

PRISE

PRISE operates as a self-funded research group within the Research School of Earth Sciences, providing commercial and collaborative access to the Research School's specialised equipment and expertise in areas of geochronology, geochemistry and petrology. PRISE scientists also undertake their own research projects and supervise postgraduate students, both within the Research School and internationally.

All PRISE staff members are actively involved in wide-ranging collaborative research projects with academic colleagues throughout the world, as well as providing research and analytical skills to industry and Government agencies on a commercial basis. During 2008 PRISE hosted twenty-nine local and international visitors, most of whom undertook collaborative projects using the SHRIMP, Laser ablation- and solution ICPMS, electron microprobe and TIMS analytical facilities. PRISE staff also participated in a number of field-orientated studies in Australia, Africa, South America and Europe.

Some areas of current research include:

- > Investigations of the origins of pyroxenite bodies in peridotite massifs of the Western Gneiss Region, Norway (PhD student A. Rosenthal)
- > High pressure experimental investigations of kimberlite and carbonatite petrogenesis (PhD student K. Kiseeva)
- > Impactor fluxes in the inner solar system from the ages and compositions of lunar glasses (PhD student S. Hui)
- > Multi-isotopic and trace element zircon studies to constrain magmatic evolution of plate margins and continental reconstructions; combined U-Th-Pb, Lu-Hf, Ti geothermometry, trace and REE chemistry, and oxygen isotope studies.
- > Development of in situ sulphur isotope analytical protocols for the SHRIMP
- > Use of sulphur isotopes to aid in understanding the origin and conditions of formation of metal sulphides
- > Chronology of the Archaean-Proterozoic transition and the rise of oxygen in the atmosphere
- > Geological Connection between West Antarctica and Patagonia since the late Paleozoic: Tectonism, Paleogeography, Biogeography and Paleoclimate
- > Placing realistic constraints on the timing of world-wide Neoproterozoic glacial events: a critical examination of the "Snowball Earth" hypothesis
- > Bioarchaeology in early Cambodian populations and in situ oxygen and strontium analysis of human teeth
- > Development of new mineralogical tools for diamond exploration
- > Ages of granites and related mineralisation in NSW.
- > Origin and evolution of plume magmas and Hawaiian volcanoes.
- > Hydrochemistry of groundwater resources in the Sydney basin and Murrumbidgee Irrigation area of NSW.

Further developments in the *in situ* analysis of sulphur isotopes using SHRIMP II

Richard A. Armstrong, Peter Holden and Ian S. Williams

Research School of Earth Sciences, Australian National University, Canberra, ACT 0200, Australia

For several years the successful measurement of sulphur isotope ratios on the SHRIMP has been frustrated by the lack of suitable standards and the difficulty in producing reproducible, accurate and precise data through instrumental problems and idiosyncrasies. Establishing suitable standards is a difficult and time-consuming process, as internationally available material might be uniform on the bulk scales they were measured at, but might show some variation in composition at the 20 μm scale commonly measured on the SHRIMP. For analyses of sulphides, the early work by Eldridge et al. (1988, 1989) on SHRIMP I showed that matrix effects require the standards to be matched to the composition of the unknown sulphides. We have spent some considerable time in analysing available sulphide standards (e.g. those described by Crowe and Vaughan, 1996) and have managed to overcome many instrumental problems, enabling us to report consistent $d^{34}\text{S}/^{32}\text{S}$ isotope measurements with external precisions of $\sim 2\text{‰}$ in standards in a variety of sulphides. Figure 1 shows results from two different composition pyrites (Balmat and Ruttan) run in a single session on SHRIMP II. These results are in excellent agreement with the reported values for these standards.

