Beamline Review Panel BM30B

Introduction

BM30B is a French CRG instrument dedicated to X-ray Absorption Spectroscopy. It started its operation at ESRF in 2002 and has been reviewed twice since then, in 2005 and 2009. Its scientific programme is centred around the analysis of element speciation in complex matrixes at low concentrations. It is a heavily oversubscribed beamline with ratios of 6 and 3 for the ESRF and national channels, respectively. The beamline maintains its leading role in molecular environmental science and in the study of metal speciation in geological fluids and has also extended in the past 5 years its field of expertise towards biogeochemistry and inorganic biochemistry with definite success in unravelling the structure of various metal-organic complexes. The main developments of the past 5 years are (i) the purchase of a Raman spectrometer that complements XAS measurements at high pressure and temperature for a better understanding of geological fluids; (ii) the development of a unique hydrothermal high pressure cell; (iii) the development of the crystal analyser setup that has evolved from one crystal to 5 crystals in the present set-up. It is increasingly used in various experiments dealing with chemistry, nano(eco)toxicology or environmental science. This latter development will further expand, as a new beamline Fame-UHD specifically designed around fourteen crystal analysers is currently being built on BM16 and should start its operation at the beginning of 2016.

This report is based on the analysis of the written documents provided before the meeting, on the oral presentations made by the project leader, three permanent scientists working on the beamline and users representing specific communities, on a visit to the beamline and on extensive discussions with the beamline staff that must be thanked for their helpful presentations and answers.

Research by users.

The beamline maintains a high productivity with around 30 publications per year in leading journals in their respective fields. The number of publications reflects the various scientific fields covered by the beamline, as on average each run produces a publication. The beamline staff have succeeded in attracting new users while maintaining strong links with a sound panel of regular users. In terms of highlights the panel has particularly appreciated the application of the new high pressure cells which enables fundamental research in geochemical modelling and hydrothermal enrichment processes for metals e.g. Liu et al. Chem Geol 376 (2014) 11-19 and Tian et al. Geochim. Cosmochim. Acta 129 (2014) 263. In addition, the work of Louvel et al. Geochim. Cosmochim. Acta 104 (2013) 281 extends this to higher pressures and enables study of element mobility in melts.

FAME was the first beam line to evaluate the transformation of nanomaterials in complex media such as human cells or bacteria. As early as 2005-2006 FAME provided data concerning the speciation of metals in various media and the links between toxicity and chemical speciation and its in-vivo evolution in relation to the cell.

Thanks to the efforts of the FAME group French geochemists and biologists are now recognized as leaders in Europe and have developed strong links with the US CEINT group. (Auffan, M et. al. Nanotoxicology 8 (2014) 167-176 ; Collin, B et. al. Environmental Pollution 187 (2014) 22-30 ; Tella, M et al..ES and T (2014) 48, 9004-9013 ; Trepeau J et. al, Metallonics 6 (2014) 263-273. The transformation of nanomaterials is now recognized by the EU FP7 and FP8 as a key parameter for evaluating the risk in the use of nanoparticles. FAME has played in this aspect a very important role in France and in Europe.

The development towards X-ray emission spectroscopy and HERFD XANES, demonstrated for both biological and catalytic applications is at a high level and enables new studies in both areas. The new beamline (FAME-UHD) together with the 14 element analyser crystals is key for both communities. In the field of catalysis this is complementary to Soleil, and the expertise from Lyon with in-situ cells, as illustrated by the results presented by Christophe Geantet, is a strong basis for further Science capability.

The development of FAME-UHD should enable the attraction of new international users that so far hasn't been possible on FAME alone.

Research by staff.
The beamline staff are mainly involved in studies of geothermal fluids and clearly their involvement in this research topic has provided them with a leading position world-wide. Recent developments around this topic involve collaborations with theoretical chemists that should deepen the fundamental knowledge of the molecular scale mechanisms occurring in these fluids. This is recognised by the panel as highly important. Numerous PhD students and post-docs have been active as guest researchers at the beamline. It must also be emphasized that the beamline staff managed to develop close collaborations with many user groups, even those who haven't used XAS previously. In that regard this can be consider to be close to in-house research. This appears in the experimental reports and is also illustrated by the faithfulness of many users.

Technical status of the beamline.
The present state of the beamline is competitive, but the first installations are now aging. The flux and optics are extremely competitive and will remain world leading. The team are to be congratulated on developing automation procedures for making the most efficient use of the beamtime and the training of users and the FAME+ course is highly commended. The He cryostat works well and is used extensively for biochemistry where its use is crucial. The ESRF standards for motors are now being implemented. The crystal analysers for X-ray emission spectroscopy are being addressed with the new FAME-UHD (see below); the high pressure autoclave is outstanding and unique asset to the beamline. The beamline team are also to be commended for developing a separate Raman system, and are to be encouraged to continue with this so that Raman and XAS can be combined into the same experiment. However, the panel expressed some concerns in two areas: (i) the panel were not convinced that the micro-focus KB-mirrors were competitive, although some good research has been done and (ii) the fluorescence detector is now very old and is in urgent need to be replaced for the beamline to maintain its competitiveness in studying dilute samples.

