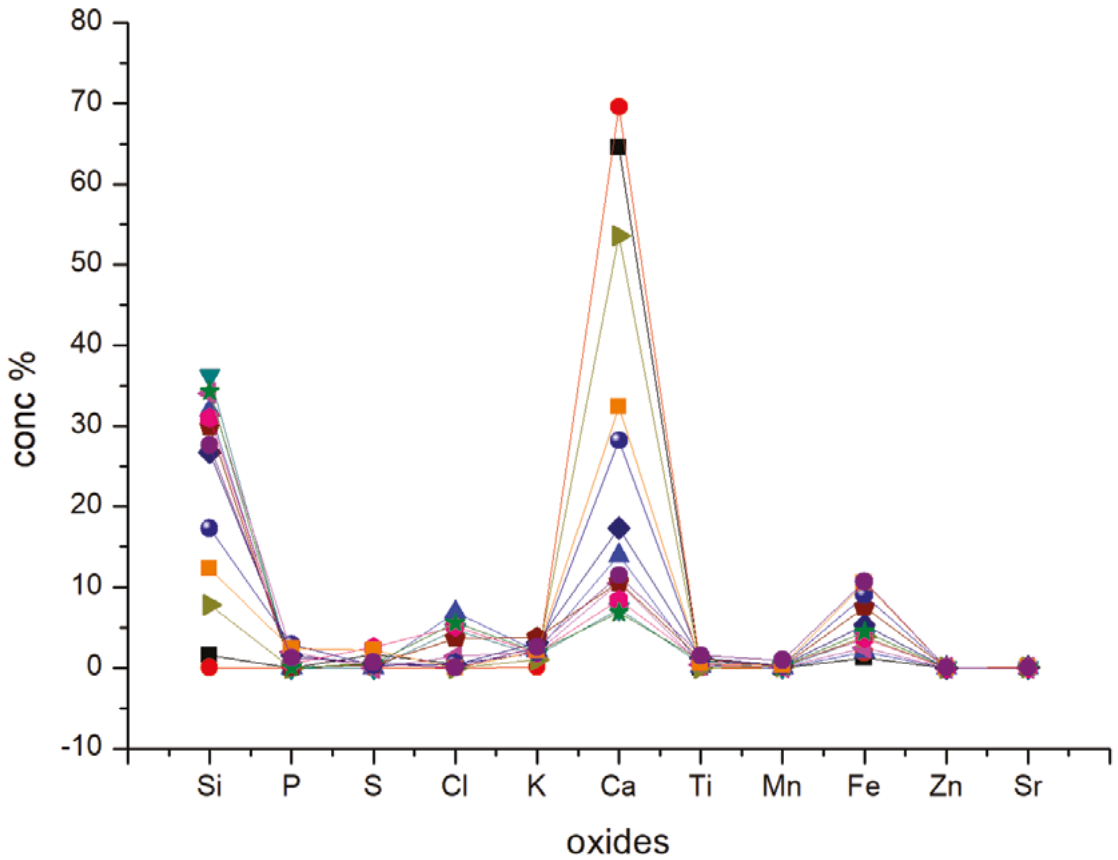
Bridging Science and Heritage in the Balkans

Studies in archaeometry, cultural heritage restoration and conservation



edited by

Nona Palincaş and Corneliu C. Ponta

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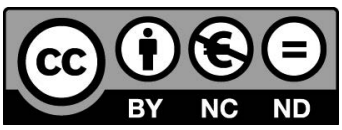

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Foreword

This volume is largely based on the scientific communications given at the *Fifth Balkan Symposium of Archaeometry 2016 (BSA5).* The Editors gracefully asked me to write this foreword given my contribution in organizing the event and despite my limited contribution to the making of the volume itself. I could hardly refuse the honour and in doing so I will include in this foreword information about the symposium, a few of the ideas that emerged from the discussions there and will only succinctly refer to the content of the book and the conditions it was put together in over two years of work by Dr Nona Palincaş and Dr Corneliu C. Ponta, the Editors, plus the authors and the referees participating in the peer review process.

The symposium

The symposium took place between 25 and 29 September 2016, in the Carpathian resort town of Sinaia, Romania. The first BSA was organised in 2008 in Ohrid (North Macedonia), the next ones in 2010 in Istanbul, in 2012 in Bucharest and in 2014 in Nessebar (Bulgaria). These symposia have therefore a tradition, even though not a long one. A question may arise whether these events, dedicated to specialists residing or working in such a restricted geographical area as the Balkans, however broadly conceived (we addressed specialists from or working in Albania, Bosnia-Herzegovina, Bulgaria, Croatia, Greece, Hungary, North Macedonia, Romania, Serbia, Slovenia, Turkey), is warranted or not, given the existence of several more general meetings and conferences on such topics. Or whether the topic is too broad and the area too small. At the time I did not doubt a single moment that yes, these meetings are needed and can be useful if we are to develop a strong local archaeometry in a systematic way. That certainly has also come from my personal connection with the field: about four decades ago my first consistent scientific project as a young physicist, newly employed at Horia Hulubei Institute for Physics and Nuclear Engineering (IFIN-HH) for a job of fundamental research in nuclear physics, was one of archaeometry (analyses of a few large numismatics hoards). And from my love of history. And while away from the field for 20 years, but with the advantages and responsibilities of the position I was having as IFIN's scientific director, I considered that we need to do as much as possible to bridge the gaps between science and heritage (see below the title chosen for this event). I had the same opinion during the organisation time, during the event itself and after! I still hold it now! We know that the region of Balkans is not merely rich, but *extremely rich* in history, in monuments and artefacts, and we know also that in most countries we are far behind the curve when it comes to the use of modern techniques in the study and preservation of material cultural heritage. While the richness, age and diversity of region's heritage is hardly matched by any other region of the world of the same size, the research in the area we are talking about here is not so developed, not enough attention is given to it by the responsible authorities! Not in all countries the authorities and the people at large understand the importance of cultural heritage and the need for its preservation and study. Not everywhere the importance of these for the economy, through tourism e.g., is understood and we face many times the impression that they are only burdens on budgets. Local budgets or national science budgets! We also know that in some areas, and by this I mean certain methods, we may have very good specialists and equipment but is also true that in some cases they are better known and appreciated abroad than inside their own countries (a good example is that from our institute for gamma irradiation techniques applied to conservation or consolidation of artefacts – see C. Ponta, in this volume). But these cases do not change the overall assessment that there is both insufficient use and demand of modern techniques in heritage sciences and practice.

The title chosen for this event was *'Bridging Science and Heritage'* and the organisers of the symposium were the Horia Hulubei National Institute for Physics and Nuclear Engineering (IFIN-HH) in Bucharest-Măgurele, the University of Bucharest (UB) and the Vasile Pârvan Institute of Archaeology in Bucharest (IAB) of the Romanian Academy.

The symposium focused on the application of modern physical and chemical methods in archaeometry, including nuclear methods and techniques used in the dating, analysis, investigation and characterisation of ancient artefacts, as well as their conservation and consolidation. Subjects from the related fields of archaeology and art history were also touched upon.

The programme included invited lectures (speaking time 40 min.), oral (20 min.) and poster presentations on the following topics:

- Analytical methods for cultural heritage diagnostics
- Lithic materials

- Archaeometallurgy
- Radiocarbon Dating
- GIS applications
- Preservation of cultural heritage – conservation and restoration
- Optoelectronic applications
- Experimental archaeology
- Multidisciplinary research in archaeology

A few more words about the organisers of BSA5. To start with, it is mandatory to mention here the members of the local Organizing Committee and Program Committee:

Organizing Committee:

Livius Trache	FIN-HH, Chair
Emilian Alexandrescu	University of Bucharest, co-chair
Ioana Stănculescu	University of Bucharest and IFIN-HH
Bogdan Constantinescu (†)	IFIN-HH
Mihaela Constantin	IFIN-HH
Roxana Morteanu	University of Bucharest
Nicolae Ionescu	University of Bucharest
Nona Palincaş	Vasile Pârvan Institute of Archaeology
Vasile Opriş	Vasile Pârvan Institute of Archaeology
Cătălin Nicolae	Vasile Pârvan Institute of Archaeology

Program Committee:

Attila László	Alexandru Ioan Cuza University, Iaşi
Nona Palincaş	Vasile Pârvan Institute of Archaeology

It is mandatory to note that among those mentioned in the longer list above we had Nona Palincaş, Corneliu Ponta and Ioana Stănculescu working extra time, with extra dedication and extra efficiency in these committees to address as wide an audience as possible, to make the right invitations, to have the booklet of abstracts ready and printed in time, to have the program ready, with appropriate sessions and chairs, etc.

At the time when the event was in its organizing phase, we insisted through invitations that we cover as many as possible of the countries in the Balkans and that we cover most of the topics in range. We succeeded to do these, but some limitations occurred for the event itself and during the editing of this volume. I note that one of our colleagues from Turkey had to cancel her trip to Sinaia in the last moment, for reasons we understood to be neither personal, nor scientific in nature. Some countries had fewer than expected representatives and unfortunately Greece and Croatia had none. Later, some of the participants would not contribute to this volume because they have other priorities imposed by their working environment (like where to publish). It is important to say here that we had a consistent support in the presence at the symposium of well-known specialists from outside the region: Walter Kutschera (University of Vienna), Laurent Cortella (ARC-Nucleart Grenoble), Ulrike Sommer (University College London), Pieter Vandenabeele (Ghent University), or attending the BSA for the first time: Milica Stojanović-Marić (National Museum Belgrad), Žiga Šmit (University of Ljubljana). The latter assumed the responsibility of organizing the next edition (at this time BSA6 has already taken place in September 2018 in Ljubljana, Slovenia, with the institutional support of the National Museum of Slovenia). The presence at BSA5 of about one hundred specialists (some attending only part-time) from different fields of expertise made us believe that our goal was reached to a large extent. We could reunite archaeologists, historians, museum curators, physicists, chemists, biologists, science managers... researchers and/or university professors, custodians of national and global heritage monuments and artefacts.

BSA5 had five ordinary sessions of half a day each and a session in round table format on the last day, a Thursday. The round table, in the organisation of which Emilian Alexandrescu from the University of Bucharest was particularly involved, was entitled *Multi-disciplinarity in archaeology: Situating archaeometry in education and research*. On that occasion, many more people joined the participants to the ordinary sessions. Officials of the host country involved in research policy and in the management of research and higher education, representatives of history departments from Romania's universities, members of the Romanian Academy, politicians and media representatives were

invited. And some responded to the invitations: Octaviana Marincaş – representing the Ministry of Research (ANCSI - Agenţia Naţionala pentru Cercetare Ştiinţifică şi Inovare/the National Agency for Scientific Research and Innovation), Petre T. Frangopol from the Romanian Academy, Vasile Cotiugă from University of Iaşi – ARHEOINVEST Platform, Dorin Micle from Timişoara –ARHEOVEST Platform, Emilian Alexandresu, Carol Capiţă and Daniela Zaharia from the University of Bucharest, arheologists Eugen Teodor, Nona Palincaş, Vasile Opriş from various institutions in Bucharest, many researchers from IFIN-HH. The round table itself had two parts, a first for general discussions on the topic in the title and one specific for the situation in Romania. The first had a few interventions from participants commenting on the status of the field in their respective countries. The second one was longer and was related to the assessment of the status of archaeometry, or more generally said, of the status of the use of modern chemical and physical methods in the study and preservation of the material cultural heritage in Romania. To assess the need (large), the technical possibilities (good) and the human resources (poor) for this endeavour! Right up for the title of the whole event: we need to have these bridges between specialists in the positive sciences and those in humanistic ones. Bridges are needed between us physicists, chemists, biologists, engineers etc ... and those who are the specialists and the curators of the monuments and artefacts that constitute our common heritage. One important conclusion was that the educational system lacks a good, modern curriculum of archaeology in its universities. Fundamental changes are needed to create the specialists that can respond quickly and adequately to the challenges of the present time and society. Most challenging: the preventive archaeology connected with the increased and increasing number of construction sites and the need for specialised classes, at master level and above, on the methods of the 'positive sciences' with application in archaeology. Moreover, a wider cooperation between the people and institutions with responsibilities and possibilities in the field is needed and within reach. I cannot skip here the fact that I presented the offer of our institute (IFIN-HH) in the fields of study and preservation of cultural heritage, which is large and diverse (see http://patrimoniu.nipne.ro/), but not sufficiently known or used by the 'beneficiaries', national or regional. And is the contribution that IFIN-HH could bring to a national Centre for the Study and Preservation of Cultural Heritage, a localised or a virtual centre, set up as a network of research infrastructures and specialists dedicated fully or partially to heritage studies that we strived to organise at that time. Two years after, I have to say that, no, the center was not formally setup, despite the initial support of the ministry of research, but that in practice it works at the grass-root level. While in September 2016 we did not know about the E-RIHS (European Research Infrastructure for Heritage Sciences) initiative, at this moment we struggle to join it, as its ideas and principles are similar.

To conclude this section: the support of the University of Bucharest, directly through its Rector Mircea Dumitru, academician, was crucial in extending the number of participants – young ones in particular - by hosting at no cost some participants in its Guest house in Sinaia. The Romanian ministry of scientific research (ANSCI) supported the workshop with seed funding. IFIN-HH and IAB supported the Organisers. Not in the last, we need to acknowledge the excellent conditions offered by hotel *International***** (https://www.internationalsinaia.ro/) in Sinaia that hosted the meeting in its Conference centre and accommodated most of the participants.

This volume

The volume contains 16 papers, all solicited to the participants and carefully reviewed by the Editors and their evaluators. For the customs of the community I come from (nuclear physics), the time it took to have it put together is long. Apparently it is not so for archaeologists or people working in the fields represented here. The extra care the Editors put into having the papers selected and worked out is commendable.

The purpose of the volume itself and the restricted number of papers would not allow to treat exhaustively or extensively each topic, each section, or to offer reviews of the status of each particular topic globally or in the Balkans. It was more so done in the actual presentations at the symposium than it is here, as each presentation started with an overview of the topic or problem, while the printed text concentrates on news.

The papers in the volume are of various complexity and length. Some are focused on methods, presenting either the results of a new method (Atanassova *et al.*) or improvements of an established method (*Šmit*), new ways of resorting to established methods (Sommer *et al.*), discussion of established methods in relation to concerns raised by those still unfamiliar with them (Cortella) as well as the history of a method (Ponta). Other papers are case studies of various extents. Rather than following the division between focus on method vs. focus on applications, the editors opted for grouping the papers according to the analysed material, whenever this was possible, to help the readers – usually specialised in a certain field – to quicker identify in the book content the papers of interest. The volume is thus loosely divided in nine sections, some more consistent, many containing one or two papers only. It starts with two papers grouped under 'Multiple investigation methods combined' by Sommer *et al.* and Palincaş *et al.*,

respectively. They treat directly what could be called the fundamental problem of archaeometry: what methods to be used, how to be combined, what can we learn from them? What are the limits of methods, what do we learn from apparently contradicting results and so on? In particular Sommer *et al.* ask to what extent the archaeological excavation would be different if we had archaeometry involved during excavation and not afterwards as it is usually the case, while Palincaş *et al.* show the benefits of considering together the results of methods that are usually applied separately – in this case diet studies and archaeometallurgy – in understanding people's biographies.

The second section is the most consistent one, with four papers on the use of radiocarbon dating. Three of them refer to Bronze Age cases of wide European interest: Dáni *et al.* dated cremated bones from Early and Middle Bronze Age on the territory of present day Hungary in tandem with associated organic material as part of a wider attempt to develop the radiocarbon dating of cremated bones, Palincaş *et al.* assessed the methodological accuracy in dating by radiocarbon the Middle Bronze Age in Central Romania and its impact on the long debated Aegean connections, while László revisits one still unsolved case of systematic difference between absolute dating by historical-astronomical and radiocarbon methods of the Late Bronze - Early Iron Ages in and around the Carpathian Basin. The last case study of this section is an application of the radiocarbon method to the history of an object – a wooden church of modern era (Simion *et al.*). These are followed by case studies in archaeometallurgy (Constantinescu *et al.* establishes the Danubian origins of Iron Age gold and silver pieces found today in the collections of famous museums in the USA), ceramics archaeometry (Opriş *et al.* and Dragoman *et al.* present analyses of pigments used in the decoration of Chalcolithic pottery and architecture pieces from the fifth millennium BC), glass (*Šmit* presents an improvement of the PIXE method applied to early Medieval glass from Slovenia) and pigments (Kostadinovska *et al.* study pigments used on Late Medieval manuscripts). These are followed by one case study on the DNA analysis of one human skeleton from the Cucuteni culture (usually known for its 6-7 millennia old beautiful ceramics) by Bolohan *et al.* and one on the use of GIS technology for the identification of previously unknown archaeological sites by Bakardzhiev and Valchev.

The last section is a more consistent one and includes three papers on 'Heritage conservation methods', from three different countries: Bulgaria, Romania and France. The first of the three by Atanassova *et al.* is a specific application of modern methods to the restoration of stone monuments damaged by contemporary graffiti, while the papers by Cortella and Ponta describe a wider range of applications of gamma irradiation for cultural heritage disinfection and preservation of archaeological organic materials. These latter two draw on the expertise of two trail blazing teams of scientists and the state-of-the-art installations they built in Bucharest and Grenoble respectively to introduce and test modern methods in the field of cultural heritage preservation, restoration and consolidation.

All in all, I believe that this volume is a good mirror of what the 5th Balkan Symposium of Archaeometry (held 25-29 September in Sinaia, Romania) was about and to a significant extent of the current situation in the Balkan region in the field of the use of modern scientific methods for the study and conservation of cultural heritage. And I would dare to say that what is missing from this volume reflects well what is missing in this field in our countries.

Prof. Livius Trache
Bucharest-Măgurele, December 2018
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Editors' note: With great sadness we learned that one of our colleagues, Dr Bogdan Constantinescu, a co-organiser of BSA5 and a contributor to this volume, had passed away unexpectedly a few days before the arrival of his chapter for proofreading. The community will miss his contribution.

Micro- and Macroarchaeology – How Can the Two Be Combined?

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Abstract

We present the scientific analyses conducted on the ongoing excavation of the late Criș settlement at Tășnad-'Sere', Satu Mare county. The excavation aims to understand the relationship between the occupation layer and sub-surface features.
We seek to achieve constant feedback between the scientific analysis and the excavation, adapting our excavation methods as needed. The ultimate aim is to develop methods that can also be applied to more conventional excavations. Soil analysis (XRF) revealed a good correspondence between sulphur, inorganic phosphorus, potassium and calcium and the archaeological features. Lipolythic microorganisms and thermophilic bacteria were identified both around and within a pit. Petrographic thin section analysis showed that a very similar fabric with fine organic inclusions was used in all areas analysed.

Keywords: taphonomy, ceramic petrography, pottery colour, phytoliths, soil biology, lipolythic microorganisms, soil analysis, X-ray fluorescent spectrophotometer.

Introduction

The following is an account of the use of methods drawn from Natural Science during an ongoing research excavation. We are thus not able to present any final results here. The account is written from the perspective of a field archaeologist and therefore very much concerns what the primary author (U.S.) learned from her co-authors and other collaborators during the process. The ceramics are analysed by Silvia Amicone; the soil by Elena Chernysheva.

Archaeometric studies are very often only undertaken after an excavation has been completed, while the results of scientific studies feed into ongoing excavations far too rarely. In the following, we reflect on how to bridge the gap between field archaeologists and archaeometrists and natural scientists, and how to arrive at research questions that are beneficial to both.

Archaeometry still has no clear place in mainstream archaeological theory (Martínon Torres and Killick 2016). At best it is accorded the status of a method (e.g. *Hilfswissenschaft* in German). The natural sciences are perceived as realist and empiricist, looking at the material properties of artefacts, while archaeologists, at least in Britain, see themselves as part of the humanities and often take a subjectivist, idealist stance, emphasising the active use of material culture (Hodder 1982) and the nature of artefacts as socially and culturally constructed (cf. Jones 2004). This is the case despite the so-called material shift in cultural studies and the recent interest in materiality, 'thingyness' and entanglement (Hodder 2011, 2012, 2014). In recent years, the concept of materiality has become very fashionable in archaeological theory, especially in the UK. Elisabeth DeMarrais *et al.* (2004: 2) offers the following definition: 'in current archaeological theory, materiality approaches concern not only the study of the characteristics of objects, but also the more general notion that humans engage with the things of the world as conscious agents and are themselves shaped by those experiences.' The concept was originally adopted from consumer studies. In the field of the history and philosophy of science, Bruno Latour (1991; 1999) has emphasised how the artificial contrast between mind and matter introduced during the Enlightenment has served to mask the complex interplay between researcher, instruments, social context and the investigated object. This was taken up in archaeology in terms of the demand for a 'symmetrical archaeology' (Shanks 2007; Olson and Witmore 2015). However, Tim Ingold (2007: 1, 3) criticised the discussion of materiality and material culture for seemingly having little to say about materials, and it was claimed that materiality had become a hindrance rather than a help in terms of understanding materials (Cooney 2016). In many respects, the discourse on materiality resembles

a complicated way of returning to a position that had always been held by materialists, i.e. that humans interact with the environment via tools of their own making.

Archaeologists are often rather ignorant of the rapidly advancing possibilities provided by the scientific analysis of materials, while scientists can be badly informed or frankly uninterested in the research questions of archaeology. Indeed, scientists are often more concerned with developing and applying a new method rather than entering into a dialogue with archaeologists, something which is already difficult to achieve given their different epistemological backgrounds, let alone any terminological disparities. These problems can be alleviated by involving them in the archaeological process, allowing them to work on the excavation itself and therefore to influence the development of research questions, supervise sampling and, most importantly, suggest analytical methods, highlight their limitations and oversee their implementation on-site.

In the following, we outline the aims of the excavation in question and how these influenced the choice of scientific methods used. The results of these preliminary analyses have in turn influenced the design of the excavation. While there is constant feedback during the dig, we will probably need to rejig our excavation procedures fundamentally once the scientific analyses have been completed and explored in more depth.

The site

Tășnad-'Sere' is located in the Satu Mare region of north-western Romania. It belongs to the Late Starčevo-Criș culture, which represents the earliest Neolithic in the upper Tisa valley. The settlement is located about 0.5 km west of the last hills of the Dealurile de Vest region, in which the town of Tășnad is situated. The remains of the Criș settlement cover an area of around 4-5ha (Virág 2015: Fig. 1) in the valley of the Cehal River, a tributary of the Ier River, which feeds into the Tisa. Two ^{14}C dates for animal bone, analysed as part of the EuroFarm project (Vander Linden *et al.* 2013), lie between 5200 and 5000 cal BC (Vander Linden *in prep*.).

At Tășnad-'Sere', sunken features like pits, postholes and so-called semi-pithouses, dug into a heavy clay alluvium, are covered by a dark occupation layer containing numerous finds, which in turn are covered by an alluvial layer that decreases in depth the further the distance from the Cehal River.

Finds from occupation layers are often perceived as unstratified and their provenance thus recorded in less detail than that of artefacts recovered from sunken features. In addition, given its location, there is a possibility that the artefacts in the occupation layer were displaced by the floodwaters that ultimately covered the site.

Aims of the Excavation

Relationship between features

As the dating of early Neolithic houses is often based on the content of adjacent pits (Astaloș and Sommer 2015: 82), the origin and chronology of pitfills should be of great general interest. However, these have rarely been studied in any detail (cf. Schäuble 1997; Hoga 2014). In Tășnad, previous excavations by Ierkosan (1994/95), Németi (1990: 89-90), Virág (Virág *et al.* 2007; Virág 2016) and Astaloș (2005) have uncovered pits and houses under a substantial occupation layer. This made it a promising site at which to study the relationship between dug features and surface finds. In 2012, a trench for the joint UCL/Satu Mare excavations was laid out in an area where Neolithic sediments were buried by an alluvial deposit of more than 1m thick. This made any secondary disturbance highly unlikely. In addition, the area had been used as meadow or woodland for as long as records exist (Stanciu and Virág 2013: 173; Virág 2015). By three-dimensionally recording every find >1cm including its orientation and dip (Sommer and Astaloș 2015), we intend to trace potential post-depositional movements, caused, for example, by flowing water or argilliturbation, or changes during the use of the site, like trampling, and to elucidate the relationship between the occupation layer and dug features, such as postholes and pits. While there were some unexpected problems in recording artefact orientation due to the inexperience of the excavators, it is clear that fluvial action can be ruled out for the formation of the occupation layer.

Two layers can be differentiated in the alluvium. We tested the section for pH as well as trace elements (Figure 1) using portable X-ray fluorescence spectroscopy (Hunt and Speakman 2015). While the strong fluctuation of many trace elements may be due to either repeated short-term sedimentation events or a pronounced inhomogeneity of the sediment, there are some clear trends that seem to indicate a change in the sediments being eroded in the catchment area of the Cehal River and hence a change in land use. There is a visible change in sediment at *c.* 0.7m beneath the surface. This corresponds to a decrease in iron and rubidium and a rise in strontium and zirconium, while the values for titanium, zinc and yttrium do not show any clear correlation. The lower alluvium, which contains a few rolled sherds and is probably an eroded archaeological horizon, and the occupation layer proper have lower levels of iron and yttrium, while the occupation layer has lower levels of rubidium and zirconium. While the results need to be verified using a larger number

of samples in order to understand the nature of the fluctuating values, they demonstrate the value of pXRF (portable X-ray fluorescence) measurements in understanding the origin of sediments and verifying the visual assessment of the stratigraphy. The pH is alkaline throughout but drops with increasing depth.

Soil micromorphology will improve our understanding of deposition processes and the formation of the interface between the occupation layer and archaeological features. Samples at the interfaces between dug features and the occupation layer were collected but have not yet been analysed.

The excavation in UCL Trench 1 has so far revealed a pit in the southeast corner and a row of four postholes that may indicate the location of a house (Figure 2).

Settlement structure

The mapping of each individual find will allow us to study the settlement structure and the activity areas associated with individual houses. The results of the previous excavations indicate a regular layout of small houses arranged in parallel rows (Virág and Stanciu 2013). Given the sheer size of the settlement at Tășnad, it seems improbable that the whole area was used simultaneously. In the middle Neolithic Alföld linear pottery culture, rows of houses were occupied one after the other, as, for example, at Tiszaszőlős-Domaháza-Puszta (Domboróczki 2010: 210). A similar pattern may have been common in the preceding period as well.

At Tășnad and other comparable sites, dug features only appear once the occupation layer has been removed, as both occupation layer and dug features are normally dark greyish brown or black and consist of heavy clay. In addition, soil formation and a changing ground water level have probably masked former disparities in terms of colour and composition. Most finds in the occupation layer occur in dense concentrations of *c.* 0.6-0.9m in diameter and separated by areas almost entirely devoid of bigger finds, both horizontally and vertically. We interpret these concentrations as being individual dumping episodes outside a dwelling, maybe on an empty plot of land. If this assumption is correct then each of these dumping episodes represents a unique moment in time relating to a specific household, even if the corresponding houses cannot be identified as yet.

Despite an extensive programme of flotation – with ten litres of soil from each excavated square and spit being processed – very few plant remains have been found so far. Systematic bucket flotation has delivered hardly any carbonised seeds, and charcoal is rare except for the top spits. Amanda Leon, who is in charge of the archaeobotany programme, has tested a variety of procedures in the hope of improving the recovery rate, albeit without significant success. After processing samples from other sites in the area with similar soils – a Pișcolt pit from Blaja (corresponding to Linearbandkeramik in Alföld, the Great Hungarian Plain: Németi and Hágo 2015) and Eneolithic pits from Moftin – with the same negative results, we suspect a deleterious influence of the heavy clay soil, either in terms of the destruction of carbonised remains or their failure to float after prolonged soaking to break up the lumps. A separate programme of wet sieving yielded scarcely better results (Pomazi 2014). The effect of soil and especially of argilliturbation on charred remains is under-researched, however, and we are planning taphonomic experiments using modern charred cereal remains.

Alternatively, the dearth of plant remains – compared, for example, with the *Linerarbandkeramik* (LBK) settlements (Bakels 1995; Bogaard 2004, 2011; Kreuz 1990) – could also indicate the existence of separate crop processing areas outside of the core settlement. The heavy fraction of the archaeobotanical flotation shows that microrefuse from chipped or ground stone work is also very rare in UCL Trench 1. This tallies with the densely built-up space inside the settlement, which does include not any of the yards associated with individual houses as in the later LBK.

Soil analysis

The thick soil cover over the Neolithic remains provided effective protection from later disturbances. This encouraged us to devote more attention to the actual composition of the soil itself. Since 2017, we have therefore been systematically taking samples to analyse the soil composition (granulometry, loss on ignition), magnetisation and pH from each excavated square and spit. Elena Chernycheva is analysing the content of major and trace elements as indicators of human activity on the site.

Soil samples were taken from spit 8 (*c.* 1.80m beneath the surface) in each excavated square. After cleaning the surface of the excavated area, a sample was taken from the centre of each quarter-square if the sediment was homogeneous. If any features were visible, separate samples were taken for every feature or layer. Sub-samples from the same contexts were then combined to eliminate any local variation.

Spit 8 was chosen because it is situated near the lower limit of the occupation surface. However, this choice was based on an educated guess. As yet, the vertical movement of prehistoric anthropogenic trace elements in soils is badly understood. In settlement contexts, it is mainly the distribution of phosphates that has been investigated (Stäuble and Lüning 1999; Lüning and Reich 2011; Weiner 2010: 59-61). The effects of different

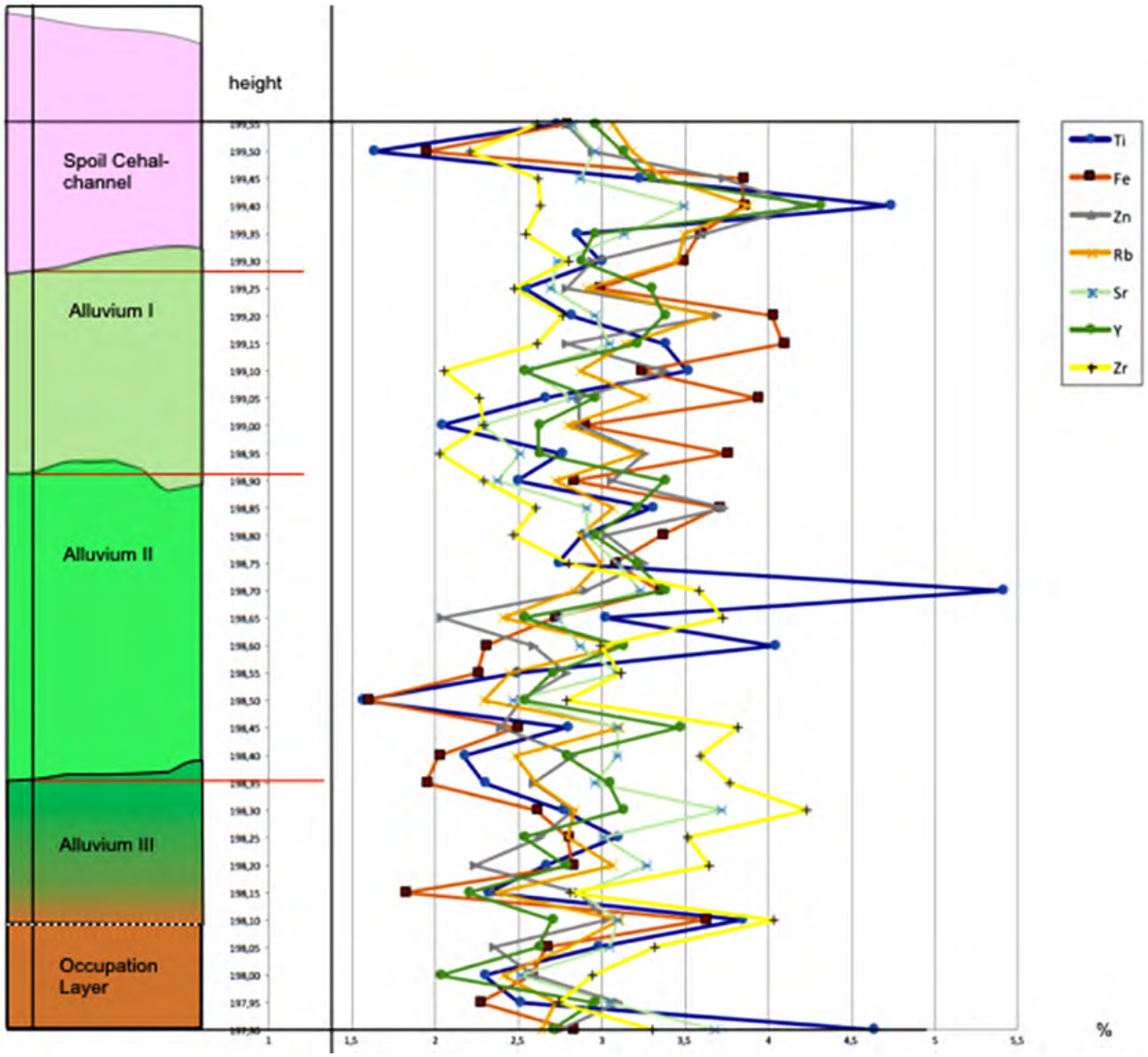

Figure 1. Tăşnad-'Sere', South-section of UCL Trench 1, horizontal distribution of selected elements (normalised values) detected by p-XRF.

soils and groundwater regimes have not been explored systematically. Therefore, in future the horizontal distribution of trace elements will be sampled in more detail. As the Neolithic surface is sloping to the East, the artificial horizontal spits may intersect different parts of the occupation surface.

The bulk content (%) of major and trace elements (Na, Mg, Al, P, S, K, Ca, Ti, Mn, Fe, Cu, Rb, Sr, Ba, Hg, Zr, and Sn) was determined using an X-ray fluorescent spectrophotometer. The determination of the concentrations of macro- and micro-elements in the soil was carried out by measuring the mass fraction of metals and metal oxides in powder samples. The soil samples were dried and ground to a particle size of about 50 microns. The ground sample (200mg) was then pressed into pellets and analysed using a spectrometer.

The inorganic phosphorus content was determined after extraction using a strong acid (2N HCl) at a soil-liquid ratio of 1:20 and determined colorimetrically through reaction with ammonium molybdate. It is possible to measure about 70-80% of the total phosphorus after this treatment.

Sulphur, inorganic phosphorus, potassium and calcium have high values in the area of the pit and of feature 2, which is probably a small pit (Figure 3). The sulphur and phosphates may have originated from rotting organic refuse. Ash is a possible source for S, K, Ca and P (Braadbaart *et al.* 2012: tab. 3). The calcium could also originate from decomposed bone. Most of the bones in the occupation layer and in the upper layers of features are badly preserved and often completely lacking in collagen. Spit 8 in fact contains the maximum number

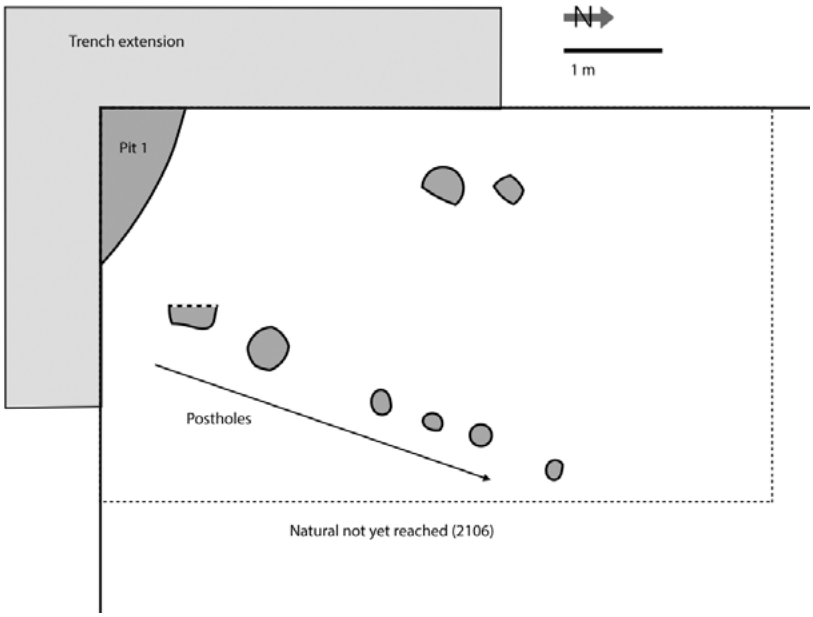

Figure 2. Features in UCL-Trench 1, south-east corner.

of preserved bones, while the number of most other materials peaks in higher layers. This, together with a lack of bones of small mammals or birds in the animal bone assemblage (El Susi 2017), hints at a considerable loss of bone. However, the pit does not show up in the strontium distribution.

Other elements, such as Al and Mg, show a regular W-E decline, which corresponds to the absolute height. The distribution is thus most likely related to groundwater action and probably postdates the archaeological deposits. The distribution of Fe_2O_3 shows a similar pattern, but the area of the pit and its environ has low values. This corresponds to the macroscopic observation that iron staining is less common in the anthropogenic sediments, which may relate to a different redox-potential. Most of the heavy elements, as well as sodium and magnesium, bear no relation either to features or to absolute height. Of course, they may reflect activities in the occupation layer or corresponding finds/concentrations, which are yet to be analysed.

Overall, the results are promising, but can only be fully interpreted once the excavation is finished. The exploratory 1m sampling grid is too coarse to catch small features like postholes, so we will try using a finer grid. However, worm casts and fossil polygonal cracks introduce a pattern of their own, which can easily mask small-scale anthropogenic signals. We will explore the use of a pXRF device in areas where we expect subsurface features that are not yet visible. This offers a reasonably fast way to analyse the sediment and could be of great help in the excavation and interpretation of comparable layers.

Soil biology

The analysis of soil microorganisms has been used successfully in the study of Medieval relic soils (Chernycheva *et al.* 2014, 2015 and 2016). We held out little hope of success in this much older sediment; however, preliminary studies have found soil microorganisms still to be present, albeit in lower concentrations.

The amount of lipolythic microorganisms was examined to identify fatty compounds introduced into the soil in the past. The determination of lipolythic microorganisms was performed using the plate count method. Briefly, soil samples (1g) were mixed with 10ml of 0.5% tetrasodium pyrophosphate, with the resulting suspension then being serially diluted: 1ml of each dilution was added to 9ml water and then poured into sterile Petri dishes containing (w/v): 0.5% polysorbate 20, 5% polysorbate 80, 1.0% peptone, 0.5% NaCl, 0.01% CaCl2 and 2.0% agar. Soil samples plated on agar were incubated at 28°C for seven days.

While differentiating between vegetable and animal fats is not possible with this method, it still provides an important way of exploring the organic component of prehistoric refuse. The analysis revealed a concentration of lipolythic microorganisms around Pit 1. As the area above the dug feature was relatively poor in finds, this may indicate that it was once full, with the area being used to deposit organic refuse. This is supported by the presence of thermophilic bacteria.

Adaptation to a new type of environment

Tășnad is located in the boundary region between the hills of Transylvania (*Crișana*) and the Great Hungarian

plain to the West. According to most Romanian authors (Lazarovici 1996, 1998; Virág 2008), the first Neolithic settlers in this area came from central Transylvania, with Gura Baculuі (Lazarovici and Maxim 1995) representing one of the oldest known Neolithic settlements in the country (Luca 2011). In contrast, many Hungarian archaeologists favour a model of Neolithic colonisation from the South, following the course of the Tisa. Only a greatly increased number of ^{14}C-dates combined with a detailed stylistic analysis of the pottery can help decide between these two possibilities. However, whichever route was followed, the settlers in Tășnad and a number of comparable locations in the piedmont had to adapt to a new environment. The 'Neolithic package' ultimately derived from Western Asia was made up of cultigens and domesticated animals adapted to dry steppic conditions. In contrast, the Alföld, before the large scale drainage and meliorisation begun under Joseph II, was a patchwork of riverine woodlands, steppe and swamps (Feurdean *et al.* 2015; Magyari *et al.* 2010). Several sites in the Northern Alföld have already illustrated the great importance of hunting to the human diet in this area (Bartosiewiecz 2005; Kovács *et al.* 2010) as well as other areas (El Susi 2011; Orton 2008: fig. 5.9) and, as the work of Georgeta El Susi indicates (El Susi *in prep*.), this is also true for Tășnad, where 42% of the identified bones are from wild animals. Both steppe (wild horse, wild ass) and hill species (brown bear) are present. If we receive the necessary funding, we plan to perform isotope analyses to obtain a better picture of the habitats of both domestic (cf. Knipper 2011) and wild animals.

Given the extreme rarity of charred plant remains, we had to turn to alternative sources of evidence for the environment and agricultural activities at Tășnad – namely, phytoliths and the frequent plant impressions in the pottery. Phytolith samples have been taken systematically since 2015, but have not yet been analysed. The utility of plant impressions on the surface of pottery depends on their origin, i.e. whether they were caused by the use of organic temper, the accidental inclusion of plant remains present in the settlement for other reasons at the time the pottery was produced or the use of chaff and similar materials as a separating agent during the production process. This problem is being investigated by Bruno Vindrola as part of his PhD dissertation.

Mobility and social structure

Currently, genetic studies indicate a solution to the heated debate surrounding the mechanism by which agriculture spread to Europe in terms of population movement, given a strong genetic input from Southwest Asia in most early Neolithic populations. However, this does not explain the nature of this mobility. Demic diffusion (Ammerman and Cavalli-Sforza 1973),

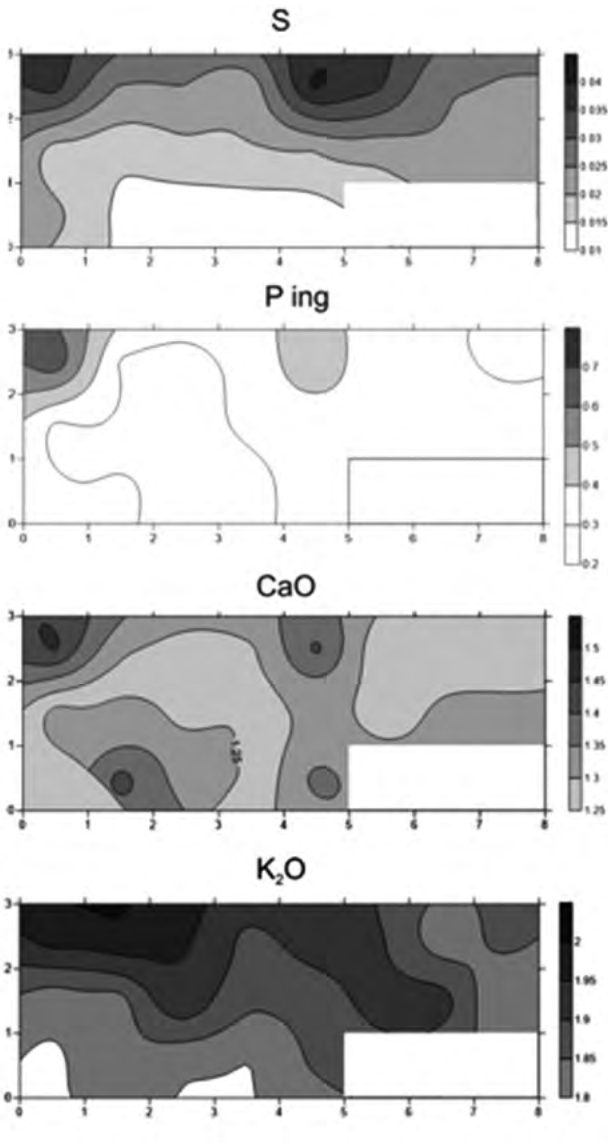

Figure 3. Distribution of sulphur, inorganic phosphorus, potassium and calcium. The values are averaged per square, the distribution map is created with Surfer, using kriging. The shape of the concentrations are thus determined partly by the values in adjacent squares and do not represent the variation inside the square.

colonisation, leap-frog colonisation (see Forenbaher and Miracle 2005: tab. 1 for a useful overview) have been discussed as possible causative mechanisms.

Given the lack of formal cemeteries in the entire Starčevo-Körös-Criș (SKC) area, and the concomitant lack of human remains, genetics is unlikely to be of much help here. There are four skeletons from Tășnad (Astalos and Virág 2006-2007: 79-80; and analysis currently in preparation by R. Pinhasi), but it is unclear how representative these and other isolated burials are. The isotope data for the LBK, commonly derived from either the Starčevo-Körös-Criș or the Starčevo culture alone (Bánffy 2006, 2014; Bánffy and Oross 2010)

indicate high individual mobility (Hofmann 2016), which may go a long way to explaining the extreme homogeneity of this culture over large areas. For the LBK, this high mobility is also reflected in the presence of different forming techniques and paste composition within the same settlement (Gomart 2014; Gomart *et al.* 2017). Corresponding studies for the SKC are being prepared by Sébastien Manem.

While individual mobility cannot yet be proven for the SKC, it should certainly be included in the list of possible mechanisms for the northward and westward spread of the culture complex. We are therefore looking for indications of variation within the settlement. Such variation can also provide indications about the organisation of the villages. Are land and other resources held in common, or controlled by individual households? Are artefacts manufactured together, or do individuals learn from family members?

Pottery, while the most frequent category of find, is unfortunately highly fragmented. In addition, the late Criș-pottery (phase IIIB/IV according to Lazarovici 1979) is only very sparsely decorated. Both factors limited the scope for stylistic analysis. Consequently, we concentrated on paste composition and surface treatment. During excavation, we noticed that a pottery concentration would very often be dominated by sherds of one colour and similar thicknesses, i.e. probably the remains of a single pot. In all cases, however, they were accompanied by other artefacts like chipped stone, ground stone and burnt clay, as well as a few sherds of differently coloured pots. It appears that the breakage of a particular pot had initiated a general clean-up. The assemblage would therefore represent the taphocoenosis (Sommer 1991) present at one specific moment in time on the floor of an individual house. The colour of the pottery ranges widely, from light grey to orange, red, brown, dark grey and black. Pottery surface colour rarely receives much attention, but we were interested in whether the colour corresponded with vessel shape/pottery use and was caused by clay selection or paste preparation, or whether it was intentionally created during the production process through the addition of pigments or a manipulation of the firing process. If colour is related to the use of a vessel, there should be a correlation between shape/size, temper and colour. If pigments are used, this could indicate personal or household preferences.

Pottery

Composition

In a pilot study, petrographic thin section analysis (Quinn 2009, 2013; Whitbread 1995, 2001) was carried out on 13 samples (Figure 4). The samples are characterised by a soft fine fabric (apart from TS 9 and 10, which have a thicker wall and are coarser), with small white and red inclusions and numerous 'channel' and 'vesicle' type pores. The colour of the samples varies from light brown to red and very dark grey. Particles previously identified as grog by the archaeologists turned out to be natural clay pellets contained in the clay.

Viewed under the microscope, the 13 specimens analysed do not display any significant compositional variability (Figure 5). Therefore, it was not possible to subdivide them into meaningful separate petrographic groups. Samples are characterised by the presence of equant and elongate sub-angular inclusions of quartz, polycrystalline quartz, feldspars, muscovite and, less frequently, chert, amphibole, clay pellets and opaque minerals. More rarely, fragments of metamorphic rocks, probably schist, occur. In all the specimens, the average grain size of the inclusions is around 0.4mm and the maximum size is 0.8mm, while TS 9-10 shows a coarser texture (average 0.6mm, maximum 1.2mm). All specimens apart from TS 3 are characterised by organic temper, which is particularly abundant in samples TS 1, 5, 6, 11, 12 and 13 (Figure 5). The bimodal distribution of the inclusions characteristic of coarser samples (TS 9 and 10: Figure 5e-g) could indicate tempering with a material derived from metamorphic rocks, probably schist.

The matrix of the majority of samples is optically active (Quinn 2013: 190-198). This indicates low firing temperatures. Some samples (TS 1, 4, 7 and 8) have a matrix that is optically inactive, but these may have been re-fired in a destruction event, as indicated by several extremely highly fired pieces of daub from UCL Trench 1 (Figure 6), probably the result of a house fire that reached temperatures of well over 1100°C, possibly 1200°C or even higher (Veronesi 2014).

The analysis of clay samples collected *c.* 15m to the east of UCL Trench 1 shows that suitable clay sources for pottery making whose compositional characterisation is compatible with that of the samples analysed were available in the immediate vicinity of the settlement. These alluvial clay samples are characterised by the presence of a coarser sandy fraction that includes quartz, chert, muscovite, amphibole and rare fragments of metamorphic rocks (Figure 4h). Sources of tertiary clay, used until recently for brick making and still used for mud-bricks, exist in several locations on the hilltops west of the town of Tășnad (Marinescu *et al.* 1967).

While it would require a larger number of samples to monitor the compositional and technological variability in pottery paste preparation at the site, we can still make some preliminary observations. First of all, it is clear that the organic material was the most common temper used in Tășnad. Surface impressions on other

sherds indicate the use of fine chaff or grasses. This organic temper was used in combination with mineral and rock tempering when producing vessels with thicker walls (cf. TS 9 and 10). Indeed, large fragments of micaceous schist occurring in the hills located some 500m away were found in the occupation layer.

These results fit well with those of petrographic studies carried out on samples from contemporary sites in Southern Romania (Kreiter *et al.* 2013; Spataro 2014). In particular in Southern Romania, Spataro (2014) observed a low variability in the temper employed in pottery manufacturing, moderate firing temperatures and the absence of any strong correlation between shape and fabric in Miercurea and Parţa, as well as a general lack of evidence for any pottery exchange in the Starčevo-Criş culture in general.

Colour

The ceramic matrix is not homogenous, its colour changes considerably within each specimen and from sample to sample. In PPL (plane polarised light), the samples' matrix is light yellow to yellow and grey. In XPL (cross polarised light), the matrix is light red to brown; in the majority of samples, it is red (in TS 4 and 7) or very dark grey (TS 8). Most of the samples with organic temper are characterised by a black core and light red edges (TS 2, 6, 9 and 10). Even if it is tempting to interpret the high variability in the colour of the fabrics as the outcome of different deliberate firing procedures used with the aim of obtaining vessels of different colours, this phenomenon could also be the result of the non-controlled atmospheric conditions in which these vessels were fired. The presence of a 'black core' in the majority of the samples could indicate that pottery was fired in a bonfire, where the firing is too short to permit the complete oxidation of the ceramic body (Cuomo di Caprio 2007: 494).

The results suggest a differentiation of ceramic paste according to vessel thickness and form, but no correlation between colour and paste. The slight differences in the ceramic matrix could have been caused by the use of different clay sources, but in an alluvial environment the differences are too slight to allow us to make any definitive statement. More analysis, comparing pottery from different squares, is being conducted by Silvia Amicone and Johannes Seidler (University of Tübingen).

In order to explain the observed colour variability it is important to ascertain whether this pattern reflects the original repertoire of colours the producers wanted to achieve or if secondary factors are responsible for the pattern detected in the archaeological record.

Pottery colour is primarily determined by the choices taken by the artisans during the production process (e.g. Rice 2015: 276-290). First of all, the selection of clay plays a very important role in determining the vessel's colour. Different methods of processing clay (e.g. levigation or the addition of temper) can also alter the compositional characteristics of the original clay and have an impact on the final colour of the pottery. Very importantly, surface treatments like the addition of a slip or pigment can also have an impact (Cuomo di Caprio 2007: 305-376).

The most important factor is probably the firing process (Rice 2015: 289). It is during this phase of the production process that pottery acquires different colour according to the properties of the raw material and the firing technique employed. The amount of oxygen present and the temperature reached are the determining factors here. For example, firing under oxidising conditions will result in light coloured pots. When there is a lack of oxygen, the fuel does not burn completely and the atmosphere becomes full of free (elemental) carbon, which combines with oxygen to produce CO. Under these conditions, dark iron oxides are formed (Jones 1986: 762-763). Another way to obtain black colours is the introduction of carbon during the firing process (smudging: Jones 1986: 764).

However, it is important also to take into consideration other factors that may have altered the original surface colour of the pottery. Firstly, there is the possibility of erosion. The colour of the body of the pot can differ from a slip that became removed by erosion or stick to the ground when removed, as is common in Tășnad. More severe erosion can remove parts of the surface of the pot proper and expose the core, which is often less oxidised and thus darker. We have uncovered some sherds with different surface colours that were clearly caused by the partial erosion of the surface. Experiments are currently under preparation to elucidate the change of colour and outer appearance of pottery due to abrasion using badly provenanced sherds. The colour of the sherds from UCL Trench 1 also needs to be compared with that of better preserved assemblages from the same site located at slightly higher elevations.

In addition, pots fired in an open fire can have several surface colours ('flaming'), which is caused by different exposure to oxygen and direct contact with the flames. Overall, this phenomenon seems to be quite rare in the Tășnad assemblage, but, again, this observation is in need of careful study and quantification. A preliminary firing experiment with pots made of local clay in shallow pits produced pots with dark red and black surfaces that were far more mottled than the archaeological samples. Further firing experiments in more controlled conditions will be conducted in order to find out whether all the surface colours observed

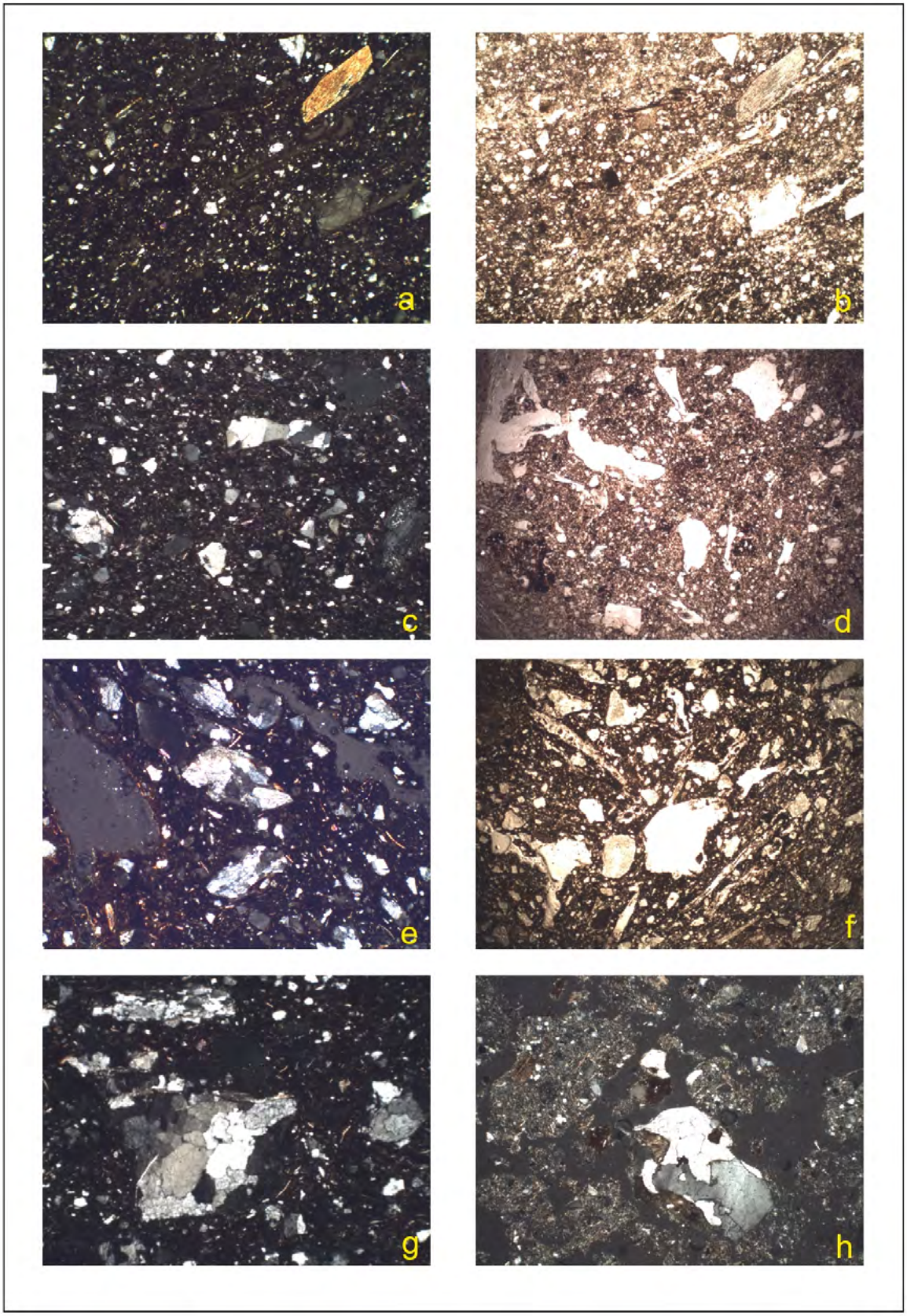

Figure 4. Thin section photomicrographs of selected ceramics from Tăşnad analyzed in this study. a) TS 8: organic tempering (XP). b) TS 8: organic tempering (PPL). c) TS 3: non tempered (XP). d) TS 5: abundant organic tempering (PPL). e) TS 10: mineral and organic tempering (XP). f) TS 10: mineral and organic tempering (PPL). g) TS 10: metamorphic rocks (XP). h) Geological sample (XP). Image width = 3mm (a, b, c, g, h); except d, e, f = 6mm.

