Contents

Page 2	Sponsors acknowledgement
Page 3	Oral Presentation Programme
Page 8	Oral Presentation Abstracts
Page 74	Posters
Page 77	Poster Presentation Abstracts
Page 102	Burlington House Fire Safety Information
Page 103	Ground Floor Plan of The Geological Society Burlington House
Page 104	2014 Geological Society Conferences



We gratefully acknowledge the support of the sponsors for making this meeting possible.





15-16 September 2014

eepearth14

Page 2



Oral Presentation Programme



Monday 15 Sept 2014

08.30	Registration & tea & coffee (Main foyer & Lower Library)

09.05 Welcome

Session 1: EARTH'S CORE

(Chair: Dr Sally Gibson. Sponsor: British Geophysical Association)

09.10 Three potential solutions to the Core heat paradox

Keynote: John Hernlund (Tokyo Institute of Technology, Japan)

09.40 Contstraints on the timing of late accretion from highly siderophile elements and W isotopes in the early rock record

Chris Dale (University of Durham, UK)

10.00 Fe-Silicide-bearing Ureilite Parent Body: an analogue for the early building blocks of the Earth?

Hilary Downes (University College London_Birkbeck, UK)

10.20 Making the Moon from the Earth – an internally consistent isotopic and chemical model

Jon Wade (University of Oxford, UK)

10.40 Tea, coffee, refreshments & posters (Lower Library)



Session 2: STRUCTURE & COMPOSITION OF EARTH'S CORE

(Chair: Prof Simon Redfern. Sponsor: Cambridge University Press)

- 11.10 Seismic structure of the Earth's inner core and its dynamical implications Invited: Arwen Deuss (University of Cambridge, UK)
- 11.40 **The melting curve of Ni to 1 Mbar** Oliver Lord (University of Bristol, UK)
- 12.00 **Development of an early density stratification in the Earth's Core** David Rubie (University of Bayreuth, Germany)
- 12.20 Discussion

12.35 Sandwich lunch (provided) & posters (Lower Library)

Session 3: LOWERMOST MANTLE

(Chair: Prof Simon Redfern. Sponsor: Geological Society of London)

- 13.25 Introduction
- 13.30 The chemical composition of the lower mantle based on laboratory elasticity measurements

Invited: Daniel Frost (University of Bayreuth, Germany)

- 14.00 **Partitioning of iron components between Mg-perovskite and post-perovskite** Chris Mohn (University of Oslo, Norway)
- 14.20 Constraining the electrical conductivity of the deep mantle from above and below

Richard Holme (University of Liverpool, UK)

14.40 Long wavelength structure of Earth's deep mantle from normal mode inversions in combination with geodynamic model comparisons

Paula Koelemeijer (Cambridge)

15.00 On the temporal evolution of large-scale mantle structure and its relation to Pangea assembly and breakup

Shijie Zhong (University of Colorado at Boulder, USA)

15.20 Tea, coffee, refreshments & posters (Lower Library)

Session 4: TRANSITION ZONE

(Chair: Prof Mike Walter. Sponsor: Mineral Physics Group, Mineralogical Society of Gt Britain & Ireland)

15.50 Effects of composition and temperature on the phase boundaries at 600-700 km depths

Invited: Dan Shim (Arizona State University, USA)

16.20 Density jump across the 410 and 660 km seismic discontinuity beneath China: A new constraint on long term mantle mixing and basalt-enriched transition zone

Alex Song (University College London, UK)

16.40 Evidence for the transport of water to the lower mantle from midmantle seismic anisotropy

Andy Nowacki (University of Bristol, UK)

17.00 A hydrous mantle transition zone indicated by ringwoodite included within diamond Invited: Graham Pearson (University of Alberta, Canada)

17.30 **Discussion**

- 17.45 Drinks reception and posters (Lower Library)
- 19.00

Tuesday 16 Sept 2014

08.30 Registration, Tea & coffee (Main foyer & Lower Library)

Session 5: UPPER MANTLE & MANTLE STRUCTURE

(Chair: Dr Saskia Goes. Sponsor: Geological Society of London)

- 08.55 Welcome
- 09.00 Seismic evidence for sulphide melt in the upper mantle Invited: Mike Kendall (University of Bristol, UK)
- 09.30 Ferric iron and its influence on Earth's deep structure Robert Myhill (University of Bayreuth, Germany)

15-16 September 2014

09.50 **Global radially anisotropic whole-mantle structure from multiple datasets** Ana Ferreira (University College London, UK)

10.10 Tea, coffee, refreshments & posters (Lower Library)

Session 6: MANTLE VOLATILES

(Chair: Prof Mike Walter. Sponsor: Geochemistry Group, Mineralogical Society of Gt Britain & Ireland)

- 10.40 **The noble gas record of terrestrial volatile origin and reservoir interaction.** Invited: Chris Ballentine (University of Oxford, UK)
- 11.10 Understanding δ15N variations in the mantle using internal variabilities in deep mantle diamonds
 Rebecca Southworth (University College London, UK)
- 11.30 **Probing the water content of the Earth's mantle** Jennifer Brooke (University of Edinburgh)
- 11.50 Helium diffusion in mantle minerals from first principles Invited: John Brodholt (University College London, UK)
- 12.20 Discussion
- 12.35 Sandwich lunch (provided) & posters (Lower Library)

Session 7: SURFACE CONSTRAINTS ON DEEP EARTH PROCESSES

(Chair: Dr Sally Gibson. Sponsor: Volcanic & Magmatic Studies Group, Geological Society of London)

- 13.35 Introduction
- 13.40 Relating the chemistry and structure of the deepest mantle to the geochemistry of mantle melts erupted at the surface

Invited: Matt Jackson (UC Santa Barbara, USA)

14.10 Paleozoic plate motion history and the longevity of deep mantle heterogeneities

Abigail Bull (University of Oslo, Norway)

15-16 September 2014

14.30 Helium isotopic composition of the earliest picrites erupted by the Ethiopia plume

Nick Rogers (Open University, UK)

14.50 **Isotope signatures from a melting mantle** Huw Davies (Cardiff University, UK)

15.10 Tea, coffee, refreshments & posters (Lower Library)

Session 8: MANTLE DYNAMICS

(Chair: Dr Saskia Goes. Sponsor: Geological Society of London)

- 15.40 **Mantle mixing: processes and modelling** Invited: Peter Van Keken (University of Michigan, USA)
- 16.10 The potential for palaeo-geomagnetism to help constrain lower mantle dynamics

Andrew Biggin (University of Liverpool, UK)

- 16.30 **Quantifying lithological variability in the mantle** Oliver Shorttle (University of Cambridge, UK)
- 16.50 Of mantle plumes and secondary scale convection: Insights from whole mantle SEM-based seismic waveform tomography

Barbara Romanowicz (Institut de Physique du Globe, Paris, France)

- 17.10 Discussion
- 17.25 Closing comments
- 17.35 **Close**



Oral Presentation Abstracts

Three Potential Solutions to the Core Heat Paradox

John Hernlund

Tokyo Institute of Technology, Japan

Recent theoretical and experimental work on the



conductivity of iron at Earth's core conditions suggests that the core-mantle boundary of Earth has cooled by at least 1,000 K since 3.5 Ga, the earliest paleomagnetic evidence for a geomagnetic field. Such temperatures are very difficult to explain, as they imply temperatures much greater than the liquidus for any plausible mantle composition. Such high temperatures are difficult to account for, even if a dense basal magma ocean was formed above the coremantle boundary. However, the interpretation of a hot early core relies on the assumption that, prior to crystallization of the inner core, geodynamo sustaining convection in Earth's liquid core was provided for by core cooling alone. Thus one potential solution to the core heat paradox is to invoke the existence of other buoyancy mechanisms besides top cooling, such as ex-solution of nominally non-siderophile elements. The ex-solution mechanism relies on certain conditions being met during core formation, and has many corollary effects that have not yet been considered. Another potential solution is suggested by saturation resistivity theory, which has been invoked to explain ab initio and experimental work on core conductivity. In the saturation model, two-thirds of the contribution to core conductivity arises from a saturation resistance that scales inversely with inter-atomic distance. If this scaling holds true for liquid iron alloys, then core conductivity should depend upon the molar density of the alloy, with light species such as hydrogen possibly having a significant influence. In this scenario, very light species such as hydrogen would decrease the core conductivity, lessening the degree of core cooling required to maintain a dynamo. A third potential solution to the core heat paradox is to relax the assumption that liquid regions deep inside the Earth must always be convecting, but instead could be at least partly stably stratified in density. Such scenarios should be a natural outcome of planetary formation, and may be compatible with the outcomes of recent giant impact simulations. Stable stratification could allow a greater amount of heat to become trapped deep inside a terrestrial planet, which can accommodate high core temperatures suggested by high core conductivity. These three different scenarios need not be mutually exclusive, however, the end-member hypotheses can be tested. For example, ex-solution should be more powerful early in the Earth's thermal evolution, predicting an earlier onset of the geodynamo. Stable stratification, on the other hand, delays the onset of a geodynamo by establishing a thermal diffusion time threshold for cooling to traverse the stratified region and penetrate into the core. An amount of hydrogen in the core sufficient to reduce core conductivity will also have many corollary effects, and will be subject to rapid baro-diffusion and thus may not be stable over Earth's entire history.





Constraints on the timing of late accretion from highly siderophile elements and W isotopes in the early rock record

Christopher W. Dale¹ Thomas Kruijer² Kevin W. Burton¹, Thorsten Kleine², Stephen Moorbath³

¹ Dept. Earth Sciences, Durham University, DH1 3LE, UK; christopher.dale@durham.ac.uk

² Westfälische Wilhelms-Universität, Münster, Germany ³ Dent Forth Sciences, University of Oxford, OX4 200, UK

³ Dept. Earth Sciences, University of Oxford, OX1 3PR, UK

Highly siderophile elements (HSEs) are strongly sequestered into metallic planetary cores, leaving silicate mantles almost devoid of HSEs. Late accretion of primitive meteoritic material, after core



formation had ceased, partially replenished HSEs in planetary mantles and occurred within a few million years of solar system formation on most parent bodies (1), but probably later on Earth, after a final episode of core formation associated with the giant Moon-forming impact (50-150 million years later (2)).

Ancient isolated domains in Earth's mantle, which may have formed prior to the giant impact, have recently been recognised by anomalies in the short-lived ¹⁸²Hf-¹⁸²W isotope system. These domains - such as the source of 3.8 billion-year-old Isua basalts (3) - might represent mantle that largely escaped late accretion. Here we show, however, that the Isua source mantle had HSE abundances at ~60% of the present-day mantle, inconsistent with a pre-late accretion model. The combined ¹⁸²W-HSE data for Isua, however, does appear to be consistent with incomplete addition of the late veneer to an early Earth mantle of similar composition to that of the Moon.

Nevertheless, the global data for rocks possessing elevated ¹⁸²W cannot be explained by simple mixing of late veneer with a homogenous mantle subsequent to the giant moon-forming impact. This may require early W isotope heterogeneity in the mantle – perhaps particularly in the lower mantle, as most komatiites are anomalous – which was imposed either by accretionary events or early differentiation. The HSEs were added to these parts of the mantle either by early 'pre-lunar' late accretion, while the Hf-W system was still extant, or somehow added without homogenising the ¹⁸²W isotope composition of the mantle. The presence of these early-formed heterogeneities suggests that parts of the mantle may have remained solid and retained their HSEs through the Moon-forming event.

C.W. Dale et al. (2012), Science, 336, 72.
 M. Touboul et al. (2007), Nature 450, 1206
 M. Willbold et al. (2011), Nature 477, 195.





Fe-Silicide-bearing Ureilite Parent Body: an analogue for the early building blocks of the Earth?

Hilary Downes^{1,2}, Nachiketa Rai^{1,2}, Caroline Smith², Aidan Ross^{1,2} and Jason Herrin³

1. Centre for Planetary Sciences, UCL-Birkbeck, London, UK

- 2. Natural History Museum, London, UK
- 3. Nanyang Technological University, Singapore



In heterogeneous accretion models for the Earth, oxidation during accretion is a critical component of the process. The earliest stages of core segregation on Earth appear to have taken place under strongly reducing conditions (Wade and Wood, 2005). To reconcile the metal-silicate partitioning data for Ni, Co, V, Cr, Nb, W and Si simultaneously with the observed depletions of these elements in the terrestrial mantle, the most plausible explanation is that conditions were initially reducing and became more oxidising as accretion progressed (Wade and Wood, 2005). Si-isotopes provide independent evidence for the presence of Si in the Earth's core (Fitoussi et al., 2009).

Ureilites are ultramafic achondrites composed largely of olivine and pyroxenes that are thought to be derived as residues of partial melting within the mantle of a carbon-rich ureilite parent body (UPB) (Goodrich, 1992; Middlefehldt et al., 1998). Despite having undergone high temperature processes and relatively high degrees of partial melting (20–30%), ureilites retain not only a significant amount of iron metal and relatively high abundances of siderophile elements but also contain phases such as iron silicides (Herrin et al., 2008; Smith et al., 2010; Ross et al., 2009). The presence of FeSi phases and other Fe-X phases (X = S, P, C) in ureilites indicates very low redox conditions. These conditions must have occurred at low pressures, since the UPB is estimated to be ~100 km in radius (Singletary and Grove, 2003). It has been suggested that smaller bodies with already differentiated core-mantle structures contributed to the accreting Earth (Taylor and Norman, 1990). Here we explore, using experimental partitioning data, isotopic and elemental composition, whether small planetesimals akin to the UPB could have been the feeding bodies for the accreting Earth during its early reduced phase.

References:

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Smith C. L., Ross A. J. and Downes H. (2010) Iron silicides in polymict ureilites – Recording the complex history of the ureilite parent body. *Meteorit. Planet. Sci.* 45(Supp.), #5221 (abstr.).

Taylor, S.R., Norman, M.D., 1990. Accretion of differentiated planetesimals to the Earth. In: Newsom, H.E., Jones, J.H. (Eds.), *Origin of the Earth*. Oxford Univ. Press, New York, pp. 29–43.

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Making the Moon from the Earth – an internally consistent isotopic and chemical model

JON WADE AND BERNARD J. WOOD¹

¹Dept of Earth Sciences, University of Oxford, South Parks Road, Oxford, OX1 3AN jon.wade@earth.ox.ac.uk, berniew@earth.ox.ac.uk

The fraction of the Moon made from Earth at the time of the moon-forming impact and the amount of impactor it contains are major questions concerning the origin of the Earth-Moon system. Earth's mantle and the Moon are distinctive in their FeO contents and some trace element ratios but identical in their isotopes of O, Si, W, Ti and Cr. The latter observation implies that they are made from exactly the same material, but the former implies the opposite. Here we show that the moon can be >90% made from Earth's mantle at the time of the giant impact, provided the Earth underwent a small amount of post-impact core formation. This produced a Moon identical to the Earth's mantle in both chemical and isotopic composition. Post-impact high-pressure core formation reduced both the Earth's mantle FeO content and its Nb/Ta ratio from lunar to present-day values without significantly altering either body's isotopic signature. We also explore the role that impactor composition plays in setting the tungsten and silver isotopic composition of both bodies. The modeled lunar core contains about 10% sulphur which is required to maintain the identical Hf/W ratios of both the Earth's mantle and silicate Moon. The Moon may therefore be regarded as a chemical model for Earth's mantle prior to the impact.





Seismic structure of the Earth's inner core and its dynamical implications

Arwen Deuss¹, Jessica Irving², Karen Lythgoe¹, Lauren Waszek¹

1.Department of Earth Sciences, University of Cambridge, United Kingdom (afd28@cam.ac.uk) 2.Princeton University, New Jersey, US

The core, comprising the innermost parts of Earth, is one of the most dynamic regions of our planet. Inner core solidification releases latent heat that, combined with motions in the fluid outer core, drives the geodynamo, generating Earths magnetic field (Buffett et al. 1992, Gubbins et al. 2003). Solidification of the inner core also supplies some of the heat that drives mantle convection and subsequently plate tectonics at Earth surface. Thus, the inner core is key to understanding the inner workings of our planet, and details of its heterogeneity and anisotropy may provide constraints on Earth's thermal and compositional structure.