Future technical developments (and ESRF Upgrade phase II).

Following the recommendations of the last review panel the beamline community is now in a much stronger position with the agreement to build the new beamline FAME-UHD. The present team are to be strongly commended for developing the crystal analysers which will be implemented on this beamline and which will lead to a stable environment for the utilisation of high resolution XAS, RIXS and HERFD in environmental, geochemical and catalysis systems. This beamline, in giving extra capacity, will reduce the oversubscription on FAME and allow it to concentrate on conventional dilute fluorescence XAS. The previous review recommended the replacement of the detector. Whilst the panel recognise this is not necessarily straightforward due to technical issues with new monolithic detectors, developments in detector electronics such as XMAP and XSPRESS do allow countrates of upto 200-300 kHz per element which is a factor of 10 increase on the present detector. The FAME monochromator and optics deliver a highly stable and competitive flux, and with a new detector system this will enable greater exploitation and maintain the beamline at the cutting edge of dilute spectroscopy measurements through enabling diluter species to be studied.

The link with Soleil is to be commended and strategically the complementarity of Soleil XAS beamlines with faster time resolution and FAME with its dilute capability provides a unique capability for a wide variety of important scientific areas.

With the ESRF upgrade the shared bending magnet with FIP (BM30A) is no longer recommended, and one of the beamlines should move to a new port. The move of FAME to another port would be highly advantageous as it would allow the optics to be placed closer to the source and a commensurate gain in flux, however it also provides an opportunity to consider new optics to take better advantage of the lower emittance source, and could make a micro-focus set-up much more competitive.

Future scientific directions.

The highlights of the beamline, which are presently geochemical processes, nano(eco)toxicology, and environmental chemistry should be pursued and in all these aspects the complementarities between FAME-UHD and FAME are a strong asset. Concerning geochemical processes, this scientific direction will be even more relevant in the future due to the new economic needs of rare metals and also rare earth elements. The prospection of ore deposits is directly related to the understanding of metal transport and enrichment processes which can be investigated by (high pressure/high temperature) in-situ studies at FAME. The combination of experimental data with molecular dynamics simulations has been proven to be very successful and allows new insights into metal transportation and enrichment processes. We strongly encourage the team to continue and extend this research in the future. The start of the new beamline FAME-UHD will enable complementary studies of metal speciation. Linked to this field of research are studies on metal demobilisation in natural environments. The life-cycle of metals and reuse of waste will be expanding in future years and FAME clearly has opportunity to address these issues. Also the studies in supercritical fluids should be pursued with the newly developed cells and combination of Raman spectroscopy and X-ray absorption spectroscopy will be an important add-on. FAME should be a key beamline to evaluate the new evolution towards a « safer by design » of nanotechnology (H2020 and US-

COR group discussions). Working at lower concentrations will certainly open new opportunities in environmental chemistry for understanding the geochemical cycle of elements in sub-surface environments.

The expertise has been recently extended to bioinorganic and biological applications, which should be further extended. Moreover, catalysis with nearby activities in Lyon and its complementarity to SOLEIL (SAMBA and ROCK) appear an interesting application, particularly with the new 14-crystal analyzer spectrometer allowing not only studies on ultradilute samples but also X-ray emission spectroscopy. This is an upcoming field in catalysis, and areas in biology and geosciences will also strongly benefit from this development.

Staff

The panel was truly impressed by the dedication, enthusiasm and technical skills of the beamline staff. Staff dedication is illustrated by the fact of providing more user shifts than required. Such a strategy however should be balanced with the need for in-house research. It must also be emphasized that the beamline staff are really active in securing various financing through grants, often obtained in close collaboration with the users. The purchase of a new detector through the ANR Mesonnet or the purchase of the Raman spectrometer are perfect illustrations of this proactive strategy. The panel strongly supports the request that for the operation of two beamlines in the future this requires the addition of at least one more engineer. Furthermore, in terms of science, reinforcing the team dealing with hydrothermal fluids would significantly strengthen this research activity. The panel agrees that it represents a key move to secure the present world-leading role of FAME researchers in these activities that, as mentioned earlier in this report, are bound to develop in the medium to long term.

Summary of recommendations.

The panel:

- Strongly recommends the upgrade of the fluorescence detector system on FAME.
- Supports the crystal analyser development at FAME-UHD
- Recommends the hiring of a new engineer for the two beamlines
- Supports the combined XAS-Raman spectrometer development
- Recommends the establishment of a dedicated port for FAME in the framework of the ESRF phase II upgrade
- Highlights the excellent in-house research in hydrothermal fluids and encourages the staff to further extend their own research in this direction

Signatures:

Karen Appel	**Jean-Yves Bottero**	
Andrew Dent	**Jan-Dierk Grunwaldt**	**Laurent Michot**