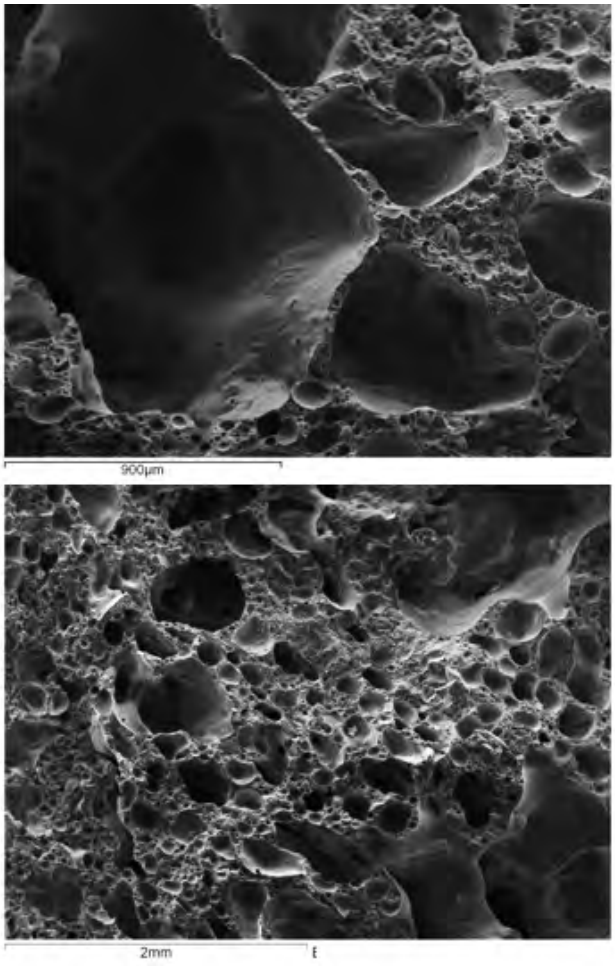

Figure 5. Secondary electron images of the fresh fracture of a piece of slagged clay from Trench 1 at different magnitudes. The extent of the bloated area, the size of the pores and the smoothness and glass-like appearance of the surfaces are clearly visible and indicate temperatures over 1100°C.

can be produced with local clays using different firing conditions alone. This is supported by the analysis of sherds from other sites. For example, Luca and Tudorie (2012: 23) report finding only 7% of flamed sherds from Sălişte a (Cioara) in Alba County. Hence, the firing of prehistoric pots was better controlled than commonly believed. However, we also need to determine how deep into the matrix the effects of flaming reach, something which determines the effects of subsequent erosion.

Cooking pots can also change colour during their use on the hearth. In this case, as with flaming, change is restricted to the outer surface (Forte *et al.* 2018). Finally, the original colour of pottery could be altered by secondary firing during random or intentional destruction episodes – for example, a house burning down. The presence of over-fired sherds and burnt clay in the archaeological record can be seen as indicative of this phenomenon.

We also plan to analyse the pottery surfaces to ascertain whether pigments were used to produce the different colours observed. Pigments used in pottery painting have been studied mainly using ED-XRF spectrometry (López-Montalvo *et al.* 2014; Olivares 2013; Roldàn 2014), SEM-EDS, X-Ray diffraction or Raman spectrometry (e.g. Buzgar *et al.* 2013 for the area under consideration). The use of pigments in slips to colour the whole surface of a pot could be demonstrated by using the same technique; however, this has not yet been studied systematically. With most possible admixtures, the way the pot is fired substantially affects the results.

Phytoliths

Ongoing work on microfossil extraction (Lionello Morandi, University of Tübingen) also revealed the

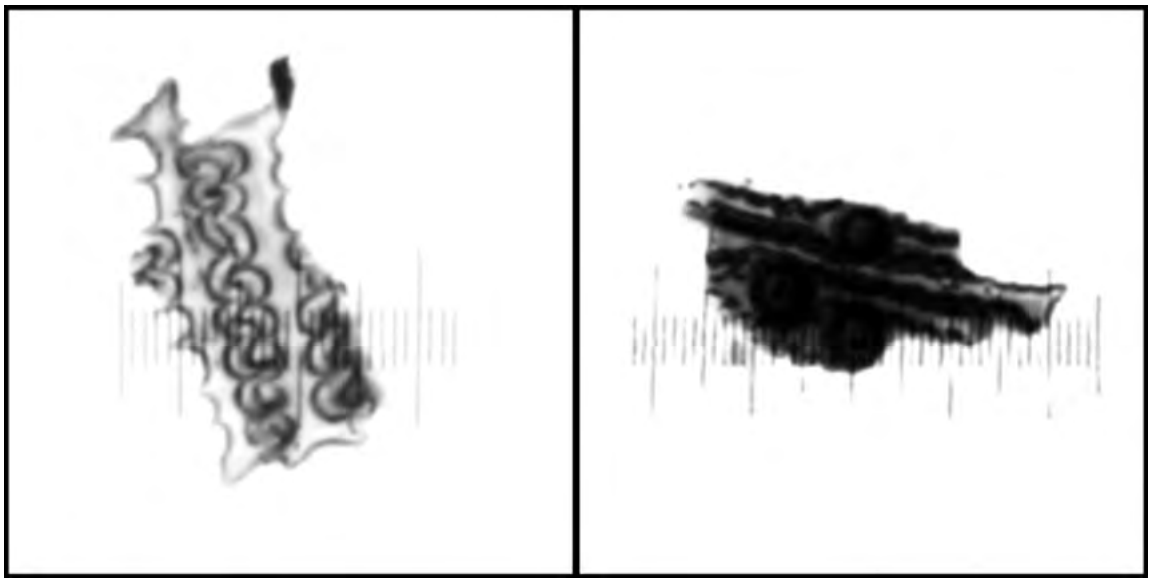

Figure 6. Micrographs showing burnt phytoliths within the ceramic body of Criş-pottery from Tăşnad.

presence of both pollen and phytoliths in the pottery. The pollen was badly preserved and could only be identified at a family level; however, these results match with the charred remains identified by Péter Pomazi (2014). Phytoliths (Figure 6) have also been identified in a Körös ritual object (cf. Kreiter *et al.* 2017), as well as in or on the surface of pottery (Kreiter *et al.* 2013, 2014; Starnini *et al.* 2007; Szakmány and Starnini 2007). Phytoliths melt between 750 and 800 °C (Starnini *et al.* 2007; cf. Pető and Vrydaghs 2016), which means that this temperature was not reached in the interior of the pottery during the firing process.

Phytoliths have been used to trace imported ceramics (Vrydaghs *et al.* 2014; Wallis *et al.* 2014). They can be also be used to identify the type of organic temper used, and, in some cases, the season of use (Vrydags *et al.* 2014: 36). However, this raises the question of how they got into the clay in the first place: as parts of plants selected as a temper, in cow dung (Delhon *et al.* 2008; Shahack-Gross 2011: 207) used as a temper or as part of the original sediment (cf. Ting and Humphris 2014: 35)? Surface deposits can also result from separating agents like chaff. Bruno Vindrola is currently studying the voids in Criş pottery using microtomography so as to obtain a better idea of the shape of the organic temper. If the organic temper is derived from cow dung, the phytoliths could potentially offer information as to the season of pottery making and the location of grazing areas and their organisation, i.e. communal or dispersed. As our trench is located on commonly owned land in Tășnad, which is still used for grazing today, we have been systematically collecting modern dung samples in order to investigate the identifiable plants and their potential seasonal variation in comparison with the current vegetation (cf. Verges *et al.* 2016).

Conclusion – does it work?

All in all, the use of archaeometry during the excavation has opened up intriguing new vista. The main difficulty seems to be that archaeologists are often simply not aware of methods already in existence in other disciplines. Once we discover them, we tend to become overenthusiastic due to a lack of understanding of the limitations of said methods. Scientists seem very reluctant to give definite answers, but the same is probably true the other way around. In addition, archaeologists do not understand the rationale behind scientific protocols. Most frustratingly, the hermeneutic circle of any empirical methodology sits badly with the archaeological process, which depends on the application of a consistent excavation method, ideally to the whole site. An excavation method once adopted is rarely changed, as evidenced by the various national schools of excavation. Very often we must first realise that we need to dig differently and solve a whole battery of subsidiary methodological problems before we can return to our seemingly simple main question. In the case of the Tășnad excavation, this probably means that, drawing on all that we have learned, we will need to begin a second trench, collect all the samples and data we need and continue to discover new problems and questions. Starting this process earlier rather than later has proved extremely beneficial, if occasionally exasperating.

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Archaeometry and Individual Biographies: Evidence from Radiocarbon Dating, Isotope-Based Diet Reconstruction and Metal Composition from the 14th-17th-Century Cemetery in Bărăşti (Southern Romania)

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Abstract

This article discusses the results of the radiocarbon dating and a few analyses of carbon and nitrogen stable isotopes for diet reconstruction and elemental composition of metal from the late medieval cemetery (14th/15th to mid-17th century cal AD) with church in Bărăşti (Argeş County, Southern Romania) and argues that, even if only few in number, these analyses still allow us to study people at the level of the individual. This first stage in the archaeometric investigation of the site in Bărăşti also represents the first case study to be published on isotope-based diet reconstruction for medieval Wallachia (present-day Southern Romania).

Keywords: radiocarbon dating, isotope-based diet reconstruction, archaeometallurgy, Medieval cemetery, individual biography.

Introduction

This article presents the results of a series of archaeometric analyses – i.e. radiocarbon dating and analyses of carbon and nitrogen stable isotopes for diet reconstruction and elemental composition of metal – carried out as part of the investigation of the medieval cemetery in Bărăşti (Cicăneşti commune, Argeş County, Southern Romania: Figure 1). The investigations presented here are at an early stage, but, despite methodological difficulties arising from the small number of samples and analyses, they were considered worth publishing because data of this kind are largely missing for the study region and period. In the interpretation of this paper, the available data are relevant primarily at the level of the individual rather than the level of the group buried at Bărăşti, although some inferences on the wider social and economic context are also possible. The paper will also indicate the archaeometric analyses to be carried out in the near future in order to obtain a more complex image of this medieval community.

Bărăşti (Cicăneşti commune, Argeş County, Romania) is a village in the southern part of present-day Romania, in the Subcarpathian highlands (Figure 1). It lies approx. 17 km north-west of Curtea de Argeş, one of the capitals of Wallachia during the 14th-16th centuries, and approx. 65 km west of Câmpulung, which was the first capital of Wallachia and which, by the period of interest here, i.e. the 14th-mid-17th century, had become the main customs checkpoint on the trade route linking Transylvania to Wallachia, the Lower Danube and the Black Sea, and further to the Asian part of the Ottoman Empire (Papacostea 1983: 9-34). The site of interest here is located in the 'Sălişte' area of the northern part of the present-day village on a plateau bordering the steep slopes of the Bărasca Valley – site code in the Romanian National Archeological Register: 15457.01.

Prior to the excavations undertaken in 2012, the only archaeological information on Bărăşti consisted of a report from 1871 mentioning the existence of stone ruins in a place called 'Sălişte' (Cristocea *et al.* 2012). Medieval written sources first mention the village at Bărăşti in 1561-1562, albeit only in passing and in connection with property issues relating to neighboring localities (Roller 1952: 155, document 187); by 1629 Bărăşti is denoted as being a village with serfs (Mioc 1969: 505, document 268) – a status that was most probably achieved already in 1595 thanks to a bill

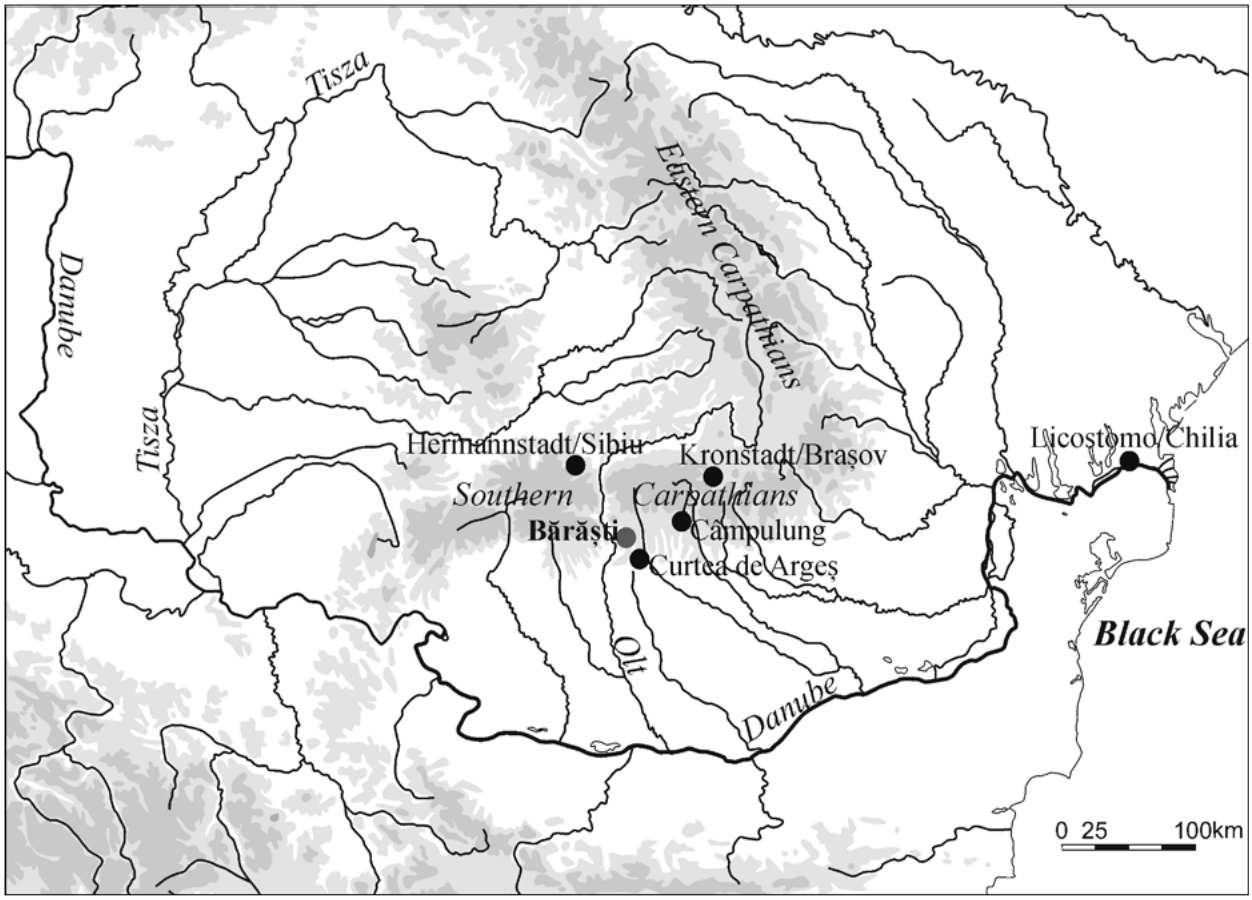

Figure 1. Location of Bărăşti and the other localities mentioned in the article (base map by Iuliana Barnea).

forcing into serfdom any peasants still free by that date (Panaitescu 2002, ch. Mihai Viteazul şi ţăranii).

Excavations (carried out in June 2012 and lasting one week) uncovered the remains of a church with only small parts preserved *in situ* and nine graves, albeit further graves most probably also existed in the unexcavated area (Figure 2). According to the reconstruction performed by the excavators, this was a regular countryside church: approx. 11 x 4m on the outside, with wooden elevation – as deduced from the large number of pegs found during excavation and the lack of mortar, bricks and rubble (Cristocea *et al.* 2012). Nevertheless, because the width of the foundations (1.10-1.15m: Cristocea *et al.* 2012) is rather large for a wooden church (e.g. the average width for the 13th-17th century Orthodox churches of Southwestern Transylvania is around 0.80-0.90m: Rusu 1997: 174, 179, 206, 224, 238, 247, 259), this could also have been a stone church (with bounding material not preserved), in which case it would differ from the typically wooden Wallachian countryside churches (Creţeanu 1968; Vătăşianu 1959: 127, 149). Based on the artefacts found, the excavators argued that the church had been in use from the 15th/16th century through to the early 18th century (Cristocea *et al.* 2012, with illustration).

The nine graves each contained the remains of one individual at depths of between -0.60 and -1.00m below the present-day surface. Due to high soil acidity, all the skeletons were in a bad state of preservation, most being reduced to the skull (or parts thereof) and parts of the larger bones (mostly the femur, tibia and pelvis) (Cristocea *et al.* 2012). The dimensions of the bones indicate that all of the deceased had passed through childhood and probably also adolescence, albeit no anthropological analysis was carried out. Apart from traces of wood from the coffins (missing only in Graves 4 and 9), the graves contained only few artefacts, all of which were of common, not narrowly datable types: in Grave 3, a silver ring; and, in Grave 4, four gilded silver buttons that were globular in shape, two with attached gilded silver wire originating from a decoration on the deceased's garment (see below Figure 4). The latter were erroneously dated by Cristocea *et al.* (2012) to the 16th century: these buttons were in use at least during the 11th-16th centuries (Ioniţă 1996-1998: 312; fig. 49.12-15), while Dumitriu considers them chronologically irrelevant (Dumitriu 2001: 81; pl. 13.11).

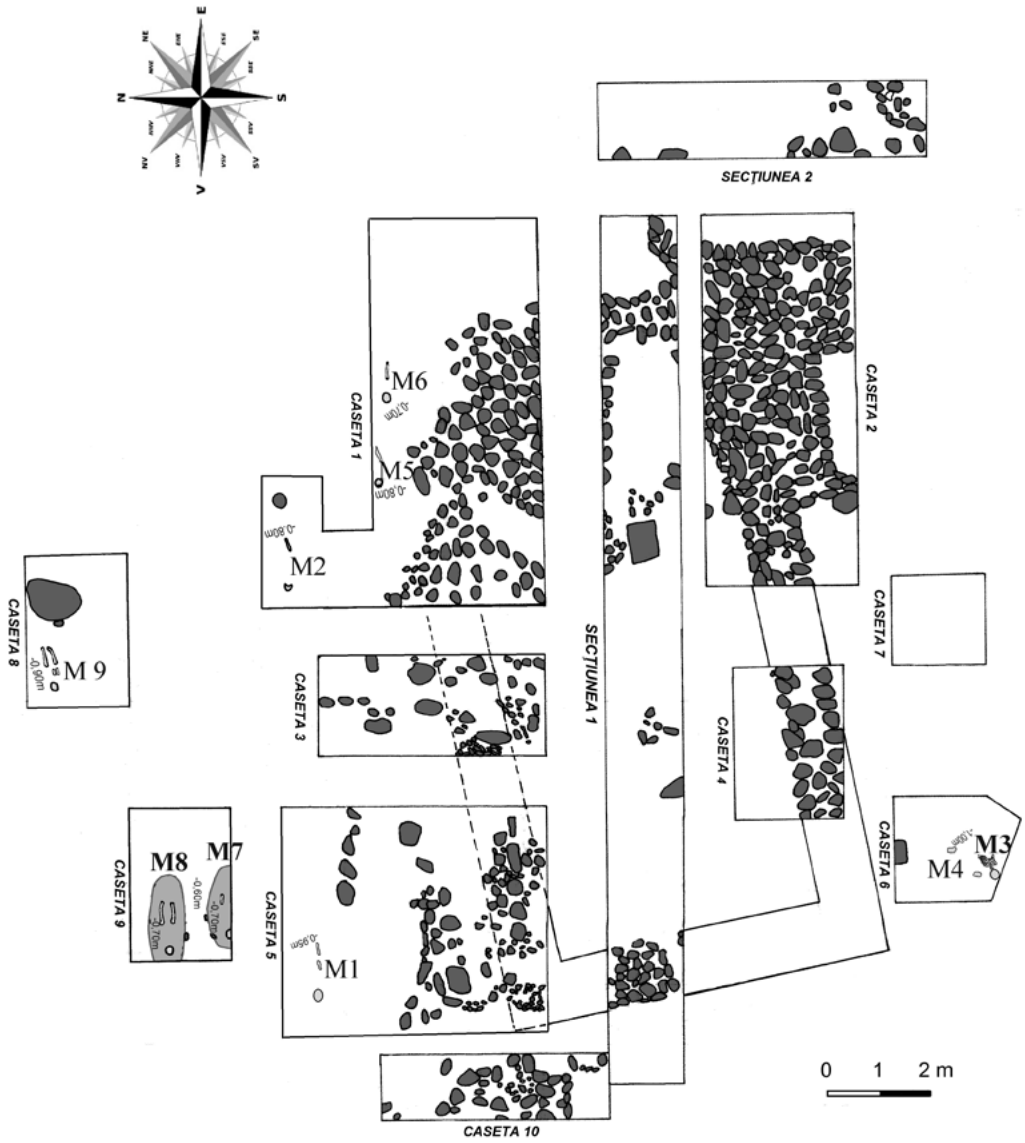

Figure 2. Bărăşti: General plan of the 2012 excavations (from Cristocea *et al.* 2012, with clearer marked graves).

The excavators recorded no stratigraphic relationship neither between the church and any of the graves nor between graves.

From the above description it transpires that the radiocarbon dating of the organic material from the graves currently represents the only means of establishing a clearer chronology of the site. Analyses of C and N stable isotopes for diet reconstruction were carried out to verify possible age offsets in the radiocarbon dates of human bones and to obtain data on human diet. So far this was only possible for three individuals (Graves 3, 7 and 8), as only in these cases was there any collagen left after the radiocarbon dating (to analyze the other skeletons the collagen will need to be prepared from the remaining bones). Metal composition analysis supplements the data on objects and their owners.

Radiocarbon dating and diet

The data

The most reliable radiocarbon dates would have been obtained from the remains of coffins, as the wood they were made of was most probably cut shortly before burial. Unfortunately, these could not be dated because the cellulose was badly preserved and disintegrated during bleaching. Consequently, the radiocarbon dating had to rely entirely on human bones. Eight of the nine skeletons were dated, the skeleton in Grave 6 being too badly preserved for collagen extraction. The skeleton in Grave 7 was dated twice to verify its much earlier radiocarbon age compared to the others and to reduce the error term of the first dating (Table 1). The dated material was Type I collagen. No contamination that

Grave no.	Sample label	$\delta^{13}C$ (‰) VPDB	$\delta^{15}N$ (‰) AIR	Conventional ^{14}C age (yr BP)	Calibrated ^{14}C dates (cal AD; atmospheric calibration)	
					1 σ (68.2%)	2σ (95.4%)
Grave 1	14-bis_M1			301±25	1522-1575 (50.2%) 1626-1646 (18.0%)	1494-1602 (70.4%) 1616-1651 (25.0%)
Grave 2	14-bis_M2			437±34	1430-1469 (68.2%)	1415-1512 (91.3%) 1601-1616 (4.1%)
Grave 3	14-1 / M3	-19.01	7.80	335±34	1490-1529 (21.8%) 1545-1603 (32.9%) 1611-1634 (13.5%)	1470-1642 (95.4%)
Grave 4	14bis-M4			309±22	1522-1575 (52.4%) 1625-1643 (15.8%)	1495-1602 (73.1%) 1616-1647 (22.3%)
Grave 5	14-2 / M5			375±35	1451-1521 (49.6%) 1592-1620 (18.6%)	1444-1529 (55.4%) 1545-1634 (40.0%)
Grave 7	14-3 / M7	-17.83	10.27	602±69	1300-1370 (50.9%) 1381-1404 (17.3%)	1280-1430 (95.4%)
Grave 7	14-bis_M7+M8 (G)			563±26	1323-1346 (35.1%) 1393-1413 (33.1%)	1310-1361 (51.6%) 1386-1424 (43.8%)
Grave 8	14-bis_M7+M8 (A)	-19.04	8.06	328±25	1513-1530 (11.7%) 1539-1601 (43.2%) 1617-1635 (13.2%)	1483-1643 (95.4%)
Grave 9	14-bis_M9			327±27	1513-1530 (11.5%) 1538-1601 (43.9%) 1617-1635 (12.9%)	1482-1643 (95.4%)

Table 1. Bărăşti-'Sălişte': The radiocarbon age of eight skeletons and the $\delta^{13}C$ and $\delta^{15}N$ values for diet reconstruction obtained for the skeletons in Graves 3, 7 and 8 (the radiocarbon dating was carried out at the RoAMS Laboratory in Măgurele, Romania, but the dates do not have a laboratory identifier and reference number because they were among the first samples dated at the laboratory, prior to its accreditation by the SIRI).

could alter the ^{14}C age was identified during chemical pretreatment (see Appendix).

The results of the C and N stable isotopes for diet reconstruction for the individuals in Graves 3, 7 and 8 are presented in Table 2. The C:N ratio falls in the interval 2.9-3.6, indicating no contamination of the collagen (DeNiro 1985).

The individuals in Graves 3 and 8 were most probably adults, as can be inferred from the space occupied by the preserved parts of their skeletons and, in the case

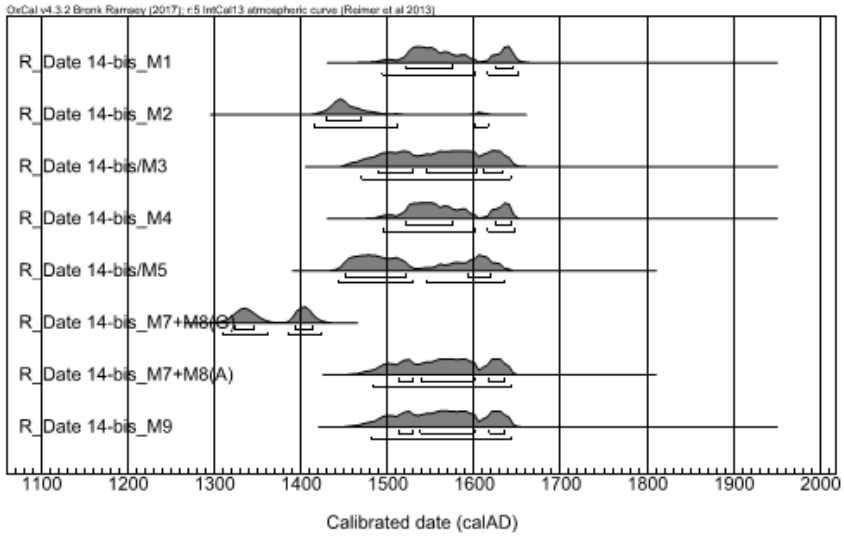

Figure 3. Bărăşti-'Sălişte' cemetery. Atmospheric calibration of the radiocarbon dates (Curve IntCal13; Calibration with OxCal v4.3.2) (see also the caption for Table 1).

Grave no.	$\delta^{13}C$ (‰) VPDB	$\delta^{15}N$ (‰) AIR	%C	%N	C/N
Grave 3	-19.01	7.80	33.4	11.7	3.3
Grave 7	-17.83	10.27	38.0	13.7	3.2
Grave 8	-19.04	8.06	36.4	13.1	3.2

Table 2. Bărăşti-'Sălişte': The $\delta^{13}C$ and $\delta^{15}N$ values for diet reconstruction obtained for the skeletons in Graves 3, 7 and 8 (analysis carried out by Dr. Marie Balasse, CNRS, Paris).

of Grave 8, also the dimensions of the grave pit (1.70 x 0.70m). The individual in Grave 7 is presumed here to have been an adult at the time of death, although later adolescence is also a possibility. The data provided by the excavators are contradictory: the grave pit in the excavation report is described as being clearly visible, rectangular and measuring 1.65 x 0.50m, while on the general plan it appears as partly unexcavated (Figure 2), meaning that at the least the reported width is incorrect.

Method

Radiocarbon dates obtained for human bones can be subject to an aging effect induced by diet (through the marine reservoir effect or the fresh water reservoir effect), meaning that only the absolute dates obtained for the three individuals (from Graves 3, 7 and 8) for whom analyses of C and N stable isotopes for diet exist can be checked for accuracy. The remaining radiocarbon dates must be considered as provisional, with the observation that, given the location of the site, it is highly probable that the majority of the population had an entirely terrestrial diet and their radiocarbon dates will therefore require no correction.

The very small number of individuals for which *C and N stable isotope analyses for diet* exist raises methodological concerns for the possibilities of diet reconstruction and has an impact on the correction of the radiocarbon dates. These aspects will be outlined in what follows.

$\delta^{13}C$ (i.e. the $^{13}C/^{12}C$ ratio measured against the V-PDB standard) indicates the source of C in the sample. This can be terrestrial – usually C_3 and C_4 plants in human diet – and aquatic – i.e. marine or freshwater sources. Each of these food sources has a specific $\delta^{13}C$ value for pure diet, also called the end value. The fact that the C-flow through the trophic chain occurs with a small isotopic enrichment from each trophic level to the next (up to 2‰: Bocherens and Drucker 2003; Post 2002) facilitates the evaluation of the ultimate source of C in the sample (Laffranchi *et al.* 2016: 2; Post 2002: 704).

Given that similar $\delta^{13}C$ values in the samples can result from both C_4 plant consumption and marine food consumption (Laffranchi *et al.* 2016: 2), or from both C_3 plant consumption and freshwater fish consumption (e.g. Cook *et al.* 2002: 454), the value of $\delta^{15}N$ is used to distinguish between them.

The $\delta^{15}N$ value (i.e. the ratio of $^{15}N/^{14}N$ isotopes compared with the abundance of ^{15}N in air as standard) indicates the trophic level of an organism, as it primarily expresses the amount of protein of animal origin as a share of the total amount of protein consumed by an organism. The principle is that plants have very low $\delta^{15}N$ values and that with every step up the food chain from food to consumer an isotopic enrichment of 3 to 5‰ occurs. Thus the $\delta^{15}N$ values increase from plants to herbivores, and then again to carnivores, being at their highest among consumers of marine and freshwater food, given that aquatic food chains are longer than terrestrial ones (from the very rich literature available on this issue, see: Minagawa and Wada 1984; Bocherens and Drucker 2003; Hedges and Reynard 2007). The $^{15}N/^{14}N$ ratio is relevant for radiocarbon dating because high values thereof indicate the consumption of marine or freshwater fish, both of which can cause the aging of apparent radiocarbon dates (e.g. Cook *et al.* 2002; Lanting and van der Plicht 1998). However, both diet reconstruction and the correction of radiocarbon dating have become more complicated since the substantial enrichment (*c.* +3‰) of $\delta^{15}N$ in cereals through manuring (Bogaard *et al.* 2007) and the wide variation of $\delta^{15}N$ values among freshwater fish (Ervynck *et al.* 2018) was discovered.

C and N stable isotope ratios allow for the reconstruction of the main characteristics of diet not only at group level, but also at the level of the individual (Hedges and Reynard 2007; Laffranchi *et al.* 2016). The accuracy of diet reconstruction depends on knowledge of the isotopic baseline of the ecosystem to which the organisms belonged (Post 2002: 704); however, for past ecosystems this cannot be measured directly. This is why paleodiet studies in humans rely on measuring the $\delta^{13}C$ and $\delta^{15}N$ values directly in human and animal remains (usually herbivores, more rarely fish) that can be reasonably associated with humans, while the $\delta^{13}C$ and $\delta^{15}N$ values of plants are not (usually) measured directly in plant remains (among other reasons because these are rarely available as such) but calculated by subtracting the value of the isotopic enrichment for C and N for one trophic step from the mean values of $\delta^{13}C$ and $\delta^{15}N$ for terrestrial herbivores, given that the $\delta^{13}C$ and $\delta^{15}N$ values for humans with a purely plant-based diet is thought to be equivalent to those for terrestrial herbivores (see, for example, Hedges and Reynard 2007: 1241). This procedure produces reliable results for the analyses of diet in sets of humans and animals. It also allows for the interpretation of diet at the level of the individual, although this is difficult in the case of small differences in isotopic values because isotopic

fractionation varies among individual organisms (Bocherens and Drucker 2003; Hedges and Reynard 2007: 1241). The results become even more uncertain when the $\delta^{13}C$ and $\delta^{15}N$ values for one organism are compared to those obtained from other ecosystems: owing to the variation in the baseline for $\delta^{13}C$ and $\delta^{15}N$, it cannot be established whether differences in isotopic values are due to differences in the trophic level of the individual organism or to differences in the isotopic baseline (Post 2002: 704).

For Bărăşti, the values of $\delta^{13}C$ and $\delta^{15}N$ are known only for three individuals, while similar data from the same period and region exist only for one skeleton, in Grave 10 at the Church of St. Nicholas in Curtea de Argeş, attributed to Prince Vlaicu, a Wallachian ruler from the mid-14th century, for which δ13C = -18.9‰ and δ15N = 11‰ (Ioniţă *et al.* 2014). There are no data whatsoever available for contemporaneous terrestrial animals in the study region, not even any zoo-archaeological analyses, which otherwise exist for all the other Romanian provinces (Bejenaru 2003).

Under the circumstances, the methodological difficulties outlined above – in particular the missing end values for $\delta^{13}C$ and $\delta^{15}N$ – will be circumvented by resorting to values from the literature concerning mostly neighboring regions.

Discussion

The apparent ages obtained by *radiocarbon dating* situate the graves at Bărăşti in the interval ranging between the beginning of the 14th and the middle of the 17th century. Grave 7 appears to be the earliest in the cemetery: 1310-1361 cal AD (51.6% probability) and 1386-1424 cal AD (43.8% probability); followed by Grave 2: 1415-1512 cal AD (91.3% probability) and 1601-1616 cal AD (4.1% probability); while the rest of the graves are roughly datable to the period ranging from slightly before 1500 to the mid-17th century (Table 1; Figure 3). As already mentioned, the results of the radiocarbon dating need to be evaluated in relation to the $\delta^{13}C$ and $\delta^{15}N$ values for diet in order to ascertain whether the apparent radiocarbon age is older than the real one. As such analyses are thus far only available for Graves 3, 7 and 8, the verification of the apparent radiocarbon age will be limited to these. The same is valid for diet reconstruction.

The individuals in Graves 3 and 8 at Bărăşti yielded values for $\delta^{15}N$ (7.80‰ and 8.06‰, respectively) and $\delta^{13}C$ (-19.01‰ and -19.04‰, respectively) that are typical of an entirely terrestrial diet, corresponding to an approx. 30% terrestrial animal protein (Hedges and Reynard 2007: fig. 1) and a C_3 plants based diet (Laffranchi *et al.* 2016: 2-3; Lanting and van der Plicht 1998: 155; van der Merwe 1982). This has no effect on the radiocarbon dating, so the ages obtained for these graves need no correction.

The case of the individual in Grave 7, seemingly the earliest in the cemetery (1310-1361, 1386-1424 at a 95.4% confidence level), with $\delta^{15}N$ = 10.27‰ and $\delta^{13}C$ = -17.83‰, is more difficult to assess. Typically, a $\delta^{15}N$ value of 10‰ in post-Neolithic farming societies is indicative of a high – i.e. 60-80% – terrestrial animal protein consumption level (Hedges and Reynard 2007), although the quantity of meat and dairy consumed could be lower in the case of a high number of young suckling animals in the diet (given that suckling animals are one trophic level higher than lactating animals: Lidén and Angerbjörn 1999). Alternatively, it could also indicate terrestrial animal protein combined with fish consumption (Hedges and Reynard 2007). Theoretically, a $\delta^{15}N$ value of between 9 and 11‰ can also result from a diet based entirely on cereals sourced from intensely manured fields (Bogaard *et al.* 2007: 340); however, in the European Middle Ages this would have been extremely unlikely, as, even in monasteries, dairy (i.e. animal protein) and fish were consumed in addition to cereals. In any case, the $\delta^{15}N$ value for the individual in Grave 7 is not high enough to clearly indicate an aging of its apparent radiocarbon date. More relevant is the value of $\delta^{13}C$ = -17.83‰, as this lies outside the range of $\delta^{13}C$ values typical of a terrestrial, C_3 plant diet. The $\delta^{13}C$ value corresponding to a purely C_3 plant diet is approx. -21.4‰ (van der Merwe 1982: 602) and in general values of around -20‰ or less negative indicate a certain amount of C_4 plants in a mainly C_3 plant-based diet (Laffranchi *et al.* 2016: 3). For a purely C_4 plant-based diet, the value of $\delta^{13}C$ = approx. -10‰ has been suggested (Laffranchi *et al.* 2016: 2). Alternatively, any value of $\delta^{13}C$ situated above the endpoint for purely C_3 plant consumption could indicate the consumption of marine food, with the endpoint for a purely marine food consumption, measured in Eskimos, being $\delta^{13}C$ = -12.5‰ (Arneborg *et al.* 1999: 158). Consequently, the $\delta^{13}C$ value of the individual in Grave 7 could indicate either a marine reservoir effect (MRE) – for example via marine fish – or the presence of C_4 plants in the diet.

Given both the $\delta^{13}C$ value and the $\delta^{15}N$ value obtained for the individual in Grave 7, the following interpretations are possible:

1. The $\delta^{13}C$ value reflects an MRE and consequently the radiocarbon date needs to be corrected. The correction requires determination of the percentage of marine carbon in the bone collagen and this in turn depends on the end values appropriate for calculation. One possibility is to take as an end value for a fully terrestrial C_3 plant-based diet of $\delta^{13}C$ = -20.1‰, which is the lowest $\delta^{13}C$ value documented in the Sub-Carpathian Arc, albeit during the Bronze Age

and approx. 180 km east of Bărăşti (Aguraiuja *et al.* 2018: tab. 1, Sărata Monteoru, Grave 41), and an approximate end value for a fully marine diet of $\delta^{13}C$= -12.0 ‰, which is close to the end value of -12.5‰ documented for Eskimos (Arneborg *et al.* 1999: 158). From a simple linear interpolation between these endpoints it results that for every 1‰ difference in the $\delta^{13}C$ value of the bone collagen sample there is a change of approx. 12.3% in its marine C content. For Grave 7 this would amount to an approx. 28% marine C, corresponding with a corrected radiocarbon age (obtained through a mixed atmospheric and marine calibration) of 1421-1478 cal AD (95.4% probability). Grave 7 would still be the earliest in the cemetery, but it would date entirely to the 15th century. Another possibility would be to use the end values documented for various periods in the Mediterranean Basin: $\delta^{13}C$ = approx. -21‰ for a fully terrestrial diet, and $\delta^{13}C$ = approx. -14.5‰ for a fully marine diet (Keenleyside *et al.*: fig. 6), which implies an approx. 15% change in marine C for each change 1‰ change in the value of $\delta^{13}C$. For Grave 7 at Bărăşti this would mean nearly 48% marine C and a corrected date of 1459-1623 cal AD (95.4% probability) – i.e. a date that includes Grave 7 in the same period as most of the graves in the cemetery. This latter correction seems rather improbable given the very high amount of marine C on which it is predicated, but so far there are no objective grounds for its dismissal.
Whatever the correct date may be, the interpretation of $\delta^{13}C$ as being indicative of an MRE is only valid if the value of $\delta^{15}N$ is compatible with marine food consumption. Given the almost complete lack of data, this is best verified not by comparison with end values, but by direct comparison with the isotopic values known for the Greeks of Apollonia (5th-2nd century BC), the colony on the west coast of the Black sea where a mixed terrestrial and marine diet is recorded in written sources and confirmed by isotopic analyses. Several individuals from this population have approximately the same $\delta^{15}N$ and $\delta^{13}C$ values as the individual from Grave 7 in Bărăşti (Keenleyside *et al.* 2006: tab. 2, in particular Sample ID 92, 222 and 250).

A value of 28% marine C in the sample does not indicate a 28% marine diet because in bone collagen C stems not only from animal protein but also from carbohydrates and lipids (Ambrose and Norr 1993). Even so, the supply on this scale (let alone a larger supply) of marine fish in the Southern Sub-Carpathians in the Middle Ages is not probable, so the presence of marine C can only be explained in terms of this person having lived on the coast during the last ten years of his life (Manolagas 2000: 116) (possibly even 20-30 years, as collagen turnover depends on age and state of health: Lidén and Angerbjörn 1999: 1780). If this explanation is true, the individual in Grave 7 must have been either a foreigner who was buried in Bărăşti or a local merchant who traveled frequently to the Black Sea as a participant in the aforementioned trade linking Central Europe with the Black Sea via Wallachia.

$\delta^{34}S$ analysis is needed to distinguish between local and marine food (Nehlich 2015) and $\delta^{87}Sr$ analysis to determine paleo-mobility, with the overall aim being to differentiate between locals and non-locals buried at Bărăşti, if not also to establish the latter's regions of origin (Beard and Johnson 2000). Nevertheless, it is not certain that these methods can be used, given the extremely poor state of preservation of the skeletons found in Bărăşti.

On a more general note, future research should try to establish end values for diet in regions of interest to Romania, as there is no guarantee that values from other regions can be used in place of local ones.

2. If the higher value of $\delta^{13}C$ is due to the presence of C_4 plants in the diet, then the radiocarbon date obtained for Grave 7 needs no correction. Europe is almost entirely a continent of C_3 plants (vegetation and cultivated plants). The only C_4 plant that could have been part of human diet in the 14th century was millet – in the form of broomcorn (*Panicum miliaceum* L.) or foxtail millet (*Setaria Italica* L.) (for a history of early millet in Europe, see Laffranchi *et al.* 2016: 1; Motuzaite-Matuzeviciute *et al.* 2013) – for maize was only introduced to Wallachia in the late 17th century (Olteanu 2003: 419). Whether millet was cultivated in Bărăşti in the 14th century cannot be established for lack of written, archaebotanical and isotopic data. The closest evidence for human consumption of millet comes from the south-east Transylvanian town of Braşov (Kronstadt), where the purchase of two wagons of millet flower (Lat. *millium*, Germ. *Hirse* or *Hyrse* for millet) is attested in writing in 1506 (Braşov 1886: 106). If we accept millet consumption as an explanation for the $\delta^{13}C$ value of the individual in Grave 7 at Bărăşti, then the individual must either have consumed it directly or its isotopic signal was transmitted via animals fed on millet, or a combination of the two. In this case, the isotopic characteristics of the individual from Grave 7 can be explained in the following ways:

a) The person came from somewhere, possibly Transylvania, where millet consumption is known to have occurred. This would not be unusual, as we know from written sources that people travelled along the trade route linking southern Transylvania and Wallachia (Papacostea 1983) and sometimes settled in Northern Wallachia (Pascu *et al.* 2001: 531). Moreover, Transylvania had a tradition of building stone churches (e.g. Vătăşianu 1959: 211-286), which could explain the solid foundations of the church in Bărăşti (whether with stone elevation or not).

b) The person in Grave 7 was a local, as presumably were those from Graves 3 and 8 (we have no reason to believe they were not locals). Their $\delta^{13}C$ value of -19‰ indicates a certain quantity of C_4 plants in their diet (Laffranchi *et al.* 2016: 3), either through direct consumption or transmitted through animals fed on C_4 plants. Nevertheless, this isotopic indication of possible millet consumption is very weak, and the same is true for the aforementioned skeleton from Grave 10 in Curtea de Argeş, a rather surprising fact given the general belief that millet was cultivated in Wallachia from at least the 17th century onwards (Olteanu 2003: 419). For Bărăşti, the isotopic values suggest a change in economy and diet occurring between the 14th/early-15th century (Grave 7) and the late 15th/mid-17th century (Graves 3 and 8): both the amount of animal protein (meat and dairy) and millet in human diet decreased over time.

Again, in order to choose between these interpretations further data are required: $\delta^{87}Sr$ might not be applicable given the state of the skeleton from Grave 7, but archaeozoological, archaeobotanical and isotopic data for animal diet could be obtained and with them a better knowledge of the local economy and human diet.

3. It should be noted that the $\delta^{15}N$ and $\delta^{13}C$ values of the individual in Grave 7 could also indicate a complex diet consisting of terrestrial sources – C_3 and C_4 plants as well as terrestrial animals – combined with freshwater fish. For decades it was believed that freshwater fish consumption results in high $\delta^{15}N$ and low $\delta^{13}C$ values in human bone collagen, but recent research has shown that $\delta^{15}N$ and $\delta^{13}C$ values are highly variable in freshwater fish and associated with extensive and at the same time erratic aging effects in terms of radiocarbon dates (i.e. age offsets ranging between several hundred and nearly 2000 radiocarbon years for the same $\delta^{15}N$ and $\delta^{13}C$ values), which can hamper diet reconstruction and make radiocarbon dating impossible (Ervynck *et al.* 2018). Whether this is also the case for the individual in Grave 7 at Bărăşti cannot be established with certainty: the closest source of freshwater fish is the Argeş River, at some 8 km away, but to what extent this source was used by the locals remains unclear. Future research will need to tackle this issue. So far we know that freshwater fish from the Danube is attested as one of the main forms of merchandise traded between Wallachia and Transylvania (Papacostea 1983: 33, with reference to documents from the 15th century), but that it was not sold before reaching Transylvania. Whether fish from the same source also reached smaller localities in Wallachia, for whose inhabitants it was affordable, and in what quantities it was consumed remains unclear. For the purposes of this paper, this last possible reconstruction of diet is considered rather unlikely.

Metal composition analyses

The ring in Grave 3 and the four metal buttons, two with attached metal embroidery, from Grave 4 (Figure 4) were analyzed using a portable X-ray spectrometer to identify their constituent chemical elements by means of their specific X-ray.

The XRF measurements were performed using an X-MET-TX3000 portable spectrometer – Oxford Instruments; the X-ray beam was generated by a 40 kV – Rh anode tube (Table 3). The detection system was a PIN silicon diode detector with Peltier cooling. The resolution of the detector was 270 eV for the K_α line of Mn (5.89 keV). The measurement spot size was around 30 mm^2. The spectrometer had a Hewlett-Packard (HP) iPAQ personal data assistant (PDA) for software management and data storage (Constantinescu *et al.* 2012).

The buttons were made from a high-quality alloy containing over 90% silver plus copper and tin – the latter being absent in the case of only one button. The alloying of Ag with Cu and bronze (also called copper-tin alloy) was carried out in order to increase hardness, as Ag is a soft metal. The composition of the metal embroidery came as a surprise, as it was made of gilded silver wires. The gilding was achieved using the amalgamation technique: a liquid alloy of Au and Hg was laid on the silver wires and then heated to the

Figure 4. Bărăşti: 1. Grave 3: silver ring; 2-5: Grave 7: silver buttons with attached gilded silver wires from a costume.

Grave	Metal item	Ag (%)	Au (%)	Cu (%)	Sn (%)	Fe (%)	Pb (%)	Bi (%)	Zn (%)	Hg (%)
Grave 3	Ring – (sample F 2450)	96.4	0.7	0.2	-	traces (impurities?)	traces	-	-	-
Grave 4	Button with gilded silver wires (sample F 2451)	96.3	0.6	0.7	2.4	1.5	0.6	0.6	-	-
	Button with gilded silver wires (sample F 2452)	83.3	6.1	3.1	-	2.4	1.0	-	0.1	2.7
	Button (sample F 2453)	89.5	0.6	4.0	4.3	0.9	0.3	0.4	-	-
	Button (sample F 2454)	89.5	0.7	3.2	-	2.3	0.5	0.3	-	-

Table 3. Bărăşti: Elemental composition of metal objects from Graves 3 and 4.

point where the Hg evaporated, while only the Au and traces of Hg (detected during analysis) remained on the silver object. The buttons also contained traces of Bi at the level of ppm, which indicates a Balkan origin for the silver (Vasilescu *et al.* 2015).

Results

Considering the results of the radiocarbon dating, the C and N stable isotopes for diet reconstruction and the metal elemental composition analyses together, the following individual biographies can be reconstructed:

The person in Grave 3 had a diet consisting mostly of C_3 plants, a small amount of C_4 plants and approx. 30% animal protein. This is considered highly probable in farming societies, as even poor villages sometimes have a 60-80% animal diet (Hedges and Reynard 2007: 1244). According to the radiocarbon dating (1470-1642 cal AD at 95.4% probability), this person lived either decades before or during the period when the peasants from Bărăşti were transformed into serfs (i.e. 1595), albeit the presence of the silver ring suggests this person was most probably not a serf.

For the person in Grave 4, whose expensive costume clearly indicates a rich man or woman, there are no data on diet, so the radiocarbon age is only probable, not certain: 1496-1602 (73.1% probability) and 1616-1647 (22.3% probability). However, if diet affected the apparent radiocarbon age, the real age could only be a later one. This means that this wealthy person either lived before serfdom or lived during serfdom as one of its beneficiaries.

For the person in Grave 7 the possible biographies were discussed above in more detail. In short, according to diet analysis this person may have originated from somewhere close to a sea or have travelled often to the coast (e.g. as a merchant), in which case he (she?) would date to the 15th century (or even the 16th/early-17th century). Alternatively, he/she may have consumed a considerable amount of millet, which means that the radiocarbon age (1310-1361 at 51.6% probability, or 1386-1424 at 43.8% probability) needs no correction. In this latter case, he/she would have been a foreigner from Transylvania or some other place where millet was part of human (and possibly also animal) diet; either that or he/she was a local who consumed a considerable amount of millet, either directly or indirectly, by eating animals fed on millet. In any case, the high quantity of animal protein differentiates the diet of this person from that of those from Graves 3 and 8 at Bărăşti, thus situating it close to the aforementioned Grave 10 from

the Church of St. Nicholas in Curtea de Argeş belonging to the ruling family of Wallachia.

The person in Grave 8 is more difficult to characterise. He/she died in the interval 1483-1643 (95.4%) – i.e. either decades before or during the period when the villagers were turned into serfs – and had a diet based on C_3 plants and approx. 30% animal protein. This diet is fully compatible with that of a modest medieval villager who practiced subsistence farming (Hedges and Reynard 2007: 1244), although it is also compatible with that of a higher social status, as seen in the case of the person in Grave 3.

In Bărăşti, the level of animal protein consumption (terrestrial or fish) for the 14th/early-15th century individual in Grave 7 is almost equal to that of the ruling class, while in the later graves this decreases clearly. Further research is needed to ascertain in what way the person from Grave 7 is representative of his/her period in Bărăşti and what this says about economic and social development in the region; however, it should be noted that this person's higher quality diet fits well with the presence of a well-built rural church near to which he/she was buried provided we date the church by the earliest artifact – i.e. to the 14th-15th century (Cristocea *et al.* 2012).

Concluding remarks and outlook

The argument put forward in this paper is based on a relatively small number of samples and an even smaller number of archaeological analyses than the samples would have allowed. Thus, while radiocarbon dating was carried out on all suitable organic material, i.e. eight of the nine skeletons, only three skeletons have so far been analyzed in terms of C and N stable isotopes for diet reconstruction. In addition, basic information necessary for diet reconstruction, such as archaeozoological and archaeobotanical data, as well as any analyses of C and N stable isotopes for diet carried out on domestic animals and fish bones, let alone plant remains, are entirely missing. The elemental analyses of metals were extensive but the number of metal items is small. Nevertheless, the results of the archaeometry are very encouraging: while when using traditional archaeological methods only the church was datable (15th-16th century, possibly also 14th century-early-18th century), the radiocarbon dating provided a chronology of the graves, even if five of them still need to be checked for possible diet-related age offsets; and diet analyses based on stable isotopes combined with metal analyses of the costume remains of the deceased painted a far more complete and individualised picture of the people buried at Bărăşti compared with that obtained from archaeology – i.e. people buried around a village church sometime during the Middle Ages.

More data are needed in order to obtain a more accurate picture of the lives of these people and an understanding of their social and economic contexts. The next step would be the full excavation of the cemetery and the performance of isotopic analyses on the human bones for diet reconstruction followed by performance of the same isotopic analyses on the animal bones from a nearby site and $\delta^{87}Sr$ for human paleo-mobility, so as to be able to distinguish between locals and foreigners buried in the cemetery at Bărăşti. This could turn this small rural cemetery with badly preserved skeletons into a reference point for the 14th/early-17th century in Southern Romania. What this study has also shown is that our understanding of diet and the correction of radiocarbon dating critically depends on the availability of regional end values for marine and terrestrial diets – thus representing a further task of research in the near future.

Appendix: Chemical pretreatment

Owing to the rather poor state of sample preservation and contamination with a moderate quantity of humic matter, a pretreatment strategy was chosen that would avoid further degradation of the protein through lasting treatment with acid and contact with alkaline solutions. After treatment with acid to achieve demineralisation and remove exogenous carbonates and fulvic acids, the bones were rinsed with ultra-pure water to remove soluble contaminants and precipitates (humic matters especially) until a neutral pH was obtained; the product was then gelatinised in acid conditions to recover the bulk collagen from the bio-apatite demineralised matrix. A supplementary stage of ultrafiltration using VIVASPIN filters was necessary in order to separate the components of high molecular mass (> 30kDa), including the non-degraded alpha chains of the Type I collagen, from the smaller mass components (degraded fragments or fragments of smaller molecular mass stemming from raw collagen, salts, non-collagenous proteins, amino acids stemming from the soil, as well as other contaminants) (Brock *et al.* 2007; Brock *et al.* 20101a; Brock *et al.* 2010b; Brock *et al.* 2013). Finally, the pure collagen with a molecular mass > 30kDa recovered from the filter was lyophilised and graphitised using the system CHNOS ELEMENTAL ANALYZER (EA: VarioMicroCube, Elementar, Germany) / AGE 3 (ETHZ, Switzerland) (Němec *et al.* 2010b; Wacker *et al.* 2010). The final product, natural carbon, of which there is about 1mg, was measured by AMS using a Cockcroft-Walton Tandetron (HVEE, Netherlands) accelerator (Sava *et al.* n.d.; Stan-Sion *et al.* 2015).

