

## 4.7 Mineral Sciences, Earth Sciences, Environment and Cultural Heritage

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### Abstract

The materials under study in Mineral Sciences, and Earth Sciences in general, pertain to all aggregation states of matter; solid, glass, molten, liquid and gas. Hence the methods of investigation are those adopted in all other branches of science dealing with such states. In the case of the Earth Sciences, however, we must consider a further degree of complexity introduced by the unrestricted nature of the chemical and physical parameters, i.e. chemical composition, temperature and pressure, underlying the formation and transformations of these objects.

Neutron scattering has only recently been added to the methods of investigation used in the Earth Sciences, mainly thanks to the latest generation of diffractometers and spectrometers at modern neutron sources which allow the accurate determination of subtle, yet very important, structural details in minerals as a function of temperature and pressure.

Still, many areas of Mineral Science research, and related fields, remain out of the reach of present-day neutron instrumentation. We have selected a few representative examples, and in turn a few keynote or “flagship” experiments that could be tackled with an ESS-type instrumental set-up, leading to a significant advance in this field of research. The three broad themes identified are:

1. In-situ measurements of structure-property relationships in mineral phases under geological conditions.
2. Structure, reactivity and physical properties of multi-component melts and fluids under geological conditions.
3. Texture and stress analysis of polymineralic rocks; modelling of tectonic processes and rock anisotropies.

Within these broad themes, four “flagship experiments” are offered as actual examples, namely:

1. - a) *In-situ diffraction and spectroscopic studies of molecular components in methane clathrates.*  
- b) *Spin dynamics of iron-containing deep Earth phases.*
2. - *Space- and time-resolved tomography of volatile-containing crystallising magmas.*
3. - *Time-resolved simultaneous structure, texture and stress analysis of polymineralic systems under variable P/T conditions.*

### I. Introduction

The use of neutron scattering by the Earth Sciences community has a relatively short history, but it is now clear that the potential of neutron scattering methods for the solution of Earth Sciences problems, including many environmental problems, is enormous. Many of the problems encountered in Earth Sciences have, until recently, simply been too complicated for earlier neutron sources and instrumentation. Only with the advent of the latest generation powder diffractometers at modern spallation sources such as ISIS, has it become possible to study the crystal structures of minerals as a function of temperature and pressure with sufficient accuracy to be really useful in solving subtle problems such as cation ordering. However, there are many areas in the Earth and environmental sciences for which the present sources and instrumentation are still inadequate. Examples include measurements of the structural changes in minerals at very high pressures and simultaneous high temperatures, locations of light elements in complex structures, strain measurements and scanning of polycrystalline aggregates under non-ambient conditions, and

***The Earth Sciences can profit greatly from neutron scattering studies using the latest and future generation neutron sources.***



studies of the dynamical properties (neutron spectroscopy), also at non-ambient conditions. This information will enable modelling of fundamental processes in the Earth, ranging from large scale phenomena such as deep-focus earthquakes and volcanic activity, through to the transport (and disposal) of pollutants in the Earth's crust and stone preservation in monuments.

Recent experience with state-of-the-art sources, such as ISIS and ILL, has shown that the outlook for applications of neutron scattering in Earth Sciences is extremely promising. There are many features of neutron scattering that find ready application to the study of natural materials. One clear example is that many natural materials contain hydrogen. Hydrogen is virtually invisible to X-rays, but it will scatter neutrons reasonably strongly, both coherently and incoherently. This means that neutron scattering from hydrogen can act as a probe of both single-atom dynamics and collective excitations. Hydrogen is central to so many problems in geology and environmental science that there are countless important applications of neutron scattering in these areas. As the facilities for collecting high-quality data are further developed, so our ability to resolve these scientific issues increases.

***Typical examples include hydrogen containing phases.***

The ESS will enable us to tackle many long standing issues related to geological and environmental processes. The ability to construct sample environments that will reproduce the temperature and pressure conditions of the deep Earth, and the increase in neutron intensity allowing reduced interaction volumes and shorter data collection periods, will allow us to perform many "in-situ" studies of mineral behaviour, which will greatly increase our understanding of the behaviour of the constituent materials of the Earth. The ability to probe the structures and motions of relatively complex minerals will provide many new insights and allow us to understand the numerous interactions that govern the behaviour of Earth materials in their natural environment. We anticipate being able to study both solids and fluids by neutron techniques, as well as for the first time the interfaces between these two states of aggregation.

***In-situ studies of dynamic processes and phenomena.***

## **II. Points of merit for neutron scattering in Mineral, Earth and Environmental Sciences**

### ***Hydrogen in minerals***

Neutrons, as opposed to X-rays, are efficiently scattered by hydrogen  $^1\text{H}$  and deuterium  $^2\text{H}$  atoms. Many minerals contain hydrogen, often in the form of bound or free hydroxide ions or in the form of bound or free water molecules, within either structurally active sites or interstitial cavities in the crystal structure. Water in minerals and rocks is extremely important in regulating a large variety of behaviours and properties of interest to the Earth Sciences spanning from the atomic to the continental scale. Because hydrogen has an extremely large

***"Water" in minerals and rocks is of paramount importance in determining their properties.***



cross section for incoherent scattering, neutron scattering can be used to study the motions of individual hydrogen atoms. Slow motions of the hydrogen atoms, such as diffusion or reorientational motions, can be probed by quasi-elastic scattering. Fast motions can be probed by high-energy spectroscopy. On the other hand, since deuterium has a reasonable cross section for coherent scattering and no appreciable cross section for incoherent scattering, deuterated samples can be used in diffraction studies for the location of hydrogen sites in crystal structures and their modifications under inner earth conditions [1].

### **Scattering cross section**

The fact that the scattering cross section for neutrons does not change with scattering vector, whereas with X-rays it falls off approximately as the inverse of the atomic radius, means that neutron scattering allows us to collect diffraction data to large scattering vectors. This is useful for a number of reasons. (i) When investigating complex crystal structures and crystal chemistries, evident in many minerals, it allows for a significant increase in the amount of information available in a diffraction pattern. (ii) A wide coverage of scattering vector is essential for information about thermal motion. (iii) To extract information about site occupancies, and to decouple this information from the thermal motion, it is again essential to have data over a wide range of scattering vectors. Furthermore, in crystals with considerable disorder, or in amorphous materials or liquids, there is a lot of information about short-range order contained within the total scattering,  $S(q)$ . The Fourier transform of  $S(q)$  provides information about the pair distribution function,  $g(r)$ , the resolution of which will depend directly on the range of the scattering vector in the data. Thus one can obtain better data for  $g(r)$  from neutron scattering than from X-ray scattering, although it is most profitable, sometime essential, to combine data from both techniques, especially where complex systems are concerned.

