# Volatiles, Geodynamics and Solid Earth Controls on the Habitable Planet

The Earth is a layered, planetary body from the core to the atmosphere, with mantle, lithosphere and hydrosphere between. Water and gas are in abundance on the fertile surface we inhabit that overlies the barren, tracts of solid silicate mantle. This familiar arrangement has fundamentally compartmentalised the study of the Earth, with the hot interior frequently assumed to be dry. Such thinking has been reinforced by the practical difficulties of measuring the low abundances of volatiles within the Earth. Yet it has become increasingly apparent that the small amounts of volatile constituents can have a dominant effect on the behaviour of the mantle. As the largest reservoir on Earth, even small abundances of volatiles in the mantle can represent a major inventory of the planet's volatiles. Thus the influence of volatile species on the operation of the mantle, which controls the storage and release of these volatiles to the surface represents Earth System Science on the grandest, most challenging scale.

Advances in measurements of volatiles in nature and experiments, an understanding of their effects on rheology and an ability to compute these effects on the dynamics of the Earth now converge for the community to address this inter-connected system holistically. This Research Theme will thus quantitatively move geological thinking from a largely separate dry interior and wet exterior to a fully interacting model of the Earth. We will address the critical state of balance of the planet. Under what range of starting conditions can the Earth evolve to a planet with oceans and plate tectonics, and how robust is this system to perturbations? Can we lose our oceans and greenhouse-regulated atmosphere to the interior just as readily as we seem to have acquired them? Not only is the time ripe to tackle these zeroth order problems but there are the critical density of skills within the UK Geoscience community in order to efficiently address the interlinked components in this truly inter-disciplinary endeavour.

## 1. Introduction

Interactions between the mantle and the Earth's surface have dominated the evolution of the crust, the oceans, and the atmosphere and those same processes control many aspects of the habitable environment. The mantle is, by many orders of magnitude, the largest reservoir of many volatiles on Earth (e.g., $H_2O$, C, N, S), and volcanic degassing and subduction 'ingassing' play a major role in their cycles. The input and output of volatiles at plate boundaries provide major links in the cycles of many important elements, including oceanic nutrients and climate-mediating species. Processes occurring at plate-boundaries underlie the generation of many mineral, hydrocarbon, and geothermal resources, and play an important role in most volcanic and seismic hazards. Feedbacks among the mantle, the lithosphere, the cryosphere, the hydrosphere, and the atmosphere exert long-term controls on climate and the biosphere. Examples include:

- By modulating mantle rheology, partial melting and redox state, volatiles influence the operation and style of mantle convection and plate tectonics (perhaps even playing a crucial role in its initiation).
- The composition of magmas at subduction zones and ultimately the composition of the continental crust depends on volatile budgets. Without water the silica-rich low density melts that produce continental crust would not form.
- Carbonate sediment recycling back into the mantle (via subduction) followed by emission via volcanic degassing is part of a long-term feedback modulating atmospheric $CO_2$ levels that has been increasingly important since ~ 200 Ma – how was $CO_2$ cycled in the Earth before this time?
- The link between mantle redox evolution and large changes in surface chemistry, leads to major transitions such as the rise of atmospheric oxygen at 2.5 Ga and the transition from "iron rich, stagnant and low oxygen" (ferruginous/euxinic) waters to "oxygenated oceans" (oxic) oceans at ~0.5 Ga.

Despite the planet's self-regulation during many carbon-driven 'hyperthermal' crises in the past, it is unlikely to do so fast enough for humankind given our current anthropogenic rates of carbon release to the atmosphere. An improved understanding of the role of volatiles in geodynamics, and especially the sensitive connections between the deep Earth, habitability and the environment, is a vital component of our knowledge, both as an intellectual endeavour and in terms of managing our future relationship with our planet.

## 2. The Research Programme (RP)

The proposed RP, *Volatiles, Geodynamics and Solid Earth Controls on the Habitable Planet*, will focus on the fundamental science of volatiles and deep Earth processes, plate tectonics, melting and volcanism and their feedbacks to the surface environment. This action specifically addresses ESS Theme Challenge 2: *Understanding the long term development of the Earth and its habitability*[1] which, amongst its goals, seeks to "Improve knowledge and understanding of: how deep-earth processes influence the surface environment; and the controls on subduction and mantle convection, melting and volcanism."

The goal of this RP is to understand the dynamic role of volatiles in mediating fundamental Earth processes that affect habitability, including mantle convection, plate tectonics, mantle melting and magma delivery, geohazards, and geothermal and ore-forming systems. Specifically the RP will aim to define and understand the controls on the volatile flows and budgets in the mantle, and their feedbacks with mantle behaviour, through well-defined programmes including observations on active geological systems (subduction zones, mantle plumes and spreading centres) and palaeo-analogues, together with closely-aligned laboratory experiments and computer simulations, and coupled geodynamic modelling and seismic imaging. It is expected that successful bids to this programme will combine scientists from a wide range of sub-disciplines within Earth Sciences, and that their chosen areas of study will be justified on the grounds of the relevance of those areas to global Earth System Science problems. It is through truly interdisciplinary work that innovation will come; the RP will act as a catalyst to initiate work between communities of scientists that do not necessarily traditionally work together.

## 3.The Science and Delivery

The programme will require a highly collaborative and interdisciplinary approach involving expertise across a wide range of fields including geophysics, geochemistry, mineral physics and petrology, and involving fieldwork, laboratory studies and computer modelling. It is envisaged that the program will involve delivery via competitive consortium-scale (or larger) proposal(s) to address and integrate the following three interlinked major themes:

1) How has cycling of volatiles between the Earth's surface and interior influenced the evolution of the habitable planet?
2) How have volatile flows both within the solid Earth and its surface reservoirs controlled, and been influenced by, redox (reduction-oxidation) reactions through geological time?
3) How have the content and distribution of volatiles influenced mantle convection and plate tectonics since the Earth formed?

Some of the key interplays relevant to these themes are summarised in Figure 1. The scope and delivery of each of these high-level themes is addressed in turn in the following sections.

### 3.1 How has cycling of volatiles between the Earth's surface and interior influenced the evolution of the habitable planet?

The importance of the mantle in determining the ability of the planetary surface to support life depends on the mass and composition of volatiles initially available in the mantle, and the exchange fluxes of volatiles into and out of the surface reservoirs. The interplay between the surface reservoir and deep Earth volatile budgets has evolved over geological time. Thus our understanding of volatile cycling between the deep Earth and the surface breaks down into four related questions:

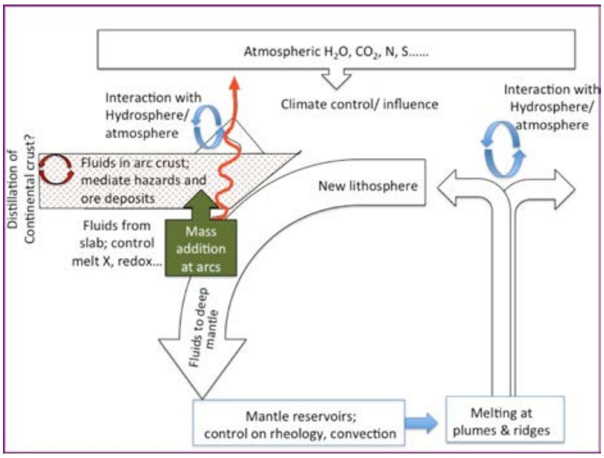


Figure 1. Schematic summary of volatile cycling and influences – which should be considered in the critical context of time, since the magnitude and type of influence will have varied over the 4.5 Ga of Earth history.

*(i) What was the Earth's initial volatile inventory?*

Our understanding of the origin of volatiles within the planet has evolved dramatically in the last few years, linking the origin of mantle volatiles to those brought to the Earth trapped in meteorites[2]. There is evidence from intraplate volcanic systems that the mantle also contains volatiles from the earliest Solar Nebula[3]. These initial volatiles have been complemented by recycled surface volatiles[4]. Establishing the initial volatile element inventory of the mantle provides a key boundary condition for any assessment of the mantle volatile output to the surface.