Inner core anisotropy was discovered in the1980's, with seismic observations in both short period PKIKP body waves (Morelli, Dziewonski & Woodhouse, 1986) and long period normal mode splitting functions (Woodhouse, Giardini & Li, 1986). Ever since this discovery, our ideas on the structure of the inner core have become more and more detailed. It was recently discovered that the inner core is not a homogeneous sphere, but displays regional variations with stronger anisotropy in the Western hemisphere and weaker anisotropy in the Eastern hemisphere of the inner core, especially focusing on reconciling normal mode and body wave observations in the light of the first discovery of inner core anisotropy now almost 30 years ago.

Two mechanisms have been proposed to explain the hemispherical pattern: either (a) inner core translation, wherein one hemisphere is melting and the other is solidifying, or (b) thermochemical convection in the outer core, leading to different solidification conditions at the inner core boundary. Neither is (yet) able to explain all seismically observed features, and a combination of different mechanisms is most likely required.





The melting curve of Ni to 1 Mbar

Oliver T. Lord^{1,2}, Ian G. Wood², David P. Dobson², Lidunka Vočadlo², Weiwei Wang^{1,2}, Andrew R. Thomson¹, Elizabeth T. H. Wann², Guillaume Morard³, Mohamed Mezouar⁴, Michael J. Walter¹

- 1. School of Earth Sciences, University of Bristol (oliver.lord@bristol.ac.uk)
- 2. Department of Earth Sciences, University College London
- 3. IMPMC, Université Pierre et Marie Curie, Paris, France
- 4. European Synchrotron Radiation Facility, Grenoble, France



The melting curve of Ni has been determined to 125 GPa using laser-heated diamond anvil cell (LH-DAC) experiments in which two melting criteria were used: firstly, the appearance of liquid diffuse scattering (LDS) during *in situ* X-ray diffraction (XRD) and secondly, plateaux in temperature vs. laser power functions in both *in situ* and off-line experiments (Lord et al. accepted) which in many cases were observed simultaneously (Fig. 1). Our new melting curve is defined by the following Simon-Glatzel fit to the data:

$$T_M(K) = \left[\left(\frac{P_M}{18.78 \pm 10.20} + 1\right)\right]^{1/2.42 \pm 0.66} \times 1726$$

This fit is in good agreement with the majority of the theoretical studies on Ni melting (e.g. Pozzo & Alfè, 2013) and matches closely the available shock wave melting data (Fig. 2). It is however dramatically steeper than the previous off-line LH-DAC studies in which determination of melting was based on the visual observation of motion aided by the laser speckle method (e.g. Errandonea et al., 2001). We estimate the melting point of Ni at the inner-core boundary (ICB) pressure of 330 GPa to be 5800±700 K, within error of the value for Fe of 6230±500 K determined in a recent *in situ* LH-DAC study by similar methods to those employed here (Anzellini et al. 2013). This similarity suggests that the alloying of 5-10 wt.% Ni with the Fe-rich core alloy is unlikely to have any significant effect on the temperature of the ICB. Our melting temperature for Ni at 330 GPa is ~2500 K higher than that found in previous experimental studies employing the laser speckle method. We find that those earlier melting curves coincide with the onset of rapid sub-solidus recrystallization, suggesting that visual observations of motion may have misinterpreted dynamic recrystallization as convective motion of a melt.

In addition, we present melting data on a range of other transition metals (Mo, Ti, V, Cu) using the same techniques that we employ for Ni. As with Ni, these results indicate that earlier experimental melting curves based on visual observation of melt motion significantly underestimate the true melting curves. They are also in good agreement with the available shock and theoretical studies and thus go a long way to eliminating the long-standing disagreement concerning the melting of transition metals between these methods on the one hand, and static LH-DAC methods on the other.

Anzellini et al. (2013) Science, 340:464-466. Errandonea et al. (2001) Phys. Rev. B, 63:132104. Lord et al. (2014) Phys. Earth Planet. Inter. <u>http://dx.doi.org/10.1016/j.pepi.2014.05.005</u> Pozzo M, Alfè D (2013) Phys. Rev. B, 88:024111.



Fig. 1 (Above): In situ run 59A (Ni in MgO at 45.8 ± 1.3 GPa). (a) Temperature vs. laser power plot. The melting temperature (grey bar) is determined from the points within the melting plateau (filled circles). The arrow represents the laser power at which LDS was first observed; LDS was observed in all subsequent data which are colour coded as a function of laser power. (b) XRD patterns colour coded to match (a). The black spectrum is the pattern collected immediately before the onset of LDS; the dashed line is a fit to its background. Tick marks from top to bottom represent Ni and MgO. A constant intensity offset is applied to each pattern such that all the patterns match at $2\theta = 8^{\circ}$.



Fig. 2 (Above): Ni melting data collected in situ at the ESRF (circles) and off-line at Bristol, corrected for thermal pressure (squares). The thick black line is an equally weighted fit using the Simon-Glatzel equation while the grey field is a 2σ error envelope. The thin black line is a similar fit to the data with the thermal pressure excluded (not shown). The red open triangles represent the estimated temperature of the onset of rapid recrystallization in our in situ experiments. The grey lines represent other Ni melting curves reported in the literature based on experiments (thick) and MD simulations (thin). L93; Lazor et al. (1993), E01; Errandonea et al. (2001), J05; Japel et al. (2005), B11; Bhattacharya et al. (2011), K06; Koči et al. (2006), P&A13; Pozzo & Alfè (2013), W09; Weingarten et al. (2009), L10; Luo et al. (2010). Closed triangles: shock melting points recalculated by Pozzo & Alfè (2013) on the basis of the equations of state of liquid and solid Ni reported by Urlin et al. (1966). The black cross at 330 GPa represents the melting point of pure Fe based on the in situ experiments of Anzellini et al. (2013).



Development of an Early Density Stratification in the Earth's Core

D.C. RUBIE^{1*}, J. HERNLUND², S.A. JACOBSON^{1,3}, A. MORBIDELLI³, J. DE VRIES¹

¹Bayerisches Geoinstitut, Bayreuth, Germany (<u>dave.rubie@uni-bayreuth.de</u>)
 ²Tokyo Institute of Technology, Tokyo, Japan
 ³Observatoire de la Cote d'Azur, Nice, France

Formation of the Earth's core was a multistage process that involved Ferich metal equilibrating with silicate liquid at pressure-temperature conditions that progressively increased with time [1, 2]. Because the partitioning of silicon and oxygen between metal and silicate liquids depends strongly on temperature, the concentrations of these light



elements in core-forming liquids must also have evolved during accretion. If the final liquids added to the core were enriched in such light elements relative to earlier liquids because of increasing temperatures, stable density stratification could have resulted that would have inhibited the onset of core convection. In fact, a relic of such stratification may still be present today in the form of a low density layer at the top of the outer core [3] and/or a high density layer (F-region) above the inner core boundary [4].

We have modelled the evolving compositions of core-forming liquids by combining the multistage core formation of [2] with N-body accretion simulations of terrestrial planet formation. We focus especially on Grand Tack simulations because of their success in producing bodies that closely resemble the terrestrial planets of the Solar System [5,6]. These simulations typically start with a few tens of embryos (Moon to Mars size) that are embedded in a disk of several thousand much smaller planetesimals. The starting bodies, which are typically distributed over heliocentric distances from 0.7 to 13 AU, collide to form larger bodies. Due to the high energies involved, impacts result in extensive melting and magma ocean formation that facilitate episodes of core formation. In order to model each core formation event, we combine rigorous mass balance with metal-silicate element partitioning data for the major elements Fe, Si, Ni, and O in order to determine the compositions of equilibrated silicate and metal liquids [2]. The mass balance requires the bulk compositions of all starting embryos and planetesimals to be defined as a function of their heliocentric distances of origin. To do this, we assume that non-volatile elements are present in solar system (CI) relative abundances in all bodies and that oxygen content is the main compositional variable. The primary constraint on the combined model is the calculated mantle composition of an Earth-like planet (i.e. located at ~1 AU and of 1 Earth mass) with secondary constraints being the mantle compositions of Mercury and Mars. The model is refined by least squares minimization using up to 5 fitting parameters that consist of the metalsilicate equilibrium pressure and parameters that define the starting compositions of primitive bodies. Results are highly sensitive to the compositional model for starting bodies and acceptable fits are only obtained when bodies that originated close the Sun (<1-1.5 AU) are highly reduced and those at greater distances are increasingly oxidized [7].

The models predict that the Earth's core contains 8-9 wt% silicon and 3-4 wt% oxygen. However, batches of metallic core-forming liquids show a progressive increase in light element concentrations as accretion proceeds. This is especially the case for oxygen which is essentially absent at early stages of accretion but is present at concentrations of up to 14 wt% during the final 20% of accretion. Thus, stable density stratification in the early core is highly likely, and only a major core-merging event is likely to provide sufficient energy to mix the core to the extent necessary for convection and production of a geodynamo.

[1] Wade & Wood (2005) *EPSL* **236**, 78– 95. [2] Rubie *et al.* (2011) *EPSL* **301**, 31-42. [3] Helffrich (2014) *EPSL* **391**, 256–262. [4] Souriau & Poupinet (1991) *GRL* **18**, 2023-2026. [5] Walsh *et al.* (2011) *Nature* **475**, 206-209. [6] Jacobson *et al.* (2014) *Nature* **508**, 84-87. [7] Rubie *et al.* (2014) *LPSC* Abstract #1734.





The chemical composition of the lower mantle based on laboratory elasticity measurements

Daniel J. Frost

Bayerisches Geoinstitut, Universität Bayreuth, Bayreuth, Germany. (dan.frost@uni-bayreuth.de)

The only rigorous method for determining the composition of the Earth's lower mantle is to compare experimental estimates for the S and P wave velocities of potential lower mantle assemblages with seismic observations. The dominant mineral of the Earth's lower mantle is likely



to be magnesium-silicate perovskite. If the lower mantle has the same composition as the upper mantle, then silicate perovskite should also contain significant concentrations of Fe and Al. In addition evidence for lateral heterogeneities in the mantle could potentially arise from either chemical or thermal anomalies. If chemical anomalies exist these are most likely to arise from variations in the Fe and Al content of the mantle. Brillouin spectroscopy and X-ray diffraction measurements have been performed in the diamond anvil cell to determine the densities and transverse and longitudinal acoustic phonon velocities of (Mg,Fe)SiO3 and MgSiO3 perovskite single crystals. Further data on the elasticity of polycrystalline MgSiO₃ perovskite and Fe and Fe and Al-bearing perovskite have been obtained using ultrasonic interferometry in the multianvil. The results of both types of study have been integrating into a single model to interpret seismic wave velocities in the lower mantle in terms of temperature and composition.





Partitioning of iron components between Mg-perovskite and post-perovskite

Chris E. Mohn¹, Reidar G. Trønnes²

- 1. Centre for Earth Evolution and Dynamics (CEED), Univ. of Oslo (c.e.mohn@geo.uio.no)
- 2. Centre for Earth Evolution and Dynamics (CEED) and Natural History Museum, Univ. of Oslo

Perovskite (pv) and post-perovskite (ppv) are ABO₃-componds with large, irregularly 8coordinated A-sites occupied mainly by Mg, Fe²⁺, and Fe³⁺ and small octahedral B-sites with Si and AI. The incorporation of octahedral AI in perovskite in the Earth's lower mantle is dominantly charge-balanced by A-site incorporation of ferric iron. We performed Monte Carlo simulations with density functional theory in the grand canonical ensemble to investigate compositions in the systems MgSiO₃-FeSiO₃ (MS-FS) and MgSiO₃-FeAIO₃ (MS-FA), focusing on the pv-ppv transition and the partitioning of the FS and FA components between MS-based pv and ppv under pressures and temperatures corresponding to the D" zone. The Clapeyron slope of the transition for MS is 9.6 MPa/K, and it decreases to 8.4 and 8.1 MPa/K at 6.3 and 12.5 mol% FS and to 8.2 and 7.3 MPa/K at 6.3 and 12.5 mol% FA. The FS and FA components partition in opposite directions, towards ppv and pv, respectively. The contrasting partitioning of ferrous and ferric iron, with Fe³⁺ coupled to octahedral AI, is broadly consistent with previous, and seemingly conflicting, experimental studies.

In Al-poor and Fe-rich peridotite compositions, the simple pv to ppv partitioning of divalent Fe will lead to increased Mg/Fe-ratio of the coexisting ferropericlase (fp). The exchange partition coefficients $K_D^{pv/fp}$ (Fe/Mg) and $K_D^{ppv/fp}$ (Fe/Mg) will therefore decrease from pv-bearing to ppv-bearing lithologies, in accordance with the exchange reaction: MgSiO₃ (pv) + FeO (fp) = FeSiO₃ (ppv) + MgO (fp)

A net chemical reaction from FA-rich pv coexisting with reduced Fe-metal to form FS-rich ppv produces additional Al_2O_3 and MgO:

 $2 \text{ FeAlO}_3 + 3 \text{ MgSiO}_3 + \text{Fe} = 3 \text{ FeSiO}_3 + \text{Al}_2\text{O}_3 + 3 \text{ MgO}$

The fate of Al_2O_3 and MgO depends on the lithological environment. In peridotite, MgO might increase the proportion and Mg-number of coexisting fp, whereas some Al_2O_3 may dissolve as an additional component in ppv and/or in coexisting pv. Separate Ca-ferrite- (CF-) or Ca-titanite-(CT-) structured phases containing the MgAl_2O_4 component might form if the solubility of Al_2O_3 in ppv is exceeded. In basaltic to komatilitic lithologies the MgAl_2O_4 component might dissolve in a preexisting CF-CT-phase, with excess MgO reacting with SiO_2 from the silica-dominated phases to increase the proportion of the MS-component in ppv.

The observations of double seismic discontinuities within the D" zone, both within the northeastern part of the Pacific Large Low Shear-wave Velocity Province (LLSVP) and under regions with high S-wave velocities have been ascribed to the upper and lower boundaries of ppv-dominated lenses. Recent experiments, indicating very high pressures for the ppv-transition in FeAIO₃-rich compositions, have made the interpretation of ppv-lenses within hot, and presumably Fe-rich, LLSVPs questionable. Our results, however, may explain the presence of ppv-lenses within the hot LLSVPs, provided that they contain pv and ppv that are poor in aluminum, but rich in ferrous iron. Iron-rich magma ocean cumulates may have such compositions. Further studies will seek to clarify the iron partitioning between a possible "H-phase" (Zhang et al., 2014, Science) and ppv.

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Constraining the electrical conductivity of the deep mantle from above and below

Richard. Holme¹ and Nils Olsen²

1 School of Environmental Sciences, University of Liverpool, L69 3GP, UK. email: holme@liv.ac.uk 2 DTU Space, Juliane Maries Vej 30, 2100 Copenhagen, Denmark



The electrical conductivity of the deep Earth can be constrained in two ways: from above, using aeomagnetic depth sounding, by modelling the induction from long-period fluctuations in the external geomagnetic field (e.g., Olsen, 1999) and from below, by considering the limitations imposed by the observation of rapid secular variation from the core at Earth's surface. Recently, the second method has been revolutionised by observation of complementary rapid variations in the rate of Earth rotation. Analysis is no longer restricted to the "sharpness" of so-called geomagnetic jerks: the similarity of the times of geomagnetic and rotational signals impose a strong upper bound on the electrical conductance of the deep mantle (Holme and de Viron, 2013). Here we consider models constructed using both constraints simultaneously. The conductivity in the lower mantle is strongly limited, although high conductivity is still possible in the very lowermost mantle - for example, a thin layer of approximately core conductivity located at the core-mantle boundary. However, given that much of any time lag between rotational and geomagnetic signals is accounted for by mantle conductivity required by surface observations, the extent of any such basal layer is strongly constrained to be substantially less thick than D". We present these conclusions to the community to determine whether they are able to provide a useful constraint on deep mantle structure and mineralogy.