### **Iso-electronic (and quasi-iso-electronic) species**

The contrast between the neutron scattering cross sections of mineralogically common atoms or cations which have equal or similar numbers of electrons, such as the following groups of ions;  $Ti^{4+}$ - $Ca^{2+}$ - $K^+$   $K^+$ - $Cl^-$   $Na^+$ - $Mg^{2+}$ - $Al^{3+}$ - $Si^{4+}$   $Fe^{2+}$ - $Mn^{2+}$   $O^{2-}$ - $F^-$ , as well as the corresponding atomic species and also the rare earth elements, allows neutron diffraction to be used for the direct determination of their site occupancies and order-disorder distributions. Untangling the ordering of these cations using X-rays can only be achieved indirectly by the analysis of bond lengths, but these are not definitive since bond lengths are affected by factors other than the specific site occupancy. Neutron diffraction provides the direct determination of site occupancies for these frequently coexisting cations in minerals. Furthermore, although synchrotron X-ray resonant scattering can certainly be used to enhance scattering contrast in favourable cases, it cannot be performed systematically since it is dependent on available edges and bonding features.

***Thermal motions, site occupancies, short- and long-range order information are more easily detectable by neutron scattering.***

***Scattering contrast is not electron-dependent.***



### ***In-situ experiments***

To study the behaviour of minerals requires the reproduction of their “natural” environment and thus the need for simultaneous high temperatures and high pressures. “*In-situ*” studies are most appropriate to obtain a thorough knowledge of the relations between thermo-baric variables and structural properties such as phase transitions, cation partitioning, bond valence, electronic structure, etc. Traditionally high pressures have been easier to work with using X-ray diffraction and diamond anvil cells, but the use of time-of-flight neutron techniques has recently allowed considerable progress in high pressure mineralogy. The low attenuation of neutron beams by many materials can effectively make extreme sample environments (HT, HP, Reaction Cells, differential loading frames etc.) easier to handle for neutron scattering than for other experimental techniques.

**“Natural occurrence” for a mineral often means high temperature and high pressure.**

Examples of frontier applications of neutron diffraction are nowadays mostly in the field of *in-situ* studies where mineral structures are investigated while the sample is kept at high temperature (Figure 1) [2], [3] and/or high pressure (Figure 2) [4].

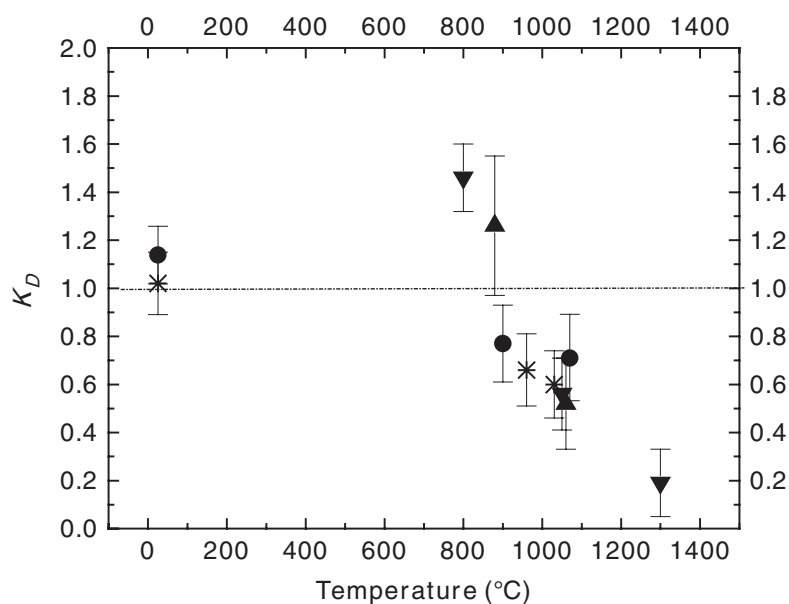


Figure 1: Example of data obtained by high temperature *in-situ* neutron diffraction on single crystals. The plot shows the variation of ordering with temperature between Fe and Mg in Fa12 and Fa10 natural olivines. *Up triangles*: Fa12 ISIS-SXD data (880, 1060°C); *stars* Fa12 ISIS-SXD data (25, 960, 1030°C); *down triangles* Fa12 ISIS-SXD data (800, 1050, 1300°C); *filled circles* Fa10 ILL-D10 data (25, 900, 1070°C); *line at  $K_D=1$*  marks total disorder; *points above 1* indicate  $\text{Fe}^{2+}$  segregation into site M1; *points below 1* indicate  $\text{Fe}^{2+}$  segregation into M2. The crystals undergo a peculiar, previously undetected, ordering reversal with temperature which is non-quenchable (Rinaldi et al. [2]).

With the ESS, the foreseeable increment in neutron flux (a factor of 30 over ISIS) and detector efficiency are expected to provide a much wider scope for these studies, extending the



capabilities of pressure/temperature devices by a factor of twenty fold at a conservative estimate, hence opening a whole new area of Earth Science studies (Figure 2).

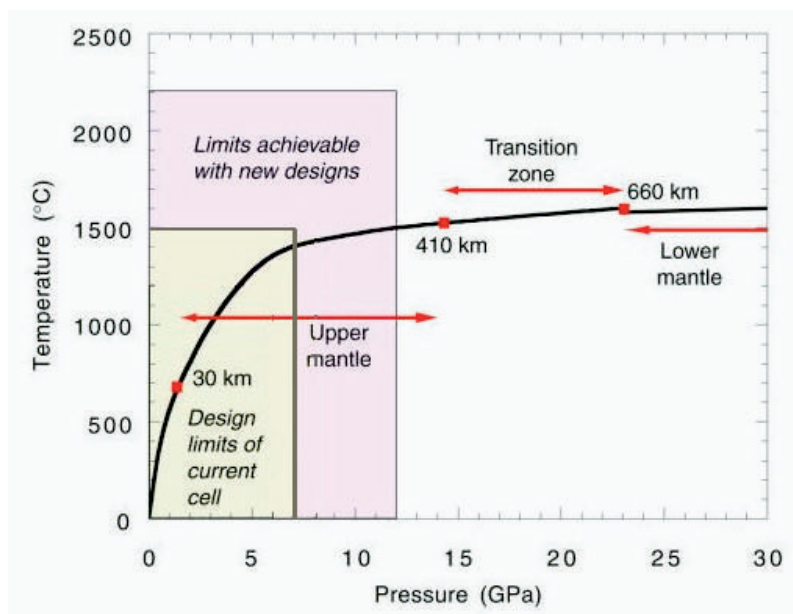


Figure 2: Pressures and Temperatures achievable with present-day and future designs cells usable at Neutron Facilities.