Delivery: The grand challenge is to resolve the different contributions to the major volatile species from accretionary or recycled sources. This can now be done using and integrating key geochemical tracers such as noble gases, halogens and incompatible elements. These geochemical observables, and our understanding of the fundamental controls on their transport, partitioning and storage, provide the starting point for dynamic models that incorporate chemical tracking. The models in turn allow us to assess the temporal impact of recycling and degassing on the major element volatile concentrations, isotopic compositions, and their spatial variance in the mantle.

*(ii) How have volatile reservoirs changed through time?*

Once the initial volatile boundary conditions have been established it is essential to develop an understanding of how volatile reservoirs subsequently evolve and interact over time. This is a key question since it constrains fluxes among reservoirs, and will allow direct comparison of Earth with other planetary bodies.

Delivery: We are well positioned to address this challenge using state-of-the-art approaches. Precise high-spatial resolution chemical analysis of trace constituents (e.g., volatile elements, incompatible elements and redox-sensitive species) in melt inclusions, undegassed magmatic samples and mantle xenolith minerals can be used to define past and present volatile inventories. Laboratory partitioning measurements using natural samples and experimental products are essential for constraining fluxes between reservoirs, and for understanding the mineral-scale reactions that control volatile release in the solid Earth. Inverting the compositions of ancient rocks can be used to constrain changing source volatile contents. Data mining will provide a critical complement to new studies. Modelling studies of different types and complexity will complement these data.

*(iii) What controls the volatile budget of a subduction zone in space and time?*

As the Earth's primary "valve" controlling the long-term input and output of volatiles, it is perhaps surprising that our understanding and quantification of processes at subduction zones is relatively poor. Volatile-bearing lithosphere is demonstrably returned to the mantle. Some volatiles are released into the overlying mantle wedge, triggering melting and emerging ultimately in arc magmas, while others are recycled into the mantle. The efficiency of recycling and its long-term variability are unknown, but the extent to which volatiles are released or retained by subducting slabs is thought to be controlled primarily by the thermal structure of subduction zones[5].

Delivery: Addressing this question will require wide interactions between petrologists, geochemists, structural geologists, seismologists and geodynamic modellers. Examining the products of arc magmatism and metamorphic rocks at exhumed subduction zones back through time would allow us to understand the changes in arc volatile budgets mediated by recycling of surface-derived components, melting and changing thermal regime. Seismic imaging of subduction zones (most likely involving both active and passive source methods) can be combined with petrological models to provide constraints on the distribution of volatiles in the system, and allow the estimation of input fluxes. Observations of magmatism and seismicity can also be compared to the predicted volatile distribution.

*(iv) How is volatile cycling affected during periods of major perturbations in the Deep Earth system?*

One of the best ways of understanding how a given system works is to disturb it and see how it behaves. Will it revert to some preferred "steady state" or will it cross a tipping point? There are periods in Earth History when dramatic and relatively short-lived changes in the Earth System have occurred that had a clear mantle-driven component. This has the particular advantage of being able to identify and assess the significance of major feedback loops.

Delivery: The stratigraphic record across suitable events provides quantitative detail about the timescale, volatile composition and mass of material involved in these global events. This work may challenge the current surface-centric view that the Earth system can be understood purely in terms of carbon cycling in crustal rocks. In the Cretaceous, for instance, there was a major period of Deep-Earth-triggered large volume magmatism[6], magnetic quiescence (no reversals), increased spreading, ocean basin flooding and climate warming, with consequent seafloor anoxia, and subduction of anoxic sediments. Other examples include the Great Oxidation Event (2.5 Ga), Snowball Earth Recovery (0.65 Ga) and the Permo-Triassic Siberian traps and mass extinction (250 Ma). The interrelationships among volatile outgassing, climate, sea level and subduction zone magmatism predicted from global geodynamic models of volatile exchange between mantle and surface reservoirs could be directly tested in such cases by combinations of targeted field observation and laboratory analysis.

### 3.2 How have volatile flows both within the solid Earth and its surface reservoirs controlled, and been influenced by, redox (reduction-oxidation) reactions through geological time?

The form and abundance of volatile elements that are exchanged between the surface and deep Earth reservoirs depends critically on oxygen fugacity[7]. This is because the speciation of volatiles, and therefore the phases they can exist in and their migration through the mantle and exchange at the surface, are regulated by oxidation-reduction reactions. For example, the redox state of the mantle determines whether carbon is present in its oxidized and potentially mobile form as carbonate or carbonatite melt (which lower the mantle solidus by several hundred degrees), or whether it is present in its reduced and immobile form as graphite or diamond (which do not affect melting temperatures)[8]. The proto-atmosphere composition and the emergence of a habitable surface was intrinsically linked to the early mantle redox state as a consequence of early atmospheric outgassing[9]. Redox sensitive volatile elements such as carbon and sulphur can potentially buffer oxygen fugacity in the mantle or in magmas that degas to the surface[10], and it is clear that they must adjust to changes in oxygen fugacity dictated by mineral equilibria involving elements with multiple valence states, especially iron through $Fe^{2+}$-$Fe^{3+}$ equilibria[11]. The redox state of deep Earth reservoirs would have been established initially after core formation, but would have evolved with time by processes of internal differentiation and through the two-way link with the surface[12]. The potential for the mantle to become oxidized by subduction input has been recognized[13], and there is now compelling evidence linking subducted slab materials to oxidation in the mantle wedge beneath subduction-zone volcanoes[14].

Even though the importance of redox equilibria for mantle-surface evolution has long been recognized, significant knowledge gaps exist in terms of identifying and quantifying the roles that redox equilibria play in deep Earth volatile reservoirs, and how they relate to the surface environment. Currently we lack the required information to model the redox state throughout Earth's interior adequately, and therefore the corresponding speciation and potential budget of volatile elements. For example, models for the speciation of 'simple' C-O-H-S fluids as a function of oxygen fugacity are calculated on the basis of equation of state estimates of fluid fugacities, which are founded upon molecular dynamics calculations of pure fluid properties[15]. There are virtually no high-pressure and -temperature experimental data to confirm the simulated properties even in simple systems; gross extrapolations are necessary to model deep mantle conditions, and information on critical S-bearing systems are lacking. Sulphur is a key element in redox reactions due to its highly variable oxidation state and capacity for electron transfer ($S^{6+}$ to $S^{2-}$), and may play a critical role in oxidative transfer from subducted slab to the mantle wedge and in regulating the redox state of mantle-derived magmas[16]. Volatile speciation and fluid properties as a function of oxygen fugacity in the more complex silicate systems that comprise the mantle are currently not available. We envisage activities within this part of the RP might be organised around the following fundamental questions:

*(i) What are the boundary conditions for the redox state of the early mantle?*

Endeavours in this field are fundamentally linked to our understanding of the origin and distribution of volatiles in the early Earth (see section 3.1). Key topics that need to be addressed include determining the likely oxygen fugacity of accretionary materials[17], and the effects of early magma ocean differentiation, core formation and the moon-forming impact on the mantle's volatile inventory and initial redox state[18].

Delivery: The main approaches that might be applied to this problem include high-pressure experimental studies, geochemical measurements of natural samples, and modelling. For example, the impact of core formation and the crystallisation of the magma ocean on mantle volatile contents and redox state can be studied through high-pressure experiments that constrain how volatile elements partition among mantle and core phases at conditions corresponding to the early magma ocean stage[19]. Investigation of primitive meteorite samples together with mantle-derived samples using novel isotope tracers in radiogenic and stable isotope systems that have recently been developed can place important new constraints on initial volatile contents in Earth and mechanism of volatile differentiation[20].

