



HAL
open science

1 Using Soil Chemistry through EDXRF to Identify Archaeological Features at the Site of Ulpiana in Kosova

Arthur Langer, Arnaud Martel, Aline Durand, Fabien Boucher

► **To cite this version:**

Arthur Langer, Arnaud Martel, Aline Durand, Fabien Boucher. 1 Using Soil Chemistry through EDXRF to Identify Archaeological Features at the Site of Ulpiana in Kosova. *Kosova Anthropologica*, 2024, 2 (1), pp.1-22. 10.62303/ncb1ap93 . halshs-04858808

HAL Id: halshs-04858808

<https://shs.hal.science/halshs-04858808v1>

Submitted on 30 Dec 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License

Using Soil Chemistry through EDXRF to Identify Archaeological Features at the Site of Ulpiana in Kosova

Arthur Laenger¹, Arnaud Martel², Aline Durand¹, and Fabien Boucher³

1 Centre de Recherche en Archéologie, Archéosciences et Histoire
(CReAAH UMR CNRS 656), Le Mans Université

2 Institut des Molécules et Matériaux du Mans (IMMM UMR CNRS 6283),
Le Mans Université

3 Institut Universitaire de Technologie Chimie, Le Mans Université
arthur.laenger@gmail.com

Abstract

Chemical analysis of archaeological sediments is a research area that has long interested archaeologists but has seen recent developments. It locates concentrations of chemical elements in soils that can be linked to ancient activities responsible for their deposition. The use of X-ray fluorescence spectrometry, a more accessible analytical technique than others, makes it possible to analyze large batches of samples. At Ulpiana, two trenches were studied. In the first area, the presence of a lime pit and a mortar preparation area was identified. The signature of the lime seems to correspond to that produced in a kiln discovered further north. In the second area, a bronze recycling workshop was identified, along with a suspected dye molecule.

Keywords: *archaeology, elemental analysis, construction material, bromine, copper metalworking, EDXRF, late Antiquity*

Introduction

The chemical analysis of soils, particularly the measurement of phosphates, has been a widely used technique in archaeology since the 1930s (Arrhenius 1931, 1934) and was adopted by French archaeologists starting in the 1950s (Louis 1946). Even today, it is routinely applied to identify livestock-related structures by linking phosphorus deposits to animal excrement (Craddock et al., 1985). However, as early as the 1970s, this technique was extended to other chemical elements in Mexico (Barba & Bello, 1978) to characterize anthropogenic activities on a broader scale. While the analytical methods described at the time may seem outdated from a contemporary chemical standpoint, they have been continually refined and developed over the decades (Rippon

et al. 2001; Wilson et al. 2008; Oonk et al. 2009; Middleton et al., 2010; Misarti et al. 2011; Dirix et al. 2013; Salisbury 2020; Bintliff & Degryse 2022). The latest advancement in this field is the replacement of inductively coupled plasma analytical techniques (ICP-MS, ICP-AES, and ICP-OES) with X-ray fluorescence spectrometry (XRF). While XRF provides semi-quantitative results compared to ICP, these results are sufficient for archaeological soil analysis, based on concentration variations. Additionally, comparative studies have shown a strong correlation between results obtained from traditional techniques and XRF analysis (Frahm et al. 2016). In most cases, a portable device is used, requiring minimal sample preparation (Cannell et al. 2018; Gutiérrez-Rodríguez et al. 2019; Hafez et al. 2017; Hayes 2013; Rippon et al. 2001; Save et al. 2020; Smejda et al. 2017; Wilkins 2009; Wilson et al. 2008). One of the key advantages of XRF is its ease of use, as sample preparation is limited to drying and grinding, in contrast to the acid digestion required for ICP. Another benefit is that XRF can analyze almost all chemical elements in a single analysis. More importantly, XRF holds significant potential for exploration, as its broad range of scanned elements can reveal notable differences in the concentration of elements previously considered uninterpretable, paving the way for the identification of new markers of anthropogenic activity. Furthermore, because all data are recorded for each site analyzed, it is possible to revisit sites retrospectively once a marker has been clearly identified at another location. Since the concentrations of chemical elements in soils are intrinsically linked to the geological environment, the goal is not necessarily to establish target concentration values to distinguish specific activities, but rather to identify distribution anomalies in the soils. This can be achieved by analyzing variations in elemental concentrations, which can be derived from semi-quantitative data.

The archaeological site of Ulpiana, studied by archaeologists since the 1950s, had not benefited from any chemical sediment analysis campaigns until the operation conducted jointly by French and Kosovar teams in 2017 (Goddard et al. 2017). We collected samples from the soil layers exposed in the two sondages excavated in 2017 and 2018. These sondages were guided strictly by archaeological questions, meaning they were not placed with consideration for their archaeometric potential. Therefore, the chemical analysis of sediments at Ulpiana is part of a heuristic approach.

How EDXRF works

ICP-MS (Inductively Coupled Plasma – Mass Spectroscopy) is the most commonly used technique for elemental soil analysis in archaeological structures. While this technique is indeed the most suitable in terms of sensitivity, it has several drawbacks: the handling of hazardous materials for sample preparation, the need for calibration for each element studied, and the time required for data acquisition. These drawbacks result in a high analytical cost per sample, often beyond the budgetary reach of archaeological projects, given that soil studies can involve hundreds or even thousands of samples.

With these limitations in mind, we sought to develop a protocol that is more accessible for most archaeological situations. Energy-dispersive X-ray fluorescence spectrometry

(EDXRF) operating in semi-quantitative mode was chosen as the analytical technique to meet this requirement. This device can take measurements directly on powders obtained by simply dehydrating and grinding soil samples. The device has its own calibration, which does not require the creation of standard ranges. The measurement is quick, and most importantly, it covers almost all chemical elements in the periodic table, with the notable exception of the lightest elements like sulphur and phosphorus.

From a technical perspective, EDXRF analysis relies on energy emissions during electronic orbital transitions (Fig. 1). An X-ray source is directed at the sample to be studied, known as the incident ray. The energy of the ray ejects electrons from the inner shells of the atoms in the sample. The resulting electronic vacancies are filled by electrons from higher energy levels. This transition is accompanied by the emission of a new X-ray, called the emitted ray, which is detected by the spectrometer's detector. The characteristics of these emitted rays depend on the electronic configuration of the atom from which they originate. They thus allow for the differentiation of the various chemical elements present in the sample.