### ***Spectroscopy and modes***

Neutron scattering is extremely good for studying the dynamical properties of materials. Unlike spectroscopy with electromagnetic radiation, inelastic neutron scattering is not subject to tight selection rules on mode symmetries and wave vectors. For this reason neutron scattering can be used to determine phonon dispersion curves and phonon densities of states, providing both a fundamental understanding and the prediction of mineral behaviour and phase transformations of minerals under the pressures and temperatures of the Earth's interior.

***Fundamental structural properties of minerals can be investigated by INS.***

The extension of “*in-situ*” techniques to inelastic and quasi-elastic scattering appears very promising. Such measurements, although requiring highly sophisticated means of data interpretation, offer a unique opportunity for solving details of the dynamics (atomic and protonic dynamics, soft modes, etc.) and allow better modelling and interpretation of fundamental thermodynamic parameters. Limiting factors are mainly associated with the availability of large enough and homogeneous natural single crystals of the phases of interest. Powder inelastic neutron scattering could also provide a viable complementary route, especially when associated with non-ambient techniques.

The limitations in INS studies of minerals are essentially correlated with the lack of large pure samples as both single crystals and powdered pure specimens. The limited scope of the studies carried out so far on minerals reflect this drawback in the use of present-day neutron sources. Here again, an



increment in neutron flux, as expected from an ESS-type source, would serve the purpose of extending INS to smaller purer samples of many more mineral species and phases [5].

### ***Magnetic properties***

Neutron scattering is the best probe of the microscopic ordering of magnetic moments, and can be used to determine magnetic structures, collective magnetic excitations, and crystal field energy levels. The magnetic structures and transitions of Fe minerals present in high pressure environments in the deep Earth is of paramount importance for elucidating their physical properties and behaviour. Although magnetic X-ray scattering can certainly be performed with synchrotron radiation, it is in practice limited to resonant species (i.e. Fe and a few rare earth elements), therefore the use of the ESS neutron source will allow much better measurements, especially under pressure.

***Neutrons are especially suited for studies of the magnetic properties and magnetic structure of minerals.***

### ***Direct Imaging and stroboscopic techniques***

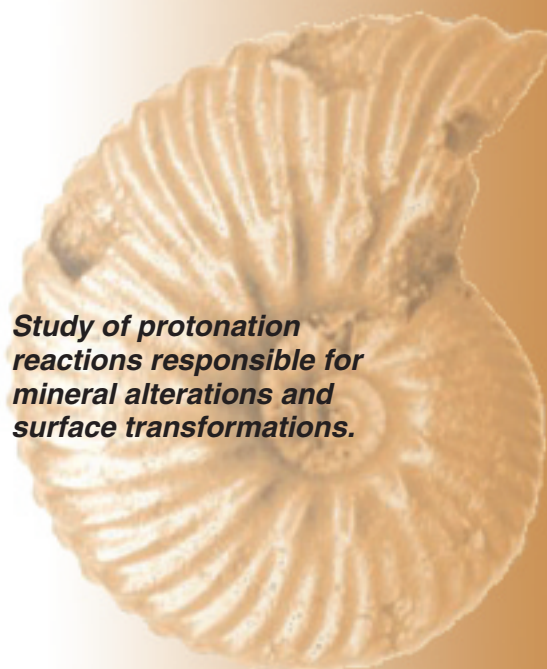
Neutron penetration and the time-structure of a pulsed source can be advantageously exploited for time-resolved neutron absorption measurements to determine the viscosity and density of magma-type melts at high pressure and temperature. Neutron imaging experiments at pressures up to 5-10 GPa and temperatures of 1300-1500°C in a cm scale cell would yield precise in-situ measurements that could also be extended to the study of reaction fronts in silicate crystallisation [6]. Decomposition and exsolution occur in minerals (and rocks) when cooled from the melt. The resulting domain structures (and textures), can be important geothermal indicators. The pulsed nature of a spallation source is ideally suited for following the kinetics of these phenomena *in-situ* by using stroboscopic methods. Such a study, on the spinodal decomposition of the system AgBr-AgCl [7], has been performed, with difficulty, at a steady state reactor source, but would be much easier with the ESS, in particular allowing us to tackle the much more complicated mineral systems. Time scales from *ms* to *h* would be accessible. Examples could include the exsolution in pyroxenes (e.g. pigeonite and augite), the kinetics of cation ordering and the development of (incommensurate) superstructures (e.g. plagioclases). More readily available measurements would be those on the static inner fabric of materials and artefacts, beyond the reach of less penetrating probes, for applications in many fields including archaeology and the preservation of cultural heritage.

***In-situ physical properties and dynamics of magma melts; direct imaging of internal fabrics in minerals, rocks and historical artefacts in bulk.***

### ***Mineral surfaces***

The breakdown, weathering and transformation of minerals on the Earth involves the migration of hydrogen through the mineral surface and into the subsurface of the crystals, thus changing the physical properties of the minerals in the surface region. As these reactions occur at the mineral/mineral, mineral/fluid or mineral/biota interface, the study of such

***Study of protonation reactions responsible for mineral alterations and surface transformations.***



protonation reactions is fundamental to our understanding of weathering and mineral breakdown. At present X-rays are used in reflectivity mode to investigate mineral surfaces but, as previously mentioned, neutrons are far superior to X-rays for the investigation of protons.

### ***Texture – stress – structure analysis***

Texture, defined as preferred orientation in a crystalline material, carries a fingerprint of the rock's history. The complexity of geological texture analysis results mainly from the overprinting of different textures upon several mineral components from different periods of geological activity. Quantitative texture analyses provide fundamental information for the modelling of rock anisotropies and reconstruction of tectonic events.