*(ii) What is the speciation of volatiles in the mantle as a function of redox state?*

In order to develop models for the deep Earth control on the global volatile cycle, we need to know the chemical speciation of volatiles in the mantle as a function of redox state. Specifically we need to know the species that are present in C-O-H-S fluids that are in equilibrium with mantle lithologies as a function of depth, temperature and oxygen fugacity[21]. This information will allow us to place important constraints on how mantle redox state and volatile speciation in the mantle affected the composition of the proto-atmosphere, and how the mantle redox state may have evolved with time and interacted with the evolving atmosphere through surface magmatism.

Delivery: This topic requires a coordinated program of experimental geochemistry and first principles calculations, coupled with constraints on secular variations in mantle redox state (discussed below in question iii). *Ab initio* calculations coupled with high-pressure and –temperature experiments can be used to determine volatile element stability and partitioning among mantle phases[22] (see also section 3.1.ii), volatile element solubilities in deep mantle and core phases[23], the effects of volatiles on mantle melting[24], and volatile speciation in melts and fluids[25], all as a function of redox state.

(*iii) How does recycling of volatiles change the mantle redox state through time?*

While we know that the redox state of the planet's surface has varied significantly over geological time, our understanding of the secular and spatial variations in mantle redox remains in its infancy. Existing proxies based on $Fe^{3+}$ mineral equilibria[26], vanadium partitioning[27] and the stable isotope signatures of redox sensitive elements such as iron[28] and vanadium[29] provide some constraints on secular variations in mantle oxidation state, but the existing data coverage is restricted. Recent progress in using synchrotron-based XANES measurements to measure the valence state of redox sensitive elements in mantle samples directly is a promising way forward[30], especially with world-class facilities available at the Diamond Light Source synchrotron. Such information is crucial in evaluating whether the mantle controlled or responded to surface redox changes such as the great oxidation event.

Delivery: State-of-the-art observations such as synchrotron-based X-ray absorption techniques on mantle derived samples can be used to explore spatial and secular variations in the redox state of magmatic and mantle samples from the Archean to the Phanerozoic[31], providing much needed information about coupling of deep mantle redox processes to the surface. This information can be linked with geochronological constraints to provide information about secular variations in both in the chemistry of material recycled from the Earth's surface into the deep mantle by plate tectonics[32]. Surface-derived volatile species can potentially be identified in deep-Earth reservoirs, for example through studies of diamonds and their inclusions, and they can be linked to both the redox chemistry of recycled material and to geodynamic processes involved in crustal recycling[33].

### 3.3 How have the content and distribution of volatiles influenced mantle convection and plate tectonics since the Earth formed?

Volatiles may weaken the rheology of mantle minerals by as much as an order of magnitude or more[34]. As the mantle volatile composition evolves through volatile loss to the planet's surface and subduction of volatiles back into the mantle system, the feedback into rheology may change the convective style and vigour with which the mantle convects and affect the style of plate tectonics [35]. A critical feedback between volatile content and rheology may aid in plate-boundary formation, as well as result in mantle regions with higher water content flowing faster than drier regions promoting shear decoupling of water poor regions from overall mantle flow. Another potential result is that the convective overturn rate and heat transport out of the mantle as a whole may see a secular rise as the mantle becomes more hydrated.

The combination of recent advances in numerical simulations and a fundamental understanding of the effect of water on rheology, if brought together, have the real prospect of a transformative change in our understanding of convection within the Earth's mantle, a new insight into how our deep planet works, and how it controls or moderates planetary habitability. Advances will be even greater if we add the volatile boundary conditions and observational constraints provided by the carefully-planned geochemical campaign outlined above. Indeed, our understanding of mantle volatile flux to the surface, and its role in controlling planetary habitability, is only as good as our understanding of volatile return into the mantle and the feedback effect this has on mantle geodynamics over time. In addressing this, there are several key questions:

*(i) How can we build a complete understanding of how volatile content and heterogeneity control mantle rheology?*

Although we know that small variations in the water content of mantle minerals play a fundamental role in determining their viscosity, quantifying this has proven difficult with estimates ranging from less than an order of magnitude weakening to several orders of magnitude. This is a particular problem at higher pressure and temperature, but also in complex mineral assemblages where the partitioning of water between different phases, relative phase proportions and the connectivity of different phases must all be considered.

Delivery: Advances in computational techniques have now made it possible to use first principles techniques at the atomic scale to obtain the rheology of mantle minerals throughout the mantle for both diffusion creep[36] and dislocation creep[37], and multiscale physics can then be utilized to apply these single crystal results to polycrystalline rocks[38]. Improvements in laboratory techniques are allowing us to measure rheological properties experimentally under upper mantle conditions[39], and plans to extend these to the lower mantle using diamond anvil technology are underway.

*ii) How can the predicted geophysical and geochemical signatures of a dynamic feedback between volatile content, mantle rheology and convection distinguish mantle evolution scenarios?*

Numerical simulations of mantle convection may be three dimensional, two dimensional or sophisticated box models – depending on the application and focus of the hypothesis to be tested. The degree of UK expertise and computing power now available enables, for example, models to work at Earth-like convective vigour and in providing global simulations using complex rheology in spherical geometry. Both seismic imaging and mineral physics have a key role to play in testing model confidence: For example, fluid dynamical models are being used to identify the mantle conditions that influence the results of seismic tomography imaging[40]. This harnesses recent developments in both inversion technologies and waveform propagation modelling. Further cross-disciplinary constraints on how seismic parameters relate to physical conditions are being supplied by molecular dynamics and mineral physics[41]. A combination of geodynamic flow models and mineral physics are being used to predict the large-scale development of mineral fabrics, which can be compared with observations of seismic anisotropy[41].

Delivery: Numerical modelling approaches have had for some time the capacity to track geochemical information[42]. These types of model not only return concentration information through the effects of melting or degassing, but are also able to follow the isotopic change of different elements over time by tracking radioelements such as U and K. The key advantage of this approach is in providing a three dimensional understanding though time of volatile, trace element and isotope distribution - all within the constraints imposed by our understanding of the fluid dynamics. In exactly the same way as the geophysical constraints of seismic imaging and mineral physics, observed volatile and trace element distribution and observed scale of isotopic heterogeneity provide the key conditions that the models must match to gain confidence in their robustness and ability to define volatile flux out of and into the mantle.

## 4. Why Theme Action mode of funding is necessary

This proposed RP will focus on the fundamental science of volatiles and deep-Earth processes, plate tectonics, melting and volcanism and their feedbacks to the surface environment. Although the research outcomes will be relevant to other themes such as Natural Hazards (volcanoes and earthquakes), Sustainable Use of Natural resources (mineral and hydrocarbon resources) and other components of the ESS theme (oceanic and atmospheric composition, paleo-climate), the focus of this action on fundamental science means the programme is better delivered as an exclusive ESS programme, rather than as a joint action with those themes. *Volatiles, Geodynamics and Solid Earth controls on the Habitable Planet* is appropriate for a RP for two main reasons: (i) the need to develop large interdisciplinary teams to tackle strategically important science objectives; (ii) the legacy it will leave in terms of the UK solid- and deep-Earth communities.

*(i) The need to develop large interdisciplinary teams to tackle strategically important science objectives.*

The opportunity presented by a theme action for a “large targeted investment where coordination and integration are essential” is precisely what is needed to deliver research “broader in scope than is normally achievable via responsive mode funding”. The key to a step change in our understanding is effective integration.

