High pressure/temperature studies of minerals at ISIS

Case for support

1 Introduction

1.1 Although neutron scattering has been an extremely useful tool in the disciples of solid state physics and chemistry (and even the biological sciences) since the 1960's, the Earth Sciences community world-wide has been relatively slow in seizing the opportunities. However, the UK mineralogical community has been substantially ahead of the rest of the world in this respect, and have pioneered several applications of neutron diffraction (e.g. Swainson et al 1992; Henderson et al 1996; Woods et al 1996; Dove et al 1997; Palmer et al 1997; Stretton et al 1997) and neutron spectroscopy (e.g. Dove et al 1992; Swainson and Dove 1993; Line et al 1994) to the study of processes and behaviour of important minerals.

Neutron scattering is, in fact, a very appropriate tool for Earth Scientists. For diffraction it has a number of significant advantages over X-rays (laboratory or synchrotron). In particular: *a*) neutrons are sensitive to hydrogen atoms, which are hard to detect in X-ray diffraction experiments; *b*) isoelectronic ions have substantially different scattering power in neutron diffraction, which means that they can be separately identified; *c*) the scattering power of atoms does not fall off with increasing scattering vector (or scattering angle), which means that high-quality diffraction data can be collected to larger values of $\sin\theta / \lambda$ than usually possible with X-rays. Another practical advantage is that the use of the larger samples required for neutron scattering means that conditions of temperature and pressure can be properly controlled without significant temperature or pressure gradients, and can be measured with high accuracy.

The exciting prospects for the use of neutron scattering in the immediate future with existing sources such as the UK ISIS source (see §1.2 below), and in the horizon beyond the next decade with future sources such as the proposed "European Spallation Source" have been discussed by Artioli et al. (1996) in the ESF document "Scientific Prospects for Neutron Scattering with Present and Future Sources". Some of the key areas for Earth Sciences will be the ability to study the structures and dynamics of hydrous minerals, studies at simultaneous high pressures and high temperatures, and atomic-scale measurements on high-temperature geological melts. These will all give important information about the structure of minerals that are important in the Earth's Mantle, and of the transfer of water between mineral phases at the high temperatures and pressures found within the Earth. This information will be of considerable value in understanding the way that the changes in the atomic structures of minerals are linked to changes in physical properties, holding the key to understanding the factors that then determine the processes that impinge, sometimes catastrophically as in earthquakes, on the Earth's surface. For these reasons there has been a considerable growth in the use of the neutron sources by Earth Scientists, as documented by Artioli et al. (1996), and as seen in the example references cited in §9 below.

1.2 The ISIS neutron source at the Rutherford Appleton Laboratory (CLRC) is the most powerful pulsed spallation source of neutrons in the world, with a peak flux that is comparable with that of the most powerful reactor source (the ILL in Grenoble). There is a considerable advantage in using a pulsed source rather than a continuous reactor source for diffraction, and for diffraction from materials with special sample environment constraints. Diffraction measurements with a pulsed source can be confined to a fixed scattering angle (typically around 90°), allowing efficient masking of any scattering from the sample environment equipment. This cannot be achieved at a reactor source. The combination of the high intensity and pulsed nature of the ISIS neutron source has allowed the development of a high-pressure facility that is unmatched anywhere else in the world, and will remain unmatched for many years.

1.3 Over the past few years a world-leading programme in high-pressure neutron diffraction has been developed at ISIS under the direction of Profs Nelmes (Edinburgh) and Besson (Paris) based on the novel Paris-Edinburgh high-pressure cell (Besson and Nelmes 1995; Besson et al 1995; Klotz et al 1996; Loveday et al 1995, 1996). This facility has reached pressures in excess of 20 GPa, which is substantially higher than has been achieved at other neutron sources. This has been recognised internationally as a real UK scientific success, and is one of the flagship achievements in UK physical science over the past decade. The quality of the diffraction data from the Paris-Edinburgh cell is sufficient to allow structure determination of unknown high-pressure phases, and accurate refinements of the structures. For example, many studies have been used to identify changes in hydrogen bonding at high pressures. This facility has been fully funded by EPSRC to date. Whilst EPSRC will fund developments to enable the cell to reach even higher pressures at ambient conditions, and will fund the extension to low temperatures (for studies of magnetic order at high pressures, for example), the developments that will allow simultaneous high temperatures and high pressures are of such considerable interest to Earth Scientists that they more properly fall within the remit of NERC.