Olsen, N., 1999. Long-period (30 days -- 1 year) electromagnetic sounding and the electrical conductivity of the lower mantle beneath Europe, *Geophys. J. Int.*, **138**, 179--187.

Holme, R. & de Viron, O., 2013. Characterization and implications of intradecadal variations in length of day, *Nature*, **499**, 202--204.





Long wavelength structure of Earth's deep mantle from normal mode inversions in combination with geodynamic model comparisons

- P. J. Koelemeijer¹, A. Deuss¹, J. Ritsema², H.-J. Van Heijst³, B.S.A. Schuberth⁴ & D. R. Davies⁵
- 1. Bullard Laboratories, Department of Earth Sciences, University of Cambridge, Cambridge, UK (pjk49@cam.ac.uk)
- 2. Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, USA
- 3. Department of Earth Sciences, University of Oxford, Oxford, UK
- 4. Department of Earth and Environmental Sciences, Ludwig-Maximilians-University, Munich, Germany
- 5. Research School of Earth Sciences, Australian National University, Canberra, Australia

Large-low-shear velocity provinces (LLSVPs) dominate tomographic shear wave velocity (Vs) models of the deep mantle. The question, whether these long wavelength features are dominantly thermal or thermochemical structures, still remains unresolved. Information on their density structure and shear to compressional wave velocity (Vp) ratio is vital for assessing their influence on mantle dynamics.

Earth's normal modes provide an invaluable tool for probing the Earth's deep interior since they are global in character and affected by density variations in addition to velocity. In particular, Stoneley modes, confined to solid-liquid interfaces such as the core-mantle boundary (CMB), are primarily sensitive to structures in the D" region. Observations of these modes increase the depth resolution and provide unique constraints on the long wavelength structures in the deep mantle.

We make use of a recent normal mode splitting function data set of 143 modes including 33 modes sensitive to Vp and 9 CMB Stoneley modes. We combine these data with independent constraints from body waves and surface waves and invert jointly for lateral Vs and Vp variations in Earth's mantle. We investigate the characteristics of the Vs/Vp ratio and compare the obtained tomographic model SP12RTS to thermal and thermochemical models of mantle convection. In addition, we perform hypothesis tests for possible density structures in the lowermost mantle.

SP12RTS shows an increase in the Vs/Vp ratio up to 2500 km depth followed by a decrease towards the CMB as well as an anti-correlation between Vs and bulk sound velocity variations (Vc). Our tomographic-geodynamic model comparison implies that these characteristics can be explained by the presence of post-perovskite but allows no discrimination between isochemical and thermochemical models of mantle convection. Our density hypothesis tests indicate that previous studies, which suggested dense LLSVPs, can be reproduced using normal mode data available at the time, whereas current normal mode data are best explained by density models containing light LLSVPs.







On the temporal evolution of large-scale mantle structure and its relation to Pangea assembly and breakup

Shijie Zhong, Xi Liu

Dept. of Physics, University of Colorado at Boulder, Boulder, CO 80309-0390, USA szhong@colorado.edu

Maxwell Rudolph

Department of Geology, Portland State University, Portland, OR 97201, USA

Arguably the most important and challenging goal in geodynamics is to understand the two-way dynamics between tectonic plates and mantle convection. While it has long been recognized that the present-day degree-2 mantle structure as imaged seismically is closely related to the plate motions (Hager and O'Connell, 1981) and their history (<119 Ma) (Ricard et al., 1993; McNamara and Zhong, 2005), recent studies have expanded this concept, from two different perspectives, by seeking connections between Pangea assembly and breakup and mantle structure. First, it has been proposed that the large igneous provinces (LIPs) and kimberlite volcanism erupted mainly along the edges of the two major seismically slow anomalies above the core-mantle boundary (often referred to as the Africa and Pacific LLSVPs) (Torsvik et al, 2010). This has led to the proposal that the present-day degree-2 mantle structure has existed for >500 Ma (Torsvik et al., 2014), although its statistical significance has been challenged (Austermann et al., 2013; Davies et al., 2014). The proposals of the spatially stable Africa and Pacific LLSVPs and of the LIP eruptions along their edges have also been exploited in attempts to build global plate motion models since the Pangea assembly by providing a plate motion reference frame or inferring true polar wander (TPW) corrections to the plate motions (Torsvik et al., 2014). Second, mantle dynamics studies indicate that degree-1 mantle convection, which is expected with realistic lithospheric and mantle viscosity, may be needed for assembly of a supercontinent (e.g., Pangea) (Zhong et al., 2007). This suggests that the present degree-2 mantle structure may have been formed only after the Pangea assembly from an initially degree-1 structure – a scenario that is consistent with convection calculations with a proxy plate motion model that considers Pangea process (Zhang et al., 2010). In this presentation, in addition to critically reviewing these arguments, we present additional calculations of mantle structure evolution using different plate motion history models (Domeier and Torsvik, 2014; Bull et al., 2014). We show that while these different plate motion history models lead to two LLSVPs and degree-2 structures for the present-day, these plate motion models perturb significantly largescale mantle structures at different times, especially during the assembly of Pangea. We will also discuss calculations of long-wavelength geoid for the mantle with thermochemical piles and LLSVPs and their potential effects on TPW determinations and hence reconstruction of plate motion (i.e., net lithospheric rotation).





Effects of Composition and Temperature on the Phase Boundaries at 600-700 km Depths

S.-H. Dan Shim and Yu Ye, Arizona State University

The phase boundaries at 600-700 km depths (the post-spinel, post-garnet, and post-ilmenite boundaries) may play important roles in the thermochemical evolution of the Earth. Seismic studies have shown complex structures in the region and dynamic simulations have shown profound impacts of the phase boundaries on mantle convection. Despite numerous efforts, recent in-situ multi-anvil press studies have suggested that the depth and Clapeyron slope of the post-spinel boundary may not be consistent with those of the 660-km discontinuity. In seismology, while some of the structures have been attributed to lateral variations in temperature, many seismic observations cannot be explained solely by thermal origins. In addition, high temperature may alter the phase relations in the mantle transition zone. We have conducted in-situ X-ray diffraction measurements on mantle-related multi-phase systems in the laser-heated diamond-anvil cell at synchrotron beamlines, in order to measure the depths and Clapeyron slopes of the phase boundaries in different composition at a wide range of temperature. Our new data reveal (1) changes in phase relations at high temperatures and (2) compositional effects on the phase boundaries. We will also discuss implications for the structure and dynamics of the warm mantle in Archean.





Density jump across the 410 and 660 km seismic discontinuity beneath China: A new constraint on long-term mantle mixing and basalt-enriched transition zone

Shen, X., Teh-Ru Alex Song, L. Stixrude, C. Lithgow-Bertelloni, X.-Y. Yuan

- 1. Lanzhou Institute of Seismology, China Earthquake Administration, Lanzhou, China
- 2. Department of Earth Sciences, University College London, London, UK (alex.song@ucl.ac.uk)
- 3. Department of Earth Sciences, University College London, London, UK
- 4. Department of Earth Sciences, University College London, London, UK
- 5. Deutsches GeoForschungsZentrum GFZ, Potsdam, Germany



Subduction process operating over much of the Earth's history induces long-term mantle mixing, chemical heterogeneities and recycles volatiles into the mantle. Transition zone discontinuities, among all, hold the key to resolve the mystery of mass and heat transport in the Earth's mantle as well as the composition of Earths interior. Fundamental question concerning mantle mixing involves the distribution of chemical heterogeneities (e.g., harzburgite, basalt) or/and compositional layering in the deep upper mantle and transition zone. While pyrolite is thought to be representative of the bulk composition of the mantle, observed velocity jumps or impedance contrast across the 410 and 660 km discontinuities are often difficult to reconcile with such a composition.

To constrain composition and chemical heterogeneities in the transition zone, it is critical to constrain velocity jump, density jump and discontinuity gradient altogether. To tackle these observables, we involve direct converted waves (P410s, P660s) and the topside reflections (the multiples, PpP410s, PpP660s) in the context of receiver function technique and such a tactic minimizes common tradeoffs between velocity and density contrast involved in reflection data analysis. Furthermore, frequency-dependent analysis of receiver functions (0.05-1Hz) allows a detailed description of discontinuity gradient, which is a function of mantle composition (e.g., Mg#), temperature and hydration. Finally, discontinuity topography imaged by receiver functions allows access to the impact of incoherent stacking in the amplitude analysis.

We processed waveforms from 1000 stations of the Chinese seismic array using an automatic scheme to remove noisy waveforms and retained close to ~300,000 high quality receiver functions. During slowness stacking of direct converted wave and the multiples, we avoid interference from other mantle waves (PP, PPP, PcP, PP410s, PP660s) and stack receive functions across epicentral distances of 74-90 (62-76) degrees for the 410 (660) seismic discontinuity. The bootstrap method was used to obtain the amplitude estimates and their uncertainties. Finally, we correct the effect of incoherent stacking due to discontinuity topography on receiver function amplitudes. To estimate the velocity/density jump and discontinuity gradient across the 410/660, we compute reflectivity synthetics over a range of velocity/density jumps and discontinuity gradients and compare with observations.

We find that the 410 is very sharp (<< 5 km, Δ Vs=5-6%, $\Delta\rho$ =1.5-2%) and there is no significant gradient near the sharp transition. On the other hand, the 660 is best described by a sharp boundary (<< 5 km, Δ Vs=4.25-4.75%, $\Delta\rho$ =4.5-5%) with a much more substantial gradient near it



(> $2x10^{-3}$ 1/s). Note that these estimates are subject to regional mantle attenuation Qs of 100-200.

Our observations are not consistent with a mechanical mixing mantle in a pyrolitic composition (82% harzburgite, 18% basalt). Instead, observed density jumps across the 410 and the 660 are more consistent with a substantially higher basalt fraction (~40%) in the transition zone beneath China. Compatible with a sharp 410, we propose that the harzburgite component in the transition zone is very depleted (Mg# ~ 0.95) and likely ancient, and the basalt enrichment is a consequence of long-term mantle mixing.






Evidence for the transport of water to the lower mantle from midmantle seismic anisotropy

Andy Nowacki, J-Michael Kendall, James Wookey and Asher Pemberton

School of Earth Sciences, University of Bristol (andy.nowacki@bristol.ac.uk)

To first order, the Earth exhibits seismic anisotropy (the variation of wave speed with direction) only in the uppermost and lowermost mantle, as well as the inner core. However, a growing body of evidence suggests that it is also present in the transition zone (TZ) and uppermost lower mantle (LM). We use the method of 'source-side' shear wave splitting to observe anisotropy in the regions of deep earthquakes (>200 km) distributed globally. This technique removes the effects of anisotropy near well-characterised receiver stations to infer the splitting at the source, allowing us to probe the midmantle where slabs appear to be impinging on the LM.

Over 130 observations, mainly beneath South America, Tonga and Japan, reveal a consistent pattern: the data are best fit with a style of anisotropy which has a rotational symmetry axis pointing upwards along the slab. This pattern of anisotropy is typical of approximately uniaxial flattening of material which develops a lattice preferred orientation (LPO) by dislocation creep. This is consistent with the expected mechanics of slab sinking and supported by the P-axes of moment tensor solutions for the events we analyse. The amount of anisotropy does not appear to be related to the depth, meaning we can confine the source region to either the slab itself, or the top of the LM.

The amount of anisotropy makes it unlikely that perovskite in the LM is the source, as it would require a high-strain layer over 1500 km thick. We can rule out other phases on similar grounds. Dense hydrous magnesium silicate (DHMS) phases, which are known to become stable at the base of the TZ in cold conditions (the so-called 'alphabet' phases, such as D and superhydrous B), do however have very large single crystal anisotropy, would likely develop LPO, and if distributed over a few tens of km could produce the splitting we observe at subduction zones. If these phases are as ubiquitous as our data imply, then significant water volumes may be brought into the LM over geological time, influencing our understanding of subduction zone dynamics and lower mantle composition.





A hydrous mantle transition zone indicated by ringwoodite included within diamond

D.G. Pearson¹, F.E. Brenker², F. Nestola³, J.C.R. McNeill⁴, L. Nasdala⁵, M.T. Hutchison⁶, S. Matveev¹, K. Mather⁴, G. Silversmit⁷, S. Schmitz², B. Vekemans⁷ and L. Vincze⁷

1: Department of Earth & Atmospheric Sciences, 1-26 Earth Sciences Building,

University of Alberta, Edmonton, Alberta, Canada, T6G 2E3.

2: Geoscience Institute - Mineralogy, Goethe University, Altenhoeferallee 1, 60438 Frankfurt, Germany

3: Dipartimento di Geoscienze, Università di Padova, Italy

4: Department of Earth Sciences, Durham University, Durham, UK

5: Institute of Mineralogy and Crystallography, University of Vienna, Austria

6: Trigon GeoServices Ltd., Las Vegas, NV 89146, U.S.A

7: Department of Analytical Chemistry, Ghent University, Krijgslaan 281 S12, B-9000 Gent, Belgium

The ultimate origin of water in the Earth's hydrosphere is from the deep Earth - the mantle. Theory and experiments have shown that whereas the water storage capacity of olivinedominated shallow mantle is limited, the Earth's Transition Zone (TZ) could be a major repository for water, due to the ability of the higher-pressure polymorphs of olivine wadslevite and ringwoodite - to host up to ~2.5wt. % H₂O. A hydrous TZ may play a key role in terrestrial magmatism and plate tectonics yet despite experimental demonstration of the water-bearing capacity of these phases, geophysical probes such as electrical conductivity have provided conflicting results, and the issue of whether the TZ contains abundant water remains highly controversial. We report X-ray diffraction, Raman and infra-red spectroscopic evidence for the first terrestrial occurrence of any higher pressure polymorph of olivine: ringwoodite, included in a diamond from Juína, Brazil. The ringwoodite has a Mg# of ~ 75, suggesting that it may be mantle hybrised with a more fertile component such as subducted oceanic crust. The water-rich nature of this inclusion (~1.5 wt%), along with the preservation of ringwoodite, is the first direct evidence that, at least locally, the TZ is hydrous. Water solubility decreases with increasing temperature in ringwoodite and wadsleyite, hence a transition zone equilibrated to the mantle adiabat may contain less than 0.5% water. The water-rich nature of our ringwoodite may be the first clear chemical evidence of the presence of cool, thermally unequilibrated subducted slabs in parts of the TZ. This amount of water helps to reconcile measured TZ seismic velocities with those predicted from lab experiments. The finding also indicates that some kimberlites must have their primary sources in this deep mantle region, as indicated by radiogenic isotope systematics.







Seismic evidence for sulphide melt in the upper mantle.

Michael Kendall¹, George Helffrich¹ and James Hammond²

¹School of Earth Sciences, University of Bristol, UK. ²Department of Earth Science and Engineering, Imperial College London, UK.

A number of seismic measurements can be used to map melt distribution in the deep Earth. These include seismic P- and S-wave velocities derived from tomography, Vp/Vs ratios obtained from receiver functions, and estimates of seismic anisotropy and



attenuation. In many active regions these observations are readily explained by silicate melt in the upper 100 km of the mantle. While low wavespeeds may be attributed to thermal effects in tectonically young or actively volcanic regions, in older, tectonically stable regions low velocity anomalies apparently persist even past the decay time of any thermal perturbation, rendering such a mechanism implausible. Low volume melts can also reduce wavespeeds, but their buoyancy should drain them upward away from source regions, preventing significant accumulation if they are able to segregate. Sulfide, ubiquitous as inclusions in lithospheric mantle xenoliths, forms dense, non-segregating melts at temperatures and volatile fugacities characteristic of even old lithospheric mantle. We show that 1–5 volume percent sulfide melts can act to permanently create reductions up to 5.5% in seismic wavespeeds in areas of the lithosphere and the asthenosphere disturbed by prior melting events that carry and concentrate sulfide.