The high penetration capability of neutrons and the availability of wide beams allow the investigation of large specimens which produce global volume textures with high grain statistics, even on coarse-grained materials. Using position-sensitive detectors and time-of-flight techniques, texture can be analysed from reflection-rich diffraction patterns of polymineralic rocks containing low symmetry mineral constituents [8].

Residual stress analysis of geological material is crucial because natural effects on rocks are orders of magnitude smaller than in technological materials and drilling gives rise to stress relaxation. Furthermore, transient stresses and strains can be directly observed through in-situ measurements at various pressures and temperatures.

A future prospect at a new high flux neutron source is the performance of simultaneous phase, structure, texture, and stress analyses. A recently developed method of refinement of the orientation distribution function makes use of an iterative procedure (called WIMV) to correct spectra for anisotropy. Cycles of Rietveld- and WIMV-like algorithms ensure the full determination of all the parameters involved in diffraction patterns. Around 1000 patterns are needed at different sample orientations. At least one curved position sensitive detector helps minimise acquisition times. This method already works at neutron centres (ILL for instance), and also using x-rays (<http://lpec.univ-lemans.fr/texture/texture.htm>). Time of flight neutron diffraction gives the benefit of multiple detectors, as proposed for the HIPPO line at Los Alamos. The ESS would allow us to tackle the more complicated natural systems. Furthermore, increasing the number of detectors around a given experimental set-up would allow us to carry out dynamic studies. We could follow phase transitions versus temperature, or textural transitions with pressure or re-crystallisation processes. How do phases re-crystallise under magnetic, thermal or pressure fields? How does texture develop? What can we learn about such processes from experiments on natural and man-made materials?

***Using the penetrating and resolving power of neutrons to extract the geological history and behaviour of rocks.***



### ***Non-destructiveness in bulk***

In general, the non-destructive nature of many neutron scattering experiments makes the technique well suited for handling large, undisturbed samples and/or rare and unique objects. These can be natural or man-made and encompass areas as diverse as sediment layers, fossils, meteorites, and historical artefacts. There is a strong need to measure large samples in the Earth Sciences, where grain growth is important. Increasing the volume is the only way to acquire statistical reliability in terms of the number of grains. Grains of the order of one mm<sup>3</sup> are not rare in rocks, and spherical samples of 30 mm diameter are sometimes required.

### ***Non-destructiveness in bulk.***

### **III. Further prospects of advancement in the Earth Sciences (and related fields) with the ESS**

Some of the most significant issues in the Earth Sciences are those related to the prediction of earthquakes and volcanic eruptions. The reliability of the relevant models largely depends on knowledge of the physical and chemical properties of the materials involved (oceanic crust, upper mantle, continental crust). First and foremost amongst these properties is the role of water in these materials and in the related magmas.

***More examples of frontier applications with an ESS-class neutron source are again in the field of in-situ studies, where mineral structures and material behaviours are investigated while samples are kept at high temperature and/or high pressure.***

To draw an effective parallel, one may consider the problem of weather prediction based upon atmospheric models. It is quite evident that the present day prediction of up to five days was not even foreseeable two decades ago. As regards the prediction of earthquakes due to plate subduction, if and when it becomes possible it will be entirely dependent on the accuracy of the models that are currently being developed.

At present we can expect to obtain considerable knowledge in this direction, in part by the use of neutron scattering techniques to study the structure and properties of minerals under mantle conditions. The main obstacle is the comparatively low flux of existing neutron sources.

Given the availability of an ESS-type neutron source, three areas of key research activity may be envisaged which would provide a leap forward in this direction for the Earth Sciences:

1. *In-situ measurement of structure-property relations in mineral phases under high pressure and temperature conditions representative of the Earth's interior.*

This mineral physics project would be of great interest to many fields of research in the areas of mantle rheology, subduction modelling, seismology, tectonophysics, etc.

2. *The study of the structure, reactivity and physical properties of multi-component melts and fluids under pressure and temperature conditions representative of the Earth's interior.*

This petrology and mineral chemistry project would be of

### ***Flagship Research Programmes***



great interest for magmatology, volcanology (including ancient and present-day volcanic activity), rocks and minerals genetics, and many other related fields.

3. *Texture – stress and structure analysis of polymineralic rocks for the reconstruction of tectonic processes and modelling of rock anisotropies.*

This project concerns the characterisation and interpretation of the textural and mechanical properties of complex polyphasic materials, and their evolution during geological processes. These processes are often analogous to those occurring during HP/HT industrial processing of materials. This project is of interest for geology, geophysics, petrology, mineralogy and materials science.

***Some examples of novel representative experiments***

Within the framework of these widely varying fields of research, a number of representative novel experiments can be proposed. Within the research fields described, four flagship experiments have been selected to show the future experimental possibilities.

***Representative experiments***

***Study of the pressure-induced spin dynamics and spin-collapse in  $(\text{Fe}_x\text{Mg}_{1-x}\text{O})$  and  $\text{Fe}_2\text{SiO}_4$***

As a first step, this includes the determination of the magnetic and crystal structure under pressure up to 100 GPa (lower Mantle). Even more advanced would be a study of magnons under pressures up to 140 GPa (Mantle-Core boundary). Rationale: The pressure-induced spin collapse in 3d ions has long been proposed as a mechanism for adaptation of simple crystal structures to high pressures. Violations of Hund's rule (spin maximisation) could reduce the 'volume' of an  $\text{Fe}^{2+}$  ion by around 25 %. However, recent experimental evidence (Mössbauer spectroscopy [9], [10]) has shown that this occurs at around 100 GPa. The experiments did not allow a detailed understanding of the nature of the phase transition. The problem is also very challenging from a theoretical point of view, as the methods currently used (DFT with generalised gradient approximation) only give semi-quantitative results.

***High pressure, Fe spin-dynamics in the Earth's lower mantle.***

Hence, what is required for this experiment is a study in which firstly the crystal and magnetic structures of  $\text{FeO}$ ,  $(\text{Fe}_x\text{Mg}_{1-x}\text{O})$  and  $\text{Fe}_2\text{SiO}_4$  are investigated under pressures up to 100 GPa, using a high neutron flux magnetic powder diffractometer. Secondly a study of inelastic magnetic scattering on a single crystal at the same pressures, using a HET like instrument (high energy chopper and cold chopper spectrometers) to obtain the transition energies between spin levels and (most demanding) a constant Q instrument with very high flux to measure magnons at high pressures.



