# MINERALOGY & MINERAL PHYSICS

**E.K.H. Salje, M.A. Carpenter, S.A.T. Redfern, I. Farnan & R. J. Harrison.**

Mineral physics research focuses on elucidating the properties and behaviour of minerals and fluids at a fundamental level. Our main research topics include the magnetic behaviour of small particles, the passivation of nuclear waste, phase transitions and microstructure, and the elastic response of minerals in a geophysical context. The nature and breadth of these topics illustrate the need for interdisciplinary approaches to solve these highly complex problems.

We have developed a wide range of in-house experimental facilities and also make extensive use of national and international facilities for neutron scattering and synchrotron X-ray diffraction. We collaborate extensively with the Departments of Physics, Materials Science, Chemistry and Mathematics in Cambridge. We are expanding our activities into micromagnetics and TEM holography for the analysis of magnetic microstructures at the nanometre scale. A major strategic development is a new elasticity laboratory to measure elastic properties over wide frequency ranges in collaboration with our geophysicists.

We are a lively, active and friendly group of students, post docs and academic staff. Our group has strong collaborative links with researchers in physics, chemistry, materials science, and earth sciences around the world, and we welcome applications from students with backgrounds in any of these areas.

For more information visit our group website at:
http://www.esc.cam.ac.uk/research/mineral-sciences.

## MINERALOGY & MINERAL PHYSICS

**M1 Mechanisms of acoustic attenuation**
**Also see G11**
Ekhard Salje & Michael Carpenter.

**M2 Elasticity of magnetic minerals.**
Michael Carpenter & Richard Harrison.

**M3 Elasticity of nanomaterials**
Michael Carpenter & Richard Harrison.

**M4 Extreme Palaeomagnetism: How Low Can You Go?**
**Also see G12**
Richard Harrison.

**M5 Elastic and anelastic behaviour of high performance alloys.**
**(Joint funded studentship with Rolls Royce, EPSRC, and the Department of Materials Science and Metallurgy).**
Richard Harrison, Michael Carpenter, Simon Redfern & Howard Stone.

**M6 Global study of mantle discontinuities and their mineralogical interpretation.**
**Also see G2**
Arwen Deuss & Simon Redfern.

**M7 Seismic-frequency mechanical consequences of pre-melting in basalt.**
**Also see G13**
Simon Redfern & John Maclennan.

**M8 High-pressure/temperature behaviour of silica.**
Simon Redfern & Martin Dove (Queen Mary's, London).

**M9 Geomechanics and metastability of methane hydrates.**
Simon Redfern & Martin Dove (Queen Mary's, London).

**M10 Can seismic waves move mineral microstructures?**
**Also see G14**
Richard Harrison & Ekhard Salje.

**M1**

**TITLE: MECHANISMS OF ACOUSTIC ATTENUATION.**
**Also see G11**

**SUPERVISORS: EKHARD SALJE & MICHAEL CARPENTER.**

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**Importance of the research:** Attenuation of seismic waves is generally attributed to the influence of grain boundaries and is assigned a smooth dependence on depth through the earth. If the temperature and pressure dependence of the dissipation behaviour was properly defined, observed variations from seismology could give independent evidence for the temperature profile within the core and mantle. However, other processes can also give rise to attenuation such as movement of twin walls in perovskites, mobility of interfaces between phases undergoing first order phase transitions and Snoek-type losses due to impurity elements in Fe-Ni alloy or hydrogen in nominally anhydrous minerals. These will have a quite different temperature dependence from grain boundary effects and could give rise to steep variations in attenuation over narrow temperature/pressure intervals. Again, recognition of these in seismic data would provide insights into the thermal and chemical structure of the earth.

**The project:** This objective of this project is to investigate mechanisms of anelastic loss and to understand the physics of loss processes which are intrinsic in minerals, i.e. due to strain relaxations of some aspect of a crystal structure, and those which are extrinsic, i.e. specifically due to twin walls and other interfaces. The principal experimental tool will be Resonant Ultrasound Spectroscopy (RUS). Information about acoustic loss processes is contained in frequency, amplitude and phase information of mechanical vibrations of small (mm – sized) single crystals or polycrystalline samples. Resonance spectra will be analysed in the light of new understanding of the physics of energy loss processes and variations of spectral parameters. This will involve a new approach to analysing resonance spectra which are more conventionally used to determine elastic constants and their temperature dependence.