1.4 Our objective in this proposal is to procure and commission high-pressure / high-temperature facilities for Earth Sciences applications at ISIS, a process that will also require a certain amount of development work. These facilities will simultaneously achieve pressures up to 9 GPa and temperatures up to 1200 K in the initial stage, although there is every prospect that it will be possible to extend this P/T range without major new technological. The developments in this proposal will build upon the pioneering work of Besson and Nelmes, and in collaboration with these workers. The feasibility has already been clearly determined by Besson, and the development of these facilities now only requires support for the implementation of the design plans and the developments that will be required during the commissioning period. The resultant high-P/T facilities for neutron scattering will be unrivalled anywhere in the world for at least a decade if no subsequent development work is carried out, and the facilities will be operated as a general user facility for UK Earth Sciences research.

It should be noted that this proposal comes from a consortium of UK workers in Earth Sciences departments who have established programmes of work at ISIS, together with experts in high P/T research and in studies of hydrous minerals. As noted, the consortium will collaborate very closely with Profs Nelmes and Besson, and with K Knight, who is the diffraction expert at ISIS with particular interest in Earth Sciences research.

1.5 Until recent policy changes implemented by EPSRC, access to neutron beam time at ISIS was "free at the point of delivery" for scientific work that might normally fall within the remit of NERC. The same access was afforded to Earth Sciences workers from other countries. The new policy requires that UK access to beam time at ISIS (and other CLRC facilities) must be funded through the normal grant procedures, which for EPSRC and NERC work requires the funding of beam time as line items in grant proposals. Thus proposals such as this present proposal, with itemised requests for neutron beam time, are now inevitable. The irony of the present situation is that international arrangements mean that ISIS beam time remains "free at the point of delivery" for Earth Scientists from European countries such as Germany (e.g. Winkler and Hennion 1994) and Italy (e.g. Artioli et al 1995, 1996b; Catti et al 1994, 1995; Pavese et al 1997; Rinaldi and Wilson 1996). Without NERC support for research using ISIS we will have the situation in which ISIS will support world-leading Earth Sciences research in neutron scattering that is based in other countries, but UK Earth Scientists will be forced to use cheaper second-rate neutron sources, and will not have access to quality high-pressure neutron scattering facilities. The issues have been discussed in the report "Use of Central Radiation Facilities in the Earth and Environmental Sciences" (which is available within NERC, and can be accessed electronically from http://www.esc.cam.ac.uk/minphys/RAL.html), and by Dove and Redfern (1996).

2 Objectives of proposal

2.1 Our first objective is to develop high-pressure/high-temperature facilities for Earth Sciences applications at ISIS. This will involve the procurement and commissioning of the essential equipment, and the development of methods to measure the temperature using radiological methods (see §3.2). The high-P/T facilities established for NERC research at ISIS will be world leading, and will remain world leading for at least one decade.

2.2 Our second objective is to develop appropriate expertise in the Earth Sciences community in the UK in order to allow further exploitation and development for high-P/T neutron research.

2.3 Our third objective, which is specific to this project, is to use the technical developments of this project study the crystal structures of hydrous minerals at high temperatures and pressures. We are proposing to study the changes in the crystal structures of the minerals Lawsonite ($CaAl_2Si_2O_7(OH)_2.H_2O$), hydrated olivine, ... Lawsonite is important because it is one of the metamorphic minerals formed when hydrated oceanic crust descends into the Earth's mantle at subduction zones, and it's high water content may mean that it is be a significant carrier of water deep into the Earth's mantle. To date accurate structure refinements (in space group *Ccmm* at ambient temperature, and *Pcmn* and $Pc2_1n$ at lower temperatures) have only been possible at ambient pressures. Investigations with our proposed high P/T facilities will enable us to determine the structural changes associated with structural phase transitions and dehydration processes detected at high pressures and temperatures.