***In-situ high P/high T and high P/low T neutron spectroscopic investigation of the molecular dynamics of volatile species (H<sub>2</sub>O, OH, CO<sub>2</sub>) in minerals and nanoporous compounds through inelastic and total scattering***

Inner surface molecular interactions require studies at variable T and P (0-1500 K, up to 1 GPa). High temperatures are required for deep Earth's materials, and low temperatures are required for Earth's crust and planetary surface materials. In addition, total scattering at high P/high T could be used to study minerals under geological conditions. Currently available fluxes and resolutions limit "molecular neutron spectroscopy" to energy transfers of about 1500 cm<sup>-1</sup> and to low temperatures. This prohibits the full utilisation of neutron molecular spectroscopy as a complementary tool to Raman and IR-spectroscopy. The need is for spectroscopic measurements of the molecular dynamics of H<sub>2</sub>O in nanoporous, hydrous, and nominally anhydrous (NAM) mineral compounds including studies of surface hydration and reactions.

***Molecular dynamics, vibrational spectroscopy, volatiles.***

To understand the molecule-inner surface interaction typically encountered in nanoporous solids, experiments in a heatable/coolable high pressure cell (0-1500°C, up to 1 GPa) are required. Very low temperatures are important to understand the transition into the quantum regime (tunnelling), high pressures are important to be able to tune the strength of the host-guest interaction.

***High P/high T and high P/low T structural behaviour in minerals***

Current technology has a foreseeable upper pressure limit of about 20 GPa, achievable with a Paris-Edinburgh type cell (PE) with heating. At present the maximum operating pressure is 7 GPa and simultaneous P/T measurements can be carried out up to 1500°C (Figure 2). An increase of the T limit to 2200°C can be envisaged. Reduction of the sample volume, improvements in pressure cell technology, and the higher neutron flux of ESS would allow access to higher pressures, possibly above the 150 GPa range.

***HP/HT structures, mantle-core phases, water in minerals, phase transitions, gas hydrates.***

***A few pertinent examples are given below***

- a) In-situ studies of mantle hydrous and nominally anhydrous Mg-silicates (alphabet phases, wadsleyite, spinel) at pressures and temperatures of the transition zone (~ 15 GPa; ~1500°C) would help to characterise the nature of the seismic discontinuity known to occur at a depth of 410 Km, and the water budget of subduction zones [11] [12]. The structural behaviour of protons in hydrous phases at high P/T governs upper mantle melting, volcanic and earthquake activity, although little is known about the effect of pressure and temperature (20 GPa, 1300 K) on the stability or the equilibrium amounts of "water" incorporated in these phases. This is presently impossible since the low H content of such minerals precludes neutron diffraction



experiments with existing sources. A gain of 10 in flux and a further gain of 5 to 10 with improved instruments (diffractometers, detectors, data processing) will make it possible.

- b) Cation ordering at high P and T. The thermodynamic consequences of cation order-disorder as a function of P, T and time, must be investigated in order to understand the geophysical and geochemical mechanisms involved. Important phases such as the pyroxenes, olivines and spinels are just beginning to be investigated. A large amount of work is required to cover the chemical and physical variants of the corresponding natural phases and the kinetics of phase transitions encountered.
- c) Accurate determination of the structure of pressure-stabilised micro-porous compounds (gas hydrates) and of their physico-chemical properties. The kinetics of their phase transformations are needed to elucidate many aspects of these poorly understood significant components of shallow geological environments in both oceanic and continental sediments (Figure 3). Gas clathrates have been postulated to be of societal relevance in at least three ways: resource, climate, and hazard.

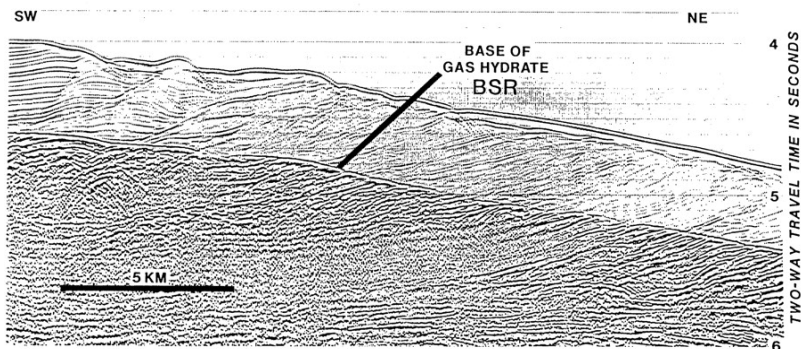


Figure 3: A 12-fold multichannel seismic reflection profile from the crest and eastern flank of the Blake Outer Ridge. The strong BSR (bottom-simulating reflection) is inferred to represent the base of the gas hydrate stability zone. (Kvenvolden, 1998 [13]).

Kvenvolden [13] reports on the immediate importance of submarine geo-hazard aspects in considerations of human activities and installations subject to the instability of deep water oceanic sediments (communications cables, ocean drilling rigs, etc.) which may be affected by slope failures, debris flows, slumps, slides and possible tsunamis and also, perhaps, ancient and historical events of global warming associated with the release of green-house effect gases. The need is for accurate phase diagrams and stability under variable P/T conditions and saline concentrations. Structural studies can also elucidate the mechanisms responsible for the seismic reflectivity attributed to these compounds.



### ***In-situ diffraction and spectroscopic studies of molecular components in methane clathrates***

This experiment indicates the high level of accuracy required to investigate fine structural and vibrational details in complex compounds.

***Methane clathrates***

Gas hydrates have hydrogen bonded rigid cage structures of water molecules entrapping gas molecules. The molecule, for example methane, has a different symmetry point group with respect to the cage symmetry and rapid flipping of the molecule over several configurational states possibly occurs. This is reflected both in the spectroscopically observable vibrational modes and in the long-range disorder of the molecules observable by diffraction, where anharmonic motion may be also observed.

Both experiments need to be of high quality to yield fine structural details, and they must be carried out under low T/high P conditions, although in this case the P range is easily accessible. The experiment requires high resolution single crystal and powder diffraction for the structural part, and resolution-enhanced TOSCA-like molecular spectroscopy for the vibrational part. A 50 Hz, short pulse, 5 MW source is advised.