Cross-disciplinary work to date addressing these science problems has been in the most part bi-lateral[43]. **It is now very apparent that to make a significant advance in this field we need a coordinated program that brings together and exploits the recent advances across laboratory experiments and geochemistry, seismic observation, mineral physics, molecular dynamical simulations and fluid dynamics.**

*(ii) The legacy it will leave in terms of the UK solid and deep Earth communities.*

A RP focussed on *Volatiles, Geodynamics and Solid Earth controls on the Habitable Planet*, by its explicit co-ordination, will bring together the UK Deep Earth community and form links that will far outlast the RP itself. The delivery of the required interdisciplinary science in the RP will provide an excellent training and development opportunity for graduate students and post-doctoral researchers ensuring a legacy of UK scientific leaders in this area. Critical in this legacy is establishing a strong network of interdisciplinary science that will establish a culture of resource, training and infrastructure sharing that will change the way this area of science will be delivered in the UK and further enhance its international competitiveness.

To ensure this legacy further we suggest that the RP budget should explicitly provide funding for frequent joint workshops for the students, PDRAs

places also for attendance by scientists not funded within the consortia.

## 5. UK Contribution and Capability

The UK is world-leading in many of the scientific communities needed to deliver conceptual step changes in these areas. The scoping phase of this RP has shown how stimulating bringing these different communities together can be and the time is ripe to build upon this momentum. To deliver innovation in this area will require groups working in areas such as volcanology, geodynamics, isotope geochemistry, mineral physics, seismology, experimental petrology and igneous geochemistry to work together as well as engaging with the wider NERC community when communicating their science. Some specific areas are discussed in more detail below (and summarised in Figure 2):

- *Seismic Imaging:* Seismology provides the most direct observations of large-scale mantle properties. UK groups play a leading role in advancing global seismic tomography and are at the forefront of seismic imaging of anisotropy at a range of scales[44] – critical for testing models of the interaction of volatiles and geodynamics. There is also a wealth of experience in crustal-scale active source seismology.
- *Computational Mineral Physics:* Calculating the stability and physical properties of volatile-bearing materials at deep mantle and core conditions is critical for understanding the form of volatiles in these super-deep reservoirs. The UK is an international leader in *ab initio* simulation of phase equilibria and material properties at the extreme conditions of planetary interiors[46].
- *High P-T Experimental Geochemistry and Mineral Physics*. High P-T experimental investigations at conditions from the crust to the core are essential for understanding volatile speciation, phase equilibria, partitioning, and mobility. Mineral physics and experimental petrology are underpinned by at least five world-class University laboratories, further theoretical groups and national facilities like the Diamond Light Source.
- *Fluid Dynamical Modelling:* Quantifying volatile exchange between deep reservoirs depends on the mechanism and rates of mantle and lithosphere flow. The UK is amongst the leaders in developing

simulations, which include non-linear viscosity, the effects of phase transitions and, increasingly, chemistry[47]. The geodynamics community is underpinned by NERC's advanced computing facilities.

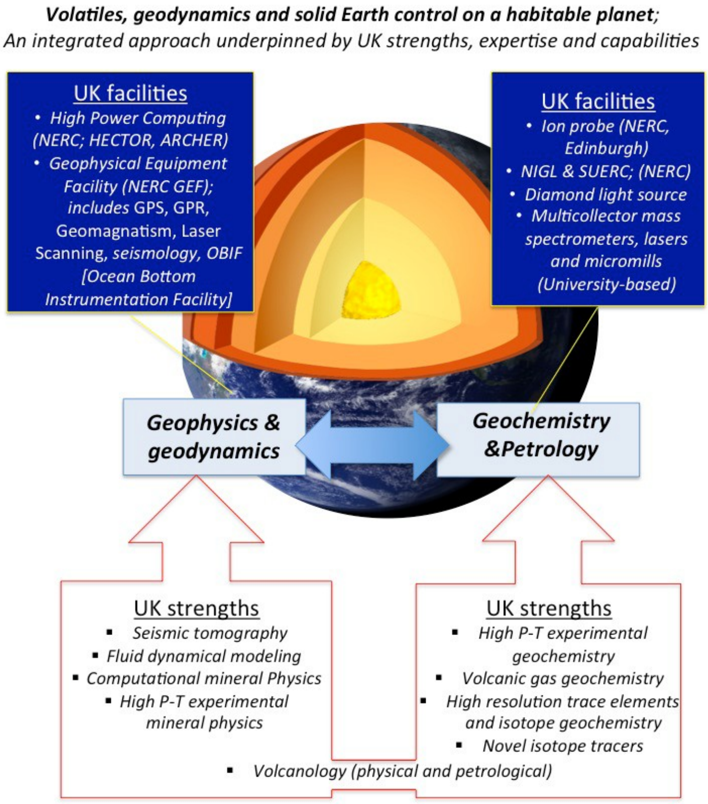


Figure 2.
Summary of relevant UK strength and facilities.

- *Trace Element and Isotope Geochemistry:* Chemical and isotopic analyses are central to tracking the geochemical and geodynamic processes that moderate volatile budgets and provide temporal constraints. The UK has an extensive NERC-funded state of the art equipment-base. Over eight UK groups lead the development and application of novel tracers and microanalytical techniques[48].
- *Volcanic Gas Geochemistry:* Volcanic outgassing plays a key role in the interplay and the planet's surface environment both in terms of long-term stability and short-term perturbations. Over seven UK groups play a world-leading role driving this scientific field[49].
- *NERC and RCUK Facilities:* Central to a successful deep Earth volatile Programme are the world-class national analytical and computational facilities, including the Diamond Light Source, NIGL, SUERC, the Edinburgh Ion Microprobe Facility, and the HECTOR and ARCHER computational facilities.

## 6. Timeliness

The strongest justifications for timeliness lie in the previous section. The UK community has an assembly of expertise and facilities, and a track record of inspiration and innovation, that together are poised to make a difference in this field. The UK is already at the cutting edge in many of the disciplines that focus on Deep Earth problems, and the goal of this action, is to instigate transformative science by bringing these communities together. There are also key recent technological advances and international programs that naturally link into the core science of this action and further enhance the timeliness of the proposed RP.

*(i) Recent technological advances*

Technical advances, such as in seismic interpretation, modelling capability and geochemical analysis techniques, are contributing to improved acquisition and analysis of geophysical and geochemical data. Rich new datasets are now developing that offer an opportunity for a major synthesis effort within this proposed RP. This will allow the science to take a major conceptual step forward, moving from developing hypotheses to tackling major research questions with more effective interdisciplinary research amongst the core disciplines. The UK is playing a major role in the exploitation of these developments and is well placed to spearhead this proposed initiative. Some examples are given below:

- **New developments in geochemical** analyses: a trend towards progressively smaller sample sizes, precisions and length scales. The development of laser ablation and mechanical micro-sampling techniques, alongside multicollector mass spectrometry and more sensitive detection techniques has enabled the UK community to be among the leaders in analysing samples within petrological contexts[50]. This has enabled us to examine mineral zoning and use this to back out petrogenetic processes from core-rim profiles[51], and to analyse melt inclusions to determine melt evolution[52] and particularly volatile budgets. Equally important has been the step improvement in mass spectrometry technology with the advent of multi-collector systems. For example, within the last few years we have seen an improvement in the precision of some noble gas isotope ratio determinations by up to a factor of fifty[53].
- **Combining computer modelling and experiments to probe volatile partitioning between different mantle phases.** *Ab initio* calculations coupled with high-PT experiments using state-of-the-art multi-anvil and diamond anvil cell techniques provide a powerful complementary approach. Recently developed state of the art internally and externally-heated diamond anvil cell techniques coupled with laboratory-based and synchrotron-based spectroscopic methods now permit *in situ* measurements of fluid speciation, and allow investigation of volatile-bearing phase equilibria to core conditions. Recently developed synchrotron X-ray microtomography techniques coupled with high-pressure multi-anvil apparatus permit direct measurement of fluid volumes, and multi-anvil techniques combined with micro-analysis (e.g. SIMS, FTIR) permit measurement of volatile partitioning among mantle phases. Thermodynamic data such as enthalpies, chemical potentials, and volumes of mixing can now all be obtained via *ab initio* molecular dynamics techniques and fit to equations of state. These equations of state can then be used to predict volatile partitioning between different mantle phases and at different conditions, which can be directly verifiable and supplemented by high-pressure experimentation. This complementary approach between experiment and theory is key to providing results with the

highest possible degree of confidence. NERC's investment in the new national high performance computer to be installed in 2013 (ARCHER) is a timely development in UK computational capability and will make these calculations possible.