**What the student will do:** The starting point of this project will be analysis of RUS spectra from minerals and analogue phases that show different types of phase transitions. Perovskites such as $LaAlO_3$, $SrZrO_3$ and $BaCeO_3$ contain twin walls due to phase transitions driven by octahedral tilting and should be ideal analogue phases for the likely behaviour of $(Mg,Fe)SiO_3$ and $CaSiO_3$. The mineral lawsonite contains 11 wt% $H_2O$ and is a possible candidate for transporting water into the mantle at subduction zones; it also displays remarkable attenuation of acoustic resonances due to changes in hydrogen bonding. $Co^{3+}$ is isoelectronic with $Fe^{2+}$ and in phases such as $LaCoO_3$ undergoes high spin/low spin transitions. The equivalent transition in (Mg,Fe)O and $(Mg,Fe)O_3$ is known to cause significant changes in bulk and shear moduli but could also give rise to attenuation. RUS spectra from these and other relevant phases will be analysed from a fundamental point of view using methodologies related to those used for other spectroscopies (Cole-Cole plots, Kramers-Kronig relationships, etc.). The search is for characteristic features which would be different for different loss mechanisms and which would lead to better understanding of likely loss processes in acoustic signals.

**Training**: Will be provided in the practical application of a experimental methods for determining elastic and anelastic properties (particularly RUS), theory and practical aspects of solid state phase transitions and in fundamental aspects of spectroscopy. The project is linked closely with a NERC funded project on Elastic and Anelastic Dissipation Mechanisms in Minerals.

**References:**


McKnight, R.E.A., M.A.Carpenter, T.W.Darling, A.Buckley, P.A.Taylor (2007) Acoustic dissipation associated with phase transitions in lawsonite, $CaAl_2Si_2O_7(OH)_2.H_2O$. *American Mineralogist* **92**, 1665–1672.

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**M2**

**TITLE: ELASTICITY OF MAGNETIC MINERALS.**

**SUPERVISORS: MICHAEL CARPENTER & RICHARD HARRISON.**

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**Importance of the research:** Magnetic minerals have an importance in Earth Sciences which far outweighs their abundance or economic value. This is because they record the magnetic signal originating from the Earth's core while they experience different geological processes. The magnetic signal is usually preserved as a consequence of a magnetic phase transition. Conventional methods for investigating the ordering processes involve magnetic spectroscopies, while computer simulations have also provided powerful insights into the nature of the magnetic record which is preserved. Accompanying magnetic ordering, however, is some degree of elastic strain and it follows that there must also be variations in the elastic properties. It is known, for example, that magnetite undergoes phase transitions which give rise to substantial elastic softening, but elastic and anelastic effects in other phases, such as hematite and ilmenite, have generally not been characterised. Could magnetic phase transitions have a significant impact on the propogration of seismic waves in the crust? This is an open question that can be addressed by experimental measurements of the elastic properties of magnetic minerals as a function of temperature. Elastic properties should provide a different perspective on the magnetic behaviour because they link, in principle, magnetic susceptibility to elastic susceptibility, which could be an additional factor in magnetic remanence.

**The project:** The main goal of this project is to understand the relationship between the magnetic and elastic properties of minerals. In particular, do magnetic ordering processes cause elastic softening by coupling of the magnetic dipole with strain or stiffening due to a more straightforward renormalisation of the elastic constants? Some new data on magnetic ordering in $YMnO_3$ suggest that the latter mechanism leaves a readily detectable anomaly which scales with the magnetic order parameter and therefore provides a quick and effective method for following different ordering processes. The starting point will involve making elasticity measurements as a function of temperature on magnetite and hematite using Resonant Ultrasound Spectroscopy (RUS). A helium cryostat will allow measurements of magnetic ordering in silicates at low temperatures. The overall approach to individual single crystals or monomineralic polycrystalline samples may also be tested on magnetite and ilmenite bearing rocks to test whether RUS can provide a new non-destructive method of investigating properties related to magnetic remanance.

**What the student will do:** The student will focus on experimental aspects of elasticity. In particular, magnetic minerals will be investigated by RUS in the temperature interval ~4 – 1000 K using existing facilities. Spectra will be analysed with the software package IGOR with a view to determining variations in elastic constants and measuring anelastic losses. The former will provide information on the magnetic order parameter and its coupling with strain while the latter will provide information on microstructure dynamics. These results will then be correlated with data from more conventional methods of characterising magnetic properties. At the scientific heart of the issue is the question of how an externally applied stress can lead to changes in the degree of magnetic order or the orientation of magnetic dipoles.