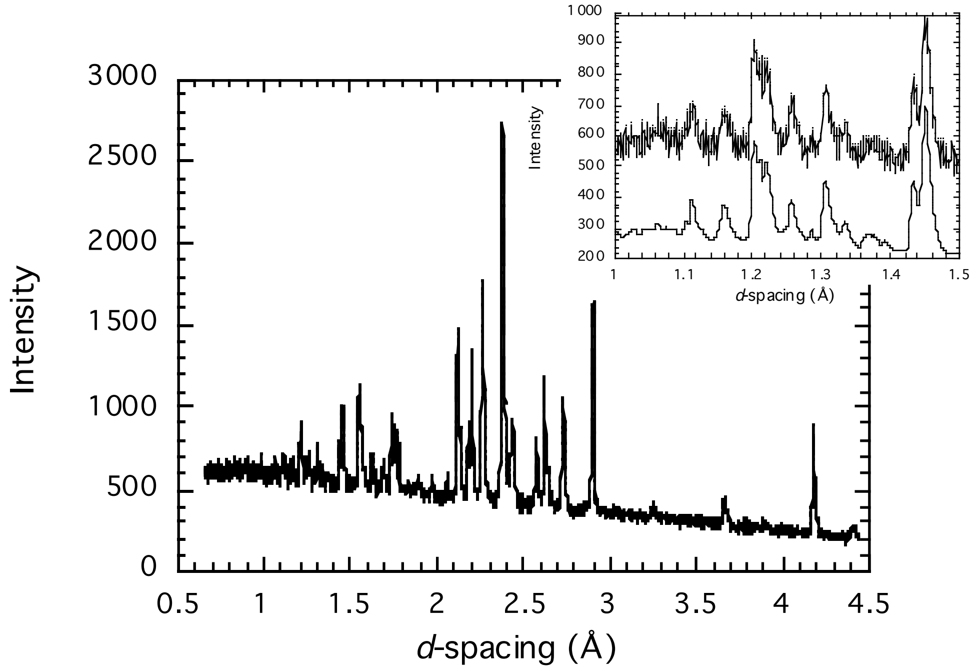

Figure 1. Simulated diffraction pattern for Lawsonite in the proposed high-P/T cell, assuming counting time of 8 hours. The simulation adds normal statistical errors. The intensity and background were estimated by comparison with data from existing high-pressure ambient-temperature cells. For this purpose we assumed the smallest sample volumes that will be practical to run – in practice we will usually be able to run with larger sample volumes, giving an increase in the signal to noise ratio. The insert shows a small region of the simulated diffraction pattern compared with the diffraction pattern calculated without statistical error.

3 Methodology and approach

3.1 The basic principles of the operation of high-pressure facilities at ISIS using the Paris-Edinburgh cell are now well developed (Besson and Nelmes 1995; Besson et al 1995; Klotz et al 1996; Loveday et al 1995, 1996, and as noted in §1.4 the feasibility of adding the capability of heating has already been technically demonstrated. For this proposal we need to implement these developments. The high-P/T cells (we are proposing to purchase two) will be built and tested in the Paris laboratory of Prof Besson, but he will require some manpower support for this (see §5.1). The cells will then be tested in detail on the ISIS facility (specifically on the PEARL station, that is dedicated to high-pressure work) before beginning the major experiments outlined in this proposal (§2.3).

We have tested the feasibility of the cell for structural work by undertaking a simulation of the diffraction pattern of Lawsonite under the actual conditions of the Paris-Edinburgh cell (i.e. accounting for sample volumes, beam attenuation, background signal etc) operated on the PEARL beamline with the existing banks of detectors. The simulated diffraction pattern, which includes the effects of normal counting statistics, is shown in Figure 1. Tests on this diffraction pattern show that it is capable of yielding a refined crystal structure (atomic coordinates, isotropic temperature factors) of reasonable quality, including data for the hydrogen atoms. Thus we are confident that the technology will yield the quality of the scientific results we are seeking.

3.2 We are proposing to use a novel non-invasive method to measure the temperature of the sample in the high P/T cell that avoids certain problems associated with the use of thermocouples. The method involves measurement of high-energy neutron absorption resonance lines in a thin metallic foil embedded in the sample. An example material is Tantalum, with principal resonance energies at 4.28, 10.34, 35.9 and 39.1 eV (alternatives are Pd, Co, and Au). Although the Bragg scattering from such a foil will be too weak to be observed, the absorption resonance will be strong and easy to measure using a special detector positioned in the beam-line behind the sample. The point is that the width of the resonance is very sensitive to temperature, which means that precise measurements of temperature can be obtained to an accuracy within a few K, which is an order of magnitude better than would be obtained with the use of a thermocouple. This method was pioneered at ISIS by Fowler and Taylor (1987), and applied to studies of catalysis (Mayers et al, 1989; Frost et al, 1989). In their arrangement the neutron resonance was measured using a ^{6}Li glass scintillator detector. Several prototypes were built, and it will not be difficult to built a detector with geometry (i.e. of the shielding, light guides, and overall casement) optimised for the high P/T cell. Some development work will also be needed to determine the optimum thickness of the scintillator, and there are ideas at ISIS on how to make some improvements to the light guides. The electronics will be copied directly from the original detectors. The development work will be carried out in close collaboration with the ISIS detector group (specifically with Nigel Rhodes).

