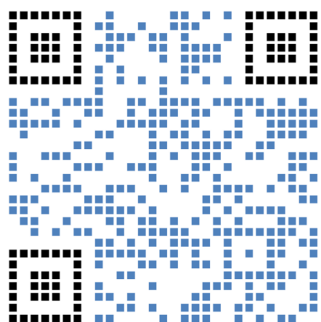




# Conference

## Methodological Innovations in P-XRF-Studies

24th of September 2024 at the Vienna Institute for Archaeological Science  
with an Ice-breaker event on the 23rd at Naturhistorisches Museum Wien



Conference program

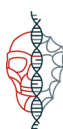


General information



universität  
wien

Vienna Institute for Archaeological Science



HEAS  
human evolution &  
archaeological  
sciences



FWF ESP 476

Standardising p-XRF for archaeometry

FWF Österreichischer  
Wissenschaftsfonds

nhm  
naturhistorisches  
museum wien



# Ice-breaker event & Conference program

## 23<sup>rd</sup> of September 2024

Naturhistorisches Museum Wien, Department of Prehistory - access through side-entrance Burgring 7, 1010 Wien. Please arrive 15 minutes early!

04:00pm	<b>Workshop</b> on Conservation and Restoration as Limiting Factors For pXRF and Other Instrumental Analysis Methods ( <i>Daniel Oberndorfer</i> ) <b>Presentation</b> of the research facilities at the Central Research Labs, Natural History Museum and their interdisciplinary applications: MicroCT and 3D Lab ( <i>Viola Winkler</i> ); Scanning Electron Microscopy ( <i>Wencke Wegner</i> ) <b>Behind-the-scenes tour</b> at the Department of Prehistory, including visit of the underground storage facilities and rooftop tour ( <i>Karina Grömer and Georg Tiefengraber</i> )
07:00pm	<b>Dinner reservation</b> at Cafe Leopold, Museumsplatz 1, 1070 Vienna (self-funded). Please note that only registered participants will be able to attend the workshop and have a reserved seat at the restaurant.

## 24<sup>th</sup> of September 2024

Vienna Institute for Archaeological Science, Franz-Klein-Gasse 1, 1190 Wien

08:00am	Registration open
08:15am-09:00am	Time for posters
09:00am-09:20am	Opening & Introduction
09:20am-09:50am	<b>Lecture 1:</b> <i>Le Bourdonnec F.-X.</i> - pXRF and Obsidian: A Success Story
09:50am-10:20am	<b>Lecture 2:</b> <i>Horák J., Fišer J.</i> - p-XRF and archaeological geochemistry – our experience and what is next?
10:20am-10:50am	<b>Lecture 3:</b> <i>Dallai L., Doonan R., Volpi V.</i> - Innovation strategies and the use of Hand-Held Portable X-Ray Fluorescence (HH-pXRF) in archaeological fieldwork
10:50am-11:15am	Coffee break
11:15am-11:45am	<b>Lecture 4:</b> <i>Schauer M.</i> - Defining p-XRF Precision and Accuracy: Empirical Thresholds and Statistical Techniques
11:45am-12:15pm	<b>Lecture 5:</b> <i>Wilke D.</i> - The necessity of raw data access for matrix specific calibration, interference, absorption and distance correction in non-destructive geochemical pottery analysis
12:15pm-12:45pm	<b>Lecture 6:</b> <i>Scott B., Kay L.</i> - Painting by numbers: investigating the reliability of Fundamental Parameters in paint analyses
12:45pm-13:15pm	<b>Lecture 7:</b> <i>Lebon M. et al.</i> - Quantitative analysis of iron-based coloring material by means of pXRF spectrometry
13:15pm-14:15pm	Lunch (in-house)
14:15pm-14:45pm	<b>Lecture 8:</b> <i>Drake L.</i> - Machine Learning & XRF
14:45pm-15:15pm	<b>Lecture 9:</b> <i>Faucher T.</i> - For a proper use of pXRF on archaeological copper alloy objects: coins as case study
15:15pm-15:45pm	<b>Lecture 10:</b> <i>Finkeldey I.</i> - Distortion through conservation. Chemical changes in XRF data due to old and new conservation methods on bronze objects
15:45pm-16:15pm	Coffee break
16:15pm-16:45pm	<b>Lecture 11:</b> <i>Abdelgawad M. et al.</i> - Intercomparison in p-XRF spectrometry: methodological approaches for the study of ceramics
16:45pm-17:15pm	<b>Lecture 12:</b> <i>Richards M., McAlister A.</i> - Establishing an Australasian pXRF Archaeological Research Collective
17:15pm-18:00pm	Final Discussion
18:00pm-18:45pm	Time for posters
19:30pm	Dinner reservation at Zattl Wirtshaus & Biergarten, Freyung 6, 1010 Vienna (self-funded). Please note that only participants registered for the restaurant will have a reserved seat.

