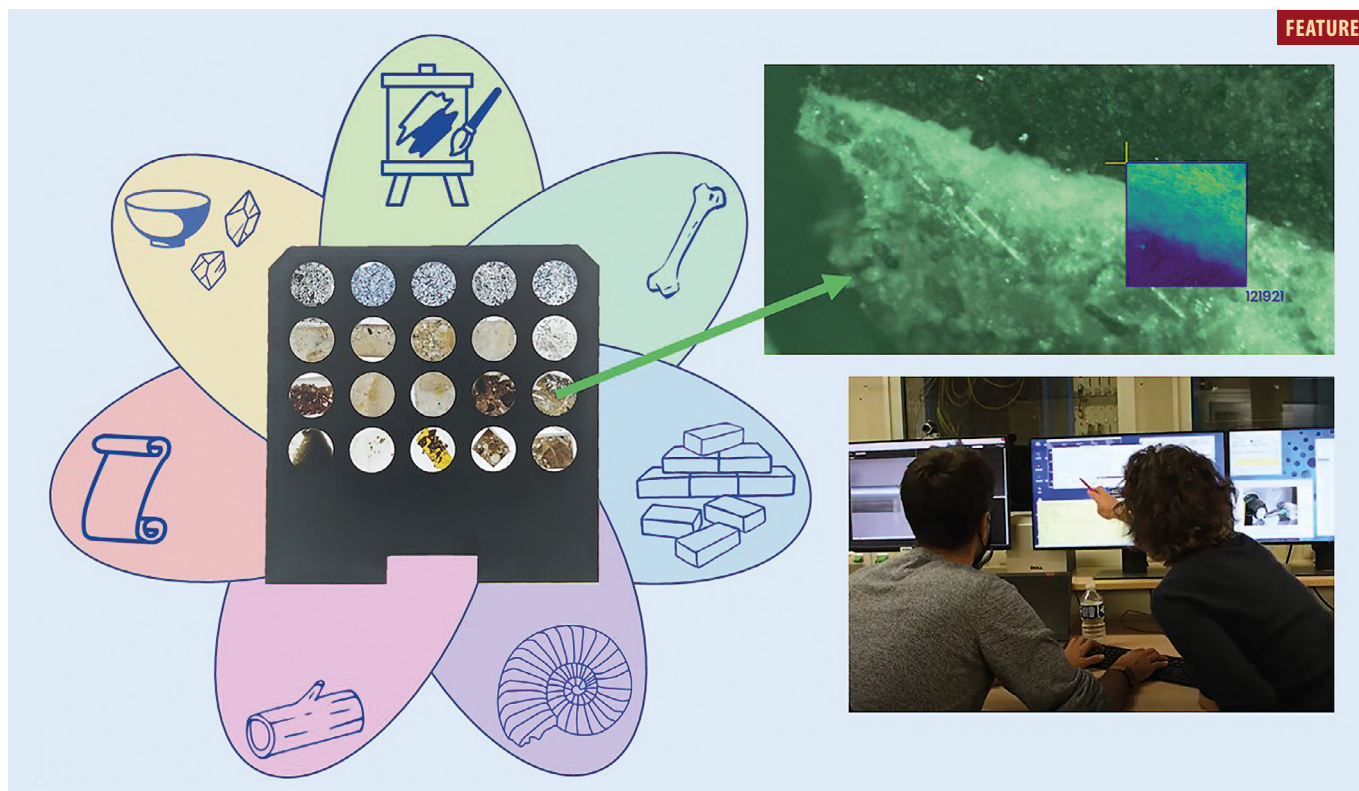




SIMPLIFYING ACCESS AND USABILITY OF ADVANCED SYNCHROTRON RADIATION MICROSCOPES FOR HERITAGE SCIENCE

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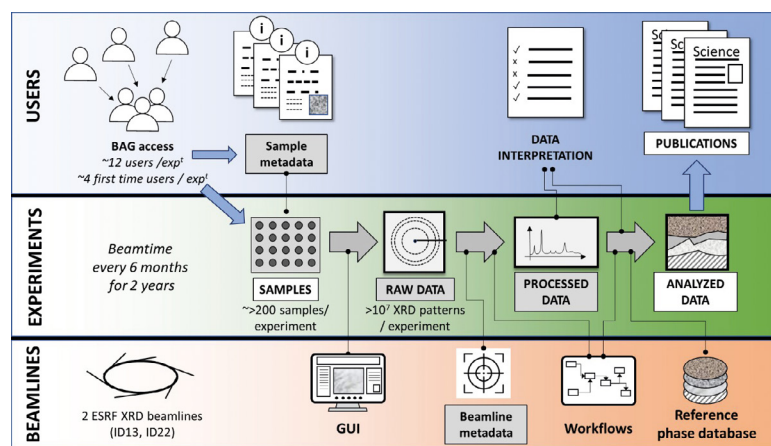
At the European Synchrotron Radiation Facility (ESRF), heritage research has become far more accessible and effective. Following the recent ESRF upgrade, this user community is benefiting from regular and facilitated access, and efforts are dedicated to Open Science, to make the data collected on these valuable materials accessible to everyone.