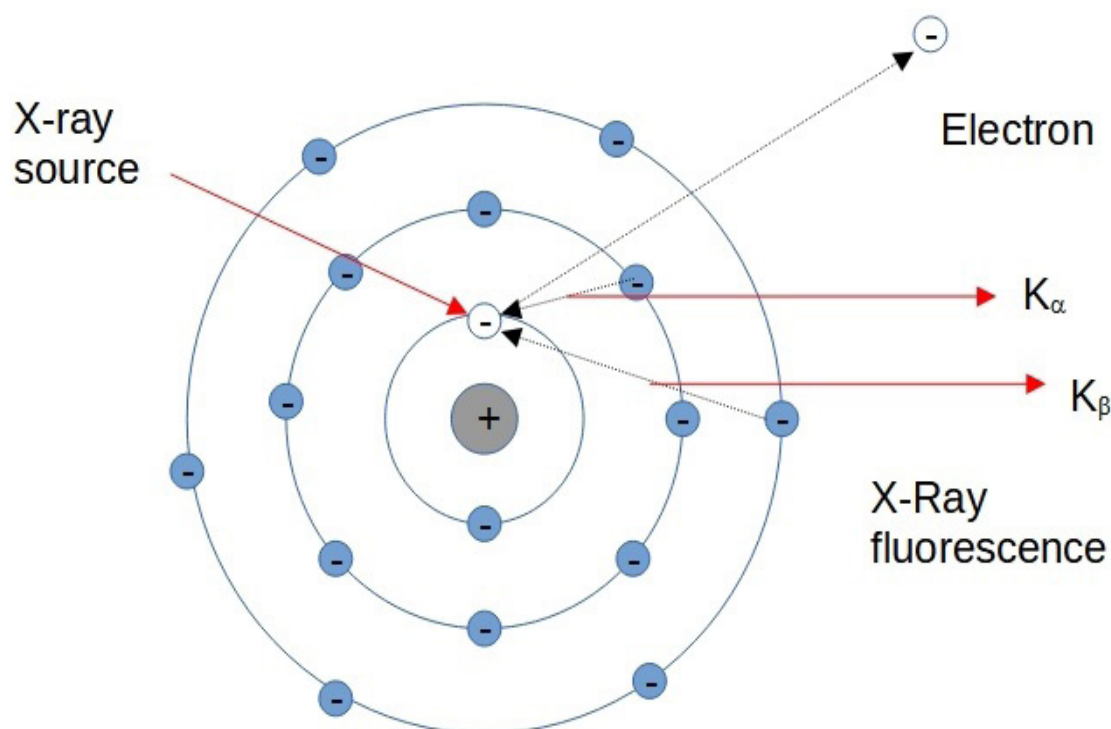


Fig 1. – Diagram of the XRF Measurement Process

Hydrogen and helium are naturally invisible to this technique, as these elements have only one electron orbital. In theory, starting from the second row of the periodic table, it should be possible to measure elemental concentrations. In practice, however, only a few particularly expensive devices are capable of this. In line with the concept of providing a financially accessible protocol, the device used can only measure elements from the third row of the periodic table (Fig. 2). While the inability to measure carbon

and nitrogen levels is a drawback, it is worth noting that other elements in the second row are unlikely to be associated with specific ancient activities. The sensitivity of EDXRF to light elements is lower, but it can be improved by performing measurements under a neutral atmosphere or vacuum. Indeed, in these configurations, the incident X-ray radiation discussed earlier does not weaken upon contact with elements present in a normal terrestrial atmosphere. However, it is challenging to achieve these conditions directly in the field, which is why we chose not to use portable devices (pXRF) that are popular in archaeology but currently not sensitive enough to complete our protocol.

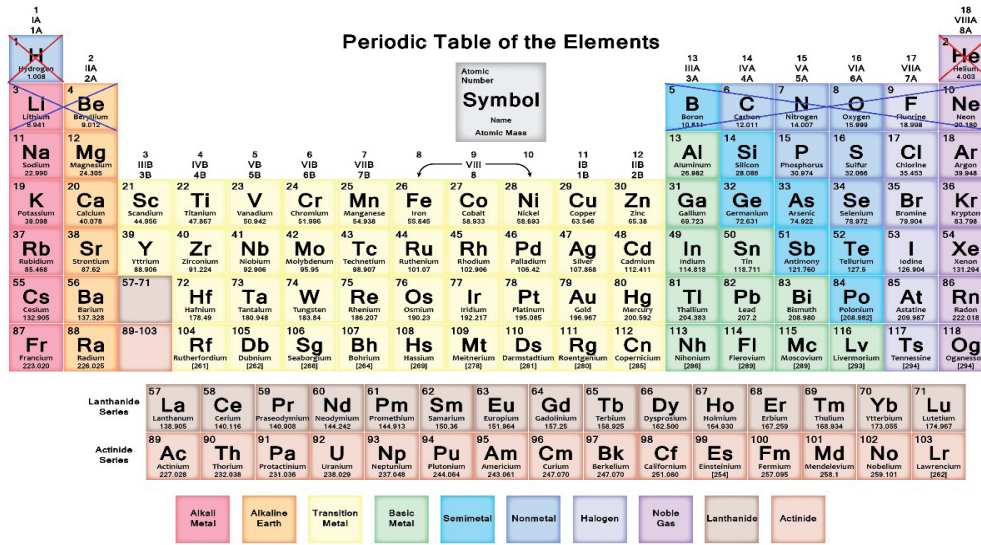


Fig 2. – Periodic Table of Elements; EDXRF can theoretically measure the concentrations of all elements except hydrogen and helium (marked in red). In practice, the measuring device used cannot analyze the elements in the second row either (marked in blue).

Materials and methods

The archaeological site of Ulpiana, located in the municipality of Gračanica, lies about eight kilometers southeast of the capital of Kosovo, Prishtina (Fig. 3). It spans an area of thirty-five hectares in an agricultural plain, at the foot of a hilly system to the south, and along the Sitnica River, which is situated three hundred meters north of its walls. The city of Ulpiana occupied a strategic position at the crossroads of two important communication routes. The first road connected the Dalmatian coast, north of Dyrrachium, to the Danube limes and Dacia. The second road linked Thessalonica, passing through Stobi in Macedonia. Its foundation dates to the Roman period and was related to the conquest of Dacia. The city was part of the province of Upper Moesia, which served as a rear base for consolidating this domination. Due to its geographical location, Ulpiana was a key passage for east-west journeys. However, it faced numerous barbarian incursions in the 5th, 6th, and 7th centuries AD, which marked its tumultuous history. Today, the archaeological site of Ulpiana is a major historical landmark, attesting to the city’s significance during the Roman era and its role in the



Fig 3 – Location map of the Ulpiana site

The samples studied for this article come from the archaeological excavation campaign conducted in 2018 and 2019 at Ulpiana as part of the Franco-Kosovar cooperation mission MAFKO led by Arben Hajdari and Christophe Goddard. These two campaigns focus on understanding the late phase of the city. The study examines the reuse of part of the colonnade of the ancient temple to build a paleochristian church, as well as the rectangular enclosure wall that surrounds it. The whole complex is dated to the first half of the 6th century AD.

Analytical protocol

Samples are taken directly from the stratigraphic unit being studied (Fig. 4). A one-meter grid is deployed over the area to be examined. This gridding module allows for covering the entire surface of the excavations while limiting the number of samples and thus the analytical cost, all while providing multiple samples per uncovered archaeological structure. A trowel is then used to collect 200 grams of sediment at each intersection of the grid. The sample is placed in a plastic bag labeled with the site name, the date of collection, and a number for identification. The trowel is cleaned, and then we move on to the next sample. The position of each sample is recorded using a total station to ensure spatial accuracy. Bags are left open and closed only when collecting

the entire sample. In Ulpiana, samples are collected during the summer, in dry weather. The risk of mold is therefore almost zero. At other times, under other conditions, the risk of mold is not zero but does not impact the elemental composition of the sample and therefore has no effect on the analysis. The sealed bags are then sent to the laboratory.



Fig. 4 – Sampling in progress in Zone 1, near the southern rampart, in Ulpiana archaeological site. Photo credit: Christophe Goddard.

The contents of the bags are transferred into beakers, which are carefully labeled with the sample number. It is crucial throughout the entire analysis protocol to ensure that samples are not mixed up. Strict attention to detail is required to obtain reliable results. The beakers are placed in an oven for 12 hours at 85°C. This process gently dehydrates the samples to remove the water content. By doing so, we ensure that the moisture level of all samples is uniform, which prevents any issues during data analysis.

Once the samples are dried, they are manually sorted to remove ‘impurities.’ This involves carefully inspecting the sample to remove stones, roots, and other debris that might be present. There may also be fragments of archaeological materials, such as bone splinters, charcoal, or ceramic sherds, which also need to be removed. However, these elements are not discarded, as they contain archaeological information. A new plastic preservation bag is created, labeled with the previously described identifiers

and marked 'artifacts.' This information can be included in the data representation but is mainly sent to the archaeologist in charge of the operation to enhance the definition of the stratigraphic units. After sorting, the sample consists only of the dry sediment. The sample is placed into a Retsch RM100 mortar grinder with a corundum mortar. The sample is ground for 60 seconds, achieving a particle size of 100 μm . The grinder is thoroughly cleaned between each sample to prevent cross-contamination. After grinding, the sample becomes a fine powder. This powder is then placed into a plastic sample holder with an internal diameter of 30 mm, with the bottom made of a 6 μm thick Mylar film. It is crucial that the film is perfectly taut and free of wrinkles. If any wrinkles are present, the film must be discarded, and the sample holder reassembled. The sample holder should be filled to its maximum capacity and then sealed with a cap to prevent accidental loss.