**Training:** Will be provided in the application of a variety of experimental techniques, including pellet preparation at different temperatures and pressures, powder diffraction and Resonant Ultrasound Spectroscopy. Other techniques for characterising magnetic properties, such as magnetic susceptibility and hysteresis measurements will also be applied, and background knowledge of elastic properties and phase transitions will be developed. It is likely that the project will have significant cross-disciplinary aspects due to the importance of magnetism in other areas of solid state science.

**References:**

Carpenter, M.A. 2006. Elastic properties of minerals and the influence of phase transitions. *American Mineralogist,* **91**, 229-246.

McKnight, R.E.A., Carpenter, M.A., Darling, T.W., Buckley, A. & Taylor, P.A. 2007. Acoustic dissipation associated with phase transitions in lawsonite, $CaAl_2Si_2O_7(OH)_2.H_2O$. *American Mineralogist*, **92**, 1655-1672.

McKnight, R.E.A., C.J.Howard, M.A.Carpenter (2009) Elastic anomalies associated with transformation sequences in perovskites: I. Strontium zirconate $SrZrO_3$. *Journal of Physics: Condensed Matter* **21**, 015901.

**M3**

**TITLE: ELASTICITY OF NANOMATERIALS.**

**SUPERVISORS: MICHAEL CARPENTER & RICHARD HARRISON.**

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**Importance of the research:** Nanomaterials have gained a significance in modern environmental and technological research which far exceeds their natural occurrence. This is largely because their physical and chemical properties can be dramatically different from those of bulk samples which might have the same basoc crystal structure. In Earth Sciences, most of the focus is on surface chemistry – how do the nano particles (fine iron oxides/hydroxides, clays, particulates in volcanic ash, etc.) interact with chemical components in the air, in solution or in biological systems? Of equal importance in the context of technological materials, however, is their physical properties and, in particular, their elastic properties. In this context the key question is how does the dominance of surface relaxations affect the elastic relaxation of the entire nanoparticle and, hence, its bulk elastic, ferroelectric, ferromagnetic and ferroelastic characteristics.

**The project:** The main goal of this project is to understand the relationship between grain size and elastic properties. To achieve this, elastic anomalies associated with structural phase transitions will be used as a probe of the influence of grain size. There are no experimental methods available for measuring the elastic moduli of nanoparticles directly, but a new method has recently been developed for measuring the elastic behaviour of fine particles dispersed in a pressed pellet of KBr, using Resonant Ultrasound Spectroscopy (RUS). Magnetite undergoes a phase transition near 125 K which gives large changes in elastic moduli and these are easily detected in the elastic properties of a KBr $_+$ magnetite pellet. Moreover, preliminary experiments have revealed systematic changes as a function of grain size, as expected from theory. The project will consist of two parts: (a) Development of the methodology for supporting nanoparticles in pellets (trials of KBr, CsI, superglue, …. as the matrix material) and (b) RUS measurements at room temperature and over wide temperature intervals to determine absolute values of shear and bulk moduli of the particles and to identify nano-elastic behaviour of materials such as magnetite (bacterial and synthetic) and functional perovskites.

**What the student will do:** The student will focus on experimental aspects of elasticity. A systematic investigation of pellet making techniques and matrix materials for supporting fine powders will form the starting point. Once an optimal experimental protocol has been developed for preparing pellets for RUS, phase transitions in a variety of material will be explored using powders with progressively finer grain sizes into the nano regime. These will complement experimental investigations of strain and elasticity associated with phase transitions being carried out by other members of the mineral sciences group.

**Training:** Will be provided in the application of a variety of experimental techniques, including pellet preparation at different temperatures and pressures, powder diffraction and Resonant Ultrasound Spectroscopy. Other techniques for characterising magnetic properties, such as magnetic susceptibility and hysteresis measurements will also be applied, and background knowledge of elastic properties and phase transitions will be developed. The project is completely different from any research currently being undertaken on nano materials, which have such widespread importance that further opportunities for the student could arise in medicine, physics, earth sciences, materials science or chemistry.