The early applications of synchrotron techniques to Heritage

Among the many analytical techniques available to study cultural heritage, those based on synchrotron sources have seen a marked increase in their use[1, 2]. Their advantages include a high X-ray beam brilliance allowing rapid analysis, high signal-to-noise ratio data, and sub-micrometre beam focussing. These are exploited together in a variety

of structural and chemical mapping methods, for example micro X-ray diffraction (μ XRD) or micro X-ray fluorescence (μ XRF), allowing identification and location of components within precious, complex and heterogeneous ancient and artistic materials. X-ray, UV-Vis and infrared spectroscopy techniques, enabled by the energy tunability of the synchrotron sources, also facilitate investigation of the artefacts' manufacture and degradation. The ●●●

▲ Heritage research facilitation at ESRF



▲ **FIG 1:** Process of a typical ESRF Historical Materials BAG experiment (illustrative numbers are given for ID13). Boxes in grey highlight the information (data and metadata) that will be gathered in the SHARE database.

● ● ● coherence of synchrotron beams has also led to new tomography methods, such as those based on phase contrast, which regularly offer invaluable discoveries in the field of palaeontology. Many of these techniques have been used for the first time on heritage materials at the ESRF (Grenoble, France), for example to reveal the composition of Ancient Egyptian cosmetics or Bamiyan Buddhist wall paintings [2]. During this early research, experiments usually involved only a few expert groups, with most heritage scientists considering synchrotrons exotic and synchrotron scientists being unfamiliar with the field of heritage. Access to experiment time is challenging to obtain and use effectively for newcomers unfamiliar with proposal procedures, sample preparation, beamline equipment, or data processing software, further discouraging heritage researchers from exploring synchrotron techniques. However, things have changed since these pioneer experiments! Heritage and synchrotron communities are now used to working together [3]. At synchrotron facilities, efforts are daily dedicated to improving instruments and making experiments faster and more user-friendly. Yet, it is important to consider data acquisition as only one of a series of many steps that all need to be improved. Here, we outline recent and on-going actions implemented at the ESRF to ease and improve synchrotron use for heritage researchers and improve the data FAIRness (Findable, Accessible, Interoperable, and Reusable) and results of these experiments.

The Historical Materials “BAG”: a group access mode

The ESRF’s extremely brilliant source upgrade increased beam brilliance by two orders of magnitude, allowing vastly more samples to be measured during an experiment due to much faster data acquisition. This motivated

the implementation of the new ‘block allocation group’ (BAG) access mode for the crystallographic analysis of historical materials. This access allows researchers from multiple institutions to share experimental time with a standardised data collection procedure (Figure 1), further increasing the efficiency of sample measurements. The Historical Materials BAG started in 2021 and gives access to two XRD beamlines, ID13 and ID22, every six months for a two-year period. It has been renewed twice since inception [4]. At ID13, μ XRD maps are collected in transmission (with simultaneous μ XRF) using a micrometric beam to determine the nature and 2D distribution of crystalline phases. Sample holders and graphical user interfaces (GUI) have been developed to make the X-ray microscope as easy to use as an optical microscope [5]. Samples are mounted in groups of ~20–50, to reduce time lost in exchanging sample holders. Thanks to a custom user interface, it is easy to navigate over the samples, define regions of interest, and queue multiple acquisitions. During a 4-day experiment at ID13, over 200 samples are typically analysed, a factor of 10 more samples than a standard heritage experiment. At ID22, high angular resolution powder XRD data allows detailed phase identification and quantification, with automated sample change for uninterrupted acquisition.

With more than 87 users over 16 visits in 4 years resulting in 25 publications thus far, the BAG has been used to investigate paintings, ceramics, marbles, manuscripts, and more, from artists as major as Leonardo da Vinci, Rembrandt, Picasso, and Miro. The BAG brings together researchers from many specialisations, promoting collaboration and bonds within the wider community. In addition to experience gained during experiments, ESRF hosts workshops for BAG users for synchrotron data acquisition and software training as well as sharing of their own research.