The sample holders are then placed in the Epsilon 4 EDXRF spectrometer from Malvern Panalytical. The device is equipped with a silver anode X-ray tube with maximum power of 10 W, 50 kV voltage and a 2 mA current. Signal detection is via an SDD10 HR detector with a resolution of 135 eV at 5.9 keV. During an analysis routine, each sample is bombarded directly and through the instrument's primary filters, namely 300 and 500 μm copper, 50 and 200 μm aluminium, 7 μm titanium, and 100 μm silver. Using these filters makes it possible to concentrate the analysis on one part of the spectrum, limiting masking effects. In addition, the use of a helium stream is conducive to observing light elements with greater sensitivity. Measurements are performed using the Omnian method, the manufacturer's standardless semi-quantitative analysis software that automatically scans six conditions with different voltage, filter and current. The Omnian method produces XRF analysis results that are comparable to those produced by other laboratories, under the same analytical conditions. The Omnian method was calibrated on delivery of the spectrometer and the gain is adjusted automatically with a Cu/Al alloy copper plate every 12 h on Cu $K\alpha, \beta$. The energy is calibrated on Al $K\alpha$ and Cu $K\alpha, \beta$. The measurements of the light elements are carried out under a helium flow according to the Omnian method and the sample spinner is activated. The measurements are taken in sample holders with an internal diameter of 30 mm, fitted with 6 μm Mylar films in the form of loose powder.

The Omnian method has been adjusted by the introduction of a tag in Omnian calibration from a soil standard (light sandy soil 1, certified reference material, BCR-142R). The processing parameters used for our samples are as follows: loose powder, film correction: Mylar 6 μm , drift correction, compound list: geology, normalization required to 100%, Compton intensity. The compound list geology displays the most abundant elements as oxides (P: P_2O_5 , S: SO_3 , Al: Al_2O_3 , Si: SiO_2 , Na: Na_2O , K: K_2O , Mg: MgO , Ca: CaO , Fe: Fe_2O_3). One of the main advantages of XRF is to provide concentrations of most chemical elements directly on solid samples. However, energy dispersive X-ray fluorescence (EDXRF) is unable to quantify the elements below F. This drawback is addressed by the Omnian software, which issues an evaluation of the latter to calculate the content of the analyzed chemical elements. In order to reduce this randomness and make the results more reliable, by bringing the semi-quantitative

results even closer to the quantitative value, Omnian can integrate the measurement of some elements into the processing parameters. Carbon dioxide (CO₂), organic matter (CHON) and water (H₂O) concentrations were then measured by Thermogravimetric analysis on a set of samples spread over the sampling areas. The mean values from these samples were then integrated to the Omnian processing parameters. Although an EDXRF semi-quantitative method is not as accurate in absolute terms as traditional analysis techniques such as ICP, the results obtained display good repeatability and provide the most important data for this study, that is, concentration variations depending on sampling coordinates. At the end of the XRF analysis, the sample holders are emptied into bags containing the remaining powders. Since the analysis is non-destructive, the sample can be preserved in case a second measurement or further analyses are considered. The XRF analysis data is presented in a table showing the elemental concentrations measured for each sample. Since our analysis is semi-quantitative, we focus more on the variations in chemical element concentrations rather than their absolute values. To reflect this, the results are normalized as $V_{\text{normalized}} = (V_{\text{raw}} - V_{\text{min}}) / (V_{\text{max}} - V_{\text{min}})$. The values are then distributed between 0 and 1, corresponding to the lowest and highest values, respectively. While these measurement tables can be interpreted directly, it is more convenient to create a map of the results, which can be easily read in the context of archaeological findings.

The measurement table obtained from the XRF analysis is then supplemented with the coordinates of each sampling point, previously recorded in the field using the total station. The enriched table is opened using GIS. Several interpolation options allow the conversion from discrete data, i.e., points, to continuous values, in our case, surfaces. We chose the Inverse Distance Weighting (IDW) interpolation. This model assumes that the phenomenon being modeled is governed by local variation that can be highlighted through a statistical approach called “neighborhood analysis.” In other words, this interpolation technique is particularly valid when the influence of the variables represented at each point decreases with distance. Since the dispersion of chemical elements in soils is generally limited, this basic principle is relevant for modeling concentration variations. This interpolation method works best when it has a regular point grid. This condition is met during field sampling when we deploy a regular grid for collecting samples.

The maps then take the form of color-coded areas ranging from blue to red, with cooler colors indicating low concentrations and warmer colors indicating high concentrations. The color-coded areas are typically overlaid on archaeological surveys of the sampling area, allowing for an initial interpretation. This interpretation is discussed with the archaeologists in charge of the site, which may lead to additional analyses to refine the interpretations. It is also at this stage that bibliographic and historical research can be conducted regarding the use of certain elements appearing in the results. While some elements and their sources (or causes of deposition in the archaeological layers) are well-known due to their frequency, others are rarer and require more in-depth research. Once these additional investigations are completed, the final interpretation can be proposed.

Sampling locations

The samples were taken from two distinct areas (Fig. 5). The first area corresponds to a soil level revealed in the initial survey in 2017 and its extensions, identified during the scientific cooperation mission in 2018. The archaeological goal of this survey was to date the construction of the enclosing wall and the junction between it and the corner tower. The sampling took place in 2018 (Fig. 6). It extends along a rampart that borders the south of the survey. Suspect color variations caught the archaeologists' attention. The entire area was sampled, resulting in a total of 114 samples.