# Lecture Abstracts

## Lecture 1:

### **p-XRF and Obsidian: A Success Story**

*Le Bourdonnec, F.-X.*

Understanding how obsidian was obtained in prehistoric times is an important challenge for archaeological sciences. This aphyric volcanic magmatic rock is a key marker of exchanges, contacts, and the movement of human groups during Prehistory. Cann and Renfrew demonstrated in 1964 that elemental analyses provided geochemical fingerprints that could be used to study the provenance of obsidian. Since this pioneering study, numerous geochemical methods (EMPA, INAA, LA-ICP-MS, PIXE, SEM-EDXS) have been deployed to measure major, minor, and trace elements in obsidian. The advent of pXRF was a complete revolution in Archaeometry that profoundly changed the analytical strategies put in place to study the provenance of this precious raw material. This presentation will examine the success stories of pXRF through several examples. In many ways, this method seems ideal: in addition to its portability, it is easy to use, fast, non-invasive, and particularly effective for the measurement of diagnostic elements, and can be adapted to numerous chronological periods and geographical areas. However, despite the many advantages of this method, it is important to discuss the calibration of the equipment and the accuracy and precision of the data produced. In addition, the size and/or thickness of the pieces analysed can have a significant impact on the results.

*Dr François-Xavier Le Bourdonnec* is an Associate Professor of Archaeological Sciences at the Université Bordeaux Montaigne. He has been engaged in research on the circulation of Prehistoric lithic raw materials, particularly obsidian, for over 20 years

## Lecture 2:

### **p-XRF and archaeological geochemistry – our experience and what is next?**

*Horák J., Fišer J.*

We present the topic in two ways: 10-year experience with XRF and our present plans and actions based on it. The archaeological geochemistry shifted far from just „phosphates“. Chemical laboratories enabled to look on archaeology through multi-elemental prism, p-XRF opened a potential for broad use. This happened with all its pros and cons (discussed strongly main archaeological journals). The usage of it grows regardless of such discussion – we don't want to solve it – we seek ways to implement it at the best level possible.

During the years, we knew what XRF needed to become more rigorous. After these years, we now have a possibility make it happen. The lecture presents our experience with researches of landscape archaeology (medieval villages, prehistoric burial areals, hillforts, Levant tells), contamination research (medieval mines in Kutná Hora), both scientific and rescue archaeology.

We are building a laboratory focused on XRF (shifted from portable ED to table-top WD methodology) with all the lab environment it needs to perfectly prepare the samples (from sieves through mills to presses and ovens). We are turning this technology to be a standard in archaeological rescue excavations of big infrastructure (prospection and excavation phase). It is linked to possibility to sample the sites in completeness with thousands of samples, but also to problems rising from such complexity and numbers, or with implementation of such methodology to already well-established rescue workflow. We also plan to connect such analyses with spectral soil analyses of airborne technology.

Last, but not least, our plans include to shift our activities also to standardization topics: active involvement in standard samples production focused on archaeological materials and round robin

tests with archaeological departments. The XRF in archaeology needs two things: standardization, more archaeo departments with such laboratories, networks or societies of specialists and maybe journals (archaeogeophysics is a good example to follow).

*Jan Horák* is an archaeologist focusing on human-environment relations in the past, working mainly with geochemical analyses in study of human impact on soils in relation to agriculture and mining. He also focuses on statistics and data in general and likes to work with R. He is now also working on ways to introduce these methods as a standard in rescue excavations.

*Jan Fišer* is an archaeologist focusing on using remote sensing data of various kinds - from aerial to satellite data. He is working on present landscape archaeology and prospection as well as on using historical aerial photography to reveal archaeological landscapes and features. He is now working on connecting geochemistry with spectral analyses of soils.

### Lecture 3:

#### **Innovation strategies and the use of Hand-Held Portable X-Ray Fluorescence (HH-pXRF) in archaeological fieldwork**

*Dallai L., Doonan R., Volpi V.*

Hand-Held Portable X-Ray Fluorescence (HH-pXRF) offers unprecedented access to chemical analysis and the potential of transforming the way archaeological investigations are conducted. This paper argues that this accessibility should not serve as a pretext for the indiscriminate and uncritical use of chemical analysis, especially when used as a direct replacement of existing laboratory analysis or as a short cut for historical archaeological interpretations. HH-pXRF demands a thoughtful innovation strategy that addresses new questions or questions formerly unapproachable by conventional laboratory analysis.

Rather than being a direct alternative to lab-based analyses, HH-pXRF offers an approach that can extend insight into the chemistry and associated processes of archaeological materials. This interdependent relationship, underlines an approach to method development that promotes innovation while recognising the strengths of complementary techniques.

Using case studies to outline the versatility of pXRF, we highlight the importance of site-landscape specific methodologies that are sensitive to geological conditions, archaeological questions, and project-specific constraints. We suggest strategies should be flexible and applicable to the breadth of archaeological applications, especially those field-based and truly innovative.

HH-pXRF has a capacity to generate results on-site rapidly so as to inform survey and excavation strategies in real time. This immediacy allows better informed decision-making, enhancing the efficiency and effectiveness of survey and excavation. We discuss the strategic implications for archaeological methodology including the role of pXRF in supporting ambitions to achieve a sustainable Carbon-Net-Zero-Archaeological approach, a critical consideration in both research and large civil infrastructure projects. These strategic insights should inform future pXRF innovation ensuring its relevance to fieldwork processes while offering field-directors the opportunity to survey and/or excavate with more agility and efficiency.