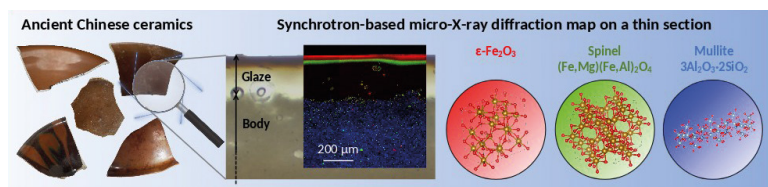
Processing and re-processing data

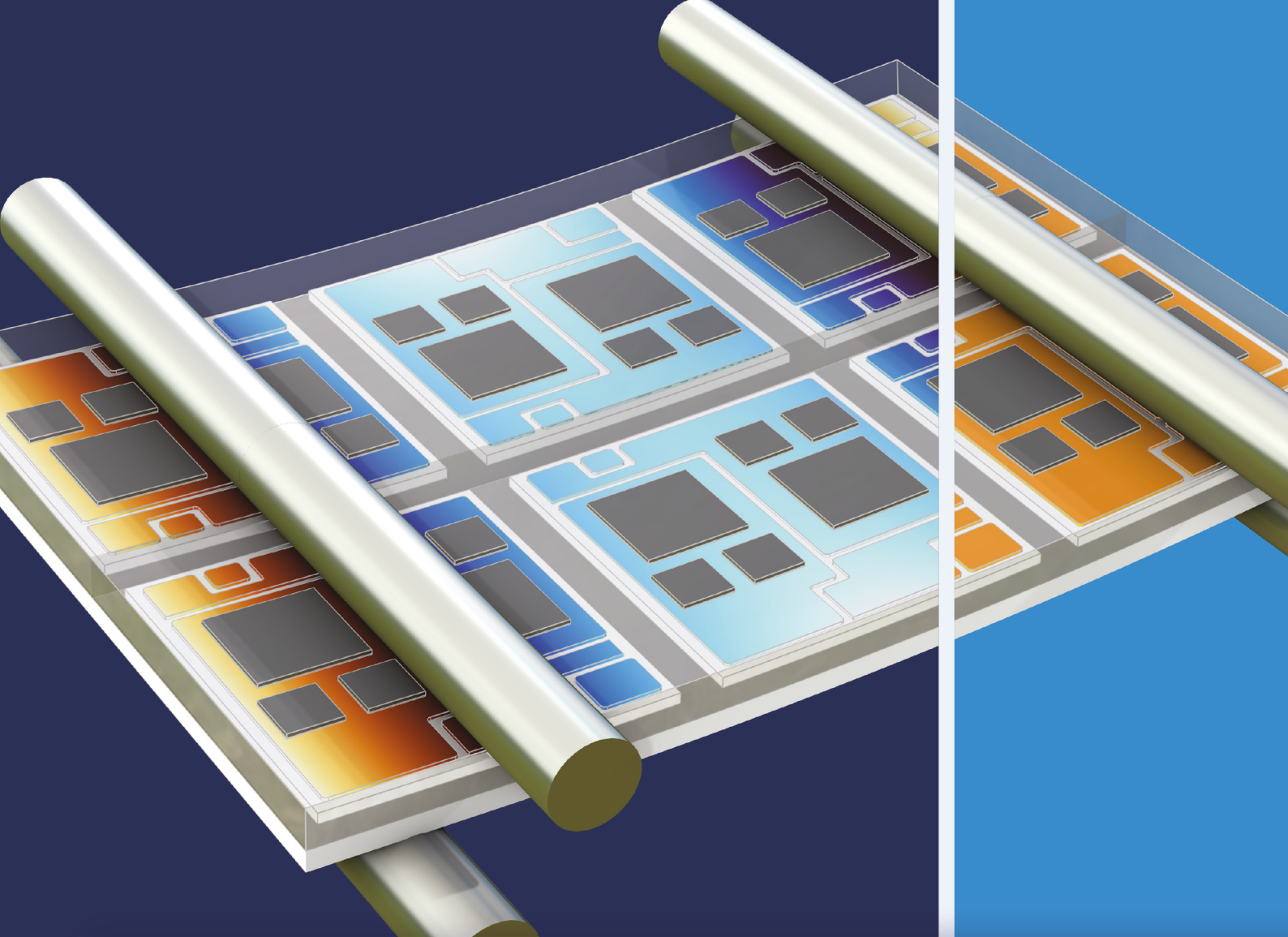
The maps generated by ID13 (one XRD pattern per pixel, $>10^4$ patterns per map) require batch integration methods. These have been integrated into the workflow so 1D XRD patterns are generated automatically. Processed data is then returned to the user interface, giving a real-time view of the phase mapping. By comparison with crystallographic databases, main components are identified, and different software packages/workflows are available to calculate the phase maps. It is also possible to re-integrate/reprocess data from outside ESRF.