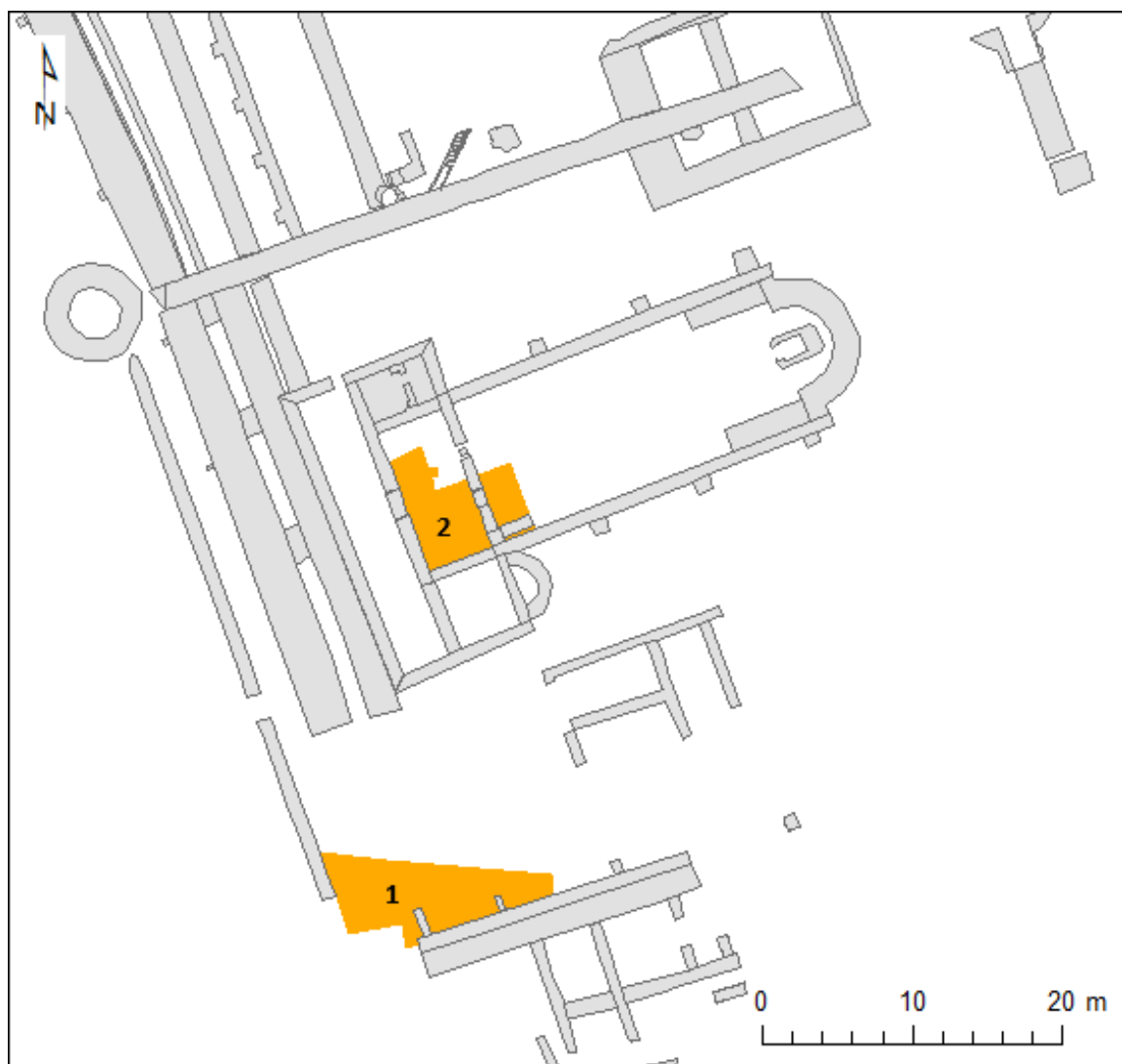


Fig. 5 - Location map of the MAFKO mission trenches in 2018-2019 at the Ulpiana site

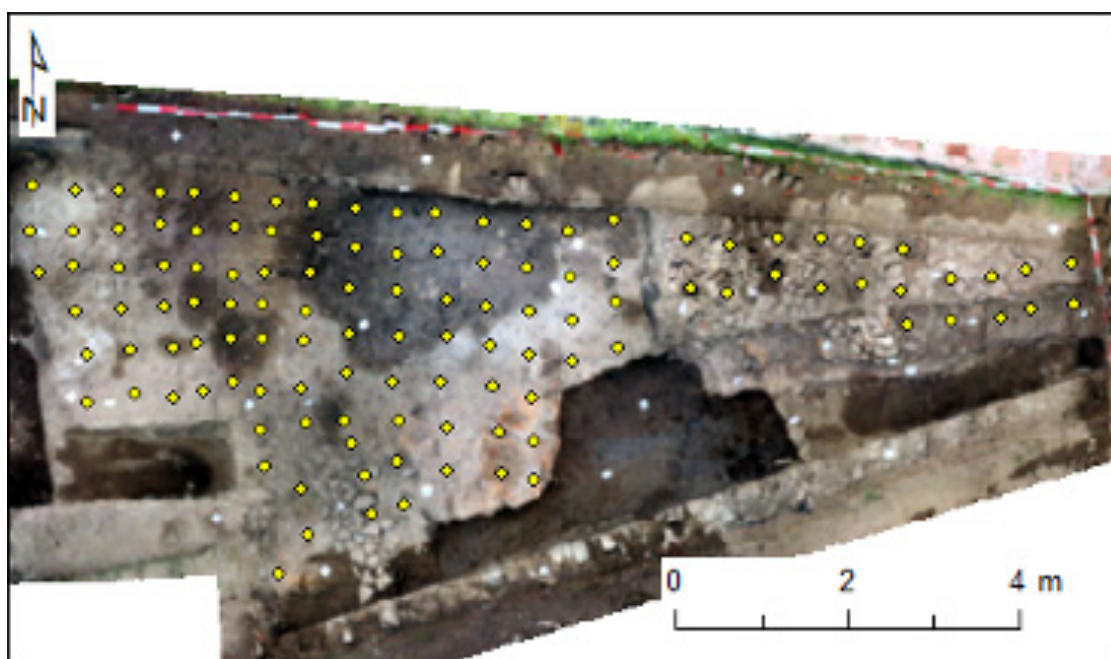


Fig. 6 – Distribution of samples in Zone 1

The second area corresponds to a part of the survey conducted in the temple-church, 30 meters north of the first area (Fig. 7). This time, the issue that motivated the opening of this sondage was the dating of the church and the understanding of its installation within the former portico of the Roman temple that predates it. A burial and an in situ ceramic prompted the deployment of a sampling grid. Samples taken at the southeast end of the area were collected from the level that appeared after the removal of mosaic elements. A total of 35 samples were collected from this area.

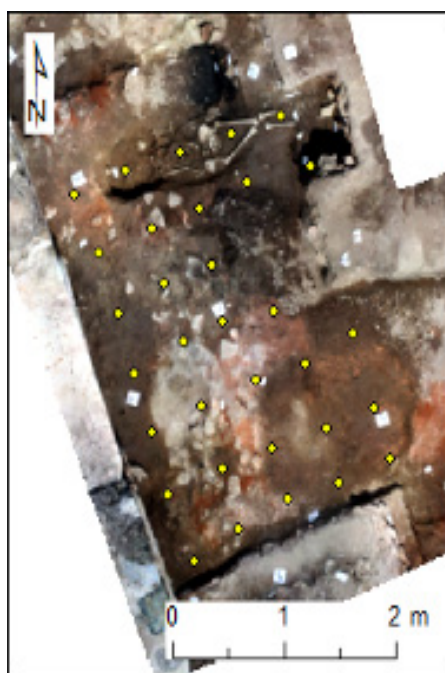


Fig. 7 – Distribution of samples in Zone 2

In addition to these two main areas, a third sampling location should be noted. This is a well-preserved potter's kiln uncovered by Milot Berisha's team (Fig. 8). Numerous white deposits suggest that it may have been repurposed as a lime kiln. Here, we did not sample using a grid but only collected from the deposit traces and the base of the structure. The results of these samples are not mapped but are presented alongside the interpretation of Zone 1, where they provide valuable information.



Fig. 8 – Distribution of samples in the kiln

Results and interpretation

In the first area, at the location of the white stains identified during excavation, we can observe that the signals for calcium and strontium are both intense and correlated (Fig. 9). It is also worth noting that sulphur shows high concentrations in the central stain. This difference between the two stains should help guide our interpretation. Finally, various minor contaminations are present. These contaminations can be both current pollution caused by agriculture or industry and minimal traces of ancient activities. In Ulpiana, the soils are irrigated by a river passing near a contemporary mining site, which suggests that we are dealing with present-day contaminations.

In the second area, metals are prominently featured (Fig. 10). The concentrations of copper, tin, and lead are clustered in the center of the study area, at the location of a ceramic found in situ. The other metal-rich areas, to the north and east of the trench, are located in close proximity to a wall and within the burial site, respectively. Also note the presence of bromine, a rare element in soils, which is located in conjunction with the burial site.