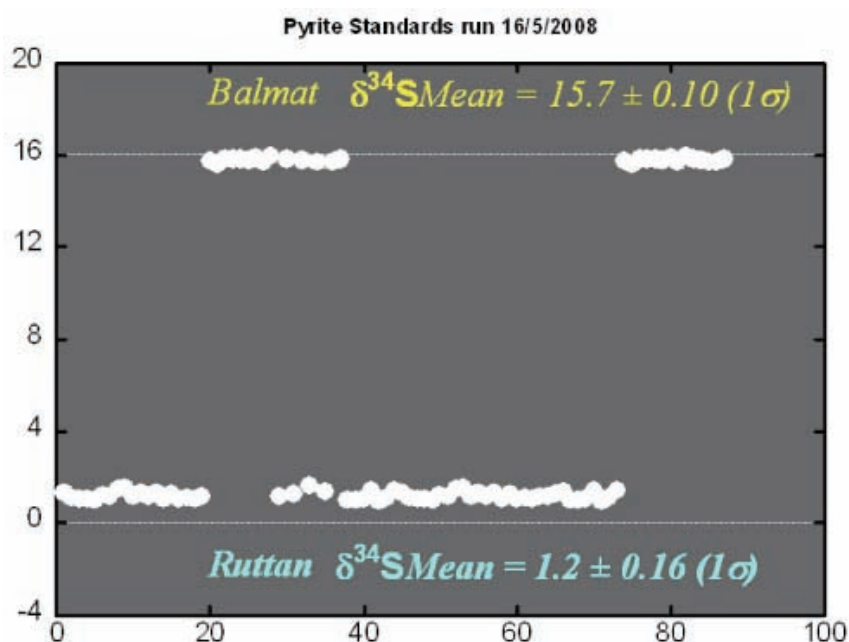


Figure 1. Sulphur isotope compositions of two pyrite standards as measured on SHRIMP II during a single analytical session.

Eldridge et al. (1988, 1989) were also able to show that isotope variations on the SHRIMP scale can be large and not necessarily comparable to bulk analyses in some ore deposits. Our investigations of a number of ore deposits from around the world have confirmed this finding. Detailed small-scale analyses within and across various types of pyrite grains from the Witwatersrand deposit show ranges up to 19‰ from core to rim. Many of these traverses show characteristic rhythmic saw-toothed changes in composition, suggesting a repeated process of formation in these particular concentric, structured grains. Figure 2 illustrates both the structure and isotope variation across a concentric Archaean pyrite grain from the Witwatersrand sequence.

The successful development of this analytical capability on SHRIMP II will be extended to other more exotic applications, with an emphasis on establishing a routine for the added analysis of ^{33}S . This currently requires modifications to the multicollector configuration, but should be possible in the near future. This will extend our research capabilities, enabling us to assess and measure complex mass-dependent and mass-independent fractionation patterns relating to the early development of the Earth's atmosphere, as described by Farquhar and Wing, 2005.

Crowe, D.E., Vaughn, R.G. (1996). Characterization and use of isotopically homogeneous standards of in situ laser microprobe analysis of $^{34}\text{S}/^{32}\text{S}$ ratios. *American Mineralogist*, **81**: 187-193.

Eldridge, CS, Compston, W, Williams, IS, Both, RA, Walshe, JL, Ohmoto, H. (1988) Sulfur-isotope variability in sediment-hosted massive sulphide deposits as determined using the ion microprobe SHRIMP: 1. An example from the Rammelsberg orebody. *Economic geology* **83**: 443-449.

Eldridge, CS, Compston, W, Williams, IS, Walshe, JL, (1989) Sulfur isotope analyses on the SHRIMP ion microprobe. *U.S. Geological Survey Bulletin* **1890**: 163-174.

Farquhar, J, Wing, BA (2005) The terrestrial record of stable sulphur isotopes: a review of the implications for evolution of Earth's sulphur cycle. In: McDonald, I, Boyce, AJ, Butler, JB, Herrington, RJ, Poyla, DA (eds): *Mineral Deposits and earth Evolution*, Geological Society, London, Special Publication 248: 167-177.