Ferric iron and its influence on Earth's deep structure

Robert Myhill¹, Fanny Sorbadere¹, Daniel J Frost¹, Tiziana Boffa Ballaran¹, Alan Woodland²

- 1. Bayerisches Geoinstitut, University of Bayreuth, 95440 Bayreuth, Germany
- 2. Institut für Geowissenschaften, Goethe-Universität, 60323 Frankfurt am Main, Germany

Several lines of evidence suggest that Earth's mantle was progressively oxidised early in its history. Likely factors contributing to this oxidation are recycling of an oxidised surface at subduction zones and iron disproportionation in the lower mantle. For example, efficient loss of iron after the formation of ferric-rich perovskite could leave the lower mantle with about 40% of iron as Fe³⁺.

The evolution of oxygen concentration and homogeneity within the Earth's mantle remains poorly understood. This evolution is important as mantle redox state would have been a key control on the composition of late core-forming liquids and the early atmosphere. The current oxidation state of the Earth's interior continues to control the stability and composition of migrating fluids and melts.

The current study investigates the effect and partitioning of ferric iron into solid and melt phases in the upper mantle. Multi-anvil experiments are designed to provide new constraints on interaction parameters within Fe^{3^+} -bearing solid solutions, and on the stability of silicates, oxides and melts under different oxidation states. We focus particularly on Fe3+-rich phases, such as spinel, garnet and silicate melts.

A common observation made on experiments run under relatively oxidising conditions (around the Re-ReO₂ buffer and above) is the presence of a partial melt at temperatures well below the mantle solidus. Experiments performed at 6 GPa show that the addition of ferric iron to reduced bulk compositions causes a profound decrease in melting temperatures, especially in Al-poor compositions where ferric iron cannot be incorporated into garnet or spinel. Melts in equilibrium with olivine, pyroxene and garnet are stabilised at <1673K. We suggest that the formation of dense Fe³⁺ -rich melt during upwelling of partially oxidised material could act as a mantle oxygen filter, reducing residual ferric concentrations and redistributing oxygen to more reduced regions.





Global radially anisotropic whole-mantle structure from multiple datasets

Ana MG Ferreira¹ and Sung-Joon Chang²

¹Department of Earth Sciences, University College London, UK ²Dept. of Geophysics, Kangwon National University, South Korea

When detected, seismic anisotropy can potentially be an indicator of mantle flow and thus can help us discriminating different geodynamical processes and competitive thermo-chemical convective models of the Earth's interior. However, the imaging and



interpretation of global anisotropy is challenging. For example, Ferreira et al. (2010) reported that a data misfit reduction of only around 2% is obtained when lateral variations in radial anisotropy in global tomographic inversions are included compared to inversions only allowing 1-D variations in anisotropy. This small misfit reduction is comparable to the effect on data misfit of using different crustal corrections, thereby indicating a strong influence of the crust in the models. We discuss new inversions for models of 3-D isotropic and radially anisotropic shearwave velocity in the whole mantle derived from new surface-wave and body-wave data with complementary sensitivities to Earth's structure. Our data set includes over 53 million fundamental mode and overtone surface wave phase velocity measurements and group velocity data from several published studies. It includes relatively short period data down to T~25 s that constrain crustal thickness. In addition, over 200,000 body-wave travel times are utilized to constrain lower mantle structure. We experiment with model regularization, different data weighting schemes and test the impact of the various datasets on the retrieved models. Variations of shear-wave velocity and anisotropy are parameterized using 21 depth splines and spherical harmonics up to degree 35; crustal thickness perturbations are also parameterized in terms of spherical harmonic functions up to degree 35. We find that the various datasets used are highly complementary, allowing us to achieve good resolution in both isotropic and anisotropic structure throughout the upper ~1000 km of the mantle. Our images of Vs share common features with previous 3-D S-velocity models, such as high-velocity anomalies beneath cratons and subduction zones, with stagnant slabs being often better defined than in previous global tomographic models. The anisotropic models show some similarities with previous global 3-D models, and, importantly, seem to be more consistent with various persistent features in previous regional studies of radial anisotropy. We discuss these robust features of our models and their implications.





The noble gas record of terrestrial volatile origin and reservoir interaction.

C. J. BALLENTINE 1, R. BURGESS 1, H. SUMINO 2, D. HILTON 3, D. GRAHAM 4, P. VAN KEKEN 5, D. CHAVRIT 1, L. RUZIE 1, P.L. CLAY 1, B. JOACHIM 1, B. WESTON 1, L.D.A. JEPSON 1 AND M. BROADLEY 1

1 U. Manchester, (<u>chris.ballentine@manchester.ac.uk</u>) 2 U. Tokyo, (sumino@egchem.s.u-tokyo.ac.jp)

2 U. TOKYO, (Summo @equinem.s.u-loi

3 UCSD, (<u>drhilton@ucsd.edu</u>)

4 OSU, (<u>dgraham@coas.oregonstate.edu</u>) 5 U. Michigan, (<u>keken@umich.edu</u>)

Noble gas isotopes provide a powerful tool to investigate the origin of volatiles within the deep Earth and the processes that have controlled their distribution and chemical evolution through geological time. Advances in mass spectrometry and discovery of samples that provide a unique record of different mantle environments have provided a new view on the accretionary processes that fix volatiles within the planet and the subsequent modification of the mantle through volatile recycling. Halogens provide an important adjunct to the information provided by the noble gases, also being highly incompatible during melting and hydrous fluid mobile. I report recent results that bring together the information from the noble gases and recent halogen studies.





Understanding $\delta^{15}N$ variations in the mantle using internal variabilities in deep mantle diamonds

R. E. Southworth¹, S. Mikhail², D. Howell³, A.B. Verchovsky⁴, F. Brenker⁵, and A.P. Jones¹

- 1. Dept. of Earth Sciences, University College London, UK (*correspondence: rebecca.southworth.11@ucl.ac.uk)
- 2. School of Geosciences, University of Edinburgh, UK
- 3. CCFS ARC Center of Excellence, and GEMOC, Macquarie University, Australia
- 4. Dept. of Physical Sciences, The Open University, UK
- 5. Geoscience Institute / Mineralogy, Goethe University, Frankfurt, Germany



The average for both $\delta^{15}N$ and $\delta^{13}C$ values of mantle-derived diamonds is -5 ‰ [1-2]. However, some individual mantle diamonds can show a very large range in $\delta^{15}N$ value with very narrow ranges for their corresponding $\delta^{13}C$ values [1]. These data can be explained by either (a) nitrogen isotope heterogeneity in the mantle (subduction induced or primordial) or (b) N-isotope fractionation during diamond growth. The former is the subject of this contribution.

To further investigate the possibility of mantle heterogeneity, we will have determined the internal C-N stable isotope variability for 10 monocrystalline diamonds from Juina, Brazil. Bulk stable isotope data show diamonds from Juina have a narrow range of δ^{13} C values for upper and lower mantle-derived diamonds (4 ‰), with a corresponding range of *ca*.10 ‰ for their δ^{15} N values [2]. These narrow ranges for both upper and lower mantle peridotitc diamonds were used to propose a homogeneous mantle source beneath the Amazonian craton (Brazil) produced by whole mantle convection [2]. However, it was shown in [1] that δ^{15} N within an individual monocrystalline diamond from Juina can vary by up to +20 ‰ (one eclogitic and one unknown), while the corresponding range of δ^{13} C values vary by <3.4 ‰ [1]. The data in [1] cast doubts on whether or not the mantle is well-mixed with respect to nitrogen and further suggests that carbon and nitrogen are de-coupled during eclogitic diamond formation.

We have used stepwise combustion gas-sourced mass spectrometry to determine the carbon and nitrogen isotope values and nitrogen concentrations within 10 diamonds from Juina, Brazil. We will interrogate the δ^{13} C- δ^{15} N-[N] data from these samples to investigate the stable isotope systematics that are recorded in diamond growth beneath the Amazonian craton. [1] Mikhail *et al.* (2014). *Chem. Geol.*, **366**, 14-23. [2] Palot *et al.* (2012). *EPSL*, **357-358**, 179-

[1] Mikhail et al. (2014). Chem. Geol., **366**, 14-23. [2] Palot et al. (2012). EPSL, **357-358**, 179-193.





Probing the water content of the Earth's mantle

J Brooke, G Bromiley, K Whaler

School of Geoscience, University of Edinburgh (jennifer.brooke@ed.ac.uk)

It has been established that the majority of nominally anhydrous minerals (NAMs) in Earth's mantle can incorporate water in the form of structurally bound hydrogen and that, as a result, there may be a significant volume of water stored in the mantle



(estimates range from almost none to several ocean volumes). This water could play a key role in the geodynamics of the Earth's interior and quantifying the amount of water in mantle minerals is therefore an important step in understanding many deep-Earth processes. However, the deep Earth is clearly not an accessible area of study and models of the interior structure of the planet are primarily based on geochemical and geophysical considerations, as well as analysis of what samples are available. The water content of the mantle can be estimated through the analysis of MORB, OIB and xenolith material but these estimates may not be representative of the whole mantle as MORB/OIB samples typically derive from shallow depths and there is significant potential for modification of water content during xenolith ascent.

As hydrogen is highly mobile it acts as the dominant charge-carrying species in mantle minerals and, consequently, electrical conductivity is particularly sensitive to even small changes in water content. It is, therefore, possible to use geophysical techniques such as magnetotellurics (MT) to 'map-out' the water content of the mantle although accurate interpretation of such data relies on good quality conductivity data from mineral physics studies. Difficulties in measuring conductivity in wet (hydrogen-bearing) samples, coupled with the fact that traditional diffusion experiments do not provide thermodynamic data on hydrogen self-mobility, mean that the influence of hydrogen on conductivity remains poorly constrained - with different groups of researchers in different laboratories obtaining calculated mantle reservoir water contents that differ by as much as several orders of magnitude.

Our experimental design investigates electrical conductivity in synthetic hydrous olivine by considering hydrogen-deuterium exchange in single crystals. Hydrogen-saturated crystals are synthesised under mantle conditions (so that the hydrogen incorporated is relevant to the conditions being studied), then sealed in a gold capsule with deuterium oxide, allowing deuterium to exchange with hydrogen under controlled pressure and temperature conditions for a specified time period. The resulting H-D exchange profiles can be characterised using SIMS and fitted to Fick's law; extrapolated diffusion data for hydrogen self mobility can then be directly related to electrical conductivity through the Nernst-Einstein equation.

Following experiments on synthetic olivine, the method will also be used to investigate high pressure polymorphs of olivine, allowing us to constrain hydrogen mobility across all parts of the mantle.





Helium Diffusion in Mantle Minerals from First Principles

John Brodholt and Kai Wang

1. UCL, UK

2. Nanjing University, China

We have used ab initio DFT methods to calculate the diffusion coefficients of He in olivine, perovskite and post-perovskite under lower mantle conditions. We have done this using two methods. The traditional way to calculate diffusion coefficients in a crystal is to calculate the migration enthalpy from the energy barrier of lowest energy pathway, and the attempt frequency from phonon frequencies at the start and saddle point positions along the migration path. However, at high temperatures He diffusion is so fast that we can simulate its diffusion directly in an ab initio molecular dynamics (MD) simulation as well. This is very unusual in a crystalline material since atomic diffusion is generally too slow to occur during normal simulation timescales. Although the statistics of a single He atom diffusing in perovskite do not allow us to calculate the diffusion coefficient from the root mean squared displacement, as in a fluid of melt, we can calculate the diffusion coefficient from the two methods are similar. For olivine, our diffusion coefficients agree well with the most recent experiments.

The diffusion coefficients of He are fast, depending strongly on temperature. For instance, in the upper mantle He can diffuse between 1 and 50 meters in 1 million years. In the deepest Earth, diffusion coefficients are sufficiently high so as to be able to homogenise reservoirs of up to 50 km over the age of the Earth. The source of 3/4He reservoirs must, therefore, be larger than this if they are to exist for the age of the Earth.





Relating the chemistry and structure of the deepest mantle to the geochemistry of mantle melts erupted at the surface

Matthew G. Jackson

Department of Earth Science, UC Santa Barbara, Santa Barbara, CA 93106, 93106, USA (jackson@geol.ucsb.edu)

The deepest mantle is emerging as a seismically anomalous and geochemically important region of the Earth. Two large low-shear-velocity provinces (LLSVPs) are identified in the lower mantle. The LLSVPs may host primitive material that has been preserved since early differentiation of the planet. Additionally, regions of partial melt that have survived long-term cooling of the planet—called a basal magma ocean (BMO)—may have persisted in LLSVPs. Subducted surface materials, including oceanic crust, sediment and depleted mantle lithosphere, are also suggested to reside in the LLSVPs. While the LLSVPs are inaccessibly deep, mantle plumes may provide a means to probe the composition of these deep reservoirs.

If a BMO persists in the deepest mantle, and if deep-seated mantle plumes are anchored to the core-mantle boundary, then it may be possible to identify the geochemical signatures associated with the BMO in plume-fed hotspot lavas erupted at the surface. However, there are key impediments to identifying the geochemical fingerprints of a BMO in hotspot lavas. The community requires both a better understanding of the mineralogy and phase relations of the deepest mantle, and better constraints on the mineral-melt partition coefficients of lower mantle phases at the relevant depths and pressures. There is enormous opportunity to link geochemical signatures identified in hotspot lavas to the deepest Earth. For example, melts in equilibrium with Ca-perovskite exhibit rather dramatic enrichments in the elements Ti, Ta and Nb (TITAN); BMO melts in equilibrium with Ca-perovskite may explain enrichments in TITAN elements that are observed in OIB lavas with the highest ³He/⁴He.

In addition to hosting primitive ³He/⁴He, the LLSVPs are also suggested to be a repository of subducted materials that have accumulated over geologic time. The higher viscosity of the deep mantle may provide a means to effectively isolate subducted materials so that their geochemical signatures can be preserved in the deepest Earth for >2.5 Ga. These "graveyards" of slab material may intermingle with primitive material so that both primitive and recycled surface materials are entrained into upwelling mantle plumes.

If mantle plumes entrain material from the LLSVPs via a non-turbulent process, the geographic distribution of geochemical components in hotspot volcanoes may relate to the geochemical geometry of enriched domains in the lower mantle. Mantle plumes may emerge from the margins of the LLSVPs so that the side of the plume anchored to the LLSVP will entrain (enriched?) material from the LLSVP, while the side of the plume facing away from the LLSVP will entrain (depleted?) ambient mantle material. This mechanism has been invoked to explain the geochemical distribution of components in the Hawaiian plume, which emerges from the northern margin of the Pacific LLSVP: The southern side of the Hawaiian plume, which faces the LLSVP, melts to form the geochemically-enriched Loa volcanic lineament, and the northern side of the volcanic plume melts to form the less enriched Kea volcanic lineament. A number of hotspots in the Pacific have been found to exhibit bilateral heterogeneity, and the patterns of geochemical enrichment at each hotspot may relate to the location of the mantle plume relative to the LLSVP.





Paleozoic Plate Motion History and the Longevity of Deep Mantle Heterogeneities

A. L. Bull¹, M. Domeier¹, T. H. Torsvik¹⁻³

¹ Centre for Earth Evolution and Dynamics (CEED), University of Oslo, 0316 Oslo, Norway. a.l.bull@fys.uio.no

 ² Geodynamics, Geological Survey of Norway, 7491 Trondheim, Norway.
³ School of Geosciences, Witwatersrand University, WITS 2050 Johannesburg, South Africa.