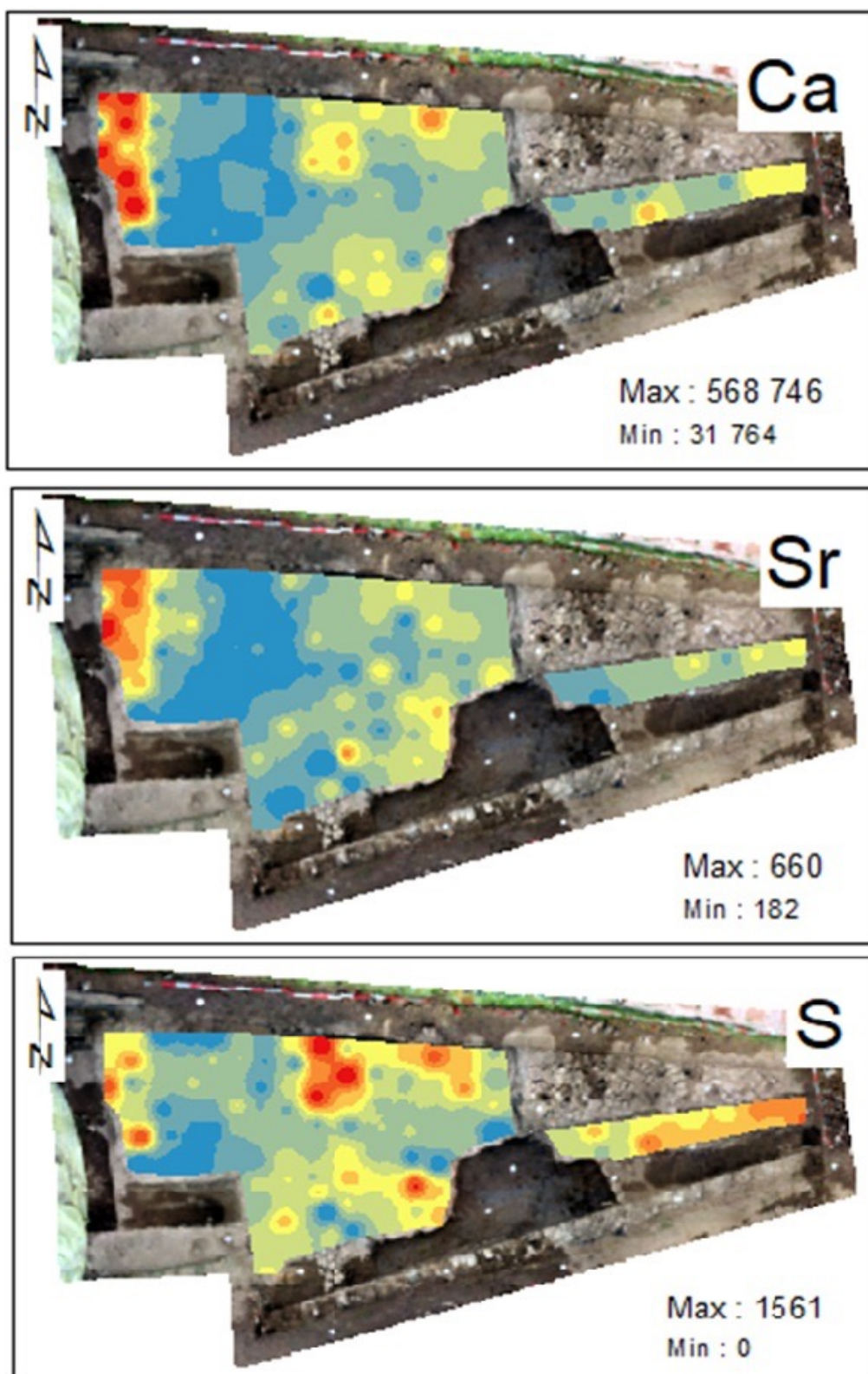


Fig. 9 – Distribution of notable chemical element concentrations for Zone 1, namely calcium, strontium, and sulphur

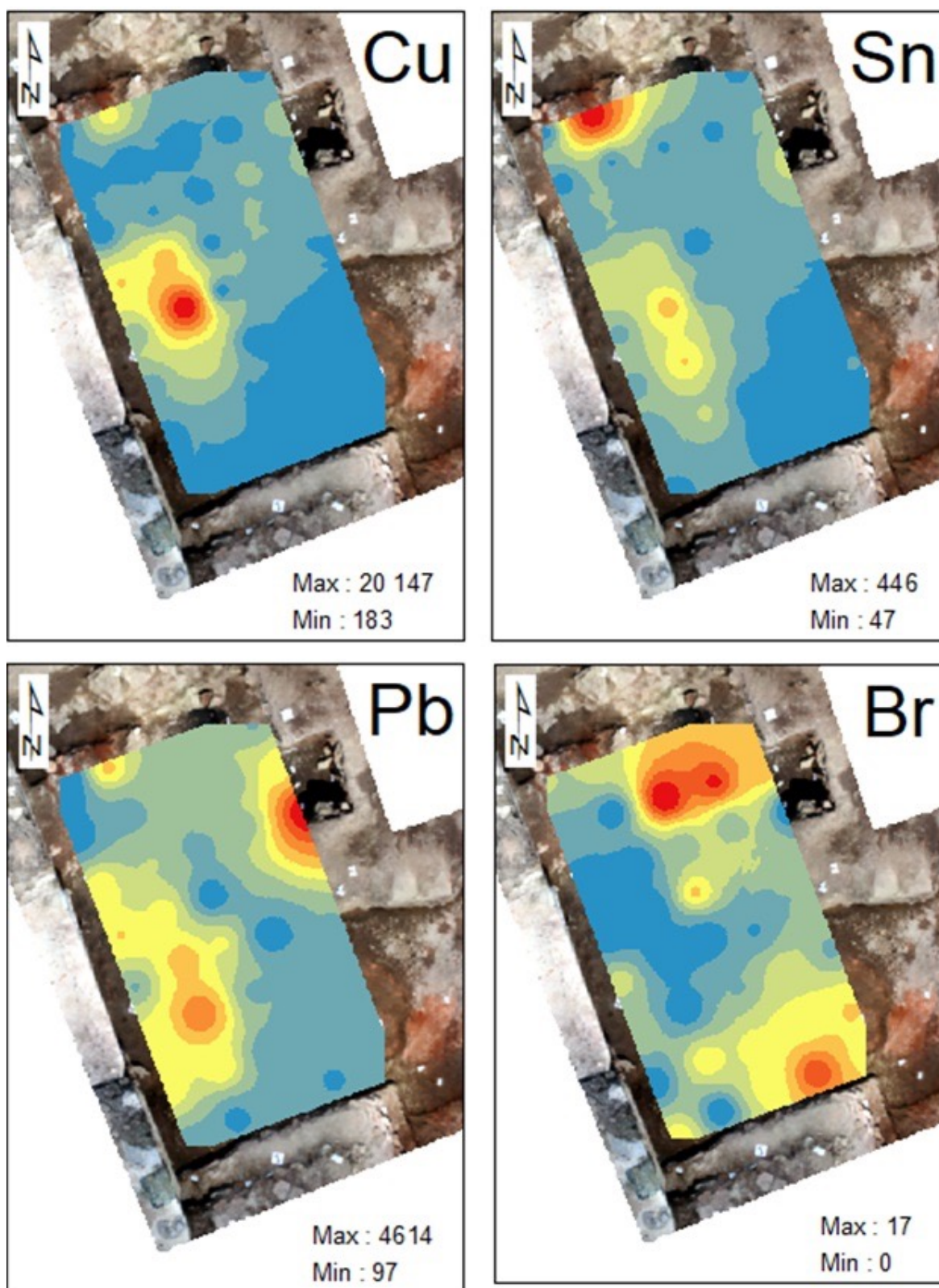


Fig. 10 – Distribution of notable chemical element concentrations for Zone 2, namely copper, tin, lead, and bromine

Interpretation

Zone 1

As previously mentioned, the two stains identified during excavation exhibit different concentrations of chemical elements. The western stain contains calcium and strontium, while the central spot also includes sulphur (Fig. 9). The correlation between calcium and strontium is naturally observed in limestone (Pracny et al. 2019). These two elements are somewhat equivalent and can substitute for one another in larger chemical structures. These data should not surprise archaeologists; the calcium-to-strontium ratio in teeth is typically used to assess individuals' diets (Bentley 2006). The substitution of calcium by strontium in this case tends to indicate a more plant-based diet, though in our case the correlation of Ca and Sr simply indicates the presence of lime, as observed at other archaeological sites (Barba et al. 2008, Abrahms et al. 2012, Ahern 2021, Herrick & Berna 2024). The central spot, which also shows sulphur concentrations, suggests the presence of plaster. With the formula CaSO_4 , plaster was used in antiquity, so its presence does not seem out of place.