Given the poor state of bone preservation, the quality of the raw material and intermediary products was checked at every step during the pretreatment. This was done by FTIR-ATR analysis of the raw bone material, FT-Raman analysis of the intermediate products and

FTIR analysis of the final compound – i.e. the Type I collagen – by using a FTIR/FT-Raman Bruker Vertex 70 spectrometer with interferometer rock solid. The results for nearly all samples, and especially the collagen from Graves 3 and 5, were in agreement with the commonly accepted results for pure collagen (Brock *et al.* 2013; D'Elia *et al.* 2007). The only exception was the sample from Grave 7: the FTIR and FT-Raman analyses showed a slight contamination with bio-apatite and protein products resulting from collagen degradation, but not with other exogenous contaminants; the FTIR analysis of the final compound, obtained after a subsequent purification in acid media, showed it to have acquired all the characteristics of the Type I collagen (Cucos and Budrugeac 2011; Figueiredo *et al.* 2012; Stathopoulou *et al.* 2008).

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Author contributions

Nona Palincaş: discussion of the archaeological data, evaluation of $\delta^{13}C$ and $\delta^{15}N$ analyses in relation to diet reconstruction and radiocarbon dating, and the writing of the text; *Corina Simion*: documentation of written sources, sampling, the chemical pre-treatment concept and laboratory work, and the technical section; *Gabriela Sava* and *Oana Gâza:* the chemical pre-treatment; *Maria Mihaela Manea*: checking the collagen for contaminants; *Tiberiu Sava*: AMS dating; and *Bogdan Constantinescu* and *Daniela Stan*: metal analyses.

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Case Studies on the Radiocarbon Dating of Bronze Age Cremation Burials in Hungary

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Abstract

The cremation of dead bodies was a common practice in the Carpathian Basin throughout the Bronze Age (2500-800 BC). Researchers, however, often face a number of challenges when investigating cremated remains concerning ^{14}C dating. Our pilot project was designed to measure samples of cremated bone (dating of inorganic bioapatite) in tandem with associated organic material – i.e. charcoal pieces or the organic (collagen) component of unburnt bone samples. Our aim was to provide a more accurate absolute chronological sequence for the Bronze Age period during which the tradition of cremation was practiced by communities across large parts of the Carpathian Basin. In this paper we present four case studies from Early and Middle Bronze Age Hungary dated between 2500-1500 BC.

Keywords: radiocarbon dating, cremated bones, Bronze Age, Carpathian Basin.

Introduction

The cremation of dead bodies was a common practice in the Carpathian Basin throughout the Bronze Age (2500-800 BC). Researchers, however, often face a number of challenges when studying cremated remains. The first of these concerns the collecting of tiny pieces of bone fragments from a cremation burial and their small but important potential for yielding bioanthropological information, as well as the difficulty of radiocarbon dating the cremated bones themselves, irrespective of their dimensions (Lanting *et al.* 2001; Olsen *et al.* 2008; Olsen *et al.* 2013, Snoeck *et al.* 2014). Despite the advances in ^{14}C dating procedures over the past 70 years, fewer than 6% of all bone dating has been performed on purified bioapatite (Zazzo and Saliège 2011).

In this context, our pilot project was designed to measure samples of cremated bone (dating of inorganic bioapatite) in tandem with associated organic material – i.e. charcoal pieces or the organic component (collagen) of unburnt bone samples. The dating of these assemblages can help us to construct a more accurate absolute chronological sequence for the nearly two thousand-year-long Bronze Age period during which communities in large parts of the Carpathian Basin practiced the tradition of cremation. A further, methodological aim of the project was to develop and compare dates originating from different types of material. In this paper we present four case studies of cremation burials in Early and Middle Bronze Age Hungary (hereafter EBA and MBA, respectively, dating to 2500-1500 BC) (Figure 1).

A refined chemical pre-treatment of cremated bones was tested and applied to bioapatite samples at the Hertelendi Laboratory of Environmental Studies (HEKAL, department of ICER) of the Hungarian Academy of Sciences, Debrecen, using the EnvironMICADAS AMS device (Molnár *et al.* 2013). The Fourier transform infrared spectroscopy in attenuated total reflectance mode (FTIR-ATR) and $d^{13}C$ analyses of the samples

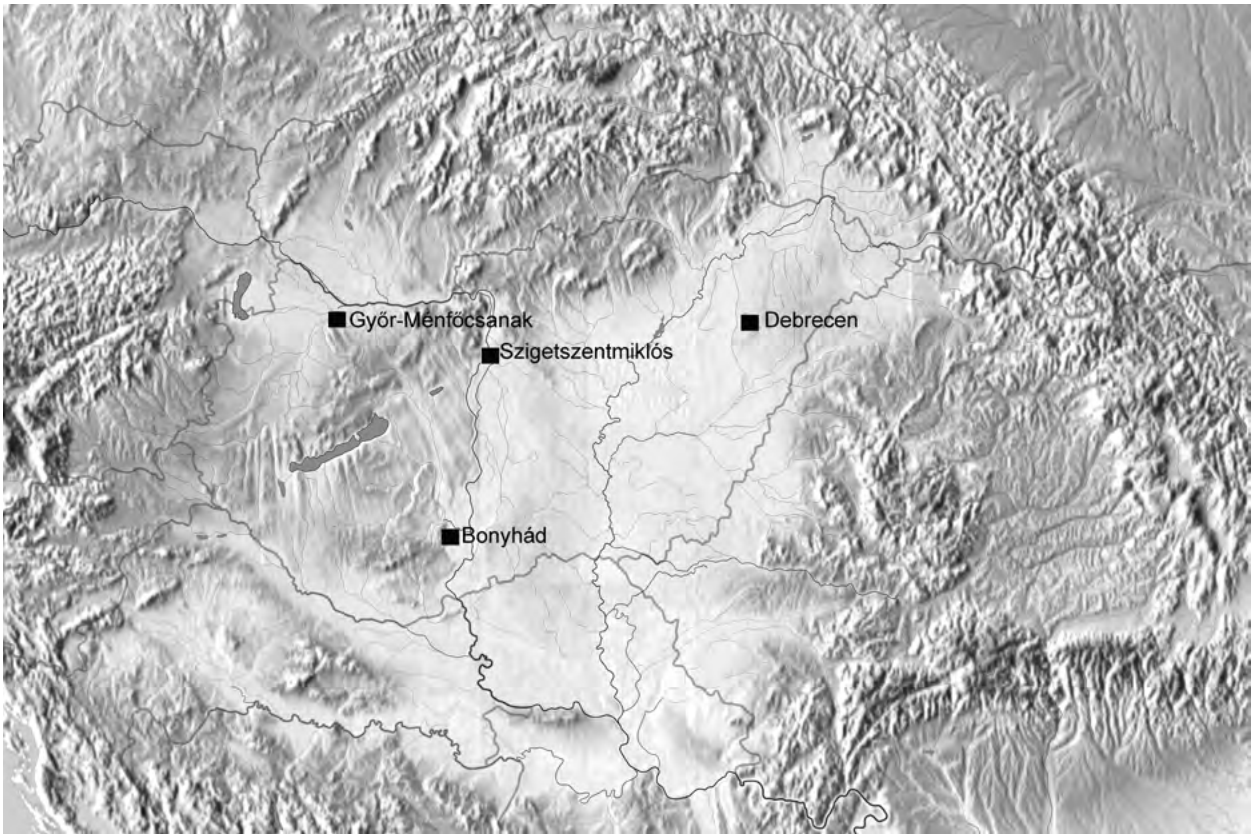

Figure 1. Location of the EBA sites of the case studies from Hungary: Bonyhád, Debrecen, Győr-Ménfőcsanak, Szigetszentmiklós.

confirmed that there was no organic material left in the selected bone fragments and that each piece had been fully cremated (for a more detailed description of the methodology, see Major *et al.* 2019).

According to the most recent chronological model in Hungary, there was a short, approximately 200-300-year-long *Transitional Period* between 2800 and 2600/2500 BC during which the social and material framework designated as the late Copper Age changed dramatically due to the eastern European influences of the Yamnaya community (Heyd 2013; Kulcsár and Szeverényi 2013; Kristiansen *et al.* 2017), while the difficulties associated with dating this period have also been pointed out (Szabó 2017). Communication networks, defined by their pottery, cover large areas within the whole of the Carpathian Basin, with the two main groups being the Makó-Kosihy-Čaka and the Late Vučedol/ Somogyvár-Vinkovci ceramic styles (Kulcsár 2009). The samples in our first case study are representative of the Makó culture (Figure 2), which can be described as a special post-Vučedol cultural phenomenon. The Makó communities were small in size, their loose networks of farmsteads were spread across extensive areas and cremation was their dominant burial practice.

The appearance of the Bell Beaker population around 2500 BC brought new cultural influences from the west (Heyd 2007). Several intensively populated settlements appeared, along with large cemeteries, often containing hundreds or even a thousand burials, concentrated in the area around present-day Budapest, e.g. at Szigetszentmiklós. A cultural syncretism with north-western and southern influences can be noted in both the burial rite and the grave goods in the EBA 2 cemeteries, and a few strontium isotope and ancient DNA analyses indicate some degree of mobility in this period (Kulcsár 2011; Olalde *et al.* 2018).

During the third phase of the EBA we observe the cremation and inhumation burials of the Kisapostag or the earliest Transdanubian Encrusted Pottery culture, traditionally dated before 2000 BC. Recently discovered inhumations suggest a transition from inhumation to cremation (Hajdu *et al.* 2016). Our samples derive from two sites at which both inhumations and cremations were discovered.

Samples and their archaeological context

The Makó samples

Case study 1: The site at Debrecen-'Szepes', excavated by Zoltán Farkas in 2015, was a typical, sporadic Makó settlement represented solely by a few domestic features and a single cremation grave belonging to an

cal BC	Central Europe	Hungary	Western Hungary	Danube region	Eastern Hungary
1500/1450	RB B	MBA 3	Encrusted Pottery Gáta-Wieselburg II	Vatya	Füzesabony-Gyulavarsánd/ Otomani Hatvan Maros
	RB A2	MBA 2			
2000/1900		MBA 1			
	RB A1	EBA 3	Kisapostag Gáta-Wieselburg I	Late Nagyrév Kisapostag	Late Nagyrév Hatvan Nyírség/Szaniszló Otomani I Maros
2200/2100		EBA 2a-b	Late Somogyvár/Proto Kisapostag Somogyvár-Vinkovci	Bell Beaker Late Makó Proto and Early Nagyrév	Late Makó Nyírség Early Nagyrév Early Maros
2300/2200	RB A0				
2500/2400	Eneolithic	EBA 1	Late Vučedol/Early Somogyvár-Vinkovci	Makó	Makó Yamnaya

Figure 2. An overview of Early and Middle Bronze Age chronology and pottery styles in Hungary (after Fischl, *et al.* 2015)

infant (≤ 3 years) (Feature 238/319). The calcined human bones recovered from the burial urn were analysed and compared with a small charcoal sample selected from various types of hardwood (mainly oak, *Quercus pertaea,* based on anthracological analysis) originating from the funerary pyre and a piece of a domesticated, probably herbivorous (ovicaprid or bovine) animal bone found among the grave furnishings (Figure 3.1-4). The ^{14}C age of the cremated bone sample (DeA-9428) and its associated context materials is shown in Table 1, below. The cremated bone sample yielded a ^{14}C age of 3910±35 BP, which is slightly older but still consistent with the ^{14}C dates of 3875±40 (DeA-9021) and 3855±30 BP (DeA-9189) for the charcoal and bone collagen samples, respectively. There is thus a significant overlap between the dates: all fall within the period between 2470 and 2200 BC (95.4% probability).

The Bell Beaker samples

Case study 2: The Szigetszentmiklós, Felső Ürge-hegyi-dűlő cemetery, situated to the south of Budapest, occupying an area of 5 hectares and excavated by Róbert Patay between 2006 and 2007, is a remarkable cemetery of the EBA 2-3 period due to its 215 Bell Beaker graves representing a range of different burial rites: inhumations, scattered cremations and urn burials (Köhler 2011; Patay 2013). Grave 107 was an inhumation containing the remains of an adult male (probably an archer) together with a scattered cremation burial (Figure 3.5-8). The unburnt bone taken from the inhumation burial yielded a ^{14}C date of 3840±35 BP, 2460-2200 cal BC (Table 1). The duplicated dating of a calcined bone sample falls between 3725±25 and 3780±30 BP (DeA-9062, DeA-9202). The average date of the cremated samples is 3753±20 BP (2280-2040 cal BC, 95.4% probability), which shows a discrepancy of approx. 90 years in comparison with the date produced by the intact bone sample. The probable overlap between the dating of the two samples is still 95% (Table 1). Considering the characteristics of the samples and the radiocarbon dates listed above, the following observations are possible:

1. The two dates yielded by the cremated remains overlap, but, as already noted, owing to the process of cremation it is possible that different parts of a cremated body provide different radiocarbon dates (Snoeck *et al.* 2014).
2. The inhumation remains generally appear to be older than the cremation. There is no indication that the radiocarbon date obtained for the inhumed bone is older than its real age (see, for example, the case study by Higham, *et al.* 2010; for more details see Major *et al.* 2019).
3. If the radiocarbon date of the unburnt human bone represents the real age, then its comparison with the combined radiocarbon dates of the cremation gives rise to two possible interpretations: either both the inhumation (2460-2200 cal BC) and the cremation (2280-2040 cal BC) burials were contemporaneous, in which case they date to some point during the period 2460-2040 cal BC (95.4% probability), or the cremation represents a later burial performed in the inhumation grave, in which case each of them could date to any time within their respective intervals.

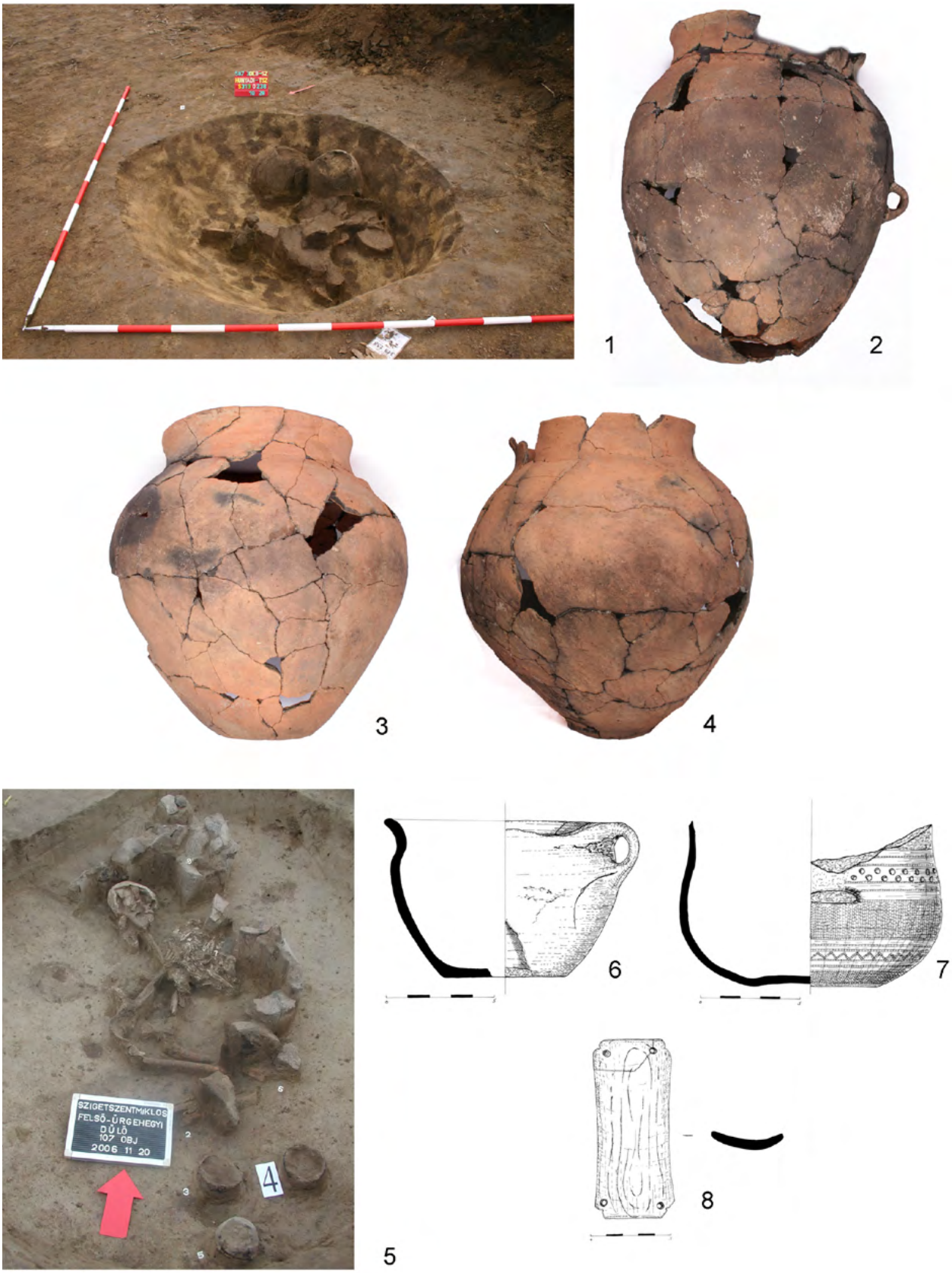

Figure 3. 1-4. Debrecen-Szepes, feature 238/319; 5-8. Szigetszentmiklós, Grave 107.

The Kisapostag or the earliest Transdanubian Encrusted Pottery samples

Case study 3: In 2008, an extensively used burial ground with 184 recently excavated burials was unearthed by Géza Szabó's excavations performed prior to the construction of the local biogas factory in Bonyhád, southwestern Hungary. The earliest inhumation burials were associated with the EBA 3 Kisapostag culture also referred to as the earliest Transdanubian Encrusted Pottery culture. Immediately afterwards, during the early MBA, both the burial rite and the material culture underwent a series of transformations, one of the most relevant being the introduction of cremation burials. The use of the cemetery continued until the end of the MBA (Hajdu *et al.* 2016; Kiss *et al., in press*). Burial no. 85 was found without grave goods and represented an *in situ* cremation (i.e. the cremation process took place in the gravepit itself, Figure 4.1-2). From this burial, a charcoal sample (DeA-5151, originating from the *in situ* remains of the pyre), and a cremated bone sample (DeA-5921) of the juvenile deceased (Hajdu *et al.* 2016, Fig. 3.) were collected. The charcoal sample produced a date of 3422±21 BP, 1870-1640 cal BC (95.4% probability), while the sample taken from the calcined human bone (bioapatite) dated slightly earlier, albeit to a very similar period, i.e. 3450±20 BP, 1880-1680 cal BC (95.4% probability). The mere 30-year difference between the dates was probably due to the dating of different materials (in which the charcoal, i.e. the organic material, could be younger). While the dates show a good overlap, both are younger than their expected relative chronological period (Table 1).

Case study 4: In the period 2009-2011, in Győr (north-western Hungary), at the huge Ménfőcsanak-Szélesföldek archaeological site covering nearly 27 ha, Gábor Ilon and Eszter Melis excavated two separate grave groups from the EBA 3 period with a total of nine cremation burials. Grave 6250 represented an urn burial of an adult female with rich bronze jewellery (Figure 4.3-9; Tóth *et al.* 2016). From this grave, a piece of human calcined bone and a piece of charred grain (based on archaeobotanical analysis) from the fill of the urn were subjected to dating. The ^{14}C age obtained for the grain at the temperature of 800ºC (Major *et al.* 2019) was DeA-9039: 3515±60 BP corresponding to 2020-1690 cal BC (95.4% probability). The organic material of the grain is considered to have good dating potential due to a well-defined ^{14}C content representing a short period of growth. The cremated bone (DeA-9429) yielded a date of 3450±30 BP, making this sample at most 67 ^{14}C years younger than the date of the grain sample (Table 1). The corresponding calibrated date for the cremated bone is 1880-1680 cal BC (95.4%), which falls within the 2σ error range of the date obtained for the grain (Table 1 and Figure 5).

Conclusions

From the four case studies, the most reliable comparison we were able to produce was for the samples from Debrecen-'Szepes' (Table 1). The samples taken from an unburnt herbivorous animal bone, charcoal and cremated human infant bone provided an unusually precise correspondence with a combined date range of 56 years. This correspondence also confirms the reliability of the dating method (for details, see Major *et al.* 2019).

Lanting, Aerts-Bijma and Van der Pflicht (2001) observed that in some cases there exist large differences between the radiocarbon dates obtained for cremated bone and those obtained for the charcoal samples used as reference material. They explain these large differences in terms of the old wood effect. In our case studies, two of the cremated bone samples (Debrecen and Bonyhád) also produced older dates compared with the organic samples. However, the two other case studies (Szigetszentmiklós and Győr-Ménfőcsanak) yielded younger dates for the calcined bones than for their associated organic material. At Szigetszentmiklós, comparison of the radiocarbon dates obtained for the unburnt and cremated human bone is limited by the possibility that the calcined remains were secondarily buried in the older inhumation burial. At Győr-Ménfőcsanak, it is probable that the differences in age between the grain and the cremated bone stem from the two different lifespans of the samples: a few months in the first case, several decades in the second (adult woman). Since there is a 95% overlap between the dating of the four samples of cremated bone and the associated context samples deriving from intact bone collagen, charcoal or charred grain, the radiocarbon dating of calcined human bones would appear to offer a reliable way of further refining the chronological framework of the Bronze Age in the Carpathian Basin (Figure 5).

The material and dates obtained in the case studies corresponds to the recent relative chronological sequence for the Early Bronze Age periods 1-3. The current convention of absolute dating for the Central European Bronze Age defines the boundary between the Early and the Middle Bronze Age at around 2000/1900 cal BC (Stockhammer *et al.*, 2015). In this case, the examined burials at Győr-Ménfőcsanak and Bonyhád belong to the first part of the Middle Bronze Age (Figure 5). The dates produced by cremated bones offer the potential of a more detailed chronology especially in cases where burnt bone remains represent the sole possibility of obtaining an absolute dating of archaeological assemblages.

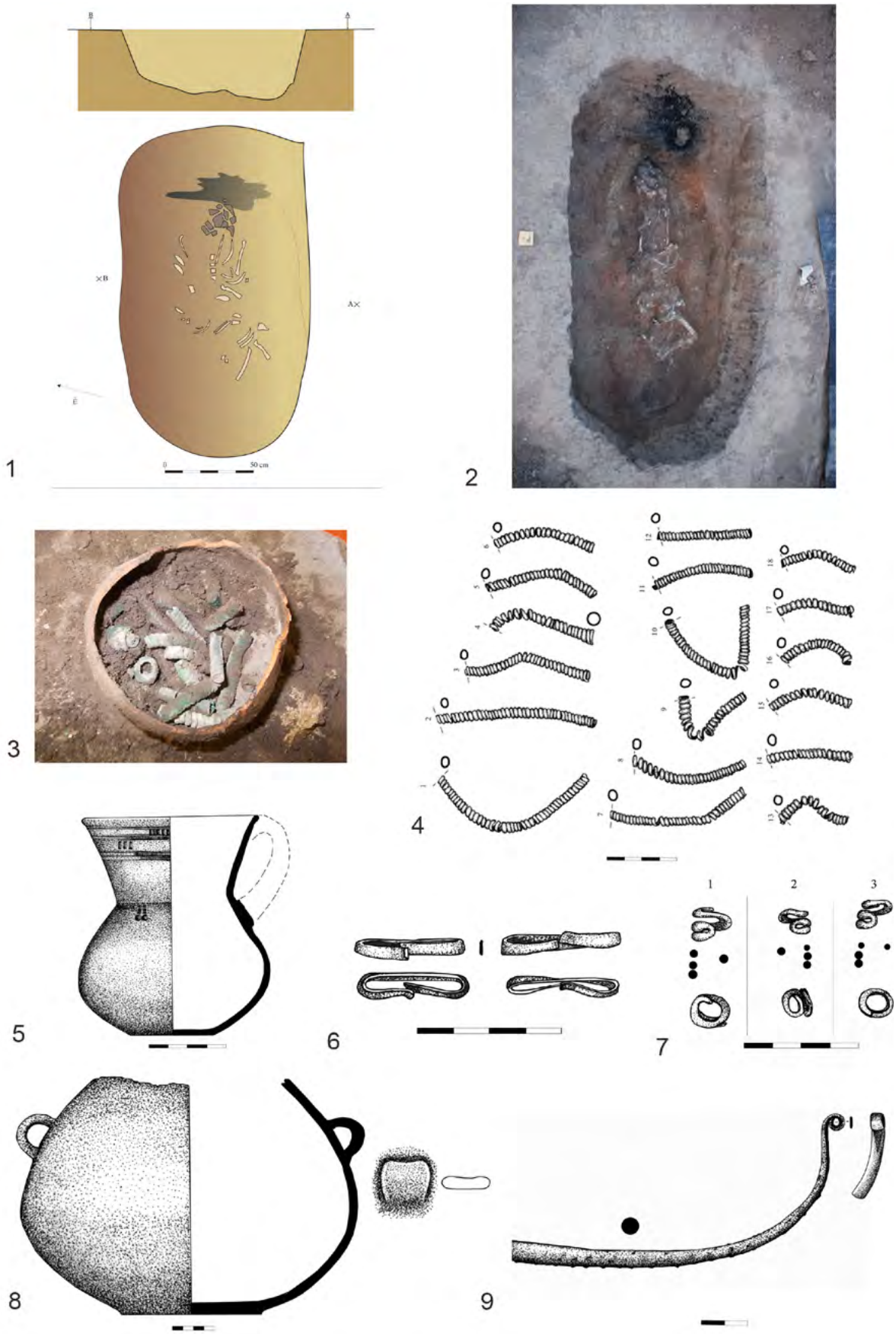

Figure 4. 1-2. Bonyhád-Biogas factory, Grave 85 (after Szabó 2012), 3-9. Győr-Ménfőcsanak, Grave 6250 (after Tóth *et al.* 2016: fig. 3.)

Location	Material type	Lab. code	C (w/w %)	^{14}C age (BP) ±1 sigma	Calibrated ages (BC) 1 sigma (68.2% probability)	Calibrated ages (BC) 2 sigma (95.4% probability)
Debrecen-Szepes,	Charcoal	DeA-9021	34.3	3875 ± 40	2460-2290	2470-2200
Grave 238/319	Bone collagen	DeA-9189	43.4	3855 ± 30	2460-2210	2460-2200
	Crem. bone	DeA-9428	0.47	3910 ± 35	2470-2340	2490-2280
Szigetszentmiklós,	Crem. bone	DeA-9202	0.41	3780± 30	2280-2140	2300-2060
Grave 107		DeA-9062	0.40	3725 ± 25	2200-2040	2210-2030
		Average	0.405	3753 ± 20	2200-2140	2280-2040
	Bone collagen	DeA-9530	42.3	3840 ± 35	2400-2200	2460-2200
Bonyhád-Biogas	Charcoal	DeA-5151	59.4	3420 ± 25	1750-1680	1870-1640
factory, grave 85	Crem. bone	DeA-5921	0.50	3450 ± 25	1870-1690	1880-1680
Győr-Ménfőcsanak,	Grain high temp	DeA-9039	19.4	3515 ± 60	1920-1750	2020-1690
Grave 6250	Crem. bone	DeA-9429	0.32	3450 ± 30	1880-1690	1880-1680

Table 1. Carbon percentage, AMS radiocarbon and calibrated age data for the archaeological organic and cremated samples (calibrated by OxCal v4.3.2 [Bronk-Ramsey 2017]; r:5 IntCal13 atmospheric curve [Reimer *et al.* 2013])

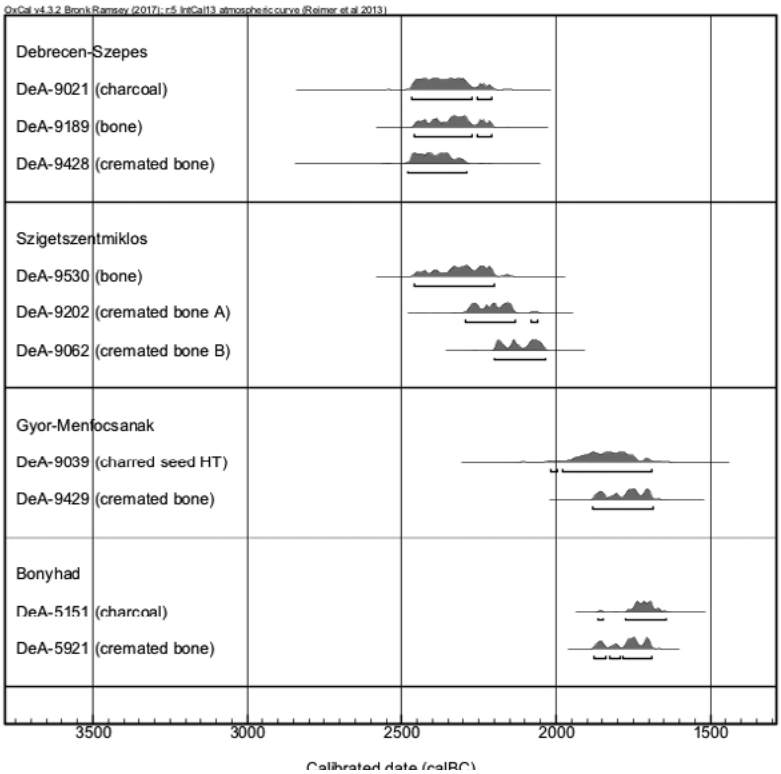

Figure 5. Calibrated ages of the four case studies, including the analysis of intact (unburnt) bone, charcoal, grain and cremated bone samples. The horizontal bars below indicate the 95.4% probability density range.

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Revisiting the Radiocarbon-Based Chronology of the Wietenberg Culture (Middle Bronze Age Transylvania): A Debate of Supra-Regional Relevance

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Abstract

This paper discusses the absolute dating of the Wietenberg culture based on five new radiocarbon dates and the assessment of the 34 previously published dates. In contradistinction to earlier research that situated the Wietenberg II phase between approx. 1900 and 1700 cal BC, some of the new dates limit this interval to between 1800 (or a few decades earlier) and a few decades after 1750 cal BC, while others indicate that the post-Wietenberg habitations are broadly datable to around 1400 cal BC. With respect to the 34 previously published dates, it is argued that only four can be retained as reliable mostly on account of a failure to respect the methodological requirements specific to the sample material. This paper recommends that future dating attempts focus on features with a variety of datable materials.

Keywords: Middle Bronze Age, Late Bronze Age, Transylvania, radiocarbon dating methodology.

Introduction

The importance of the absolute dating of the Wietenberg culture reaches far beyond Middle Bronze Age Transylvania (Figure 1), of which it is characteristic, primarily due to the large number of artifacts associated by archaeologists with remote regions such as the Aegean (e.g. the 'spiral-meander' decoration [Chidioşan 1980: 74; Daróczi 2010-2011; Rotea 2017: 67; Vulpe 2001], the so-called Mycenaean swords [Alexandrescu 1966: 119-121; Bader 1991]), Anatolia (the 'pulley motif': David 2007; Kull 1989) and Northern Europe (the Apa-Hajdúsámson hoards: Kristiansen and Larsson 2005: 205, 208; Sørensen 2013). In this respect, probably the most important consequence of a clear absolute dating would be the settling of the heated, decades-long debate surrounding the origins of the spiral-meander style that characterises the Wietenberg pottery and other objects from phase II onwards, namely the question of whether it is the result of the Mycenaean (Chidioşan 1980: 74; Hänsel 1982: 24; fig. 15) or a pre-Mycenaean influence (Vulpe 2001; Daróczi 2010-2011; Rotea 2017: 67).

The establishing of an absolute chronology requires the selection of relevant archaeological contexts and samples and an operational periodisation. These are dependent on the present state of research as well as the authors' judgment and experience.

The Wietenberg culture is known from approximately 600 (Rotea 1993: 28; Rotea 2019, *in press*) sites, most of them single-layered settlements (Rotea 1993: 34). Because multi-layered settlements are relatively exceptional and those better preserved are situated at the periphery of the Wietenberg area – i.e. Derşida-'Dealul lui Balotă' at the north-western (Chidioşan 1980), and Rotbav-'La pârâuţ' at the south-western limit (Dietrich 2014a) – questions were raised as to their relevance for the periodisation of the entire Wietenberg culture. Human skeleton remains are few, found alone or in small groups, and indicate a complex handling of human bodies that resulted in a few cases of primarily inhumed skeletons or parts of skeletons in anatomic connection, subsequent inhumations of partly recomposed skeletons, combinations of unburned and cremated body parts, and a majority of cremations. Associated artefacts are few in number, with the exception of the sanctuary at Oarţa de Sus, where a variety of objects were buried in pits together with human and animal body remains (Palincaş 2014). The vast majority of metal objects appear in hoards with no direct association with pottery (Rotea 2019, *in press*).

These characteristics of the Wietenberg sites have a bearing on the periodisation of the culture in that this is based almost entirely on pottery. Several systems

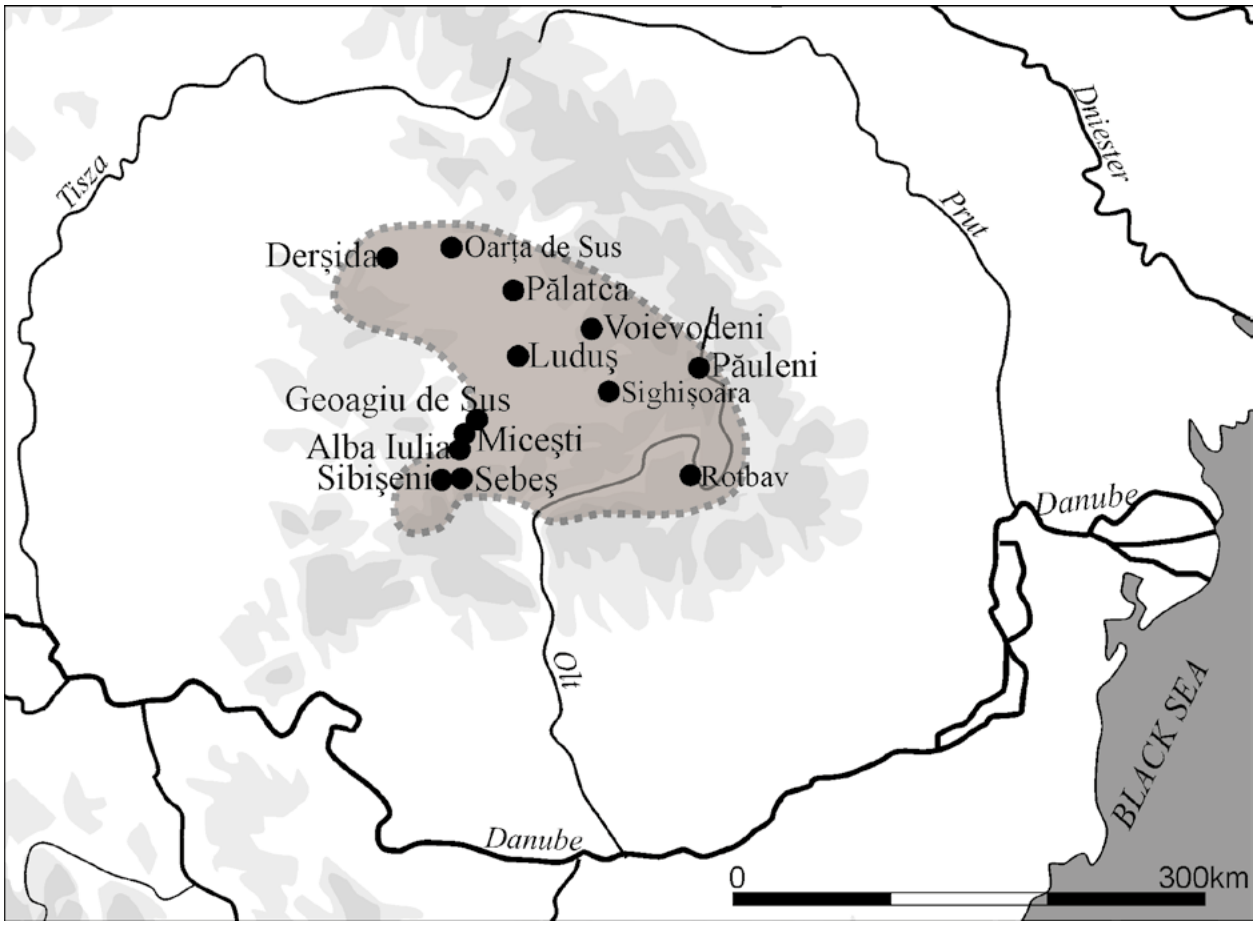

Figure 1. Distribution area of the Wietenberg culture and location of sites with radiocarbon dates (base map by Iuliana Barnea).

have been proposed so far, some of which were rejected, while others are still used. Most used is the system of periodisation by Nicolae Chidioşan, who defined the Wietenberg I-III phases based on the five superimposed layers of the settlement at Derşida-'Dealul lui Balotă' and a phase IV not present in this settlement; he paralleled the phases I-IV with the Reinecke Br A2-D horizons of bronze objects of the Central European chronology (Chidioşan 1980: 71, 75-77, 80-81, 83). Nikolaus Boroffka defined phases A-D based on a seriation of all Wietenberg finds with known contexts (Boroffka 1994). Mihai Rotea redefined the early and late stages of the Wietenberg culture; he separated several of the sites previously attributed to phase IV into a later, post-Wietenberg group, which he named Deva-Bădeni and attributed to the Late Bronze Age (Rotea 1994: 42-57; Rotea 2017: 55-57). Florin Gogâltan also recognised the existence of a mixture of Wietenberg, Otomani and Noua traits at the beginning of the Late Bronze Age situated at the chronological level of Reinecke Br D bronzes, which he called the Gligoreşti ceramic style (Gogâltan 2015: 76; Gogâltan and Popa 2016: 53-60). Recently, Bălan *et al.* proposed a different periodisation, regrouping the Wietenberg finds into three phases: early, classical and late (Bălan *et al.* 2016). As the debate on periodisation – despite its obvious relevance for the dating of the Wietenberg culture – lies outside the scope of this paper, the attributions to phases made here will be kept the same as in the publication of origin. This should not create any confusion because the various periodisations can be correlated sufficiently well for the specific needs of this paper.

Despite the rich material repertoire attributed to the Wietenberg culture, the assemblages useful to cross-dating (the traditional dating method of archaeology) are limited to the site at Oarţa de Sus: there Wietenberg II pottery is associated with Reinecke Br A2 bronzes (Kacsó 2004: 60), while this horizon of bronze objects was dated in Southern Germany by radiocarbon and dendrochronology to between the late 20th/early 19th and 16th centuries (Becker *et al.* 1989: 440-441). However, for the dating of the Wietenberg II phase, this interval is too large. Given these very limited possibilities of cross-dating, efforts were made during the last two decades to construct an absolute chronology based on radiocarbon dates. This paper presents a few new radiocarbon dates, assesses the reliability of the previously published dates

and suggests a strategy for future research with the aim of obtaining a clearer absolute dating.

The data

The five new radiocarbon dates presented here were obtained from ovicaprid bones (one from a young individual, the others from adults) (Table 1; Figure 2).

Three of the samples come from features excavated in 2000 at the Derşida-'Dealul lui Balotă' settlement, layer 3, attributed to the Wietenberg II phase (Chidioşan 1980: 72): House 1, Pit 2 belonging to House 1, and Pit 6. The associated ceramics belong to the general repertoire of the Wietenberg II phase. The two other radiocarbon dates come from layers IIa and IIb of the settlement at Pălatca-'Togul lui Mândruşcă', attributed by Rotea to the Deva-Bădeni Group. Although good practice requires extensive publication of the inventories for these features, for reasons of space these will have to be published separately (Rotea *et al.* 2019).

Methodological aspects

Radiocarbon dating of bone collagen only produces accurate dates if the diet of the living organism exclusively contains C derived from sources in equilibrium with the atmosphere. This is generally the case with herbivores, to which ovicaprids belong, as they feed on grass, which takes up C from the atmosphere through photosynthesis (see the basic principles of radiocarbon dating in, for example, Bowman 1990: 13-15).

Discussion

We are able to make the following interpretation with respect to the dating of the samples from layer 3 at Derşida:

– Because the site formation processes are not known in sufficient detail, it is not possible to establish a finer relative chronology of the

No.	Phase	Site	Context	Sample	Label	CRA (yr BP)	Calibrated date (cal BC)	
							1σ (68.2%)	2σ (95.4%)
1	W II	Derşida	Pit 2/2000; layer 3: -0.69 m	Bone of adult ovicaprid	RoAMS 144.47	3426±30	1766-1686	1875-1842 (8.4%) 1818-1798 (3.2%) 1780-1639 (83.9%)
2	W II	Derşida	Pit 6/2000, layer 3; -0.90m	Bone of young ovicaprid	RoAMS 142.27	3470±30	1877-1841 (25.1%) 1821-1796 (15.8%) 1782-1744 (27.3%)	1884-1736 (87.5%) 1716-1695 (7.9%)
3	W II	Derşida	House 1/2000; layer 3	Bone of adult ovicaprid	RoAMS 143.47	3514±30	1890-1868 (15.3%) 1848-1774 (52.9%)	1921-1751
4	Deva-Bădeni	Pălatca	layer IIa	Bone of adult ovicaprid	RoAMS 145.47	3181±29	1496-1474 (26.9%) 1461-1429 (41.3%)	1505-1410
5	Deva-Bădeni	Pălatca	layer IIb	Bone of adult ovicaprid	RoAMS 147.47	3086±24	1406-1376 (25.6%) 1350-1303 (42.6%)	1416-1281

Table 1. Radiocarbon dates from Derşida-'Dealul lui Balotă' (Wietenberg II phase) and Pălatca-'Togul lui Mândruşcă' (Deva-Bădeni period) (bone identification by Diana Bindea).

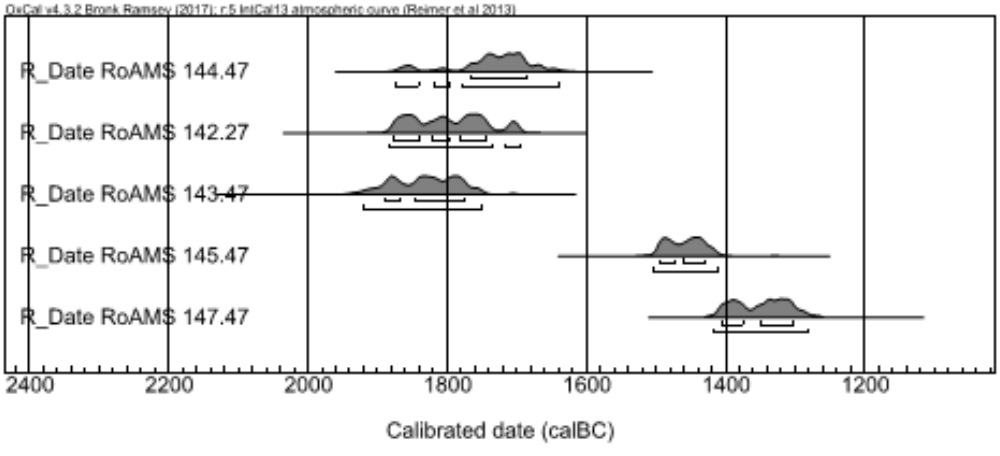

Figure 2. Multiple plot of the radiocarbon dates from Derşida-'Dealul lui Balotă' (Wietenberg II phase) and Pălatca-'Togul lui Mândruşcă' (Deva-Bădeni period).

features from which the radiocarbon dates were taken. Of particular interest here is whether House 1/2000 was already a ruin some time (maybe a few decades) before the filling of Pit 2/2000 was formed. Consequently, all three samples will be considered individually rather than resorting to a combination of their radiocarbon dates – the latter being appropriate for cases where strict contemporaneity can be expected

- With 95.4% probability, the dates overlap – with interruptions – in the interval ranging between 1875 and 1751 cal BC (more precisely, they overlap between 1875 and 1842, between 1818 and 1798, and again between 1780 and 1751 cal BC)
- With 95.4% probability, the sample from House 1 (RoAMS 143.47) cannot be dated later than 1751 cal BC. As there is no reason to believe that the dated bone fragment was in House 1 long before its destruction, we can say that 1751 cal BC is the latest possible date at which House 1 was in use. The sample from House 1 (and the corresponding habitation at Derşida) could nevertheless date earlier, with any date within the interval up to 1921 cal BC being probable
- In terms of the highest probability, the samples from House 1 (RoAMS 143.47) and Pit 6 (RoAMS 142.27) date much closer to each other than the sample from Pit 2 (RoAMS 144.47), which could be of a slightly later date
- With 68.2% probability, the sample from Pit 2 clearly dates to later than that from House 1 (the sample from Pit 2 dates to 1766 cal BC at the earliest, while that from House 1 cannot date later than 1774 cal). This significantly increases the probability that the former sample is of a slightly later date
- Given the 95.4% probability that the sample from House 1 does not date after 1751 cal BC (unless we wish to use 100% probability) and the 68.2% probability that the sample from Pit 2 dates to after 1766 cal BC, it is highly probable that the corresponding habitation at Derşida (i.e. layer 3) dates to a few decades before 1750 cal BC as well as around or slightly later than this date – rather than at a much earlier time, such as the late 20th or 19th century BC, as the 95.4% interval would suggest
- Again, due to a lack of detailed site formation analysis, it cannot be ascertained whether the habitation corresponding to layer 3 immediately followed that corresponding to layer 2. However, if we assume no interruption in the habitation, then it can be estimated that layer 2 existed around 1800 BC and might even have begun slightly earlier. This means that the Wietenberg II pottery (and the Wietenberg II phase) already existed around that date.

It is possible to make the following interpretation in respect of the two dates from Pălatca-'Togul lui Mândruşcă':

- With a confidence level of 95.4%, the dates overlap only from 1416 to 1410 cal BC; while at a confidence level of 68.2%, they do not overlap at all (the latest possible date for the sample from layer IIa being 1429 cal BC, while the earliest possible date for the sample from layer IIb is 1406)
- If no time gap exists between the occupation of layers IIa and IIb and neither lasted for a century or more, then the dating of the two samples to the decades around 1410 is more probable. A more secure dating would require site formation studies and further samples dated by radiocarbon.

Before discussing the implications of these new dates for the absolute chronology of the Wietenberg culture, it is necessary to assess the previously published radiocarbon dates. These number a total of 34, stem from all Wietenberg phases, including the recently defined post-Wietenberg phase called the Deva-Bădeni Group, and were obtained from a variety of materials: charcoal (and wood?), grains, unburned as well as cremated human bones, and unburned animal bones (Table 2). In most cases, the samples lack sufficient description, were hardly ever considered in terms of the logic of radiocarbon dating specific to the sample material, and the resulting dates were accepted or rejected based on archaeologists' expectations rather than on methodological grounds. The following section of this paper comprises a methodological assessment that aims to determine which samples can be considered relevant to the absolute dating of the Wietenberg culture. To facilitate discussion, the list of the available samples and dates is provided here (Table 2), although similar lists were also published more recently (e.g. Bălan *et al.*: fig. 282; Bălan *et al.* 2016: pl. V).

Wooden charcoal samples were dated in five cases, assuming what is stated as being a wooden sample at Păuleni is charred wood: one from a Wietenberg II context in Păuleni (Gogâltan 2015: 77; fig. 31; Whitlow *et al.* 2013: 38), three from the superimposed layers of a pit mostly containing Wietenberg C (Wietenberg III after Chidioşan) pottery but also with later elements (Ciugudean and Quinn 2015: 151), and one from a feature with Wietenberg C pottery in Sighişoara-'Cartierul Viilor' (Popa and Boroffka 1996: 56 and note 40; Motzoi-Chicideanu 2004: 82; the initial assessment that the pit also contained later elements has since been withdrawn: N. Boroffka, personal communication November 2018). Questions pertaining to site formation processes, despite these being fundamental in modeling the relationship between the date of the

No.	Phase	Site	Context	Sample characteristics	Laboratory label	CRA (yr BP)	Calibrated date (calBC) 2σ (95.4%)	Reference
1	Early (W I-II/W A)	Sebeş-'Între răstoace'	Grave 2	Cremated human bone	AA-103611	3445±41	1883-1660	Bălan *et al.* 2014: fig. 280
2	Early (W I-II/W A)	Sebeş-'Între răstoace'	Grave 17	Cremated human bone	AA-103613	3517±41	1950-1741 (94.3%) 1710-1700 (1.1%)	*loc. cit.*
3	Early (W I-II/W A)	Sebeş-'Între răstoace'	Grave 25	Cremated human bone	AA-103614	3533±41	2007-2005 (0.2%) 1974-1746 (95.2%)	*loc. cit.*
4	Early (W I-II/W A)	Sebeş-'Între răstoace'	Grave 32	Cremated human bone	AA-103615	3555±41	2021-1992 (5.5%) 1984-1768 (89.9%)	*loc. cit.*
5	Early (W I-II/W A)	Sebeş-'Între răstoace'	Grave 34	Cremated human bone	AA-103616	3562±42	2026-1771 (95.4%)	*loc. cit.*
6	Early (W I-II/W A)	Sebeş-'Între răstoace'	Grave 36	Cremated human bone	AA-103617	3425±41	1878-1838 (11.4%) 1829-1792 (7.4%) 1785-1629 (76.6%)	*loc. cit.*
7	Early (W I-II/W A)	Sebeş-'Între răstoace'	Grave 43	Cremated human bone	AA-103618	3520±41	1953-1742 (94.5%) 1710-1701 (0.9%)	*loc. cit.*
8	Early (W I-II/W A)	Sebeş-'Între răstoace'	Grave 44	Cremated human bone	AA-103619	3495±40	1923-1736 (91.4%) 1716-1695 (4.0%)	*loc. cit.*
9	Early (W I-II/W A)	Sebeş-'Între răstoace'	Grave 45	Cremated human bone	AA-103620	3501±40	1933-1737 (92.4%) 1715-1697 (3.0%)	*loc. cit.*
10	W II	Oarţa de Sus-'Ghiile Botii'	Pit 22	Burnt grain(s)	Ly-9190	3265±30	1619-1495 (90.8%) 1478-1458 (4.6%)	Kacsó 2015: 432
11	W II	Oarţa de Sus-'Ghiile Botii'	Pit 22	Burnt grain(s)	Bln-5626	3507±37	1931-1742 (94.3%) 1709-1701 (1.1%)	*loc. cit.*
12	W II	Rotbav-'La Pârâuţ'	Layer 2	Animal bone	Hd-28203	3547±24	1954-1867 (69.5%) 1848-1774 (25.9%)	Dietrich 2014a: 171; Annex 2 in vol. 2; Dietrich 2014b
13	W II	Păuleni	Layer	Wood, well preserved timber	PAC-25	3440±25	1877-1840 (14.0%) 1823-1796 (6.0%) 1783-1683 (75.5%)	Gogâltan 2015: 77; fig. 31; Whitlow *et al.* 2013: 38)
14	W III	Rotbav-'La Pârâuţ'	Layer 3	Animal bone	Hd-27967	3195±19	1501-1430 (95.4%)	Dietrich 2014a: 182; Annex 2 in vol. 2: Dietrich 2014b
15	W III	Rotbav-'La Pârâuţ'	Layer 3	Animal bone	Hd-27989	3174±16	1492-1482 (2.2%) 1454-1394 (93.2%)	Dietrich 2014a: 182; Annex 2 in vol. 2; Dietrich 2014b
16	W III	Alba Iulia-'Recea'		Animal bone	Hd-29515	3448±21	1876-1841 (17.8%) 1821-1797 (7.0%) 1782-1689 (70.6%)	Ciugudean and Quinn 2015: 149; tab. 1

No.	Phase	Site	Context	Sample characteristics	Laboratory label	CRA (yr BP)	Calibrated date (calBC) 2σ (95.4%)	Reference
17	W III	Sibişeni	Grave ?	Cremated human bone	AA-103610	3454±46	1891-1658 (94.8%) 1651-1645 (0.6%)	Ciugudean and Quinn 2015: 151; fig. 4
18	W III	Voievodeni-'La Şcoală'	Pit, Skeleton 1	Unburned human bone, adult female	DeA-2002.1.1	3337±38	1736-1716 (3.9%) 1695-1521 (91.5%)	Németh 2015; Bălan, Quinn and Hodgins 2016: 85
19	W III	Voievodeni-'La Şcoală'	Pit, Skeleton 4	Unburned human bone, post childhood	DeA-2004.1.1	3407±38	1874-1843 (5.0%) 1815-1800 (1.7%) 1779-1617 (88.7%)	*loc. cit.*
20	W III	Voievodeni-'La Şcoală'	Pit, Skeleton 5	Unburned human bone, young individual	DeA-2003.1.1	3412±42	1877-1841 (7.6%) 1822-1796 (3.9%) 1782-1619 (83.9%)	*loc. cit.*
21	W III	Luduş-'Fabrica de zahăr'	Feature Cx. 5	Pig jaw	RoAMS 16-03	3346±73	1876-1841 (3.0%) 1820-1797 (1.6%) 1781-1492 (88.6%) 1483-1452 (2.3%)	Berecki 2016: 137; Simion and Sava 2016: Tab. 23
22	W III	Luduş-'Fabrica de zahăr'	Feature Cx. 22	Bovine femur	RoAMS 16-07	3422±36	1876-1841 (8.9%) 1821-1797 (4.1%) 1782-1629 (82.4%)	*loc. cit.*
23	W III	Luduş-'Fabrica de zahăr'	Feature Cx. 22	Human femur	RoAMS 16-08	3345±78	1876-1841 (3.3%) 1821-1796 (1.9%) 1782-1451 (90.1%)	*loc. cit.*
24	W III (?)	Luduş-'Fabrica de zahăr'	Next to Cx. 22	Notched scapula	RoAMS 16-06	3101±66	1506-1195 (95.0%) 1141-1134 (0.4%)	*loc. cit.*
25	Post W III	Luduş-'Fabrica de zahăr'	Feature Cx 6	Notched scapula	RoAMS 16-04	3186±73	1626-1279 (95.4%)	Berecki 2016: 137
26	W C	Sighişoara-('Cartierul Viilor' sau 'Dealul Viilor')	Feature	Charcoal	Bln-4622	3330±51	1742-1707 (6.2%) 1701-1501 (89.2%)	Popa and Boroffka 1996: 56 ; Motzoi-Chicideanu 2004: 82; Ciugudean and Quinn 2015: 149 (site referred to as 'Dealul viilor'); Boroffka, pers. com. 2018
27	W III/IV	Geoagiu de Sus-'Viile Satului'	Pit in Unit 2 and 3/2013, intermediate fill (Level 7)	Charcoal	OS-107554	3470±25	1882-1738 (89.2%) 1714-1697 (6.2%)	*loc. cit.*
28	W III/IV	Geoagiu de Sus-'Viile Satului'	Pit in Unit 2 and 3/2013, upper fill (Level 6)	Charcoal	OS-107666	3370±45	1767-1530 (95.4%)	Ciugudean and Quinn 2015: 151; tab. 1)
29	W IV (?)	Geoagiu de Sus-'Viile Satului'	Pit in Unit 2 and 3/2013, upper fill (Level 9)	Charcoal	OS-107555	3260±25	1614-1496 (91.3%) 1476-1460 (4.1%)	Ciugudean and Quinn 2015: 151; tab. 1

No.	Phase	Site	Context	Sample characteristics	Laboratory label	CRA (yr BP)	Calibrated date (calBC) 2σ (95.4%)	Reference
30	W IV	Micești-'Cigaș(e)'	Pit C.7/2009	Unburned human bone	OS-108311	3460±25	1880-1732 (82.2%) 1721-1693 (13.2%)	Bălan and Quinn 2014
31	W IV	Micești-'Cigaș(e)'	Pit C.11/2012	Unburned human bone	OS-108811	3390±25	1745-1627 (95.4%)	Bălan and Quinn 2014
32	Deva-Bădeni	Gligorești-'Holoame'	Layer	Notched scapula	DeA-5021	3298±38	1682-1673 (1.0%) 1666-1498 (94.4%)	Gogâltan 2015: 76; fig. 29; Gogâltan and Popa 2016: 53-54
33	Deva-Bădeni	Vlada-'Pad'	?	?	DeA-5096	3249±30	1612-1490 (79.7%) 1485-1451 (15.7%)	Gogâltan and Popa 2016: 60
34	Deva-Bădeni	Vlaha-'Pad'	?	?	DeA-5152	3236±41	1612-1433 (95.4%)	Gogâltan and Popa 2016: 59

Table 2. Previously published radiocarbon dates for samples attributed to Wietenberg and the immediately following archaeological context.

sample and the archaeological event to be dated (see, e.g. Waterbolk 1971), were not explicitly considered for any of the aforementioned samples, e.g. was the feature in Sighișoara-'Cartierul Viilor' formed over a shorter or longer period of time, and how does the sample relate to its duration? (The reverse order given for the samples in Geoagiu de Sus-'Viile Satului', with the Wietenberg IV layer as the lowest and Wietenberg III/IV as more recent [Ciugudean and Quinn 2015: comp. tab. 1 with p. 151], is most likely a typo, given that there is no explanation for this stratigraphic sequence in the text). Moreover, the old wood effect (caused by dating of reused wood or of earlier parts of the wood than the rings found immediately under the bark), which is one of the earliest known causes of age offsets in radiocarbon dating, was not properly taken into account despite being known to the authors (e.g. Ciugudean and Quinn 2015: 151) and despite wood anatomy analyses being available in Romania. Thus there is no information on the wood species or the part of the wood from which the samples were taken (pith, heartwood, sapwood, young wood, branch or twig). Such data can provide clues on the distance in time between the dated sample and the target event (see, for example, Palincaș 2017: 2-4) and are crucial in deciding whether the sample was worth dating at all. Further, the number of dated tree rings is also relevant, as samples with few tree rings are more influenced by possible short term high oscillations in radiocarbon content in the atmosphere, such as the 'Miyake event' (Miyake *et al.* 2012), than samples of ten or more tree rings. In summary, based on the published data, none of the five aforementioned wood samples can be considered reliable for the absolute dating of their archaeological contexts.