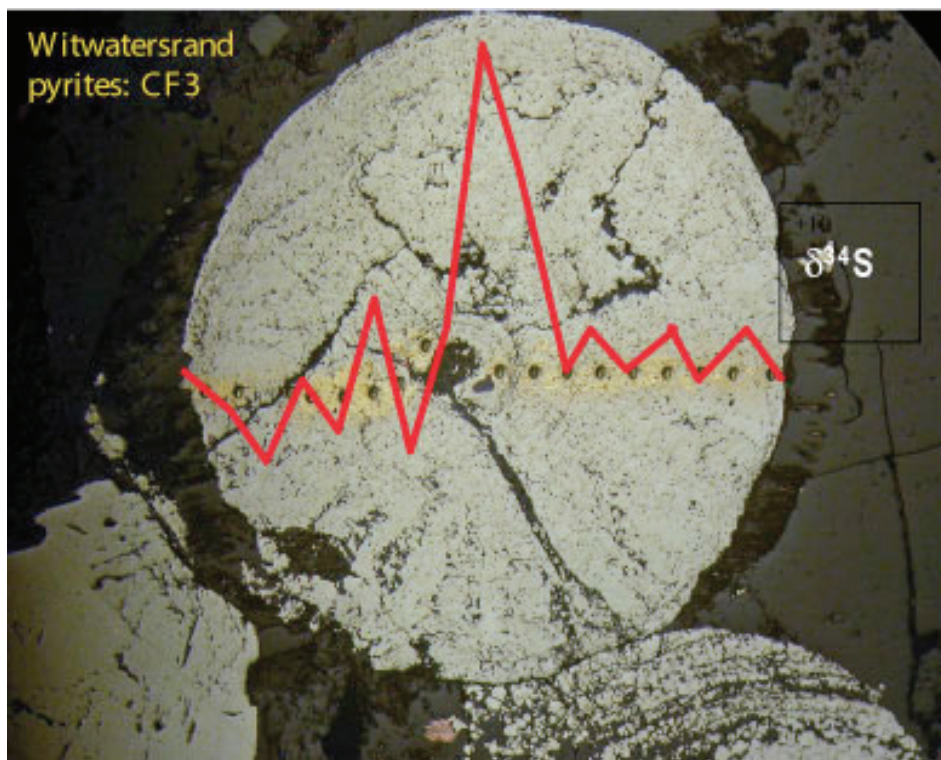


Figure 2. A concentrically-grown pyrite grain from the Witwatersrand gold deposit, South Africa, showing a series of SHRIMP analytical spots across the grain. The SHRIMP spots are approximately 20 mm in diameter. Sulphur isotope compositions were measured across the growth bands and show a large range in values from +10‰ in the centre to ~-7‰ in one of the bands near the margin.

Geochemistry and Analysis of Apollo 16 Lunar Impact Glasses

Simeon S. M. Hui¹ and Marc D. Norman¹

¹ *Research School of Earth Sciences, Australian National University, Canberra, ACT 0200, Australia*

Lunar impact spherules are micron to centimetre sized glass particles formed during impact events where shock induced melting of the lunar regolith and impactor produce melt splashes that can be deposited locally or be ejected far beyond the point of impact. These particles can be found within the lunar soil and in microbreccias and are a medium from which we can study lunar chemistry and impact history.

We have separated over 900 lunar spherules, most of them likely to be from impact origins, from the Apollo 16 fines, 66031. Using new mounting and analysis techniques we aim to obtain major and trace element compositions while preserving the maximum amount of sample for ³⁹Ar-⁴⁰Ar dating on singular particles. Preliminary tests were conducted using shards of crushed USGS standard TB-1G which represents extremes in irregularity. Using wavelength-dispersive electron microscopy techniques to obtain major element compositions of the TB-1G shards, we are able to achieve errors of less than 5% relative.

Following this success, petrographic descriptions and dimensions were obtained for 272 lunar glasses greater than 75µm in diameter along with major element compositions. There are broad positive correlations between MgO vs. FeO and negative correlations between Al₂O₃ and CaO vs. FeO. The majority of the impact spherules have chemistry consistent with derivation of the glasses from the local regolith.

Most impact spherules are irregular and splash-like in shape, often with a coat of adhering grains while highly spherical forms are rarer but have cleaner surfaces. We also find that irregular shapes tend to be more internally heterogeneous in major element composition than the highly spherical forms. This may indicate that highly spherical forms cooled before contacting the lunar surface suggesting a more distant origin. However, rare exotic compositions are more likely to be irregularly shaped which might be due to fragmentation of the glass.

Results of this study were presented at the 8th Australian Space Science Conference, Canberra, Australia, 29th September-1st October 2008.

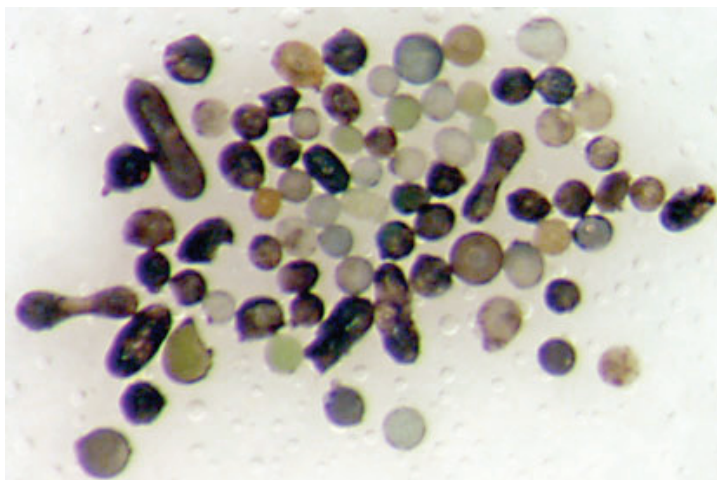


Figure 1.