Towards open science: Metadata identification and collection

Analysing our heritage is not just important for understanding the past; it is also vital in preserving it for the future. This research is inherently collaborative, meaning that data should be openly accessible to advance our collective understanding. To this end, and thanks to funding from the OSCARS project (Open Science Clusters’ Action ● ● ●

▼ **FIG 2:** Ancient Chinese ceramic shards (left) and μ XRD phase map representing the distribution of ϵ -Fe₂O₃ (red), iron-bearing spinel phase (green) and mullite (blue) phases, overlaid on an optical microscopy image of a thin section (right).





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••• for Research and Society, grant 101129751), we are developing the SHARE (Synchrotron X-ray analysis of Heritage Accessible to and Reusable by Everyone) database.

While it is critical that both raw and processed data are stored efficiently and organized for easy access, it is equally important that the context surrounding a dataset is recorded as well. We have therefore identified the core information needed to fully describe an experiment and ensure that data can be identified, reprocessed and reanalysed by anyone. This includes metadata about the sample (artist, period, material, *etc.*) and the experimental setup (X-ray energy, detector geometry, *etc.*). Standardised sample metadata is collected pre-experiment through an online form that can be added to afterwards with significant findings. Ultimately, this will allow searching via keywords, as is already the case for the ESRF's Paleontology and Human Organ Atlas databases. Setup metadata is automatically recorded during measurements, then stored within the raw data files, within an online logbook, and within the ESRF data portal. It will be available to view alongside the sample metadata within the SHARE database website, currently under development. Ultimately, the SHARE project will allow any researcher (after an embargo period) to re-investigate data with new scientific questions and new data analysis processes that will certainly emerge in the coming years.

A BAG case study: Deciphering the firing conditions of Song ceramics

The brown-glazed ceramics manufactured during the Song Dynasty constitute an essential group in the history of Chinese ceramics. These objects, manufactured all across the Song Empire, were particularly appreciated for tea drinking, as their dark glazes aesthetically contrast with the white froth of the whipped tea. Interestingly, the characteristic brown hue of these ceramics is due to the presence of $\epsilon\text{-Fe}_2\text{O}_3$ dendrites at the surface of the glazes, an otherwise rare ferric oxide. Understanding the growth of such structures is key to providing insights on the firing conditions of these products. Knowing the nature and spatial distribution of the crystalline phases across the glazes is therefore essential.

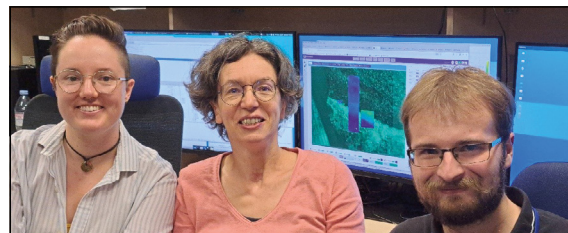
18 shards excavated from several Northern Chinese archaeological sites (Yaozhou kilns and Yingou site, Shaanxi province; Xin'An kilns, Henan province) were analysed at ID13 through the BAG. μXRD maps as large as $800 \times 800 \mu\text{m}^2$, $2 \mu\text{m}$ step size, were recorded in only 1 hour. Besides the standard data processing described above, the data were further exploited to develop statistical procedures aiming at extracting phase maps more efficiently [6].

This analysis revealed a typical stratigraphy, common to most of the samples: a layer of $\epsilon\text{-Fe}_2\text{O}_3$ at the glaze surface, above a layer containing an iron-bearing spinel phase, covering the mullite-containing ceramic body (Figure 2). Interestingly, the spinel layer extends to different depth depending on the ceramic's provenance, indicating that different firing processes were used in neighbouring provinces to

produce similar-looking glazes. This is also the first recording of the presence of the iron-bearing spinel layer to such an extent, and its thickness confirms our previous hypothesis that the growth mechanism of $\epsilon\text{-Fe}_2\text{O}_3$ is diffusion-driven [7].

This case study is only one among the many projects which benefitted from the BAG access, more examples can be found on the Historical Materials BAG webpage [8]. We welcome new potential users, and encourage anyone interested to get in contact! ■

About the Authors



Georgina Robertson (ESRF, left) is a post-doctoral researcher, developing tools for streamlining the ID13 beamline and using μXRD mapping to investigate the degradation of pigments. **Marine Cotte** (ESRF and LAMS, CNRS, middle) is a beamline scientist, developing and applying synchrotron micro-analyses, with a particular interest on cultural heritage. **Clément Holé** (ESRF, right) is a post-doctoral researcher, applying micro-X-ray spectroscopy and diffraction techniques to study the manufacturing process of ancient Chinese ceramics.

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