We conducted additional analysis on a sample from this spot to verify whether it is indeed plaster. As noted, while EDXRF provides the concentrations of chemical elements, it does not provide the molecular structure of the sample. We can hypothesize molecular forms based on the concentrations alone; here, we proposed plaster. However, when possible, such hypotheses should be tested. In this case, we used X-ray diffraction to identify plaster. The spectra highlight that the presence of sulfur in these samples is likely not related to gypsum (CaSO_4), which would have confirmed the presence of plaster, but rather to chalcopyrites. We then examined the data more closely, particularly focusing on the silicon content. This element is generally excluded from interpretations because it is extremely abundant in soil and sand, as aluminum silicates. In this particular case, the silicon concentration helps us understand what the two white spots are. The bar chart represents the measured elemental concentrations for seven samples (Fig. 11). Lime 1 and Lime 2 come from the lime kiln we previously discussed. Samples A1, B1, and B2 come from the western spot, while I1 and J2 come from the central spot.

It is then clearly visible that the samples from the central area have significantly higher concentrations of silicon and aluminum compared to those from the western area. Therefore, it is likely that the lime in the central area was mixed with sand to prepare mortar. In the western area, there is little silicon and aluminum, and all the concentrations are similar to those measured in the lime samples from the kiln. We can then propose that the western area is the remnant of a lime pit, while the central area represents the remains of a mortar mixing area.

It seems, however, possible to go further. By creating the same bar chart but excluding the concentrations of calcium, silicon, and aluminum, which are the three highest, we observe that the minor elements present in the lime from the kiln also appear in the lime pit samples and in the same proportions (Fig. 12). As for the mortar mixing area

samples, we note that the concentrations are generally higher, particularly for iron, potassium, and manganese. The overall increase is likely due to the lower proportion of calcium. The significant increases in iron, potassium, and manganese are consistent with the addition of sand, as these elements are relatively abundant in sand.

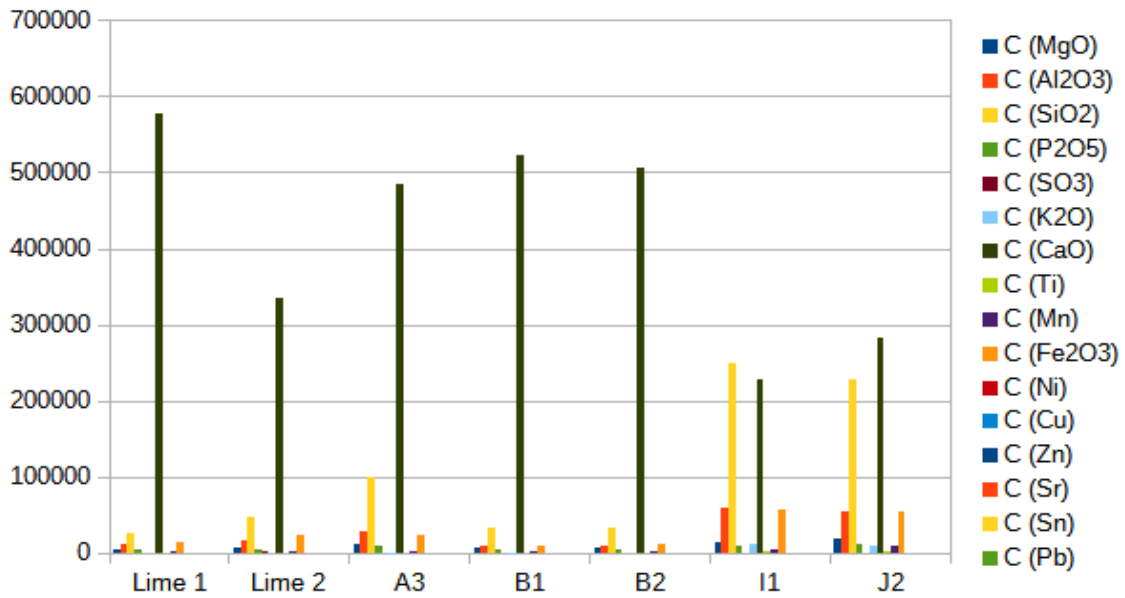


Fig. 11 – Bar chart representing the concentrations of notable chemical elements in the samples Lime1, Lime2, A1, B1, B2, I1, and J2

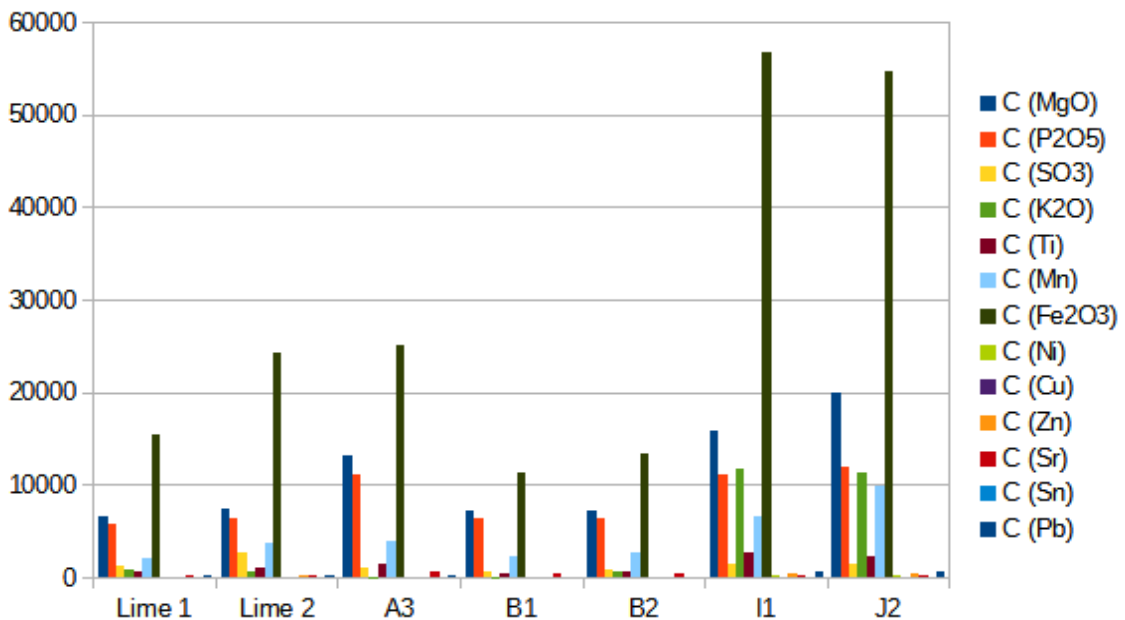


Fig. 12 – Bar chart representing the concentrations of chemical elements in the samples from Fig. 11, excluding the three most concentrated elements (Ca, Si, Al).

Zone 2

The metal concentrations in the center of Zone 2 leave little doubt about the activity that took place there. Indeed, the presence of copper, tin, and lead indicates metallurgical activity (Fig. 10). However, it is unlikely that this was a forge dedicated to the production of copper alloy objects. Examples of such archaeological structures have been studied, and while they exhibit similar chemical signals, they also show additional archaeological evidence linked to this production, whether in the form of waste or structural remains (Shalev et al. 2006, Gauss et al. 2013, Zhang et al. 2017, Smejda et al. 2018, Tighe et al. 2018, Laenger et al. 2024). At Ulpiana, there are no traces of production structures, except for a piece of pottery found flat at the centre of the elemental signal (Fig. 13). Moreover, the location of this activity within the church's narthex is rather surprising, but it is easily understood. This small workshop is situated within the stratigraphic sequence just after the layers indicating a particularly devastating earthquake. The metallurgical production identified in the narthex is likely connected to post-catastrophe recovery activities. The pottery mentioned earlier most likely served as a crucible for melting debris from copper alloy objects retrieved from the rubble.