The role of carbonated eclogite in kimberlite and carbonatite petrogenesis

Ekaterina S. Kiseeva¹, Gregory M. Yaxley¹ and Vadim S. Kamenetsky²

¹Research School of Earth Sciences, The Australian National University, ACT 0200, Australia,

²CODES and School of Earth Sciences, University of Tasmania, Hobart, TAS, Australia

The exotic and rare rock types – kimberlites and carbonatites are undoubtedly of mantle origin and are sometimes considered to be genetically related, but the compositions of their parental melts and melting conditions are still widely debated. A component in the source of kimberlitic and carbonatitic melts may be carbonate-bearing eclogite, reflecting heterogeneity in the mantle derived from recycling during subduction of oceanic crust.

The aim of this study is to use high pressure experimental petrology to investigate the behaviour of carbonate-bearing eclogite in upper-mantle conditions and to test its possible involvement in the mantle sources of kimberlite and related magmas. The first part of our investigation aims to locate the solidus positions and partial melt compositions as functions of bulk compositional parameters such as SiO₂ and CO₂ contents, Ca/Mg, Na₂O/CO₂, etc.

Altered oceanic crust typically contains a few % calcite, formed during hydrothermal alteration. The starting experimental composition (GA1) is an average "altered" MORB composition. Ten % CaCO₃ was added to GA1 in the experiments to facilitate detection of carbonate in the runs. The second mix, Volga, is GA1 minus 6.5% SiO₂, to which 10% CaCO₃ was also added (Volga+10%cc). Experiments were run at 3.5 to 5.5 GPa and 1000–1400°C in piston-cylinder presses at RSES. The run results were analyzed with a HITACHI 4300 SE/N FESEM and JEOL 6400 at the ANU Electron Microscopy Unit, using EDS detectors for quantitative analysis of mineral phases.

Experimental runs after quenching contained the three main phases: garnet, clinopyroxene and melt (Fig. 1, A, B), and sometimes various accessory phases such as K-feldspar, rutile, coesite and carbonate.

Several types of melt were observed in our experiments. A large fraction (>30%) of silicate melt is present in higher temperature runs (T1250 °C). In these cases silicate melt segregated to a pool at one end of the capsule (Fig. 1, A). The totals are about 88–92%, suggesting 8–12% CO₂ dissolved in the melt. At T = 1150 to 1250 °C and 3.5 GPa in GA1+10%cc and 1100 to 1200 °C in Volga+10%cc experiments tiny particles of incompatible-element rich material (ie K-rich and P-rich) are distributed throughout much of the graphite capsules (Fig. 1, C, D) which was often vesiculated or fragmented, indicating decarbonation of a silicate-carbonate melt during quenching. Capsule piercing of some of these runs into a gas chromatograph detected significant CO₂-fluid. With decreasing temperatures at high pressures (4.5 and 5 GPa) carbonate-silicate melts formed small pools of melt within the graphite spheres. Interestingly, at near-solidus conditions in all the investigated pressure intervals two immiscible carbonate and silicate melts are formed. Potassium usually fractionates into the silicate melt, while phosphorous prefers the carbonate.

In sub-solidus conditions in GA1 + 10%cc 1050 °C and 3.5 GPa experiment apatite (Ap), potassium feldspar (K-Fspar), rutile (Ru) and carbonate were observed. At higher pressures potassium feldspar as well as apatite is no more stable and K and P presumably fractionate into the fluid. GA1 + 10%cc solidus at 3.5 GPa is at about 1075 °C, Volga + 10%cc solidus is at least 50 °C lower at all the studied pressures.

Carbonate-rich melts formed from a low degree of eclogite melting will infiltrate neighbouring peridotite, resulting in metasomatism and refertilization. Our next aim is

to investigate how these melts would interact with peridotite and compare the outcomes with melt compositions that may be parental to kimberlites.