Charred grains are ideal for radiocarbon dating as they are short-lived samples (with life spans of a few months) and it is presumed that they cannot be much older than their context (long-term preservation before deposition would normally be excluded). The context from Oarța de Sus is also ideal: a ritual pit (Pit 22) with characteristic Wietenberg II pottery and a large quantity of grains (Kacsó 2015: 432), meaning that the radiocarbon dates obtained for the grains are very close to the moment of ritual deposition of the grains and pottery and therefore relevant for the dating of the associated pottery. It is unclear why the two results obtained for grains from the same pit are so different that they do not even overlap at a confidence level of 95.4%. Nevertheless, there are no clear methodological grounds to reject either of the two dates obtained for these grains.

Unburned human bones constituted the dating material for five samples originating from two sites: Voievodeni, where three skeletons out of a total of five found in one pit with Wietenberg III pottery were dated (Németh 2015; erroneously described in Bălan *et al.* 2014: fig. 283 as animal bones); and Micești-'Cigaș(e)', where two single skeletons were found in separate pits with Wietenberg IV pottery (C.7/2009 and C.11/2012) (Bălan and Quinn 2014; Bălan *et al.* 2016: 85, pl. V, where it is attributed to the classical phase of the Wietenberg culture) (Figure 3). Unlike other cases in the Wietenberg area, where skeletons were recomposed after excarnation of the human bodies (e.g. Sibișeni [Palincaș 2014: 315] and consequently could be – but do not necessarily have to be – *significantly* earlier than the associated pottery, the features from Voievodeni and Micești seem to raise no such problems (whether Skeleton no. 4 at Voievodeni with its several missing parts was laid somewhere else before deposition in this pit, or the missing parts were removed just before its deposition, remains to be established by detailed anthropological analysis; of relevance here is that it still has most parts in anatomic connection so that the

distance in time between this first stage of handling of the dead body and the deposition of the associated pottery is small and unable to hamper the radiocarbon dating). Nevertheless, the authors' confidence that the radiocarbon dates obtained from bone collagen accurately date the death (*sic*) of the individual because they are not affected by the 'old wood' effect (Bălan and Quinn 2014: 119; Ciugudean and Quinn 2015: 153), by which probably the absence of an age offset is meant, stands in contradiction to previous research. First, the turnover time of bone collagen is usually ten years (Manolagas 2000: 116, although it can also be of 20-30 years in case of old age or illness: Lidén and Angerbjörn 1999: 1780), which means that the radiocarbon date obtained from bone collagen is calculated based on the C uptake that occurred during the last decade of a person's life and not at the moment of death itself.

Second, radiocarbon dates obtained from human (or any other omnivore's) bone collagen can have significant age offsets caused by diet if this includes carbon from sources that are not in equilibrium with the atmosphere. These sources are mainly marine and fresh water. They can be recognised in bone collagen by their values of $\delta^{13}C$ and $\delta^{15}N$ (see Palincaş 2017: 5-7 with further literature). Although it is fairly unlikely that a marine reservoir effect (MRE) would be present in radiocarbon samples from Transylvania, it cannot be ruled out entirely: for example, if we accept an Aegean connection for the Middle Bronze Age in Transylvania, then we also have to take into consideration that some people, albeit only a few, may have traveled to and lived for a while in those remote regions, and if they consumed marine food while there, this might yield an MRE. What is more likely to appear in the Middle Bronze Age in Transylvania is a freshwater reservoir effect (FRE) due to freshwater fish consumption: both sites are within walking distance of rivers – in the case of Voievodeni, the Mureş River and the Leţ Creek (Németh 2015: 179); in the case of Micești, the Mureş and the Ampoi Rivers (Bălan 2014: 95) – and the presence of fish bone in a ritual context (Haimovici 2003: 58) suggests a special meaning being attributed

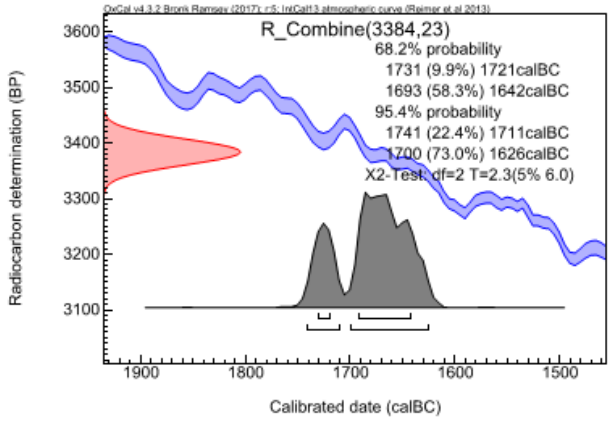

Figure 4. Voievodeni. Combination of the radiocarbon dates of the samples from Skeletons 1, 4 and 5 (the T value of 2.3 of the Ward and Wilson test for two degrees of freedom being lower than 6 indicates that there is less than 5% chance that the three samples are not contemporaneous or, in other words, that the three samples are statistically contemporaneous).

to fish among Wietenberg communities. Freshwater fish consumption, recognizable in principle due to higher $\delta^{15}N$ and lower $\delta^{13}C$ values than those typical of an entirely terrestrial diet, is known to cause higher age offsets in radiocarbon dates than marine food consumption (see, for example, Cook *et al.* 2002) and until recently correction of the radiocarbon age was considered possible (Bronk Ramsey *et al.* 2014). However, a recent case study showed that the $\delta^{15}N$ and $\delta^{13}C$ values in freshwater fish are highly variable and each is associated with highly variable radiocarbon age offsets. This hampers diet reconstruction and makes correction of radiocarbon dates impossible (Ervynck *et al.* 2018). Consequently, while according to the χ^2 test the skeletons from the Wietenberg III feature at Voievodeni are statistically contemporaneous and the dates resulting from their combination – i.e. 1741-1711 cal BC with 22.4% probability and 1700-1626 cal BC with 73.0% probability (Figure 4) – is compatible with the Wietenberg II phase suggested based on the samples

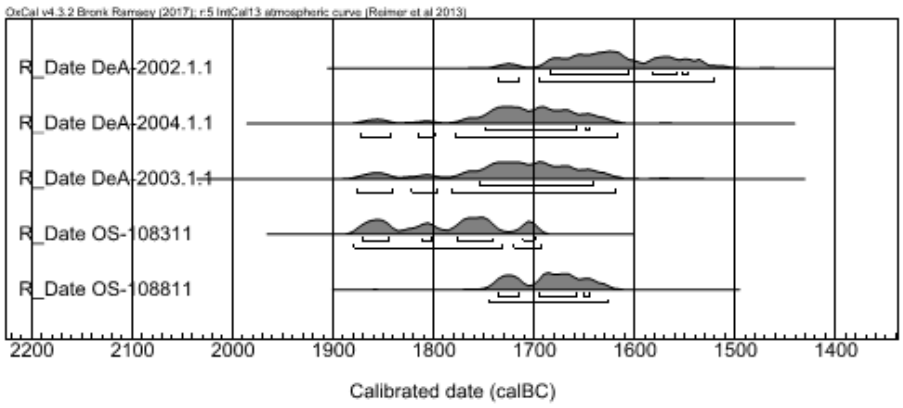

Figure 3. Multiple plot of radiocarbon dates from the Wietenberg III pit at Voievodeni (samples with the laboratory identifier DeA) and two Wietenberg IV pits at Micești (samples with the laboratory identifier OS).

from Derşida, this does not mean that the Voievodeni samples are reliable, because we do not know whether they include any reservoir effects (FRE in particular). The latter should be verified before resorting to any statistical approach to calibration. As so far none of the human bone samples from the Wietenberg area were published with C and N stable isotope analyses of diet reconstruction, these cannot be retained as reliable samples for radiocarbon dating.

Cremated human bones are poor candidates for radiocarbon dating: as an exchange takes place during cremation between the C endogenous to the bones and the C from the combustion milieu depending on the combustion conditions (temperature, duration, presence of water vapors and wind), the radiocarbon date cannot be accurate unless the fuel is contemporaneous with the cremation – i.e. no old wood, coal etc. is used as fuel (e.g. Snoeck *et al.* 2014). The possibility of an old wood effect in cremated bones should therefore be considered, even if it seems that most cremations used relatively young wood – i.e. not considerably older than the date of the cremation (van Strydonck *et al.* 2010: 583-584). To ascertain the accuracy of the radiocarbon dates obtained from cremated bones it is necessary to also analyze the charcoal resulting from the same cremations in terms of wood anatomy and then to date it by radiocarbon. Ideally, several pieces of charcoal, if present, should be analyzed: if different pieces produce different radiocarbon dates it then becomes clear that the old wood effect is present in the radiocarbon dating of the cremated bones. Moreover, it is believed that depending on the position of the body on the pyre, the exchange of C with the combustion milieu affects different body parts differently and consequently cremated bones from different parts of the body could return different radiocarbon dates (see, for example, Zazo *et al.* 2012). None of these aspects have been taken into account so far when dating cremated bones from the Wietenberg area and therefore the present results do not constitute a firm basis for an absolute dating.

Animal bones appear to have been dated in eight cases: two with more specific descriptions - one pig jaw and one bovine femur (from Luduş: RoAMS 16-03 and RoAMS 16-07, respectively); three with the rather generic indication of having stemmed from notched scapulae (RoAMS 16-06 and 16-04 from Luduş and DeA-5021 from Gligoreşti); and a further three with only the general description of 'animal bones' (from Rotbav: Dietrich 2014b: 59). Based on current information, with the exception of the herbivore samples, for the remainder it is not possible to know whether or not they were correctly chosen for dating. Pigs are omnivores, which means their diet could have contained human food leftovers, including fish. However, whether or not this was the case, and to what extent it would affect the radiocarbon dating, cannot be established without knowing the $\delta^{15}N$ and $\delta^{13}C$ values of the sample. The other animal bones are not even attributed to species. All we know of the notched scapulae is that in the Noua culture (partly contemporaneous with and partly succeeding the Wietenberg culture in Transylvania), with the exception of a pig scapula, bovine bones were mostly used (given that with this type of implement it was bone dimensions, not species that was of relevance: Bălăşescu and Dietrich 2009). As to the samples from Rotbav described as 'animal bones', doubts can be raised as to whether they were classified as such by an archaeozoologist (an archaeozoologist normally identifies the species rather than simply classifying bones as animal or human) or whether they were assumed to be animal bones simply because they were found in settlement layers (Rotbav). If the latter is the case, then it is possible that at least one of them could have been a human bone (see, for example, Comşa 2005). Interestingly, the radiocarbon dating of these 'animal bones' indicated a large gap between phases II and III of the Wietenberg culture (Figure 5).

This could have been caused by diet, but the lack of relevant data hinders any further discussion. In addition, the authors mostly do not specify whether they took site formation processing into consideration when attributing animal bones to features, although the possibility that animal bones – particularly smaller ones – could have moved between layers during the post-depositional period (Bowman 1990: 52-53) has long been noted. In summary, there is only one animal bone sample – i.e. the bovine femur found in a pit at Luduş (RoAMS 16-07) – that meets the methodological criteria for radiocarbon dating.

Finally, the two dates from Vlaha (Table 1) have to be left out of this discussion because thus far the samples lack any description.

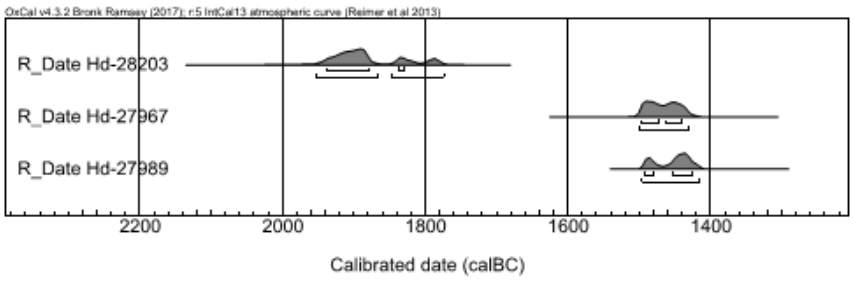

Figure 5. Rotbav. Multiple plot of radiocarbon dates: Hd-28203 from layer 2, Wietenberg II phase and Hd-27967 and Hd-27989 from layer 3, Wietenberg III phase.

Results

By applying the methodological requirements discussed above to the total of 34 samples previously published we are able to identify six samples as being reliable in the radiocarbon dating of the Wietenberg culture:

- the two grain samples from the Wietenberg II pit at Oarţa de Sus-'Ghiile Botii' (Ly-9190 and Bln-5626)
- one bovine bone sample from the Wietenberg III settlement at Luduş-'Fabrica de zahăr' (RoAMS 16-07)
- two samples from the Wietenberg III and slightly later contexts at Luduş-'Fabrica de zahăr' (RoAMS 16-06 and RoAMS 16-04, respectively) taken from the notched scapulae of unspecified species, but most probably bovine
- one sample similar to the latter two stemming from a post-Wietenberg (i.e. Deva-Bădeni) settlement at Gligoreşti-'Holoame' (DeA-5021).

With two of these samples (RoAMS 16-04 and RoAMS 16-06) having too large error terms to be useful for dating (±73 and ±66, respectively: Table 2), we are left with only four. To these the five new samples from Derşida and Pălatca, published here, can be added. The resulting nine samples no longer cover all of the Wietenberg phases.

For the Wietenberg II phase there are five remaining dates: three from Derşida and two from Oarţa de Sus. The three samples from Derşida are much earlier than sample Ly-9190 from Oarţa de Sus but broadly contemporaneous with sample Bln-5626. From their comparison with the latter sample it emerges that:

- within the 1 σ error range, the Bln-5626 sample from Oarţa de Sus (dated to 1887-1861 at 15.8% and 1853-1772 at 52.4% probability) is earlier than that from Pit 2 at Derşida (RO-AMS 144.47, dating to 1766-1686 cal BC) and is contemporary with the dates for House 1 and Pit 6 at Derşida (RO-AMS 142.27 and 143.47);
- within the 2 σ error range, the Bln-5626 sample from Oarţa de Sus (RO-AMS 144.47, dated to 1932-1742 at 94.3% and 1709-1701 at 1.1% probability) could also be contemporaneous with the sample from Pit 2 in Derşida.

This comparison, while it does not contribute to a more precise dating of the Wietenberg II phase, nevertheless indicates that the dating suggested based on Derşida – approx. 1750 cal BC as the date when layer 3 existed, and approx. 1800, or somewhat earlier, as the date when the previous layer (layer 2) existed – is probably correct. Whether the latter date (i.e. late 19th century) is also valid for the beginning of the Wietenberg II phase remains unclear, as it depends on how layer 2 from Derşida relates to other Wietenberg II sites. At the same time, it can be estimated that the previous dating of the Wietenberg II phase to approx. 1900-1700 BC is too large, particularly for its earliest part, and that at least the first half of the 19th century should be ruled out (Gogâltan 2015: 77). One of the most important consequences of this dating is that the emergence of the Wietenberg II phase under Mycenaean influence (e.g. Chidioşan 1980: 74; Palincaş 2018: 85) should be rejected: even if we accept the results of the radiocarbon dating that situate the transition from the Middle Helladic III to Late Helladic I (when the Mycenaean period begins) between 1742 and 1623 cal BC (Wild *et al.* 2010: 1019-1020), instead of early to mid-16th century BC as suggested by earlier research (Sandars 1971: tab. 3), this is still too late a date for the Wietenberg II habitation at Derşida (which existed decades before 1750 cal BC) and consequently for the beginning of the Wietenberg II phase.

The only remaining Wietenberg III sample, i.e. that from Luduş, most probably dates to the interval 1782-1629 cal BC (82.4%: Table 2; Figure 6). This date, while compatible with the dating of the Wietenberg II phase resulting from the analysis of the dates from Derşida, does not allow for a more precise dating (e.g. establishing of the limit between the Wietenberg II and III phases).

The three post-Wietenberg samples can be dated to between 1666 (the earliest possible date for the sample at Gligoreşti with a 94.4% confidence level) and 1281 cal BC (the latest possible date for the sample at Pălatca with a 95.4% confidence level) and would seem to date subsequent rather than contemporaneous habitations. As discussed above, for the habitations al Pălatca, the dating of around 1400 cal BC is more probable (Tables 1, nos. 4-5 and 2, no. 32; Figures 2 and 6). These dates suggest that the Wietenberg IV phase as defined by Mihai Rotea ended either around 1500 cal BC or somewhat earlier; however more dates are needed to confirm this possibility (Horia Ciugudean dated the end of the Wietenberg IV phase to around 1450 cal BC, but it should be noted that he defines this phase differently: Ciugudean 1999). The contemporaneity of this post-Wietenberg phase (called Gligoreşti by Florin Gogâltan and Deva-Bădeni by Mihai Rotea) with the Reinecke Br D horizon, dated to the 13th century BC (Müller-Karpe 1959; David-Elbiali 2013), is thus questionable, primarily, for the site at Gligoreşti itself, for according to the radiocarbon date DeA-5021 this can be dated no later than 1498 cal BC with 94.4% probability (Table 2) – i.e. it is roughly two hundred years earlier than the Reinecke Br D period.

It should be added to the interpretation presented above that thus far it has not been possible to exclude a certain

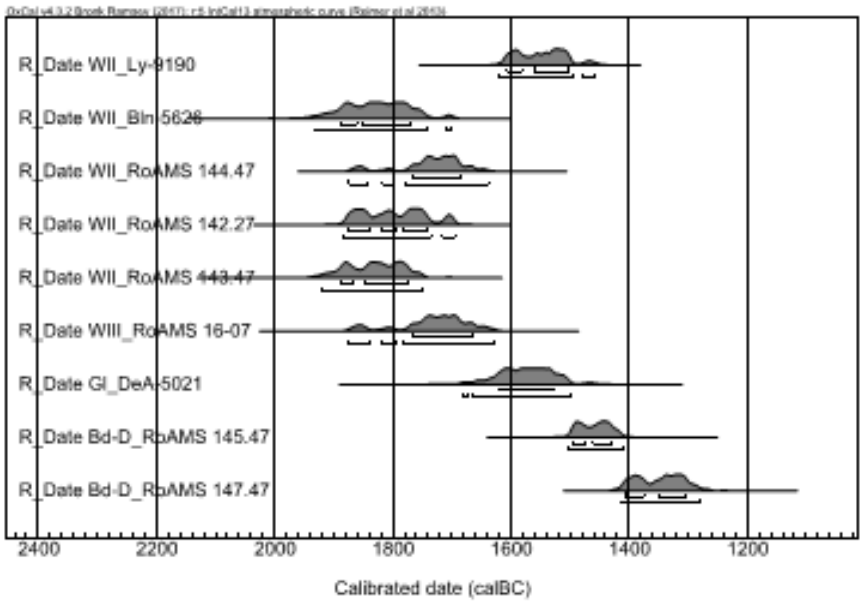

Figure 6. Multiple plot of the Wietenberg and post-Wietenberg radiocarbon dates considered reliable after the selection of samples based on criteria specific to the sample material: WII – Wietenberg II phase; WIII – Wietenberg III phase; Gl – Gligoreşti Group (Deva-Bădeni after M. Rotea) and Bd-D – Deva-Bădeni Group.

aging of the samples due to animals having fed on grass located close to mineral waters, i.e. due to a hard water effect (Carreira *et al.* 2008; Hood *et al.* n.d.; Philippsen 2013), given that Transylvania is particularly rich in mineral waters (Roşca *et al.* 2016). More dated samples are needed to establish whether this is the case, as not all samples are likely to be affected by a hard water effect.

Concluding remarks

Based on new radiocarbon dates, this article proposes a fairly precise absolute dating for layer 3 at Derşida, which is attributed to the later Wietenberg II habitation in the settlement (Chidioşan 1980), i.e. around 1750 cal BC. This suggests that the Wietenberg II phase already existed around 1800 cal BC and most probably also slightly earlier. Compared with the earlier dating of this phase, i.e. between 1900 and 1700 cal BC (Gogâltan 2015: 77), while the new dates from Derşida do not prove that the Wietenberg II phase did not begin slightly after 1900 BC, they do suggest that this date is probably too early. The dates from Derşida also rule out the second half of the 17th century as a possible date for the beginning of the Wietenberg II phase. This implies that the Wietenberg II phase could not have developed under the influence of the Mycenaean civilisation as previously argued (for example, by Chidioşan 1980: 74; Hänsel 1982: 24; Palincaş 2018: 85), even if we accept the earliest suggested date of 1742-1623 cal BC (Wild *et al.* 2010: 1019-1020) for the beginning of the latter. At the same time, this dating does not rule out an earlier Aegean influence on the Wietenberg culture (as argued by Vulpe 2001; Daróczi 2010-2011; Rotea 2017: 67).

The two dates from subsequent layers at Pălatca seem to indicate that the Deva-Bădeni Group, following the Wietenberg IV phase, existed around 1400 cal BC.

This article also argued that of the 34 previously published radiocarbon dates, only four can be considered reliable on methodological grounds: two for the Wietenberg II phase (Bln-5626 and Ly-9190); one for the Wietenberg III phase (RoAMS 16-07); and one for a post-Wietenberg context (DeA-5021) (Figure 6). Apart from two dates with excessively wide error ranges, the other dates were rejected on methodological grounds, i.e. due to insufficient consideration of the logic of radiocarbon dating specific to the sample material. A correct application of the methodology in radiocarbon sampling is mandatory, for otherwise acceptance of the results becomes dependent on the archaeologists' expectations, thereby eliminating the independent nature of this dating method. Whether or not the eliminated dates are in agreement with those considered reliable and the fact that two dates adjudged to be reliable (Bln-5626 and Ly-9190 from Oarţa de Sus) are in clear disagreement with each other is methodologically irrelevant: absolute dates obtained by faulty methodology remain uncertain even if by chance they deliver dates that later prove to be correct; alternatively, a well applied radiocarbon dating methodology does not always lead to successful dating. There are some famous case studies in which the differences of over one hundred years between the historical-archaeological absolute dating and radiocarbon dating could not be explained (see, for example, Kutschera 2012; Higham *et al.* 2010). Based on archaeological expectations alone, these radiocarbon dates are often rejected without much concern; however, they have the potential to lead to improvements in the radiocarbon dating method.

Finally, the analysis presented here gives rise to certain lessons for future strategies of dating the Wietenberg culture by radiocarbon. First, it is clearly necessary that more attention be paid to the logic of dating

specific materials. Second, a more complex dating strategy is needed, one that starts with archaeological features with which several types of material datable by radiocarbon are associated: for example, the pits in Oarţa de Sus with their complex association of human and animal bones, charred wood, grains, etc. (Kacsó 2015: 428-435) or cremation graves that also contain charcoal pieces, as in Fântânele (Marinescu 2008). Their dating needs to take into consideration not only whether individual samples meet the methodological criteria for relevance, but also the complexity of the human practices that led to the formation of the dated feature – human mobility between settlements, animal husbandry practices, the reburial of human bodies and body parts, etc. – which seem to have been more complex in the Wietenberg area than elsewhere.

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Author contributions

Nona Palincaş: discussion of radiocarbon dates and writing of the text; *Mihai Rotea*: discussion of Wietenberg periodisation and archaeological excavations at Derşida and Pălatca; *Tiberiu Sava*: AMS dating of the Derşida and Pălatca samples; *Gabriela Sava* and *Oana Gâza*: chemical pretreatment of said samples; *Monica Bodea*: excavations at Derşida; and *Constantin David*: discussion of the statistical contemporaneity of radiocarbon dates from Voievodeni.

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Archaeological-Historical Information and Radiocarbon Dating: Problems of the Late Bronze-Early Iron Age Chronology of the Carpathian-Danubian-Balkan Region

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Abstract

This paper discusses the dating of the end of the Bronze Age and beginning of the Iron Age (i.e the Reinecke Br D and Ha A phases) in present-day Central and Eastern Romania and the neighboring regions to the north (in present-day Ukraine). It compares the results of radiocarbon dating and cross-dating and concludes that the two methods produce significantly different results, with the radiocarbon dates being in most cases approx. 150 years higher than those obtained by cross-dating. The cause of this systematic difference cannot currently be explained. Further, the paper highlights the need for more radiocarbon dates for the study period.

Keywords: Late Bronze Age; Transylvania; Moldavia; Dobrudja; the Noua-Coslogeni, Gáva-Holihrady, Corlăteni-Chişinău and Babadag cultures; radiocarbon dating; historical-astronomical chronology

Introduction

The archaeological research conducted during the past half century shows that the vast area between the Dnester river valley and the Transylvanian Plateau was inhabited in the Late Bronze Age (LBA) by the people of the Noua culture. Several archaeologists believe that this culture is of an eastern origin and that it spread from the north-western Black Sea regions to the intra-Carpathian region. The stratigraphic data prove that during the following period, referred to by some Romanian authors as LBA III (Ciugudean 2010, with further literature) and by others as the Early Hallstatt period (where Early Hallstatt represents the Reinecke Ha A-B phases corresponding to the Central European Urnfield period: László 1989, 2010, the latter also with further literature), other archaeological cultures with different settlement types, burial practices and object repertoires appeared in the former distribution territory of the Noua culture (Figure 1). Thus, in the regions of the upper Sereth, Pruth and Dnester rivers, today part of Sub-Carpathian Ukraine, north-west Moldavia (the historical region of Bukovina) and Transylvania, the Noua culture was followed by the Gáva (-Holihrady) culture; while between the Sereth and Dnester rivers, today part of Romania's Moldavia region and the Republic of Moldova, by the Corlăteni-Chişinău culture. These *post*-Noua cultures can be characterised archaeologically by the specific pottery with channeled decorations that has its origin in the ceramics of the Middle and Late Bronze Age cultures of the Middle Danube region, and especially that of the Tisza river basin, and which spread eastwards beyond the Carpathian Mountains. In Central and Southern Moldavia, the Noua (-Coslogeni) culture was followed by the successive Tămăoani-Holercani and Cozia-Saharna-Solonceni cultures/groups, while in Dobrudja the Noua-related Coslogeni culture was followed by the Babadag culture. These cultures are characterised by ceramics with incised and impressed decorations specific to the Eastern Balkan and North-Western Pontic regions. Some channeled decoration is also present. The origin of the latter was searched for in a westerly direction, more precisely in the Cruceni-Belegiš II and Gáva areas (for further reading see László 1989, 1993a and 1994: 91-95, 156-163, 164: chronological table; Kaiser and Sava 2006; Ciugudean 2010; Kašuba and Zanoci 2010; László 2010: p. 125-130; László 2011; Bader 2012; Ciugudean 2012; Marta 2012; Ailincăi 2013; Sava 2014; and Leviţki and Kaşuba 2015, with further literature. Also Figure 1).

This picture suggests a *historic* turning point that is discernable not only in the appearance of new *archeological cultures*, but also in the change of direction of the *cultural movement*, from a mainly East-West trend during the Noua-Coslogeni culture to a predominantly West-East trend represented by the spread of the cultures with channeled ceramics and, to a certain extent, a South-North trend with the spread of the cultures with incised and impressed pottery. There is no satisfactory answer as to the reasons these changes came about, whether historical (as a 'counter-offensive of the Thracian block'), environmental (climatic change) or relating to population movement, etc. (László 1989, 1993 and 1994; Kaiser and Sava 2006; Ciugudean 2010; Kašuba and Zanoci 2010; László 2010, 2011; Bader 2012; Ciugudean 2012; Marta 2012; Ailincăi 2013; Sava 2014; and Leviţki and Kaşuba 2015).

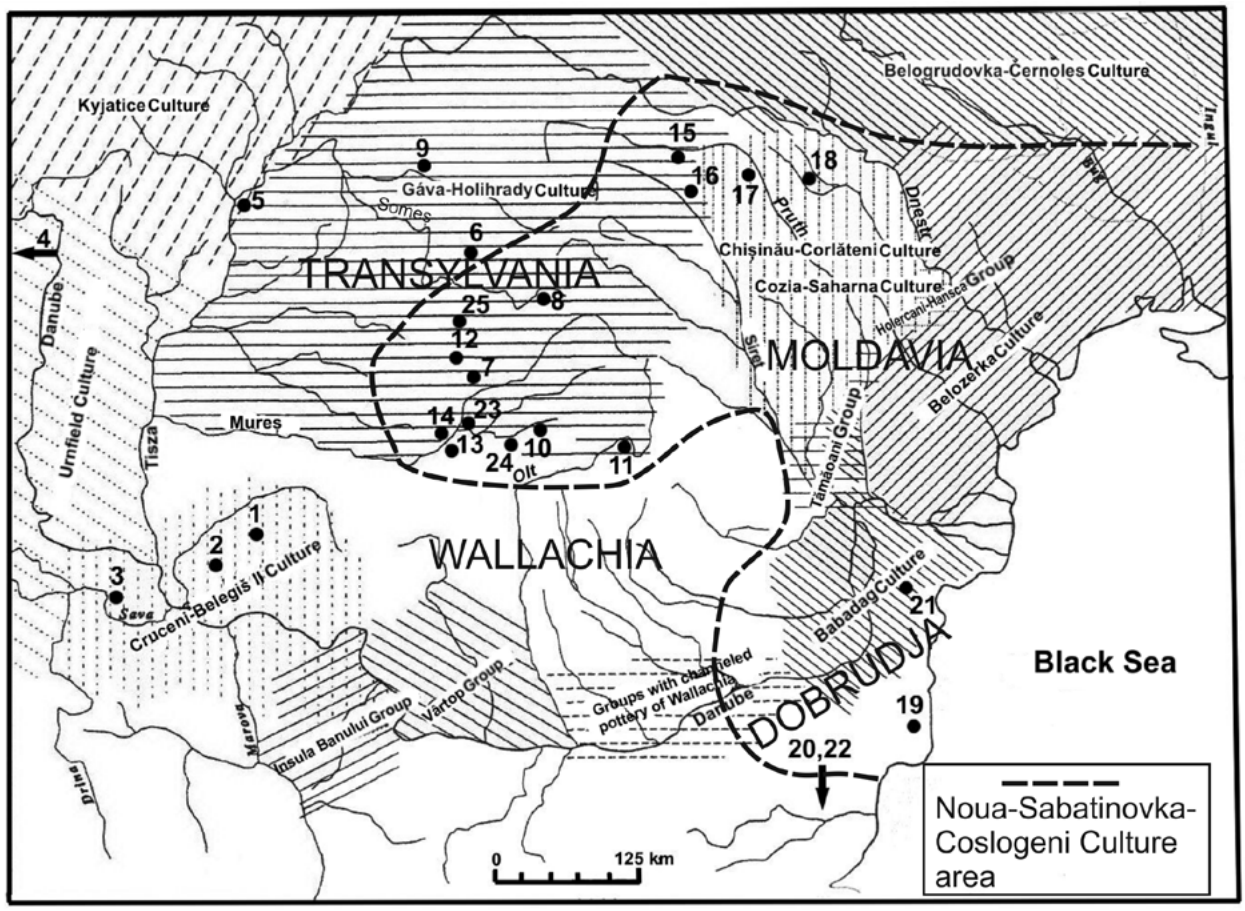

Figure 1. Distribution map of some Late Bronze Age and Early Hallstatt cultures and the sites represented in the Diagram (Figure 2). 1. Giroc; 2. Foeni; 3. Hrtkovci-'Gomolava'; 4. Németbánya; 5. Polgár; 6. Lăpuş; 7. Valea Florilor; 8. Băile Figa; 9. Királyvölgy/Valea Regilor; 10. Sighişoara; 11. Rotbav; 12. Vlaha; 13. Teleac; 14. Alba Iulia; 15. Mahala; 16. Siret; 17. Crasnaleuca; 18. Odaia; 19. Durankulak; 20. Kastanas; 21. Babadag; 22. Troy; 23. Teiuş; 24. Valea Viilor; 25. Floreşti-'Polus'.

The development of a solid chronology for the process under discussion is of obvious importance and this paper seeks to contribute to this endeavor. A specific feature of this study period is that the calibrated radiocarbon dates can be compared with the results of cross-dating – i.e dating based on the circulation of objects between cultures, which is ultimately linked to the historical-astronomical absolute chronology of Egypt. In particular, in terms of cross-dating, what is of interest here is the historical chronology of the 2nd and 1st millennia BC in the Aegean – i.e. the Late Helladic, Sub-Mycenaean, Protogeometric and Geometric periods – and its links to the Egyptian historical chronology.

Radiocarbon samples and procedures

This paper discusses 90 radiocarbon dates from 26 archaeological sites in the study region. Some were discussed previously from various different perspectives (László 2015 and 2017b).

The dating of the aforementioned 90 samples was carried out in different laboratories, with the accuracy varying due to the specifics of the sample material (bone, charcoal, etc.), the differing quality of the samples and different measurement techniques. As far as the charcoal samples are concerned, for instance, we cannot rule out the old wood effect. Working with such a large series of ^{14}C dates has the advantage of allowing for the identification of outlying dates, which deviate from well grouped dates and should not be taken into consideration or should be dealt with cautiously. The available 90 radiocarbon dates were entered into a Data List indicating the site, type of feature (settlement, burial, etc.), cultural-chronological attribution of the site, sample material, laboratory label, conventional BP and calibrated BC (1 and 2 σ error range) radiocarbon dates, and bibliographical reference. The same 90 radiocarbon dates were also recorded under the same running numbers used here in two diagrams showing their distribution in space and time, both in their conventional form (on the BP time scale, see László 2015: Fig. 2 and Pl. 2), and in their calibrated variant (on the cal BC time scale, see László 2017b: Tab. 1 and Fig. 2). In this paper, from the aforementioned Data List we have only included the *bibliography* and the

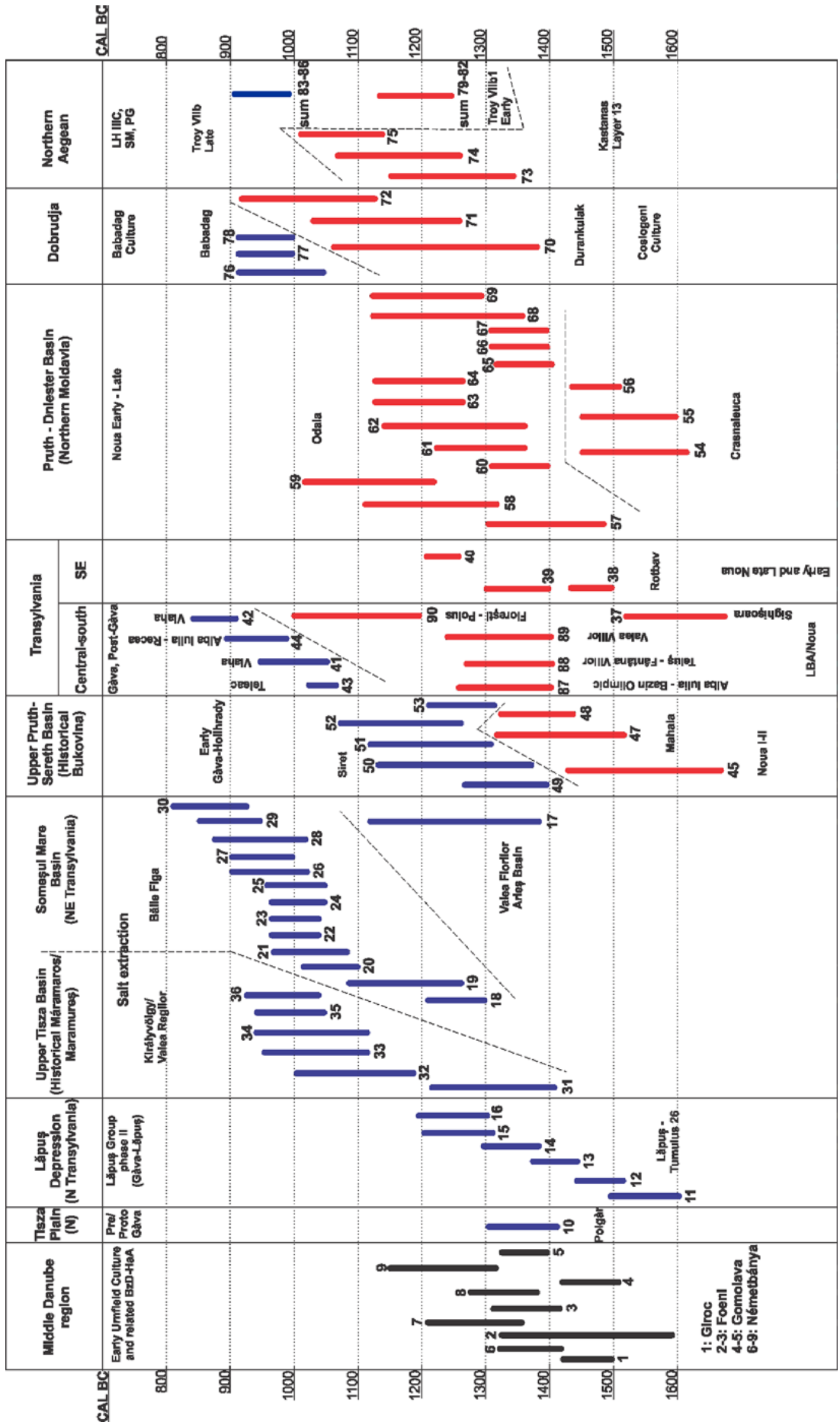

Figure 2. The spatial and temporal distribution on the cal BC time scale (1σ error range) of the sites of the Noua-Cologeni culture (red), the sites of cultures with channeled, incised and impressed pottery (blue), and various sites dating from the Urnfield Period in Transdanubia and Banat (black).

diagram showing the distribution in space and time of 90 radiocarbon dates on the cal BC time scale with a 1 σ confidence level (Figure 2). The time intervals expressed in terms of ^{14}C dating were represented by vertical lines, the lengths of which it was not always possible to trace accurately, but even so they paint a good overall picture. To aid understanding, the lines on the diagram representing the data for the Noua-Coslogeni period are shown in red and the data for the sites of the cultures with channeled, incised and impressed pottery in blue. The comparative dating nos. 1-9 are shown in black. In order to paint a chronological picture better able to reflect regional differences, the radiocarbon dates were as far as possible represented in the graphic according to the geographical position of the dated sites, generally from West to East. In this way, we can easily identify not only the time frames for which an archaeological phenomenon is documented in a given area, but also the geographical regions and periods of time for which we do not have radiocarbon age determinations. Viewed from this perspective, it is clear that the chronological picture outlined contains many gaps and that a new series of ^{14}C dating is required in order to produce a more coherent image. In the present state of the research, the radiocarbon dates show significant chronological differences with respect to the beginning, evolution and end of one and the same culture in different regions within its distribution territory.

In order to be able to distinguish better between the dating of the various archaeological sites and features, age determinations with a 1σ confidence level will be used. Thus, the chronological scheme outlined below may differ from the timelines suggested in other papers, where the dating is calibrated according to a 2σ confidence level.

The radiocarbon dating of the Noua and succeeding cultures

The earliest available dates for the beginning of the Noua culture are those from Mahala (level II, dating nos. 45 and 47-48: 1680-1430, 1520-1310 and 1434-1313 cal BC) and Crasnaleuca (nos. 54-56: 1610-1450, 1600-1450 and 1515-1435 cal BC). These series show that in the north of Moldavia (including the historical region of Bukovina), in the Upper Pruth river basin, the Noua culture had existed since the 16th century cal BC. The series of dates for the Noua settlement with 'ash-hills'('zolniki', 'cenuşar') in Odaia, on the Răut River, a tributary of the Dnester (nos. 57-69), indicates a long period of habitation, perhaps starting in the 15th century and certainly existing in the 14th century cal BC (see date nos. 57, 60 and 65-67: 1444-1300, 1398-1315, 1412-1319, 1400-1315 and 1403-1312 cal BC). This means that for the eastern Carpathians, at least in the northern part of the territory between the Sereth and Dnester Rivers, we can assume the Noua culture began in the 16th/15th century cal BC. However, the historical fate of this culture was not the same in all the different regions of said territory.

Comparing the aforementioned radiocarbon dates obtained for level II (attributed to the Noua culture) of the Mahala site with the existing dates for the Siret settlement (Mahala III type, i.e attributed to the early Gáva-Holihrady culture, nos. 49-52: 1400-1260, 1370-1130, 1310-1120 and 1260-1020 cal BC, and no. 53, combined dating of four samples: 1310-1210 cal BC), we can say that the development of the Noua culture first ended in the north-western periphery of the extra-Carpathian area of this culture, in the regions located at the foothills of the north-eastern Carpathians, i.e. the present sub-Carpathian Ukrainian and North-Western Moldavian region (the historical region of Bukovina), during the timespan stretching between approximately 1350 and 1300 cal BC, if not somewhat earlier. At the same time, the incipient (Pre-/Proto-?) Gáva-Holihrady culture appears in the aforementioned regions, in the Upper basins of the Dnester, Pruth and Sereth rivers. This culture spread throughout the passes of the Carpathian Mountains from the Upper and Middle Tisza region, which is considered the formative area of the Gáva culture.

In terms of the Noua culture in the Moldavian Plain, radiocarbon dates are only available for the early period (Crasnaleuca, nos. 54-56: 16th-15th century cal BC). However, as the dating of the site in Odaia shows, the development of the Noua culture can be followed in the Răut River Basin (in the north of the Republic of Moldova) until the 12th century cal BC (see the dating nos. 58-59, 63-64 and 68-69: 1310-1119, 1214-1108, 1261-1130, 1260-1130, 1365-1131 and 1289-1132 cal BC). Therefore, the end of the Noua culture and the settlement of the people of the Corlăteni-Chişinău culture specific to the so-called Early Hallstatt period east of the Sereth River could not have occurred in the northern part of the region between the Pruth and Dnester before the second half or, more likely, the end of the 12th century cal BC. Unfortunately, this is only an approximation, for we do not have any radiocarbon dates for the sites of the Corlăteni-Chişinău culture.

For the Central Moldavian Plateau, where both the Noua and the Corlăteni-Chişinău cultures (and later also the Cozia group, which was related to the Babadag culture) are well represented by numerous archaeological sites, we do not possess any radiocarbon age determinations.

The longest lifespan of the Noua-Coslogeni cultural complex to the east of the Carpathian Mountains can be seen in Dobrudja (and possibly also in Southern Moldavia). This derives from the radiocarbon dates for two sites in Dobrudja: Durankulak, which belongs to

the Coslogeni culture and is part of the Noua-Coslogeni phenomenon (nos. 70-71: 1380-1055 and 1270-1030 cal BC); and Babadag, the eponymous site of the Babadag culture (nos. 76-78: 1007-927, 997-921 and 997-921 cal BC). These data show that the replacement of the Noua-Coslogeni culture in its south-easternmost area by the cultures with incised and impressed pottery (Babadag in Dobrudja and Tămăoani-Holercani and Cozia-Saharna-Solonceni in the southern part of Moldavia between the Sereth and Dnester) probably occurred towards the middle or during the second half of the 11th century cal BC.

The date when and the paths whereby the Noua culture moved from Moldavia into Transylvania, as well as its subsequent fate in the region, are not well known. The radiocarbon dates for the early Noua phase at Rotbav (level Rt 4) suggests that the Noua culture appeared in south-eastern Transylvania during the 15th-14th centuries cal BC (see the very distant date nos. 38-39: 1497-1441 and 1405-1303 cal BC, respectively). This period corresponds with the end of the settlement at Crasnaleuca, the later period of the settlement at Mahala and the beginning of the settlement at Odaia, and is therefore contemporaneous with a developed period during the presence of the Noua culture in Moldavia. The settlement of the late Noua culture at Rotbav (level Rt 5) ends during the second half or towards the end of the 13th century cal BC (date no. 40: 1264-1208 cal BC). Unfortunately, the results of the ^{14}C measurements of the samples from the features belonging to the Gáva culture at Rotbav (level Rt 6) have not been published yet. The dating of the Noua settlement at Rotbav suggests that in south-eastern Transylvania the replacement of the Noua culture by the Gáva culture did not occur before the end of the 13th or the beginning of the 12th century cal BC.

During this time, the Gáva culture may already have existed in Central Transylvania (assuming that it spread from this region towards the south-east). However, this is merely a hypothesis: the available data do not confirm any chronological contact between the Noua and Gáva cultures in this region. On the one hand, recent dates would seem to demonstrate an extension of the presence of the Noua culture (or of a 'Noua-time', in the sense of an *ante*-Gáva period) until towards the beginning of the 13th century cal BC: Alba Iulia-'Bazinul Olimpic' (no. 87: 1385-1285 cal BC), Teiuş-'Fântâna Viilor' (no. 88: 1397-1302 cal BC) and Valea Viilor (no. 89: 1386-1281 cal BC), all covering the 14th century and the first decades of the 13th century cal BC. The dating obtained for the Noua grave of Floreşti-'Polus' (no. 90: 1200-1000 cal BC) is unreasonable and unacceptably late for a Transylvanian Noua feature. As far as the Gáva culture is concerned, radiocarbon dates in Central Transylvania only exist for its more developed and later phases. These can be placed towards the middle and second half of the 11th century and the 10th century cal BC based on the dates from Teleac (no. 43: 1060-1030 cal BC) and Alba Iulia-'Recea' (no. 44: 975-896 cal BC), on the Middle Mureş River, and Vlaha (no. 41: 1060-940 cal BC), in the basin of the Someşul Mic River. However these dates only reflect the current status of the issue. Until the results of the ^{14}C dating of some earlier habitation settlement levels (such as Alba Iulia-'Recea/ Monolit', dated to the Hallstatt A period: Lascu 2012: 135) and of the Gáva settlement at Rotbav (dated to the Ha B period: Dietrich 2012: 102-103; Dietrich 2014a: 61-62; Dietrich 2014b: 192, 213-214) are published, the dating of the beginning of the Gáva culture in Central and South-Eastern Transylvania remains an unsolved problem.

To the north of the Mureş River, in the Transylvanian Plain, the Noua culture is well represented by numerous archaeological discoveries. The northern border of this region, the valley of Someşul Mic and Someşul Mare, represents the north-western border of the entire distribution area for the Noua culture. The archaeological evidence suggests that the Noua culture in the Transylvanian Plateau was replaced by the Gáva culture, probably arriving from the north-west, i.e. from the Tisza region, along the (united) Someş Valley (a tributary of the Tisza River), and through the Poarta Meseșului Pass. Unfortunately, we do not have any radiocarbon age determinations either for the Noua or the Gáva cultures in this region, meaning that a beginning date for the Gáva culture (in this peripheral region of its distribution area) in the 13th-12th centuries BC is purely hypothetical. Whether the beginning of salt exploitation in the area and, with it, the radiocarbon dating of the salt extraction is linked with the Gáva culture must remain a matter of speculation (see the radiocarbon dates from the salt extraction sites at Valea Florilor [no. 17: 1380-1120 cal BC], and Băile Figa [nos. 18-30] [Ciugudean 2012: 117-119, Fig. 13], spanning the 13th-12th centuries [nos. 18-19], 11th-10th centuries [nos. 20-27] and also reaching into the 9th century cal BC [nos. 28-30]). If we accept the estimate for the beginning of the Gáva culture in the Transylvanian Plateau as being the 13th-12th centuries BC, then this places it close to the moment when the Gáva-Holihrady culture arrived in the historical region of Bukovina, during the second half of the 14th century cal BC, probably coming from the Upper Tisza region, through the north-eastern Carpathians. This change in area might be linked at least in part to the rich salt deposits and salt springs in the region (Alexianu *et al.* 2015). At this point, the evolution of phase II of the Lăpuş group continued outside the distribution area of the Noua culture, in the Lăpuş Depression (Northern Transylvania), as shown by the ^{14}C series of dates for Tumulus 26 at Lăpuş (nos. 11-16). Taken as a whole, the series spans the 16th-13th centuries cal BC. However, individual dates indicate different periods: nos. 11-13

date to the 16th-15th centuries, no. 14 dates to the 14th century, while nos. 15-16, two very close dates, cover the time span between the end of 14th and beginning of 12th centuries cal BC. In this region the first elements of the Gáva culture already began to appear in the form of the ceramic repertoire of the second phase of the Lăpuş group, also called the Lăpuş II-Gáva phase (Metzner-Nebelsick *et al.* 2010: 221-223), while the Gáva culture proper probably first appeared starting with the 12th century cal BC, immediately after the end of the Lăpuş group.

The Gáva culture can also be assumed to have made an early appearance in the historic Maramureş (Máramaros, Marmarosch) region, provided we accept the supposition that the series of ^{14}C dates (nos. 31-36) obtained for the salt extraction at Solone/Királyvölgy/Valea Regilor (Upper Tisza region, currently part of Trans-Carpathian Ukraine) are connected to the mining activities of the Gáva culture, in the same way as with the series of dates for Băile Figa (Harding and Szemán 2011; Ciugudean 2012: 117-119, Fig. 13). The earliest date in the series, no. 31, mainly covers the 14th-13th centuries, while no. 32 covers the 12th-11th centuries and nos. 33-36 the end of the 12th to the end of the 10th century cal BC. If we accept these dates, based on the purely speculative connection between salt exploitation in Maramureş and the presence of the Gáva population, it becomes easier to explain the spread of the Gáva culture beyond the North-Eastern Carpathians into Subcarpathian Ukraine and North-Western Moldavia (Bukovina) at an early date, i.e. approximately during the period 1350-1300 cal BC.

In summary, the radiocarbon dates available thus far for the Late Bronze Age and Early Hallstatt period paint a relatively broad picture with many gaps, but one which fits well with the picture obtained by archaeologists by means of typological and stratigraphic comparisons between sites. Namely, the calibrated radiocarbon age determinations show that the replacement of the Noua culture with the Gáva-Holihrady culture took place earlier in the Northeastern extra-Carpathian regions in present-day Subcarpathian Ukraine and the northwestern part of Romanian Moldavia (i.e. around the middle or second half of the 14th century cal BC), and somewhat later in Southeastern and Central Transylvania (i.e. probably not before the end of the 13th or beginning of the 12th century cal BC). On the other hand, the presence of the Noua(-Coslogeni) culture lasted longer (i.e. until the middle of the 12th century cal BC) in its eastern territory, in the Pruth-Dnester River Basin, and in Dobrudja (i.e. until the middle of the 11th century cal BC). The late phase of the Noua-Coslogeni culture in these areas may be synchronised with the early phase of the Gáva-Holihrady culture in the Northern Carpathian region. It is most likely that only the late phase of the Noua-Coslogeni culture in its south-eastern periphery came into contact with the Northern Aegean LBA (LH III C) civilisation, as seen in Greek Macedonia at Kastanas, layers 14-13 (nos. 73-75: approx. mid-14th to mid-11th century cal BC) and Troy VIIb1 (date nos. 79-82: second half of 13th to first half of 12th century cal BC). The Early Hallstatt Babadag culture and related groups (with their incised, impressed and knobbed wares) began around the middle of the 11th century cal BC – i.e later than the Gáva-Holihrady culture. The lifespan of these cultures/cultural groups (in accordance with both the typological data and the radiocarbon dating) can in effect be synchronised with the Troja VIIb layers 2-3 (date nos. 83-86: 10th century cal BC). (For a more detailed discussion on the relationship between the Late Bronze Age and Early Iron Age in the Lower Danube and Northern Aegean regions, including Kastanas and Troy, see László 2003, 2006, 2007, 2012 and 2013b with further literature).

The radiocarbon dates confirm and refine our previous observations regarding the regional differences in the transition from the Late Bronze Age to the Early Iron Age, i.e. that this took place earlier in the western part and later in the eastern and south-eastern parts of the area under study and that it occurred in a non-linear manner. These regional chronological differences could only with great difficulty have been revealed without the contribution of radiocarbon dating.