**References:**

Carpenter, M.A. 2006. Elastic properties of minerals and the influence of phase transitions. *American Mineralogist*, **91**, 229-246.

McKnight, R.E.A., Carpenter, M.A., Darling, T.W., Buckley, A. & Taylor, P.A. 2007. Acoustic dissipationassociated with phase transitions in lawsonite, $CaAl_2Si_2O_7(OH)_2.H_2O$. *American Mineralogist*, **92**, 1655-1672.

McKnight, R.E.A., Moxon, T., Buckley, A., Taylor, P.A., Darling, T.W. & Carpenter, M.A. 2008. Grain size dependence of elastic anomalies accompanying the α–β transition in polycrystalline quartz. *Journal of Physics: Condensed Matter*, **20**, art. no. 075229.

Carpenter, M.A., A.Buckley, P.A.Taylor, T.W.Darling (2010) Elastic relaxations associated with the Pm m – R c transition in $LaAlO_3$ III: superattenuation of acoustic resonances. *Journal of Physics: Condensed Matter* **22**, 035405.

**M4**

**TITLE: EXTREME PALAEOMAGNETISM: HOW LOW CAN YOU GO?**
**Also see G12**

**SUPERVISORS: RICHARD HARRISON.**

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Fig. 1. Electron holography image revealing the complex magnetic microstructure of an array of ~ 100 nm sized cubes of magnetite (Ref. 1).

**Importance of the research:** Paleomagnetism is a powerful tool for studying the structure and dynamics of the Earth and other planets. As we strive to push the boundaries of what can be achieved using paleomagnetism, an understanding of its mineral physics underpinnings becomes ever more important. One of the central challenges in paleomagnetism is that the reliability of palaeomagnetic signals decreases rapidly with increasing age of the rock. Some of the most interesting and controversial periods of Earth's history occur beyond the limit of our confidence in the paleomagnetic signals used to study them (as epitomized by the on-going debate surrounding the 'Snowball Earth' – a controversial theory based on disputed paleomagnetic data). The fidelity of paleomagnetic data is most severely compromised by physical and chemical alteration of the primary magnetic carriers. To overcome this problem it is necessary to perform measurements at ever decreasing length scales (< 1 mm). It then becomes possible to isolate the primary magnetic carriers and fully characterise their chemical and magnetic microstructures, thereby reducing the complexity of the system to the point where it is amenable to theoretical modeling. Although this drive to smaller length scales will ultimately enable us to establish the true nature of ancient paleomagnetic signals, it brings its own set of experimental and theoretical challenges. This project will tackle these challenges using an innovative combination of experimental and/or computational techniques.

**The project:** This project will involve the development of experimental and computational techniques that will enable us to perform paleomagnetic analysis at small length scales. The central component of the project will involve the application of X-ray and electron tomography to develop a detailed three-dimensional picture of the size, shape and spatial distribution of magnetic grains within a sample with nanoscale resolution. The three-dimensional information will feed into a large-scale computer simulation, enabling us to predict macroscopic behaviour and therefore extract meaningful paleomagnetic information (such as paleointensity).

**What the student will do:** The student will join the mineral magnetism group and be trained in the use of state-of-the-art techinques for the study of magnetic minerals at small length scales. The student will be responsible for sample preparation using a variety of techniques, including transmission electron microscopy, electron and X-ray holography, and X-ray and electron tomography. The student will perform experiments at major national and international facilities (e.g. Diamond) and take responsibility for analysing the data. The student will perform micromagnetic and Monte Carlo computer simulations in order to interpret the data and develop tools that can be applied to extract paleomagnetic information from small areas.

**Training**: Training will be provided in the practical application of both experimental and computational methods for determining magnetic properties of minerals. The student will be trained in a variety of electron microscopy, X-ray and neutron methods. The student will be trained in the development of data analysis techniques and in the use of micromagnetic simulations.

**References:**

Harrison, R.J., Dunin-Borkowski, R.E., and Putnis, A. (2002) Direct imaging of nanoscale magnetic interactions in minerals. *Proceedings of the National Academy of Sciences*, **99**, 16556-16561.

Harrison, R.J. and Feinberg, J.M. (2009) Mineral Magnetism: Providing New Insights Into Geoscience Processes. *Elements*, **5**, 209-215.