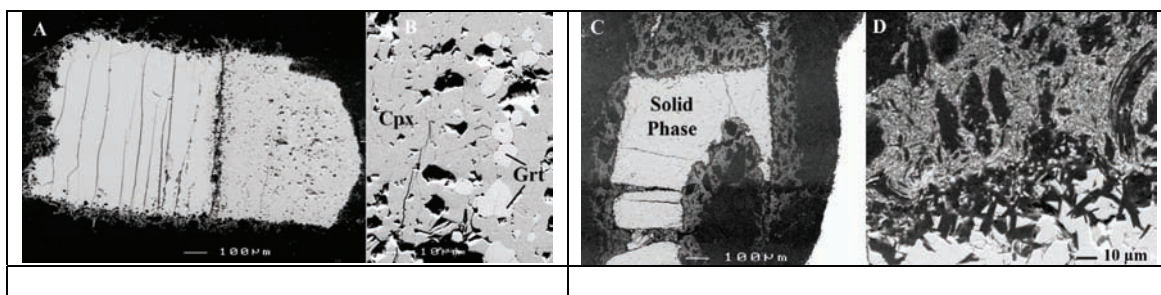


Fig. 1. Backscattered electron image of GA+10%cc 1350°C 3.5 GPa (A, B) and 1200°C, 3.5 GPa (C, D) run material. **A.** Melt (left) and solid phase (right). **B.** Magnified view of part of the solid material in **A**, showing clinopyroxene (Cpx) and garnet (Grt) crystals. **C.** Solid phases represented by Grt and Cpx crystals. **D.** Magnified area of melt distributed within the capsule. Melt is in contact with residue.

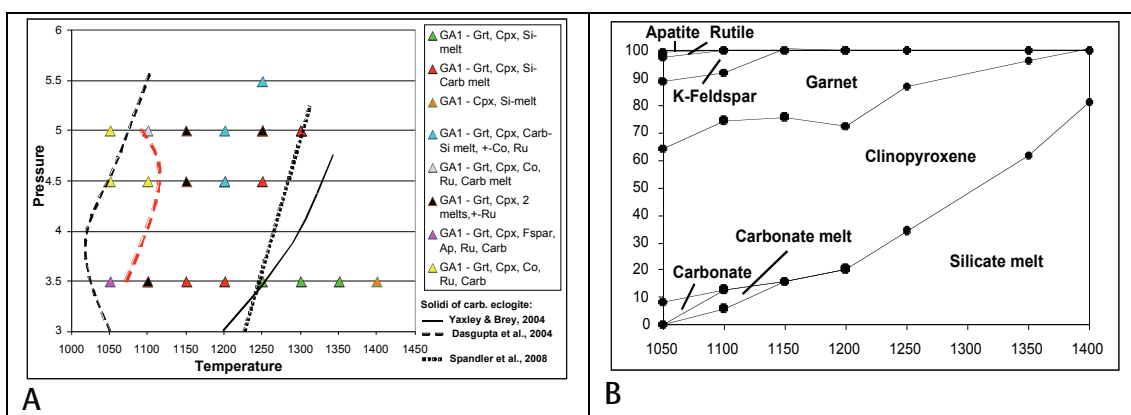


Fig. 2. **A.** Results of experiments with GA1+10%cc. Approximate solidus is shown by the red dashed line. **B.** Phase proportions for GA1+10%cc at 3.5 GPa pressure. The sole liquidus phase is Cpx.

The Lunar Cataclysm: Reality of Mythconception?

Marc Norman¹ and Robert Duncan²

¹ Planetary Science Institute, Research School of Earth Sciences, Australian National University, Canberra, ACT 0200, Australia

³ College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, OR 97331 USA

Understanding the early impact history of the terrestrial planets is a priority goal for solar system exploration. More specifically, ascertaining whether or not the Earth and Moon experienced a cataclysmic Late Heavy Bombardment of impacting planetesimals ~3.9 billion years ago remains an open question with significant implications for the dynamical history of the Solar System, environmental conditions on the early Earth, and the development of crustal structures on Mars.

The idea of a Late Heavy Bombardment is controversial. Lunar impact melt breccias have crystallisation ages that cluster between 3.8 and 4.0 Ga (Norman et al., 2006; Figure 1), corresponding to an episode of intense crustal metamorphism defined by U-Pb isotopic compositions of lunar anorthosites. The late cataclysm interpretation invokes a spike in the mass flux to the Earth and Moon at precisely the time when the Earth's oldest preserved continental crust was forming and life was emerging. Alternatively the age distribution of lunar impact melts may reflect a steadily declining flux of impactors, with the older record being erased by younger events.

Relating lunar surface deposits to specific basins is critical for assessing the reality (or otherwise) of the late cataclysm. An excellent example is the Descartes Formation, a regional unit of fragmental impact breccia that was sampled by the Apollo 16 mission in 1972. Taking advantage of recent improvements in mass spectrometry we measured high-precision ³⁹Ar-⁴⁰Ar ages and trace element composition of anorthositic clasts from two of the Descartes breccias. These measurements show that the breccias were deposited 3.866 ± 0.009 billion years, most likely as ejecta from the massive Imbrium basin, located some 1000 km to the NW of the Apollo 16 landing site (Fig. 2). The trace element compositions support this interpretation.