### ***Time-resolved neutron radiography and tomography of the behaviour of fluids and melts at HT/HP conditions***

Imaging based on neutron transmission measurements is potentially an excellent tool to study macroscopic changes down to length scales of 5 micrometers with a time resolution of 1/10th of a second. One example is falling sphere experiments at high pressures. Currently, synchrotron-based falling-sphere experiments for the in-situ determination of the viscosity and density of melts is the only way to determine viscosities at very high pressures. These experiments suffer from problems with sample size and constraints due to the high-pressure cell. From our own experience, we know that neutron imaging measurements can be much more accurate, especially as convection can be monitored by doping with highly absorbing compounds, such as Gd-oxide. A set-up which would allow a falling sphere experiment at pressures up to 5-10 Kbars / 1500°C in a cell of about 10 cm height would allow very precise measurements. In addition to a homogeneously illuminated area of about 10 x 10 cm<sup>2</sup>, this would also require the development of a position sensitive detector with 5 micrometers resolution (current state of the art is about 250 micrometers). In these dynamic experiments the pulse structure and high peak flux of ESS can be fully exploited by synchronisation with the camera shutter, an advantage over a continuous source.

***Absorption, tomography, radiography, rheology, melts, magmas, solutions.***

Neutron tomography is also a promising technique for investigating the internal structure of multi-component systems in a non-invasive manner [14]. Time resolved neutron imaging could also be used study reaction fronts, such as occur during crystallisation of silicates or alloys as well as magma mixing



and mingling properties in order to model natural systems in magma chambers involving the need for high temperature and moderate pressures.

New techniques such as resonance absorption for precise temperature measurements and transmission Bragg edge detection for partially crystalline melts would also have to be further developed to improve characterisation of samples in-situ.

Similar to those regarding silicate melts are many problems involving mineral-water interface reactions still unsolved. Experiments on aqueous solutions in either reflectance mode (surface) or transmission mode (bulk) would yield better models for surface capacitance and cation adsorption energetics, for instance.

### ***Space- and time-resolved absorption measurements of volatile-containing crystallising magmas***

Neutron imaging and tomography are used to study the rheology and the processes (magma mixing, convection, gas segregation, reaction fronts, crystal growth, etc.) occurring during the high-temperature crystallisation of silicate magmas. Measuring the P, T, X dependence of the viscosity and density of silicate melts would provide crucially important data for petrology and, particularly volcanology issues. Use of sealed vessels would allow gas fugacities (H<sub>2</sub>O, CO<sub>2</sub>, F, etc.) to be controlled. Degassing experiments (e.g. speed with which bubbles grow during vesiculation) should also be possible. Other mineral physics/chemistry questions to be addressed would be, for example, mechanisms of nucleation and growth, phase competition during growth as a function of melt composition, inhibition of crystal growth by specific elements or molecules, etc.

### ***Magma rheology and dynamics.***

A parallel very intense beam is needed on an area of 10 x 10 cm<sup>2</sup> for recording the image of the autoclave vessel. Present space resolution, of the order of 1 mm, should be improved by one order of magnitude. New high resolution position sensitive detectors are needed to resolve fine details of the evolving system. With the logarithmic dependency of the viscosity on temperature one can fine-tune the time-scale of the experiment by selecting the appropriate temperature. A 50 Hz, short pulse, 5 MW source is necessary for time-resolved measurements.

### ***Strain partitioning upon deformation of polymineralic rocks***

One of the major aims in the Earth Sciences is to refine our understanding of the structure and composition of the Earth's interior using seismological data. The interpretation of this data is heavily reliant upon laboratory measurements of the elastic properties of the relevant rock types [15]. These rock-types are essentially polymineralic aggregates with a range in composition and microstructure that is far too large for it to be

### ***In-situ measurements of stress and strain partitioning in rock deformation.***



feasible to determine the properties of every rock-type individually.

Consequently, it makes sense to seek a method that will permit the elastic properties of polymineralic materials to be specified in terms of the elastic properties of the component phases. In order to formulate mechanical equations of state for polymineralic materials that are based on some function of the properties of the component phases, it is necessary to establish the relative contribution of each phase to the aggregate's properties. However, in rock deformation experiments it is usually only aggregate properties that can be measured. There is a glaring dearth of experimental evidence as to what happens to the strain partitioning between the component phases in a composite in the elastic regime, and also when one or more of the phases starts to yield plastically. Once yielding occurs there is the possibility of load transfer between the phases, and the extent to which this occurs exerts a profound influence on aggregate properties (Figure 4).

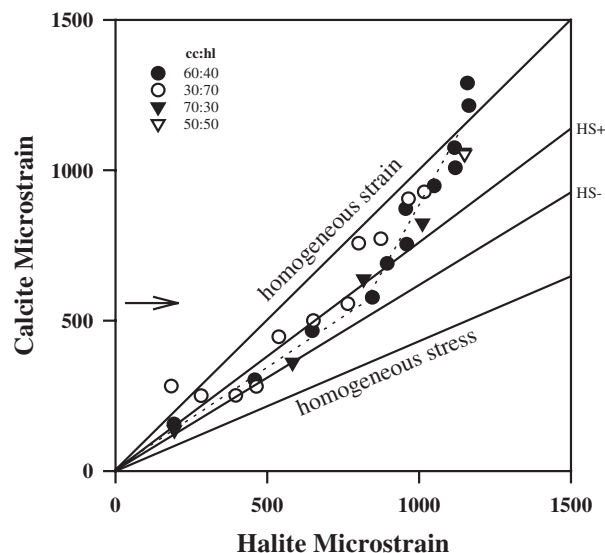


Figure 4: Calcite and halite axial elastic strains at different applied loads [16]. Also shown are the predicted phase strains assuming homogeneous stress, homogeneous strain, and as given by the upper (HS+) and lower (HS-) Hashin-Shtrikman bounds on the composite properties. The dashed line shows the trend in the data (calcite  $\geq$  50%) and the arrow shows the calcite strain at the elastic limit of calcite.

The elastic limit of the halite was at a halite strain of about 350 $\mu$ strain. The elastic strain partitioning between the two phases was unaffected by the yielding of the halite. However, above a calcite elastic strain of about 550 $\mu$ strain, the strain partitioning between the two phases started to tend towards homogeneous elastic strain, a condition that was attained by a total (elastic+plastic) strain of about 1%. The curve describing the elastic strain partitioning between the calcite and halite was independent of composition. The change in elastic strain partitioning at a calcite strain of 550 $\mu$ strain corresponds to the point at which the elastic limit of calcite is attained.