Kasama, T., Church, N.S., Feinberg, J.M., Dunin-Borkowski, R.E., Harrison, R.J. (2010) Direct observation of ferrimagnetic/ferroelastic domain interactions in magnetite below the Verwey transition., *Earth and Planetary Science Letters* **297** 10–17. doi:10.1016/j.epsl.2010.05.004.

**M5**

**TITLE: ELASTIC AND ANELASTIC BEHAVIOUR OF HIGH PERFORMANCE ALLOYS.**
(Joint Funded Studentship with Rolls Royce, EPSRC, and The Department Of Materials Science And Metallurgy).

**SUPERVISORS**: **RICHARD HARRISON, MICHAEL CARPENTER, SIMON REDFERN & HOWARD STONE.**

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**Importance of the research:** Understanding the mechanical properties of materials are of critical importance in the design of high-performance alloys for the aerospace industry. Surprisingly little is known, however, about how the mechanical properties of high-performance alloys, such a Ni-based superalloys, vary as a function of frequency. Anelastic relaxation processes can lead to very different mechanical properties from those measured using static techniques, depending on the temperature and frequency of the applied stress. What processes are important in determining the properties and behaviour of such materials under the operating conditions of a jet engine? Can we measure and model such processes using laboratory experiments and use the information to guide the development of new materials for the aerospace industry?

**The project:** This 4 year project is joint funded by Rolls Royce and EPSRC. Mechanical spectroscopy using Resonant Ultrasound Spectroscopy (RUS) and forced oscillation techniques allow exceptional insight to be obtained into the elastic and anelastic properties of materials across a wide range of time scales. The observed acoustic and mechanical spectra can be interpreted to provide detailed information on both the bulk material behaviour as well as microstuctural changes. In this project these techniques will be applied to characterise the temperature dependence of the elastic and anelastic properties of a series of high performance nickel-base and titanium-base alloys and determine the effect of microstructural parameters including phase transitions, precipitation, grain size and processing texture on the material response.

**What the student will do:** The student will focus on experimental aspects of mechanical response. In particular, a series of high-performance alloys will be investigated by RUS and torsion pendulum methods in the temperature interval ~4 – 1600 K using existing facilities, spanning frequencies from mHz to kHz. Spectra will be analysed with the software package IGOR with a view to determining variations in elastic constants and measuring anelastic losses. The former will provide information on the alloy order-disorder and its coupling with strain while the latter will provide information on microstructure dynamics. These results will then be correlated with data from more conventional methods of characterising elastic properties. At the scientific heart of the issue is the question of how an externally applied stress can lead to changes in microstructure that could influence the performance of the material.

**Training**: Training will be provided in the application of a variety of experimental techniques, including preparation of alloys of different compositions, powder diffraction and RUS and mechanical spectroscopy. The student will interact closely with research teams within Rolls Royce and therefore will gain valuable industrial experience. As part of the 4 year funded course the student will also be expected to take a number of relevant taught graduate courses within the Department of Materials Science and Metallurgy. Hence no specific expertise in metallurgy is required at the start.

**References:**

Carpenter, M.A. 2006. Elastic properties of minerals and the influence of phase transitions. *American Mineralogist*, **91**, 229-246.

Golovin, I.S., Neuhauser, H., Redfern, S.A.T. 2009 Mechanisms of anelasticity in Fe-Ge-based alloys. *Materials Science and Engineering* A, **521**: 55-58.

McKnight, R.E.A., Carpenter, M.A., Darling, T.W., Buckley, A. & Taylor, P.A. 2007. Acoustic dissipation associated with phase transitions in lawsonite, $CaAl_2Si_2O_7(OH)_2.H_2O$. *American Mineralogist*, **92**, 1655-1672.

McKnight, R.E.A., C.J.Howard, M.A.Carpenter (2009) Elastic anomalies associated with transformation sequences in perovskites: I. Strontium zirconate $SrZrO_3$*. Journal of Physics: Condensed Matter* **21**, 015901.