Discussion

The radiocarbon dates obtained for the LBA sites analyzed above are 100-200 years higher than the ages expected based on historical (contact) chronology (also called cross-dating). This was already noted with respect to the settlement at Siret (László 2010; here nos. 49-53). The settlement at Siret – as well as the settlement at Grăniceşti, both located in the Suceava Plateau (László 1994: 48-104) – was assigned to the early Gáva-Holihrady culture based mainly on the similarity of its pottery with that found in layer III at Mahala (Smirnova 1974, 1976). The ceramics and metal objects known from the early phase of the Gáva-Holihrady culture are typical of the Reinecke Ha A phase. The four ^{14}C dates from Siret span the period 1400-1020 cal BC (1 σ error range); within this period there are several shorter intervals with higher or lower probabilities that will not be discussed here (v. László 2010: Appendix 2). The four dates overlap within the time interval *c.* 1310-1130 cal BC and therefore it can be said that the settlement most likely existed during the 13th-12th centuries cal BC. This interpretation is also supported by the combined dating of the four samples: 3003±24 BP, i.e. 1310-1210 cal BC (68% probability) and 1320-1120 cal BC (88.1% probability) (László 2010: Appendix 3). However, this more limited interval (by comparison with the 1400-1020 cal BC interval) is

still higher than the dating expected according to the traditional historical-astronomical chronology for the Hallstatt A period (approx. 12th-11th centuries BC). A similar phenomenon – i.e. a systematic deviation of 100-200 years between calibrated radiocarbon dates and the historical dates – was also noticed in some sequences of the Egyptian and Aegean chronology, with no satisfactory explanation available: it remains unclear whether the cause of these discrepancies lies in the imperfections of the historical chronology, the deficiencies of the radiocarbon dating or both (Bietak 2000 and 2003; Bietak and Czerny 2007; Bietak and Höflmayer 2007; Kutschera *et al.* 2012; Müller 2005: 209; Shortland *et al.* 2008). According to the traditional archaeological chronology, which relies on the cultural links established between Central Europe and the Late Helladic III B-C and Sub-Mycenaean civilisations of the Aegean (and, ultimately, on the historical-astronomical Egyptian chronology), later extending into Eastern Europe, the periods Reinecke Br D and HaA were dated (e.g. by Hermann Müller-Karpe 1959) to the 13th-11th centuries BC. However, the radiocarbon dates obtained for the corresponding (i.e Late Bronze and Early Hallstatt) sites in the study region are higher, falling between the 14th and 12th centuries BC. Thus, while for the end of the Noua culture (represented by the settlement at Mahala and dated to the Reinecke Bz D phase) and the beginning of the Gáva-Holihrady culture in Bukovina (dated to Reinecke Ha A phase) we expected a date of around 1200 BC, the radiocarbon dating indicates a date of around 1350 cal BC. The credibility of this unexpectedly high dating is ensured by the equally early radiocarbon dating obtained for some sites of the Early Urnfield culture/period from Transdanubia and Banat, for the Pre- (or Proto-) Gáva culture of the Tisza Plain, and for phase II ('Lăpuş-Gáva') of the Lăpuş group in Northern Transylvania: see here the series of dates from Giroc and Foeni (nos. 1-2, Cruceni-Belegiš I phase); Foeni and Hrtkovci-'Gomolava' (nos. 3-5, Cruceni-Belegiš II phase, Bz D-Ha A); Németbánya (nos. 6-9, Late Urnfield Period, Bz D-Ha A1); Polgár (no. 10, 'Pre-Gáva' period, Bz D–Ha A1); Lăpuş (nos. 11-16, Lăpuş II/Lăpuş-Gáva phase, traditionally dated to the period Bz D–Ha A) (László 2010: 123-125).

At the same time, when judging the correspondence between the results of radiocarbon dating and cross-dating, we should bear in mind that the latter is not necessarily settled once and for all, as it depends on the state of research. This becomes clearer when we consider the new, dendrochronology-based dating of the Ha A2 and Ha B1 period in Western Switzerland, where it was established that the late phase of the Ha A2 and the early phase of the Ha B1 period overlap during the second half of the 11th century BC – i.e they are not periods that follow, one after the other, as assumed in the chronology by H. Müller-Karpe (David-Elbiali and Dunning 2005; David-Elbiali 2013). For Bz D and Ha A1, the periods of interest here, the dating to the 13th-12th century BC is still accepted (David-Elbiali 2013: 194), but to date they have not been the subject of any particular study.

The picture becomes even more complicated when independent dating methods are used for the same archaeological context. For example, discrepancies between the results of radiocarbon dating and cross-dating also appeared for the destruction layer of Phase Ib of the late Mycenaean site at Aigeira (North-West Peloponnese). Phase Ib was dated to the early LH III C period, mainly based on pottery. According to the dating of the Mycenaean pottery sequences, which relies on the historical chronology, the early period of the LH III C is placed in the first decades, possibly also the first half of the 12th century BC, immediately after the collapse of the Mycenaean palaces. By combining the eight ^{14}C dates from the aforementioned layer, the date 2967±16 BP, i.e. approx. 1300-1050 cal BC (1σ), was obtained. This interval can be narrowed down to approx. 1260-1120 cal BC with reasonable probability. In any case, compared with the archaeologically expected date, the beginning of this interval is too high and its end too low. Therefore, the ^{14}C dates could not be used in a more accurate dating of Phase Ib at Aigeira and, by consequence, a more accurate dating of the early phase of the LH III C within the much debated chronology of the LH III C period (Deger-Jalkotzy 2003, especially p. 467).

The timespans resulting from the aforementioned ^{14}C dates from Siret and Aigeira overlap considerably, indicating the partial contemporaneity of the two layers, with the beginning of the settlement at Siret slightly preceding the beginning of the destruction layer of Phase Ib at Aigeira. Consequently, the early phase of the Gáva-Holihrady culture in the north-eastern extra-Carpathian regions began at a time that corresponds to the end of the LH III B and continued into the LH III C period. However, the broader chronological consequences of this synchronism cannot be discussed here.

Concluding remarks

The initial optimism among experts in radiocarbon dating and archaeologists with regard to the compatibility of calibrated ^{14}C dates with the dates resulting from the historical chronology is now much more tempered. This holds true in particular for the later prehistoric periods (Late Bronze Age and Iron Age), where the two chronological systems may be compared and even a difference of less than a century, sometimes even a few decades, can influence the understanding of historical phenomena. At the same time, we should bear in mind that both methods – radiocarbon and cross-dating – are continuously being refined.

Moreover, because radiocarbon dating produces time intervals and not actual dates, such as those obtained for later periods from written texts or in other parts of Europe from dendrochronology, it cannot be used to solve subtle chronological problems (Hassan and Robinson 1987: 130). Under the circumstances, it has been argued that for the Mycenaean and even post-Mycenaean periods the pottery sequences give more accurate dates than dating by radiocarbon (Korfmann 2001: 27; for the preference of a pottery-based dating of the LH III C over ^{14}C dating, see also Deger-Jalkotzy 2003: 467).

In light of the systematic differences between historical and radiocarbon chronology, it is recommended to specify (and mark accordingly) the chronological system used in the dating of the LBA and EIA: either calibrated radiocarbon dates (expressed in *cal BC* years), or historical (contact) chronological dates (expressed in *BC/a.Chr*. and *AD/p.Chr.* years).

Establishing a solid chronology of the pre- and proto-historic periods in Romania will only be possible by implementing a comprehensive radiocarbon dating project (where possible also cross-checked with other dating methods) covering all periods and regions. It is our hope that the scientific program of the tandem accelerators of the Horia Holubei National Institute of Physics and Nuclear Engineering will also include such a project. Its success depends on the close cooperation, during all research stages, between the experts in charge of sample measurement and dating on the one hand, and the archaeologists providing the samples on the other.

Acknowledgements

The initial text was much longer but had to be summarised on account of editorial constraints.

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6-9. Németbánya: Ilon 1996: 153-157; Ilon 2015: 248-249.

10. Polgár: Szabó 2007: 154-158, 164-165.

11-16. Lăpuş: Metzner-Nebelsick *et al.* 2010: 222-225, Fig. 7.

17. Valea Florilor: Wollmann and Ciugudean 2005: 100-101, Fig. 1; Ciugudean *et al.* 2006: 50; Harding and Szemán 2011: 15 (slightly different calibrated dates).

18-30. Băile Figa: Harding and Kavruk 2010: 151-152, Tab. 1; Ciugudean 2012: 117, Fig. 13.

31-36. Királyvölgy/Valea Regilor: Harding and Szemán 2011: 12-16, Tab. 1, Fig. 11.

37. Sighişoara: Popa and Boroffka 1996: 56, n. 40; Motzoi-Chicideanu 2004: Figs. 18-19; Motzoi-Chicideanu 2011: 528, note 967; Ciugudean and Quinn 2015: 150, Fig. 2.c, Tab. 1.

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41-42. Vlaha: Németh 2015: 370-371, 381-384, Tab. 2 (p. 371); see also Gogâltan *et al.* 2008: 115-116; Gogâltan *et al.* 2011: 167; Nagy and Gogâltan 2012: 35-39; László 2013a.

43. Teleac: kind information H. I. Ciugudean, 23.10. 2008; László 2010: 125, note 18.

44. Alba Iulia-'Recea': Ciugudean 2012: 117, Fig. 11.

45-48. Mahala: Smirnova 1972: 29; Smirnova 1976: 126; Smirnova 1990: 9-11; László 1993b: 23-29, Tab. 1; László 2010: 125.

49-53. Siret: László 2010: 122-125, Tab. 1 and p. 130-132, Appendices 1-3; see also Görsdorf 2006, 2007.

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Radiocarbon Dating of the Wooden Church in Borovineşti (Southern Romania, 19th Century): An Attempt to Elucidate the History of the Church

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Abstract

This article presents the results of radiocarbon dating and wood anatomy analyses of the wooden church built in Borovineşti (Argeş County, Southern Romania) in 1869. The aim was to verify whether the church was made of reused wood – either from an old church in Cicăneşti, for which contradictory written information exists, or, alternatively, some other church, even if this is not mentioned in written sources. Dendrochronology is not yet available in the study region and radiocarbon dating does not work between 1700 and 1950. Nevertheless, the risk of using the radiocarbon method was taken in the hope that the dated material would contain much older wood and thus the life history of the church in Borovineşti could be elucidated. The results were indecisive and, owing to the lack of preserved bark and the only partially preserved sapwood, it is not certain if even dendrochronology would have produced much better results.

Keywords: monument history, object history, 19th century wooden church, radiocarbon dating, wood anatomy, Southern Romania.

Introduction: two wooden churches and a case of object history

Cicăneşti and Borovineşti are two small villages in the outlying hills of the Southern Carpathian Mountains. Situated to left and right of the Argeş River, respectively, they are separated by approx. 10 km of road, with access possible only through valleys (Figure 1).

The case study presented in this article consists of the radiocarbon dating of the wooden structure of the Holy Angels Church in Borovineşti (Argeş County, Southern Romania: Figure 2) with the aim of elucidating whether the church was built using reused wood from the Annunciation Church in Cicăneşti (Argeş County), as noted in an ecclesiastical document (Cristocea and Păduraru 2009: 282, who cite the National Archives of Argeş County, Bishopric of Argeş collection, file 20/1869, f. 3r, 6r and 7r), or whether it was built without the use of said wood, as implied by the inscription on the church in Borovineşti. The church in Borovineşti was built in 1869, while the construction date of the church in Cicăneşti may lie between 1775 and 1789, albeit there is no guarantee that the written sources are accurate and it could also have been built much earlier or even made by reusing wood from an earlier church. If the latter is not the case, then both construction dates fall within the interval 1700-1950 (the so-called 'Stradivarius gap') during which precise radiocarbon dating is not possible (e.g. Jull n.d.). Nonetheless, as long as dendrochronology is unavailable in the region and there exists a chance that the church in Cicăneşti is much older, the risk of using radiocarbon dating was deemed worth taking, as for the time being it may provide the only chance of elucidating the history of the church and establishing a starting point for a possible study of object biography (Joy 2009).

Data from written sources

There is no certain construction date for the church in Cicăneşti given in the written sources. In General Friedrich Wilhelm von Bauer's (Bawr) *Mémoires historiques et geographiques et militaires sur la Valachie avec un Prospectus d'un Atlas Géographique et Militaire de la dernière Guerre entre Russie et la Porte Ottomane*,

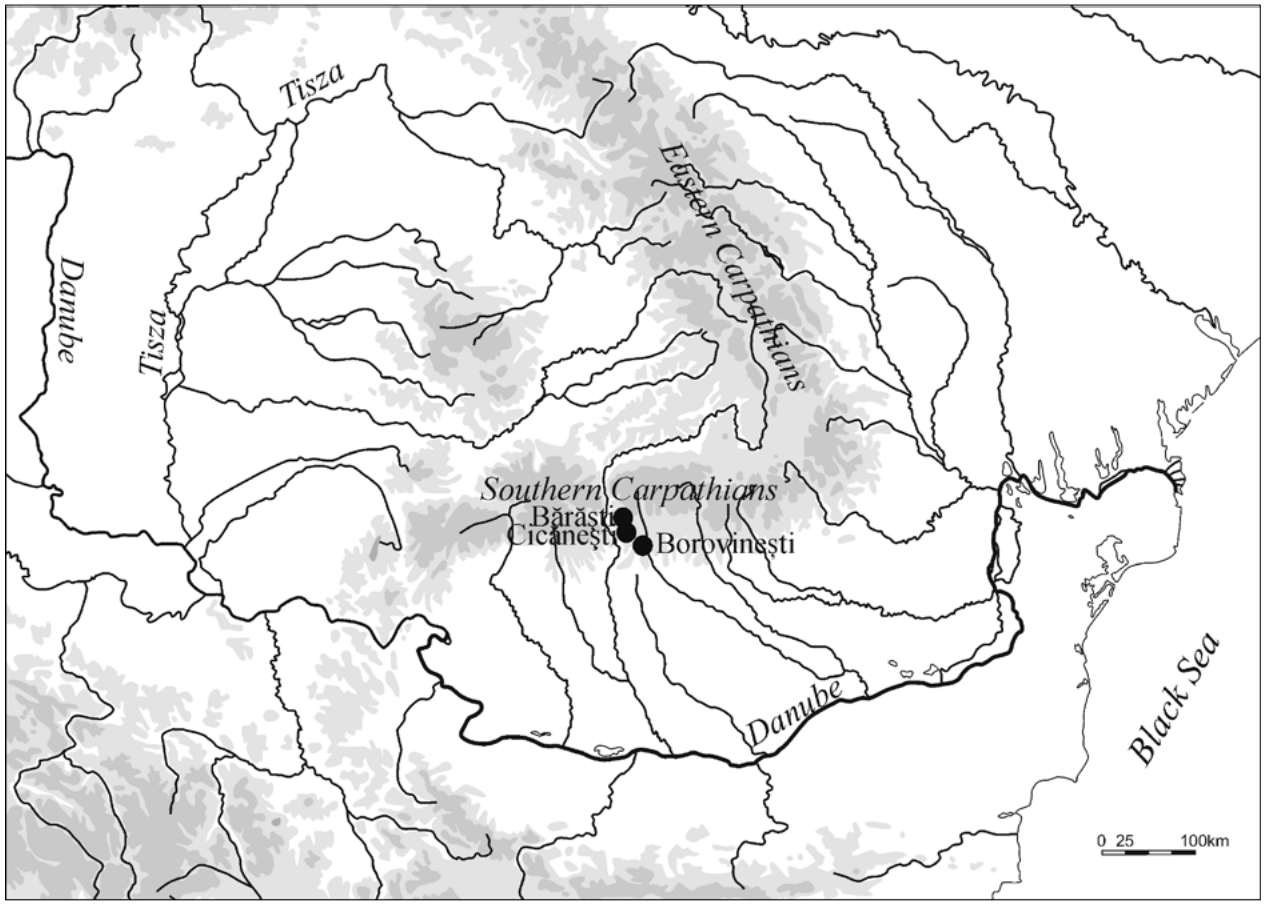

Figure 1. Location of sites mentioned in the article.

Figure 2. Borovineşti, The Holy Angels Church – view from the south-west.

published in 1778 and based on data gathered during the Russian occupation of 1769-1774 (during the Russo-Turkish war of 1768-1774), an interval that includes the 1773 census, Cicăneşti is described as a small village. There is no mention of a church, although other villages are mentioned as having a church (Georgescu and Georgescu 1995: 73, 76). The church in Cicăneşti appears for the first time in 1790-1791 on a map drawn by Colonel Sprecht. From this it was inferred that the church must have been built sometime between 1775 and 1789, although this date should be treated with caution as General von Bauer's memoirs often contain erroneous information (Cristocea and Păduraru 2009: 280). Later documents also prove inaccurate: while Cicăneşti appears in documents dating from 1808 and 1824 as having a wooden church dedicated to the Annunciation, in the census of 1832 it appears as having two churches, and in that of 1833, which was meant to correct the inaccurate information in the census conducted the previous year, it appears as having no church at all. This overview of the written sources shows that they are not necessarily accurate. As the village of Cicăneşti itself was founded hundreds of years before the first mention of its church (the village is first mentioned in a document from 1565 under the name of Cecăneşti: Roller 1952: document no. 250), it is possible that the latter was built much earlier than 1775-1789, the date inferred based on written documents – i.e. there is a chance that the Annunciation Church was constructed before 1700 and consequently radiocarbon dating could provide a decisive dating for the wood used in construction.

It would seem certain that the Annunciation Church in Cicăneşti existed in 1845, that signs of decay caused by moisture originating from two neighboring streams became visible beginning with 1858, and that the roof collapsed and the church was demolished by the villagers for safety reasons in 1866. A document from the Bishopric of Argeş states that the remaining building material was donated in 1868 to the inhabitants of the hamlet of Boroghineşti (today Borovineşti), whose own church was too far away from the hamlet, with the donated wood thus being used to build the Holy Angels Church in 1869 (summary based on Cristocea and Păduraru 2009: 280-282, who base their reconstruction of the church's history on documents from the National Archives of Argeş County, Bishopric of Argeş collection).

The Holy Angels Church in Borovineşti (Valea Iaşului commune, Argeş County; Figure 2) is small and made of wood covered with plaster and paintings. According to the church's inscription, it was constructed between 10 March and 20 September 1869 with the contribution of several people. No connection whatsoever with the church in Cicăneşti is mentioned. There is also no mention of the reuse of any older building materials.

Data from archaeology

At the same time, it is also possible that the church in Cicăneşti was built using wood recycled from some other earlier building(s). The most likely candidate is the church in Bărăşti, provided the archaeologists who brought this archaeological church to light are right about it having been a wooden church built during the 15th-16th centuries that was moved somewhere else in the 17th-early-18th century. (Cristocea and Păduraru 2009). In a region of high hills and villages situated in narrow valleys, there might not have been many options for moving a wooden church. Moreover, reused wood is often limited to a few pieces (e.g. Baboş 2004: 19, note 35 and the caption of Fig. 20), so attempting to identify any such pieces is risky.

Method: radiocarbon dating and wood anatomy analyses

In order to try to elucidate the history of the churches in Borovineşti and Cicăneşti, the wooden structure of the church in Borovineşti was dated by radiocarbon. The dating by radiocarbon of wooden churches known to have been built in 1869 and the late 18th century, respectively, can be considered methodologically erroneous because – as already mentioned – the construction dates fall within the interval 1700-1950, when dating by radiocarbon is impossible owing to rapid fluctuations in ^{14}C content caused by intense solar activity, on the one hand, and the release of old, 'dead' carbon during the industrial revolution, on the other, with all samples falling within this period returning radiocarbon dates that cover the entire period, albeit in certain cases some intervals can be excluded (Jull n.d.). Clearly, radiocarbon dating would only be useful in this case if the churches in Borovineşti and Cicăneşti were built, if only partially, using wood felled before 1700. As this possibility cannot be ruled out based on analysis of the written and archaeological sources, and as there is no other possibility of obtaining an absolute dating for the construction timber (dendrochronology is not yet available in this region), the risks of applying radiocarbon dating had to be accepted.

The dated material was holocellulose (i.e. it not only contains cellulose, but also all of the carbohydrates in the samples, including hemicellulose and pectic substances). The standard procedure for wooden samples was applied: cellulose purification by base (mercerisation) – acid (leaching of carbonates and fulvic contaminants) – base (leaching of humic materials) – acid (neutralisation and final purification) – bleaching (destructuration of organic remains) (Adolphi *et al.* 2013: 391; Brock *et al.* 2010: 103; Němec *et al.* 2010a: 1358). At the end, the holocellulose was lyophilised and graphitised using the CHNOS ELEMENTAL ANALYZER (EA: VarioMicroCube, Elementar, Germany)/AGE 3

(ETHZ, Switzerland) (Němec *et al.* 2010b: 1380; Wacker *et al.* 2010a: 976; Wacker *et al.* 2010b: 931) and the radiocarbon age was then measured using an 1MV Cockcroft-Walton Tandetron (HVEE, Netherlands).

Twelve samples were taken from various parts of the Holy Angels Church: three from the sills of the altar and nave, three from the wooden structure of the wall, two from the roof covering the nave and the sanctuary, and a further four from the porch (Table 1). All were taken from visible wooden beams (most of the wooden structure being covered by plaster and painting), with no part of the visible wooden structure bearing any obvious signs (such as holes from other fittings) of having previously belonged to another building. Sampling by drilling the wood was not possible and the rule of dating the most recent tree rings could be applied only in part: the samples come from recent, albeit for the most part not the most recent tree rings, as sampling was made difficult by the hardness of the wood and the requirement that we not leave any visible marks on the building.

The location of the samples within the wooden beams is of paramount importance. Trees generally develop a ring every year and tree rings live – i.e. exchange C with the atmosphere – for only a very short period (usually from one to several months). As a consequence, trees yield in cross section radiocarbon dates that grow increasingly younger from the pith (found in the center of the tree trunk) to the tree ring found immediately under the cambium (the tissue that produces growth in trees, situated immediately under the bark), i.e the most recent tree ring. This latter ring indicates the date of felling of the tree and will be the closest to the construction date, although it is entirely possible that a certain amount of time – impossible to determine by radiocarbon dating - elapsed between the felling of the tree and the construction of a building (e.g. Waterbolk 1971). None of the visible wooden beams bore any traces of bark and most were cut to form rectangular surfaces or other shapes so as to fit to the shapes of neighboring beams and ensure a strong structure. This indicates that in all cases the most recent tree ring of the original tree is missing and that, whatever the absolute dating method used (radiocarbon or dendrochronology), it would yield an earlier date than that for the felling of the trees used in construction. In an attempt to estimate the gap between the date obtained by radiocarbon dating and that for the building of the church, the samples were subjected to wood anatomy analyses, as these can provide clues as to how the sample was situated within the tree trunk (estimate of the distance to the most recent ring/bark) and whether the wood was left unused for a time before its integration into the church (based on signs of decay presumed to be absent in living trees felled for building purposes but which can occur after the death of trees) (Schweingruber and Schoch 1992). Additionally, wood anatomy analyses also allow for the determination of the wood species used to build the church, thus providing supplementary information useful to our knowledge of the building itself.

Results and discussion

The radiocarbon dating of all samples is very imprecise (Table 1 and Figure 3). This is not surprising given the possibility that not only the felling year(s) of the trees used in the building of the church in Borovineşti but also the felling year(s) of the trees used for the church in Cicăneşti could, as already mentioned, fall within the interval 1700-1950.

Not all the samples are equally relevant for the issue under discussion: to establish whether the church was built from reused wood we require samples that come from the most recent tree rings (ideally the ring immediately under the bark). According to the wood anatomy analyses, only two samples meet this condition. One is Sample 44-5, which *most probably* stems from the sapwood of an oak tree (Table 1): due to its tannin content, oak is well protected against fungi and insect attack; given that such an attack occurred, it most probably happened in the nutrient rich sapwood longitudinally, as the tree is well protected against attacks occurring in a tangential and medial direction by its medullary rays (Schweingruber 1992: 13; Schweingruber and Schoch 1992: 13). If we accept this interpretation, then sample 44-5 comes from rings not much older than the felling date of the tree and this makes it the most relevant sample for dating the felling year of the wood, or at least part of the wood, used to build the church in Borovineşti. A probably similar case is that of sample 44-bis10, which stems from a birch tree (*Betula* sp.) and yielded traces of fungi and attack by xylophagous insects. (However, as birch is less resistant than oak, and although there is a high chance that this sample stems from the sapwood, the heartwood cannot be totally ruled out). Both these two most relevant samples for the felling year of the trees used in the construction of the church in Borovineşti (samples 44-5 and 44-bis10) have very similar radiocarbon dates roughly covering the period between 1650 and 1950, with a few decades just before 1800 and around 1900 being excluded (Figure 3). This very imprecise dating is perfectly compatible with the historically recorded date of construction of the church in Borovineşti (1869) and the date of construction inferred for the church in Cicăneşti (between 1775 and 1789), at both 1σ and 2 σ confidence levels. It is also compatible with a somewhat earlier construction date for the church in Cicăneşti, so long as this is no earlier than 1650. (A very similar date was obtained for Sample 44-bis6.3 taken from the recent (even if not quite the most recent) part of the preserved tree rings (Figure 4.1), but as it cannot be ascertained whether these are also the most recent rings of the tree of origin, the sample as such is not relevant).

Location of samples	Sample label	Characteristics of the wood	CRA (yr BP)	Calibrated ^{14}C date (cal AD)	
				1σ (68.2%)	2σ (95.4%)
Base of the apse and the nave					
Sill separating the nave from the altar	44-5	Light color; medium hardness; massive xylophagous insect attack; oak (*Quercus* sp.)	133±27	1681-1706 (11.0%) 1720-1739 (9.2%) 1752-1762 (4.0%) 1803-1819 (8.0%) 1833-1880 (24.4%) 1915-1938 (11.7%)	1675-1778 (38.8%) 1799-1893 (41.5%) 1907-1942 (15.0%)
Southern sill, outside	44-bis7	dark color; oak (*Quercus* sp.)	159±25	1669-1690 (12.7%) 1729-1780 (35.6%) 1798-1810 (7.5%) 1926-1944 (12.3%)	1665-1706 (16.4%) 1720-1785 (39.0%) 1793-1819 (10.8%) 1832-1880 (10.2%) 1915 (19.0%)...
Sill separating the nave from the porch	44-bis6.3	Hard; dark color; oak (*Quercus* sp.)	126±25	1683-1707 (12.4%) 1719-1734 (7.9%) 1806-1826 (9.4%) 1832-1885 (29.6%) 1913-1930 (8.8%)	1678-1765 (33.6%) 1774-1776 (0.4%) 1800-1894 (46.6%) 1905-1940 (14.8%)
Walls of the sanctuary and the nave					
Lintel at the iconostasis	44-4	Resinous wood (sample too small for further analysis)	142±26	1679-1697 (9.8%) 1726-1765 (20.2%) 1800-1814 (7.4%) 1836-1877 (18.1%) 1917-1940 (12.7%)	1669-1710 (16.1%) 1717-1781 (28.2%) 1797-1890 (35.0%) 1910-1945 (16.1%)
Uppermost joist, inside the southern wall (above the painting)	44-3	Soft; light color; Norway spruce (*Picea abies*)	81±26	1698-1724 (20.1%) 1815-1835 (14.5%) 1878-1917 (33.6%)	1691-1729 (25.0%) 1810-1923 (70.4%)
Grid supporting the plaster, NE wall, outer side of the sanctuary wall	44-bis9.1	resinous wood, soft, light, fine texture; silver fir (*Abies alba*)	100±27	1695-1726 (21.2%) 1814-1853 (22.2%) 1868-1894 (16.4%) 1905-1918 (9.5%)	1682-1735 (27.2%) 1806-1930 (68.2%)
Roof covering apse and nave					
Hip rafter	44-1	Hard; dark color; oak (*Quercus* sp.)	112±19	1693-1708 (10.5%) 1718-1727 (6.1%) 1813-1827 (9.3%) 1833-1888 (38.4%) 1911-1917 (4.0%)	1684-1733 (27.5%) 1807-1895 (55.6%) 1903-1929 (12.3%)
Roof, longitudinal beam in attic, in the area above nave and porch	44-bis2.1	Hard; dark color; oak (*Quercus* sp.)	110±26	1694-1711 (10.9%) 1717-1727 (6.0%) 1813-1891 (46.3%) 1910-1918 (4.9%)	1682-1736 (27.6%) 1805-1936 (67.8%)
Porch					
Sill at the entrance of the porch, left-hand side	44-bis6.1	Hard; dark color; oak (*Quercus* sp.)	96±25	1697-1726 (24.5%) 1815-1836 (17.5%) 1877-1895 (15.0%) 1903-1917 (11.2%)	1689-1730 (26.0%) 1809-1926 (69.4%)
Pillar on right-hand side	44-bis6.2	Hard; dark color; oak (*Quercus* sp.)	62±25	1700-1720 (13.3%) 1819-1833 (10.9%) 1881-1915 (44.0%)	1694-1728 (22.3%) 1812-1862 (21.6%) 1867-1919 (51.5%)
Longitudinal beam in the attic	44-2	-	87±21	1699-1721 (20.0%) 1818-1833 (14.0%) 1880-1916 (34.2%)	1693-1728 (25.6%) 1812-1920 (69.8%)

Location of samples	Sample label	Characteristics of the wood	CRA (yr BP)	Calibrated ^{14}C date (cal AD)	
				1σ (68.2%)	2σ (95.4%)
Hip rafter	44-bis10	Medium hardness; yellowish; mixed attack of xylophagous insects and fungi; birch (*Betula* sp.)	136±25	1681-1699 (9.7%) 1722-1763 (16.7%) 1802-1817 (7.6%) 1834-1879 (22.3%) 1916-1938 (11.9%)	1674-1778 (39.9%) 1799-1891 (40.0%) 1909-1942 (15.5%)

Table 1: Borovineşti, Holy Angels Church. Results of radiocarbon dating and wood anatomy analyses (The radiocarbon dating was carried out at the RoAMS laboratory at Măgurele, Romania, but the dates do not have laboratory identifier and reference numbers because they were among the first samples to be dated at the laboratory, prior to its accreditation by the SIRI).

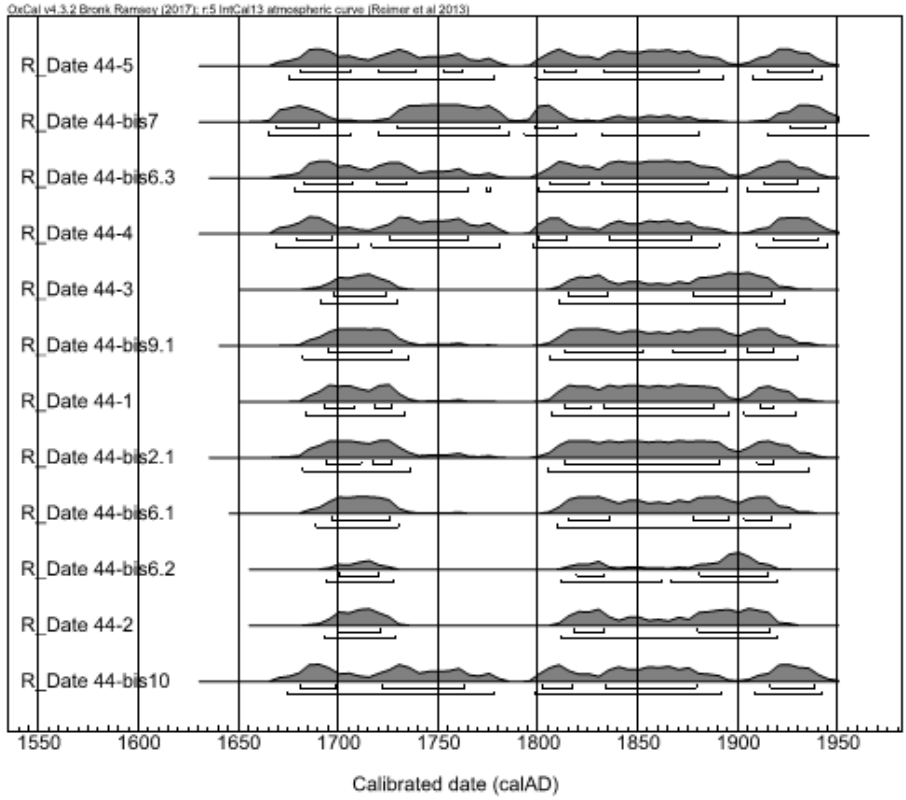

Figure 3. Borovineşti. Multiple plot of the calibrated radiocarbon dates for the wood samples (the order of samples is that given in Table 1; Curve IntCal 13; Calibration with OxCal v4.3.2) (see also the caption of Table 1).

For most samples – samples 44-3, 44-bis9.1, 44-1, 44-bis.2.1, 44-bis6.1, 44-bis6.2 and 44-2 – radiocarbon dating excludes the interval of around 1730 to around 1810 from the possible dates. Both samples 44-1 (oak) and 44-2 (undetermined species) were taken from the area close to the most recently preserved tree rings (Figures 4.2-3). These samples might indicate a felling date for the trees of origin not much later than 1730 and consequently they may have belonged to an earlier church than that in Borovineşti. However, this cannot be established with certainty because it is not possible to decide whether the most recent preserved rings are from among the most recent rings of the trees of origin, and because oak is a long-lived species (living for hundreds of years, as, for example, in the case of the *Quercus robur*, which can live up to 1000 years: Pătruţ *et al.* 2011; Schweingruber 1992: 119), such that the number of missing rings is potentially very large. Samples 44-3, 44-bis6.1 and 44-bis2.1 most probably come from much earlier parts of the trees of origin and consequently their dating is irrelevant. Sample 44-bis9.1 is a lath of silver fir (*Abies alba*) and the part of the wood from which its comes cannot be determined. Sample 44-bis6.2 (oak), taken from one of the pillars of the porch, did not come from the most recent available tree rings, but probably comes from a young tree, something which reduces the age offset between the dated rings and the most recent rings in the tree of origin (Figure 4.4).

Conclusions

The interpretation of the radiocarbon dates, supported by wood anatomy analyses and observations on the *in situ* wooden structure of the church, merely show that no 15-16th-century wood was incorporated into the

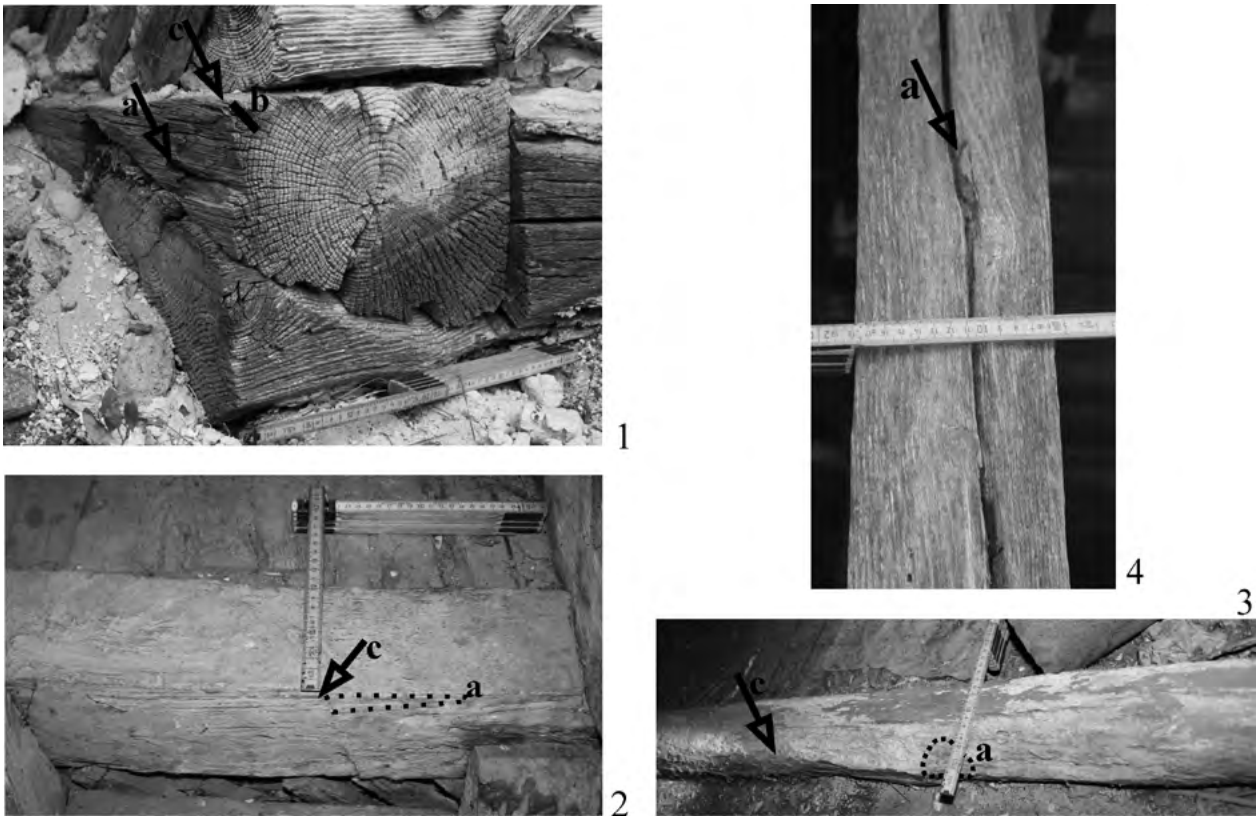

Figure 4. Borovineşti – wooden beam with the location of the samples dated by radiocarbon: 1 – Sample 44-bis6.3; 2 – Sample 44-1; 3 – Sample 44-2; 4 – Sample 44-bis6.2; a – location of the dated samples; b – approximate distance from the earliest tree ring of the dated sample to possibly the most recent tree ring preserved in the beam; c – the most recent of the accessible tree rings in the beams.

church in Borovineşti and consequently the hypothesis of the church in Bărăşti having been moved to Cicăneşti and then the church in Cicăneşti used to build that in Borovineşti is invalidated. As to the relationship between the churches of Cicăneşti and Borovineşti, this research did not produce any decisive conclusions. All samples produced radiocarbon dates that were perfectly compatible with trees felled in 1869 or shortly before. The fact that seven samples have dates compatible with wood cut around 1730 does not necessarily mean that they stem from the Annunciation Church in Cicăneşti because, in keeping with the logic of radiocarbon dating, these samples can also be dated with equal probability to the interval 1800-1869 (the latter being an *ad quem* date). Moreover, it is not certain that the matter will be settled by the use of dendrochronology, when this becomes available in the region. If the most recent tree rings from these seven samples (in fact six, as one is a lath with too few rings to be useful for dendrochronology) dates to after 1800, then this means they do not originate from the church in Cicăneşti (first mentioned in writing in 1790-1791) and that dendrochronology could provide a definitive answer. But if these samples were dated by dendrochronology to around 1730, then the issue remains unsettled, for there would be no way to determine how many tree rings were missing up to the bark (i.e. the felling date of the trees of origin) and the dates would be compatible with both the possible date of construction for the church in Cicăneşti (between 1775 and 1789) and the known date of construction for the church in Borovineşti (1869). But even if dendrochronology were to fail to elucidate the relationship between the two churches, an attempt to do so should be made when possible because you never know until you look and because we know so very little about the life history of small, countryside buildings.

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Author contributions

Corina Simion: sampling, chemical pretreatment of samples, discussion of radiocarbon dates; *Nona Palincaş:* interpretation of radiocarbon dates in relation to wood anatomy and dendrochronology, observations on the *in situ* beams, writing of the text; *Iulia Anania* and *Laurenţiu Dragomir*: wood anatomy analyses; *Gabriela Sava*, *Oana Gâza* and *Iuliana Stanciu*: chemical pretreatment and graphitisation of radiocarbon samples; *Doru Păceşilă*: AMS measurements; and *Tiberiu Sava*: AMS dating.

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Compositional Analysis of the Agighiol Hoard: Provenance and Possible Links to Pieces in the Detroit Institute of Arts and the NYC Metropolitan Museum of Art

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Abstract

We present a comparative analysis of some famous examples of silver Getae-Thracian art – a large cup (beaker) from the Metropolitan Museum of Art of New York; a helmet from the Detroit Institute of Arts; a large beaker, a (partially gilded) helmet and some appliqués from the Agighiol hoard, today housed by the National Museum of Romanian History. Initial compositional analysis was performed using a portable X-Ray Spectrometer for X-Ray Fluorescence (XRF). Later, a more sensitive analysis was performed using SR-XRF (Synchrotron Radiation induced X Ray Fluorescence) on ten microscopic samples. The silver turned out to be approx. 99% pure, with traces of gold, copper, lead and bismuth differing quantitatively from item to item (even stylistically the Agighiol hoard is heterogeneous). We also performed a careful examination of the hammering marks, especially those left by chasing tools, which were identical both for the Agighiol helmet and the large beaker, as well as for the USA artefacts. Our results demonstrated the common provenance (same workshop and probably same silversmith) of these four precious Getae-Thracian silver artefacts from the USA and Romania.

Key words: Agighiol hoard, Thracian Detroit helmet, NYC MET large beaker, silver provenance, chasing tools fingerprints.

Introduction

The Agighiol hoard (Figure 1) – currently housed by the National Museum of Romanian History in Bucharest – is of a Geto-Thracian origin and was discovered in Northern Dobrudja in 1931 in a ceremonial tomb (*Prunkgrab*) dated to the 4th century BC (Berciu 1969 [1971]; for a complete history of its discovery see Constantinescu *et al.* 2014, where preliminary results of the metal analyses were also presented).

The hoard contains various silver adornments: ornamental plaques, beads, buttons (horse harnesses), phialai, two beakers, a gilded helmet and two greaves (knee-pieces), one of which is gilded. The stylistic variation of the objects suggests a heterogeneous provenance. On the other hand, the silver helmet from Agighiol is morphologically almost identical to the Thracian helmet from the Detroit Institute of Arts, while the two cups/beakers from Agighiol are similar to one of the cups from the Metropolitan Museum of Art in New York. All the artefacts mentioned – i.e. those from Agighiol, as well as those currently in Detroit and New York – were described by Ann Farkas (Farkas 1981) and Pieter Meyers (Meyers 1981). The latter also published a compositional analysis of the silver in the 'American artefacts', and this inspired us to perform a similar investigation of the Agighiol pieces. The two 'American' artefacts, formerly part of the Franz Trau collection in Vienna, are known as 'Iron Gates material' and are of suspicious provenance (Farkas 1982). Their discovery was announced in 1913-1914 by a sailor following a storm in the region of the Iron Gates, where the Danube flows into western Romania. The helmet was first presented publicly in 1934, around three years after the discoveries at Agighiol. However, their similarity in terms of iconography and form with the Agighiol artefacts is undeniable. Given the circumstances of their discovery, only the Agighiol finds can be dated with any certainty: the Greek (mainly red figure) ceramics, found in the same grave as the hoard, date the entire context to the 4th century BC (Alexandrescu 1983: 48). The two other objects, referred to here as the 'American' items, can only be dated based on their similarity with the pieces from Agighiol, with which they are considered contemporaneous. A common origin for the American and Romanian artefacts had already been suggested in 1987 by Timothy Taylor (Taylor 1987) based on the tool marks found on both the helmets and the large beakers, which in photographs appeared to be identical (Taylor had no direct access to the Agighiol artefacts). Consequently, we decided to examine the traces of the tool marks on the Agighiol objects directly in the Treasure Room of the Bucharest museum, in order to verify whether or not they were produced by the same tools as the 'American' artefacts.

Figure 1. The Agighiol hoard (©the National Museum of Romanian History).

Method

Silver is known to have been used by man as early as the 4th millennium BC. However, silver objects appear to have been relatively rare in Europe before Greek and Roman times. In fact, we know of only a few such items dating from the Bronze Age. It would seem that prior to Greek colonisation and Roman conquest, despite the regular presence in Europe of technically advanced products made of other metals (Cu, Au, Fe) and the extensive links between European societies and the Eastern Mediterranean/Aegean region, where silver was abundant, the metallurgical techniques used to work in silver and lead were either unknown or spread only very slowly across Europe.

The practice of separating silver from lead ores (in fact only from argentiferous galena) – known as cupellation – was widespread during classical Greek and Roman times. The procedure is very effective in producing above 95% wt% purity, but the resulting metal typically contains minor-to-trace amounts of Au, Cu, Pb and Bi (<1%), as well as traces of Sb, As, Te, Zn and Ni, the naturally geologically associated elements of the former group (where these are present in the ore). Thus, copper contents above 0.5-1wt % indicate a deliberate addition to increase the strength of the metal.

The accepted standard method used to determine the provenance of metal uses lead isotopes and gives a more precise localisation for the source of the ore. Unfortunately this method was not available to us. Moreover, it should be noted that, in the case of silver, given the characteristics of the galena-type sources and the technology, it is possible that contamination with Pb from other sources will have occurred during manufacture and this might mask the original lead isotope fingerprint. In this paper we will discuss the compositional analysis of the objects from Agighiol using a more limited approach.

In the case of silver, the fingerprint elements used in the identification of East European geological deposits are gold, bismuth, zinc and antimony: e.g. Bi for South Thracian and Greek, Macedonian or Aegean argentiferous galena, and Sb for the Northern

Carpathians (Maramureş and Slovakia). Nevertheless, only Au and Bi can be regarded as being reliably associated with the source of the silver (their levels not being affected either at all or only very slightly by the smelting and refining to which the silver ore is subjected during the manufacturing of silver objects). Other elements may be contaminants or intentionally added elements, while the presence of copper and lead is directly related to the technology.

Our research began with in situ measurements of the Agighiol hoard items at the National Museum of Romanian History in Bucharest using a portable X-Ray X-MET 3000TX instrument, with 10% maximum uncertainty (B. Constantinescu *et al.* 2012). To achieve a more sensitive analysis we then performed a Synchrotron Radiation X-Ray Fluorescence (SR XRF) investigation on microscopic samples using the BAM-line at the Helmholtz Centre Berlin for Materials and Energy HZB – BESSY II synchrotron facility (Radtke *et al.* 2010).

Results and discussion

Composition: minor and trace elements

The in situ XRF analysis identified the use of two different types of silver:

- Silver with traces of Bi for a group of several objects, of which some contain Pb but also some added Cu, in order to increase mechanical resistance, as in the case of the bear-head shaped ornamental plaques; the rest of the items did not contain Pb.
- Silver without Bi: again, with two sub-types:
  - Bi, Pb – phialai, gilded greave
  - Bi, no Pb – small ornamental plaques

The silver with Bi also has 3 sub-classes in respect of their Au content:

- Bi, Pb, Au 0.5% – four horse-head-type ornamental plaques
- Bi, Au 0.5%, no Pb – large beaker, non-gilded greave
- Bi, Au 1%, no Pb – helmet, small beaker

The silver composition of the Agighiol helmet is Ag 98.6%, with Au 1%, Cu 0.3%, Bi 0.05% and Pb 0.05%. We also measured the thin, approx. 30-micron (calculated from the Ag K-alpha/K-beta ratio) gold foil used in the partial gilding of the helmet applied after hammering was finished and which had a pure gold composition. For the large Agighiol beaker, the silver composition was Ag 99.3%, with Au 0.5%, Cu 0.05%, Bi 0.1% and Pb 0.05%. Meyers found the composition of the Detroit helmet to be Ag 99.5%, Au 0.231% and Cu 0.269%, and that of the New York beaker to be Ag 99.7%, Au 0.242% and Cu 0.0656%, concluding that the silver was produced from a common ore source (using the same gold content as an indicator). Our results, while similar with those described by Meyers (Meyers 1982), show a higher Au content (about twice as much), thus indicating a different silver ore source. The identified trace elements are also different, but this is due to the different techniques applied (XRF and neutron activation analysis, respectively). Unfortunately, we could not obtain any microscopic samples on which to perform an SR XRF analysis.

The Synchrotron Radiation X-Ray Fluorescence (SR XRF) investigation on microscopic (100-200-micron diameter) silver samples from ten small objects from Agighiol (the buttons, ornamental plaque and two beads) was performed using the BAM-line at the Helmholtz Centre Berlin for Materials and Energy HZB – BESSY II synchrotron facility (Radtke *et al.* 2010). The

Sample Agighiol	Number	Ca wt%	Ti wt%	Cr wt%	Fe wt%	Cu wt%	Zn wt%	Br wt%	Zr wt%	Ag wt%	Au wt%	Pb wt%	Bi wt%
Button	8470	48.8	0.010	0.009	0.026	0.083	0.002	0.003	0.012	50.6	0.223	0.017	0.174
Bead	1	0	0.034	0.026	0.047	0.387	0.009	0.032	0.019	98.5	0.837	0.017	0.063
Bead	2	0	0.107	0.029	0.077	0.311	0.049	0.201	0.011	98.4	0.725	0.014	0.035
Button	8487	0	0.033	0.060	0.102	1.36	0.009	0.006	0.071	97.5	0.498	0.124	0.251
Ornamental plaque	8472	0	0.050	0.032	0.156	0.100	0.021	0.008	0.042	98.7	0.692	0.058	0.192
Button	8486	0	0.056	0.587	0.245	2.45	0.021	0.004	0.009	95.1	0.983	0.120	0.410
Button	8486-1	0	0.013	0.010	0.029	2.02	0.008	0.002	0.012	96.8	0.637	0.115	0.327
Button	8465	0	0.042	0.020	0.103	2.89	0.026	0.081	0.013	95.2	1.04	0.395	0.188
Button	8471	0	0	0.339	0.472	0.081	0.056	0.036	0.291	98.7	0.031	0.011	0.019
Button	8467	0	0.171	0.031	0.087	12.5	0.040	0.003	0.019	85.4	0.504	0.976	0.281
Button	8468	0	0.022	0.019	0.066	1.80	0.005	0.263	0.009	96.1	1.33	0.358	0.049
Button	8468-1	0	0.023	0.024	0.069	0.938	0.008	0.318	0.020	97.0	1.37	0.199	0.023

Table 1. SR XRF results for the buttons, ornamental plaque and two beads.

excitation energy used was 20keV and the beam size 100x100μm^2. The spot-size for mapping was 2.5x2.5μm^2, with the 40x40 maps centred on previously selected points. The quantitative evaluation was based on a combination of measurements of metallic standards and Monte Carlo simulation (fundamental parameters), which are described in detail elsewhere (Constantinescu *et al.* 2011).

The SR XRF measurements yielded more precise values for the microscopic samples, and the results are given in Table 1. The uncertainty levels for these results are ~1% for major and minor elements, and ~10-20% for traces, depending on whether or not a standard was available for the element in question. Tin was not measured owing to the choice of a 20keV excitation energy in order to achieve a better resolution in the low-energy region of the fluorescence spectrum.

Items 8470, 8465, 8467, 8471 and 8468 are buttons (Figure 2), 8472 is a damaged ornamental plaque (Figure 3), and 8486 and 8487 conical beads. The buttons have silver handles, excepting two items with bronze handles (probably the harness parts, which are the most subject to torsion).

Figure 2. Agighiol: a button (front and back) (photo: Bogdan Constantinescu).

Figure 3. Agighiol: a damaged ornamental plaque (front and back) (photo: Bogdan Constantinescu).

In summary, the silver from Agighiol has the following characteristics:

- Ag content: 95-98.7%; Au content is low – as a rule, less than 1% with Au/Ag ~ 10^{-4}-10^{-3}, which is comparable to the silver from the mines in Thassos and Laurion, in Greece (Gitler *et al.* 2009; Gale *et al.* 1980 – see below).
- Cu is generally <1%, with a few samples with ~2-3wt% and a single sample with 12.5% (for silver obtained by cupellation from galena, the Cu content should be below 0.5%, unless intentionally added during the metallurgical process)
- The lead content is 0.01-0.5%, with one exception of - 0.98%
- Bi ranges between 0.02 and 0.4%.

In order to compare this with other silver provenance data (Gitler *et al.* 2009; Gale *et al.* 1980), a plot of the Au-Ag ratios versus the Bi-Ag ratios is shown in Figure 4. From this we can conclude that only one sample is in the low Au/low Bi Laurion group, and that, as already mentioned, the Agighiol hoard is heterogeneous (different workshops and silversmiths).

More detailed knowledge resulting from a combined analysis using the Au-Ag and Bi-Ag ratios and the lead isotope data could offer a better insight into the provenance of the silver (original ore). The high Au/ moderate Bi groups discussed in Gitler *et al.* (2009) were supposed to be of mixed metal, possibly from other Greek sources – e.g. Macedonia, Siphnos or Halkidiki, or even Anatolia. (We did not find any other reliable data containing both Au-Ag or Bi-Ag ratios and Pb isotope data for other sources).

In our plot, the data from Agighiol with an Au-Ag ratio in the region of 0.005-0.01 can possibly be attributed to the Macedonia group (from Gale *et al.* 1980).

The use of extremely pure silver for such 'princely' artefacts is also mentioned by Michael Vickers for the Dalboki hoard (Ashmolean Museum, analysis by Sophie Stos: Vickers 2002).

Tool marks (silversmith's punches)

We focused on traces of tool marks on the helmet and the large beaker because in ancient times a silversmith's tools – especially punch marks – were personalised (Treister 2001), which today helps us obtain information about the provenance of artefacts, their workshops and manufacturer. We used the photographs from Meyers (1982) and our own photographs of the Agighiol artefacts. With the helmets, we compared the details of animal horns on the Detroit helmet (on the piece corresponding to the left cheek) with the details of a horse (under the gilding layer) on the Agighiol helmet (also on the piece corresponding to the left cheek) (Figure 5).

With the beakers we compared the details of the border of the bird heads on the New York beaker with the

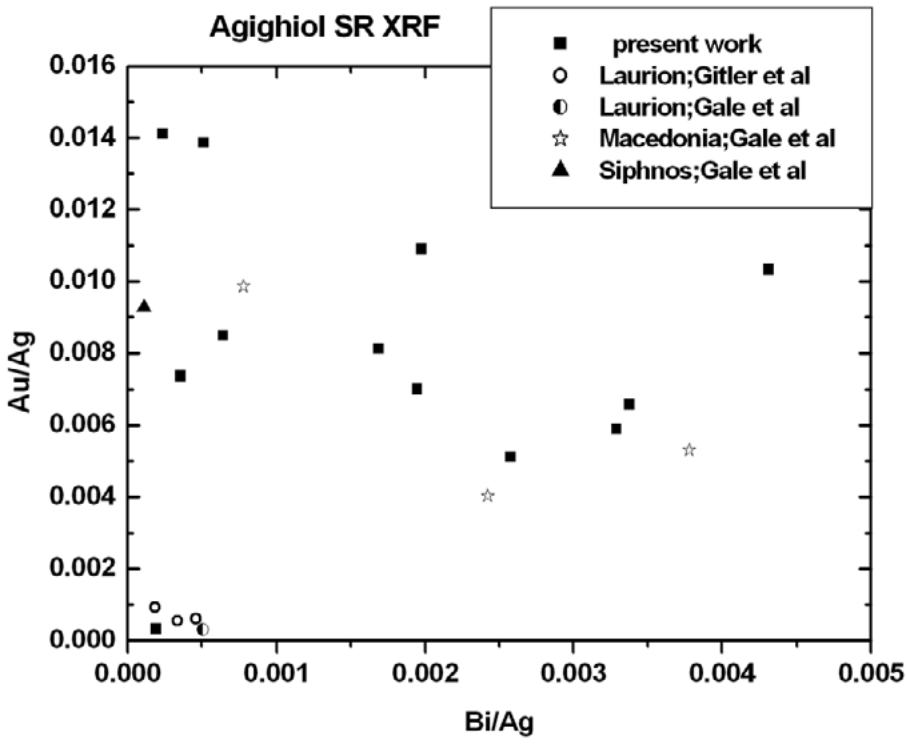

Figure 4. Au-Ag versus Bi-Ag wt% ratios.