Luisa Dallai is currently in charge of the Laboratory of Topography of Mining Territories (LTTM) at the Department of Historical Sciences and Cultural Heritage of the University of Siena and adjunct professor of environmental chemistry and chemistry for cultural heritage in Master's Degree in Archaeology. Her main lines of research include landscape and mining archaeology, archaeology of production, and the application of geochemical analysis (pXRF) to archaeological contexts.

Roger Doonan is currently Head of Innovation at Archaeological Research Services Ltd. He has led the commercialisation of pXRF in professional archaeology in the UK to transform the evaluation process of archaeological sites under development. This work has recently been recognised with The Kings Award for Enterprise: Innovation, the highest business award in the UK. He has previously held posts at The University of Sheffield, Bournemouth University and English Heritage. He has directed the EU FP-7 funded work package on pXRF as part of the NARNIA project and undertaken survey and fieldwork in Russia, China, and across the Mediterranean. He is a trustee of the Keros Foundation and directs the geochemical survey for the Keros Project.

Vanessa Volpi currently has a research grant at the Department of Historical Sciences and Cultural Heritage of the University of Siena. A key aspect of her research activities has been to test the versatility of certain analytical techniques (in particular pXRF), and to verify the reliability of the results obtained with conventional laboratory techniques. The analyses she conducted concerned soils, river sediments, waste products from ancient metallurgical processes, and metals, particularly coins. In recent years, she has also coordinated extensive geochemical survey activities in the field, aimed at analyzing environmental and anthropized contexts of archaeological sites and their relevant territories. Her ongoing research activities continue in the field of geochemical analysis applied to the environment and cultural heritage, archaeometallurgy, and more generally, archaeometry.

#### Lecture 4:

##### **Defining p-XRF Precision and Accuracy: Empirical Thresholds and Statistical Techniques**

*Schauer M.*

Although a well-established method in archaeometry, geochemistry, art and conservation, p-XRF is still the subject of criticism. In particular, there are concerns about the assumed low precision and accuracy of the method, especially when it comes to heterogeneous material such as archaeological pottery. As a result, the validity of the results produced with p-XRF is often doubted. Yet statistical procedures and empirically determined threshold values enable both criteria to be defined more precisely, and permit exact comparisons of these categories between devices and with laboratory methods. This talk will describe in detail how coefficients of variation, nominal values and standard deviation can be used to define and check not only the devices performance but also data quality in an easy, everyday routine that can even be applied when time is of the essence. The Munich Procedure will then be introduced, which standardises the development of coefficient corrections for p-XRF studies using coefficients of determination, (relative) standard errors of the estimates and bootstrap algorithms. In the longer term, the implementation of the procedures outlined here by other specialists can be a significant factor in standardising the method and, as a consequence, in creating a new perception of the method within the archaeological community.

*Michaela Schauer* is a Prehistorian and Near Eastern archaeologist by training and an archaeometrist specialised in the analysis of archaeological and geological materials using p-XRF. Since October 2023 she is the PI of her three-year FWF ESPRIT project „Standardising portable X-ray fluorescence for archaeometry” at the Vienna Institute for Archaeological Science (VIAS) and part of the research network Human Evolution and Archaeological Sciences (HEAS).

#### Lecture 5:

##### **The necessity of raw data access for matrix specific calibration, interference, absorption and distance correction in non-destructive geochemical pottery analysis**

*Wilke D.*

Handheld XRF analysis is actually the sole truly non-destructive method for geochemical provenancing of archaeological ceramics. Measurements without prior substance consuming sample preparation are not only a prerequisite for studying cultural heritage material, but also for high throughput analysis of voluminous assemblages of archaeological settlement finds. For most of the archaeological regions worldwide a plenitude of production sites must be considered, which makes it almost impossible to cover all these sites by a single laboratory with a single instrument. Therefore it is important for cross-time and cross-laboratory data use, to calibrate instruments reflecting the peculiarities of XRF analysis of micro-heterogeneous sample materials with uneven surfaces.

Matrix specific element calibration is only possible with spiked fired clay samples, since there is no geochemical reference material differing in the concentration of just a single element. Examples are given for the necessity of absorption and interference correction at varying Fe or Pb concentrations. Distance and density correction needs normalization with the tube photons, the Compton or the Rayleigh scatter. The respective arithmetic corrections are only possible if the instruments provide raw data access for subsequent peak deconvolution into net counts per energy line. Since many adjacent clay deposits are

very similar in the composition of those (few) minor and trace elements accessible with XRF analysis, careful calibration is crucial for positive and negative sample allocation to archaeological reference groups established with waster materials and cluster analysis, respectively.

*Dr. rer. nat. Detlef Wilke* is a microbiologist/biotechnologist by education. He has a long-lasting interest in cultural anthropology and archaeological theory. Since the 2000s he kept an eye on non-destructive XRF analysis as a potential tool for overcoming the limits of mere form-stylistic provenance attributions in archaeology and art history. His company provides contract analytics, calibration support and data processing for ceramic provenancing on an international basis. He is a member of SAA, SAS and GNAA, and recently joined the advisory board of the annual International Ceramic Symposium, established in 1968 as "Internationales Hafnerei-Symposium".