The significance of this discovery is that Imbrium is one of the youngest impact basins on the Moon. Previous interpretations linked the Descartes breccias to the older Nectaris basin, strongly supporting the idea of a late cataclysm. Our study pulls the pin on the cataclysm hypothesis by showing that age of Nectaris is effectively unconstrained by the sample data. Absolute ages of older basins will be necessary to define the pre-3.9 Ga impact history of the Earth and Moon.

Norman MD, Duncan RA, and Huard JJ (2006) Identifying impact events within the lunar cataclysm from ⁴⁰Ar-³⁹Ar ages and compositions of Apollo 16 impact melt rocks. *Geochimica et Cosmochimica Acta* **70**: 6032-6049.

Ages and textures of impact melts from the Moon

Several large impact events between 3.75-3.95 Ga

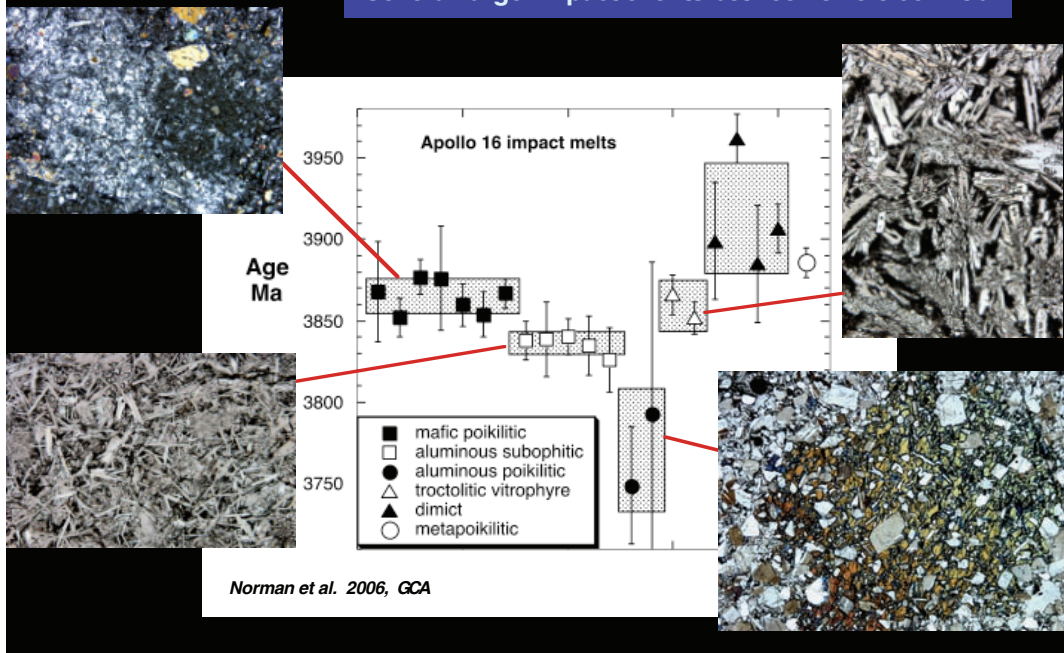


Figure 1.

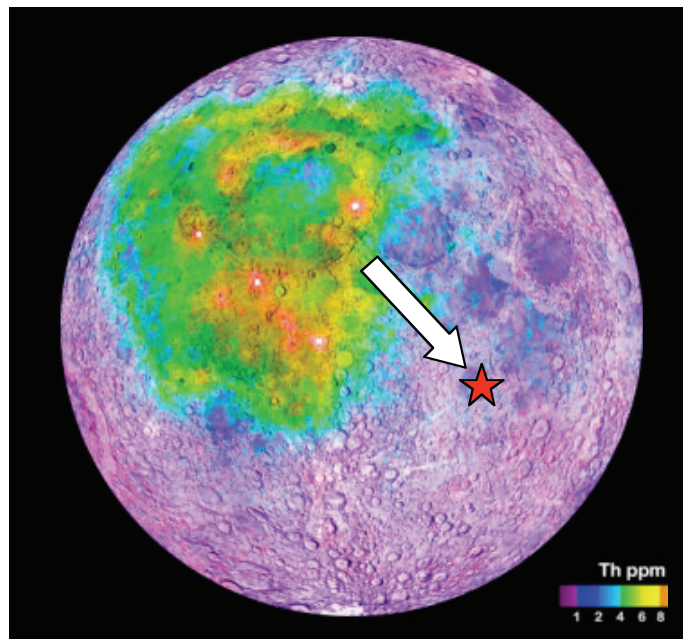


Figure 2.