3.3 There is now a large amount of experience of how to handle data from the Paris-Edinburgh cell. Examples of some of the issues are the need to take careful account of the attenuation of the neutron beam by the cell, including the effects of Bragg edges, and the need to take account of preferred orientation within the sample. These issues have been discussed by Loveday et al (1995). We do not foresee any new features in data analysis that will arise with our proposed high-P/T cells. Therefore the commissioning stage in the project will involve measurements of beam attenuation, background levels from the high-P/T cell etc, in order to be able to calibrate for the corrections that are used with data from the Paris-Edinburgh cell. The commissioning tests may well point to optimisation procedures in order to improve the quality of the raw data.

4 Programme and plan of research

4.1 01/98 – 9/98. The first stage of the project, before we have the necessary manpower, will be spent in detailed planning, ordering equipment and components, recruiting the PDRA and tied student, and liaising with Prof Besson in the detailed planning. In this stage we will establish the project's WWW pages. The milestone of this stage will be that the staff will be recruited and able to start on specific tasks on day 1 of their tenure.

4.2 10/98 – 9/99. The second stage of the project will be devoted to producing the first versions of the high-P/T neutron cell and the heating diamond anvil cell. The milestone will be to collect diffraction data from both sets of equipment that will be good enough for structure refinements. Simultaneously with the development of the high-P/T cells will be the building and testing of the resonance detectors for temperature measurement in the neutron experiments (§3.2), with the milestone that temperature measurement will be fully functional at the same time that the high-P/T neutron cells become operational. This stage will be the most challenging of the four in terms of the technological aspects.

4.3 10/99 – 9/00. The third stage of the project will be to properly commission the equipment, and optimise its operation. In this stage more of the effort will be put into the analysis of the data (§3.3). We plan to collect rather more useful data in this stage, and produce good results from structure refinements of minerals under high-P/T conditions. The milestone will be our first publications of structural data.

4.4 10/00 – 9/01. The fourth stage of the project will be more concerned with ensuring that the high-P/T neutron facilities become general user facilities. This will involve making sure hat every aspect of the equipment is made as "user-friendly" as possible, and in producing good manuals in paper and electronic (WWW) form. We plan to encourage wider use of these facilities by other groups in this stage, with the primary mechanism being a summer school for prospective users (for which we will seek NERC support at the appropriate time). In this stage we will also continue to collect data for the scientific programme outlined in §2.3, and by the end of this stage we will have published six substantial papers on the scientific issues in addition to having publications concerned with the technical achievements. The milestone in this stage will be to hold the summer school with a sizeable prospective-user participation.

5 Justification for resources being sought

5.1 We are requesting support for one post-doctoral research worker for three years, and a tied PhD studentship. The justification for two staff posts is that we are aiming to establish a facility that will be of considerable use to the Earth Sciences community for many years, and one that has the potential to evolve to cover a wider range of science than envisaged in the initial three-year period. In order to achieve all our technical objectives and establish a fully functional general user facility, and also complete the scientific objectives, this level of manpower support is deemed to be the minimum possible. We have taken advice from the experts in high-pressure research. We are also requesting six months of technician support for this project in order to support development and maintenance work.

5.2 We are requesting support for two high-P/T cells for the neutron diffraction. We are advised that two cells are required because of the greater efficiency they afford. Whilst one cell is being used to collect data on the neutron beam line the other cell can be loaded off-line. Moreover, wastage of beam time following failures in the components of one cell will be minimised by having a preloaded substitute cell ready off. The efficiency savings are easily seen to be worth while: the cost of a second cell is less than the cost of 2 days beam time, and the efficiency gains will amount to 2–3 days in any experimental period lasting 10 days. For this proposal we estimate an efficiency saving of around £140,000 by having a second cell costing around £20,500.

The basic cost of two high-P/T cells is £41,000. The high-P/T facility will require a regulated power supply and control, which is costed at £11,000. It is estimated that the scientific programme will require three pairs of leached diamond anvils, which will cost a total of £16,000 for purchase and processing, and five pairs of tungsten carbide anvils costing a total of £4,200. Additional small items and consumables such as gaskets, foils for temperature measurements, high-pressure hoses, high-tension cables, furnace elements, oil pumps and gauges have been costed at £17,500. We have been quoted construction costs of £7,000 to cover machine shop time and finite-element calculations. The total costs for the full three-year programme are £96,700. These costs have been provided by Prof Besson, who will supervise construction of the cells. The costs include VAT.

The temperature measurements will require construction of a dedicated neutron detector based on the principles outlined in §3.2. The ISIS detector group have quoted a costing for components and development costs of £10,000.