Numerical studies of mantle convection have attempted to explain tomographic observations that reveal a lower mantle dominated by broad regional areas of lower-than-average shear-wave speeds beneath Africa and the Central Pacific. The anomalous regions, termed LLSVPs ("large low shear velocity provinces"), are inferred to be thermochemical structures encircled by regions of higher-than-average shear-wave speeds associated with Mesozoic and Cenozoic subduction zones. The origin and long-term evolution of the LLSVPs remains enigmatic. It has been proposed that the LLSVP beneath Africa was not present before 200 Ma (i.e. before and during most of the life-time of Pangea), prior to which time the lower mantle was dominated by a degree-1 convection pattern with a major upwelling centred close to the present-day Pacific LLSVP and subduction concentrated mainly in the antipodal hemisphere. The African LLSVP would thus have formed during the time-frame of the supercontinent Pangea as a result of return flow in the mantle due to circum-Pacific subduction. An opposing hypothesis, which propounds a more long-term stability for both the African and Pacific LLSVPs, is suggested by recent palaeomagnetic plate motion models that propose a geographic correlation between the surface eruption sites of Phanerozoic kimberlites, major hotspots and Large Igneous Provinces to deep regions of the mantle termed "Plume Generation Zones" (PGZs), which lie at the margins of the LLSVPs. If the surface volcanism was sourced from the PGZs, such a link would suggest that both LLSVPs may have remained stationary for at least the age of the volcanics. i.e., 540 Myr. To investigate these competing hypotheses for the evolution of LLSVPs in Earth's mantle, we integrate plate tectonic histories and numerical models of mantle dynamics and perform a series of 3D spherical thermochemical convection calculations with Earth-like boundary conditions. We improve upon previous studies by employing a new global plate motion model to impose surface velocity boundary conditions for a time interval that spans the amalgamation and subsequent break-up of Pangea. Our results are distinct from those of previous studies in several important ways: our plate model explicitly includes (i) absolute longitudinal reconstructions and (ii) TPWcorrection, and (iii) our model extends back to the mid-Paleozoic (410 Ma). We find that, were only the Pacific LLSVP to exist prior to the formation of Pangea, the African LLSVP would not have been created within the lifetime of the supercontinent. We also find that, were the mantle to be dominated by two antipodal LLSVP-like structures prior to the formation of Pangea, the structures would remain relatively unchanged to the present day and would be insensitive to the formation and break-up of the supercontinent. Our results suggest that both the African and Pacific LLSVPs have remained close to their present-day positions for at least the past 410 Myr.





The composition of the earliest picrites erupted by the Ethiopia plume

N. W. Rogers¹, F. M. Stuart², I. Parkinson¹, S. Hammond¹, M. Fehr¹, M. Davies¹ & G. Yirgu³

 ¹ Department of Environment, Earth & Ecosystems, The Open University, Milton Keynes, MK7 6AA, UK. (nick.rogers@open.ac.uk)
² Isotope Geosciences Unit, SUERC, East Kilbride G75 0QF, UK
³ Dept. of Geology and Geophysics, University of Addis Ababa, Ethiopia.

Mantle plumes are widely believed to originate near the coremantle boundary and consequently provide constraints on Earth structure and differentiation history. The earliest basalts erupted



by mantle plumes are typically hotter than those derived from the convecting upper mantle at mid-ocean ridges and the majority of basalts erupted from ocean islands. They, therefore, offer a particular window into the composition of the deep mantle. For example, the first picrites erupted by the Iceland plume have a high proportion of primordial He (${}^{3}\text{He}/{}^{4}\text{He} \sim 50 R_{a}$) yet a range in radiogenic isotope and incompatible trace element ratios that overlap mid-ocean ridge basalts. This cannot be reconciled with pristine primordial mantle dominating the plume head material.

In an attempt to place further constraints on the deep mantle source of plumes we have analysed the He-Sr-Nd-Pb isotopic composition of the earliest picrites from the ~30 Ma Ethiopian flood basalt province. The picrites are from the Dilb (Chinese Road) section and are characterized by high Fe and Ti contents for MgO = 10 - 22 wt. %. This implies that the parent magma was derived from a high temperature small melt fraction, most probably from the Afar plume head. The picrite ³He/⁴He never exceed 21 R_a , and there is a negative correlation with MgO, the highest ³He/⁴He corresponding to MgO = 15.36 wt. %. ⁸⁷Sr/⁸⁶Sr_i (0.70392–0.70408) and ¹⁴³Nd/¹⁴⁴Nd_i (0.512912-0.512987) plot away from typical MORB and OIB while age-corrected Pb isotopes display a significant range (e.g. ²⁰⁶Pb/²⁰⁴Pb = 18.70-19.04) and plot above the NHRL. Such values contrast with estimates of the modern Afar mantle plume which has lower ³He/⁴He and Sr, Nd and Pb isotope ratios that are more comparable with typical OIB.

These results imply either interaction between melts derived from the Afar mantle plume and a lithospheric component, or that the original Afar mantle plume had a rather unique radiogenic isotope composition. Regardless of the details of the origins of this unusual signal, our observations place a minimum ${}^{3}\text{He}/{}^{4}\text{He}$ value of 21 R_a for the Afar mantle plume, significantly greater than the present day value of 16 R_a, implying a significant reduction over 30 Myr. In addition the Afar source was less degassed than convecting mantle but more degassed than mantle sampled by the proto-Iceland plume. This suggests that the largest mantle plumes are not sourced in a single deep mantle domain with a common depletion history and that they do not mix with shallower mantle reservoirs to the same extent.





Isotope signatures from a melting mantle

Hein van Heck¹, **Huw Davies¹**, Tim Elliott², Don Porcelli³

- 1. Cardiff University, School of Earth and Ocean Sciences (<u>DaviesJH2@cardiff.ac.uk</u>)
- 2. University of Bristol
- 3. University of Oxford



Many outstanding problems in Earth science relate to the geodynamical explanation of geochemical observations. Nowadays, extensive geochemical databases of surface observations exist, but satisfying explanations of underlying processes are lacking. Longstanding problems such as; the possible existence and sustainability of chemically distinct reservoirs in the Earth's mantle; the possible need of layered convection through much of Earth's history to explain chemical observations; and the heat flow paradox remain unsolved. One way to address these problems is through numerical modeling of mantle convection while tracking chemical information throughout the convective mantle. In the past decade, both numerical mantle convection codes and computer power have grown sufficiently to begin to grasp much of the full problem of the complex interlocking physics, chemistry and thermodynamics of the convecting mantle, lithosphere, continents and atmosphere.

We implemented a new way to track both bulk composition and concentration of trace elements in the well-developed benchmarked mantle convection code TERRA. Our approach is to track bulk composition and trace element abundance via particles. One value on each particle represents bulk composition; it can be interpreted as the basalt component. The system is set up to track radioactive isotopes (in the U, Th, K system), noble gas isotopes (He, Ar) and Pb isotopes. In our model, chemical separation of bulk composition and trace elements happens at self-consistent, evolving melting zones. Melting is defined via a composition dependent solidus, such that the amount of melt generated depends on pressure, temperature and bulk composition of each particle. A novel aspect is that we do not move particles that undergo melting; instead we transfer the chemical information carried by the particle to other particles. Molten material is instantaneously transported to the surface, thereby increasing the basalt component carried by the particles close to the surface, and decreasing the basalt component in the residue. For molten material that arrives at the surface, a part of its content of noble gasses is moved into a separate atmosphere reservoir.

Results will be presented in which we test and show the success and limitations of our implementation. We choose to use a simplified setup with calculations of incompressible mantle convection in spherical geometry avoiding for now further complexities such as elastic/plastic deformation. For these calculations we will show: 1: The evolution of bulk composition over time, showing the build up of oceanic crust (via melting induced chemical separation in bulk composition); i.e. a basalt-rich layer at the surface overlying a thin layer of depleted material (Harzburgite), and the transportation of these chemical heterogeneities through the deep mantle. 2: The evolution of the concentrations and abundances of different isotopes of the elements: U, Th, K, Pb, He and Ar, throughout the mantle as well as the atmosphere. 3: A match to analytical predictions (Rudge, EPSL, 2006) linking melting age to Pb pseudo-isochron age.





Mantle mixing: processes and modeling

Peter E. van Keken

Department of Earth and Environmental Sciences University of Michigan Ann Arbor, MI 48105 USA keken@umich.edu



The Earth's mantle is heterogeneous at multiple scales as seen by geochemical and geophysical studies. The introduction of heterogeneity is caused by early Earth differentiation and ongoing differentiation due to melting at the surface and possibly deeper in the mantle. Mantle convection partly erases the introduced heterogeneity, but the strongly variable nature of the Earth's mantle allows for the preservation of isotopic and structural heterogeneity over billions of years. The sampling of heterogeneity at mid-oceanic ridges and mantle plumes introduces additional filtering upon melting.

I will review recent progress on the studies of mantle mixing with a focus on the role of mantle dynamics and how this is assessed by dynamical modeling studies. The introduction of oceanic crust into the mantle by subduction is volumetrically important and I will specifically test the hypothesis that the long-term recycling of oceanic crust can satisfy a significant number of geochemical and geophysical observations following earlier suggestions by Hofmann and White (1982) and quantitative modeling in Brandenburg et al. (2008) as summarized in van Keken (2013).

Citations:

Brandenburg, J.P., E.H. Hauri, P.E. van Keken, C.J. Ballentine, 2008. A multiple-system study of the geochemical evolution of the mantle with force-balanced plates and thermochemical effects, Earth Planetarv Science 276. and Letters. 1-13. Hofmann, A.W., W.M. White, 1982. Mantle plumes from ancient oceanic crust, Earth and Planetary Science Letters, 421-436. 57, van Keken, P.E., 2013. Mantle mixing: processes and modeling, 351-371, in: Physics and Chemistry of the Earth's Deep Interior, S. Karato (editor), 412pp, Blackwell.





The potential for palaeo-geomagnetism to help constrain lower mantle dynamics

Andrew $\textbf{Biggin}^{a},$ Neil Suttie^a, Julien Aubert^b , Bernhard Steinberger $\overset{c}{,}$ Richard Holme^a

- a. Geomagnetism Lab., School of Environmental Sciences, University of Liverpool. L69 7ZE, UK
- b. Bureau 459, Institut de Physique du Globe de Paris, 1 Rue Jussieu, 75238, Paris, France
- c. Helmholtz Centre Potsdam, GFZ German Research Centre for Geosciences, 14473 Potsdam, Germany

<u>biggin@liv.ac.uk</u>

The Earth's internal magnetic field is generated by the geodynamo, a heat engine that is ultimately driven by the flow of heat across the core-mantle boundary. Varying conditions in the lowermost mantle may alter the magnitude of the local heat flux and profoundly affect the geodynamo. Spatial variations in core-mantle boundary heat flux, suggested from seismology, may explain the locations of intense geomagnetic flux patches observed in the present day field. Palaeomagnetism offers a unique perspective on deep Earth processes occurring back into deep time. Palaeomagnetic records show geomagnetic field behaviour varying considerably over tens to hundreds of million years, timescales comparable to that which mantle convection is expected to modify CMB heat flow. Furthermore, the timings of transitions in geomagnetic behaviour are suggestive of mantle forcing mechanisms related to true polar wander and mantle plume activity. These records and mechanisms will be reviewed and the potential of future types of palaeo-geomagnetic measurements discussed.

The primary palaeo-geomagnetic signal for the last 500 million years is magnetic polarity reversal frequency. This record does not span an entire supercontinent cycle however and there is limited scope to expand it in the future. The case will be made that considerable potential lies in the expansion of palaeomagnetic intensity records and their comparison to synthetic records output from dynamo simulations. The state-of-the-art of full vector palaeomagnetic records, and potential links to mantle dynamics since the Precambrian will be presented.







Quantifying lithological variability in the mantle

Oliver Shorttle¹, John Maclennan¹, Sarah Lambart²

1. Department of Earth Sciences, University of Cambridge, Cambridge, United Kingdom. 2. GPS, Caltech, Pasadena, CA, United States.

As the primary flux of material from the mantle to the surface, the basalts erupted at mid-ocean ridges (MORB) are a key resource for investigating the mantle's chemical composition. However, despite the



large volumes of oceanic lithosphere returned to the mantle by subduction, it has proven difficult to quantify this material's involvement in melt production. Even more enigmatic is the signal of refractory material in the source, which may barely melt if other more fusible lithologies are present. Here we demonstrate how combining thermodynamic models of melting, the density of phase assemblages at high pressure and geochemical observations, can allow the proportion of refractory and enriched material in the mantle source to be estimated and place limits on mantle potential temperature.

We focus on determining the abundance of recycled material in the mantle beneath Iceland, where we have excellent geophysical and geochemical constraints on the melting process and the chemical variability in the mantle. Firstly, the lithologies contributing to melting are identified by a quantitative comparison of the major element composition of erupted basalts to a database of experimental partial melts (Shorttle and Maclennan, 2011). Secondly, a mass balance is calculated between the endmember basalt compositions and the fully mixed melt to obtain the relative proportion, by mass, of enriched and depleted melts. A three-lithology melting model is then developed (peridotite-harzburgite-basalt), which uses the appropriate melting parameterisations to account for the differences in productivity between each lithology. The melting model enables the calculated abundance of the different endmember melt compositions to be projected back into mass fractions of solid mantle domains.

Applying this method to Iceland demonstrates that ~5% of the source is recycled basaltic material and at least 20% must be highly refractory and essentially un-melting. Combining geophysical constraints with the modelled high-pressure densities of the three lithology assemblage constrains excess mantle temperature beneath Iceland to be at least 150°C. This density modelling further shows that the proportion of recycled basaltic material carried in the Iceland plume is near the limit of what maintains plume buoyancy in the shallow mantle. Extending this density analysis to other plume localities such as Hawaii, shows that some previous estimates of plume pyroxenite fraction may mean the plume would not be buoyant unless it were to also contain a significant fraction of harzburgite.





Of mantle plumes and secondary scale convection: Insights from whole mantle SEM-based seismic waveform tomography

Barbara Romanowicz ^{1,2}, Scott French², Vedran Lekic³

¹ Institut de Physique du Globe, Paris

² Department of Earth and Planetary Science, U.C. Berkeley ³ Department of Geological Sciences, University of Maryland e-mail: barbara@ipgp.fr

Global mantle seismic tomography has long revealed coherent long wavelength structures in the uppermost mantle, reflecting surface



tectonics: slower than average ridges and back-arcs, fast continental roots, and the progressive thickening of the oceanic lithosphere with the age of the plate. The other most salient features of global mantle structure are the two large antipodal low shear velocity provinces at the base of the mantle, whose role in global mantle dynamics is not yet understood, yielding debates between proponents of "top down" and "bottom up" control on mantle circulation.

Many questions remain on the detailed morphology of convection patterns in the mantle. While higher resolution regional scale studies have shown a variety of behaviors of subducted slabs, some stagnating in the transition zone, others penetrating into the lower mantle, low velocity structures - reflecting hotter than average upwellings - have been more difficult to resolve. In particular, some numerical computations and laboratory experiments predict the presence of secondary convection at the scale of the whole upper mantle, but only one study (Katzmann et al., 1999) has hinted at its seismological detection on a particular "corridor" between Fiji Islands and Hawaii. Likewise, the depth extent of the low velocity roots of hotspot volcanoes is still debated, in the context of the existence or not of "mantle plumes".

With the advent of numerical methods for accurate seismic wavefield computations, it is now possible to apply the tools of waveform tomography to better map the distribution, throughout the mantle, of slow velocity anomalies, previously "hidden" by wavefront healing effects that are not captured by approximate wave propagation methods. Using waveform tomography based on the spectral element method (SEM), we have recently constructed a global, radially anisotropic, shear velocity upper mantle model (SEMum2, French et al., 2013) and have now extended it to the whole mantle by adding shorter period body waveforms (model SEMUCB-WM1, French and Romanowicz, in prep.). Inspection of this model shows long wavelength structures that are in good agreement with other recent global shear velocity models constructed under more restrictive approximations (e.g. S40RTS, Ritsema et al. 2011; S362ANI, Kustowski, et al. 2008). However, the model reveals better focused, finer scale structures both in the upper and in the lower mantle. In the upper mantle, we observe quasi-periodic, low velocity structures with a wavelength of ~2000 km, elongated horizontally for thousands of kilometers in the direction of absolute plate motion (APM), most prominent in the depth range 200-300 km, but extending from the base of the lithosphere into the transition zone. These structures are present in all major ocean basins, but most prominently in the Pacific Ocean, where their presence agrees in wavelength and directions with structures found in the geoid through directional wavelet analysis (Hayn et al., 2012). Their periodicity, aspect ratio, and signal in the geoid suggest the presence of secondary convection at the scale of the upper mantle as well as channeling of flow into the low viscosity upper mantle. While these upper mantle structures are elongated horizontally, the rest of the mantle is dominated by vertically elongated structures that form discrete "columns"



Page 70

rooted at the base of the mantle, many of which are positioned in the vicinity of major hotspots (e.g. Figure 1). This is particularly clear in the Pacific basin (Hawaii and Superswell hotspots) where the vertical conduits are quite straight, but wider (~1000 km) than expected from the standard "plume" model. This suggests that these features have been stable for a very long time and manifest the very sluggish dynamics of the high viscosity lower mantle. As they reach the transition zone, the simple structure is lost, and these "conduits" appear to meander through the upper mantle, interacting with the more vigorous convection therein.