- **Computer models of convection: handling large variations in strain and the feedback between chemistry and rheology.** It is now possible to model, from first principles and at the atomic scale, the rheology of lower mantle minerals. Advances in experimental methods allow the rheology of Earth materials to be measured directly for large volumes of sample under the temperature and pressure conditions of the upper mantle, and lowermost mantle conditions will soon be obtainable. However, uncertainties remain in the theory of the deformation of poly-phase polycrystalline composites (rocks) and how to best describe their deformation within larger scale models of mantle convection. Mantle convection models and computational power have recently advanced to the point where they are be able to incorporate non-linear and material dependent rheologies in global scale models thus allowing to test the implications of experimentally and numerically constrained flow laws.
- **Driving the limits of seismic imaging:** global full waveform tomography. The development of adjoint inversion and waveform modelling techniques and the meteoric rise of available computing power is driving a revolution in full waveform tomography. It is now possible to make global models to match large global datasets at long periods. Improvements over the next few years will see the frequency being driven higher, improving not only the resolution of the models but also the range of parameters which can be robustly determined.

*(ii) Complementary international programmes*

The UK has ongoing synergies with relevant international programmes including:

- **The International Deep Carbon Observatory (DCO):** This program, is managed through the auspices of the Carnegie Institution of Washington (USA) (https://dco.gl.ciw.edu/), and is a “multidisciplinary, international initiative dedicated to achieving a transformational understanding of Earth's deep carbon cycle”. The DCO provides substantial support and access to the international community and has clear synergies with the proposed RP. The DCO welcomes this interaction and the scoping workshop was attended by the DCO Director, Craig Schiffries.
- **GeoPRISMS:**The US NSF is in its second iteration of thematic funding (“GeoPRISMS (http://geoprisms.org/ )following on from ”Margins”, 2000-2010) with a major focus on subduction zones, including cycling of volatiles. Support and offers of collaboration have already been offered by the GeoPRISMS leadership for this RP. Similar to the DCO this program offers access to the networking opportunities, collaborative interactions and data outputs of a major and complementary international effort. GeoPRISMS was represented by Katie Kelley at the scoping workshop.
- **Computational Infrastructure in Geodynamics (CIG):** This NSF-funded, membership-led organisation supports and promotes Earth science by developing and maintaining software for computational geophysics (http://geodynamics.org/ ) UK universities including Bristol, Cardiff and UCL are foreign affiliate members of CIG. Collaborating with this organisation will enable the broad impact of software developed and enhanced by activity in the RP. Louise Kellogg represented CIG at the (geodynamics) scoping workshop.

## 7. Impact

The fundamental impact of this RP will be to inspire and inform both the science community and public alike. Examples of this outside the NERC arena are seen for example through improvements in understanding the solar system via remote missions such as the Cassini-Huygens probe, the upcoming ROSETTA mission to a comet, and even the Google Lunar-X prize. The obvious immediate benefits include bringing together UK researchers at the forefront of this field, training a new generation of highly skilled and interdisciplinary scientists, and maximising use of recent NERC investment in the world-class UK scientific infrastructure. We also expect the continued development of new analytical and computational methods will require input from UK industry and enterprise. In particular interactions with the strong UK analytical equipment industry base will benefit from a buoyant scientific community in this area allowing, for example, UK industry to continue to lead the world in supplying state of the art mass spectrometers.

## 8. Indicative budget

**Core person hours:** We envision a roughly equal split in the budget between Geophysics and Geochemistry. We have used a notional £100k average cost per postdoc year to represent typical FEC costs that include the PDRA's time, a proportional amount of time spent on the project by a senior permanent academic, travel (fieldwork, conferences, twice yearly TAP group meetings, local meetings), and laboratory costs (including small equipment). This effort will need about 18 PDRAs.

5 × 5-year Senior PDRAs (could be funded through a special fellowship round) would provide the experience and continuity essential for a 5-year program. These would ideally be assigned to each of the key areas in Geochemistry and Geophysics to supervise and coordinate across disciplines. An additional 7-8 × 3-year PDRA positions in each of Geochemistry and Geophysics would support the focussed research effort of the specialist groups.

The total effort of the 3- and 5-year postdoctoral fellows would be about 70 person years (see example resource chart in Appendix 1), costing £6.4million

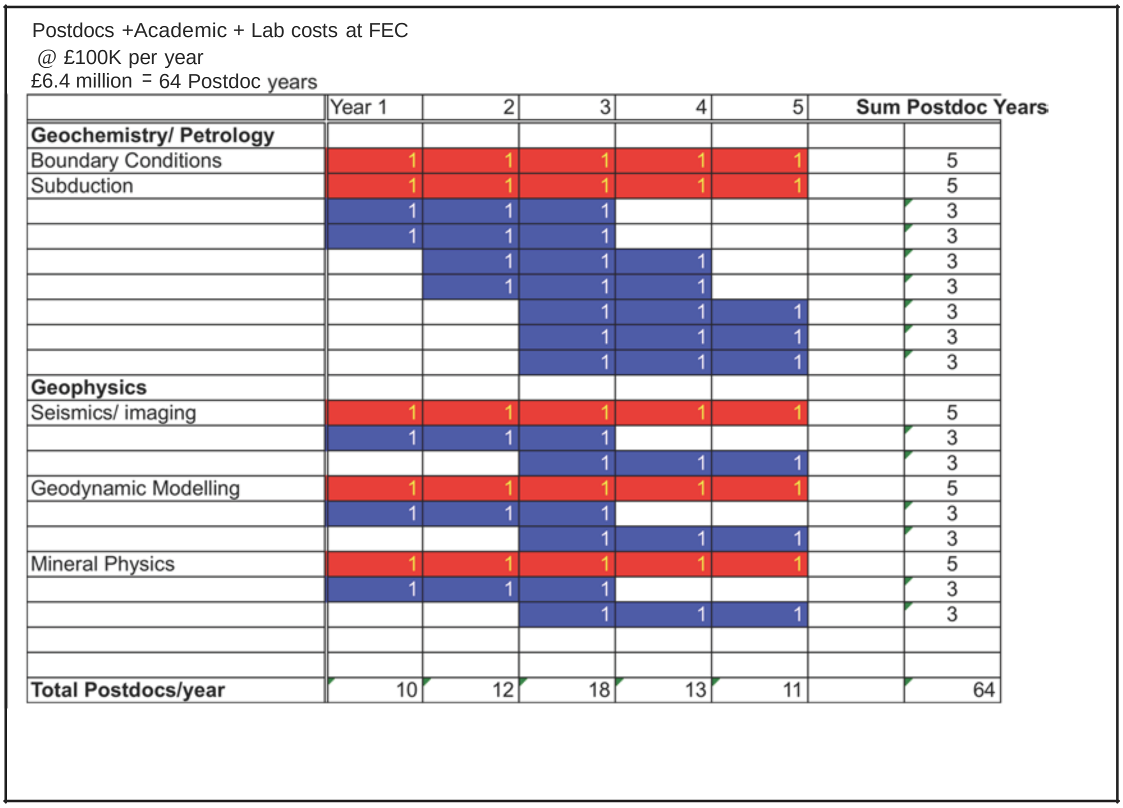
**Training:** PhD student training costs approximately £20k/year, with each student requiring 3.5 years to complete. 18 PhD students (parity in numbers with the PDRAs) would cost £1.26 million.

**Facilities:**Use of national facilities (including ship time, computing, Diamond, NIGL, EIMF, SUERC) could range from £1-3million depending on need. We budget here for the average value of £2million.