**M6**

**TITLE: GLOBAL STUDY OF MANTLE DISCONTINUITIES AND THEIR MINERALOGICAL INTERPRETATION. Also see G2**

**SUPERVISOR: ARWEN DEUSS & SIMON REDFERN.**

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**Importance of the area of research:** A transition zone from 410 to 660 km depth separates the Earth's upper and lower mantle. Discontinuities in this transition zone have been studied on a global scale using precursors to SS and PP (Deuss & Woodhouse, 2001, Deuss *et al*. 2006). They have also been studied on a regional scale using other data types, including receiver functions, P'P' precursors and ScS reverberations. The results are usually interpreted in terms of phase transitions in olivine and indicate a complicated seismic structure at 410, 520 and 660 km depth that requires lateral variations in temperature and composition. In addition, several weak discontinuities in the upper and lower mantle have been found using a systematic search for long-period SS- and PP-precursors (Deuss, 2009). In principle, the observations can be used as a probe for local mantle composition and temperature. However, using SS and PP data alone we do not have enough information to distinguish which mechanism causes these discontinuities. Comparisons with other studies are hindered because every study is performed using a different technique, data selecting procedure, test of robustness and often only focuses on one or two discontinuities using array data in a small region.

**What the project will involve:** At the moment it is unclear which mineral physical mechanisms explain observed upper mantle discontinuities (i.e. the Lehmann discontinuity at 220 km depth) and also the transition zone discontinuities seem more complicated that simple phase transitions in olivine (Deuss & Woodhouse, 2001, Deuss *et al*, 2006). In this project, a systematic search technique will be applied to a number of different data types on a global scale. This will give the unique opportunity to have one investigator comparing the different results and the conclusions will be organised to facilitate interpretation by other disciplines.

**What the student will be doing:** The student will be collecting a large data set of different seismic phases and will develop techniques to select and process the data. The observed seismic discontinuities will also be interpreted by comparing with recent mineral physical results on possible phase transitions and other mechanisms, for which the student will have to do a bibliographical study of existing results from mineral physics.

**Training that will be provided:** The student will be given training in computational techniques, in computer programming, in the handling of large data sets and in observational seismology. The project will suit a physicist, geophysicist or numerate geologist who is interested in a multidisciplinary project combining seismology with mineral physical interpretation.

**References:**

Deuss, A. & J.H. Woodhouse, 2001.Seismic observations of splitting of the mid transition zone discontinuity in Earth's mantle, *Science*, **294**, 345-357.

Deuss, A., 2009. Global Observations of Mantle Discontinuities Using SS and PP Precursors, *Rev. Geophys*., **30**, 301-326.

Deuss, A., S.A.T. Redfern, K. Chambers and J.H. Woodhouse, 2006. The nature of the 660-kilometer discontinuity in Earth's mantle from global seismic observations of PP precursors, *Science*, 311, 198-201.

**M7**

**TITLE: SEISMIC-FREQUENCY MECHANICAL CONSEQUENCES OF PRE-MELTING IN BASALT.**
**Also see G13**

**SUPERVISORS: SIMON REDFERN & JOHN MACLENNAN.**

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**Importance of the area of research:** Time-dependent deformation of minerals has been suggested as the origin of seismic attenuation in the deep Earth. Such anelasticity may also place the limits on use of microstructure in technological devices, such as non-volatile RAM and smartcards. Despite the potential importance of this phenomenon, observations to shape theories of anelasticity in microstructured minerals are sparse. We have recently shown that mineral microstructures stressed at seismic frequencies display remarkable nonlinear physics. Here we seek to develop an understanding of this phenomenon as it occurs during the melting of basaltic rocks.

**What the project will involve:** Determining and understanding the anelastic behaviour of minerals is the key to interpreting seismic attenuation in the mantle. The same pheonomena have potential for understanding novel materials. Here, the low-frequency (≈ 1Hz) dynamic mechanical response of basaltic composition rocks will be measured at temperatures approaching melting. This will reveal the anelastic characteristics of their microstructures, and their dependence on frequency, applied stress, and temperature.

**What the student will be doing:** The student will use a novel torsion pendulum device to measure the dynamics of mechanical properties of a selection of basaltic composition rocks and other model systems. The role of pre-melting on the dynamical mechanical behaviour will be explored by direct observation of dynamically stressed systems, and related to geophysical observations.

**Training that will be provided:** The student will be trained in the experimental methods surrounding anelastic materials characterisation, materials synthesis and preparation, and in the theoretical background that underpins the interepretation of the acquired data. The student will also be trained in SEM & thin section interpretation.

**References:**

Wang C, Redfern SAT, Daraktchiev M. 2006 Memory effect of a mechanical anomaly related to ferroelastic domain switching in rhombohedral lead zirconate titanate ceramics *Appl Phys Lett* **89** (15): Art. No. 152906.