Melting of residual eclogites with variable proportions of quartz/coesite

Anja Rosenthal¹, Gregory M. Yaxley¹, David H. Green¹, Jörg Hermann¹ and Carl S. Spandler²

¹ *Research School of Earth Sciences, Australian National University, Canberra, ACT 0200, Australia*

² *School of Earth and Environmental Sciences, James Cook University, Townsville, Australia*

Eclogite and pyroxenite layers and veins within the peridotitic mantle may be important in genesis of many magmas. Understanding high pressure melting of residual eclogites with varying amounts of quartz/coesite (qz/co) will improve understanding of the melting behaviour of heterogeneous mantle assemblages.

We are investigating the phase and melting behaviour of a residual eclogite composition, which crystallizes garnet (grt) + clinopyroxene (cpx) at 3.0 & 4.0 GPa with no qz/co (REC). The melting behaviour of REC reveals the anhydrous solidus of a coesite-free eclogite.

The subsolidus phases of REC are garnet (grt) and clinopyroxene (cpx) at 3.0 & 4.0 GPa. The solidus is at $1325 \pm 25^\circ\text{C}$ at 3.0 GPa, and at $1475^\circ\text{C} \pm 25^\circ\text{C}$ at 4.0 GPa. Melt compositions and proportions with $\text{cpx} > \text{grt}$ are controlled by grt-cpx cotectics. At 3.0 GPa, cpx/grt ratios decrease with increasing % melting. At 4.0 GPa, cpx/grt ratios are lower at a given % melting than at 3.0 GPa.

We are also studying eutectic-like melting in coesite-bearing eclogites with varying proportions of qz/co. REC10 and REC20 are identical to REC, but have 10% and 20% higher SiO_2 contents, respectively.

Both REC10 & 20 crystallise sub-solidus as grt + cpx + qz/co at 3.0 GPa. The solidi of both are similar at 3.0 GPa, at $1275 \pm 25^\circ\text{C}$. Low-% melting (<20%) is eutectic-like until qz/co melts out. Like REC, grt-cpx cotectics control high degree melting for all compositions, with cpx abundance always exceeding grt. However, for REC, the proportion of cpx always exceeds those in REC10 & 20, but the % melt is always lower than for REC10 & 20 at given temperature.

Melts vary with increasing % melting from andesitic to basaltic for REC & REC10, but from dacitic to basaltic-andesitic for REC20. At <25% melting, melt in REC has lower Mg# at given % melting than melt in REC10 & 20. The contrary is observed at higher % melting.

Garnet and cpx in REC have higher Mg# at a given % melting than grt and cpx in REC10 & 20. Towards higher % melting (>25% melting), variations in cpx Mg# diminish.

These variations of residual grt and cpx Mg# and melt Mg# are principally because melts from REC (qz/co-free) are more mafic at a given % melting.

These outcomes reveal the strong dependence of Mg# of residual mineral phases & melt on the presence or absence of qz/co in melting of eclogites.

Rosenthal A, Yaxley GM, Green DH, Hermann J, Spandler CS (2008) Melting of residual eclogites with variable proportions of quartz/coesite. *Geochimica et Cosmochimica Acta* 72 (12): A806

Advancing diamond exploration – novel techniques for the interpretation of diamond indicator minerals

Greg Yaxley¹, Hugh O'Neill¹ and Andrew Berry²

¹ *Research School of Earth Sciences, Australian National University, Canberra, ACT 0200, Australia*

² *Department of Earth Science and Engineering, Imperial College, London, UK*

We have developed new mineralogical tools applicable to the search for diamonds in Australia and overseas. This project was an ARC Linkage Project with industry partners BHP-Billiton, de Beers and Rio Tinto Exploration, through AMIRA International.

Techniques of high-pressure experimental petrology were used to develop mineral thermometers based on partitioning of Zn and Mn between upper mantle minerals. A new synchrotron-based technique for determining the redox state of the upper mantle is also being developed. These tools are being applied to fragments of garnet peridotite transported from the deep lithosphere to the surface by deeply-derived, occasionally diamondiferous kimberlite magmas. The resulting temperature and redox information will provide fundamental constraints on lithospheric diamond stability, and will be important in diamond exploration programs at a strategic level for targeting cratonic lithospheric domains more likely to contain high grades of diamonds, and at a more local level for targeting particular kimberlites for grade assessment by expensive bulk sampling techniques.