Neutron diffraction experiments at spallation sources, conducted on samples held under differential load in the



neutron beam line, offer a solution to these two problems. By determining the change in lattice parameters of each component phase as a function of applied load, the elastic strain of each phase, and hence its contribution to the total deformation, may be ascertained [17]. These experiments are only feasible due to the penetrating and polychromatic nature of the neutrons produced at spallation sources. Future developments foreseeable at the ESS would be an improved strain resolution from lower counting times, the development of high temperature equipment, and smaller beam sizes enabling greater spatial resolution. Such developments could be a large step beyond that available at ENGIN-X at ISIS.

### ***Deformation mechanisms in polymineralic rocks***

Due to the high penetration capability of the neutrons, volume texture investigations can be performed on rather large natural specimens up to about 10 cm<sup>3</sup>. Such volumes are necessary to ensure sufficient grain statistics for all mineral constituents in polymineralic rocks, especially with coarse grain sizes (e.g. about 1 mm) [18].

Large sets of geological samples from different locations must be investigated in order to study mineral specific textural changes under different deformation conditions [19], or for different minerals under similar deformation conditions in order to understand the underlying deformation mechanisms [20]. A high intensity source and a large beam are needed to perform textural investigations on large samples sets within a reasonable time scale. Time-of-flight techniques are essential because pole figure measurements can be performed without any sample scanning, and because simultaneous structure and texture refinements become possible.

### ***Influence of stress and development of texture upon deforming geomaterials***

Large scale deformation of crustal and mantle materials generates the development of microstructures, involving twinning, phase transitions, and mineral structural and textural transformations. To explore the influence of differential stress and strain partitioning on plastically deforming polymineralic materials, and the development of textures, requires HT/HP conditions to simulate geological processes.

Texture analysis without sample rotation requires large banks of detectors (HIPPO-type instrument) and accurate detection of lattice variations in low-symmetry materials requires high-resolution diffractometry (resolution-enhanced ENGIN-X instrument, with ample sample space). Preferably, in certain cases the two experiments should be performed simultaneously, in order to follow the complete evolution of the sample. A 50 Hz, short pulse, 5 MW source is most suitable.

### ***Comparative texture studies of complex systems, time evolution of rock texture.***

### ***Stress and texture***



#### IV. Cultural heritage materials

*Phase, microstructure and texture analysis* of natural materials such as stone, as well as ceramics and metal objects, is still relatively new but the potential applications of such powerful techniques span many fields of interest within archaeological research, from standard fingerprinting to complex conservation problems. Diffraction techniques are important for helping to date excavation sites, to establish trading patterns, to determine cultural exchange between regions, to elucidate historic and regional abundance of traded goods and to help identify the original source of raw materials. Phase and microstructure characterisation of ancient objects by diffraction methods can hint to manufacturing techniques. Diffraction studies may address the phases of the source materials or alteration and corrosion phases produced by exposure (e.g. patina, black crusts, etc.).

***Archaeological artefacts, conservation, non-destructive analysis.***

Owing to the non-destructive character of neutron scattering techniques, and to the large interaction volume, the applicability to relatively large, intact and potentially precious archaeological objects, is easily predicted. There will be many new applications in the fields of study and conservation of historical artefacts. An example of intervention guided by such studies is given in Figure 5.



Figure 5: Foligno Cathedral; limestones, marbles and travertine – before and after restoration (Courtesy of B. Moroni and G. Poli, Perugia).

TOF neutron diffraction can provide complementary information to X-ray diffraction, especially when non-destructiveness is an important issue, e.g. if objects must not be damaged by cutting, drilling, scraping etc. No preparation of objects is needed as data can be collected from large and intact objects of almost any shape. The experimental set-up is simple and free of sample movement [21].

Correlations between phases, or ratios of phase fractions, may be used to characterise or classify an artefact (Figure 6). During firing of ceramics the starting materials undergo solid state reactions depending on the firing temperature, duration and atmosphere [22]. Ancient or pre-historic ceramics fired at moderate temperatures often exhibit very complex diffraction patterns due to a wide variety of mineral phases, among them clay minerals and sheet silicates which need high intensity and resolution for identification and quantification.



Materials may change their microstructure due to mechanical treatments utilised in the production of artefacts. Hence diffraction ‘fingerprinting’ may also provide valuable information about the manufacturing processes. Texture is a case study of its own, and may for example be an important characteristic of a mechanically treated archaeological metallic object. The potential of neutron diffraction is further enhanced by the ability to investigate the phase abundance, texture or grain distribution of metal objects, for example bronze objects and coins [23]. Neutron diffraction is particularly powerful for sandwich situations, e.g. metal sheet stacking, coins with coatings or objects locked inside containers. Another aspect is to determine whether a coin is authentic or a fake, as well as to distinguish between differently struck coins.