Figure 1: 3D rendering of low shear velocity structures in the central Pacific, viewed from the East in the direction of the Pacific Plate APM, cutting across horizontally elongated low velocity fingers in the uppermost mantle and bringing out vertically elongated conduits (plumes?) in the transition zone and below. After French et al. (2013, Science)




Posters

Monday 15 September 2014

1. Global scale observation of scattered energy from the core: seismic constraints on the F-layer

Joanne Adam (Institut de Physique du Globe de Paris, France) Barbara Romanowicz#(Institut de Physique du Globe de Paris, France, Collège de France, France and University of California, USA)

2. Melting relations in the MgO-SiO₂ and CaO-MgO-SiO₂ systems at 25-80 GPa: methods and preliminary results

Marzena Baron, (University of Oslo, Norway) RG Trønnes (University of Oslo, Norway) O. Lord and MJ Walter (University of Bristol, UK)

3. Ab initio thermodynamics and seismic properties of MgSiO₃ polymorphs at mantle transition zone conditions

Donato Belmonte (University of Genova, Italy)

4. Sediment in the source? Investigating the origins of the mantle zoo

Alex Brett, Julie Prytulak and Matthias Willbold (Imperial College London, UK)

5. Halogen and noble gas evolution of the Hawaiian Plume Source

Michael Broadley, (University of Manchester, UK) R Burgess (University of Manchester, UK) D Graham (Oregon State University, USA) CJ Ballentine (University of Oxford)

6. Probing the mantle transition zone beneath Europe with Pds receiver functions

Sanne Cottaar and Arwen Deuss (University of Cambridge, UK)

7. Stratification at the top of the outer core: constraints from SmKS and PmKP phases

Elizabeth Day, (Imperial College London) Connor Tann, Arwen Deuss (University of Cambridge, UK) Jessica C.E Irving (Princeton University, USA)

8. Evidence for primordial water in the Earth's deep mantle

L. J. Hallis, K. Nagashima, G. J. Taylor, S. A. Halldórsson, D. R. Hilton, G. R. Huss and K. Meech

9. Anelasticity of the HCP metal Zinc: a key to understanding the dynamics of Earth's core

Simon Hunt (University College London, UK) Andrew Walker (University of Leeds, UK) Oliver Lord (University of Bristol, UK) Matthew Whitaker (Stony Brook University, N.Y, USA)

10. Mantle discontinuity topography beneath Iceland from P to S receiver functions

Jennifer Jenkins, Arwen Deuss and Bob White (University of Cambridge, UK)

11. Lithological heterogeneity in the mantle plume source of continental flood basalts

Eleanor Jennings, J. Maclennan, S. A. Gibson and T. Holland (University of Cambridge, UK)

Tuesday 16 September 2014

12. The feasibility of thermal and compositional convection in Earth's inner core

Karen Lythgoe, John Rudge, Arwen Deuss (Bullard Laboratories, Cambridge, UK) Jerome Neufeld (Bullard Laboratories, Cambridge, UK, BP Institute, Cambridge, UK and Department of Applied Mathematics and Theoretical Physics, Cambridge, UK)

13. Statistical modeling of mantle-wave scattering in 3D structure at different scales

Matthias Meschede (Institut de Physique du Globe de Paris, France) Barbara Romanowicz (Institut de Physique du Globe de Paris, France, Collège de France, France and University of California, USA)

14. Si and Cr Diffusion in Liquid Iron: Implications for the Basal Region of a Magma Ocean and Planetary Core-Mantle Boundaries

Esther Posner, David Rubie, Daniel Frost and Gerd Steinle-Neumann (Unversität Bayreuth, Germany) Razvan Caracas (Laboratoire de Géologie, École Normale Supérieure de Lyon, France)

15. The mechanics of Deep Earthquakes: An experimental investigation of slab phase changes

James Santangeli, DP Dobson, SA Hunt and PG Meredith (University College London, UK)

16. Seismic array-processing: an alternative to better constrain CMB and D"

Sergi Ventosa (Institut de Physique du Globe de Paris, France)

17. Fractionation of magnesium isotopes in the lower mantle: insights from density functional theory

Andrew Walker (University of Leeds, UK) Tim Elliott (University of Bristol, UK)

18. Lateral variations at the inner core boundary: implications for inner core processes

Dr Lauren Waszek & Dr Arwen Deuss (University of Cambridge, UK)



Poster Presentation Abstracts

Global scale observation of scattered energy from the core: seismic constraints on the F-layer

Joanne M.-C. Adam¹, Barbara Romanowicz^{1,2,3}

- 1. Institut de Physique du Globe de Paris (IPGP), France (adam@ipgp.fr)
- 2. Collège de France, France
- 3. Seismological Laboratory, University of California, Berkeley, CA, USA

The seismic F-layer is a ~200km thick transition region at the base of the outer-core, characterized by a reduction in the P-wave velocity gradient with depth. It plays an important role in the investigation of the geodynamo modelisation and core evolution. In this study, we investigate the seismic velocity in this region by looking at seismic phases that travel in the core and would be sensitive to the F-layer.

We collect a global dataset of several hundreds of high quality records of PKPbc, PKPbc-diff and PKPdf phase arrivals. Those phases are most sensitive to the bottom of the outer-core and/or the top of the inner-core. Among this collection, we identify an energy packet that arrives 8-12 seconds after the PKPbc (or PKPbc-diff) coda that is not predicted by reference models. The origin of this scattered energy is unclear and may provide valuable information about structure in the core. We use array analysis techniques (*e.g.* phase weighted stacking) to enhance the signal of the scatterers and identify their origin.

Results show that the scattered energy originates along the great-circle path and has consistent arrival times and ray parameters. There are no obvious variations due to different source or station locations. After exploration of possible location for these scatterers, we show that their origin is most likely at the base of the outer-core, in the F-layer. To verify our interpretation, we model synthetic seismograms in an axisymmetric model using the spectral-element method (Nissen-Meyer *et al.* 2014) and test velocity profiles in the F-layer. We confirm that such a layer can be responsible for the scattering in the PKP coda as observed in the data.



Melting relations in the MgO-SiO₂ and CaO-MgO-SiO₂ systems at 25-80 GPa: methods and preliminary results

Baron MA¹, Lord OT², Walter MJ², Trønnes, RG^{1,3}

1. Centre for Earth Evolution and Dynamics, University of Oslo, Norway (marzena.a.baron@gmail.com)

- 2. School of Earth Sciences, University of Bristol, UK
- 3. Natural History Museum, University of Oslo, Norway



Melting and crystallization processes during magma ocean episodes of the early Earth led to extensive chemical differentiation. Some of the resulting mantle heterogeneities, in the form of dense cumulates, might have survived convective mixing. To gain insights in the origin, composition and properties of the currently inferred lower mantle heterogeneities, we perform melting experiments on compositions in the binary MgO-SiO₂ (MS) and ternary CaO-MgO-SiO₂ (CMS) systems at lower mantle pressures (25-80 GPa), using the laser-heated diamond anvil cell (LH-DAC) technique.

An important objective of this study is to determine the effect of pressure on the eutectic melt compositions involving the following liquidus mineral assemblages:

1. Mg-perovskite (pv) + periclase (pc) and pv + silica in the MS-system, corresponding to model peridotite and basalt compositions

2. pv + pc + Ca-perovskite (cpv) in the CMS-system.



Fig. 1 An example of temperature profiles recorded during laser-heating of a near-eutectic composition with 60 mol% SiO_2 (MS-system) in a 4-hole DAC experiment where the three ruby-free sample chambers were heated under different pressure conditions. Temperature measurements were taken from both sides (R: right, L: left).

To this end we have developed a novel technique for micro-fabrication of metalencapsulated samples. Multiple sample discs are produced by melting sample powder on top of a resistively heated Refilament of about 20 µm thickness. The filament is bow-tie shaped, with a central part containing 30-40 laser-drilled holes with 20
m diameter. The molten powder fills the holes and quenches to glass. The filaments with glass chambers are polished and coated by Re-metal layers deposited by electroplating. The Reencapsulated sample discs are then laser-cut from the filament and loaded in the DAC between discs of MgO (pressure medium and heat insulation). Doublesided, "external" laser-heating of the Re layers enclosing the sample gives greatly reduced temperature gradients compared to conventional LH-DAC-experiments. To locate the eutectic compositions. recovered samples of different bulk compositions, containing various liquidus phases and guenched melts are analyzed by FE- EPMA.

Additional exploratory 4-hole DACexperiments are performed to investigate the melting temperatures (T_m) of neareutectic compositions based on Liebske and Frost (2012) and de Koker et al. (2013). Four sample holes drilled trough an indented Re-gasket are filled with perature [K] identical starting material mixed with W powder (laser absorbant). One of the holes has ruby as pressure calibrant. During laser-heating of the three ruby-free different chambers under pressure conditions, we record T as a function of increasing laser power. Upon melting the W-powder migrates and aggregates, reducing laser coupling and resulting in a temperature plateau (Fig. 1). Тο complement and refine the ruby pressure determination, we also measure and calibrate the Raman peak shift of the diamond culet surface in contact with the sample. based on Akahama and Kawamura (2006) and expanded by Wang et al (in prep).

The selected near-eutectic compositions show an expected positive $p-T_m$ correlation (**Fig. 2**), with lower T_m for the



Fig. 2 Preliminary p-T_m curves of near-eutectic compositions (T_m: melting temperature). **MS-system:** pv-silica near-eutectic (Si₆₀ and Si₆₅, red line, Si₆₀: 60 mol% SiO₂), pv-pc near-eutectic (Si₄₂, green line). **CMS-system** pv-cpv-pc near-eutectic (C₂₅Si₄₂, blue line, Ca₂₅Si₄₂: 25 mol% CaO and 44 mol% SiO₂). The eutectic curves from DFT studies (pv-silica, DFT and pv-pc, DFT) and thermodynamic modeling (pv-pc, therm.) are from de Koker et al (2013) and Liebske and Frost (2012).

CMS-system. Our preliminary results indicate that the dT_m/dp slope for the pv-silica neareutectic is lower than for the pv-pc near-eutectic composition the MS-system. There is an overall good agreement between our preliminary results and those of Liebske and Frost (2012) and de Koker et al (2013). Experimentally determined melting phase relations in the simple MS and CMS systems at in the lower mantle pressure range will improve our thermodynamic models for melting through the Earth's mantle.

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Ab initio thermodynamics and seismic properties of MgSiO₃ polymorphs at mantle transition zone conditions

Belmonte D. 1

University of Genova, Corso Europa 26, 16132 Genova, Italy. E-mail: donato.belmonte@unige.it

MgSiO₃ polymorphs with the garnet, pyroxene and ilmenite structure



play a key role in controlling phase equilibria and seismic velocity gradients in the mantle transition zone (~440÷660 km). Despite the relative abundance of structural and thermoelastic informations, thermodynamic data are still poorly constrained and their extrapolation at high pressure and temperature conditions is affected by large uncertainties.

In this work, *ab initio* calculations of the thermodynamic properties of MgSiO₃ polymorphs stable at mantle transition zone conditions (tetragonal majorite, Mj; akimotoite, Ak; HP-clinoenstatite, HPCen) have been carried out with the hybrid B3LYP density functional method. Hybrid functionals are widely and successfully used in solid state chemistry, where it has been shown to provide excellent results as concerning vibrational spectra and elasticity of insulating crystalline solids, at both ambient and high-pressure conditions [1]. The static and vibrational features (equation of state, elastic constants, seismic anisotropy, IR & Raman spectra, mode Grüneisen parameters) of Mj, Ak and HPCen have been fully characterized in a broad range of P-T conditions. The vibrational density of states (vDOS) have been reproduced in the framework of quasi-harmonic approximation through a full phonon dispersion calculation or, alternatively, a modified Kieffer's model splitting the acoustic and optic modes contribution to the thermodynamic properties [2, 3].

The calculated heat capacities are in good agreement with the relatively few calorimetric investigations made so far on these minerals in the low- to medium-T range. However, the hightemperature extrapolation of calorimetric results turns out to suffer from physical unsoundness, so that their use in phase equilibrium calculations deserves great care. The calculated Gibbs free energies allow to define phase transition boundaries in MgSiO₃ diagram and locate the majorite-akimotite-perovskite triple point at P = 21.09 ± 0.13 GPa and T = 2247 ± 31 K (see Figure 1). The effect of partial structural disorder in majorite, defined through an interchange enthalpy ($\Delta H_{int} \cong 15 \text{ kJ/mol}$) and configurational entropy [S_{conf} $\cong 1.9 \text{ J/(mol}\times\text{K})$] contribution, must be taken into account to accurately reproduce the Mj-Ak-Pv triple point. The predicted Clapeyron slopes of the phase boundaries Mj-Pv, Mj-Ak, Ak-Pv and HPCEn-Mj are, respectively, 2.2, 8.3, -4.0 and -3.6 MPa/K, in good agreement with experimental observations and thermodynamic assessments as well. A general feature of first principles calculations is the accuracy and robustness of the predicted Clapevron slopes, in spite of the fact the absolute P-T location of the univariant phase boundaries highly depends on the exchange-correlation functional used (Figure 1). B3LYP assures a very accurate reproduction of Mj-Ak-Pv phase transition boundaries as well as a reliable simulation of the vibrational and thermodynamic properties of MgSiO₃ polymorphs at high pressure and temperature conditions.





Figure 1. Ab initio B3LYP calculated phase transition boundaries for $MgSiO_3$ majorite (Mj) – akimotoite (Ak) – perovskite (Pv).

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Sediment in the source? Investigating the origins of the mantle zoo

Alex Brett, Julie Prytulak, Matthias Willbold

Imperial College London (a.brett13@imperial.ac.uk) Imperial College London University of Manchester

The 'mantle zoo' is a collection of proposed chemical end-members



invoked to account for the large range in radiogenic isotope and trace element composition observed in Ocean Island Basalts (OIB). The end-member 'HIMU' (high $\mu = {}^{238}\text{U}/{}^{204}\text{Pb}$) is characterised by high time-integrated U/Pb and unradiogenic strontium isotopes, hypothesized to arise from subducted altered oceanic crust isolated in the mantle for over 2Ga. The Enriched Mantle component has low {}^{143}\text{Nd}/{}^{144}\text{Nd}; high {}^{207}\text{Pb}/{}^{206}\text{Pb} and ${}^{208}\text{Pb}/{}^{204}\text{Pb}$ for a given {}^{206}\text{Pb}/{}^{204}\text{Pb}; lavas with low ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ are designated 'EMI' and those with high ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ are 'EMII', canonically interpreted as the result of incorporation of old (>1.5Ga) pelagic sediment and terrigenous sediment respectively. These origins, however, remain a topic of debate. Traditional investigation of OIB sources has used these radiogenic isotopes, but due to the number of parameters that can be varied (e.g. mantle concentrations, degree of melting, time between fractionations) it is difficult to unambiguously identify specific inputs. For example, Samoan lavas with extremely radiogenic Sr isotopes have been explained by either metasomatic enrichment or clastic sediment addition [1,2]. Stable isotope geochemistry is independent of time and parent/daughter fractionation, and is here employed to assess the underlying causes of chemical heterogeneity in the mantle. We focus specifically on the element thallium (TI).