**Total TAP Budget: (Indicative) = £9.66million**

---

## Appendix 1: Example resource chart



Postdocs +Academic + Lab costs at FEC
@ £100K per year
£6.4 million = 64 Postdoc years

| | Year 1 | 2 | 3 | 4 | 5 | | Sum Postdoc Years |
|---|---|---|---|---|---|---|---|
| **Geochemistry/ Petrology** | | | | | | | |
| Boundary Conditions | 1 | 1 | 1 | 1 | 1 | | 5 |
| Subduction | 1 | 1 | 1 | 1 | 1 | | 5 |
| | 1 | 1 | 1 | | | | 3 |
| | 1 | 1 | 1 | | | | 3 |
| | | 1 | 1 | 1 | | | 3 |
| | | 1 | 1 | 1 | | | 3 |
| | | | 1 | 1 | 1 | | 3 |
| | | | 1 | 1 | 1 | | 3 |
| | | | 1 | 1 | 1 | | 3 |
| **Geophysics** | | | | | | | |
| Seismics/ imaging | 1 | 1 | 1 | 1 | 1 | | 5 |
| | 1 | 1 | 1 | | | | 3 |
| | | | 1 | 1 | 1 | | 3 |
| Geodynamic Modelling | 1 | 1 | 1 | 1 | 1 | | 5 |
| | 1 | 1 | 1 | | | | 3 |
| | | | 1 | 1 | 1 | | 3 |
| Mineral Physics | 1 | 1 | 1 | 1 | 1 | | 5 |
| | 1 | 1 | 1 | | | | 3 |
| | | | 1 | 1 | 1 | | 3 |
| | | | | | | | |
| | | | | | | | |
| **Total Postdocs/year** | 10 | 12 | 18 | 13 | 11 | | 64 |

# Appendix 2. References

---

[1] Earth System Science – Theme Action Plan 3 (http://www.nerc.ac.uk/research/themes/tap/fullversions.asp#tap3)

[2] Ballentine C.J., Marty B., Lollar B.S., et al. (2005) Neon isotopes constrain convection and volatile origin in the Earth's mantle Nature **455** 33-38 DOI: 10.1038/nature03182

Trieloff M., Kunz J., Clague D.A., et al. (2000) The nature of pristine noble gases in mantle plumes Science **288** 1036-1038 DOI: 10.1126/science.288.5468.1036

[3] Yokochi R., Marty B., (2004). A determination of the neon isotopic composition of the deep mantle Earth and Planet . Sci. Lett., **225**, 77–88

[4] Holland G., Ballentine C.J., (2006) Seawater subduction controls the heavy noble gas composition of the mantle Nature **441** 186-191 DOI: 10.1038/nature04761

Sumino H., Burgess R., Mizukami T., et al (2010) Seawater-derived noble gases and halogens preserved in exhumed mantle wedge peridotite Earth and Planet . Sci. Lett. **294** 163-172 DOI: 10.1016/j.epsl.2010.03.029

[5] Peacock S. M. (2003), Thermal structure and metamorphic evolution of subducting slabs, in Inside the Subduction Factory, Geophys. Monogr. Ser., **138**, edited by J. Eiler pp. 7–22, AGU, Washington, D. C., DOI:10.1029/138GM02

[6] Machetel P., Humler E., (2003) High mantle temperature during Cretaceous avalanche, Earth and Planet . Sci. Lett. **208** 125-133 DOI: 10.1016/S0012-821X(03)00041-4

[7] Frost D.J., McCammon C.A., (2008) The redox state of Earth's mantle, Annual Review of Earth and Planetary Sciences, **36**, 389-420 DOI: 10.1146/annurev.earth.36.031207.124322

[8] Rohrbach A., Schmidt M.W., (2011) Redox freezing and melting in the Earth's deep mantle resulting from carbon-iron redox coupling, Nature **472**, 209-212.

[9] Zahnle K.J., (2006) Elements, **2**., 217-222 Earth's Earliest Atmosphere DOI: 10.2113/gselements.2.4.217

Sleep N. H., Zahnle K., Neuhoff P. S., (2001) Initiation of clement surface conditions on the earliest Earth. Proceedings of the National Academy of Sciences of the United States of America, **98**, 3666-3672

Catling D. C., Glein C. R., Zahnle K. J., McKay C. P., (2005) Why O(2) is required by complex life on habitable planets and the concept of planetary "oxygenation time". Astrobiology **5**, 415-438

[10] Blundy J.D., Brodholt J.P., Wood B.J., (1991) Carbon–fluid equilibria and the oxidation state of the upper mantle Nature **349**, 321 - 324, DOI:10.1038/349321a0

Oppenheimer, C., Moretti R., Kyle P. R., Eschenbacher A., Lowenstern J. B., Hervig R. L., and Dunbar N. W., (2011) Mantle to surface degassing of alkalic magmas at Erebus volcano, Antarctica. Earth and Planetary Science Letters **306**, 261-271

[11] Canil D. et al., (1994) Ferric iron in peridotites and mantle oxidation states. Earth and Planetary Science Letters, **123**: 205-220;

Woodland A.B., Kornprobst J. A., Tabit A., (2006) Ferric iron in orogenic lherzolite massifs and controls of oxygen fugacity in the upper mantle Lithos **89**, 222–24

Rohrbach A., Schmidt M. W., (2011). Redox freezing and melting in the Earth's deep mantle resulting from carbon-iron redox coupling. Nature **472**, 209-212

[12] Frost D.J, McCammon C.A ., (2008) The redox state of earth's mantle. Annu. Rev. Earth Planet. Sci. **36**, 389–420. DOI:10.1146/annurev.earth.36.031207.124322.

[13] Lecuyer C., Ricard Y., (1999) Long-term fluxes and budget of ferric iron: implication for the redox states of the Earth's mantle and atmosphere. Earth and Planetary Science Letters**165**, 197-211

[14] Kelley K., Cottrell E., (2009), Water and the Oxidation State of Subduction Zone Magmas. Science, **325** 605-607, DOI: 10.1126/.1174156

[15] Belonoshko A. Saxena S.K., (1991), A molecular dynamics study of the pressure-volume-temperature properties of supercritical fluids: II. $CO_2$, $CH_4$, CO, $O_2$, and $H_2$, Geochim. Cosmochim. Acta, **55** 3191–3208.

[16] Kelley K.A., Cottrell E., (2012)The influence of magmatic differentiation on the oxidation state of Fe in a basaltic arc magma,Earth and Planetary Science Letters **329–330**,109–121

[17] Schoenbaechler M., Carlson R. W., Horan M. F., Mock T. D., Hauri E. H., (2010). Heterogeneous Accretion and the Moderately Volatile Element Budget of Earth. Science **328**, 884-887

[18] O'Neill H. S., (1991) The origin of the Moon and the early history of the Earth – a chemical model. 2. The Earth. Geochimica et Cosmochimica Acta **55**, 1159-1172

[19] Frost D. J., McCammon C. A., (2008). The redox state of Earth's mantle, Annual Review of Earth and Planetary Sciences ***36**, 389–420. DOI:10.1146/annurev.earth.36.031207.124322.*

Rubie D. C., Gessmann C. K., Frost D. J., (2004). Partitioning of oxygen during core formation on the Earth and Mars. Nature **429**, 58-61

Wood B. J., Walter M. J., Wade J., (2006). Accretion of the Earth and segregation of its core. Nature **441**, 825-833

[20] Shahara A., Ziegler K.,Young E. D., Angele Ricolleau. A.,Schauble, E.A.,Fei, Y., (2009) Experimentally determined Si isotope fractionation between silicate and Fe metal and implications for Earth's core formation. Earth Planet. Sci. Lett., **288**. 228-234