High-pressure experiments, focussing on Mn partitioning between garnet and olivine under upper mantle pressure-temperature conditions, have been completed. Algorithms for a Mn partitioning thermometers based on statistical fitting of experimental Mn-Mg and Fe-Mn exchange data between garnet and olivine have been determined. Experiments measuring Zn partitioning between Cr-spinel and olivine were also conducted and an olivine-spinel Zn-based thermometer was developed. These thermometers were applied to a comprehensive range of natural garnet ± spinel peridotite xenoliths samples from kimberlites erupted through the Kaapvaal and Slave Cratons. They performed extremely well in most cases, when compared with conventional thermometers (eg two-pyroxene thermometry etc).

The calibration of a synchrotron-based, X-ray Absorption Near Edge Structure Spectroscopy (XANES) method for determining Fe³⁺ contents of mantle garnets has proved unexpectedly challenging, despite a promising start (Figure 1), due to complexities relating to the compositional variations of natural garnets. We therefore adopted the alternative approach of obtaining the Fe³⁺ data by conventional Mössbauer Spectroscopy in collaboration with Prof Alan Woodland (Uni of Frankfurt) and by the newly developed electron microprobe based Flank Method in collaboration with Dr Heidi Höfer (Uni of Frankfurt). This will still allow determination of the oxygen-fugacity depth profiles through the lithospheric section represented by the garnet peridotite xenoliths supplied by the sponsor companies. These calculations are currently underway.

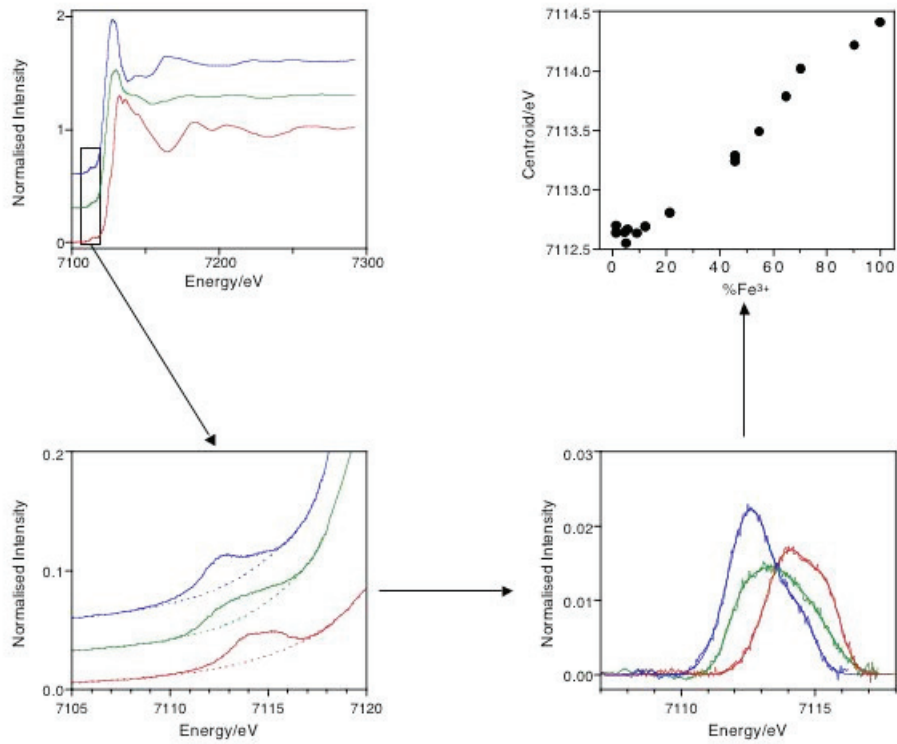


Figure 1: Top left panel: Representative raw XANES spectra for synthetic garnets with $\text{Fe}^{3+}/\text{Fe} = 1.0$, 0.46 and 0.01 (red, green, blue respectively – compositions known from stoichiometry of skiaigite - almandine - andradite series, kindly supplied by Prof. Alan Woodland, University of Frankfurt) showing Fe K-edge and near edge structure in inset. Data was collected on the Australian National Beamline Facility, KEK, Tsukuba, Japan; Bottom left panel: Expanded view of inset in A, showing pre-edge spectral features with backgrounds (dashed lines); Bottom right panel: Pre-edge peaks after background subtraction and best fit from fitting a number of Gaussian components; Top right panel: Pre-edge peak centroids as a function of Fe^{3+}/Fe , showing linear correlation, the basis of the calibration.