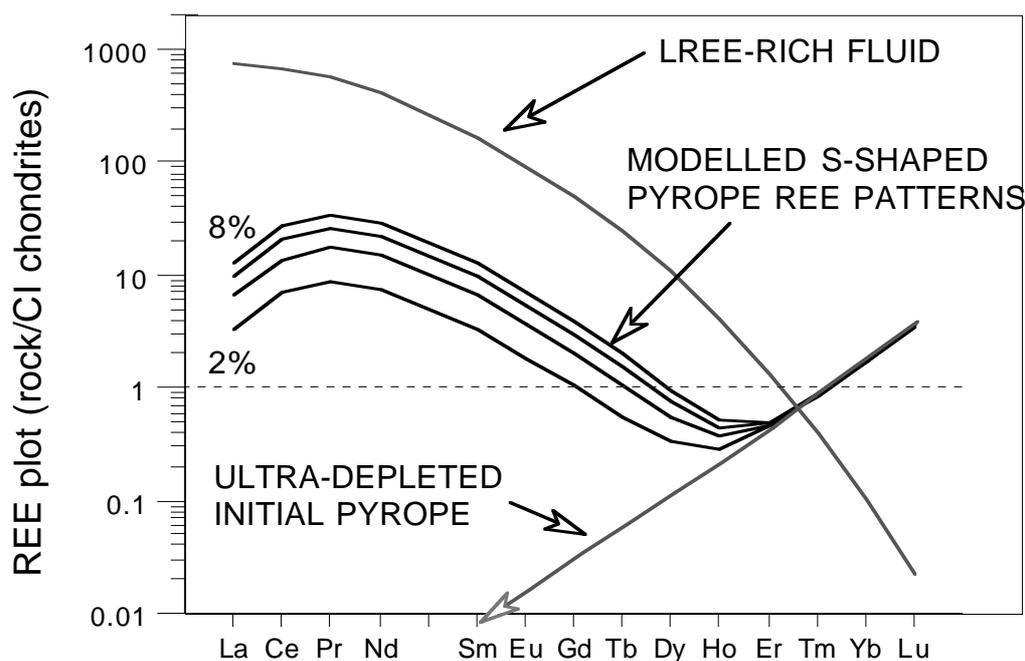


Figure 7a: Modelled REE patterns of Cr-pyrope garnet xenocrysts from the Skerring kimberlite. First stage. Generation of “S-shaped” (Nd-enriched, Dy-depleted) REE patterns can be modelled as the reaction products between a LREE-rich fluid phase and ultra-depleted harzburgitic pyrope.

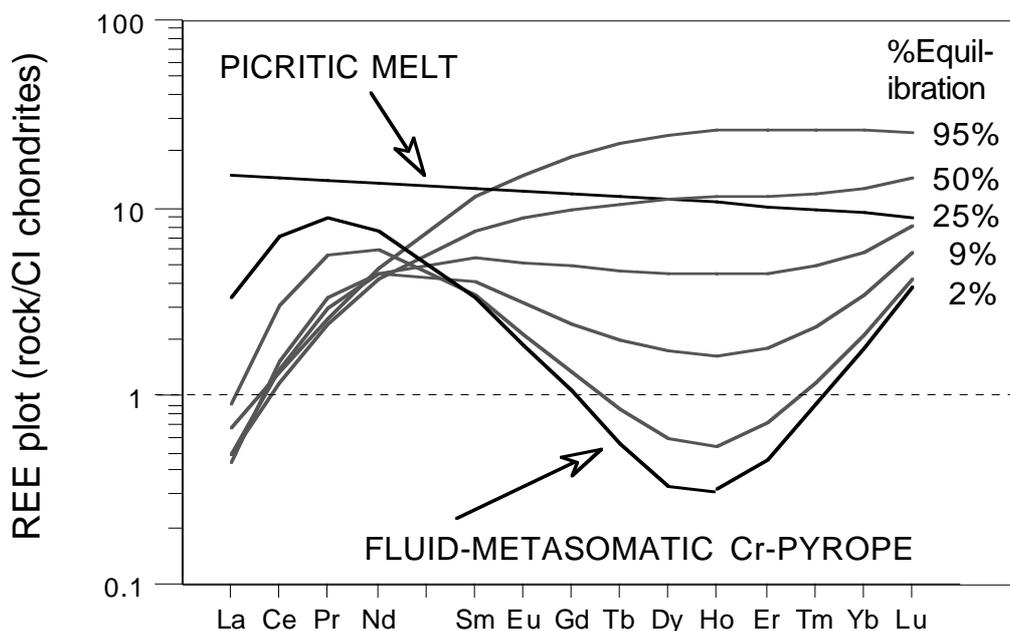


Figure 7b: Second stage. The range of pyrope REE patterns found for Skerring pyropes can be modelled as reaction products between a picritic, plume-derived magma and the fluid-metasomatic pyrope.

Xenocryst compositions and modelling of garnet and Cr-diopside REE patterns indicate that the lithosphere beneath Skerring was also chemically modified and a two-stage process is required to explain the observations. The lithosphere was probably originally composed of highly-depleted garnet harzburgite and Ti-poor lherzolite — the residues of extensive melt extraction. Cr-pyrope garnets acquired their unusual “S-shaped” (Dy-depleted, Nd enriched) REE patterns by a process of fluid metasomatism involving introduction of an LREE-rich fluid into the depleted lithosphere (Figure 7a). The fluid phase may also have caused diamond precipitation. Enrichment events of this kind are recorded in pyrope garnets from all the world's old cratonic regions where thick lithosphere exists.

At a later time, but because of thermal constraints at a time close to kimberlite eruption, the lithosphere was variably refertilized by a plume-derived, probably picritic magma which introduced Fe, Ti, Ca, incompatible trace elements, and heat. This resulted in conversion of harzburgite and Ti-poor lherzolite to Ti-rich lherzolite and to the formation of megacrystic microilmenite, garnet and zircon from crystallization of the fractionating plume-derived magma. REE patterns of xenocryst garnets and Cr-diopside record the refertilization event and this can be modelled by extensive degrees of alkalic picritic melt addition and re-equilibration (10–50 vol%) at the base of the lithosphere (Figure 7b).

A Re-Os isotope study of Cr-spinel from the xenoliths, which were formed in the refertilization event, confirm that the timing of this event was close to the eruption age of the kimberlite at 800 Ma (V. Bennett, pers. comm.). It is likely that any diamond present at this time was resorbed providing an explanation for the observed inverse correlation between microilmenite and diamond content in the North Kimberley province. The effects of the inferred mantle plume — possibly the tail of the ~825 Ma Gairdner plume which affected central and southern Australia — were restricted to the northern ‘microilmenite-rich zone’ of the province with diamondiferous lithosphere to the south, near the Ashmore pipe, being relatively unmodified, at least chemically, by this event.