Fig. 13 – Photograph of the ceramic in situ, at the center of the high metal concentrations.
Photo credit: Arthur Laenger

The burial in the narthex exhibits unusual concentrations of bromine (Fig. 10). Bibliographic research has highlighted a source of this element in an artisanal process known to ancient societies (Guckelsberger 2013, Tsourinaki 2020). This involves textile dyeing, particularly using Tyrian purple. This pigment, extracted from *Murex brandaris*, was highly prized by Roman elites, becoming a distinctive mark of the senatorial class and later the imperial elite. Although ancient societies did not know this, the molecule responsible for the purple color of this pigment, 6,6'-dibromoindigo, contains bromine atoms in its structure (Fig. 14). While a royal tomb with significant bromine concentrations has been analyzed in the past (James et al. 2009), the concentrations at Ulpiana are too low. It has not been possible to confirm or refute whether the bromine detected in the EDXRF analysis originates from this molecule. However, the hypothesis is plausible, as dyeing a garment would not leave a very strong chemical imprint. The bromine in the soil is probably from a piece of dyed fabric that did not preserve.

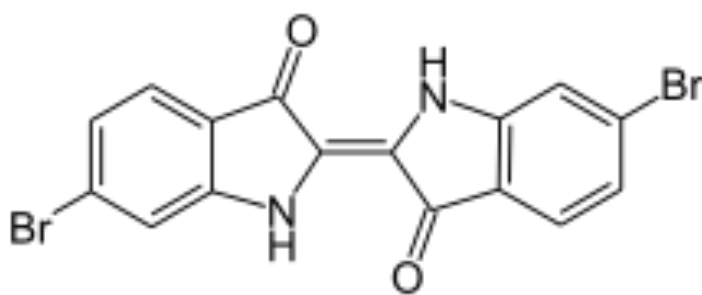


Fig. 14 – Lewis structure of the 6,6'-dibromoindigo molecule, a dye molecule present in Tyrian purple.

Conclusion

Soil chemical analyses, particularly the use of EDXRF, provide unprecedented insights for identifying and interpreting past human activities. The study conducted at Ulpiana enabled the distinction of production and transformation areas, notably a copper alloy recycling workshop and mortar remains associated with construction material preparation. Furthermore, the presence of bromine, potentially linked to prestigious textile dyes, underscores the wealth of information that geochemical analyses can reveal.

These findings demonstrate the efficacy of EDXRF in delivering reliable and accessible data while reducing the costs and complexities of analytical protocols. They also highlight how this method can play a central role in heuristic studies, offering precise interpretative hypotheses that can be confirmed or refined through complementary techniques.

In the future, the systematic application of this methodology to comparable archaeological sites, such as Justiniana Secunda, located just to the north of Ulpiana, could deepen our understanding of cultural and economic interactions in the region.

Additionally, integrating EDXRF with other analytical approaches, such as isotopic analysis or X-ray diffraction, may uncover new chemical markers of anthropogenic activities that have thus far been underexplored.

Conflict of Interest

There are no conflicts of interest to declare regarding this publication.

Acknowledgments

The use of new technologies in archaeology can sometimes be perplexing or even daunting for archaeologists, who naturally fear for the integrity of their sites. However, without experimentation, progress in knowledge is limited. Therefore, we would like to warmly thank Arben Hajdari, Milot Berisha, and Christophe Goddard for allowing us to test our study protocol on the areas investigated at Ulpiana under their supervision. We also extend our sincere gratitude to the laboratory at IUT de Chimie du Mans Université for providing access to their EDXRF equipment, without which this experiment would not have been possible.

REFERENCES

- Abrahams, Peter W., Jane A. Entwistle, and Robert A. Dodgshon. 2010. "The Ben Lawers Historic Landscape Project: Simultaneous Multi-Element Analysis of Former Settlement and Arable Soils by X-Ray Fluorescence Spectrometry." *Journal of Archaeological Method and Theory* 17: 231–48.
- Ahern, Kaitlin R. 2021. "Analysis of Late Preclassic Period Lime Plaster Floors at Holmul, Guatemala." *Journal of Archaeological Science: Reports* 36: 102883.
- Arrhenius, Olof. 1931. "Die Bodenanalyse im Dienst der Archäologie." *Zeitschrift für Pflanzenernährung, Düngung, Bodenkunde* 10 (27–29): 427–39. <https://doi.org/10.1002/jpln.19310102705>.
- Arrhenius, Olof. 1934. Fosfathalten i Skånska Jordar. *Sveriges Geologiska Undersökning C* 28: 383–415.
- Barba, Luis, and Guadalupe Bello. 1978. "Análisis de Fosfatos en el Piso de una Casa Habitada Actualmente." *Notas Antropológicas* 1 (24): 188–93.
- Barba, Luis, Salvador Domínguez-Bella, Juan Ramos, Vicente Castañeda, María Pérez, and Manuel Sánchez. 2006. "Geophysics and Archaeology at La Mesa Site, Chiclana de la Frontera, Cádiz (Spain)." In *Proceedings of the 34th International Symposium on Archaeometry*, Zaragoza, 3–7 May 2004, edited by Josefina Pérez-Arantegui, 15–20. Zaragoza: Institución "Fernando el Católico."
- Bentley, Alexander R. 2006. "Strontium Isotopes from the Earth to the Archaeological Skeleton: A Review." *Journal of Archaeological Method and Theory* 13, (3): 135–87.
- Bintliff, John, and Patrick Degryse. 2022. "A Review of Soil Geochemistry in Archaeology." *Journal of Archaeological Science: Reports* 43: 103419. <https://doi.org/10.1016/j.jasrep.2022.103419>.

- Craddock, Paul T., David Gurney, Francis Pryor, and Michael J. Hughes. 1985. "The Application of Phosphate Analysis to the Location and Interpretation of Archaeological Sites." *The Archaeological Journal* 142 (1): 361–76. <https://doi.org/10.1080/00665983.1985.11021068>.
- Dirix, Katrien, Philippe Muchez, Patrick Degryse, Borut Mušic, and Jeroen Poblome. 2013. "Integrating Multi-Element Geochemical and Magnetic Survey at Ancient Sagalassos (Southwest Turkey): Anthropogenic versus Natural Anomalies." *Archaeological Prospection* 20 (4): 233–47. <https://doi.org/10.1002/arp.1462>.
- Frahm, Ellery, Glenn F. Monnier, Nicholas A. Jelinski, Eric P. Fleming, Benjamin L. Barber, and Joseph B. Lambon. 2016. "Chemical Soil Surveys at the Bremer Site (Dakota County, Minnesota, USA): Measuring Phosphorus Content of Sediment by Portable XRF and ICP-OES." *Journal of Archaeological Science* 75: 115–38. <https://doi.org/10.1016/j.jas.2016.10.004>.
- Gauss, Reinhard K., Juraj Batora, Erich Nowaczinski, Kurt Rassmann, and Guido Schukraft. 2013. "The Early Bronze Age Settlement of Fidvár, Vráble (Slovakia): Reconstructing Prehistoric Settlement Patterns Using Portable XRF." *Journal of Archaeological Science* 40 (7): 2942–60. <https://doi.org/10.1016/j.jas.2013.01.029>.
- Goddard, Christophe, Arben Hajdari, Milot Berisha, and Tomoo Mukai. 2017. Rapport de la Mission Archéologique Franco-Kosovare à Ulpiana. MAEE; Ministry of Culture of Kosovo. halshs-02431321.
- Guskelsberger, Martin. 2013. Purple Murex Dye in Antiquity. Háskóli Íslands Hugvísindasvið Latína.
- Gutiérrez-Rodríguez, Manuel, Paul Goldberg, Francisco J. M. Peinado, Thomas Schattner, Werner Martini, Miguel Orfila, and Clara B. Acero. 2019. "Melting, Bathing and Melting Again: Urban Transformation Processes of the Roman City of Munigua: The Public Thermae." *Archaeological and Anthropological Sciences* 11(1): 51–67. <https://doi.org/10.1007/s12520-017-0527-0>.
- Hafez, Ibrahim T., Giovanni Sorrentino, Maria Faka, Carmen Cuenca-García, Christina Makarona, Antonia Charalambous, Koen Nys, and Silvia Hermon. 2017. "Geochemical Survey of Soil Samples from the Archaeological Site Dromolaxia-Vyzakia (Cyprus), by Means of Micro-XRF and Statistical Approaches." *Journal of Archaeological Science: Reports* 11: 447–62. <https://doi.org/10.1016/j.jasrep.2016.12.023>.
- Hayes, Katherine. 2013. "Parameters in the Use of pXRF for Archaeological Site Prospection: A Case Study at the Reaume Fort Site, Central Minnesota." *Journal of Archaeological Science* 40 (8): 3193–211. <https://doi.org/10.1016/j.jas.2013.04.008>.
- Herrick, Heather M., and Francesco Berna. 2024. "A Review of Methods to Analyze Archaeological Lime Production: Investigating Raw Materials Selection and Firing Conditions." *Journal of Archaeological Method and Theory* 31 (4): 1668–96. <https://doi.org/10.1007/s10816-024-09652-x>.
- James, Matthew A., Nils Reifarth, Anirban J. Mukherjee, Michael P. Crump, Peter J. Gates, Peter Sandor, Fiona Robertson, Peter Pfälzner, and Richard P. Evershed. 2009. "High Prestige Royal Purple Dyed Textiles from the Bronze Age Royal Tomb at Qatna, Syria." *Antiquity* 83(322): 1109–18.