Thallium is among the heaviest naturally-occurring element, and has two stable isotopes of mass 203 and 205 (29.5% and 70.5% abundance, respectively). The concentration of thallium in the upper mantle is approximately 2ppb, whereas in altered oceanic crust (AOC) and ferromanganese sediments, concentrations can reach 100s of ppm. Therefore even a vanishingly small contribution (<<1%) to the OIB source can potentially dominate the thallium budget. In addition to the stark concentration contrast between the possible inputs to the mantle, there are also significant stable isotope fractionations documented at low temperature. Stable TI isotope compositions are reported in parts per ten thousand versus the standard NIST SRM 997, defined as $\epsilon^{205}TI = 0$. In the upper mantle, $\epsilon^{205}TI = -2.0 \pm 0.5$ [3], based on measurement of fresh MORB and assuming that partial melting and other high temperature processes do not fractionate TI isotopes.

In contrast, ferromanganese sediments have heavy $\epsilon^{205}TI$ up to +10 [3,4] whereas AOC can have isotopically light TI, reaching values as low as $\epsilon^{205}TI = -15$ [5]. Only three OIB locations have previously been investigated for TI isotopes: Iceland, the Azores, and Hawai'i. $\epsilon^{205}TI$ of Hawai'ian picrites covers the range from -3 to +4, and has been interpreted as resulting from the incorporation of ferromanganese sediments in the mantle source [6]. The TI isotope composition of lavas from Iceland and the Azores is reported as $\epsilon^{205}TI = -1.5 \pm 1.4$, indistinguishable from the estimated mantle composition.

The extreme concentration contrast between the mantle and possible inputs, coupled with significant TI isotope fractionation, makes **TI potentially the most sensitive stable isotope tracer of low-T materials in the source of OIB.** The present study consists of a global investigation of thallium concentration and isotopic composition in OIB. Concentrations and



Page 81

isotope compositions (ϵ^{205} TI) are presented for whole-rock OIB from *Tristan de Cuhna (EMI)*, *Gough (EMI), St Helena (HIMU), and the Marquesas (EMII/HIMU).* We compare the new data with the 'mantle' value of ϵ^{205} TI = -2.0, and reevaluate the view that HIMU, EMI and EMII represent low-T AOC, pelagic and terrigenous sediment contributions, respectively.

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Halogen and noble gas evolution of the Hawaiian Plume source

M.W. Broadley1, R. Burgess1, D. Graham2, C.J. Ballentine3

- 1. SEAES, University of Manchester (Michael.broadley@manchester.ac.uk)
- 2. COEAS, Oregon State University
- 3. Department of Earth Sciences, University of Oxford

The Emperor Seamount Chain (ESC) preserves the earliest known record of volcanism emanating from the Hawaiian Hotspot (85 to 42 Ma). Isotopic data from these seamounts have shown a temporal evolution of the hotspot's magmatism, with ${}^{3}\text{He}/{}^{4}\text{He}$ ratios steadily increasing from a MORB-like signature (10 R_A) to ratios (24 R_A) which are indistinguishable from the current Hawaiian Islands [1]. The evolution of the seamounts chemistry could reflect a change in the hotspot source over time or could be a result of interaction with other mantle reservoirs. In order to better constrain the early evolution of the hotspot source; olivine samples from three seamounts which span 27 Ma have been analysed for their halogen and noble gas content.

The heavy halogens (chlorine, bromine and iodine) much like the noble gases provide an excellent tracer of volatiles throughout the Earth due to their incompatibility during partial melting and their distinct ratios within different reservoirs. The high concentration of the heavy halogens in seawater and marine pore fluids make them the ideal tracer of volatiles through subduction zones and into the mantle.

Preliminary data suggests there is a trend of increasing I/CI and Br/CI ratios as the seamounts get younger; with an evolution from a MORB-like signature within the oldest seamount (Detroit) to a more enriched value in the younger seamounts (Suiko and Koko). There is also a variation within the K/CI ratios of the samples. Detroit has an average K/CI ratio of 11.4 similar to that of the MORB value (12.8), whilst Suiko and Koko have ratios of 40.1 and 20.8 respectively.

Although the overall trend is that Suiko and Koko are distinct from the MORB-like Detroit seamount, there is no clear trend with decreasing age as Suiko (65 Ma) has twice the K/Cl ratio of the younger Koko (49 Ma) whilst maintaining similar ³He/⁴He ratios. The MORB-like signature within Detroit is most likely a result of the proximity of the plume head to a spreading ridge during the Cretaceous [2], whilst the younger seamounts are more representative of the hotspot source. I/Cl ratios within the younger seamounts are higher than the MORB ratio measured in Detroit and suggest there is a subducted sedimentary signature within the Hawaiian source. The high K/Cl ratios within Suiko and Koko compared to Detroit further reflects the addition of a subducted source due to the lower subduction efficiency of halogens compared to K. There appears to be evidence of a subducted volatile signature within the Hawaiian source which is masked in the older seamounts by the influx of MORB material. This suggests that there is no clear linear evolution of the Hawaiian hotspot source through time and any fluctuations in chemical composition are a function of the tectonic setting.

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Probing the mantle transition zone beneath Europe with Pds receiver functions

Sanne Cottaar and Arwen Deuss

University of Cambridge

The mantle is delineated by seismic discontinuities between 300 and 800 km depth. Variations in topography, width and occurrence of the discontinuities indicate lateral variations in temperature, composition and water content, as these variations influence the mantle phase transitions. Seismic studies of the conversions of pressure to shear waves (Pds phases) are an important tool to observe lateral variations in these discontinuities.

Here we collect a Pds data set across all European seismic stations since 2000 that are available through ORFEUS or IRIS; resulting in ~500,000 event-station pairs. We deconvolve the radial component by the vertical component – assumed to represent the source component-using the iterative deconvolution method to obtain receiver functions. We assess the quality of a receiver function by the signal-to-noise ratio and by evaluating how well the radial component is reproduced when reconvolving the receiver function with the vertical component. This results in ~40,000 high quality receiver functions across Europe.

Our receiver functions show little lateral variation in the depth of the transition zone discontinuities across the East European Craton, and we use this region as a reference to the more tectonically unstable regions. Around the Mediterranean, we look for signature of slabs ponding or penetrating at the discontinuity around 660 km; we aim to link the characteristics of the mantle discontinuities to the ongoing dynamics.



Stratification at the top of the outer core: constraints from SmKS and PmKP phases

Elizabeth A. Day¹, Connor Tann¹, Jessica C. E. Irving³ and Arwen Deuss²

- 1. Imperial College London
- 2. University of Cambridge (ead33@cam.ac.uk)
- 3. Princeton University



Convection in the Earth's outer core is responsible for the generation of the planet's magnetic field and is strongly dependent on interactions between the mantle and inner core. However, despite undergoing vigorous convection, the outer core is not necessarily a single uniform, homogeneous layer of the Earth. Recent seismic and geomagnetic studies suggest that the uppermost outer core is comprised of a chemically distinct layer of stably stratified material. This layer is likely enriched in light elements, which may either be accumulating due to the release of light elements during the solidification of the inner core, or due to a flux of material across the core mantle boundary.

Here we compile a new dataset of SmKS and PmKP differential travel time data to investigate the vertical and geographical extent of stratification in the uppermost outer core. By jointly considering SmKS and PmKP phases, carefully correcting for known mantle structures, exploring the effect of CMB topography, and considering changes in the core over recent time, we are able to place new constraints on this stably stratified layer at the top of the outer core.



Evidence for primordial water in the Earth's deep mantle

L. J. Hallis, K. Nagashima, G. J. Taylor, S. A. Halldórsson, D. R. Hilton, G. R. Huss and K. Meech

Earth is the only planet known to have active plate tectonics. Hydrogen isotope ratios (D/H) can be used to track the cycling of water through surface reservoirs and into the mantle. We present data from Baffin Island volcanic rocks, which suggest an isolated water reservoir with a low D/H ratio ($\Box D > -218$ ‰) exists in the deep mantle. This deep mantle reservoir reflects the Earth's initial D/H ratio, suggesting that post-accretionary processes increased the D/H ratio of Earth's surface and upper mantle reservoirs. Preferential loss of the lighter hydrogen isotope to space, and/or the addition of deuterium-rich cometary material during the Late Heavy Bombardment, could account for this increase. A lower initial D/H ratio for the mantle is in line with carbonaceous-chondrite-like building blocks for Earth.



Deep Earth Processes 2014

Anelasticity of the HCP metal Zinc: a key to understanding the dynamics of Earth's core

Simon A. Hunt¹, Andrew M. Walker², Oliver T. Lord³ and Matthew L. Whitaker⁴

- 1. Department of Earth Sciences, University College London (<u>simon.hunt@ucl.ac.uk</u>)
- 2. School of Earth and Environment, University of Leeds
- 3. School of Earth Sciences, University of Bristol
- 4. Mineral Physics Institute, Stony Brook University, N.Y.



The solid inner core is the most remote and inaccessible part of our

planet but its structure and composition may provide a key record needed to untangle the geological history of the surface environment. Information encoded in the inner core during its solidification could reveal the timing and nature of the onset of Earth's protective magnetic field generated by convection in the liquid outer core or even of changes in the way the mantle convects, driving surface dynamics. Key to developing our understanding of the inner core is our ability to use seismic observations to constrain its structure on all scales. Seismic wave velocities are mostly sensitive to the atomic scale crystal structure, temperature and composition. On a larger scale the microstructure of the inner core, reflecting its deformation and crystallization history, can be probed by seismic studies of elastic anisotropy and anelasticity [e.g. 1]. The inner core is at temperatures in excess of ~0.95Tm and interpretation of the properties and history of the inner core must therefore include careful understanding of the anelastic properties of HCP iron and its alloys.

The most recent study of the anelasticity of iron and iron alloys [2] is now over a decade old and is limited to low pressures where iron adopts the body centered cubic (BCC) or face centered cubic (FCC) structure. However, it is now widely, although not universally, accepted that iron in the core adopts the hexagonally close packed (HCP) epsilon-iron structure [3] that becomes stable above ~10 GPa at room temperature and yet there are no data on the anelasticity of this core-forming phase.

We have used Zinc as a low pressure analogue for HCP-iron and measured its anelastic response as a function of frequency (periods 10-300s), temperature (up to melting) and pressure (P<7GPa). Our proof-of-concept experiments use the D-DIA to apply sinusoidally varying strains at a range of frequencies to both the sample and an adjacent corundum elastic standard [as per 4]. We image changes in length of the sample and standard in response to the driving strain using X-radiography. The amplitude and frequency dependent phase lag of the change in the sample length relative to that of the elastic standard gives us the effective Young's modulus and internal friction. Above ~0.7Tm, we observe significant reduction in the sample's effective Young's modulus (compliance) and an increase in internal friction; both of these are frequency dependent.

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Mantle discontinuity topography beneath Iceland from P to S receiver functions

Jennifer Jenkins, Arwen Deuss, Bob White

University of Cambridge (jj405@cam.ac.uk)

Iceland straddles two tectonic plates separated by a spreading centre. The question as to the source of it's high volumes of crustal volcanism, compared to normal spreading ridges, have lead many to hypothesise the presence of an underlying mantle plume. Though multiple

tomographic studies observe a strong low-velocity region in the upper mantle (down to ~400km), structure in the lower mantle is still poorly constrained, with much disagreement between models. This study investigates mantle discontinuity topography beneath Iceland and the surrounding region using P to S receiver functions, to assess whether the underlying low velocity anomaly imaged tomographically extends through the transition zone, and can be attributed to a deep sourced mantle plume.

As in previous receiver function studies of Iceland we use data from the permanent Icelandic IRIS station BORG (which has now been active for 20 years) and data from 2 temporary Icelandic networks (HOTSPOT and ICEMELT). We also make use of new data from over 100 additional seismic stations run by the University of Cambridge. Receiver functions are calculated for Mw \geq 6 events, 30-90° distance from stations via the iterative deconvolution method. Observations passing quality criteria, produce nearly 3000 high quality point samples of the mantle discontinuities. These are converted from time to depth before being stacked by piercing point location.

Initial results reveal normal discontinuity depths, close to the global average, west of Iceland along the coast of Greenland. However stacks made beneath Iceland itself show both depressed 410 and 660 discontinuities, with deepest measurements observed in central stacks (depths of 453/699km). This indicates a low-velocity region beneath Iceland, likely due to high mantle temperatures, not fully taken into account in our depth conversion. Though we observe slight thinning of transition zone thickness beneath central southern Iceland compared to surrounding regions, the variation is subtle.



Lithological heterogeneity in the mantle plume source of continental flood basalts

E. S. Jennings, J. Maclennan, S. A. Gibson, T. Holland

Department of Earth Sciences, University of Cambridge, UK (esj26@cam.ac.uk)

Continental flood basalts (CFBs) are widely believed to be the products of high temperature and high degree melting in an impacting mantle plume startinghead [1]. Traditional models have focused on rising mantle plumes consisting of both fertile and refractory peridotites but recycled oceanic crust (pyroxenite or eclogite) may also be an important component. Moreover, if mantle plumes originate from the core-mantle boundary, then evidence of recycled, subducted material in plume-derived melts provides direct evidence for whole-mantle cycling processes. We examine the possibility of a recycled component in the mantle source of the ~ 133 Ma Paraná-Etendeka CFB province, which formed in response to the sub-lithospheric impact of the proto-Tristan plume, and is linked to the modern day plume by aseismic ridges. Here, primitive mantle melts (picrites and ferropicrites) are found in association with the main CFB pile. The ferropicrites were emplaced in the Etendeka region of Namibia immediately prior to the main flood basalt pulse and predate much of the lithospheric thinning in the region [2]. Picrite melts - thought to form by high temperature melting of a depleted peridotite source – form dykes in the area [3] and provide a useful comparison scenario for deconvolving the effects of pressure, temperature and source lithology on mantle melt composition.

Ferropicrite is a rare magma type found exclusively in a subset of global CFB provinces [2]. It is characterised by high MgO, high FeO and low Al₂O₃, which cannot be the product of high pressure melting of peridotite alone. Strongly fractionated rare-earth element patterns indicate the presence of garnet in the melt source region. The association of ferropicrites with thick lithosphere and elevated mantle temperatures, alongside this strong 'garnet signature', implies that they are derived from high pressure melting of a more fusible mantle lithology (such as eclogite or pyroxenite) making this melt type a marker of heterogeneity within upwelling mantle plumes. The presence of garnet pyroxenite in the source of ferropicrites has been invoked from high-pressure experimental investigations [4]. We have built on these findings by undertaking detailed trace element modelling to test the hypothesis that ferropicrite is formed by high pressure melting of garnet pyroxenite, and that picrite forms from lherzolite, where melting extends to lower pressures and higher fractions. Our non-modal polybaric fractional melting models investigate the modal mineralogy required of the source in order to reproduce incompatible trace element patterns observed in the picrites and ferropicrites, given a mantle potential temperature of around 1530 °C. Our findings confirm that ferropicrite melts cannot be adequately modelled by peridotite melting and so we have investigated their origin using a model optimised for pyroxenite melting. We use a pyroxenite-specific garnet-spinel transition, opx stability and solidus location based on THERMOCALC thermodynamic investigation [5] of the KG1 litholoav [6].

In addition to major element, olivine composition and experimental petrology arguments [2,3,4], our modelling supports the hypothesis that ferropicrites are the product of high P, high T melting of pyroxenite, providing strong evidence for recycling and melting of oceanic lithosphere in Earth's convecting mantle.



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The feasibility of thermal and compositional convection in Earth's inner core

Karen Lythgoe¹, John Rudge², Jerome Neufeld^{3,4,5} Arwen Deuss⁶

- 1. Bullard Laboratories, Department of Earth Sciences, Madingley Road, Cambridge, CB3 0EZ, UK (khl43@cam.ac.uk)
- 2. Bullard Laboratories, Department of Earth Sciences, Madingley Road, Cambridge, CB3 0EZ, UK
- 3. Bullard Laboratories, Department of Earth Sciences, Madingley Road, Cambridge, CB3 0EZ, UK
- 4. BP Institute, Madingley Road, Cambridge, CB3 0EZ, UK
- 5. Department of Applied Mathematics and Theoretical Physics, Wilberforce Road, Cambridge, CB3 0WA, UK
- 6. Bullard Laboratories, Department of Earth Sciences, Madingley Road, Cambridge, CB3 0EZ, UK

Understanding the structure of Earth's inner core can provide unique insights into the thermal and dynamical processes of the Earth. Inner core convection and the corresponding variations in grain size and alignment, has been proposed to explain the complex seismic structure observed, including anisotropy, lateral variations and the elusive F-layer at the base of the outer core.