## Lecture 6:

### Painting by numbers: investigating the reliability of Fundamental Parameters in paint analyses

*Scott R.B., Kay L.*

Fundamental Parameters is often used with portable XRF instrumentation. In some cases, it can be extremely difficult for the operator to access and process the spectral data independently. Since FP is cited as a "standardless" method, there becomes a temptation to rely on the "numbers" generated. This issue is further compounded with instruments where operators must utilise an inbuilt "mode" for analysis. Portable XRF has been used in several studies to determine the composition of paint: both in gallery paintings and as décor on objects and artefacts. Most studies use the technique to determine the presence/absence of elements within a given painted region, to ascertain the type of paint and whether further analysis is required. It is generally accepted that even if the accuracy of the pXRF data is questionable (i.e. the numbers), the precision is not. Patterns in the data are felt to be reliable. In some industrial applications, particularly the coatings industry, pXRF is also being used to give information relating to specific layers. This research explores the extent to which FP provides an accurate representation of the composition of varying volumes of Titanium White acrylic paint. Consideration is given to reliability of data from multilayered painted pieces, and the implications of using FP generated data to investigate paint. Ultimately, can pXRF be used to give more targeted information about different layers of paint?

*Dr Becki Scott* is a Forensic Archaeometrist, with a background in archaeology, forensic, and analytical science. She lectures in Forensic Science at Teesside University, UK. Her research interests include materials analysis, provenance studies, and heritage crime. She has a particular interest in the field use of pXRF instrumentation.

## Lecture 7:

### Quantitative analysis of iron-based coloring material by means of p-XRF spectrometry

*Lebon M., Mauran M., E. Vincent, Calligaro T., Gallet X., Beck L.*

The study of red and yellow coloring materials based on iron oxides and hydroxides found in prehistoric archaeological contexts have benefited from an important methodological renewal in recent years. The analysis of their elemental composition has proved to be a relevant tool for discriminating geological sources and identifying the origin of materials. Although its sensitivity to trace elements can be limiting, pXRF analysis is an interesting technique for in-situ analysis of large collections in the preliminary phase of studies. However, the composition of these natural materials varies widely (eg. 15%wt of iron for bauxite, over 60%wt for pure iron oxide), and the quantification these matrices is complex. Furthermore, these issues require the comparison of large set of archaeological and geological samples (sometimes analyzed by different teams or system), and the reuse of these data over a long period of time. For this purpose, we have initiated a calibration of XRF data by analyzing rock and ore standards, combined with quantification by the fundamental parameter method using PyMCA software. We have also developed an add-on to automate the analysis of large corpora. This work has helped us to increase the precision of quantifications, to better assess quantification errors and biases for the different elements, and thus to improve data interoperability and reliability.

*Matthieu Lebon* is a lecturer at the Muséum National d'Histoire Naturelle (Paris - France) in a laboratory specializing in the study of prehistory. He studies coloring materials from various Middle and Upper Paleolithic contexts, notably in France,

Namibia and Morocco. To this end, he uses a variety of analytical techniques, in particular elemental analysis techniques, to identify geological sources. He is also involved in the management of collections and associated data and, since 2022, has been coordinating a national research program on this subject (ANR Color-Sources).

## Lecture 8:

### Machine Learning & XRF

*Drake B., L.*

Advancements in machine learning and artificial intelligence expand the capabilities of X-ray fluorescence (XRF), ranging from challenging limits in detection limit, elemental range, and inference more generally. Whether the goal is determining nitrogen concentration, sub-ppm detection limits, or direct classification of materials, AI can expand the ability to infer properties in an XRF spectrum. These models, like all empirical models such as more traditional Lucas-Tooth algorithms, are bound by the limits of their training data (e.g. the universe of data they are trained upon). Nonetheless provided the data is sufficiently defined and fit for purpose, AI applications represent a significant expansion of non-destructive analysis. This brief talk will cover the expanded application space as well as the limits of AI spectrometry.

*Lee Drake* is a specialist in XRF, helping to design components of Bruker's Tracer 5g as well as collaborating globally on research using XRF. He is co-editor of the recent volume „Advances in Portable XRF“ from the Royal Society of Chemistry. His current research focus is developing AI applications in archaeology.

## Lecture 9:

### For a proper use of p-XRF on archaeological copper alloy objects: coins as case study

*Faucher T.*

Since at least the 17th century, numismatists have been interested in the composition of ancient coins. During the 20th century, it became increasingly difficult to destroy archaeological objects for study. The massive development of pXRF, particularly in the 1990s and 2000s, led to a proliferation of coin analyses. Although the effects of corrosion on surface elemental composition are well known, the protocols used for these analyses have not always made it possible to avoid them, often tarnishing the results and leading to erroneous conclusions. Two case studies presented here illustrate both the limitations and benefits of surface measurements using pXRF. The first example stems from work in progress on a sample of around 150 ancient coins that it has been possible to cut out, thus offering the possibility of comparing analyses on the surface of the coin and on the surface on a polished section. The second example is based on a series of analyses of several hundred coins excavated in Alexandria, Egypt. While these analyses do not enable quantitative measurements to be made, they do provide interesting data, particularly for classifying coins and period forgeries. The aim is therefore to reintroduce the use of pXRF in the field of numismatics and, more generally, in the study of archaeological objects made of copper alloys.