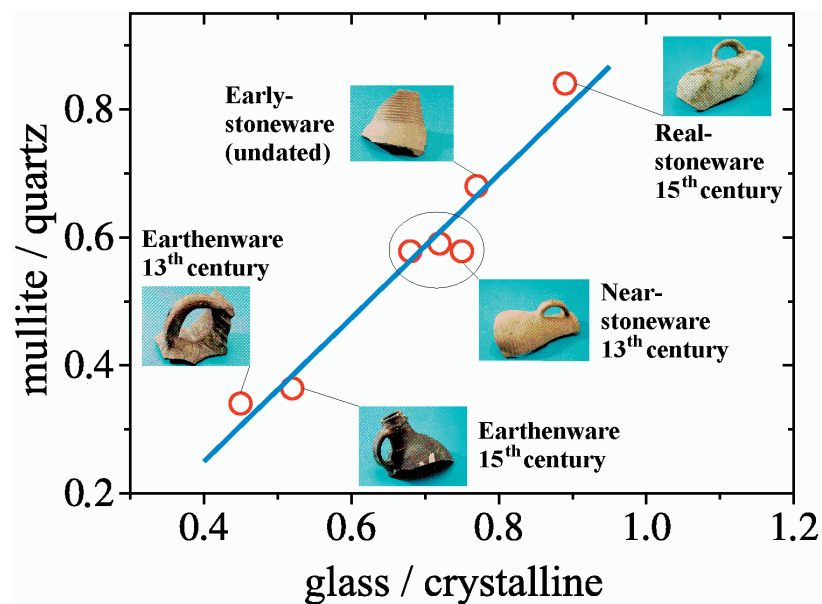


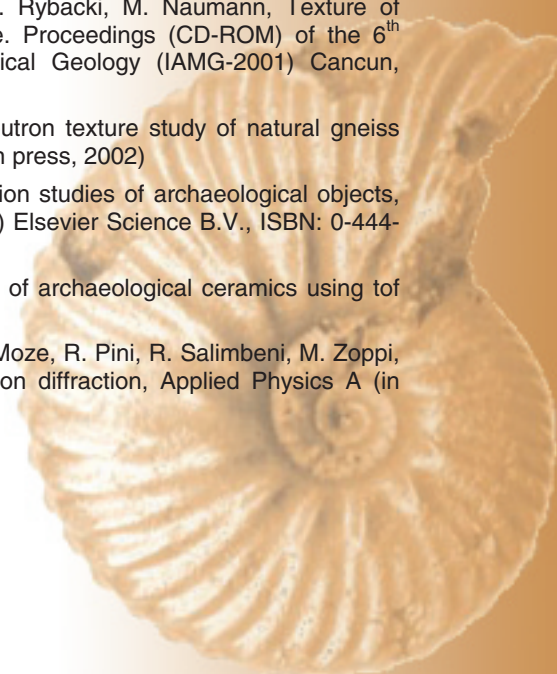
Figure 6: Classification of Medieval German pottery from Siegburg using ratios of phase fractions mullite/quartz and glass/crystalline that were obtained non-destructively by TOF neutron diffraction.

In the non-diffractive mode, information on the inner fabric of large scale materials and artefacts (a few  $\mu\text{m}$  to several cm), which is beyond the reach of X-rays, can be obtained by making use of recently developed neutron detectors which lend themselves to *neutron imaging* and *tomographic reconstruction*. Applications of this technique to archaeological artefacts are already envisaged; the availability of improved instrumentation, especially in terms of detector capabilities, would definitely represent a major improvement for this area of research.



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## Achievements of neutrons in mineral, Earth and environmental sciences

- Accurate and precise crystal structure determinations of minerals (including hydrogen bond properties) under ambient conditions and also under extreme conditions by the simultaneous application of elevated pressure and temperature (in-situ). Measurement of accurate equation-of-state data, phase stability and crystal structure behaviour under geologically relevant conditions to help our understanding of global dynamics, from catastrophic events to phenomena that span 10's of millions of years. Recent examples of geologically relevant minerals include: brucite, micas, olivines and spinels. Very recent new achievements in this field have been obtained thanks to the newly developed PEARL instrument and Paris-Edinburgh cell at ISIS, which provide excellent diffraction data at simultaneous pressures and temperatures of 7 GPa and 1700 K.
- Cation ordering of isoelectronic and quasi-isoelectronic species in crustal and mantle silicates and oxides by dynamical in-situ studies of order/disorder processes and transitions, often unveiling the non-quenchable nature of such phenomena. These experiments provide thermodynamic and kinetic data required for modelling mineral behaviour, mineral reactions and geospeedometry. The most significant examples are olivines, spinels, cristobalite and leucite.
- Low- and high-temperature hydration/dehydration processes in hydrous and nominally anhydrous minerals studied by neutron diffraction has provided the mineral structural basis for an understanding of geo-dynamic phenomena. These reversible transitions impact significantly upon a range of Earth science issues including the role of phosphates, zeolites and clay minerals in the remediation of contaminated land, the role of sulphates and clay minerals in crustal failure, and the behaviour of dense hydrous Mg-silicate phases and nominally anhydrous minerals in mantle/subduction zone derived earthquakes.
- Neutron spectroscopy has been pivotal in the evaluation of vibrational properties near and at phase transitions, measurements of soft phonon modes and the dynamics of hydrous components in minerals. The measurements of phonon dispersion curves to investigate interatomic potentials in geologically relevant phases (quartz, forsterite, enstatite, calcite, leucite, pyrope, etc.) have resolved issues associated with structural instabilities. Measurements of phonon density of states of framework minerals has enhanced thermodynamical modelling of phase transitions (i.e. cristobalite).
- Total neutron scattering measurements have for the first time been used to account for long-range crystallographic order providing a complete description of the temperature-dependent behaviour of framework silicates. Results for quartz show that a classical soft-mode treatment of its properties is too simplistic and that the structural behaviour is best described in terms of its ability to respond to low-frequency, high-amplitude vibrational modes.
- Strain/stress measurements have been performed in-situ at elevated pressures and temperatures on natural rocks (e.g. sandstone, quartzite and marble) with strains of the order of  $10^{-4}$  using the EPSILON instrument at Dubna. The partitioning of elastic strains between the component minerals in polymineralic rocks has been determined using ENGIN at ISIS providing significant insights into the controls and influences of rock composition and microstructure on the properties of the Earth's crust and mantle.
- In-situ observation of the evolution of both thermal and residual strains from within the center of large solid samples of natural rocks has recently been performed, providing a link between the thermal properties of rocks to the thermal response of the component minerals. Thermal cracking commences at 180°C when the thermal strain deficit along the

a-axes of quartz grains induces a thermal stress that is close to the bulk tensile strength of the rock.

- Texture analysis of bulk, single-phase mineral samples such as pyrite, chalcopyrite, quartz, hematite and calcite, and very recently, on polymineralic rocks such as gneiss mylonite, granulite and eclogite. These types of investigations yield information on the overall kinetics of rock deformation relating to large-scale geological processes.
- Non-destructive phase identification and quantitative phase analysis of archaeological objects (i.e. Bronze age ceramics, Attic ceramics, Etruscan bronzes, Medieval German stoneware) has been obtained using time-of-flight diffraction at ROTAX, ISIS.
- Small and wide angle neutron scattering experiments probing the structure of silicate and aluminosilicate glasses have provided information regarding the structure and dynamics of extrusive magmas and the dynamics of intrusive and mantle magmas. Additionally, the structural environment around toxic and radioactive metals is now generating accurate models and realistic materials designed for the long term containment of harmful metals.
- Neutron diffraction has recently been applied to the interaction of fluids with minerals that are associated with cements, oil and construction industries, waste containment and environmental remediation. Fluid interactions with vermiculites and montmorillonites, pillared clays, and zeolites are being studied in-situ under pressures and temperatures relevant to hydrostatic geological conditions (equating to burial depths of 10 km) and with chemistries relevant to environmental applications such as barrier materials and nuclear waste containment.