5.3 We estimate that we will require 20 days of neutron beam time each year for the scientific objectives (10 days per scientific objective, running two objectives each year), and another 20 days for development work. This level is based on our simulation of the Lawsonite diffraction pattern (Figure 1), and allows us to collect data for each sample over a useful range of temperatures and pressures. The beam time also accounts for setting-up time, and for rapid exploratory runs each time to help map out useful temperatures and pressures. The development time will be used to tackle issues such as reduction of beam time by effective collimation of the beam, in situ testing of components of the high-P/T cell, and development of the radiographic method of temperature measurement. Neutron beam time is costed at £9,300 per day, making a total of £744,000 for neutron beam time.

5.4 Diamond cell for SRS

5.5 SRS beam time

5.6 Sample production

5.7 We believe that the student will need to spend 1.5 years in the High-pressure laboratory in Paris, and that the post-doctoral worker will need to spend 0.5 years there. We believe that to cover additional accommodation and subsistence costs will require £3,000 per year for two years. These visits to Paris will require 4 return journeys, which are costed at around £100 per return journey. (Total £6,400)

The work at ISIS will require dedicated manpower support. For each period of 10 days of neutron beam time we will require an additional 5 days of setting up and dismantling of equipment. Assuming accommodation and subsistence costs of £30 per day per person, and travel costs of £50 per person (including rail from Cambridge to ISIS, and daily travel to and from the laboratory), a 10 day experiment will cost £1,000. We are proposing eight periods for experiments. (Total £8,000)

5.8 In order to publicise our results, attendance at international and national conferences is essential. This is also essential for the training component of the proposal. To inform the UK mineralogical community, we are proposing that the PDRA and PhD student should both attend the annual Winter conference of the Mineralogical Society (estimated costs for conference fee, travel and accommodation are £500 per person per conference). We are also proposing one visit by a member of the team to one of the major US Geophysical conferences each year (costing £1,200 per visit), and three visits to the mayor European conferences (EUG and EMPG, costing £800 per visit). (Total £9,000)

6 Management of project and resources

6.1 The overall project will be managed from Cambridge. It is planned to hold two management meetings for all principal applicants and staff associated with the project each year in London.

6.2 The work associated with the procurement, commissioning, development and maintenance of the neutron scattering high-P/T cell will be managed by MTD and SATR.

6.3 The work associated with the procurement, commissioning development and maintenance of the diamond anvil cell for the synchrotron radiation experiments will be managed by SATR and ARP.

6.4 The ISIS experiments and data analysis will be managed by the whole consortium.

6.5 The SRS experiments and data analysis will be managed by SATR and ARP.

6.6 The sample preparation will be managed by ARP and SCK.

6.7 Production of manuals (see §4.4, §7.4) will be managed by MTD and SATR.

6.8 The WWW site (see §4.1, §7.4, §8.2) and other publicity will be managed by MTD and SATR.

6.9 The summer school at the end of the grant period (see §4.4, §8.3) will be managed by MTD and SATR.

6.10 The training of the tied PhD student will be managed by MTD and SATR. This will periods of several months spent in the Paris Laboratory of Prof Besson to learn high-pressure techniques at first hand, and to assist in the building and testing of the high-P/T cells.

6.11 The PDRA and tied student will also receive training in high-pressure neutron and X-ray measurements, and this will be managed by MTD and SATR.

7 Long-term stewardship

7.1 Datasets from the neutron scattering measurements will be stored in optical archive form at ISIS. The results from the structure refinements will be published in mainstream journals, and the normal practice is for the technical details to be entered into crystallographic databases for easy retrieval by other scientists.

7.2 The neutron scattering high-P/T equipment will eventually be kept at ISIS. The equipment may be formally transferred into the care of ISIS, or be maintained by follow-on NERC support.

Either way, the facility will be maintained as a general user facility for Earth Sciences application. Support will be sought for further development work.

7.3 The diamond anvil cells will be maintained in the long-term in Cambridge.

7.4 Manuals will be stored with the equipment, with electronic copies held on the WWW site associated with this project (see §8.2). The WWW site will be maintained indefinitely.

8 Wider dissemination of results

8.1 In line with our current practice, all results will be published in top-quality mainstream scientific journals, targeted towards appropriate readership. We will produce publications devoted to the specific technological developments, and to the specific scientific results.

8.2 We will maintain a WWW page associated with this project (see §4.1, §4.4). This will contain details of progress and results, electronic copies of manuals in all draft stages and final copies, and information for other potential users.

8.3 We plan to hold a summer school at the end of the grant period in which other potential users can learn first-hand about the facilities (see §4.4).

8.4 We are proposing to also publicise our results at national and international conferences (noted in §5.8).

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