We develop a parameterised convection model to investigate the possibility of thermal or compositional convection in the inner core, focusing on the dominance of the plume mode of convection versus the translation mode. We present thermal and compositional convection separately so as to study the end-members of the system.

In the thermal case, the most likely mode of convection is inner core translation, but this is dependent on the viscosity of the inner core which is poorly constrained. For compositional convection, inner core translation is always the dominant mode given a reasonable range of parameter space. The style of convection resulting from a combination of both thermal and compositional effects is not easy to understand. We expect complex double diffusive processes to occur given the very different thermal and compositional diffusion rates and more work is needed to understand these processes.



Statistical modeling of mantle-wave scattering in 3D structure at different scales

Matthias Meschede (1), Barbara Romanowicz (1,2,3)

Institut de Physique de Globe de Paris Collège de France University of California, Berkeley

This study aims to combine our current knowledge of the Earth with statistical modeling of scattering due to unresolved small heterogeneities.

We present accurate regional and global spectral measurements of current tomographic models. Comparison of regional and global models demonstrate their respective resolution limits. We can further identify distinct lengths scales with increased heterogeneity strength in the uppermost mantle of the Earth.

Through special spherical filters, we can associate the most dominant scale with the size of tectonic plates but also reveal a shorter scale length with increased heterogeneities. Earth's seismic heterogeneity spectrum is therefore difficult to model by a single underlying physical process and a simple

power-law decay might oversimplify its complexity.

We then provide a formalism, which extends well-known methods in Cartesian, stationary environments, to create radially non-stationary random models in the

spherical geometry of the Earth. Combined with tomographic models that constrain the larger heterogeneity scales, these models can be used to further constrain the spectrum of the Earth on small scales. We show simulations that demonstrate the effects of scattering on amplitudes of mantle waves and the development of the seismic coda for a given model. We finally provide suggestions on how these can be used to constrain the strength of small-scale scatterers.



Si and Cr Diffusion in Liquid Iron: Implications for the Basal Region of a Magma Ocean and Planetary Core-Mantle Boundaries

Esther S. Posner¹, David C. Rubie¹, Daniel J. Frost¹, Razvan Caracas², Gerd Steinle-Neumann¹

- 1. Bayerisches Geoinstitut, Unversität Bayreuth, D-95440 Bayreuth, Germany (Esther.Posner@uni-bayreuth.de)
- 2. Laboratoire de Géologie, École Normale Supérieure de Lyon, France



According to current models of the Earth's core-mantle differentiation, substantial amounts of Si and Cr should have partitioned from a magma ocean into metallic Fe-Ni cores of impacting bodies during accretion [1]. In contrast to these predictions, however, the Si and Cr contents of iron meteorites, which are derived from the metallic cores of early-formed planetesimals, are surprisingly low (e.g. < 1 ppm) [2]. Recent studies of magnetized achrondrites [3,4] reveal that planetesimal parent bodies likely possessed liquid metallic cores that underwent convection during their formation that would result in the chemical mixing and transport of chemical components in liquid iron, such as Si and Cr, to the body's core-mantle boundary (CMB). As the solubility of Si and Cr in liquid iron has been experimentally shown to increase with temperature, the alloy component of a molten core should decrease during cooling. Ongoing metal-silicate interaction at the CMB of larger bodies, such as the Earth, and potential diffusive profiles of light elements in the outmost region of the Earth's outer core have been used to model and interpret deviations from reference model seismic wavespeeds from these respective regions [5.6]. We are conducting a series of high P-T experiments and first principles calculations to constrain the diffusivity of Si and Cr in liquid iron in order to understand the kinetics of chemical transport and equilibration during core formation and processes occurring at CMBs.

Experimental diffusion couples comprised of highly polished cylindrical disks of 99.97% Fe and metallic Fe alloy (8 wt% Si, 1 wt% Cr) were contained in an MgO capsule and annealed within the *P*-*T* range 1743–2523 K and 1–12 GPa in a multi-anvil apparatus. A series of experiments are conducted at each pressure using variable heating rates, final quench temperatures (*T_i*), and time duration at *T_f*. To minimize the occurrence of diffusion prior to reaching the target temperature, a rapid heating rate of 25 or 50°C/sec was used to ramp the temperature to the required value. Experimental durations were very short (< 180 sec) and terminated by quenching at ~500°C/sec by switching off the electrical power. Recovered capsules were cut and polished parallel to the axis of the cylindrical sample and measured using EMPA 10 µm-step line scans. To extend our dataset to *P*-*T* conditions of the Earth's core-mantle boundary, we have begun first principles molecular dynamics (FP-MD) calculations. Fe supercells of 108 atoms are overheated to induce melting, compressed along several isotherms (2000–5000K) and allowed for changes in chemistry (Si, Cr). Diffusion coefficients are computed from the atomic trajectories in the simulation cell via the Einstein relation.

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The mechanics of Deep Earthquakes: An experimental investigation of slab phase changes

Santangeli J, Dobson DP, Hunt SA, Meredith PG.

University College London (james.santangeli@ucl.ac.uk)

The mechanics of deep earthquakes have remained a puzzle for researchers since 1928 when they were first accurately identified by Kiyoo Wadati¹ in Japan. Deep earthquakes show a split distribution, with peaks centered around ~370-420km and ~520-550km. As these events are limited to subducting slabs, it is accepted that they may be due to phase changes in metastable slab material. Indeed, conditions at ~350km depth are nominally appropriate for the olivine – wadsleyite transition, consistent with the anticrack mechanism previously observed in (Mg,Fe)₂SiO₄². The additional peak around 520km suggests that there is another siesmogenic phase change; candidates include Ca-garnet \rightarrow Ca-perovskite, wadsleyite \rightarrow ringwoodite and enstatite \rightarrow majorite or ilmenite. Importantly, for large scale seismogenesis to occur candidate phase changes must be susceptible to a runaway mechanism. Typically this involves the release of heat during exothermic reactions, which acts to increase reaction and nucleation rates. It is worth noting that the post-spinel reaction (sp \rightarrow pv + fp) marks the cessation of deep earthquakes; possibly as a result of being endothermic.

This research aims to identify which of these candidates could be responsible for seismogenesis.

We use high-pressure split cylinder multi-anvil experiments with acoustic emission detection. Low-pressure analogue materials have been used to allow greater cell sizes and thus sample volumes to enable accurate location of AE to within the sample. The candidate phase is annealed below its phase boundary, and then taken through the boundary by heating. Acoustic emissions, if generated, are observed in real time and later processed to ensure they emanate from within the sample volume. Initial results indicate that the pryroxene \rightarrow ilmenite transition in MgGeO₃ is seismogenic, with several orders of magnitude increase in the energy of AE concurrent with the phase boundary.

References:

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Seismic array-processing: an alternative to better constrain CMB and D"

Sergi Ventosa 2, Barbara Romanowicz 1,2,3

- 1. Collège de France, Paris, France
- 2. Institut de Physique du Globe de Paris, Paris, France (ventosa@ipgp.fr)
- 3. Berkeley Seismological Laboratory, Berkeley, CA, United States

The topography of the core-mantle boundary (CMB) and the structure and composition of the D" region are essential to understand the interaction between the earth's mantle and core.

Observations of travel-times and amplitudes of short period teleseismic body waves sensitive to CMB and D", provide essential constraints on the properties of this part of the mantle. Current major challenges in extracting this information are due to (1) low signal-to-noise ratio (SNR) of the target phases and (2) interference with other mantle phases.

Many studies to date use data-independent seismic-array processing approaches at relatively short periods to (1) enhance the signal of weak body wave phases and (2) isolate them from unwanted neighboring phases, usually through a delay-and-sum (i.e. slant stack) approaches. While array-processing techniques have been traditionally developed with other applications in mind (e.g., communications, radio astronomy or exploration geophysics), they are becoming increasingly relevant in global seismology, owing to the deployment of dense large scale arrays, such as the USArray of Earthscope. Combining high quality data from these arrays and seismic data-processing techniques applied to teleseismic signal processing should help expand observations over large portions of the globe that are currently poorly sampled.

To address some of the challenges encountered, we introduce scale-dependent slowness filters that do not compromise time-space resolution. This data-independent strategy merges complex wavelet and slant-stack transforms to create the local slant-stack transform in the time-scale domain. This is a redundant directional-wavelet transform with an extremely adaptable direction (here slowness) resolution.

We specifically use this expansion to design coherence-driven filters able to obtain clean PcP observations (a weak phase often hidden in the coda of the P wave) for events with magnitude Mw>5.4 and distances up to 80 degrees. This significantly increases the quantity and the quality of the PcP-P travel-time difference and PcP/P amplitude ratio measurements available for modeling. In this context, we also introduce a method based on the minimization of a linear misfit between P and PcP waveforms to improve the quality of PcP-P and PcP/P relative travel-time and amplitude measurements compared to the cross-correlation method.

The accuracy of our observations is limited mainly by the highest frequency of the signals used and the level of noise. We carefully analyze and, when possible and significant, correct for the main sources of bias, i.e., mantle heterogeneities, earthquake mislocation and intrinsic attenuation.

We illustrate our approach, taking advantage of high quality data from dense arrays located in North America and Japan to conduct regional studies of the CMB and D" using compressional waves with unprecedented resolution. Regions sampled span from Alaska and the north of Canada, to regions of the Pacific outside of the Pacific large-low shear-velocity province (LLSVP) on its northwest border (near Japan) and eastern boarder (near central America).

15-16 September 2014



Page 95

Although we focus on body-wave separation with the ultimate goal of studying CMB and D" using PcP, the tools we propose are more general, and they may prove useful in other applications. Particularly, our approach can potentially contribute to further extend our observational limits in low SNR and high interference scenarios.



Fractionation of magnesium isotopes in the lower mantle: insights from density functional theory

Andrew M. Walker^{1,} and Tim Elliott²

- 1. School of Earth and Environment, University of Leeds (email: a.walker@leeds.ac.uk)
- 2. School of Earth Sciences, University of Bristol (email: tim.elliott@bristol.ac.uk)

Because mass-dependent isotopic fractionation is inversely proportional to temperature, its study of has traditionally been the realm of low

temperature geochemistry. However, improved analytical techniques offer the possibility of studying processes operating at high temperature in the Earth's deep interior which generate low degree isotopic fractionation. In order to advance such studies it is necessary to quantify fractionation between mantle phases at high temperature and pressure, and understand how changes in cation co-ordination with depth modulate this fractionation. To this end we have performed atomic scale lattice dynamics simulations based on density functional perturbation theory to probe the fractionation of magnesium isotopes between forsterite (Mg₂SiO₄), periclase (MgO) and perovskite structured MgSiO₃ at pressures between 0 and 50 GPa and temperatures up to 4000 K. Magnesium is an attractive target because of its high abundance in the mantle and the relatively large (8%) mass difference between its two major isotopes. Furthermore, the increase in magnesium co-ordination with depth (from 6-fold in forsterite and the higher pressure polymorphs to 8-12 fold in the perovskite phase) means that the effect of co-ordination on isotopic fractionation can also be explored.

Our approach is to calculate the reduced partition function (the equilibrium constant for the exchange reaction for two isotopes between a solid phase and an ideal gas) for ²⁴Mg and ²⁶Mg in each phase as a function temperature and unit cell volume. This can be used to predict the fractionation between phases and its calculation only requires knowledge of the phonon density of states for a crystal containing the two isotopes of interest. We follow the approach of Méheut et al. (2007) and use variational density functional perturbation theory to evaluate the phonon frequencies for model crystals containing the heavy and light isotopes on a grid of points in the symmetry-irreducible wedge of the first Brillouin zone and use these to calculate the reduced partition functions. Unit cell volumes are determined as a function of pressure and temperature using lattice dynamics within the statically constrained quasi-harmonic approximation. In combination with a parameterized model for how the reduced partition functions vary with cell volume and temperature this allows the equilibrium fractionation factor between pairs of phases to be evaluated at a chosen pressure and temperature accounting for the differential compressibility and thermal expansively of the three phases. All our atomic scale calculations made use of the CASTEP code (Clark et al., 2005) and its implementation of density functional perturbation theory (Refson et al. 2006).

Our results indicate the perovskite phase will preferentially fractionate ²⁴Mg compared to the phases containing magnesium in octahedral co-ordination. While increasing temperature dramatically reduces this fractionation pressure has the opposite effect. When evaluated along the chondritic liquidus (the maximum temperature and thus minimum degree of isotopic fractionation possible for solids in the mantle) the predicted fractionation factor between these phases rapidly increases with depth, reaching a maximum greater than 0.1 ‰ at a depth of 700





km (30 GPa and 2800 K). This suggests that accurate measurement of isotopic variation can open a window on processes operating in Earth's deep interior.

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Lateral variations at the inner core boundary: implications for inner core processes

Dr Lauren Waszek & Dr Arwen Deuss University of Cambridge, Bullard Laboratories, Department of Earth Sciences Contact: Iw313@cam.ac.uk



The existence of a hemispherical difference in seismic velocity anisotropy and attenuation is well

established in the inner core. However, it is not known how these differences arise, and whether they extend up to the top of the inner core and its boundary with the outer core. The hemispheres may be frozen into the inner core structure as it grows, or may form after solidification. Constraining the structure on the inner core boundary (ICB), and in the lowermost 300 km of the outer core (F-layer), will help us to determine the more likely process.

Here, we use a large global dataset of PKiKP/PcP differential travel time residuals and amplitude ratios to examine regional variations in the vicinity of the ICB. We use the travel time residuals to investigate velocity structure in the F-layer and topography on the ICB, while the amplitude ratios help to constrain velocity and density contrasts across the boundary. The data are corrected for mantle velocity structure. We examine the data for hemispherical differences, which have been proposed to exist but not observed. In addition, we also search for smaller-scale lateral variations, including topography and mosaic-type structures that have previously been detected.

As the site of inner core growth, the ICB provides insight into the origins of the inner core properties. The west hemisphere is anisotropic, with lower seismic velocity and weaker attenuation than the isotropic east hemisphere. Two mechanism have been proposed to explain the hemispheres:

1. thermochemical flows which couple the inner core to the mantle, causing a variation in rates of growth; 2. lateral inner core translation, driven by melting of the east hemisphere and freezing of the west. Both models require hemispherical differences at the ICB. In the thermochemical flow model, there could be additional regional variations from localised freezing and melting of the inner core. In the translating inner core model, on the other hand, two distinct hemispheres are expected. Thus, determining the regional variations at the ICB is an important step in understanding the inner core structures.



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If you hear the Alarm

Alarm Bells are situated throughout the building and will ring continuously for an evacuation. Do not stop to collect your personal belongings.

Leave the building via the nearest and safest exit or the exit that you are advised to by the Fire Marshall on that floor.

Fire Exits from the Geological Society Conference Rooms

Lower Library: Exit via main reception onto Piccadilly, or via staff entrance onto the courtyard. Lecture Theatre: Exit at front of theatre (by screen) onto Courtyard or via side door out to Piccadilly entrance or via the doors that link to the Lower Library and to the staff entrance. Main Piccadilly Entrance: Straight out door and walk around to the Courtyard.

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The Gents toilets are situated on the ground floor in the corridor leading to the Arthur Holmes Room.

The cloakroom is located along the corridor to the Arthur Holmes Room.

Ground Floor Plan of the Geological Society, Burlington House, Piccadilly







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29-31 October	Small to Subseismic Scale Reservoir Deformation	Burlington House
5 November	2014 Geological Society Careers Day	British Geological Survey, Keyworth
19 November	GSL London Lecture – Contaminated Land: What is it good for?	Burlington House
26 November	Careers in Earth Science 2014	Our Dynamic Earth, Edinburgh
26-27 November	Operations Geology	Burlington House
10 December	Terra Infirma: What has Salt Tectonics ever done for us?	Burlingon House