- Laenger, Alain, and Alain Martel. 2024. "Analyse Géochimique de Sol: Théroutanne, Pas-de-Calais, 22-24 Rue Saint Jean." *Technical Report*. 11.
- Middleton, William D., Linda Barba, Alessandra Pecci, James H. Burton, Alejandra Ortiz, Luca Salvini, and Ricardo R. Suárez. 2010. "The Study of Archaeological Floors: Methodological Proposal for the Analysis of Anthropogenic Residues by Spot Tests, ICP-OES, and GC-MS." *Journal of Archaeological Method and Theory* 17 (3): 183–208. <https://doi.org/10.1007/s10816-010-9088-6>.
- Onk, Sander, Cornelis P. Slomp, and Diederik J. Huisman. 2009. "Geochemistry as an Aid in Archaeological Prospection and Site Interpretation: Current Issues and Research Directions." *Archaeological Prospection* 16 (1)1: 35–51.
- Pracný, Petr, Jan Fiamon, and David Všianský. 2019. "Evolution of Mg/Ca and Sr/Ca Ratios during the Experimental Dissolution of Limestone." *Chemical Geology* 523: 107–20.
- Rippon, Stephen J., Michael H. Martin, and Andrew W. Jackson. 2001. "The Use of Soil Analysis in the Interpretation of an Early Historic Landscape at Puxton in Somerset." *Landscape History* 23 (1): 27–38. <https://doi.org/10.1080/01433768.2001.10594528>.
- Salisbury, Roderick B. 2020. "Advances in Archaeological Soil Chemistry in Central Europe." *Interdisciplinaria Archaeologica: Natural Sciences in Archaeology* 11 (2): 199–211.
- Save, Stéphane, Ján Kováčik, Françoise Demarly-Cresp, Romain Issenmann, Sébastien Poirier, Susanne Sedlbauer, and Yannick Teyssonneyre. 2020. "Large-Scale Geochemical Survey by pXRF Spectrometry of Archaeological Settlements and Features: New Perspectives on the Method." *Archaeological Prospection* 27 (3): 203–18. <https://doi.org/10.1002/arp.1773>.
- Shalev, Shirly, Sergey S. Shilstein, and Yuval Yekutieli. 2006. "XRF Study of Archaeological and Metallurgical Material from an Ancient Copper-Smelting Site near Ein-Yahav, Israel." *Talanta* 70 (5): 909–13.
- Smejda, Ladislav, Martin Hejzman, Jan Horák, and Itzhaq Shai. 2017. "Ancient Settlement Activities as Important Sources of Nutrients (P, K, S, Zn and Cu) in Eastern Mediterranean Ecosystems—The Case of Biblical Tel Burna, Israel." *Catena* 156: 62–73. <https://doi.org/10.1016/j.catena.2017.03.024>.
- Tighe, Matthew, Greg Rogan, Susan C. Wilson, Peter Grave, Lisa Kealhofer, and Piyaporn Yukongdi. 2018. "The Potential for Portable X-Ray Fluorescence Determination of Soil Copper at Ancient Metallurgy Sites, and Considerations beyond Measurements of Total Concentrations." *Journal of Environmental Management* 206: 373–82.
- Tsourinaki, Sofia. 2020. "The Use of Muricidae and Other Purple Colourants during Late Antiquity." In *Environment and Religion in Ancient and Coptic Egypt: Sensing the Cosmos through the Eyes of the Divine*, edited by Alicia Maravelia and Nadine Guilhou, 453–474. Oxford: Archaeopress.
- Wilkins, Ann P. 2009. "Identifying 18th Century Hidden Landscapes at Stratford Hall Plantation Using Portable X-Ray Fluorescence Phosphorus Readings on Plowzone

- Samples.” PhD diss., University of Massachusetts.
- Wilson, Clare A., Douglas A. Davidson, and Malcolm S. Cresser. 2008. “Multi-Element Soil Analysis: An Assessment of Its Potential as an Aid to Archaeological Interpretation.” *Journal of Archaeological Science* 35 (2): 412–24. <https://doi.org/10.1016/j.jas.2007.04.006>.
- Zhang, Shuangquan, Yuzhang Yang, Michael J. Storzum, Haifeng Li, Yanhong Cui, and Guanghui Dong. 2017. “Copper Smelting and Sediment Pollution in Bronze Age China: A Case Study in the Hexi Corridor, Northwest China.” *Catena* 156: 92–101.

About the authors

Arthur Laenger

Arthur Laenger studied history, archaeology, and chemistry at Le Mans University (France) and obtained his PhD in archaeology and the history of the Middle Ages in 2006, under the supervision of A. Durand and A. Martel. His work focuses on the characterization of structures and archaeological sites using an interdisciplinary approach that combines history, archaeology, and chemical soil analysis.

Arnaud Martel

Arnaud Martel was born in 1974 in Le Mans, France. He pursued studies in chemistry at Université du Maine, obtaining his PhD in 2001. Subsequently, he conducted postdoctoral research with Prof. G. Guillaumet at ICOA (Orleans, France) and with Prof. H. Ottosson in Uppsala (Sweden). He was appointed assistant professor in 2004 and attained the rank of full professor at Université du Maine in 2013. His research interests include organic chemistry, DFT-assisted elucidation of reaction mechanisms, and analytical chemistry. Currently, his research focuses on developing new analytical methodologies applied in a multidisciplinary approach spanning archaeology to environmental sciences.

Aline Durand

Aline Durand studied history, Latin, and anthracology at Paris I Panthéon-Sorbonne University, obtaining her PhD in 1991 under the supervision of R. Fossier and J.-L. Vernet. An assistant professor at Aix-Marseille University from 1992 to 2013, she has been a full professor of medieval history and archaeology at Le Mans University since 2013. She is particularly interested in the rural economy of the 10th to early 13th centuries in the Mediterranean French region (Languedoc, Provence, and the Southern French Alps). Her research interweaves diverse sources, including written documents (such as diplomatic documentation and agronomic treatises), archaeological data, and bioarchaeological and palaeoenvironmental results. She studies agrarian landscapes, vegetation resource management, and plant practices and knowledge. To gain a better understanding of craft production techniques and their environmental impact, she developed an ethnoarchaeological research project in Morocco, employing archaeological methods to observe and record them.

Fabien Boucher

Fabien Boucher was born in 1978 in Le Mans, France. He initially studied chemistry at the University of Maine, where he earned a DUT in Chemistry (the French equivalent of a bachelor's degree), and continued his studies at the Rennes School of Chemistry (University of Rennes). There, he obtained an engineering degree in analytical chemistry. After spending more than 10 years working in laboratories providing environmental analysis services, he returned to the University of Le Mans as a study engineer. In this role, he supported research in analytical chemistry and contributed to the development of new analytical methodologies applied across various fields, including chemistry, biology, and archaeology.