Figure 5. Left: the Detroit helmet (photos: Meyers 1981, Fig. 1, 5-6); right: the Agighiol helmet (photo: Bogdan Constantinescu).

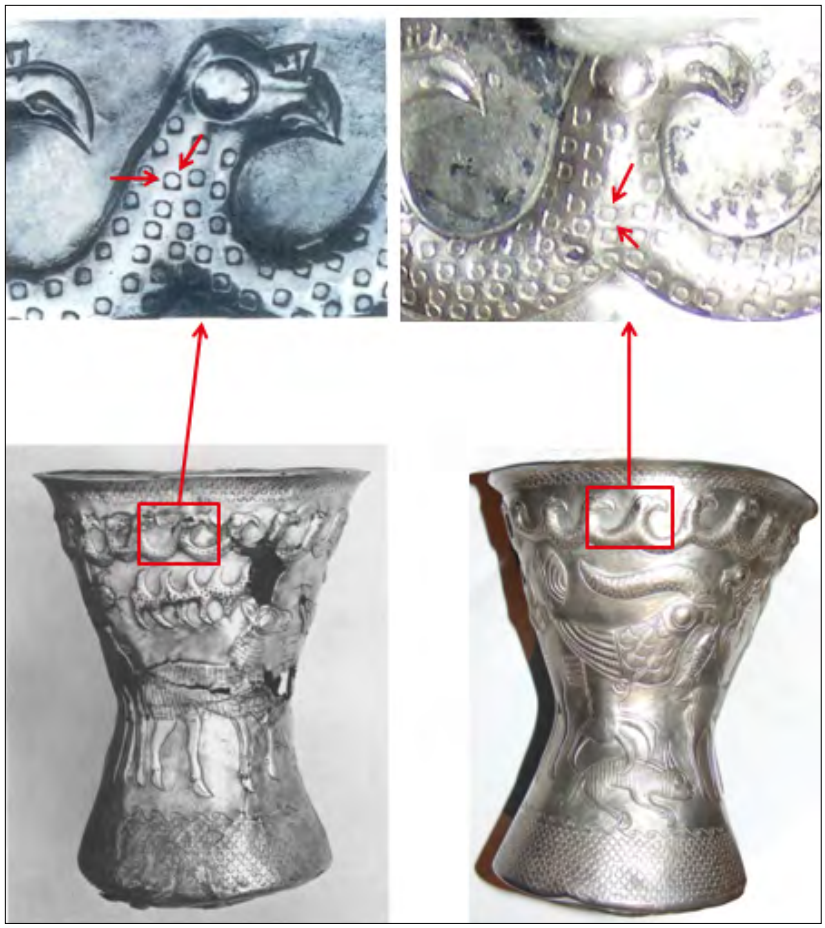

Figure 6. Left: the New York big beaker; right: the Agighiol big beaker (photo: Bogdan Constantinescu).

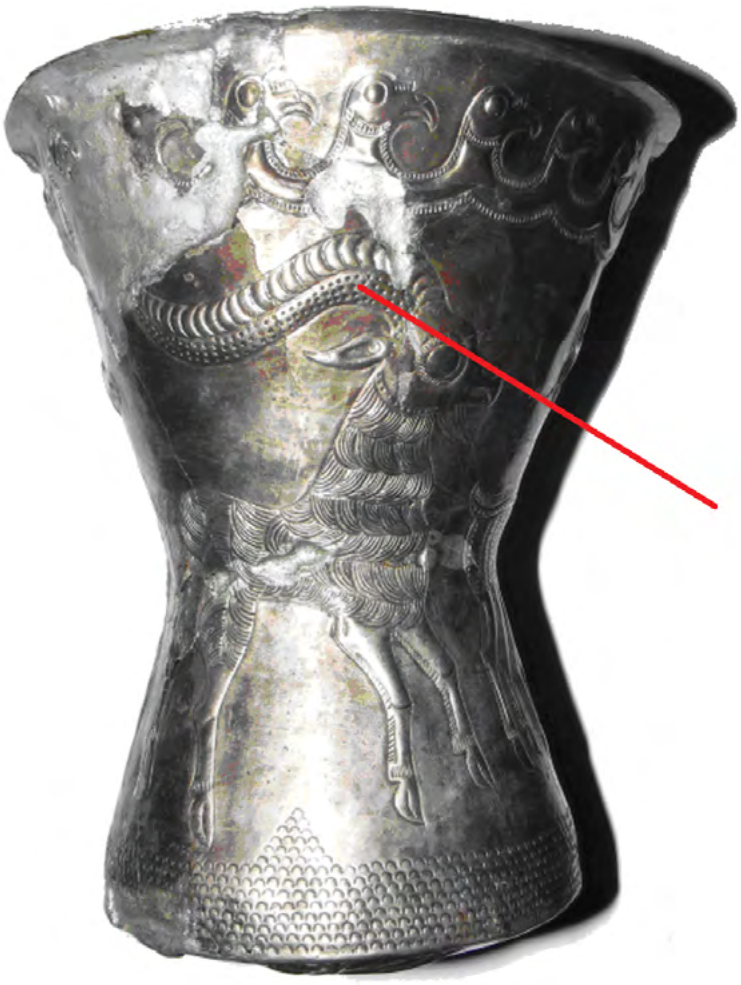

Figure 7. The small Agighiol beaker (photo: Bodgan Constantinescu).

details of the similar area on the Agighiol big beaker (Figure 6).

Each mark – from the helmets as well as the large beakers – is roughly square in terms of its outer contour (approx. 1.2 x 1.2mm) and round in terms of its inner contour (approx. 0.95-1mm diameter), and features a particular imperfection: the nicked corner of the square.

The small Agighiol beaker presents a clearly different 'pattern' of punching traces (Figure 7).

The tool mark on the Rogozen beaker also has a different pattern (see also http://commons.wikimedia.org/wiki/File:Vratsa-museum-Rogozen-treasure-8.jpg).

The fact that at least one common tool was used indicates that both the Detroit and the Agighiol helmets, as well as the New York and large Agighiol beakers, were made in the same workshop, possibly (but not necessarily) by the same person.

Conclusions

The silver material studied shows a large variability in composition and micro-structure, and, even within the same hoard, various objects can be identified as originating from different ingots – different silver ore sources and possibly also different workshops and/or itinerant silversmiths (especially in the case of the small objects used as ornamental plaques).

Essentially, all the silver is of a high purity with few added elements. Nevertheless, various traces and minor elements are present, which suggests that the silver may possibly have been imported from Greece, the Aegean and/or Macedonia, possibly as ready-made ingots, obtained by cupellation from argentiferous galena ores. Agighiol is situated in Dobrudja, and the ancient Greeks had colonised the nearby Black Sea coast. It should also be noted that during antiquity there was no exploitation of silver ore deposits, not only in Dobrudja, but also anywhere on the territory of present-day Romania. We were able to identify a significant quantity of Bi, but also some Pb, in the silver. It is interesting to note that the helmet and the large beaker from Agighiol, the helmet from Detroit and the beaker from New York not only show the same tool marks and, consequently, most likely come from the same workshop, but they also share almost the same chemical composition (note, however, the double percentage of gold content in Agighiol). At the same time, we should note that there are differences in what elements can be and were measured by the two different techniques.

The heterogeneity of the chemical composition of the sample set (heterogeneous also in terms of style) is also explained by the hypothesis that the silver used came from a variety of sources – one of which being the Greek mine in Laurion. The non-homogeneity of the composition and structure can also to some extent be explained in terms of an insufficient mastery of the silver smelting and/or metal-working skills by the local workshops.

On the one hand, our methods generated valuable information about the silver objects without almost any intervention on the samples. However, our measurements were not able to provide as complete a description of the silver objects as could have been obtained using more invasive methods. Nevertheless, in cultural heritage investigations, it is

of major importance to adhere to the principle of least intervention.

With specific differences, but in a relatively similar manner as in the case of gold, micro-analytical X-Ray techniques can – especially in combination with a database of ancient metal sources - provide information about the provenance of silver archaeological artefacts and metallurgical aspects that is of use to archaeologists, as well as information about corrosion that is of use to the restorers.

As concerns manufacturing, this will have been directly related to the circulation of silver, which took place mainly in the form of ingots and coins. We can imagine a pattern of specialised workshops near the Greek cities on the Black Sea coast, possibly in combination with small local (Geto-Thracian) workshops and itinerant silversmiths. Complex artefacts – helmets, greaves, beakers, phialai – were certainly produced near Greek cities that respected specific Thracian iconography (e.g. fantastic animals and birds), using silver ingots imported (by sea?) from Greece and Macedonia. Simpler objects, such as ornamental plaques, could have been made locally in small workshops from small commercialised ingots and/or from re-melted Greek silver coins or even by itinerant masters using the 'customer's' silver.

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Compositional Analysis of the White and Red Colours in the Chalcolithic 'Sanctuary' at Căscioarele-'Ostrovel' Tell (Southern Romania, *c.* 4800-4550 cal BC)

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Abstract

This paper presents the results of the first study of the chemical composition of the white and red colours used in the painting of architectural elements and objects (11 samples) from the Chalcolithic 'sanctuary' at Căscioarele tell, on Ostrovel Islet, in Southern Romania. The 'sanctuary' was attributed to the Spanțov phase of the Boian Culture (i.e. the transition phase to the Gumelnița culture) and dated to approx. 4800-4550 cal BC. The methods applied were in-air PIXE and FT-Raman spectroscopy owing to their sensitivity and non-destructive nature. The results enable a comparison between various categories of painted materials within the Boian 'sanctuary' at Căscioarele-'Ostrovel' tell and with coloured objects from other Boian sites. In addition, the results, together with other mineralogical and phyisicochemical analyses, are a necessary component of future research directions, such as the different technologies used in obtaining the white and red colours; the long-term use of the two colours during the Neolithic and Chalcolithic; and the religious and symbolic dimensions of the white and red materials and their technologies.

Keywords: Chalcolithic, Boian culture, tell settlement, 'sanctuary', painted ceramics, white pigment, red pigment, in-air PIXE, FT-Raman spectroscopy.

Introduction

This paper presents a first stage in the analysis of the chemical composition of the pigments used to paint Chalcolithic objects and architectural elements from the tell settlement at Căscioarele, on Ostrovel Islet, in Southern Romania (Figure 1). The 11 samples analysed so far originate from a 'sanctuary' (House 12) excavated in 1968, in the first level of habitation (for this context, see Dumitrescu 1970; Dragoman 2015-2016). Based on the decoration of some vessels and the ^{14}C dates obtained, the 'sanctuary' was attributed to the last phase of the Boian culture (Figure 2), i.e. the Spanţov phase or the transition phase to the Gumelnița culture, and dated to approx. 4800-4550 BC (Reingruber 2015; the second and third levels of habitation belong to the Gumelnița culture: for the site stratigraphy, see Dumitrescu 1986b).

The archaeological excavations conducted in the Boian-Spanțov layer in 1968 identified and partially excavated three burned rectangular-shaped structures (nos. 10, 11 and 12) of considerable dimensions. According to the director of the excavation, the 'sanctuary' (House 12) was divided into two rooms by a wall indicated by a row of six post-holes (Dumitrescu 1970) (Figure 3). One of the rooms contained undecorated walls, while the walls of the other room were painted with linear, spiral and circular motifs of a white-yellowish colour set against a red background, and a bench (Dumitrescu 1970) or 'altar-table' (Dumitrescu 1986a) painted in the same manner; on some fragments it was noticed that the wall painting had been renewed on two different occasions, each time with a different design. The room was also 'decorated' on one side with a three-colour painted 'medallion' (red and white on a brown background), with vertically fixed triangles, painted on both sides, and house models with animal heads (of which two were painted in white). The painted room contained two clay tubes described in the archaeological literature as 'columns': one of these, the larger of the two (almost 2 m long, oval shaped, with a diameter of 43 and 41 cm, and 9-10 cm thick walls), had been painted on three successive occasions with white-yellowish linear and geometric motifs against a red background, each layer of painting featuring a different design, as in the case of the walls; the other clay tube/'column', the smaller of the two (2m in length, about 10cm in diameter), was painted only once and also with white-yellowish motifs against a red-brown background. The painted room was excavated almost in full, while the non-decorated room was excavated only to a limited

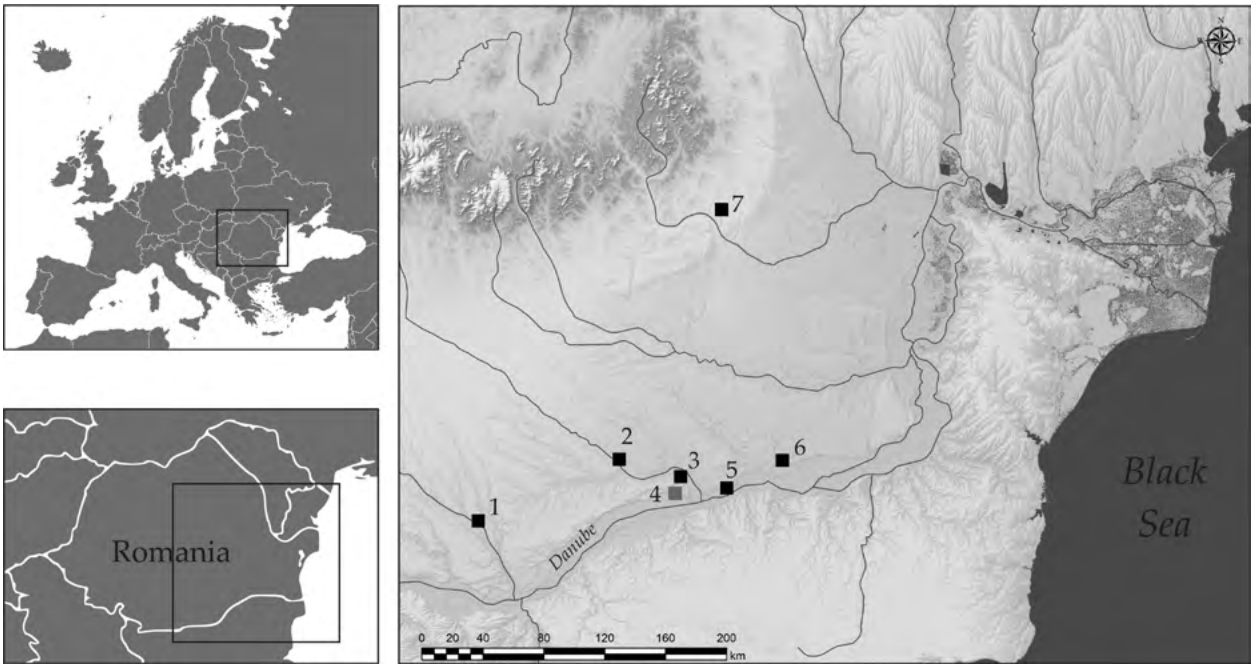

Figure 1. Map showing the Boian culture sites mentioned in the text: (1) Nanov-'Vistireasa 3'; (2) Vidra; (3) Radovanu-'La Muscalu'; (4) Căscioarele-'Ostrovel' (5) Spanțov; (6) Gălățui-'Movila Berzei'; and (7) Aldeni.

Figure 2. Boian Culture area in the Spanțov phase (redrawn from Carozza *et al.* 2012: 24, Fig. 3).

extent. Vessel fragments, a small painted plate incorporated into the 'sanctuary's' structure, fragments of a copper needle, and a stone grinder were all found in the painted room.

House 12 has been interpreted in different ways. For example, the author of the excavation interpreted House 12 as a 'sanctuary' dedicated to a 'column cult' (Dumitrescu 1970), an interpretation that became dominant in archaeological literature in Romania and beyond. However, according to Radu-Alexandru Dragoman, House 12 is a container that protects other containers (storage vessels, dishes, bowls, clay tubes/the so-called 'columns') involved in the circulation of the material and the immaterial (for more information, see Dragoman 2015-2016; for an archaeology of the immaterial, see Buchli 2016).

Since its publication in 1970, the elaborately painted Boian 'sanctuary' has been mentioned in numerous texts on the European Neolithic, Chalcolithic architecture and religious life during the Chalcolithic period (e.g. Dumitrescu 1970; Dumitrescu *et al.* 1983: 78; Gimbutas 1974: 71, 88; Lazarovici and Lazarovici 2006: 534-

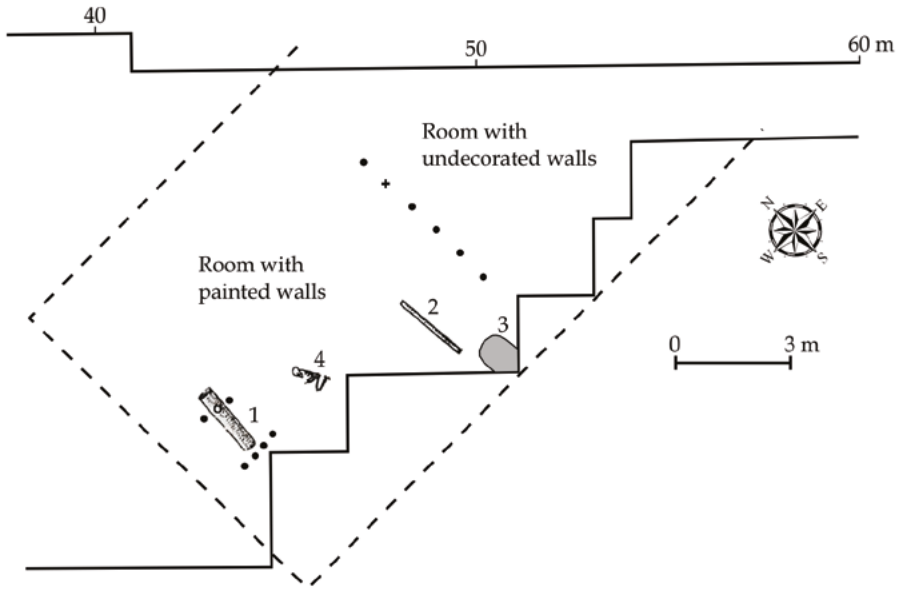

Figure 3. Simplified plan of the Boian 'sanctuary' at Căscioarele-'Ostrovel' tell: (1) the large clay tube/'column'; (2) the small clay tube/'column'; (3) painted bench/'altar-table'; (4) skeleton under the floor (redrawn from Dumitrescu 1970).

540; Lichter 2014; Monah 2001; and Whittle 1996: 94-95). However, while the architecture and function of the building appear to have been the subject of most discussion, with the painting being a central element thereof, the pigments themselves have received no attention and no technological analyses have been performed to date. It was therefore our intention to begin studying the white and red colours used in the painting of architectural elements and objects from the 'sanctuary' by analysing their chemical composition.

Materials and methods

The batch of samples contains only materials found at the Vasile Pârvan Institute of Archaeology, Romanian Academy, in Bucharest. Other materials (such as the triangles, the 'medallion', the small clay tube/'column' and the small plate painted white on the inside), found at the Lower Danube Museum and the Municipal Museum in Călărași, were not available to this study.

The material analysed consists of an almost complete dish painted on the inside with white spirals (Figure 4: P1); a leg fragment painted in white on a red background (Figure 4: P2); part of a painted stand-vessel with three holes in the upper part (Figure 4: P3); two fragments of large vessels, decorated with grooved and excised motifs filled with white pigment on the exterior, and covered with a red coat inside and outside (one of them also painted with white on the inner side) (Figure 4: P4 and P5); two white painted fragmentary house models, originally with animal heads (Figure 5: P6 and P7); three painted wall fragments (Figure 6: P8, P10 and P11); and a fragment from the large clay tube/'column' (Figure 6: P12). Initially, a pot fragment painted with black motifs from another Boian structure (House 11) was included in the batch of samples, but was later excluded because the substance, most probably a graphite based layer, cannot be analysed by the available techniques (P9).

The mass percent elemental composition, as a first step in assigning the chemical composition of the white and red colours, was determined using the Particle Induced X-ray Emission (PIXE) technique. A 3MV Tandetron™ particle accelerator at the Horia Hulubei National Institute for Research and Development in Physics and Nuclear Engineering (IFIN-HH) was used to generate and deliver the proton beam. Recently, the 3MV Tandetron™ (Burducea *et al.* 2015) was upgraded to include an 'in-air' analysis setup. This facility allows for the measurement of samples without any risk of damage due to the vacuum chamber conditions. A proton beam of 2.735MeV was generated and directed towards the samples. The resulting characteristic X-ray spectra were recorded using a Silicon PIN and analysed with the Gupix software (Campbell *et al.* 2010).

In addition, in terms of the FT-Raman spectroscopy, the pigments were analysed directly on the surface after a gentle prior scratching using a Bruker Vertex 70 FTIR spectrometer equipped with a RAM II Raman module (with N2 cooled detector and a Nd:YAG laser excitation source of 1064nm).

The two methods were chosen not only for their sensitivity, but also their non-destructive nature, given that the then curator of the archaeological materials from Căscioarele-'Ostrovel' explicitly requested that the analysis not affect the samples in any way.

It should be also mentioned that the selection of the samples was limited by several factors: the difficulty of finding sherds with well-preserved white and red pigments; the large size of some samples, making

Figure 4. Căscioarele-'Ostrovel' tell. Pottery fragments from the Boian 'sanctuary' (photos by Radu-Alexandru Dragoman).

them difficult to hold in place for measurements; and the extreme fragility of the wall fragments and – especially – the large tube/'column' fragments.

We tried to select materials with a sufficiently thick layer of colour. When the colour layer was too thin, two points were measured using the PIXE technique and compared – one on the colour and the other on the paste. However, due to the extreme thinness of the white and red layers, the pigment in the composition of some samples could not be determined by the PIXE and FT-Raman techniques at all the measuring points – or even any at all (the white pigment on sample P1). In other cases, despite a thick layer of colour, the substance could not be analysed by the FT-Raman technique because of the characteristic uneven surface of the samples (the white pigment on samples P4 and P5).

Results

The results obtained through the PIXE technique indicate calcium and iron as the most frequent elements, with the white pigments containing much higher concentrations of calcium than the red pigments (Figure 7), and the red colour palette with a somewhat higher concentration of iron than the white colour palette (Figure 8). The other chemical elements are more uniformly distributed in the white pigments than in the red pigments.

The white pigments contain P, S, K, Ti, Mn, Sr and Zn. For reasons that pertain to the interpretation of the PIXE results, their mass concentration was expressed as percentage values of the corresponding oxides (although in practice they can also be part of other chemical compounds). From

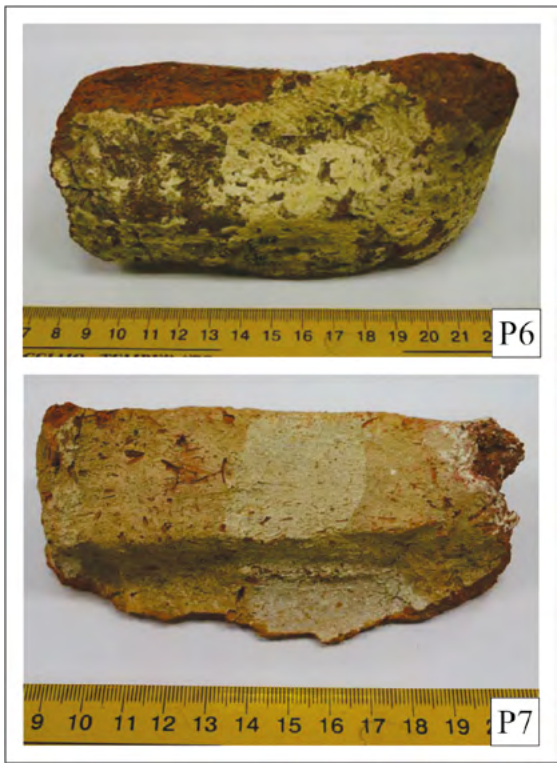

Figure 5. Căscioarele-'Ostrovel' tell. House models (originally with animal heads) from the Boian 'sanctuary' (photos by Radu-Alexandru Dragoman).

the calculation based on this reasoning it results that they are trace-elements and consequently must have been introduced to the white pigments through the raw materials used in the formula. It should be noted that the presence of Ti in white pigments is usually linked to the use of titanium oxide, which was introduced to the painting technique during the first half of the 20th century. Nevertheless, in our case, the presence of Ti can be explained as trace-element regularly occuring in soils and not as having been intentionally added to the formula by the use of a specially selected raw material.

The red pigment formula is more complex and heterogeneous than the white pigment. The predominant element is Si, followed by relatively equal proportions of Fe and Ca. Ca – generally associated with the calcite form – is present in all samples. Given its role as a mordant, calcite was added to other types of formula besides the white pigments. The calcium/calcite statistics for the white pigment correlated with the same statistical presence in the red pigment give us an indication of how the whole process of decorating the analysed elements was devised. Unlike the white pigment, P, S, especially K, then Mn and, to a certain extent, Ti become more important. The major issue in terms of 'heterogeneity' has more to do with the

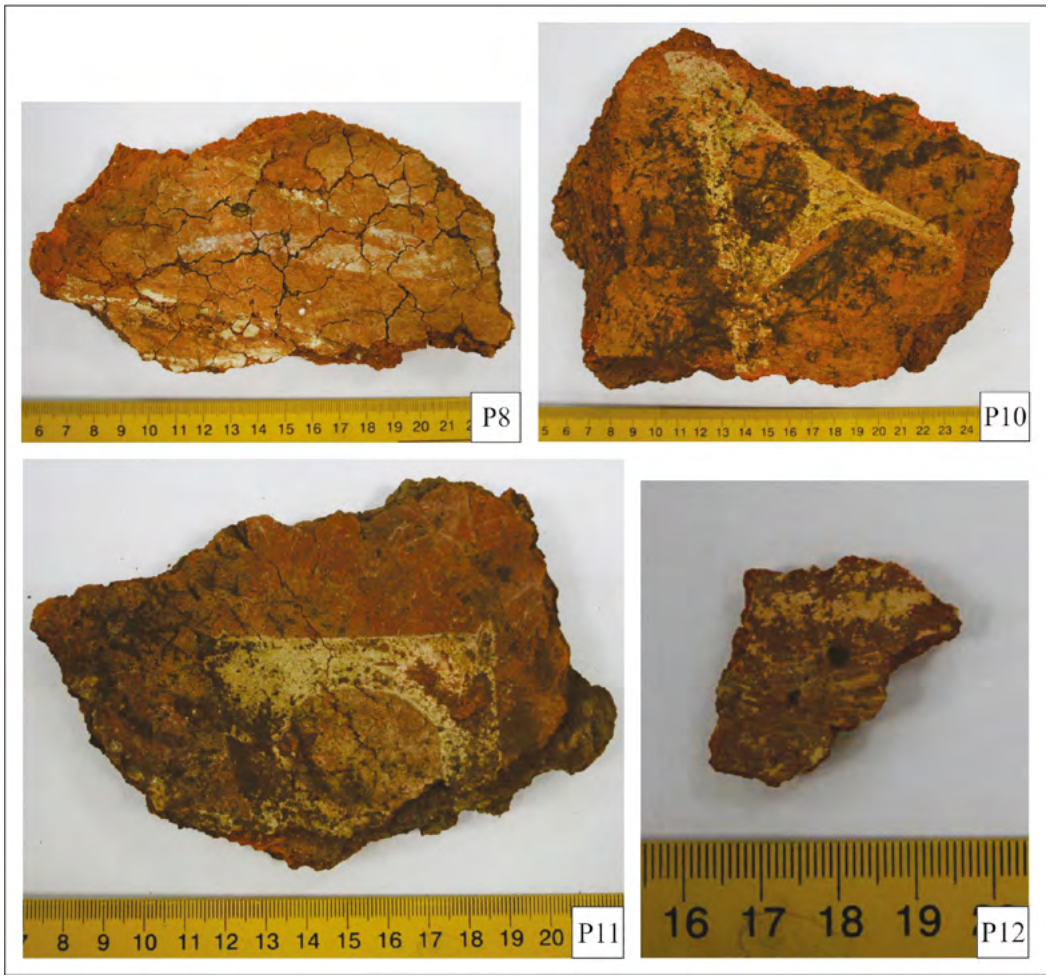

Figure 6. Căscioarele-'Ostrovel' tell. Wall fragments (P8, P10 and P11) and fragment of the large clay tube/'column' (P12) from the Boian 'sanctuary' (photos by Radu-Alexandru Dragoman).

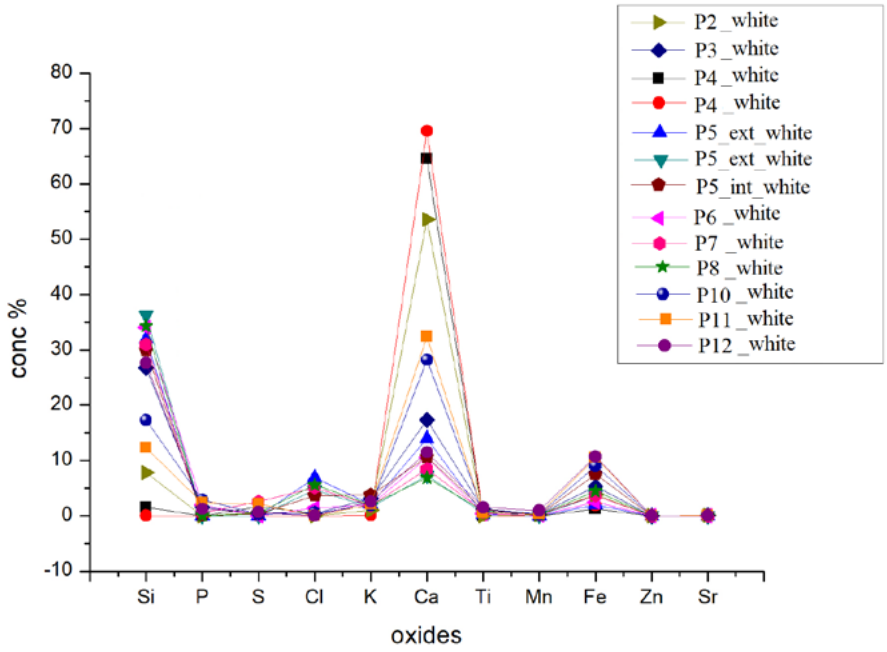

Figure 7. White pigment: the PIXE distribution of mass percentages by types of oxide; samples P2, P3, P4, P5, P6, P7, P8, P10, P11 and P12 (ext = exterior; int = interior).

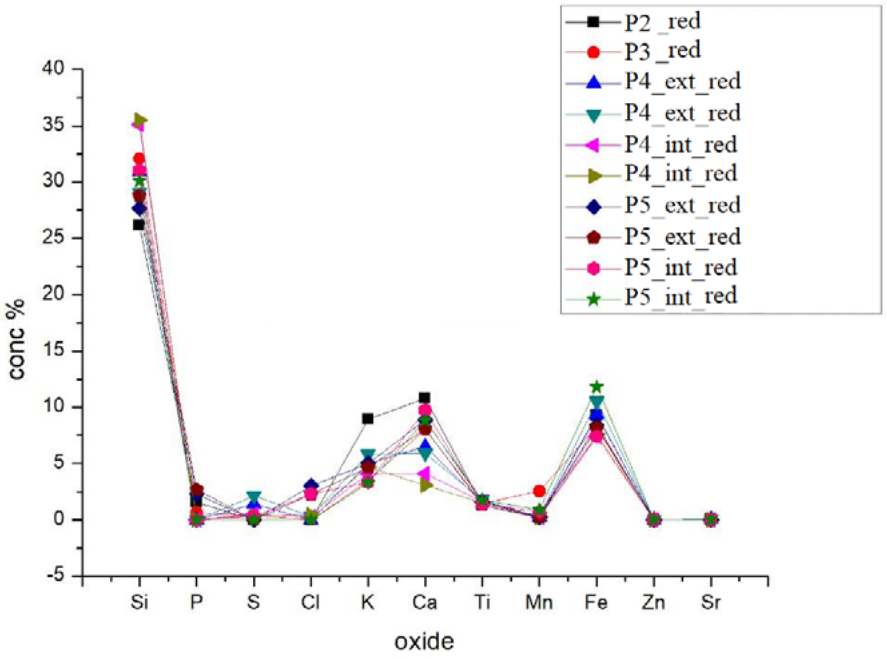

Figure 8. Red pigment: the PIXE distribution of mass percentages by types of oxide; samples P2, P3, P4 and P5 (ext = exterior; int = interior).

degree of mixing of the two different raw materials than with variations in the composition of the formula. This explains why the principal component analysis (PCA) did not identify any distinct groups among the samples. It is also worth noting the complete lack of cinnabar, i.e. mercury (II) sulfide (HgS), a substance only encountered in exceptional cases in the Neolithic period in Southeastern Europe (e.g. Mioč *et al.* 2004; Tóth *et al.* 2013).

The results obtained using the PIXE technique were subsequently complemented by the use of the FT-Raman technique. The investigations carried out using FT-Raman spectrometry were based on the results obtained using PIXE. In addition, FT-Raman is able to differentiate between different chemical combinations of the elements highlighted by the PIXE technique. Finally, obtaining the same conclusions from two different analyses only reinforces the answers to the questions that formed the basis of the experiments. The assignments of the FT-Raman peaks and the literature on which they were designated and interpreted are presented in Appendices 1 and 2.

In summary, calcite and natural varieties of silicon dioxide were identified in the case of the white colour on sample P2 (Figure 9). In six other samples (P3, P7, P8, P10, P11 and P12), the white colour was obtained

using quartz varieties mixed with kaolinite and a minor contribution of iron oxide (hematite, possibly present as a mixture with another variety of iron oxide, and magnetite, in the P3 sample), the other main component being calcium through its natural compounds (calcite or/and calcium hydroxide/ portlandite) (Figure 10). These latter interpretations of the structure of the natural chemical compounds involved could not have been obtained without the use of FT-Raman spectrometry.

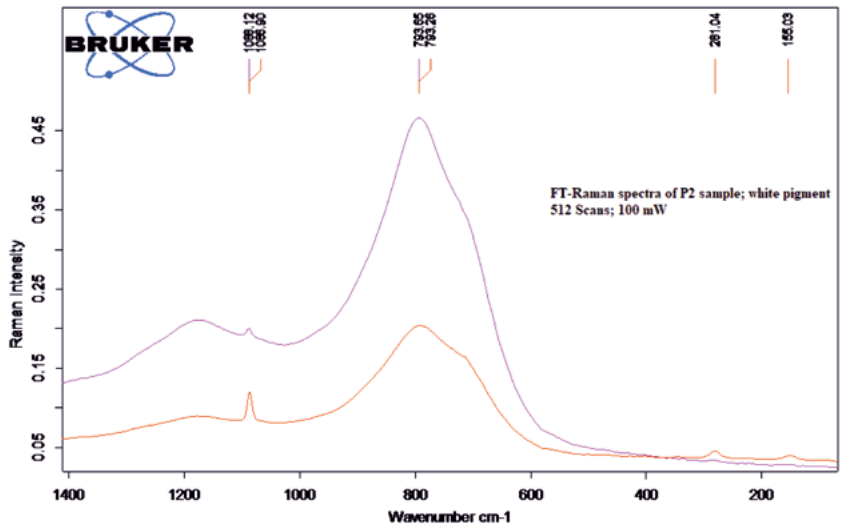

Figure 9. White pigment: the FT-Raman spectra, sample P2.

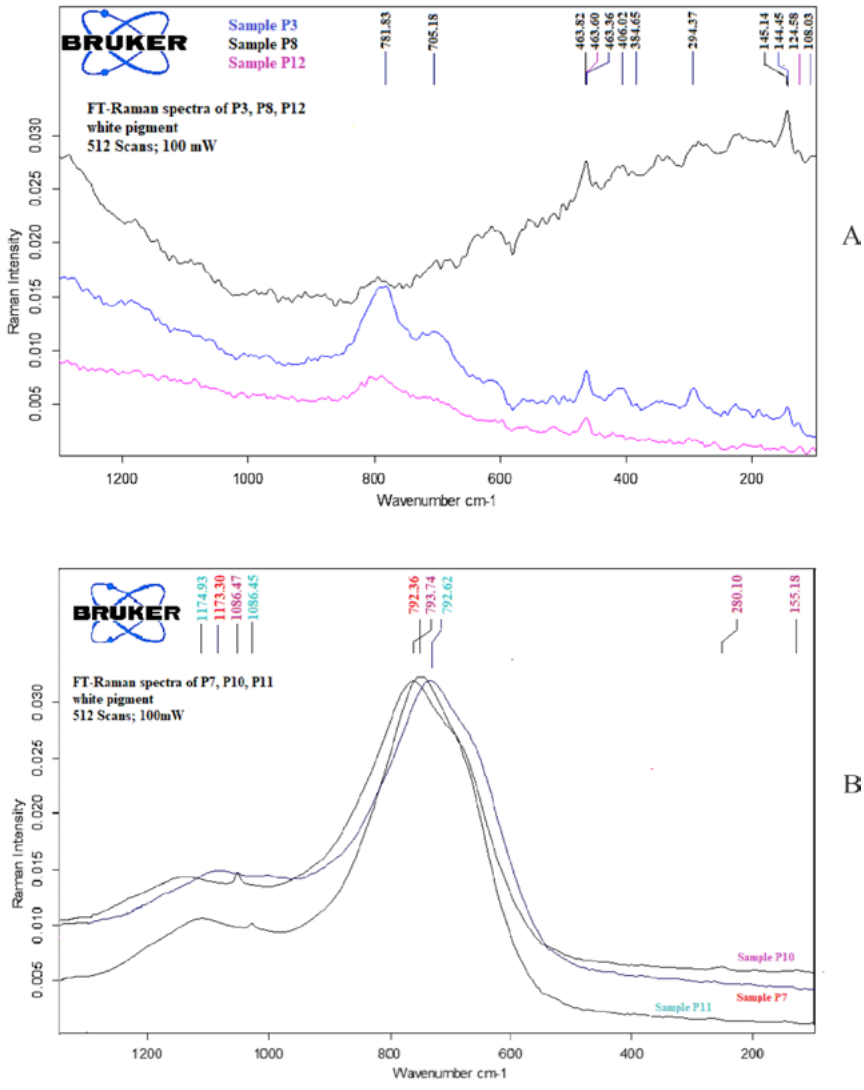

Figure 10. White pigment: the FT-Raman group of spectra, samples P3, P7, P8, P10, P11 and P12 (A – samples P3, P8 and P12; B – samples P7, P10 and P11).

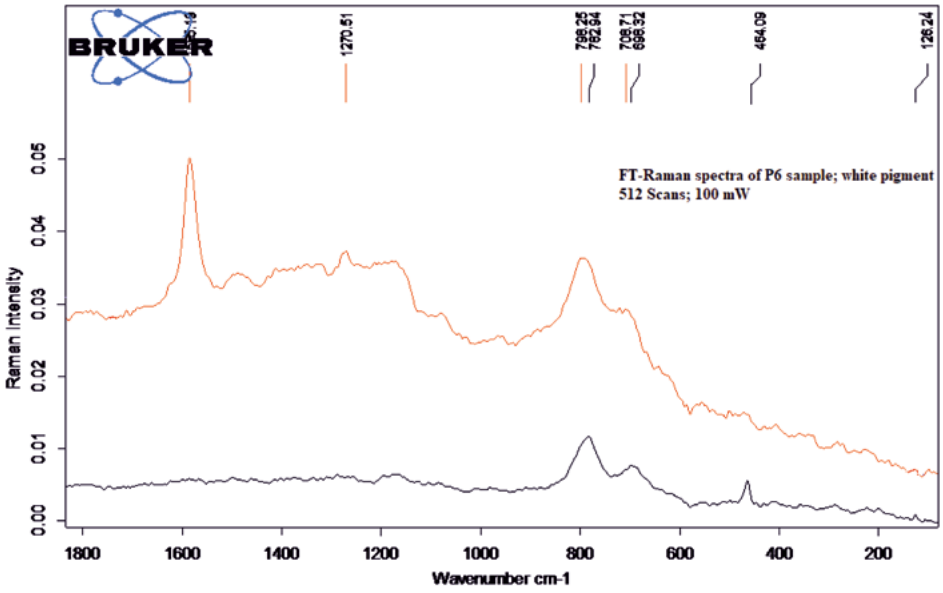

Figure 11. White pigment: the FT-Raman spectra, sample P6.

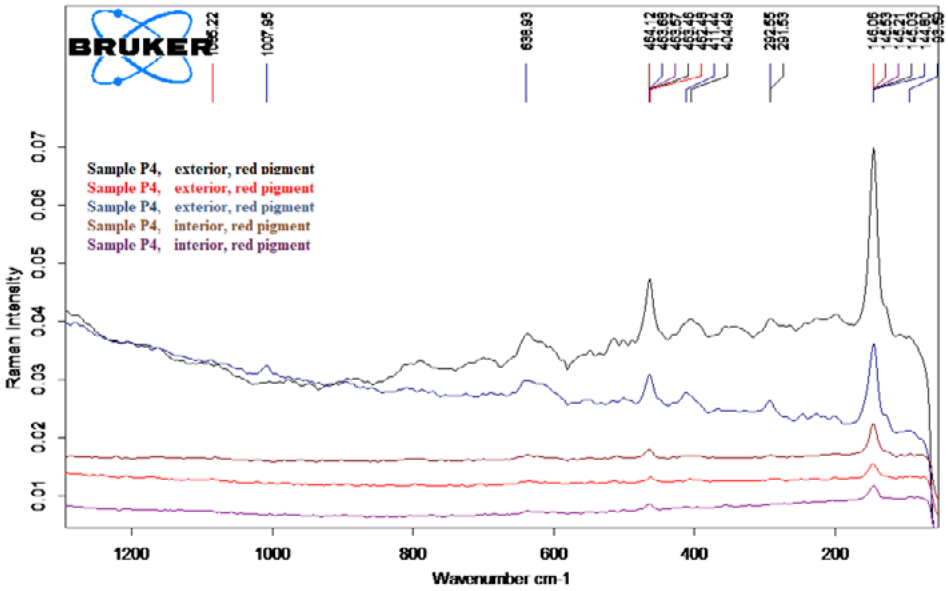

Figure 12. Red pigment: the FT-Raman spectra, sample P4.

A special case would appear to be given by sample P6 (Figure 11): alongside a possible organic component, this sample also contains quartz varieties, trace amounts of kaolinite, trace amounts of calcite with a possible dolomitisation and natural calcium oxalates. However, further information is needed to obtain an accurate understanding of why they used such a formula.

In the red colour palette (Figure 12), a mixture of natural silicon dioxide varieties together with a predominant kaolinite phase were identified, with the mineral phase being dominated by iron oxides – hematite in a possible mixture with magnetite. This statistical occurrence of quartz and kaolinite, as in the case of white pigments, suggests a possible common source for this component in both types of formula.

The results obtained appear to indicate that for the Boian 'sanctuary' at Căscioarele-'Ostrovel' tell there is no relationship between different compositions of the white and red colours, on the one hand, and specific types of objects, on the other. In other words, the pots, the large clay tube/'column' and various architectural elements are linked by the use of similar colour compositions or formulae.

The results concerning the white colour are similar to those obtained for other Boian-Spanţov sites. For example, a fragment of a *Steckdose* from the site of Radovanu-'La Muscalu' (Călăraşi County), located not far from Căscioarele-'Ostrovel' tell, has been studied in detail (Ştefan *in press*). The XRD analysis proved that the white paste used for filling the grooved and excised decoration was 'practically monomineral, namely

calcite', while the XRF analysis showed 'the abundance of CaO'. However, more sherds from Radovanu-'La Muscalu' need to be studied in order to be able to make a reliable comparison. The white colour used to decorate the pots in the Boian-Spanțov site at Nanov-'Vistireasa 3' (Teleorman County) contains calcite and kaolinite (Opriș *et al.* 2019). Moreover, the results for Căscioarele-'Ostrovel' are partly comparable with the results obtained for nine sherds from Gălăţui-'Movila Berzei' (Călăraşi County) dating from an earlier Boian-Giuleşti phase and deriving, according to the author of the excavation, from a 'sanctuary' (Marian Neagu, pers. com., 20 September 2016). There the white paste consists of calcite, calcite and hydroxiapatite, only hydroxiapatite, quartz and gismondine, quartz and diopside, aluminium phosphate, and calcite and albite (Niculescu 2003: 113;). According to the present state of the research, the difference at Căscioarele-'Ostrovel' tell seems to reside in the absence of osteological materials in the composition (i.e. the absence of hydroxiapatite).

The observations for the red colour composition at Căscioarele-'Ostrovel' tell can be related to the known data for the use of red colour during the Neolithic and Chalcolithic. According to the study of ochre on Neolithic and Chalcolithic pottery, including Boian sherds from the sites in Vidra, Aldeni, Spanţov and Radovanu: 'All the samples [...] have a mineralogical nature'; '[t]he X-ray diffraction patterns of some sherds covered with ornamental red always present a higher concentration of micaceous minerals (muscovite and illite) and quartz accompanied by hematite and goethite. Calcite, kaolinite and sometimes feldspars appear subordinately in variable quantities' (Gâţă and Mateescu 1999-2001: 186).

Conclusions

The use of in-air PIXE and FT-Raman spectroscopy generated the first data to be used in determining the chemical composition of the white and red pigments used in the Chalcolithic 'sanctuary' at Căscioarele-'Ostrovel' tell. In terms of the white colour results, the two methods led to the identification of a complex mixture of calcite and other calcium white compounds, quartz varieties, kaolinite and even monohidrated calcium oxalates (in sample P6). In the red colour, the mineral phase was dominated by iron oxides (hematite in a possible mixture with magnetite, denoting a specific thermal treatment), and by silicon dioxide varieties (a common mineral base for most white and red pigments); while the presence of kaolinite, calcite and traces of natural gypsum were also indicated.

The results obtained allow for a comparison to be drawn between various categories of painted materials from the Boian 'sanctuary' at Căscioarele-'Ostrovel' tell and coloured objects from other Boian sites. Moreover, these results, together with other mineralogical and phyisicochemical analyses, will form a necessary component of future research directions, such as investigations of the different technologies used to obtain the white and red colours; investigations of the long-term use of the two colours during the Neolithic and Chalcolithic; and investigations of the religious and symbolic dimensions of the white and red materials and their technologies.

A forthcoming phase of this study will include more samples from the materials coloured with red and white pigments, as well as samples of 'raw materials' from the Boian and Gumelnița habitations on the tell at Căscioarele-'Ostrovel'. When available, samples from other Boian/Gumelnița sites will also be studied. These analyses may contribute to a more sensitive and refined (in time and space) understanding of Chalcolithic white and red pigments – materials which connected, in various different constellations, houses, animal figurines, vessels and human bodies.

Appendix 1: FT-Raman results

Yellowish-white pigment (sample P2; Figure 9*)*

Calcite identified by characteristic signals at 155, 281, *c.* 711 ÷ 713 in coalescence, and at *c.* 1087cm^{-1}. No dolomitisation appeared (no signals at ~1440 and ~1752cm^{-1}, respectively). *Natural varieties of silicon dioxide*; with a characteristic signal at 462cm^{-1} assigned to α-quartz, large band signal at 600 ÷ 1000cm^{-1} overlapping several signals of minor concentration compounds, centred al 794cm^{-1}, and a relatively low intensity band signal centred at ~ 1200cm^{-1}. A possible quartz – coesite composition of natural silicon dioxide.

White pigments (samples P3, P7, P8, P10, P11 and P12; Figure 10)

Quartz varieties: characteristic signal at 462cm^{-1}, silicon dioxide varieties with large band signals at 600 ÷ 1000cm^{-1} and at *c.* 1200cm^{-1}, mixed with *kaolinite* (characteristic signal at *c.* 144cm^{-1}), *minor contribution of iron oxides* (hematite with assigned signals at 226, 294, 406, 497 and 614cm^{-1}; possibly present as a mixture with another variety of iron oxide, magnetite, in P3 sample, attributed signal at *c.* 670cm^{-1} in coalescence with 650 ÷ 950cm^{-1} large band), the other *main component being calcium through its natural compounds* (calcite and/or oxide/hydroxide) having characteristic signals at *c.* 1087cm^{-1} – *calcite*, and at *c.* 780cm^{-1} *calcium hydroxide/portl*and*ite*.

White pigment in sample P6 case study (Figure 11)

Among other possible organic components, this sample also contains *quartz varieties, kaolinite in trace amounts,*

calcite trace amounts with a possible dolomitisation, and *natural calcium oxalates* (signals assigned at 1400 ÷ 1650 cm^{-1}, weak signals at *c.* 200, 500, 800 ÷ 900cm^{-1}); the signal at *c.* 1200 ÷ 1300cm^{-1} may be due to a *monohydrated oxalate mineral or may be a sign of a compound with a vegetal base origin present*. More information is needed.

Red pigment (*sample P4;* Figure 12)

A mixture of *natural silicon dioxide varieties* having a characteristic signal at *c.* 462cm^{-1}, due to a-quartz, other signals being assigned at *c.* 600 ÷ 1000cm^{-1} and at *c.* 1200cm^{-1}, together with a *predominant kaolinite phase* with characteristic signals at *c.* 144 and 639cm^{-1}.

The mineral phase is dominated by iron oxides (characteristic signals at 292, *c.* 411cm^{-1} of hematite, in a possible mixture with magnetite, sentence assumed by the presence of a signal at *c.* 670cm^{-1}, denoting a particular thermal treatment applied). Low intensity signals assigned to *calcite* (1087cm^{-1}) *mixed with natural gypsum* (characteristic signal at *c.* 1008cm^{-1}).

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Archaeometric Studies of Boian Pottery from Nanov-'Vistireasa 3' (Teleorman County, Romania, *c.* 4800-4500 cal BC)

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Abstract

The vast majority of the studies on Boian pottery (Early Eneolithic in Southern Romania: *c.* 5000-4500 cal BC) are limited to analyses of shape and decoration with the aim of establishing periodisation and chronology. Only few studies are concerned with technological aspects, such as the composition of the paste and pigments. This article aims to contribute to the latter by looking at pottery samples originating from recent preventive excavations (2012) undertaken at the Nanov-'Vistireasa 3' settlement, attributed to the Boian-Spanțov phase (*c.* 4800-4500 cal BC). To this end, several archaeometric measurements were used to analyse the ceramic paste and white and red pigments. The results of this study indicate a common production for the majority of the pottery samples analysed and an exotic provenance for one sherd in particular. Different types of clay were used as building materials (hearths, walls). The chosen samples of white pigments were based on two main groups of compounds: four samples had calcium-based compositions in combination with low silicon-based products, and one sample had a high concentration of aluminium-silicates resulting from the presence of kaolinite. The red pigments were iron-based but with a high variability of the adjacent compounds.

Keywords: Eneolithic, Boian culture, pottery technology, archaeometry, in-air PIXE, FT-Raman, μ-DRIFT, SEM, EDS, white and red pigments.

Introduction

Previous studies of Boian pottery from Southern Romania have mostly been limited to analyses of shape and decoration with the aim of defining local relative chronologies (Rosetti 1934, Berciu 1961, Comșa 1974 and Pandrea 2000). Only a few fragments of Boian pottery were subjected to laboratory-based tests with a view to determining the composition of the paste. The first published results were obtained from a mineralogical analysis of 12 fragments from different sites, phases and ceramic types (Stoicovici 1974); this latter study described the types of clay used and the main inclusions, and determined a firing temperature of between 500 and 700° C. Other chemical and physical analyses looked at five Boian pottery fragments from Dobrudja, four of them found in Cheia, a fifth in Hârșova (Cărpuș and Cărpuș 2007). The results indicated the use of at least two sources of clay and the absence of any tempers in the paste matrix.

Questions regarding the composition of the white or red pigments applied to the Boian pottery have been addressed since the earliest studies, when several hypotheses were also put forward. For example, Dinu V. Rosetti believed that the red pigment of the Boian vessels 'is not ochre itself, but a colour obtained from the burning in a certain way of limonite, a common mineral in the loess deposits around Bucharest' (Rosetti 1934, p. 8). However, determinations based on archaeometric analyses are relatively recent and scarce. The very few samples of red pigment analysed were based on iron oxides (hematite, goethite) in combination with quartz varieties and small quantities of other minerals (Gâță and Mateescu 2001; Dragoman *et al.* 2019). The white pigments were commonly calcium-based (Gâță and Mateescu 1987; Dragoman *et al.*, 2019), but there were also samples from the Gălățui-*Movila Berzei* site (Boian-Giulești phase), which had various mixtures of calcite, hydroxyapatite, quartz, gismondine, diopside, aluminium phosphate and albite (Niculescu 2003).

The object of the present study is to acquire information on the paste and pigment composition of the Boian pottery. The samples it looks at come from a recent rescue excavation (2012) at Nanov-'Vistireasa 3' (Teleorman County, Southern Romania) (Figure 1), an

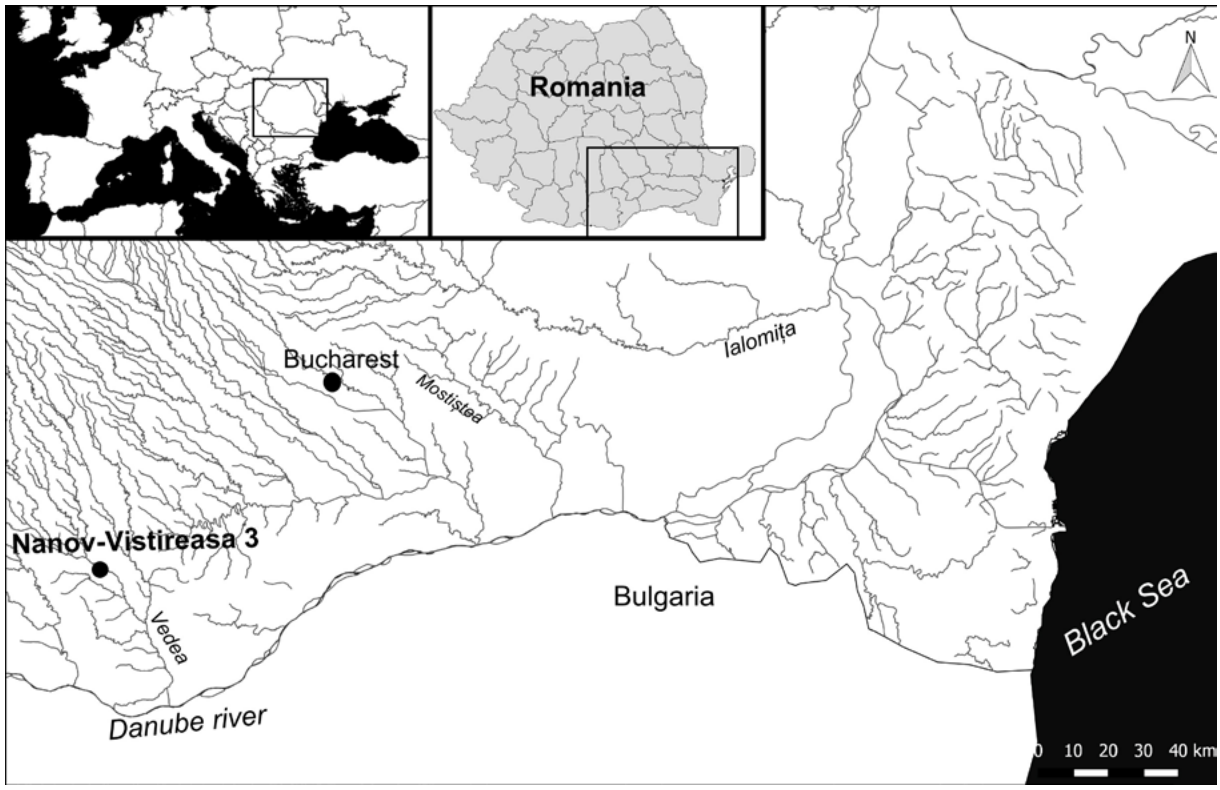

Figure 1. Geographical location of the Nanov-'Vistireasa 3' site.