Focusing on economic and monetary history, Thomas Faucher's research looks in particular at the production and circulation of coinage in ancient Egypt, as well as the methods used to extract the minerals used to make them. After completing a PhD in archaeology at the University of Paris-Sorbonne in 2006, he went on to do a postdoc as part of the Nomisma programme. In 2011, he joined the Institut français d'archéologie orientale in Cairo as a scientific member. For two years, Thomas Faucher supervised the „Egyptian Gold“ programme. He was recruited as a research fellow at the Institut de recherche sur les archéomatériaux d'Orléans in 2013, before joining the Bordeaux component of the same laboratory in 2019 (IRAMAT-CRP2A), where he continued his work on ancient Egyptian numismatics. Between 2018 and 2022, he was the Head of the French archaeological mission in the Eastern Desert (MAFDO). He joined the Centre d'Études Alexandrines in 2021 and became its director in 2023.

## Lecture 10:

### Distortion through conservation. Chemical changes in XRF data due to old and new conservation

## methods on bronze objects

*Finkeldey I.*

As part of my master's thesis from 2023/24 Traces of craftsmanship in metal - X-ray fluorescence-based analysis of the two Bronze Age hoard inventories from Schellhorn and Fahrdorf (Schleswig-Holstein), bronze objects from the two hoards discovered in Schleswig-Holstein, Schellhorn (1902) and Fahrdorf (2021), were examined using non-destructive X-ray fluorescence analysis (RF/XRF) and microscopy.

Both hoards date to Period II of the Nordic Bronze Age and were selected for analysis due to their good state of preservation and typical artifact composition. The proposed presentation will discuss the generated measurement data in the light of the manufacturing processes, the corrosion processes, as well as in relation to conservation measures and thus contribute to the process analysis of XRF data.

Portable X-ray fluorescence (p-XRF) allows the composition of solid objects to be analysed quickly and easily, but the results are influenced by the state of preservation due to the low measuring depth, especially in the case of non-destructive analyses (which were a requirement by the State Museum for all artifacts). However, both hoard inventories processed showed specific anomalies on the surface that do not match the expected compositions of prehistoric artifacts. In consultation with the responsible conservator, the influence on the more recent finds could be attributed to the desalination method used. As in the case of the older finds from Schellhorn there is no documentation of any conservation measures that could help to explain the identification of the chemical anomaly. Several possibilities had to be considered, in particular natural and artificial corrosion processes. Ultimately, all anomalies could be classified as the traces of various restoration measures and thus compensated for in the processed data. The trace elements present in the adjusted data correspond to the composition typical for this period and region. Apart from the corrosion-related changes, the compositions of the objects are so similar, with one exception, that a connection between the two hoards could be assumed through a common origin of the raw materials, or perhaps even a common production site.

Ilian Finkeldey studied Pre- and Protohistoric Archaeology and European Ethnology/Cultural Anthropology for a Bachelor's degree in Hamburg from 2014-2018 and in Vienna in 2017. He completed a Master's degree in Pre- and Protohistoric Archaeology in Hamburg between 2018 and April 2024. From 2018 to 2021, he was elected chairman of the board of the Dachverband Archäologischer Studierendvertretungen (DASV e.V.). His research focus so far has been on the early metal ages, metallurgy, and experimental archaeology.

### Lecture 11:

#### **Intercomparison in p-XRF spectrometry: methodological approaches for the study of ceramics**

*Abdelgawad M., Borschnek D., Cantin N., Charamboulous A., Dikomitrou M., Hein A., Illiopoulos I., Le Bourdonnec F.-X., Müller N., Cau Ontiveros M. A., Roumié M., Schauer M., Xanthopoulou V.*

The development of portable X-ray fluorescence (pXRF) equipment for the chemical analysis of ceramics has enabled the acquisition of larger quantities of data, despite the limitations in sensitivity compared to traditional analytical techniques such as WD-XRF, ICP-MS, and NAA.

As part of an International Research Network pXRF-CUN programme (pXRF Ceramic Users Network, 2021-2025), led by the CEALex, various partners are working together to compare and share the data obtained by their pXRF equipment on ceramic materials. To this end, an initial selection of 18 examples of ceramics and international standards has been made to create an intercalibration kit. Initially, ten kits of glass beads were prepared and distributed to partners. In parallel, the measurements obtained by ICP-MS and WD-XRF are almost identical and could be considered as reference. The same kit, in powders forms was also provided to question the preparation of the analysis medium and broaden the methodological questioning.



Thus, the results obtained were discussed, in terms of detection sensitivity, resolution, accuracy, precision, but also sample preparation.

Accordingly, a new ceramic kit comprising 18 fired bricks has been prepared from clays collected from known provenances, covering the range of the most common ceramic compositions. This stage in the intercomparison of 11 portable pXRF systems provides an opportunity to engage in a constructive debate on the quality of the data obtained and the potential for using it by other teams. However, the challenge of intercalibration of equipment dedicated to the analysis of ceramic material remains more complicated to implement. The results will be presented here and published in detail soon.