Williams, H. M., McCammon, C. A., Peslier, A. H., Halliday, A. N., Teutsch, N., Levasseur, S., Burg, J. P., (2004). Iron isotope fractionation and the oxygen fugacity of the mantle. Science **304**, 1656-1659

Schoenbaechler, M., Carlson, R. W., Horan, M. F., Mock, T. D., Hauri, E. H., (2010). Heterogeneous Accretion and the Moderately Volatile Element Budget of Earth. Science **328**, 884-887

[21] Frost D. J. McCammon C. A., (2008). The redox state of Earth's mantle, Annual Review of Earth and Planetary Sciences; ***36**, 389–420. DOI:10.1146/annurev.earth.36.031207.124322*

Rubie, D. C., Gessmann, C. K., and Frost, D. J., 2004. Partitioning of oxygen during core formation on the Earth and Mars. Nature **429**, 58-61;

Wood B. J., Walter M. J., Wade J., (2006). Accretion of the Earth and segregation of its core. Nature **441**, 825-833

Kohn, S. C., Grant, K. J. (2006) The partitioning of water between nominally anhydrous minerals and silicate melts. In WATER IN NOMINALLY ANHYDROUS MINERALS Book Series: Reviews in Mineralogy & Geochemistry (Keppler H; Smyth JR eds.) 62, 231-241 DOI: 10.2138/rmg.2006.62.10.

Poli S., Franzolin E., Fumagalli P., et al. (2009) The transport of carbon and hydrogen in subducted oceanic crust: An experimental study to 5 GPa Earth and Planet . Sci. Lett. **278**, 350-360 DOI: 10.1016/j.epsl.2008.12.022

Hirschmann M. M., Aubaud C., Withers A.C., (2005) Storage capacity of H(2)O in nominally anhydrous minerals in the upper mantle, Earth and Planet . Sci. Lett. **236**, 167-181 DOI: 10.1016/j.epsl.2005.04.022

Jephcoat Andrew P.; Bouhifd M. Ali; Porcelli Don (2008) Partitioning experiments in the laser-heated diamond anvil cell: volatile content in the Earth's core. Philosophical Transactions Of The Royal Society A-Mathematical Physical And Engineering Sciences 366 4295-4314 DOI: 10.1098/rsta.2008.0226

Dasgupta R., Hirschmann M. M., Smith N. D., (2007) Partial melting experiments of peridotite CO2 at 3 GPa and genesis of alkalic ocean island basalts, Journal Of Petrology **48**, 2093-2124 DOI: 10.1093/petrology/egm053

Dasgupta R., Hirschmann M. M. (2007) Effect of variable carbonate concentration on the solidus of mantle peridotite American Mineralogist **92** 370-379 DOI: 10.2138/am.2007.2201

Mysen, B. O., Kumamoto, K., Cody, G. D., Fogel, M. L., (2011) Solubility and solution mechanisms of C-O-H volatiles in silicate melt with variable redox conditions and melt composition at upper mantle temperatures and pressures. Geochimica et Cosmochimica Acta **75**, 6183-6199

Canil, D., O'Neill, H. S., Pearson, D. G., Rudnick, R. L., McDonough, W. F., Carswell, D. A., (1994). Ferric iron in peridotites and mantle oxidation-states. Earth and Planetary Science Letters **123**, 205-220

Canil, D., (2002). Vanadium in peridotites, mantle redox and tectonic environments: Archean to present. Earth and Planetary Science Letters**195**, 75-90

Williams, H. M., McCammon, C. A., Peslier, A. H., Halliday, A. N., Teutsch, N., Levasseur, S., Burg, J. P., (2004) Iron isotope fractionation and the oxygen fugacity of the mantle. Science **304**, 1656-1659

Nielsen S. G., Prytulak J., Halliday A. N., (2011). Determination of Precise and Accurate V-51/V-50 Isotope Ratios by MC-ICP-MS, Part 1: Chemical Separation of Vanadium and Mass Spectrometric Protocols. Geostandards and Geoanalytical Research **35**, 293-306

Prytulak, J., Nielsen, S. G., and Halliday, A. N., (2011). Determination of Precise and Accurate V-51/V-50 Isotope Ratios by Multi-Collector ICP-MS, Part 2: Isotopic Composition of Six Reference Materials plus the Allende Chondrite and Verification Tests. Geostandards and Geoanalytical Research **35**, 307-318

Cottrell E., Kelley K. A., Lanzirotti, A., and Fischer R. A., (2009). High-precision determination of iron oxidation state in silicate glasses using XANES. Chemical Geology **268**, 167-179

Metrich N., Berry A. J., O'Neill H. S. C., Susini J., (2009). The oxidation state of sulfur in synthetic and natural glasses determined by X-ray absorption spectroscopy. Geochimica Et Cosmochimica Acta **73**, 2382-2399

Berry A. J., Yaxley G. M., Woodland A. B., and Foran G. J., (2010). A XANES calibration for determining the oxidation state of iron in mantle garnet. Chemical Geology **278**, 31-37.

Kelley K. A. Cottrell E., (2009) Water and the Oxidation State of Subduction Zone Magmas, Science **325**, 605-607, DOI: 10.1126/science.1174156

Yaxley G. M., Berry A. J., Kamenetsky V. S. et al. (2012) An oxygen fugacity profile through the Siberian Craton - Fe K-edge XANES determinations of Fe3+/Sigma Fe in garnets in peridotite xenoliths from the Udachnaya East kimberlite, Lithos **140**, 142-151 DOI: 10.1016/j.lithos.2012.01.016

Becker H., Shirey S,B., Carlson R.W., (2001) Effects of melt percolation on the Re–Os systematics of peridotites from a Paleozoic convergent plate margin, Earth Planet. Sci. Lett., **188**, 107–121

McCammon C., Hutchison M., Harris J., (1997). Ferric iron content of mineral inclusions in diamonds from Sao Luiz: A view into the lower mantle. Science **278**, 434-436

Walter M. J., Kohn S. C., Araujo D., Bulanova G. P., Smith C. B., Gaillou E., Wang J., Steele A., Shirey S. B., (2011). Deep Mantle Cycling of Oceanic Crust: Evidence from Diamonds and Their Mineral Inclusions. Science **333**, 54-57

Mei S., Kohlstedt D.L., (2000) Influence of water on plastic deformation of olivine aggregates 1. Diffusion creep regime Earth and Planet . Sci. Lett.**105** 21457-21469 DOI: 10.1029/2000JB900179

McGovern P.J. Schubert G. (1989) Thermal evolution of the Earth – Effects of volatile exchange between atmosphere and interior. Earth and Planet. Sci. Lett. **96** 27-37 DOI: 10.1016/0012-821X(89)90121-0

Ammann M. W., Brodholt J. P., Wookey J., Dobson D. P., (2010). First-principles constraints on diffusion in lower-mantle minerals and a weak D '' layer. Nature **465**, 462-465.

Cordier P., Amodeo J., and Carrez P., (2012). Modelling the rheology of MgO under Earth's mantle pressure, temperature and strain rates. Nature **481**, 177-180

Wheeler J., (2010). Anisotropic rheology during grain boundary diffusion creep and its relation to grain rotation, grain boundary sliding and superplasticity. Philosophical Magazine **90**, 2841-2864.

Hunt S. A., Dobson D. P., Li L., Weidner D. J., Brodholt, J. P., (2010). Relative strength of the pyrope-majorite solid solution and the flow-law of majorite containing garnets. Physics of the Earth and Planetary Interiors **179**, 87-95.