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Harrison, R.J. & Redfern, S.A.T. 2002. The influence of transformation twins on the seismic-frequency elastic and anelastic properties of perovskite: Dynamic mechanical analysis of single-crystal LaAlO3. *Phys Earth Planet Int* **134**: 253-272.

**M8**

**TITLE: HIGH-PRESSURE/TEMPERATURE BEHAVIOUR OF SILICA.**

**SUPERVISORS: SIMON REDFERN & MARTIN DOVE (QUEEN MARY'S, LONDON).**

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**Importance of the area of research:** Silica, $SiO_2$, is a model system important in geology, technology and across the physical and chemical sciences. It has a rich phase diagram, containing both stable and metastable phases. It is important to be able to characterise and understand the origin of new phases, and studies of the behaviour of silica polymorphs at high pressure and temperature provide insight into mineral behaviour under the conditions of the geotherm more generally.

**What the project will involve:** The fundamental principles of phase transitions in silica will be explored by experimental and theoretical methods, providing insight into how and why such transitions occur generally in minerals. Our approach is to investigate P/T phase space for $SiO_2$ using combined diffraction, spectroscopic, and computational techniques. We anticipate discovering new displacive phase transitions with this approach. Complex phase diagrams point to competing ordering processes, which are usually hidden in studies with fixed pressure or temperature. Being able to study across a range of P/T enables us to identify these competing ordering processes, giving a more complete picture of the stability of the mineral structure. Because the ability to study mineral behaviour under simultaneous variations of P/T is new, this is opening up a whole new area of scientific investigation.

**What the student will be doing**: The student will study the phase space of silica using combined X-ray diffraction, vibrational spectroscopy, neutron scattering and computational modelling to gain an understanding of the phases that arise, their limits of stability, and the structural controls on their behaviour. The structural controls to be explored over a range of length scales and across a wide span of pressure-temperature space. The behaviours of quartz, tridymite, cristobalite, coesite and amorphous silica will be compared to gain a thorough picture of these controls.

**Training:** The student will have great benefit in obtaining skills in a wide range of experimental techniques, including X-ray and neutron diffraction, vibrational spectroscopy, and high-pressure techniques. In addition the student will gain experience in the use of computer modelling methods. Supporting training in the subjects of crystal physics and phase transitions will be provided.

The project would suit a physicist, chemist, earth scientist or materials scientist interested in linking both experimental and computational approaches to study the behaviour of materials under extreme conditions.

**References:**


S.A.T. Redfern (2002) Neutron powder diffraction of minerals at high pressures and temperatures: some recent technical developments and scientific applications. *Eur J Mineral*, **14**: 251-261.

M.T.Dove, M.S.Craig, W.G.Marshall, S.A.T.Redfern *et al*. (2000) Crystal structure of the high-pressure monoclinic phase of cristobalite, $SiO_2$, *Min Mag* **64**, 569-576.

A.K.A.Pryde & M.T.Dove (1998) On the sequence of phase transitions in tridymite. *Phys Chem Minerals* **26**, 171-179.

**M9**

**TITLE: GEOMECHANICS AND METASTABILITY OF METHANE HYDRATES.**

**SUPERVISORS: SIMON REDFERN & MARTIN DOVE (QUEEN MARY'S, LONDON).**

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**Importance of the areas of research:** Methane hydrates (sometimes termed "clathrates", as these are solid crystalline ice structures that retain methane molecules within the large ice interstices) occur pervasively in both oceanic sediments and high latitude terrestrial environments across the globe. They are stable as a solid material at low temperatures and high pressures, within sedimentary strata, but have the potential to become destabilised upon temperature increase of the ocean or reduction in overlying pressure of the sediments in which they occur, releasing methane into the ocean/atmosphere and causing landslips (and potentially tsunamis) in the sediments where they reside. Methane hydrates have been identified as both an untapped potential fossil fuel energy resource (which some estimates suggest are as voluminous as known gas and oil reserves) and as a potential positive feedback threat to rapid climate change, in particular because methane has a potent (although relatively short-lived) effect on active climate forcing. Indeed, methane hydrate has been implicated in past extreme climate warming within geological history (Kennedy *et al*., 2008, Nature). Given its importance, it is astonishing that accurately establishing the risks or benefits attached to methane hydrate occurrence is currently almost impossible: such occurrence is poorly surveyed and the risks of destabilisation only touched upon in current understanding.