Mai Abdelgawad, chemical engineer, archaeometrist in the Materials Characterisation Laboratory of the Centre d'Études Alexandrines. I have been working on methodological development of pXRF analysers since 2016 as well as the statistical approach for ceramic study with the objective of provenance characterisation and fabrication technology identification. I am currently at the end of my first year of doctoral studies at the university of Bordeaux Montaigne under the direction of Thomas FAUCHER, working towards a thesis entitled "Characterisation of Aegean transport amphorae from the Hellenistic and Roman periods: Chemical fingerprints and statistical treatment of compositional overlaps"

## Lecture 12:

### Establishing an Australasian p-XRF Archaeological Research Collective

*Richards M. J., McAlister A.*

We present new results from the establishment of an 'Australasian Portable x-ray fluorescence (pXRF) Archaeological Research Collective' that seeks to address common issues faced by archaeological and First Nations researchers wanting to use pXRF. This is a preferred technique for chemical characterisations of artefacts because it is non-destructive and pXRF instruments are often marketed as 'out-of-the-box-ready-to-go', however the practical realities for research are not always so straight forward. This extends to training communities on these instruments for use in the field and in collections. Key issues include custom calibrations, radiation safety (state legislation), realistic field applications and data quality. The solution requires much more collaboration between researchers and institutions in Australasia. Importantly, our current research must now confront how archaeologists curate databases for Open Science to meet the UNESCO "Findable, Accessible, Interoperable, Reusable" and "Collective Benefit, Authority to Control, Responsibility, Ethics" (FAIR and CARE) principles especially when working with First Nations communities. Work towards solutions is being achieved through this project by connecting multiple archaeology departments in different institutions across Australia and New Zealand to establish a network of accessible research-ready instruments across Australasia. During our pilot study we tested several instruments from different manufacturers (Bruker, Niton and Olympus) and found that, although their factory calibrations varied widely, all the tested instruments were able provide compatible results by calibrating their raw spectrum data with suitable reference standards.

*Dr Michelle Richards* is a postdoctoral research fellow in the Indigenous Knowledges Institute at the University of Melbourne, Australia. Her research with communities combines archaeological and earth science approaches with heritage and museum studies. Michelle is working on the development and application of non-destructive geochemical analysis to characterise and identify the origin of archaeological stone tools as a means to explore the historical complexities and interactions among First Nations peoples and early settler communities in Australia and the Pacific.

*Dr Andrew McAlister* is an honorary academic in Anthropology at the University of Auckland, New Zealand, specializing in the application of pXRF in archaeology. His research interests include identifying the raw materials used to manufacture stone tools as a means of better understanding their spatial and temporal distributions, and how different raw materials relate to form and function. Andrew's research is focused on the East Polynesian region of Oceania, where he collaborates with both academics and indigenous groups.

## Poster Abstracts

- *Becker H.* - A broad field. XRF analytics in the context of a heterogeneous collection
- *Kneale C., Martín-Torres M.* - Short-time, large-sample obsidian sourcing at Tell-Brak by pXRF: method and implications
- *Hein A.* - Machine Learning approaches in provenance studies of transport amphorae using p-XRF
- *Munene J. K., Ferguson, J. R.* - Tracing Ancient Networks: pXRF Provenience Analysis of Obsidian Artifacts in Central Rift Valley, Kenya During the Middle Stone Age
- *Potetz A.* - Observations on Trace Elements in p-XRF Data for Bronze Artefacts
- *Schauer M.* - Standardising Portable X-ray Fluorescence for Archaeometry
- *Sifogeorgaki I., van Os B., Schmid V., Fratta V., Huisman H., Dusseldorp G.* - Integrating p-XRF with micromorphology to help raw material lithic identification at Umhlatuzana rockshelter, South Africa

### **A broad field. XRF analytics in the context of a heterogeneous collection**

*Becker H.*

The Rhineland Museum Bonn (LVR-LandesMuseum Bonn) belongs with a tradition of over 200 years, to one of the oldest collections of cultural history in Germany, with a deeper focus on archaeological objects. It also holds a long tradition in conservation sciences, with well-equipped laboratories. Here the team of 12 conservation scientists has specialised in paintings-restoration, over ceramics, stones and mosaic, ancient metals and organic materials including waterlogged wood.

As part of the X-Ray department, the application of pXRF-analysis has become practise since years. XRF-analysis refers not only to questions concerning deeper understanding of the chemistry of materials resolving out of the daily work with objects from the own collection and archaeological sites, but also in cooperation with researchers from external institutes, national and international. The poster reveals an overview over the wide range of application of XRF-analysis in the conservation labs in the Rhineland Museum Bonn and shows in a more detailed focus, examples of research projects in collaboration with external institutes. Here the chemical analysis of roman and medieval pottery is of high interest, but also the investigation of glas and metal objects.