Styles, E., Goes S., van Keken P. E., et al.(2011) Synthetic images of dynamically predicted plumes and comparison with a global tomographic model Earth and Planet . Sci. Lett.**311** 351-363 DOI: 10.1016/j.epsl.2011.09.012

Wookey J., Stackhouse S., Kendall J.M., et al. (2005) Efficacy of the post-perovskite phase as an explanation for lowermost-mantle seismic properties Nature **438** 1004-1007 DOI: 10.1038/nature04345,

---

Walker A.M., Forte A.M., Wookey J., Nowacki A., Kendall, J.M., (2011) Elastic anisotropy of D″ predicted from global models of mantle flow, Geochemistry, Geophysics, Geosystems, **12**, (pp. -), 2011. ISSN: 1525-2027 DOI: 10.1029/2011GC003732

[42] van Keken P.E., Hauri E.H., Ballentine C.J., (2002) Mantle mixing: The generation, preservation, and destruction of chemical heterogeneity Annual Rev. Earth and Planet. Sci. **30** 493-525 DOI: 10.1146/annurev.earth.30.091201.141236

Brandenburg J. P.; Hauri Erik H.; van Keken Peter E.; et al. 2008 A multiple-system study of the geochemical evolution of the mantle with force-balanced plates and thermochemical effects Earth and Planet. Sci. Lett. 2008 276 1-13 DOI: 10.1016/j.epsl.2008.08.027

[43] Wookey J., Stackhouse S., Kendall J.M., et al. (2005) Efficacy of the post-perovskite phase as an explanation for lowermost-mantle seismic properties Nature **438** 1004-1007 DOI: 10.1038/nature04345

Styles E.,; Goes S., van Keken P. E., et al.(2011) Synthetic images of dynamically predicted plumes and comparison with a global tomographic model Earth and Planet . Sci. Lett.**311** 351-363 DOI: 10.1016/j.epsl.2011.09.012

van Keken P.E., Ballentine C.J., (1999) Dynamical models of mantle volatile evolution and the role of phase transitions and temperature-dependent rheology J. Geophys. Res. **104** 7137-7151 DOI: 10.1029/1999JB900003

[44] Ferreira, A.M.G., Woodhouse, J.H., Visser, K. and Trampert, J. (2010). On the robustness of global radially anisotropic surface wave tomography. J. Geophys. Res., **115**, B04313

Nowacki A, Wookey, J., Kendall, J.M., (2011) New advances in using seismic anisotropy, mineral physics and geodynamics to understand deformation in the lowermost mantle', Journal of Geodynamics, **52**, 205-228, DOI: 10.1016/j.jog.2011.04.003

[46] Alfè D., Gillan M., J., Vočadlo. L., Brodholt,J., Price, G. D., (2002), The *ab initio* simulation of the Earth's core. Phil. Trans. R. Soc. Lond. A **360**,1227-1244, DOI: 10.1098/rsta.2002.0992

[47] Davies D. R., Davies J. H., (2009)Thermally-driven mantle plumes reconcile multiple hot-spot observations. Earth Planet. Sci. Lett. **278**, 50-54, DOI:10.1016/j.epsl.2008.11.027, 2009

Davies D. R., Wilson C. R., Kramer S. C., (2011) Fluidity: A fully unstructured anisotropic adaptive mesh computational modeling framework for geodynamics. Geochem. Geophys. Geosys., **12**, Q06001, 20 PP., DOI:10.1029/2011GC003551, 2011

[48] Harlou R., Pearson D. G.. Nowell G. M., Ottley C.J., Davidson J.P., (2009) Combined Sr isotope and trace element analysis of melt inclusions at sub-ng levels using micro milling, TIMS and ICPMS. Chem. Geol. **260**, 254-268 DOI:org/10.1016/j.chemgeo.2008.12.020

Williams H.M., Peslier A.H., McCammon C.,Halliday A.N., Levasseura S.,Teutsch N.,, Burga J.-P. (2005) Systematic iron isotope variations in mantle rocks and minerals: The effects of partial melting and oxygen fugacity. Earth Planet.Sci, Lett. **235**, 435–452

Davidson J.P., Morgan D.J., Charlier B.L.A.,; Harlou R., and Hora J.M., (2007) Microsampling and Isotopic Analysis of Igneous Rocks: Implications for the Study of Magmatic Systems. Ann. Rev. Earth Planet. Sci. **35**, 273–311, DOI: 10.1146/annurev.earth.35.031306.140211

Holland *Greg; Cassidy Martin;* Ballentine *Chris J.2009 Meteorite Kr in Earth's Mantle Suggests a Late Accretionary Source for the Atmosphere Science 326 1522-1525 DOI: 10.1126/science.1179518*

[49] Pyle, D.M., Mather T.A., (2009) Halogens in igneous processes and their fluxes to the atmosphere and oceans from volcanic activity: a review, Chemical Geology, **263**, 110-121, DOI:10.1016/j.chemgeo.2008.11.013

Johnston Fraser K. B., Turchyn A. V., Edmonds M., (2011) Decarbonation efficiency in subduction zones: Implications for warm Cretaceous climates, Earth and Planetary Science Letters **303**, 143-152;

[50] Davidson, J.P., Morgan D.J., Charlier B.L.A., Harlou, R., Hora J.M., (2007). Microsampling and Isotopic Analysis of Igneous Rocks: Implications for the Study of Magmatic Systems. Ann. Rev. Earth Planet. Sci. **35**, 273–311, DOI: 10.1146/annurev.earth.35.031306.140211

[51] Martin V.M., Morgan D.J., Jerram D.A., Caddick M.J., Prior D., Davidson J.P., (2008). Bang! Month-scale eruption triggering at Santorini Volcano. Science, **321**, 1178, DOI: 10.1126/science.1159584

[52] Harlou R., Pearson D.G., Nowell G.M., Ottley C.J., Davidson J.P., (2009) Combined Sr isotope and trace element analysis of melt inclusions at sub-ng levels using micro milling, TIMS and ICPMS. Chem. Geol. **260**, 254-268 DOI:.org/10.1016/j.chemgeo.2008.12.020

[53] Holland G., Cassidy M., Ballentine C. J., (2009) Meteorite Kr in Earth's Mantle Suggests a Late Accretionary Source for the Atmosphere Science **326** 1522-1525 DOI: 10.1126/science.1179518

## **Appendix 3.** Letter of support from GeoPRISMS

RICE

Department of Earth Science
Wiess School of Natural Sciences

May 29, 2012

Professor Jon Davidson and colleagues
c/o Dept of Earth Sciences
University of Durham
Durham DH1 3LE

United Kingdom

Dear Professor Davidson,

The GeoPRISMS Steering and Oversight Committee (GSOC), on behalf of the GeoPRISMS community, is pleased to learn of your proposal for a NERC *Theme Action* on *Volatiles, Geodynamics and Solid Earth Controls on the Habitable Planet.* Your proposed objectives of assessing volatile controls on Deep Earth processes such as mantle convection, growth of the crust, and subduction zone dynamics (through seismicity, magmatic outputs, deposition of resources, etc.) clearly have an important relationship to surface processes and our planetary "habitability." These issues are highly compatible and complementary with the mission of the NSF GeoPRISMS Program (http://www.geoprisms.org). GeoPRISMS seeks an integrated understanding of volatile fluxes and of the material cycling and deformation driven by subduction processes as part of its Subduction Cycles and Deformation (SCD) Initiative.

Therefore, on behalf of the GeoPRISMS community and the GSOC, I offer full support of your proposal to NERC. GeoPRISMS clearly recognizes the need to link and integrate efforts with international partners, and values enhanced collaboration between the UK and GeoPRISMS communities. Moreover, we particularly recognize such international cooperation as a key means to achieve GeoPRISMS program goals, which by their nature span scientific disciplines and political borders, and further anticipate that our community support will similarly aid in the achievement of your own program objectives.

Sincerely,

Julia K. Morgan
Professor, GeoPRISMS Chair
E-mail: morganj@rice.edu
Tel: 713-348-6330

Rice University • Department of Earth Science-MS 126 • P.O. Box 1892 • Houston, Texas 77251-1892
6100 Main Street • Houston, Texas 77005-1892 • Phone: 713-348-4880 • Fax: 713-348-5214 • E-mail: geol@rice.edu