Eneolithic settlement from the Boian-Spanţov phase (*c.* 4800-4500 cal BC) that yielded an impressive quantity of pottery. To date, complete batches of sherds discovered in two large pits (labelled Cpl 50 and Cpl 51) have been macroscopically analysed (Opriș and Ștefan 2016). Given the large dimensions of both pits, during the excavations the archaeologists were of the opinion that they represented the remains of pit-houses inhabited by Eneolithic people. However, size analysis of the sherds and the depositional patterns showed that the pottery ended up in the pits as refuse.

Previous analysis of the technology used to manufacture the vessels was carried out using the naked eye and with the aid of a magnifying glass (×2.25). This led to the identification of eight types of paste formulae. The most frequently used temper was vegetal in nature, while grog was only very rarely encountered. Other commonly encountered inclusions that seem to depend on the clay sources used by the potters were white mica, fine or coarse sand, and, in a few cases, limestone (Opriș and Ștefan 2016). The vessels were made using the pinching, coiling and slab methods, techniques through which shapes, such as cups, beakers, bowls, dishes, lids, and cylindrical and common pots, were formed. Decorative elements were applied, such as polishes, channels and graphite painting on the cups and beakers, incisions and white filled excisions on the bowls and cylindrical body pots, and organised barbotine on the common pots. Red pigments were occasionally applied to the internal surface of cups, beakers, bowls and cylindrical pots. In two cases, the red layers were partially covered with white pigments.

The large quantity of decorated pottery from well excavated features and the results of preliminary, macroscopic analysis made the pottery assemblages from Nanov-'Vistireasa 3' a good choice for compositional analysis.

The samples

A number of 33 samples were selected for the archaeometric measurements (20 from Cpl 50 and 13 from Cpl 51) (Table 1); while 24 samples were chosen in order to determine the chemical composition of the paste matrix, with the selection criteria based on the variability of the paste composition, as macroscopically observed (Opriș and Ștefan 2016: 34-36). A further seven sherds were selected primarily due to the presence of decorative pigments (white and/or red) on their surfaces (Figures 2 and 6; Table 2), but their paste composition was also analysed using the same procedure used for the aforementioned group of sherds. A hearth fragment and a burnt adobe piece discovered in pit Cpl 51 were also chosen as testing samples in order to identify possible similarities between the clay used in common Eneolithic structures, such as hearths or house walls on the one hand, and the clay used to make pottery on the other.

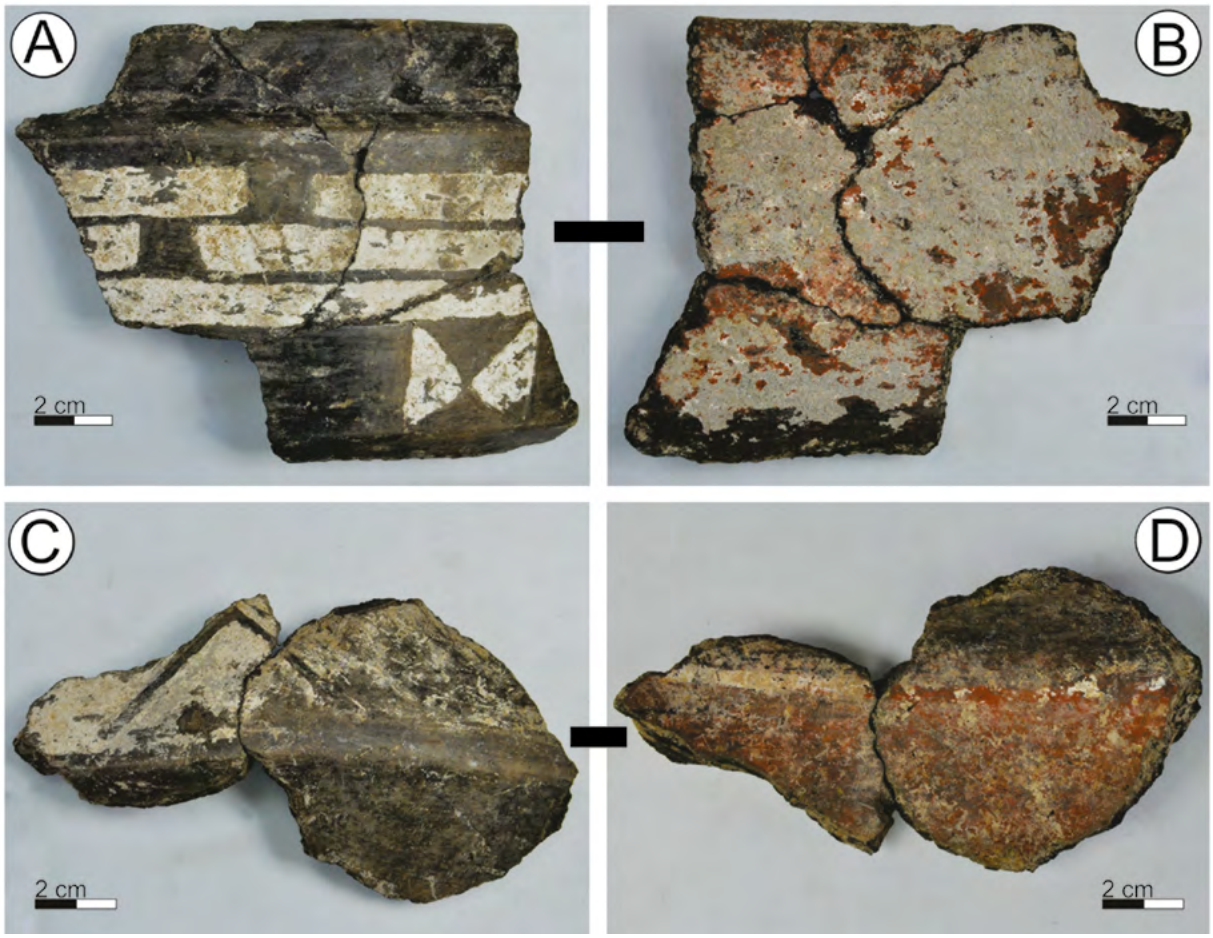

Figure 2. Fragments of a bowl (A and B, Sample 50-16) and a cylindrical body vessel (C and D, Sample 50-17) from pit Cpl 50 with white colour encrusted on the external surface (A and C) and white on red on the internal surface (B and D).

Methods

The Particle Induced X-Ray Emission (PIXE) method was used for both the paste and pigments, and the Fourier Transform Raman spectroscopy (FT-Raman), Fourier Transform Diffuse Reflectance Infrared Micro-Spectroscopy (μ-DRIFT), Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) techniques were used just for the white and red pigments. Prior to the measurements, the surfaces of the pottery samples were cleaned with water and the pigment areas scratched with a sharp metal tool in order to remove the surface layer that could have undergone post-depositional contamination.

In-Air Particle Induced X-Ray Emission

The samples were first analysed using the Particle Induced X-Ray Emission (PIXE) technique. For this, the 3MV Tandetron™ particle accelerator at the Horia Hulubei National Institute for Research and Development in Physics and Nuclear Engineering (IFIN-HH) was used to generate and deliver the proton beam (Burducea, *et al.* 2015). The 3 MV Tandetron™ was recently upgraded to include an 'in-air' setup that allows for the analysis of fragile and large samples with no geometrical limitations and without the risk of damage posed by vacuum chamber conditions.

A proton beam of 2.7 was generated and directed towards the samples at a normal incidence. The beam spot on the sample was 2mm in diameter and the penetration depth was approximately 70μm. The data acquisition time was set to 300s for each sample. The resulting characteristic X-ray spectra were recorded using a Si-PIN detector (Amptek, USA) positioned backwards at 45° with respect to the beam direction, and the collected spectra were analysed with the Gupix software (Maxwell *et al.* 1989) using the Iterated Matrix solution type.

Fourier Transform Raman Spectroscopy (FT-Raman) and Fourier Transform Diffuse Reflectance Infrared Micro-Spectroscopy (μ-DRIFT)

Compositional analysis of the pigments was performed using a FT-IR/Raman Bruker Vertex 70 instrument equipped with a Helios micro-spectroscopy accessory and a Nd:YAG laser (1064nm) with variable power (1-

500mW) and LN2 cooled Ge detector. FT-Raman and μ-DRIFT vibrational spectroscopy techniques were used in the non-destructive manner. μ-DRIFT spectra were recorded between 400 and 4000cm^{-1} with 1000 scans. FT-Raman spectra were recorded between 50 and 3500cm^{-1} with 512 scans, and power between 25 and 500mW. In all cases, the spectral resolution was 4cm^{-1}. Several spectra were recorded for each sample with the one with the best defined peaks being kept.

Scanning Electron Microscopy and Energy Dispersive Spectroscopy

The scanning electron microscope (SEM) used was the FEI Quanta 200, which is made by the FEI Company. This test allows for visualisation of the surface morphology of the samples analysed. The samples were fixed on the support using a double adhesive conductive band. This band must be conductive to ensure the electrical contact between the sample and the grounded metallic support. The electronic microscope was equipped with an integrated X-ray energy dispersive spectrometer (X-EDS), produced by EDAX. Using X-EDS analysis, the chemical elements on the sample surface can be identified and measured quantitatively.

Results

Ceramic paste analysis

The in-air PIXE method was used to determine the chemical composition of the ceramic paste. Two measurements of the external surface were taken for each sample, with the final result for each being the arithmetic mean of the concentration of each chemical element identified (Table 3). This was necessary in order to compensate for the slight differences between measurement values for the same sample due to the heterogeneity of the ceramic paste. Five chemical elements were detected in all of the samples (Al-Si, K, Ca, Ti, Fe), with two other elements (Mn and P) being identified in only a small number of samples.

Relative homogeneity, conferred in particular by a less variable Al-Si content, was observed in the samples from pit Cpl 50. No phosphorus compounds were identified and manganese was found only at very low concentrations in all samples. Iron showed the most notable variations. In the set of pottery samples from pit Cpl 51, the chemical composition of the paste of the sherds was more heterogeneous than that of the samples from Cpl 50: the calcium concentration was higher, the Al-Si was lower, the iron showed smaller variations, phosphorus was detected in two samples, and in one sherd no manganese was detected. Samples of the building materials (hearth fragment and burnt adobe) indicated a significantly different clay matrix than in the case of the pottery samples, as both have a higher concentration of calcium. Principal components analysis (PCA) of chemical concentrations, obtained by the in-air PIXE method, was performed using the Minitab 17 software. Sample 51-6 was not included in the PCA analysis because of the lack of manganese. The resulting graph (Figure 3) shows the groupings of the samples from the two pits, with many similarities visible among the fragments from pit Cpl 50 and a greater heterogeneity among the fragments from pit Cpl 51. The samples from the hearth (51-9) and the burnt adobe (51-10) can be identified as a separate group (Figure 3). These groups may be the result of clay sources or paste formulae with different compositions. The fragments analysed from pit Cpl 50 are more homogeneous in terms of the chemical composition of the paste and appear to originate from pots manufactured from a common clay source. Sample 50-8, although labelled as imported pottery based on the specific incised decoration assigned to the contemporaneous Precucuteni culture from Moldavia (north-eastern Romania), is no different in terms of the chemical composition of the paste. Similar compositional features were found in five samples from pit Cpl 51 (51-1, 51-4, 51-8, 51-14 and 51-15), indicating a common clay source with the sherds from pit Cpl 50. Other samples from Cpl 51 had chemical compositions that generated a marginal distribution following the PCA analysis. These include Samples 51-3, with a sandy paste, 51-5 and 51-11, made of common paste with vegetal debris, and 51-13d and 51-13s. The latter two samples are part of the same sherd: 51-13d is a layer of sandy clay applied to the external surface and 51-13s is the inner part of the wall of the vessel, a mixture of clay with carbonate concretions. Differences between the outer layer and the core are generated both by the types of inclusions and the differences in the chemical composition of the clay. Taking this into account, on the one hand this demonstrates the use of two types of clay formula in the manufacture of the same vessel: one for the construction of the vessel and another for the treatment of the external surface. On the other hand, as seen in Figure 3, the composition of the two types of clay from Sample 51-13 is substantially different from the composition of all the other samples. Thus, this fragment falls into the category of exotic pottery fragments, most probably being part of a vessel imported from another production site.

White pigment analysis

The white colour analysed was used for decoration and found in the form of inlaid paste in the excision patterns on the external surface of four sherds, one of which also had a white band painted on the internal surface (Table 2). In order to determine the chemical composition, the in-air PIXE and EDS methods were used, while the FT-Raman and μ-DRIFT techniques were applied to detect the mineralogical phases, with

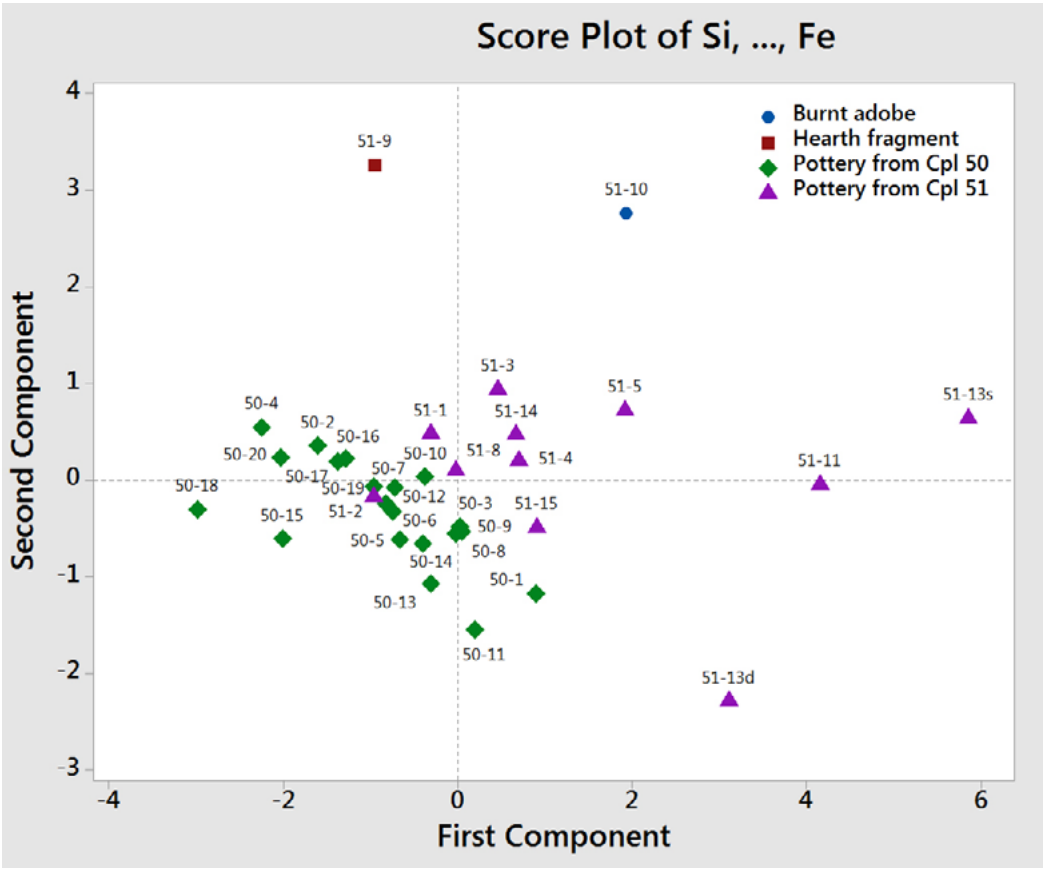

Figure 3. Bi-plot of the first and second principal components resulting from PCA on the log-ratio transformed concentrations (Al-Si, K, Ca, Ti, Mn and Fe).

SEM being used to observe the textures of the pigment microstructures.

Samples 50-4_1 and 50-16_1 returned very similar chemical compositions in the in-air PIXE and EDS measurements, with calcium being the main chemical element detected (Tables 4-5). This similarity was also confirmed by the presence of calcite/lime peaks, as seen from the FT-Raman and µ-DRIFT spectral analyses (Figure 4). However, the SEM images showed slight differences in the texture of the microstructure of the sample surfaces. Based on these results, it can be assumed that only lime and small quantities of quartz were present in the formula. This observation may also confirm an assumption made during the typological analysis – namely that the two sherds belonged to the same vessel.

One interesting case study involved the comparison of two samples of white pigment from the same sherd: 50-17_1 encrusted in an excised pattern from the external surface and 50-17_2 applied to the internal surface as a strip over a red painted layer. Firstly, the in-air PIXE and EDS measurements of both samples revealed some differences in their chemical composition (Tables 4-5). The spectral analysis (FT-Raman and µ-DRIFT) led to the observation that the external white paste (50-17_1) contained lime, acting as a mordant, and quartz/kaolin with a substantially higher content of crystallised water, while the white pigment from the inner surface (50-17_2) was mixed with iron oxides (probably from the red pigment applied here). Relatively well defined traces of O-H, in combination with C-O from calcium carbonates, were found in both samples, a mixture that suggests the presence of portlandite in a combination such as $Ca(OH)_2/CaCO_3$. This type of association has been explained in other situations (Chiriu, *et al.* 2014) as being controlled in the formula in order to achieve specific results, namely to produce a certain amount of vitrification and to reduce the amount of carbon dioxide in the pottery combustion area.

The largest compositional differences compared with the four other white pigments analysed in the paper were found in Sample 50-18_1. The very small quantity of calcium detected by the in-air PIXE and EDS indicates that the white colour was not obtained by using a calcium-based mixture. The absence of calcium based compounds (lime/calcite) was also observed on the FT-Raman and µ-DRIFT spectra, with the base composition being defined by quartz-kaolinite. The SEM analysis of the sample revealed that its surface morphology also differs from the four other samples of white pigment. (Figure 6.E-F).

Red pigment analysis

The red pigments analysed (n=5) were applied exclusively on the internal surfaces of the pots (Table

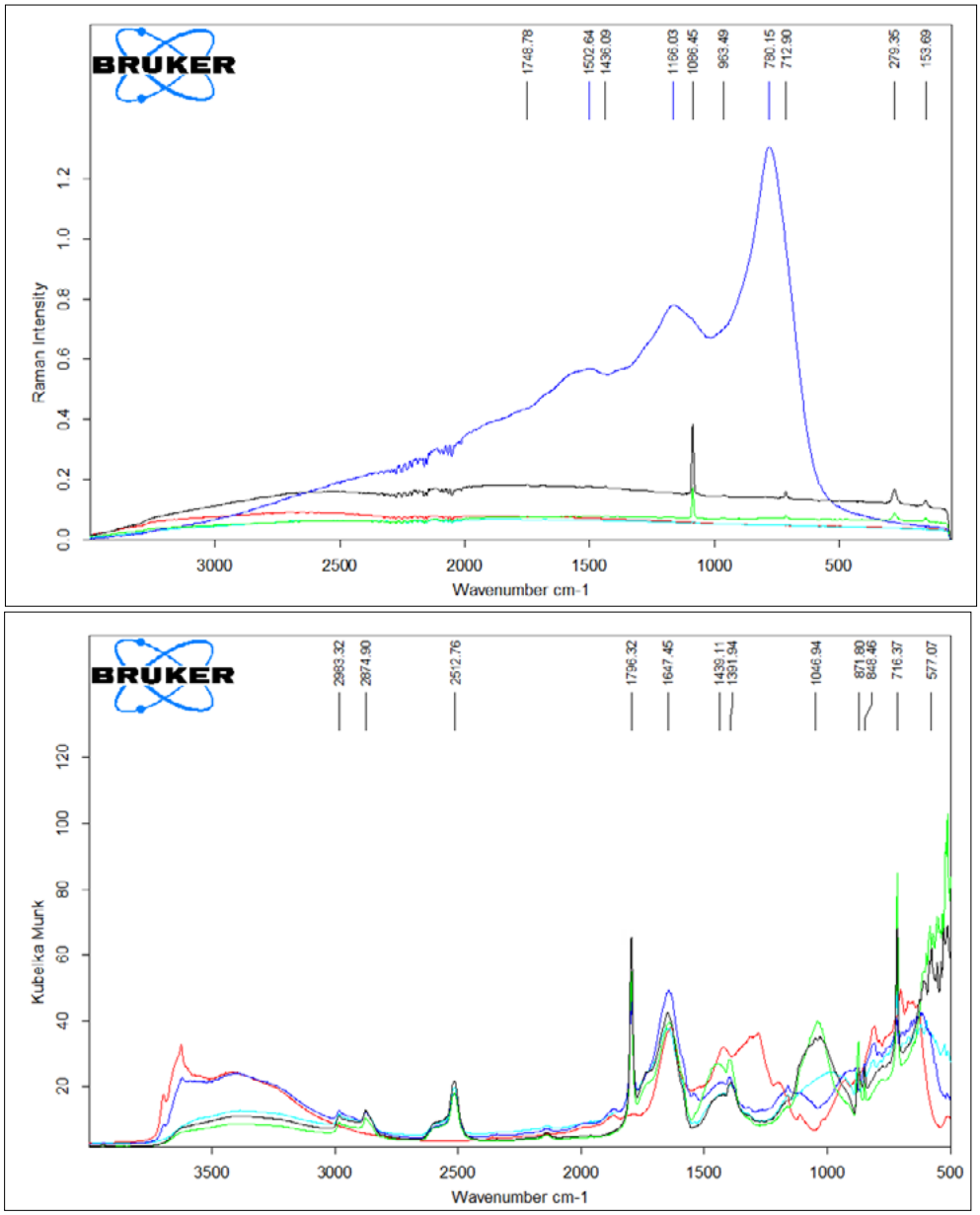

Figure 4. Vibrational spectra of the white pigment FT-Raman (top figure) and μ-DRIFT (bottom figure): NV50-4 (black line), NV50-16 (green line), external surface of NV50-17 (dark blue line), internal surface of NV50-17 (light blue line) and NV50-18 (red line).

2). The chemical composition, mineralogical phases and the texture of the microstructure were determined using the same methods applied in the case of the white pigments (in-air PIXE, EDS, FT-Raman, μ-DRIFT and SEM).

Sample 50-2_1 has a thick reddish-orange layer (1-2 mm) applied to a rim on the inner part of a beaker. The in-air PIXE and EDS measurement showed an unexpectedly high amount of calcium in the composition of the pigment, as well as other chemical elements, such as silicon and iron (Tables 6-7). Interpretation of the μ-DRIFT spectra confirms the use of a formula based on iron oxide combined with calcite/limestone/lime as a mordant in the mixing of colours (Figure 5). The SEM images for the surface microstructure showed a fine and homogeneous texture (Figure 6.H-I).

For the four other samples of red pigment (50-16_2, 50-17_3, 50-19_1 and 50-20_1) only small differences in chemical composition were observed (Tables 6-7). Based on the K-Ca ratio (Table 7) and on SEM images, two main groups can be outlined. The first comprises samples 50-16_2 and 50-17_3, both being cases of red pigment applied to large areas of the internal part of bowls with cylindrical bodies. The second group contains Samples 50-19_1 and 50-20_1, with red pigments found on the inner part of the rim of two small cups. The μ-DRIFT spectra for Sample 50-19_1 indicates a formula obtained by mixing iron oxide with quartz/raw kaolinite (kaolinite with trace α-quartz and anatase titanium dioxide, traces that suggest a primitive method of processing without kaolinite purification) (Mihály *et al.* 2009) to which calcite/lime was added.

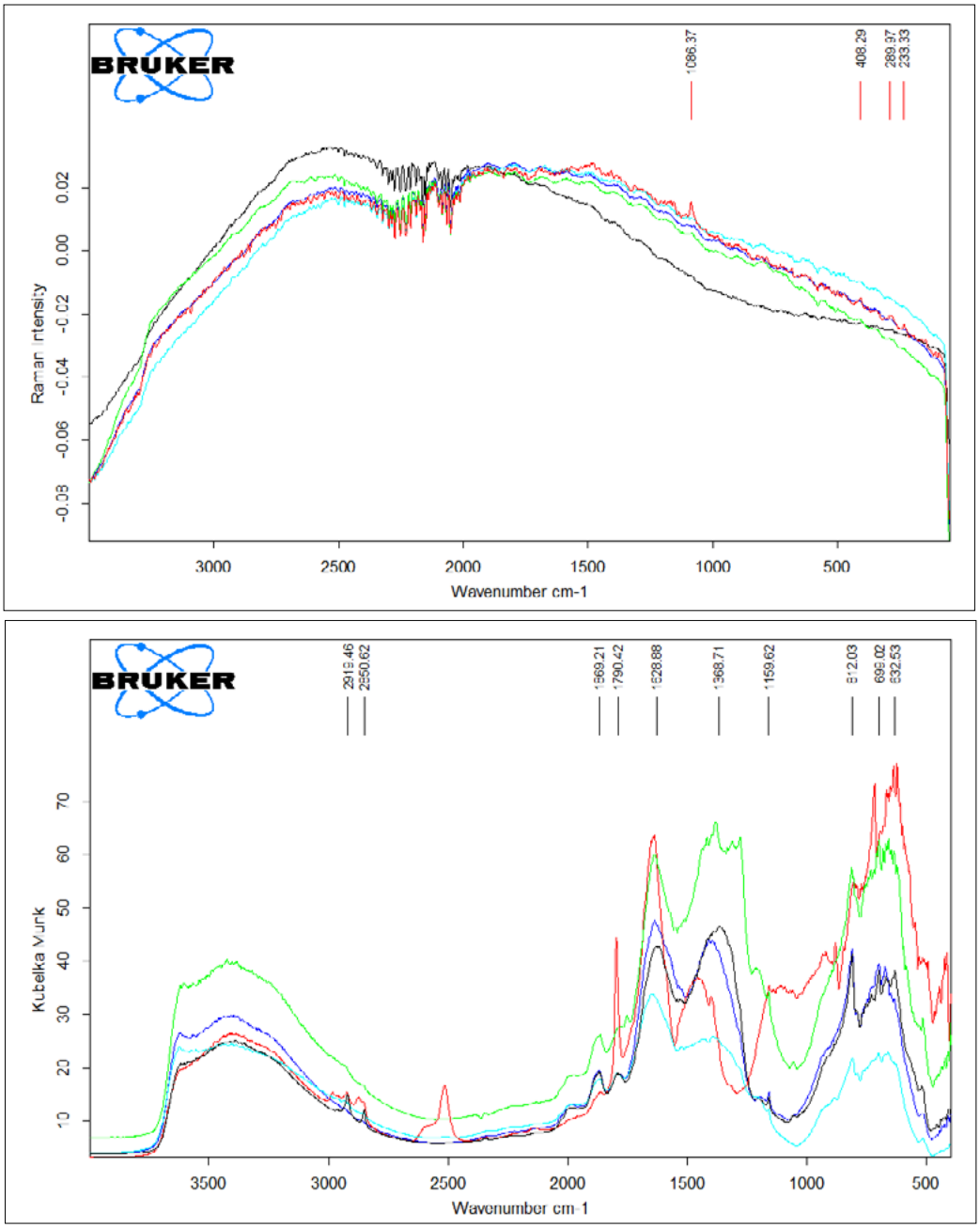

Figure 5. Vibrational spectra of the red pigment FT-Raman (top figure) and μ-DRIFT (bottom figure) NV-50-2 (red line), NV50-16 (green line), NV-17 (light blue line), NV50-19 (dark blue line) and NV50-20 (black line).

Discussion

The compositional analysis of paste formulae using the in-air PIXE method shows that the Boian-Spanţov pottery from the two pits at the Nanov-'Vistireasa 3' site was not produced using only a single clay source. However, a large number of the samples analysed had similar chemical compositions, something that can be explained in terms of the traditions specific to different pottery production sites. This situation was very well defined for the sherds found in pit Cpl 50. The samples from pit Cpl 51 had a more heterogeneous composition thanks, among other things, to a sherd with carbonate inclusions most probably made at a different production site. Unfortunately, there are no similar analyses for the Boian-Spanțov pottery from other sites, and therefore the origin of this exotic sherd cannot be discussed further. Combining these observations with the results of the macroscopic analysis (Opriș and Ștefan 2016) we can assume that most types of clay used in pottery are alluvial in nature, containing white mica and quartz inclusions of different sizes, suggesting different sources of raw material and/or the use of a special treatment to separate the inclusions (sieving, levigation). The sediment of the Vedea River is presumed to be the most likely source of clay for the pottery discovered on the site (Opriș and Ștefan 2016: 40), while those with carbonate inclusions can be considered 'imports'. The chemical analysis of a piece of hearth and a fragment of burned adobe led to the conclusion that the clay used as a building material was collected from other sources than those used for pottery. A similar situation was

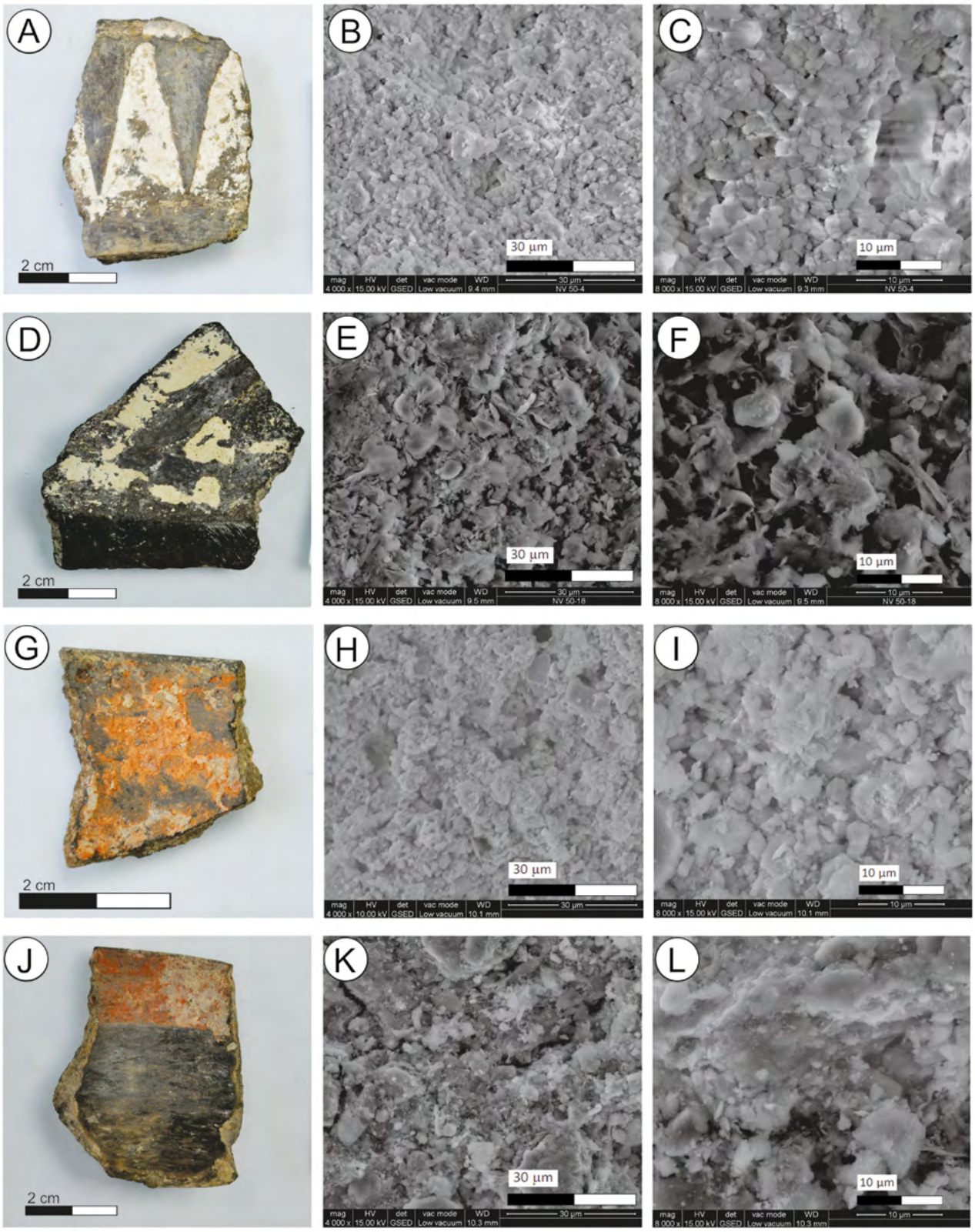

Figure 6. Examples of fragments with encrusted white colour (A and D) and red pigment applied to the internal surface (G and J) from pit Cpl 50 and SEM images of white and red material; (A-C, Sample 50-4_1) sherd with carbonate-based white colour; (D and F, Sample 50-18_1) sherd with kaolinite-based white colour; (G and I, Sample 50-2_1) sherd with red colour based on calcium and iron mixture; (J-L, Sample 50-20_1) sherd with red colour based on iron and silicon compounds.

observed in Neolithic sites in Hungary (Vorsa, Szarvas-Endrőd, Kup), where the clay building materials had different chemical compositions compared with the pottery samples, but very similar to that of the soil collected in the close vicinity of the sites (Tubald 2009; Kovács *et al.* 2009).

Further, our study shows that the selected samples of white pigments were based around two main groups of compounds. Four samples had calcium-based compositions in combination with low silicon-based products, while one sample had a high concentration of aluminium-silicates resulting from the presence of kaolinite. The presence of portlandite in two samples (Samples 50-17_1 and 50-17_2) of the same sherd may indicate that thermic treatments were used in order to adhere the pigment to the walls of the vessels. Given that the pottery firing temperature was not determined, it is for the time being impossible to establish whether the firing of the pigment occurred at the same time as or prior to the firing of the vessel. As to the sources of the calcium-based pigments, these could have been obtained from carbonate concretions formed in the loess deposits found in the eastern vicinity of the settlement. The use of carbonate concretions as sources of white pigment in decorating Eneolithic pottery has already been demonstrated by a study that compared samples of carbonate concretions with encrusted white paste on pottery sherds from various sites in southern Romania (Gâță and Mateescu 1987), one of which was a Boian-Spanțov whitened sherd from the site in Radovanu. The sherd encrusted with kaolinite-based colour (Sample 50-18_1) is the first of this type to be identified so far in the Boian pottery repertoire, with all of the white pigments analysed thus far being based on calcium carbonate or hydroxyapatite (Gâță and Mateescu 1987; Niculescu 2003; Dragoman *et al.* 2019). As the known sources of kaolin clay are situated at great distances from the site, we can assume the existence of a wide exchange network for white pigments or finished encrusted vessels.

One sample from the red colour group was of a lighter hue – reddish-orange – and had a high concentration of calcium, which occurred in addition to concentrations of quartz and iron oxides. The morphology of the microstructure was fine-grained, homogeneous, with very similar morphologies being observed in the samples of the calcite-based white pigment. In this case it is possible that a calcite-based suspension was used in the application of the red pigment, resulting in the mixture described. The four other samples had variable iron contents (from oxides such as hematite or goethite) in combination with quartz-based compounds. None of the red pigments indicated the presence of cinnabar. Similar results were obtained for the red colours (commonly denoted as red ochre) applied to pottery from other contemporaneous sites in Southern Romania (Gâță and Mateescu 2001; Dragoman *et al.* 2019).

Conclusion

The archaeometric characterisation of the Boian pottery paste is currently at an early stage. For the majority of the samples from the Nanov-'Vitireasa 3' site, the results of this study indicate a common production for the majority of the samples analysed and an exotic provenance for one sherd in particular. They also show that a different type of clay was used in building materials (hearths, walls). The use of a single method (i.e. in-air PIXE) in determining the composition places a limit on our final explanations of the paste formulae. Given these circumstances, there is a plan to apply new, complementary methods, such as thin section microscopy and X-ray diffraction, in the near future.

The archaeometric analyses performed in this and previous studies outline the high variability of the materials used in the production and application of white and red pigments on the Boian pottery. In the case of white pigment, the use of substances with diverse compositions shows that the end result (i.e. the white colour) was imposed by a common tradition, while the methods employed in obtaining it may have differed significantly (i.e. from calcite, apatite, kaolinite and dolomite). In these cases, different technological choices can be identified based on knowledge (different traditions or empirically acquired new knowledge) and the resources available to the potters (as a function of exchange networks or the natural environment). In all the samples analysed, the red pigment was obtained from mineral raw materials based on iron oxides. However, the identified adjacent compounds indicate different sources or deliberate mixtures.

Appendix

Features	Samples analysed			
	Pottery paste	Building materials	Red pigment and pottery paste	White pigment and pottery paste
Cpl 50	20	0	5	5
Cpl 51	11	2	0	0

Table 1. Number and type of sample analysed.

Sample	Vessel type	Pigment	
		White	Red
50-2	Beaker	-	1. Applied under the rim, on the internal surface
50-4	Pedestaled vessel (foot fragment)	1. Encrusted on the external surface	-
50-16	Cylindrical body bowl	1. Encrusted on the external surface	2. Applied to the upper part of the internal surface
50-17	Large cylindrical vessel	1. Encrusted on the external surface 2. Painted line on the internal surface, over the red pigment	3. Applied to the upper part of the internal surface
50-18	Cylindrical body bowl	1. Encrusted on the external surface	-
50-19	Cup	-	1. Applied under the rim, on the internal surface
50-20	Cup	-	1. Applied under the rim, on the internal surface

Table 2. Description of the samples of white and red pigment analysed.

Sample	Si (Al)	K	Ca	Ti	Mn	Fe	P
50-1	39.05	2.45	2.50	0.89	0.18	6.71	nd
50-2	41.41	2.49	2.14	0.68	0.07	3.24	nd
50-3	39.80	2.68	2.37	0.79	0.09	5.30	nd
50-4	41.78	2.64	1.72	0.61	0.04	3.08	nd
50-5	39.96	2.51	1.79	0.69	0.06	5.79	nd
50-6	40.26	2.73	1.87	0.69	0.05	5.23	nd
50-7	41.01	3.18	1.63	0.74	0.09	3.68	nd
50-8	40.33	2.68	1.98	0.78	0.21	4.74	nd
50-9	40.11	2.48	2.3	0.79	0.16	5.01	nd
50-10	40.02	2.47	2.31	0.62	0.15	5.39	nd
50-11	39.96	2.65	2.02	1.10	0.07	5.08	nd
50-12	41.11	2.82	1.57	0.71	0.13	3.90	nd
50-13	39.97	2.83	1.57	0.81	0.05	5.82	nd
50-14	40.28	2.85	1.87	0.81	0.06	4.92	nd
50-15	41.52	2.35	1.41	0.71	0.04	3.96	nd
50-16	41.32	2.85	1.74	0.67	0.08	3.49	nd
50-17	40.75	2.77	1.89	0.65	0.04	4.09	nd
50-18	42.29	1.87	1.29	0.59	0.06	3.40	nd
50-19	40.98	2.79	1.72	0.68	0.09	4.10	nd
50-20	41.73	2.62	1.38	0.58	0.07	3.49	nd
51-1	39.81	2.83	3.24	0.73	0.06	4.32	nd
51-2	40.79	2.29	2.24	0.71	0.11	4.25	nd
51-3	38.66	3.59	3.23	0.61	0.06	5.68	nd
51-4	38.92	2.81	4.11	0.86	0.11	4.65	nd
51-5	38.77	3.73	2.70	0.66	1.35	4.88	nd
51-6	39.76	3.13	2.89	0.73	0.01	4.56	nd
51-8	40.22	3.18	2.29	0.76	0.11	4.26	nd
51-9	37.07	2.74	7.39	0.52	0.045	2.55	1.21
51-10	34.95	3.52	9.81	0.59	0.145	4.80	nd
51-11	33.83	4.20	5.68	1.16	0.23	7.28	1.30
51-13d	37.09	3.56	2.22	1.41	0.21	8.25	nd
51-13s	25.26	2.89	10.48	1.09	0.31	10.23	5.41
51-14	40.43	3.47	3.25	0.77	0.145	4.45	nd
51-15	39.01	3.13	2.71	0.88	0.095	5.74	nd

Table 3. Nanov-*Vistireasa 3*. The concentrations of the chemical elements detected in the paste samples analysed by in-air PIXE (%) (nd=not detected).

Sample	Si (Al)	K	Ca	Ti	Mn	Fe
50-4_1	4.18	0.37	63.45	0.03	0.12	1.22
50-16_1	nd	0.38	70.36	nd	nd	0.84
50-17_1	22.66	1.48	32.14	0.33	0.17	3.08
50-17_2	23.24	1.44	27.71	0.49	0.16	6.79
50-18_1	40.07	3.30	0.96	0.67	0.07	6.01

Table 4. Nanov-*Vistireasa 3*. The concentrations of the chemical elements detected in the white pigment samples analysed by in-air PIXE (%) (nd=not detected).

Sample	C	O	Na	Mg	Al	Si	K	Ca	Fe
50-4_1	10.15	32.78	nd	0.49	1.24	3.72	nd	48.75	1.09
50-16_1	12.76	36.20	nd	1.06	1.68	3.78	0.93	40.68	0.97
50-17_1	13.78	26.11	nd	1.35	3.49	14.28	1.50	30.85	3.87
50-17_2	17.00	39.60	0.14	1.28	2.52	9.20	1.08	24.95	4.23
50-18_1	11.51	35.66	nd	1.88	11.10	28.50	2.91	1.03	7.41

Table 5. Nanov-*Vistireasa 3*. The concentrations of the chemical elements detected in the white pigment samples analysed by EDS (%) (nd=not detected).

Sample	Si (Al)	K	Ca	Ti	Mn	Fe
50-2_1	27.56	1.63	21.53	0.44	0.12	6.22
50-16_2	38.99	3.48	2.32	0.77	0.19	5.91
50-17_3	37.56	3.05	1.79	0.81	0.11	9.29
50-19_1	39.78	2.79	1.23	0.79	0.11	6.49
50-20_1	41.12	2.39	2.78	0.58	0.10	3.23

Table 6. Nanov-*Vistireasa 3*. The concentrations of the chemical elements detected in the red pigments samples analysed by in-air PIXE (%).

Sample	C	O	Na	Mg	Al	Si	K	Ca	Fe
50-2_1	12.01	38.19	0.30	nd	4.76	12.68	1.43	19.69	10.95
50-16_2	16.62	38.64	0.47	0.82	7.25	26.90	2.07	2.10	5.13
50-17_3	16.28	39.22	0.28	1.07	6.03	24.30	1.73	1.48	9.60
50-19_1	14.96	36.75	0.40	1.02	6.97	22.28	2.21	1.03	14.39
50-20_1	16.53	38.68	0.57	1.08	8.39	23.69	2.62	1.23	7.21

Table 7. Nanov-*Vistireasa 3*. The concentrations of the chemical elements detected in the red pigment samples analysed by EDS (%) (nd=not detected).

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Glass Analysis in Relation to Historical Questions

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Abstract

This paper describes the development and optimisation of the PIXE-PIGE method for glass analysis in air, notably the use of filters, the fitting of the gamma spectra and reducing the effect of surface roughness. From among historic examples, it looks at the automatic classification of Roman glass using the method of scores for particular elemental concentrations. It discusses the source of alkalis for plant ash glass and proposes desert plants as a source of alkalis for medieval glass beads.

Keywords: PIXE, PIGE, glass analysis, Roman glass, plant ash glass.

Introduction

Glass is generally composed of three main components – a network former, a flux and a stabiliser – and several additives classified as decolorants, opacifiers and pigments. The use of particular components or additives is historically dependent and their chemical composition is significant, rendering glass an interesting and useful subject of chemical analysis. The main task of this analysis is to determine the compositional types and manufacturing procedures involved, which may be linked to certain production areas and transport routes and in some cases can also be used for dating.

The role of a flux is to reduce the melting point of silica, and in this respect two principal sources were used during different historical periods up until the industrial revolution. Historically, the melting point would have been reduced by the addition of alkalis, which were obtained either from plant ash or mineral sources. The halophytic plants that grow on the coast or in deserts produce ash that is rich in sodium, so the resulting glass is considered to be of the sodium type. Ash from inland trees (especially beech) is rich in potassium, so the resulting glass, also known as forest glass, is considered to be of the potassium type. The only mineral sources exploited significantly were the dry sediments of the Egyptian lakes in the Nile Delta, which produced sodium reach alkalis, known as natron. This type of glass was also of the sodium type, but differed from the glass made using halophytic plants in terms of its much lower admixture of impurities: the content of MgO was generally lower than 1.6%, and the content of K_2O lower than 1% (Sayre and Smith 1961). The characteristic period for the production of natron glass ranged between 800 BC and 800 AD (Shortland *et al.* 2006). Natron glass was produced from siliceous coastal sand, which also contained fragments of seashells, thus providing Ca oxide, which acted as a chemical stabiliser. Coastal sands also contain several other impurities, notably compounds of iron, aluminum and titanium. In combination with Nd and Sr isotopes (Ganio *et al.* 2012), these three elements can be used to trace the origin of siliceous sands, which in turn indicates the centers of primary (or raw) glass production. In terms of Roman glass, this enigmatic question was raised by the writings of Pliny the Elder, who mentions production centers in present-day Israel, but also in Italy, southern France and Spain. Investigations into the isotopic composition of siliceous sands around the Mediterranean show that glass was produced in all of these regions during the Roman imperial period, but was concentrated in Egypt and the Levantine region during Late Antiquity (Ganio *et al.* 2012) (Freestone 2005). The impurity pattern of Al, Fe and Ti would appear to allow for a distinction between Egyptian and Levantine glass production (Schibille *et al.* 2016).

For the glass made using halophytic plants, the impurity pattern is the opposite: it is the ash that contains several different elements, while the silica source is purer and allows for a limited distinction based on a few trace elements, such as Zr, Hf or certain rare earth elements (De Raedt *et al.* 2001). The alkaline content or earth alkaline elements thus allows us to distinguish between different fluxes from different regions or plant species. The important historical question is to distinguish between the original production of Venetian glass of the 12th-17th centuries and glass produced in the Venetian manner (façon de Venise).

In this paper, we review various recent instrumental improvements in terms of the use of the ion beam analytical methods PIXE (proton-induced X-ray

emission) and PIGE (proton-induced gamma emission) in glass studies. More specifically, we concentrate on the automatic classification of Roman glass according to its elemental values as stated by E. Gliozzo (Gliozzo *et al.* 2015; Gliozzo *et al.* 2016) and the identification of sources of alkalis in medieval glass beads.

Instrumental details and improvements

Glass can be considered to be a mixture of oxides, so a typical analysis of a glass sample involves elements from sodium onwards. The energy of sodium K lines is 1.04 keV, so photons with such low energy levels are easily absorbed by the thinner layers of materials, including the oxidised layers on the surface of archaeological glass. This requires analysis of a polished surface, the use of thin-window X-ray detectors and measurement in a vacuum or at least a helium atmosphere. Excitation of light atom X-rays can be achieved equally efficiently by the electrons in an electron microscope or by a particle beam from an electrostatic accelerator. However, an important difference is that particles also excite gamma rays, which, given their high energy, are much more penetrative than X-rays. The strongest gamma line for sodium is at 440keV, which is negligibly attenuated in the layers reached by bombarding ions, and in the air path towards the detector. The predominant mechanism of gamma excitation is inelastic nuclear scattering, which requires higher projectile energies than X-ray excitation. For protons, the recommended energy levels are above 3MeV. Several labs perform glass analysis by combining the detection of sodium gamma lines and the X-rays of heavier elements, thus avoiding the sodium-depleted layer at the glass surface. In our approach, the measurement was performed in air, which also strongly absorbs the X-rays of magnesium and aluminum. This required that the two elements were also detected according to their strongest gamma rays, i.e. 585keV for magnesium and 844 and 1014keV for aluminum. This further required that aluminum was avoided in the construction of the beam exit station: brass and stainless steel were used instead and a 2μm tantalum foil was used as an exit window, its high Z ensuring that any undesired gamma background was below 300keV. The analysis of magnesium is critical given the detection of a competing gamma line at 583keV in the natural background. The lead shielding of the detector and a sufficient count rate of proton-induced gamma rays diminish its relative contribution.

Our recent improvement in terms of the gamma analysis consists of a peak-intensity fitting program specifically adapted to the analysis of sodium glass: the program auto-calibrates for peak energy and width according to the sodium lines at 440 and 1636keV and uses top-hat filtering to subtract the background. The only parameter provided on-line by the user is the sensitivity level used to discriminate between particular peaks. The peak width is fitted for high-intensity peaks, but when the peak height approaches background fluctuations, the program switches to the instrumental energy resolution.

Using air as the only absorber ensures good sensitivity for the X-rays of the elements between sodium and iron. Heavier elements are more efficiently detected at a higher proton current, using an absorber to attenuate the intense X-rays from light elements. An aluminum exit window of 8μm thickens was used, as aluminum does not produce any hard X-rays that could reach the detector through scattering in the air. In our earlier experiments we measured three spectra one after another: soft X-rays with a low proton current of 0.3nA, hard X-rays with a proton current of 1-1.5nA, and a gamma spectrum at 1.5nA. In order to save accelerator time, we first combined the hard X-ray and gamma measurements. We recently introduced a funny filter of 50μm aluminum foil with a relative opening slightly below 10% that provided good sensitivity for X-rays over the whole Z-range from silicon onwards. Only one irradiation of about 20 minutes per sample is thus required, however at the price of scattering the tantalum L X-rays into the detector, which reduces sensitivity for copper.

For gamma ray measurements, the unknown concentrations are calculated according to the glass standard NIST 620, using the stated concentrations of Na, Mg and Al oxides. The measurements are normalised to the collected proton number, which is measured by a thin metal mesh intersecting the beam in a vacuum before the exit window (Jezeršek *et al.* 2010). Concentrations based on the detected X-rays are determined by the method of independent physical parameters, using published values of ionisation cross-sections, stopping powers and X-ray attenuation coefficients. The matrix effects (reduction of the proton energy within the target and attenuation of X-rays in the target) are taken into account by an iteration procedure. As the combined PIXE-PIGE analysis detects all essential elements in glass, the sum of all metal oxides is normalised to unity.

The surface of archaeological glass samples is sometimes very rough, which influences the results of the analysis. Irregular surface structure modifies the distribution of X-ray escape lengths and generally increases the mean escape lengths. It is possible to monitor the roughness effects by measuring the argon K-alpha line induced in the air gap between the exit window and the target. The yield of this line is calibrated through known geometrical parameters obtained from the measurements of smooth elemental or simple chemical compound targets. The sum of all metal oxides is then also calculated according to the collected argon yield and compared to unity. Differences of up to 20% are

deemed acceptable for the normalisation procedure to unity to be applied, but larger differences signal that the effects of surface roughness are prominent. The calculation is then repeated using a broader X-ray take-off angle that simulates a larger mean X-ray escape length. The calculation is regarded as successful when the sum of metal oxides departs from unity by less than 20%.

During experiments it may also occur that the wire-mesh measurement of the proton number essential to the quantisation of PIGE data is unsuccessful. The reason for this may be the fluctuation of the proton beam or insufficient bias on the mesh suppressing the ejection of secondary electrons. We developed a specific numerical method for use in such cases that also exploits the X-ray part of the measurement at the NIST 620 standard. The argon signal is used to assess the proton numbers in the standard and unknown samples, so correction of the surface roughness effects is then not possible.

In order to monitor the accuracy of our measurements, the glass NIST 620 and 621 standards are analyzed periodically as unknown samples. The concentrations of major elements are reproduced within ±5%, though the accuracy reduces to about 10% for the elements with concentrations below 0.1%.

Classification of Roman glass

Two shipwrecks – Ouest Embiez, close to Marseille, dated to the late 2nd and beginning of the 3rd century AD, and Iulia Felix, in the Northern Adriatic, dated to first half of the 3rd century AD – provided extensive quantities of glass that allowed for classification. In 2003, Foy *et al.* proposed a classification of glass from southern France into 12 groups, four of which being characteristic of Roman glass. The most common was group 3, which included glass from the 3rd century BC until the 9th century AD. This glass was made from the siliceous sands found in the vicinity of the Belus River in present-day Israel and used MnO as a decoloriser. Group 4 is limited to the much narrower time scale of the 2nd-3rd centuries AD and used Sb_2O_3 as a decoloriser. Groups 1 and 2 corresponded to Late Antiquity, Group 1 to 5th century AD Egypt and Group 2 most likely to the 6-8th centuries AD Belus River. Freestone, working on the glass from the ancient Near East, Egypt and Palestine, identified the types of glass defined as HIMT (high iron, manganese and titanium), Levantine I and II, and Egypt II. HIMT glass was produced beginning with the 4th century AD; while Levantine I glass was produced from the 5th to 7th centuries AD using the sands found around the Belus River (Freestone 2005).

There is some overlap within the groups of Foy and Freestone: Group 1 of Foy corresponds well with HIMT glass. Within Group 3, three subgroups, 3.1-3.3, were identified as spanning the period between the 4th century and the 8th century AD. Subgroup 3.1 coincides with Levantine I (although Levantine I has a larger span of aluminum and calcium oxides), and Subgroup 3.3 with Levantine II (or Bet Eli'Ezer). In the glass from Iulia Felix, Silvestri identified two groups of colored and three groups of transparent glass (Silvestri *et al.* 2008). Both groups of colored glass coincide with Group 3 of Foy (more precisely, with the elements of Group 3 subtracted for the contribution of the late antique subgroups 3.1-3.3), while for the clear glass, one group coincides with Group 3, one with Group 4 and one extends over both.

Other research has proposed finer divisions, such as the specification of HIMT glass with the introduction of HIMT2 (Foster and Jackson 2009), weak HIMT (Foster and Jackson 2009) and high lime HIMT or HLIMT (Ceglia *et al.* 2015); the latter two have analogies in the Group 2 of Foy. A recent study by N. Schibille *et al.* (2016) looked at the impurities in sand and suggested distinctions between the primary glass made in Palestine and Egypt; it was confirmed that HIMT glass originates from Egypt. An important discovery is that the glass discolored with antimony is also of Egyptian origin, thus signaling that the two primary production areas used different formulae.