Since 1999 Holger Becker is senior conservator for metal objects in the conservation department of the Rhineland-Museum Bonn. He works both, for the communal archaeology and the collection of the Rhineland-Museum. For the communal archaeology, he is responsible for documentation, investigation and restoration of metal objects excavated in the wider region of the Rhineland in the western part of North Rhine Westphalia. In the collection of the Rhineland-Museum, he cares for archaeological metal objects as well as metal objects of art and fine arts. As radiation protection officer, Holger Becker is responsible for x-ray investigations in form of x-ray imaging as well as XRF based analysis of all kinds of materials out of the collection.

### **Short-time, large-sample obsidian sourcing at Tell-Brak by pXRF: method and implications**

*Kneale C., Martín-Torres M.*

Tell Brak is a large mound site, now in modern Syria, continuously inhabited between the 6th and the 2nd millennium BCE. It is one of the biggest sites in northern Mesopotamia and one of the earliest cities, and thus a great source of information about early urbanism and state formation, long-distance exchange and cultural interactions.

Multiple excavations since the 1930s have yielded a very large number of obsidian pieces, both blades and debitage, that suggest a workshop for the making of stone tools existed on the site. Tell Brak is at least 200km as the crow flies from the nearest volcanic region and so determining the origins of this obsidian

can provide very useful information about the movement of goods and people over a long timespan.

Sporadic analyses of obsidian from Brak have pointed to various sources in Eastern and Central Anatolia, but small sample sizes and incompatibility between methods made it impossible to assess the relative importance of different obsidian sources over time. Methodological innovations in pXRF have enabled us to use a shared calibration set requiring short analysis times (PYRO), and to deploy it to around 3000 artefacts – an unprecedented sample size that would be practically possible with any other technique.

We will present the methodology and data from this project, and how it can allow a diachronic perspective about the provision of raw materials, the choice of sources and the underlying material properties that may have driven the selection, and the trade and connections that existed in this part of the world.

Catherine Kneale is a Senior Research Technician in Archaeological Science at the University of Cambridge. She has been in that post for sixteen years, initially specialising in stable isotopes but now also working with Materials Science and helping staff and students to develop methodologies and produce high quality data. In her spare time she is studying for a BA in photography.

### **Machine Learning approaches in provenance studies of transport amphorae using p-XRF**

*Hein A.*

In provenance studies of archaeological ceramics compositional differences between ceramics manufactured at different production sites are investigated, which are basically related to the use of geochemically diverse raw material sources. In order to determine the elemental composition of archaeological ceramics commonly samples are taken from selected ceramic objects and analyzed with laboratory methods, such as NAA or WD-XRF, which provide high analytical performance in terms of precision and accuracy. As an alternative the use of handheld portable energy dispersive XRF (pXRF) systems became quite popular during the last 20 years allowing for non-invasive analyses of elemental compositions, which can be taken in large numbers and comparatively fast. On the other hand, pXRF is extremely surface sensitive, provides a limited number of element concentrations and the analytical performance is comparably low. For this, the statistical evaluation of pXRF data following established approaches of multivariate statistics applied to data collected in laboratory analyses is not always feasible. The data collected with pXRF present a higher variation introduced by the method and they are thus comparably fuzzy requiring a more flexible approach taking into account the actual data structure rather than assumptions or models based on geochemistry or chaîne opératoire. For this, various machine learning approaches, such as unsupervised and supervised artificial neural networks (ANN), are tested for the automated categorization of pXRF data of ceramics and more specifically Archaic, Hellenistic and Roman transport amphorae from the Eastern Aegean region.

Dr. Anno Hein is senior researcher at the Institute of Nanoscience and Nanotechnology at the National Centre for Scientific Research “Demokritos”. His research interests in the field of Cultural Heritage concern the investigation of archaeological materials in view of raw material management, manufacturing processes, dissemination and technology transfer. Furthermore, he works on data management, in view of open-source database development and the evaluation of ‘Big Data’, collected in the physico-chemical characterization of archaeological materials and raw materials.

### **Tracing Ancient Networks: pXRF Provenience Analysis of Obsidian Artifacts in Central Rift Valley, Kenya During the Middle Stone Age**

*Munene J. K., Ferguson, J. R.*

Tracking the processes by which Homo sapiens developed its extraordinarily broad ecological niche has been argued as key to understanding the evolution of behaviors characteristic of our species. These responses are those in technology, settlement systems, and social connectivity. The Central Rift Valley, Kenya has many chemically distinct obsidian sources. Their unique signatures can be used to determine

the provenience of obsidian tools and thus examine patterns and social connectivity of the Middle Stone Age (MSA) and early Later Stone Age (LSA) hominins across East Africa. Previous research shows that during the early MSA, small numbers of obsidian artifacts were transported from the Central Rift Valley to sites up to 190 km away and up to 250 km in the early LSA. However, the small number of artifacts in these studies, the lack of a regional framework of long-term ecological change, and a concurrent record of human behavior make it difficult to establish whether and how variation in interaction through time relates to environmental variables. Although the pXRF provides a novel tool for advancing knowledge on these social networks, its potential has not been fully exploited in the region due to the challenges the technology poses to those trying to use it, particularly due to the large number of geologic sources. Here we present the results of an attempt to employ this technology on one of the largest sample sizes of obsidian (n=3,000) from four MSA sites namely Malewa Gorge 1, Ilkek,1, 2, and 3 sites excavated in 2021.