**The project:** The objective is to determine the geomechanical properties and kinetic stability of methane hydrates in order to allow improved geophysical estimates of their occurrence in sediments and to provide a new assessment of the risks associated with this potential geohazard, and its likely impact on rapid climate change. Assessing such risks depends on first understanding the kinetic controls on maintaining the solid phase outside of thermodynamic equilibrium. Minerals frequently exist metastably in non-equilibrium conditions. Recent reports of methane hydrates in shallow sediments at lower pressures and higher temperatures indicate kinetic stabilisation as the likely cause, but the kinetics of inhibition of the dissociation reaction are unknown. If methane hydrates can be preserved in Nature metastably the risk of runaway climate forcing due to their dissociation may have been overstated in the literature.

**What the student will do:** The Cambridge group have a strong record of study of the kinetics and thermodynamics of mineral reactions, in particular employing sophisticated high pressure and variable temperature environments for the study of atomic scale structure and reactions using synchrotron X-rays and neutron beams. The student will combine experimental and computational approaches to investigate the kinetic metastability of methane hydrate in Earth environments. Neutron methods are particularly valuable for the study of low-atomic-number elements such as H, C, and O that form methane hydrates [2]: Cambridge have developed unique apparatus for deployment at neutron sources which will allow the essential measurement of kinetics of the formation and dissociation of natural methane hydrate systems, including rock-hydrate samples. Alongside these, molecular dynamics simulations will be applied to understand the atomistic features of the ice-methane system responsible for the limits of stability and physical and mechanical properties.

**Training which will be given:** Training will be provided in (i) in situ high-P/T study of minerals using synchrotron and neutron scattering methods; (ii) computational simulation of condensed matter (iii) interpretation of results in the framework of the structural properties of solids. The project would suit a physicist, chemist, earth scientist or materials scientist interested in theoretical simulations.

**References:**


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**M10**

**TITLE: CAN SEISMIC WAVES MOVE MINERAL MICROSTRUCTURES?**
**Also see G14**

**SUPERVISORS: RICHARD HARRISON & EKHARD SALJE.**

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**Importance of the area of research:** Seismology provides us with a 3-dimensional picture of seismic wave velocity, anisotropy and attenuation. This data is then used to develop physical, chemical and thermal models for the Earth. However, translating seismic data into a realistic model requires a thorough understanding of the mineralogy of the Earth's mantle and core and the mechanical properties of minerals as a function of temperature, pressure, composition, frequency and stress. At seismic frequencies, microstructural changes in response to an applied stress can lead to dramatic deviations from the ideal elastic behaviour predicted by computational mineral physics. Such deviations may be crucial in understanding the discrepancies between calculated and observed seismic properties of the deep Earth. Although it is well established that such microstructural changes can be created with relatively large strain amplitudes (i.e. $> 10^{-6}$), it is less clear that the small strain amplitudes typically associated with seismic waves ($<< 10^{-6}$) have the ability to influence microstructures.

**What the project will involve:** An interesting question for seismology is the behaviour of ferroelastic twin domain boundaries exposed to vanishingly small amplitudes of shear stress. In this regime, twins may be completely pinned by lattice defects, undergo thermally activated creep over long periods, or display an intermediate behaviour where smooth ballistic motions are interrupted by jerky motions that mimic the statistical behaviour of propogating fault planes. These processes will be studied using single crystals of different ferroelastic minerals, such as $LaAlO_3$ and $Pb_3(PO_4)_2$.

**What the student will do:** In this project the student will develop an experimental method for studying the dynamics of twin domain motion in response to low-amplitude slowly varying shear stress. Using timelapse photography, we will make direct measurements of twin velocity as a function of applied force, and interpret the results in terms of domain pinning theory. This experiment has currently been developed for room temperature analysis only. The student will be responsible for developing the experiment to allow measurements as a function of temperature. The methods will be applied to both single crystal and polycrystalline samples. With single crystal samples the focus will be on understanding the physics of domain wall unpinning under small applied stress. With polycrystalline samples, the focus will be on determining how stress concentration at grain junctions can be relieved by the nucleation and movement of twin boundaries.

**Training that will be provided**: The student will receive training in the use of timelapse microscopy in the study of dynamic microstructural development. The student will learn about the development of scientific instruments and become expert in the use of image analysis and processing techniques for feature tracking in timelapse images.

**References:**


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