James Munene is a doctoral candidate at the University of Michigan, Ann Arbor, USA. His research is focused on testing hypotheses about whether and how changes in lithic technology, ranging patterns, and social connectivity articulate with environmental shifts during the Late Quaternary in East Africa.

### **Observations on Trace Elements in p-XRF Data for Bronze Artefacts**

*Potetz A.*

The use of p-XRF in bronze studies may provide greater information than previously thought. Comparing p-XRF data to SEM and  $\mu$ XRF data suggests that p-XRF is reliable in determining antimony and nickel concentrations in bronze artefacts. This comparison was done by examining individual trace elements against one another across the three datasets. The results of which suggest a low margin of error for antimony and nickel in p-XRF datasets. As a result, p-XRF may help distinguish different alloys from one another due to the low impact of corrosion processes and elemental migration on these two trace elements. With this information in mind, recycling and (re)mixing of two parent bronzes to create a new bronze artefact may be easier to identify when examining artefacts using p-XRF.

These observations were conducted on Hallstat A1 artefacts from the south Pannonian Plain. As a result, other important trace elements (namely silver) present in earlier bronze and copper artefacts were not examined. Weaponry, chiefly spears and swords, from eighteen sites were used in this analysis. Domestic items, ingots, and other bronze artefacts were not examined despite their presence at some of the sites. These were not examined due to time constraints and warrant further investigation to confirm the above observations. Data for analysis was kindly provided by Dr. Barry Molloy and Dr. Vana Orfanou.

Amelia Potetz is currently a cultural resource archaeologist working in the Mid-Atlantic of the United States with a bachelors in anthropology and a masters of science in archaeology and hopes of pursuing a doctorate in anthropology/archaeology this coming fall. Her primary research focus is in the Bronze Age and archaeometallurgy.

### **Standardising Portable X-ray Fluorescence for Archaeometry**

*Schauer M.*

The FWF ESPRIT project „Standardising Portable X-ray Fluorescence for Archaeometry“ aims to standardise portable X-ray fluorescence (p-XRF) for archaeological research and address the current credibility issues of the method. The project focuses on establishing consistent measurement standards, investigating instrument-specific variations, and developing robust statistical protocols for data acquisition, processing and analysis to ensure accurate, precise and reliable results. It aims to optimise the combined use of p-XRF and other archaeometric methods, but also to highlight p-XRF’s unique contribution to scientific research. By working with international experts and facilitating a p-XRF network, the project aims to collaboratively establish standard methodologies. In addition, the development and delivery of workshops and training

to equip researchers with the knowledge and skills to effectively use p-XRF technology is an important objective. The initiative aims to increase the acceptance and usefulness of p-XRF in archaeological studies.

Michaela Schauer is a Senior Scientist at the Vienna Institute for Archaeological Science (VIAS) and a member of the Human Evolution and Archaeological Sciences (HEAS) research network, specialising in chemical analysis using p-XRF. With more than seven years of experience and over thirty p-XRF-related research projects, since October 2023 she has been focusing on methodological research as part of her three-year FWF ESPRIT project on „Standardisation of portable X-ray fluorescence for archaeometry“.

## **Integrating p-XRF with micromorphology to help raw material lithic identification at Umhlatuzana rockshelter, South Africa**

*Sifogeorgaki I., van Os B., Schmid V., Fratta V., Huisman H., Dusseldorp G.*

Umhlatuzana rockshelter (UMH) is an important archaeological site for the study of the Middle and Later Stone Age in South Africa with a largely continuous occupation sequence spanning ~70,000 BP to present. Changing raw material selections is an important issue in the study of the Middle-to-Later Stone Age transition that is characterised by a shift in raw material use in association with a different technological organisation.

Micromorphological thin sections of UMH allowed a petrological inspection of rock fragments embedded in the deposits. They yielded different rock type determinations than the ones proposed by archaeologists previously working on the site. While quartz and hornfels are present, they represent lesser proportions than previously reported. Instead, quartz arenite sandstone played a more important than previously assumed.

We initiated an in-depth mineralogical and elemental classification of the raw materials. We distinguish six raw material types based on the thin section analysis: sandstone, quartz, hornfels, dolerite, siltstone, and silcrete. Afterwards, we determined the elemental composition of the rock types from the micromorphology samples applying p-XRF analysis directly on the thin sections. Additionally, p-XRF analysis was conducted on specimens from the lithic assemblage. This allowed us to determine elemental characteristics of the raw materials used during the Pleistocene occupation of the site. Subsequently, p-XRF was systematically performed on a larger sample set of lithics from the site to (correctly) determine their raw material type. This integrated approach emphasizes the significance of micromorphological and p-XRF analysis in accurately understanding lithic assemblages and Stone Age techno-economies.

Irini is a freelance geoarchaeologist and guest researcher at Leiden University. Her primary research focus is on site formation processes, which she explores using micromorphology and various other geoarchaeological techniques. Other research interests include lithic raw material identification and archaeological fieldwork strategies.

Gerrit is associate professor in Pleistocene Archaeology at Leiden University. His research focuses on hunter gatherer behaviour during the Middle and Later Stone Age (~300,000-10,000 years ago).