Gliozzo recently proposed a new classification scheme based on glass from the sites of Herdonia and Esquiline Hill in Italy (Gliozzo *et al.* 2015; Gliozzo *et al.* 2016). This classification takes into account the oxides of ten characteristic elements: Na, Mg, Al, Si, K, Ca, Ti, Mn, Fe and Sb. These glass types principally include naturally colored blue-green-yellow Roman glass and clear (or transparent) glass from the Imperial and Late Antique period. The clear glass can be discolored by antimony, manganese or a mixture of both; in the latter case we are dealing with recycled glass. This division thus covers the colored glass types RNCBGY1 and RNCBGY2, and clear glass types RC-Sb, RC-Mn, RC-MnSb (Roman) and LAC-Sb, LAC-Mn and LAC-MnSb (late antique). From Late Antiquity, the classification retains the glass types Levantine I and Egypt II, and from the HIMT family, the glass types HIMT, HIMT2, weak HIMT and Ca-rich HIMT. According to the division of Foy, Group 2.1 continues as an independent type, as evidently it does not have a parallel in the other established groups.

Automatic classification program

Gliozzo published their mean concentrations and standard deviations for the oxides of the ten characteristic elements. As it is not feasible to check the concentrations of all ten elemental oxides manually, we created a simple computer program that utilises the principle of scores. The mean concentration and their

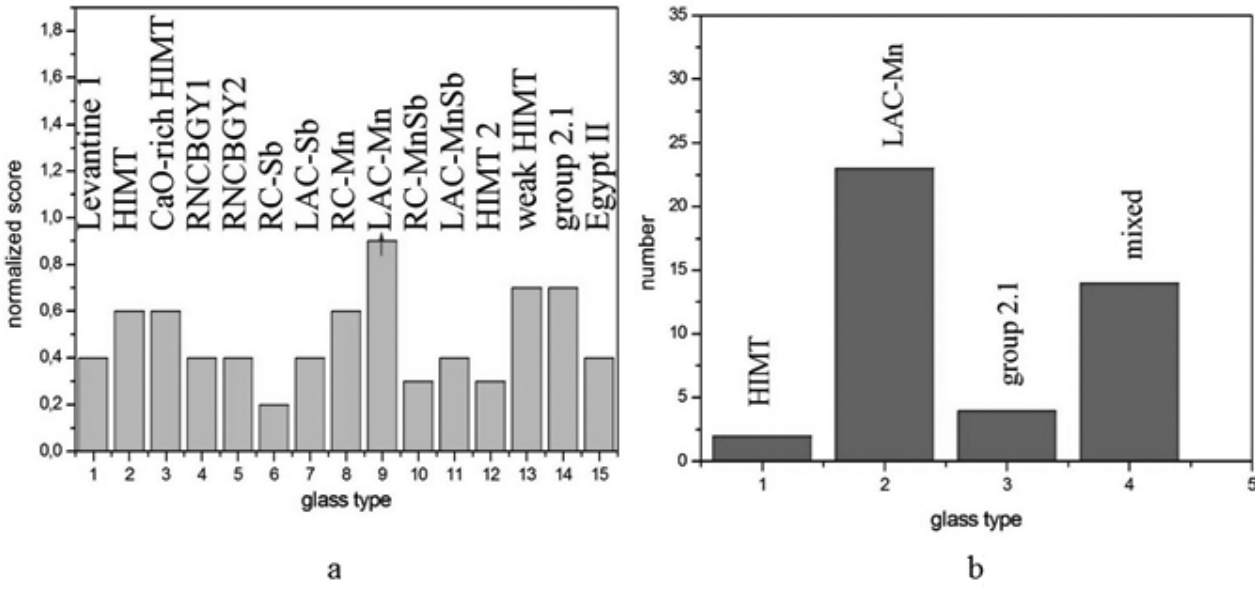

Figure 1. Characterisation of glass types according to the method of scores. a) Unknown fragment corresponds to LAC-Mn, as it agrees with most of its concentration limits. b) Occurrence of glass types for the Tonovcov grad site in western Slovenia.

standard deviations as stated in Gliozzo *et al.* 2015 and Gliozzo *et al.* 2016 are recorded in the program database. The program then inspects each individual sample of unknown glass for its type. In a cross examination, each possible glass type is examined for the ten characteristic concentrations. If the concentration in the unknown sample and the specified concentration differ by less than a certain amount, the glass type in question receives a score. At the end, the glass type with the highest score is assigned as the type of the unknown sample. The distinction criterion during calculation is optional, but we normally take two standard deviations. The program also performs a sorting of unknown glass and creates a distribution according to type.

In practice this method threw up several difficulties. Working on real examples from particular archaeological complexes, we discovered that quite a lot of glass items exhibit equal scores for two or more glass types. These glass types remain undetermined or represent a mixed type (Figure 1). We presented examples from a late antique site, Tonovcov grad, in Slovenia (Šmit *et al.* 2013). The predominant type is clear glass discolored by manganese (LAC-Mn). Undetermined glass represented the second largest group. Minor glass groups show a few examples of HIMT glass and Foy's Group 2.1. A large proportion of the undetermined glass may indicate that the properties of several glass types coincide, and some other discriminating properties would need to be taken into account. Particular elements may be correlated (notably Al, Ti and Al characteristic for particular siliceous sands) and the assumption of independent Gaussian distributions may not be realistic.

Origin of plant ash fluxes

Around 800 AD, the ash of halophytic plants again began to be used as a source of alkalis for natron-type glass; however, natron glass circulated until about 1200 AD. It is easy to detect the use of plant ash experimentally, as the ash contains much larger quantities of impurities, more than 1.6% of MgO and K_2O. The relative fraction of the light elements is characteristic for the plants used or even for particular plant parts.

Statistical properties of plant ash alkalis were extensively studied for Venetian and façon-de-Venise glass. Different groups were depicted (Šmit *et al.* 2004; Šmit *et al.* 2009) on a plot showing the amount of Na_2O and K_2O from the total content of alkaline and earth alkaline oxides (Figure 2). The group denoted as *vitrum blanchum I* undoubtedly contains original Venetian glass produced using the finest alkalis from plants from the Levantine area; this fluxing agent was known as *alume catino*. The two other groups are centered around two lines with a negative gradient that signifies an inverse correlation. The alkalis in these two groups are likely to represent a mixture of fluxes with different contents of sodium and potassium but which together produced a desired fluxing effect. The correlation line with the highest content of alkalis (top right) matches the glass from Antwerp, Netherlands, and the Albanian city of Lezha (Šmit *et al.* 2009); it is significant that the bottom of this line (with the lowest K_2O content) contains *cristallo* glass from Venice. The line clearly corresponds to the later development of the Venetian glass (around the 17th century), which used a different purifying procedure for the alkalis, a source of relatively pure silica (crushed stones instead of sand), and arsenic as a decoloriser.

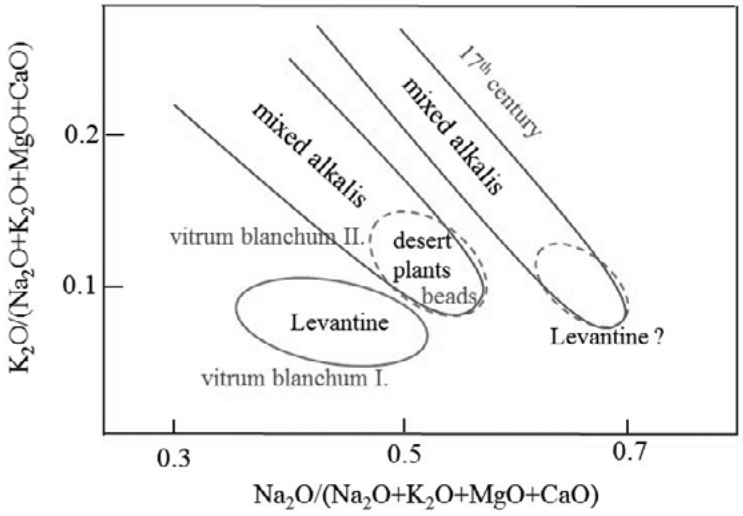

Figure 2. Sources of plant ash alkalis for Venetian, façon-de-Venise and medieval glass beads of Near Eastern origin. The proposed region of desert plants is indicated as part of the *vitrum blanchum II* group.

The middle correlation line is more problematic. It contains façon-de-Venise glass, but also glass of true Venetian origin (Šmit 2004). According to Cagno (Cagno *et al.* 2012), this line involves façon-de-Venise glass manufactured from less qualitative fluxing materials, like *barilla* from Spain. These two statements stand in contradiction to one another, a situation which may be solved by the supposition that the correlation line does not contain glass from one source only – similar to the 17th century line, the true Venetian glass may be found at its lower part. In Šmit *et al.* 2009 we named the lower part of this correlation line *vitrum blanchum II*. This two-fold composition of the middle correlation line was also accepted in the study of façon-de-Venise glass from Portugal (Coutinho *et al.* 2016).

Medieval glass beads

The switch from natron to plant ash glass technology around 800 AD can be considered an important time marker. A problematic archaeological dating based on this threshold is given by the Slavic graves in central Slovenia pertaining to the Köttlach culture. Traditionally, the graves were dated to the 7th and 8th centuries. In central Europe, the earliest phase of the Köttlach culture is dated to the first half of the 9th century AD and its later phases (Köttlach I and II) to the period lasting from the second half of the 9th century to the first half of the 11th century. Our measurements (Šmit *et al.* 2012) were performed on glass beads from two cultural groups. The first one involved beads from the graves in eastern Slovenia, dated to the end of the 8th and the 9th century AD according to its characteristic pottery and a few ^{14}C dates. The second group contained beads from central Slovenia.

Our database contains 179 different measurements, 112 of these being performed as part of the study (Šmit *et al.* 2012). The glass beads form two compositional groups, one representing the natron glass, the other glass made using halophytic plants. Although natron glass circulated until the 13th century, the occurrence of plant ash glass beads in a particular grave indicates that the grave cannot be older than about 800 AD. The distribution of the plant ash glass beads indicates their frequent presence in central Slovenia (Figure 3), which argues in favor of a later dating of these graves, in accordance with the dates in eastern Slovenia and central Europe.

The second question involves the origin of the glass used in medieval beads. Our inventory of measurements contains a few beads with mosaic eyes, draw-segmented and draw-cut beads that originated in the Baghdad caliphate and are dated to the end of the 8th, but mostly the first half of the 9th century AD (Andrae 1973). We have already noted that in the Na-K plot shown in Figure 2, the plant ash beads are located in the region of *vitrum blanchum II*, and were, in spite of the time difference of several centuries, produced from the same type of alkalis. It is unlikely that the barilla from Spain was traded as far as Mesopotamia. This glass was more likely produced at local centers other than those located in the coastal area that provided the *alume catino*. Given that we found further parallels in the glass produced on the territory of present-day Iraq and Uzbekistan, the most likely candidate is desert plants, harvested in the inner regions of the medieval Near East.

Conclusions

Glass is an attractive material for chemical analysis. Its composition can reveal the manufacturing technologies and the sources of raw material in Roman glass, and can be used in dating, for example in the case of medieval glass beads made of plant ash that cannot be older than about 800 AD. In terms of instrumentation, the combined PIXE–PIGE method was optimised to develop a fast, reliable and non-destructive analytical approach.

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Figure 3. The occurrence of glass beads at medieval archaeological sites in Slovenia that were made from plant ash glass, thus implying a dating to after 800 AD.

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A Decorated Islamic Manuscript from the Ottoman Turkish Period: Paper Characterisation, Dating and Conservation

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Abstract

The present study comprises an analytical investigation and conservation treatment of a decorated Islamic manuscript from the Ottoman Turkish period. The analytical techniques used in this study were micro-chemical (spot) tests supported by optical microscopy (OM). The results showed that the original paper was made up of rag fibres and the sizing material was of animal origin (gelatine) in combination with alum and starch as additives, indicating that the manuscript most probably dates from the late 17th century. The treatment and conservation of the manuscript included disinfection in an anoxic environment, mechanical and chemical surface cleaning, and the removal of previous restoration materials. This was followed by a stage of consolidation, the replacement of missing parts, the strengthening of the surface of the paper, and the binding with a new leather cover.

Keywords: paper characterisation, micro-chemical analysis, conservation treatment.

Introduction

A number of illuminated Islamic manuscripts, richly decorated in gold and dating back to the Ottoman period (1299-1923 AD), are stored at the Museum of Macedonia in Skopje. The present study describes the analytical investigation and conservation treatment of one of these manuscripts (Figure 1).

The decorated Islamic manuscript entitled *Tefsir-I kuran envarut tensile ve esrar ut tevil* (Inv. No. 2) was written in Ottoman Turkish by the author/transcriber Imer el Beyzavi at an unknown point in history. It is made up of 140 folios (15 x 21cm) bound together with a decorated paperboard cover framed in leather. The main damage to the manuscript was caused by the actions of microorganisms and various insects due to poor storage conditions, which led to a weakening and brittleness of the paper. The damage to the covers included insect attack, surface dirt, wear and tear from excessive or careless use, broken joints and detached covers, while the paper had suffered damage from white mould residues, accumulated surface dirt, wear and tear, oily fingerprints and ink and moisture stains.

The manuscript had been restored in the past, but in time its condition deteriorated severely, such that a new restoration became necessary (including the removal of the materials used during the previous restoration). To this end it was necessary (1) to study the composition of the paper, including the fibres and adhesive used to size the pulp used to make the folios, and the acidity of the paper, in order to be able to date the manuscript and to identify the right replacement materials, and (2) to devise the right method for the treatment and conservation of the manuscript.

Conservation research

An important aspect of conservation is the research into materials. Micro-chemical (spot) tests (Mayer *et al.* 1990) were undertaken to identify the materials present in the paper (Table 1). Based on the results we were able to make a rough estimate of the date and to establish an appropriate treatment procedure.

The general test for the identification of paper fibres was performed using a Graff C reagent (TAPPI T 401. Fiber Analysis of Paper and Paperboard. n.d.). This reagent stains the pulp fibres with moderate reddish-orange colour in the presence of rag fibres such as cotton, hemp or flax. These fibres contain very small amounts of lignin. Consequently, an additional test to determine the lignin content using a Phloroglucinol reagent was performed on a small paper sample (TAPPI T 401. Fiber Analysis of Paper and Paperboard. n.d.). Lignin fibres, which can be seen with the naked eye as individual fibres with a red hue, were detected in the original paper at a proportion of less than 5%, while the restoration paper did not contain lignin fibres at

Figure 1. The frontispiece of Islamic manuscript *Tefsir-I kuran envarut tensile ve esrar ut tevil* (photo by M. Kostadinovska).

	Original	Restoration
Fibre identification		
General test	Rag fibres (hemp or flax)	Rag fibres (cotton)
Lignin	< 5%	-
Sizing		
Hydroxyproline Test for animal glue (or gelatine)	+	+/-
Aluminon Test for alum	+	+
Raspail Test for rosin	-	+
Iodine Potassium Iodide Test for starch or modified starches	+	-
Date (most probable)	Late 17th century	After 1835

Table 1. Micro-chemical (spot) tests for the characterisation of the fibres and sizing in paper.

all. The micro-chemical test for lignin fibres confirmed that the pulp could not have been made of ground wood or other lignified fibres.

The next step was to reveal the sizing material in the paper. A hydroxyproline test is a micro-chemical test used to detect gelatine in paper (TAPPI T 504. Qualitative and Quantitative Analysis of Glue in Paper. n.d.). The development of a rose-red or pink colour was detected both in original and restoration paper samples, which confirmed the presence of gelatine in the paper (Figure 2a).

Tests for alum and starch were also performed. The results of the Aluminon test (Barrow 1969) indicated that both the original and the restoration paper samples contained alum, as could be seen from the formation of a pink colour (Figure 2b). The formation of the deep blue to black colour following the Iodine potassium iodide test (TAPPI T 419. Starch in Paper. n.d.) indicate the presence of starch. This test is extremely sensitive to small concentrations of starch. The results showed that starch was present as an additive only in the original paper sample (Figure 2c).

Treatment and conservation

Based on the results of the aforementioned research, we carried out a treatment and conservation procedure in order to inhibit future degradation and to preserve the manuscript for future use.

Anoxic disinfection

The first step in the conservation treatment was that of anoxic disinfection, which kills aerobic bacteria. This procedure involves the vacuum packing of the infected material in an Escal transparent foil together with RP System Type K oxygen scavengers and Ageless Eye indicating tablets with the help of a CXD vacuum packing machine Type 160 (Figure 3a). The oxygen scavengers eliminate the remaining oxygen in the vacuum sealed bag, while the Escal foil acts as a high barrier film to oxygen. When the oxygen level falls to 0.1% or lower, the Ageless Eye turns from blue/purple

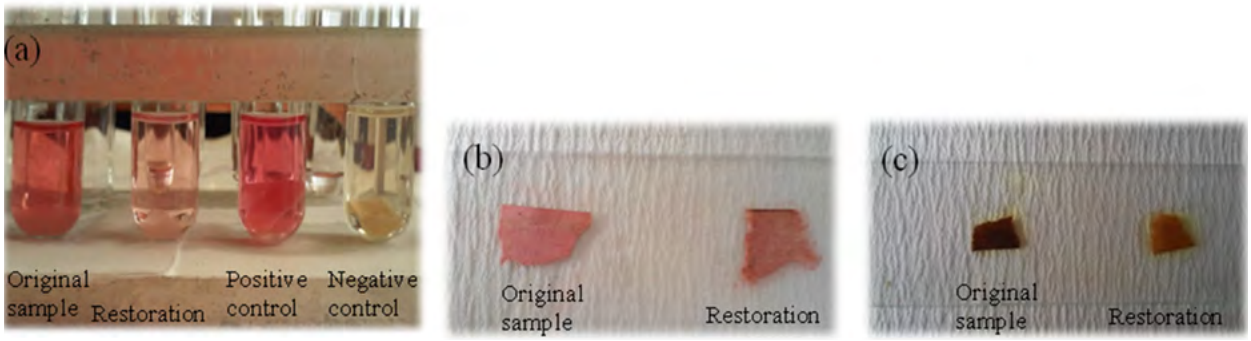

Figure 2. Conservation research: (a) Hydroxyproline test for the detection of gelatine; (b) Aluminon test for the detection of alum and (c) Iodine potassium iodide test for the detection of starch or modified starches.

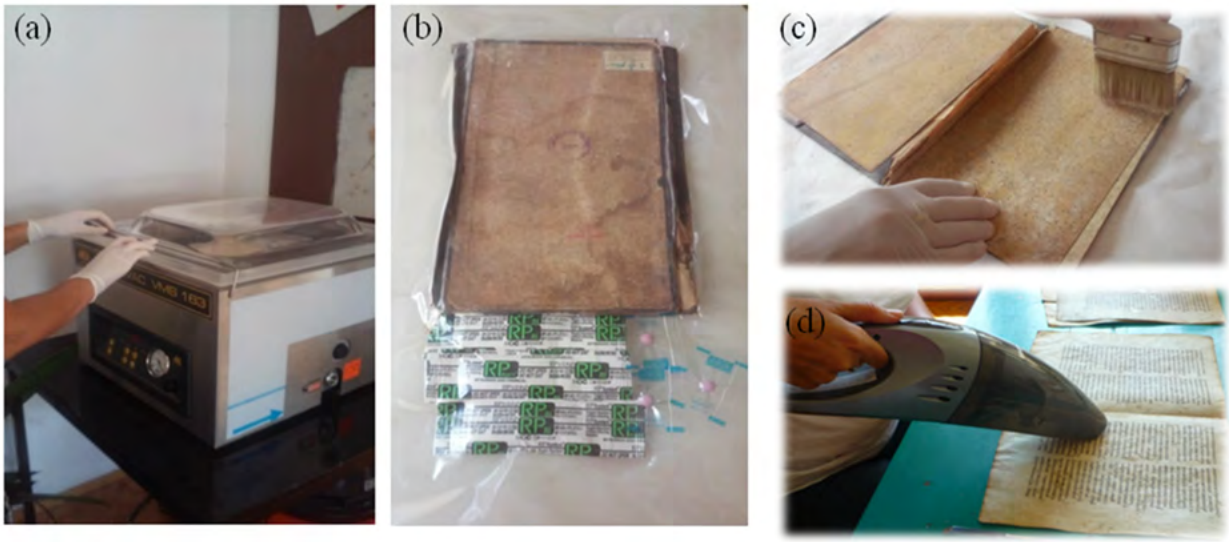

Figure 3. Preparatory treatments in conservation: (1) anoxic disinfection using a CXD vacuum packing machine Type 160 (a) and RP oxygen scavengers (b); and (2) surface cleaning using a soft brush (c) and a HEPA vacuum cleaner (d).

to pink, indicating that the conditions of an effective treatment have been achieved. The bag packed in this way is stored for at least two weeks (Figure 3b).

Surface cleaning

After the anoxic treatment, the amount of superficial grime, dirt and soot was reduced with a soft brush (Figure 3c). In addition, surface mold and insect residues were removed mechanically through the use of a small HEPA vacuum cleaner (Figure 3d). The chemical cleaning of the paper surface was achieved using a cotton swab damped in a benzene solution.

Filling losses, mending and consolidation

After the cleaning, any losses in the sheets of paper were filled with Japanese paper inserts and with methylcellulose used as an adhesive (Figure 4a). Where necessary, tears were mended and loose paper consolidated through the application of methylcellulose as a binding material. A good contact between the paper and the binding material was achieved by using a bone folder (Figure 4c). Finally, the surface of the paper sheet was resized using the same adhesive in order to give the paper additional strength (Figure 4d). The sheets were left to dry on a piece of silk fabric at normal room temperature and humidity.

Reducing creases and the dimensioning and arrangement of the folios

After drying, each pair of folios was placed in a sandwich formed of two layers of silk fabric (up and down) and then placed between two wooden ironing boards. These were placed under pressure in a paper press machine in order to reduce any creases created during the process of drying (Figure 5a-c).

Each sheet of paper was dimensioned to the original size and folded in half to form a pair of two folios. The folded paper sheets were grouped in stacks of 5 sheet folios in keeping with the foliation number (Figure 5d). Finally, an ordered pile of 14 stacks was sent to the

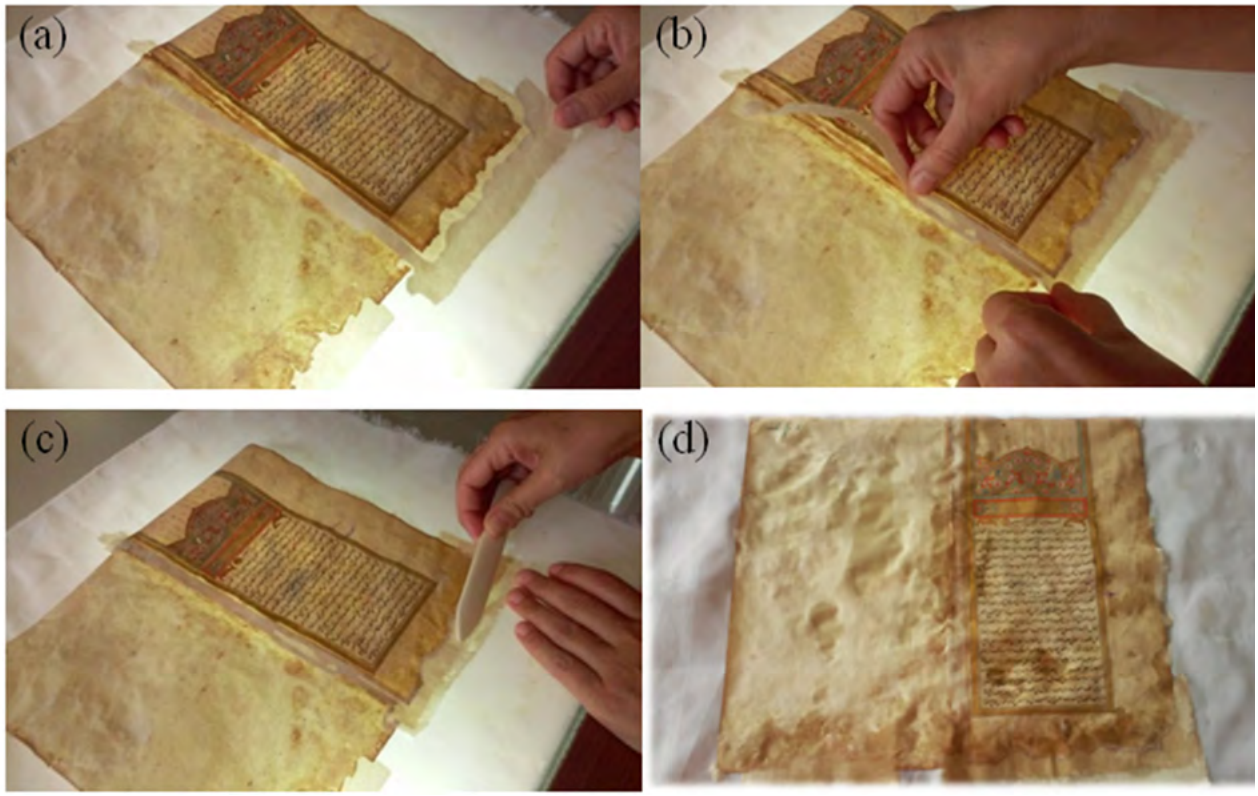

Figure 4. Filling losses with Japanese paper inserts, mending tears, consolidating flaking media and resizing with methylcellulose.

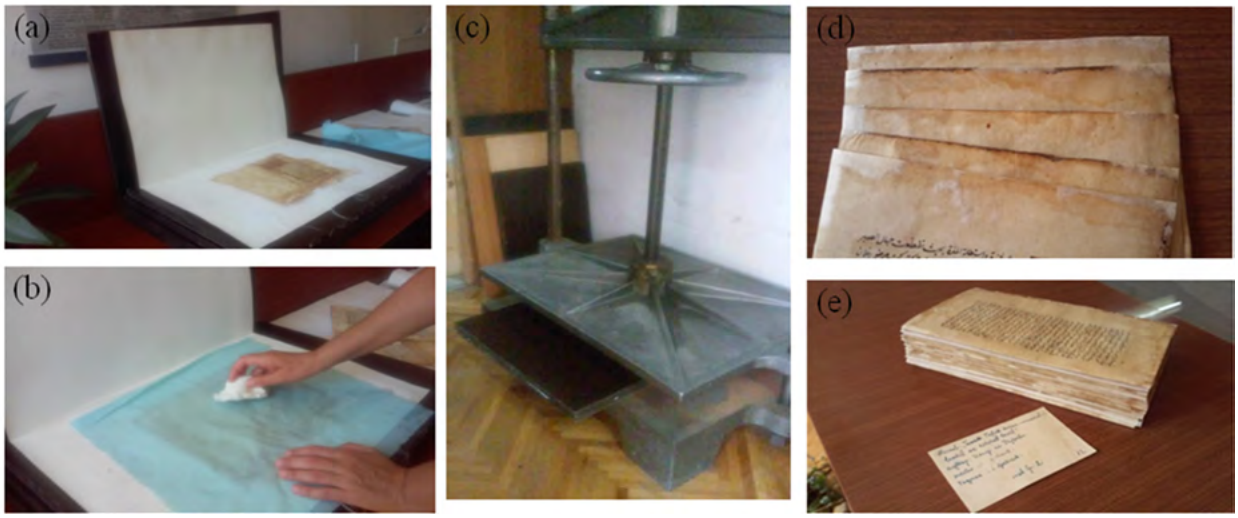

Figure 5. Reducing creases using a paper press machine, dimensioning to the original size and arrangement of folios in a pile of stacks.

bookbinding department for finishing with a new book cover (Figure 5e).

Bookbinding

The bookbinding process involves the physical assembly of the pile along one edge by sewing through the folds with thread. A new leather hardcover was adhered to the sides of a paperboard and then the original decorated paper sheets were attached to the front and back cover (Figure 6).

Conclusions

The research described in this study helped to achieve the objective of preserving this valuable manuscript for future use by applying compatible new materials to the original media in order to prevent deterioration.

Figure 6. The final view of the manuscript after the bookbinding process.

The composition of the original paper, made from flax or hemp fibre and sized with gelatine in combination with alum and starch, indicates an earliest possible date for the creation of this book in the late 17th century, given that it was at that time that alum began to be used in combination with gelatine more generally. Prior to this date, this additive was a minor component in paper production and saw only very limited use. The conclusions regarding the restoration paper support this dating: it was restored with cotton fibres and alum/rosin sizing material, which indicate that the restoration dates at the earliest to 1835.

However, dating the paper and dating a document or book are different things and the results do not necessarily coincide. A document or a book is dated by the total sum of paleographic indications: paper, handwriting, ornamentation, binding, the composition and content of the text of a book, the various kinds of notes on it, etc. On the other hand, it is usually the paper that provides the opportunity to perform the most precise and chronologically close dating of a document or book, as a manuscript cannot have been created earlier than the paper it was written on.

Finally, only time will show whether the conservation treatments performed will ensure the long-term safeguarding of the book.

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The Micro-Chemical and Spectroscopic Study of Component Materials in 18th- and 19th- Century Printed Holy Books

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Abstract

This short paper looks at the component materials (paper and inks) of three Cyrillic books – Menology for May (1705), The Bible (1822) and Mirror (1816) – which were submitted for preservation to the Conservation and Restoration Laboratory at the National Library in Skopje. Micro-chemical tests were used to identify the type of paper fibres and materials added to the paper pulp. FTIR was used to confirm the findings for the sizing and fillers found in the paper. The presence of mineral and inorganic pigments were revealed by micro-Raman spectroscopy. The original paper in the first two books was made of rags with the presence of lignin fibres at less than 5%, whereas the paper in *Mirror* was made of raw and unbleached hardwood. Distinct types of sizing were identified as having been used to form the paper material: gelatine/alum (Menology for May and Mirror) and gelatine/rosin (The Bible). The pigments identified are lamp black, vermilion, Prussian blue and calcite.

Keywords: paper, inks, micro-chemical analysis, FTIR and Raman spectroscopy.

Introduction

This study was limited to the conservation of three valuable books. Two of these are old printed books from the 18th and 19th centuries: *Menology for May* (1705 in Moscow) and *The Bible* (1822 in Moscow), both of which belong to the private collection of one of the oldest churches, St. John the Baptist Church at Bigorski Monastery (1020 AD), located close to the village of Rostuše, in the Republic of Macedonia. These books are of special significance to the monastery and are a local bibliographic rarity, because there are no re-prints in the National Library in Skopje or elsewhere in the country. The third book, *Mirror* (1816 in Vienna), currently to be found at the Goce Delčev Public Library in Gevgelija, Republic of Macedonia, is an original work created by the Macedonian cleric and writer Kiril Pejčinović on the territory of the former Ottoman Empire (present-day Republic of Macedonia) (to the best of the authors' knowledge, a second copy of this book is to be found at this monastery).

The aim of this study was to identify the component materials (paper and inks) used as a first fundamental step ahead of the forthcoming conservation/restoration treatment of the books. For a more detailed analysis of this short paper, see the extended contribution published in *Restaurator* (Kostadinovska *et al.* 2017).

Experiment

The study used the following techniques:

Light microscopy

An YS100 optical microscope (Nikon Instruments Inc.), equipped with fixed oculars of 10x and 4 achromat objectives with different magnifications (4X, 10X, 40X and oil immersion 100X), was used to perform the micro-chemical analysis. A total of 100X magnification is necessary for staining, so the operations were carried out with 4x (N. A. 0.10, W. D. 25mm) and 10x (N. A. 0.25, W. D. 5.6mm) objective lenses.

Infrared spectroscopy

An FTIR Perkin-Elmer 2000 infrared spectrometer coupled with a Golden Gate single reflection Diamond ATR cell (Series Mkll) was used to record samples of raw paper and pulp. The infrared spectra were recorded in the range of 4000-550cm^{-1} with a resolution of 4cm^{-1} and 64 scans. The recorded spectra were processed

Wave number [cm-1]	Assignment	Component
3500-3100	H-bonded OH stretch	Cellulose, free H_2O
1730	C=O vibration	Oxidation of cellulose
~1710	C=O vibration in C(O)OH groups	Non-conjugated carboxyl groups of Rosin
~1648	Typical peptide C=O (Amide I band)	Animal glue or gelatine
~1635	Absorbed H_2O in cellulose	Intermolecular H_2O, conjugated C=O
~1546-1559	Typical peptide N–H (Amide II band)	Animal glue or gelatine
~1425	CH_2 bending; asym. C-O stretch in $CaCO_3$	Cellulose; $CaCO_3$ (Calcite)
1315-1320	Typical peptide N–H (Amide III band)	Animal glue or gelatine
~875	Sym. C-O stretch of $CaCO_3$	$CaCO_3$ (Calcite)
~712	O-C-O bending (in-plane deformation)	$CaCO_3$ (Calcite)
~670	Sulfates bending vibration	Sulfates (SO_4^{2-})

Table 1. Specific ATR bands, their assignments and components present

using the software Spekwin32 (Menges 2010). The 1800-800cm^{-1} range was assumed to be the most informative in terms of analysing the presence of lignin, starch, animal glue or gelatine, alum, rosin, calcium carbonate, absorbed moisture, acidic and oxidative decomposition of the paper.

Raman spectroscopy

A LabRam 300 Micro-Raman spectrometer (Horiba Jobin-Yvon) equipped with a He-Ne laser (632.8nm) and laser power at the sample (2-6mW) was used for the *in situ* analysis of inks/pigments. An Olympus MPlanN microscope with a magnification of x50 was used to focus the laser beam on the sample. The scattering of light was dispersed by a grating of 1800 lines/mm. The spectral resolution was 3-4cm^{-1}. To avoid any damage to the rare books, the laser power was reduced using filters of different densities (D=0.3; D=0.6; D=1; and D=2). The spectra were recorded at an exposure time of 5s with 5-7 scans performed in the region of 1800-100cm^{-1}. A LabSpec package was used to obtain spectra (LabSpec 2007). The spectra were processed and analysed with the help of the Spekwin32 software.

Results

The basic material (paper)

A colouring of the fibres in a peach to moderate red and red purple hue was noticed in the paper from *Menology for May* and *The Bible*, which suggested that the fibres originated from annual plants (flax, hemp and/or cotton), whereas the paper fibres from *Mirror* were found to contain raw and unbleached hardwood chemical pulp colouring in pale yellow green to colourless (Graff 'C' reagent) and dark purplish and weak olive to gray blue green hue (Herzberg reagent) (TAPPI T 401. Fibre Analysis of Paper and Paperboard *n.d.*). Lignin fibres were detected at less than 5% in all three books (TAPPI T 401. Fiber Analysis of Paper and Paperboard *n.d.*). Distinct types of sizing were identified in the forming the paper material: gelatine/alum (Menology for May and Mirror) and gelatine/rosin (The Bible) (Barrow 1969; TAPPI T 504. Qualitative and Quantitative Analysis of Glue in Paper *n.d.*; TAPPI T 408. Rosin in Paper and Paperboard *n.d.*).

The spectra recorded by ATR-FTIR spectroscopy were used to identify characteristic absorption bands for cellulose as a main component of the paper, thus enabling the identification of the minor components, such as lignin and materials added to the pulp, i.e., gelatine, alum, rosin and starch (Table 1).

The pigments

All three books were printed in black ink using a carbon black pigment which was identified as *lamp black* (Figure 1). Occasional use of red ink was found in the books *Menology for May* and *Mirror*, which was characterised as red pigment *cinnabar* (or vermilion). *Prussian blue* pigment was identified in the decoration of the end paper in *Mirror*. As to the palette of white pigments, white from ground *calcite* (CaCO3) also known as chalk was identified while examining the black ink in *Mirror*.

Conclusion

Based on the above observations, we can conclude that:

(1) The paper in *Menology for May* (1705), which is made of used rags sized with gelatine and alum, and the use of the red pigment vermilion confirm that the book was most probably manufactured in the late 17th century, for from the late 17th century until the beginning of the 19th century gelatine sizing was used frequently with alum as an additive (Kolbe 2004). The restoration paper being made of bleached wood species sized

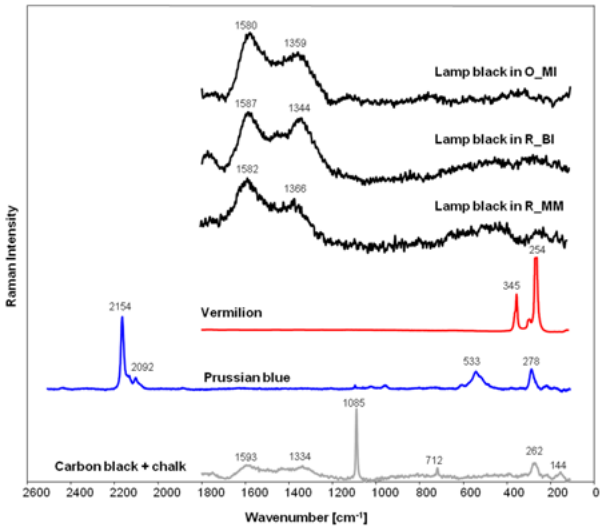

Figure 1. Inks/pigments identified in the books studied using μ-Raman spectroscopy.

with gelatine, starch and alum suggests that the restoration interventions were made during the 19th century or later, because chemical pulping processes were not introduced to Russia before the first half of 19th century (Travis *et al.* 1998).

(2) The paper in *The Bible* (1822) was made of rags sized with gelatine and rosin as an additive, which confirms that the book was manufactured no earlier than the beginning of the 19th century, for the use of rosin as a sizing agent (added to the pulp) was found more frequently after 1807 (Illig 1959). The use of the red pigment vermilion confirms that these folios were attached no later than the end of the 19th century.

(3) The paper in *Mirror* (1816), although produced in the same period as *R_BI*, was found to be made of hardwood species and gelatine sized with alum as an additive, which is in keeping with the development of paper production in West European countries (Rückert, Hodeček and Wenger 2009).

Acknowledgements

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DNA Analysis of the Human Remains Found in a Cucuteni Ritual Pit in Eastern Romania (4100-3800 cal BC)

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Abstract

This paper presents the first results of the DNA analysis of human remains dating from the Chalcolithic period in Eastern Romania, with the aim of identifying the haplogroup. The analysis was performed on the femur of an adult male found in a ritual pit in a settlement attributed to the Cucuteni culture (Vorniceni commune, Botoşani County). The results allowed us to infer the admixtures of the ancient human population from Eastern Romania using amtDNA isolated from bone remains.

Keywords: human remains, Cucuteni culture, DNA analysis, haplogroup, population admixtures.

Introduction

The Cucuteni culture is mainly distributed between the Eastern Carpathians and the Dniester River (i.e. present-day Eastern Romania and the Republic of Moldova). It displays features that are common to the Chalcolithic period in Eastern Europe, such as multi-layered long-lived settlements and large dwellings with inventories dominated by lavishly decorated pottery. In terms of settlement systems and object repertoire (pottery, flint, bone and copper artefacts), the Cucuteni culture is related to the Trypillia culture, which covered a large part of present-day Ukraine. Based on pottery style, three Cucuteni phases were defined: A (4600-4100/4050 cal BC), A-B (4100-3800 cal BC) and B (3800-3600/3500 cal BC), each of which were further divided into various substages (Mantu 1998).

In Romania, there are over 1000 Cucuteni sites (Monah, Cucoş 1985). Although only a small number of them have been studied in depth, the contrast with the very low number of human remains identified thus far (135) is self-evident (Kogălniceanu 2008: 201-217; Enea 2011: 102-103). This makes the study of the Cucuteni human remains all the more important. This paper presents the first results of the DNA analysis performed on an individual from a Cucuteni context in Eastern Romania with the aim of establishing membership of a human haplogroup.

In order to infer the genetic background of this individual, we combined the genetic analysis of the mitochondrial hyper variable region 1 (Hv1) with archaeological and anthropological observations. mtDNA is effectively a single haplotype that is transmitted from mothers to their offspring, meaning that mitochondrial lineages can be identified in a much more straightforward manner than nuclear lineages, which, in sexually reproducing species, are continuously pooling genes from two individuals and undergoing recombination.

The archaeological context of the human remains

This article presents the results of the DNA analysis of a human bone found at the archaeological site of Vorniceni (a village in the commune of Vorniceni, Botoşani County, on a terrace of the Ibăneasa River, part of the Jijia River basin; Figure 1).

The human remains identified at Vorniceni consist of 12 disarticulated human bones deposited in different ritual pits. Pit 40, where the human bone in question was found, was dug deeper than the others (at between 1.10 and 3.10 m in depth), had wattle-and-daub walls, and contained large amounts of richly decorated pottery, anthropomorphic and zoomorphic figurines, and animal bones, including a *bucranium*. Based on the corresponding inventory, Pit 40 was attributed to the Cucuteni A-B phase (Diaconescu 2012). The bone is the femur of an adult male, age 40 (Diaconescu 2012, where the identification by G. Miu is cited).

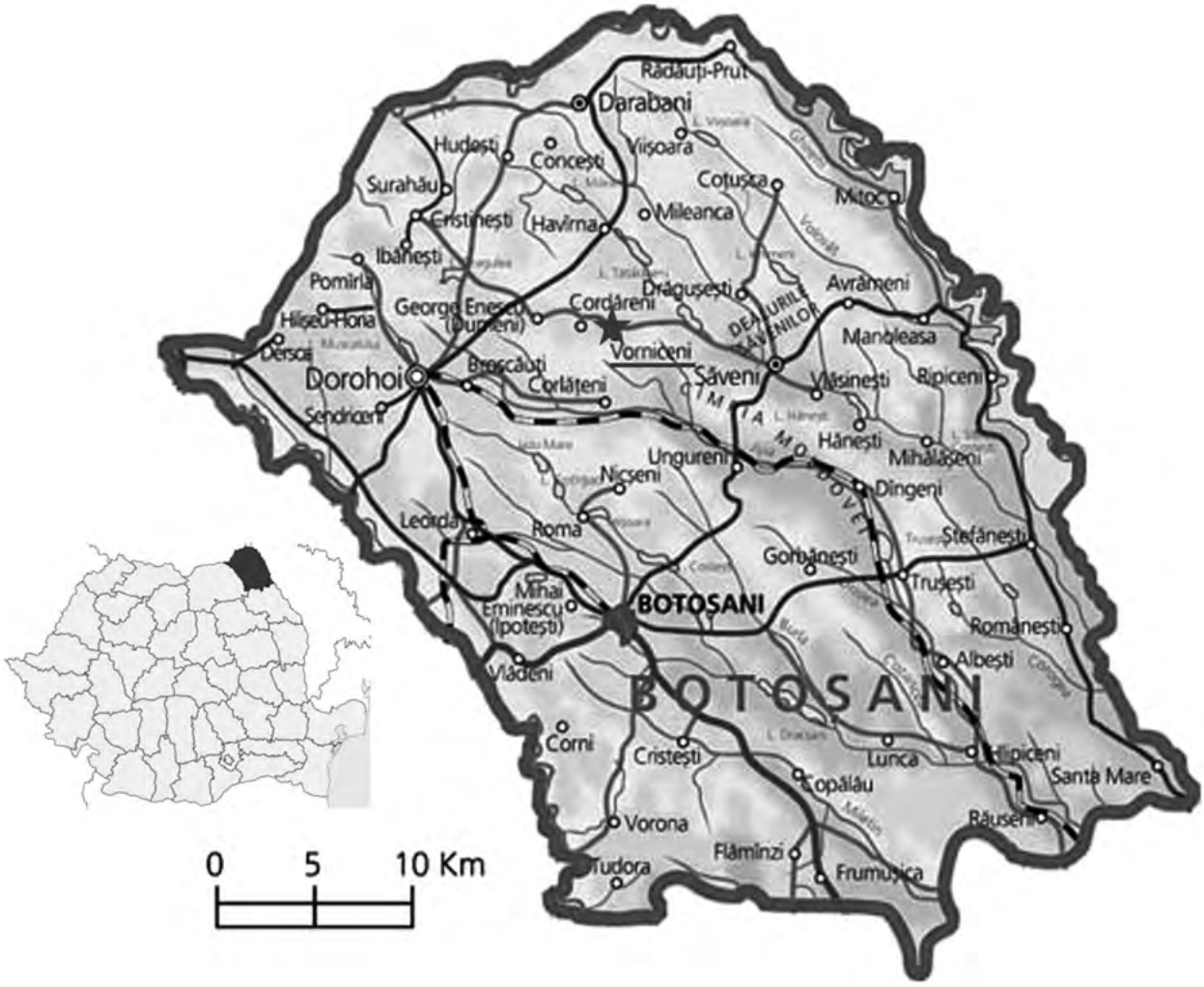

Figure 1. Location of the Vorniceni archaeological site in Botoşani County (Eastern Romania).

Method: DNA analysis protocols

In order to achieve a higher degree of confidence, two extraction protocols were used: phenol-chlorophorm-isoamyl alcohol (Treco 1987) and DNA IQ (https://www.promega.com/-/media/files/resources/protocols/technical-bulletins/101/dna-iq-system-database-protocol.pdf). For both extraction protocols, blank control samples were used to check for potential reagents or lab contamination. In order to identify any possible contamination that may have occurred during the various stages of the sample preparation and above all in the aDNA isolation, at least two extraction blank controls and multiple PCR non-template controls were included in each amplification reaction. The PCR was carried out in a 25 µL reaction volume using GoTaq® Hot Start Polymerase (https://www.promega.ro/-/media/files/resources/protocols/product-information-sheets/g/gotaq-hot-start-polymerase-protocol.pdf) to amplify the mitochondrial hyper variable region 1 (Hv1). Specific pairs of primers were used: MPS1A_f - MPS1A_r, MPS1B_f - MPS1B_r, MPS2A_f - MPS2A_r and MPS2B_f - MPS2B_r (Gabriel *et al.* 2001). The amplicons were purified using the Agencourt AMPure XP (Beckman Coulter, USA) and direct sequenced using the Genome Lab DTCS Quick Start Kit (Beckman Coulter, USA) in the CEQ 8000 Genetic Analysis System (Beckman Coulter). In order to construct a comprehensive phylogeny of the sample, a dataset comprising 16 Hv1 sequences (370 bp) was assembled. Akaike Information Criterion (AIC) (Posada and Crandall 1998) under ML optimised likelihood calculations indicated a General Time Reversible model as the optimal substitution model. Evolutionary relationship reconstruction within sequences was performed under a maximum likelihood (ML) framework using MEGA7 (Kumar *et al.* 2016). To illustrate the relationship between the haplotypes, the SplitsTree4 (Huson *et al.* 2008) was used to construct a statistical parsimony network for the Hv1 dataset. The Basic Local Alignment Search Tool (http://blast.ncbi.nlm.nih.gov/Blast.cgi) command line applications developed at the National Center for Biotechnology Information (NCBI) were used for sequence assignment.

Sequence	Predicted Haplogroup	Total Variants	Variants
S22	U4a (U4a2a)	9	T195C, A249G, A263G, T267d, T310C, T310TTC, T16126C, C16278CT, C16355CC

Table 1. The S22 sample assignation to human haplogroup variants using MITOMASTER (MITOMAP, http://www.mitomap.org).

Results and discussion

The isolated aDNA was successfully used to amplify the mitochondrial hyper variable region 1 (Hv1), free of contaminants, using the PCR method. An approx. 370 bp DNA sequence was successfully generated using the mitochondrial hyper variable region 1 (Hv1) primers set. The obtained sequence was checked for similarity using the BLAST module of the National Center for Biotechnology Information (NCBI). To ensure the haplogroup assignation for the obtained sequence, named S22, a double check was performed using MITOMASTER (Lott *et al.* 2013), a database of human mitochondrial DNA (mtDNA) able to identify nucleotide variants relative to the rCRS and to determine the haplogroup. Both comparison analysis and phylogenetic reconstruction revealed a high similarity score for the sample (S22) with the U4a haplogroup (Table 1).

A phylogenetic tree based on the Hv1 dataset was inferred through an ML approach and presented in Figure 2A. The haplogroup assignation for the S22 sample as an U4a haplogroup member is supported phylogenetically, being clustered in the U4a haplogroup clade, separate from the HV0 and R haplogroup, as expected. Additionally, the parsimony network generated with SplitsTree4 reveals no haplotype sharing (Figure 2B), thus indicating a slight difference from the other U4a human haplogroup members.

The U4 haplogroup originated during the Last Glacial Maximum and has a high frequency among the Mesolithic hunter-gatherers. The study of the spatial distribution of the U4 haplogroup in European populations showed that its highest frequency (5.5 %) was typical of Northeastern Europe (Figure 3), while in the populations of Central and Northwestern Europe the frequency of U4 did not exceed 3% (Malyarchuk 2004). The U4 haplogroup was previously identified on the territory of South-Eastern Romania in a bone sample from Sultana-'Valea Orbului', which belongs to the Gumelnița culture (Hervella *et al.* 2015). Recently, the U4 haplogroup was also identified on the territory of Southern Ukraine in a bone sample from the Revova *tumulus* attributed to the Chalcolithic Srednij Stog culture complex (Nikitin *et al.* 2017b).

Previous studies performed on bone samples from the Verteba Cave, Western Ukraine, belonging to the Trypillia B II-C I (Cucuteni B1 – B2-3) have identified different haplogroups. Several individuals displayed variants of Haplogroup H, which is common among modern Europeans; two individuals were assigned to Haplogroup T2, which is frequent in parts of the Near East; and another individual labeled VC013, assigned to Haplogroup V, was found in ancient contexts from Scandinavia (Nikitin *et al.* 2010; Schmidt *et al.* 2015). The archaeogenetic study conducted on amtDNA obtained from human remains identified in the Verteba cave revealed lineages characterizing European Neolithic farmers and did not identify any similarity with the autochthonous hunter-gatherer groups until the Bronze Age (Nikitin *et al.* 2010). The anthropological analysis of the Trypillia remains are in agreement with the amtDNA data and characterised the Trypillia populations as being predominantly integrated into the gracile Mediterranean type prevalent in the Neolithic farming communities of Europe and Anatolia (Nikitin *et al.* 2017a).

Conclusions

To our knowledge, this is the first report on DNA analysis performed on bone samples from the Chalcolithic period in Eastern Romania. It is a start, although clearly an extended aDNA database is needed in order to gain some insight into the mobility of the Chalcolithic communities. At the same time, the archaeogenetic data can help us to understand the interplay between the long-distance trade routes established for some raw materials (such as copper and hematite) and the rich, locally available salt resources, by adding new data in respect of the circulation of people. Furthermore, given the peculiarity of the human remains from the Cucuteni culture, by adding anthropological and aDNA data, a more comprehensive picture of the funerary customs will be obtained.

This case study produced a high similarity score for the sample (S22) with U4a human haplogroup based on both comparison analysis (BLAST and MITOMASTER) and phylogenetic reconstruction. Furthermore, the lack of haplotype sharing indicates a slight difference in the S22 sample compared with the other U4a human haplogroup members.

Acknowledgements

The human bone samples and the information about the archaeological research were provided by the archaeologist Maria Diaconescu (Botoșani County Museum), to whom we are most grateful.

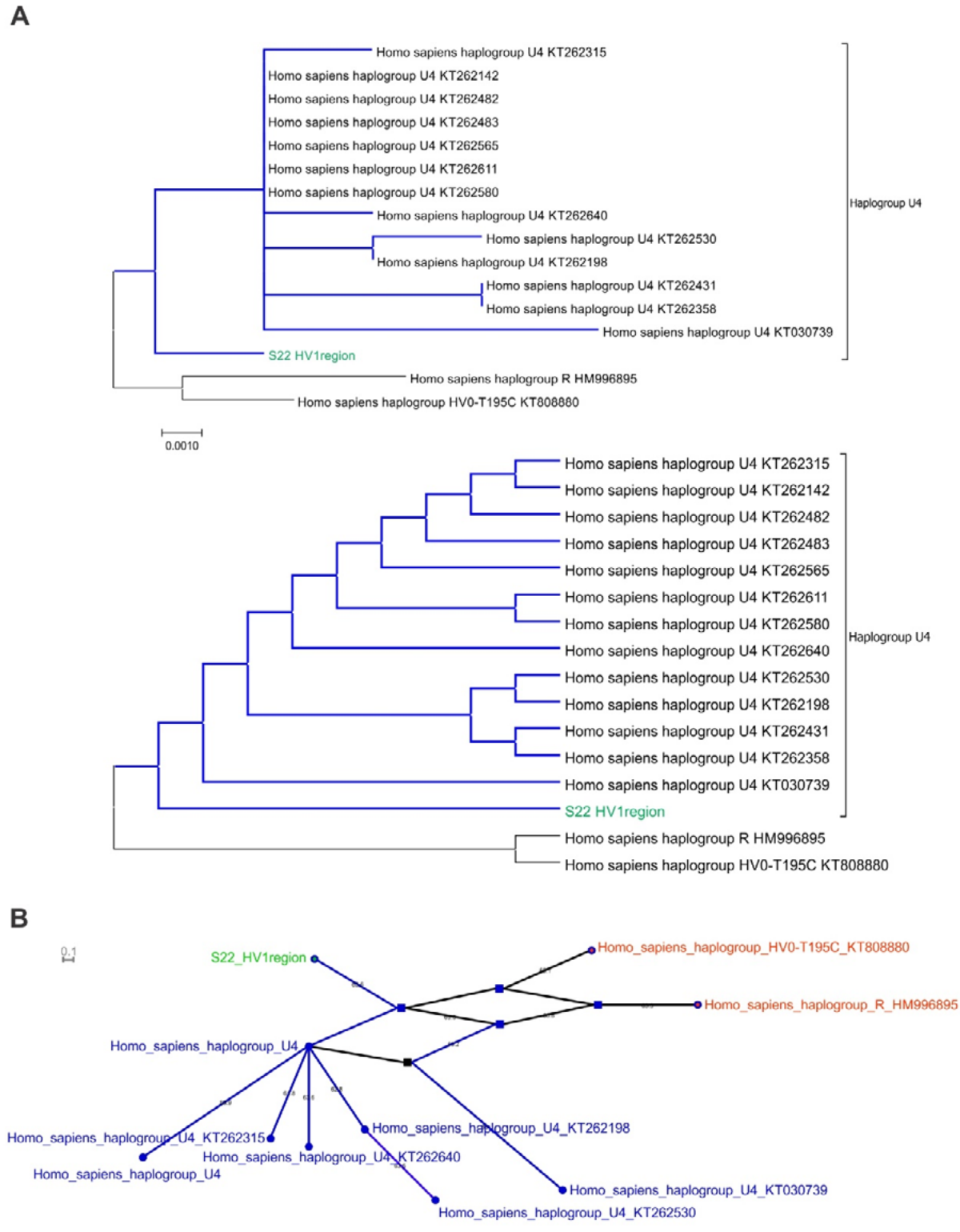

Figure 2. Reconstruction of evolutionary relationships within Hv1 sequences. A – Maximum Likelihood tree (up: phylogram; down: cladogram) estimated using the GTR substitution model; B – Statistical parsimony network for the Hv1 dataset.

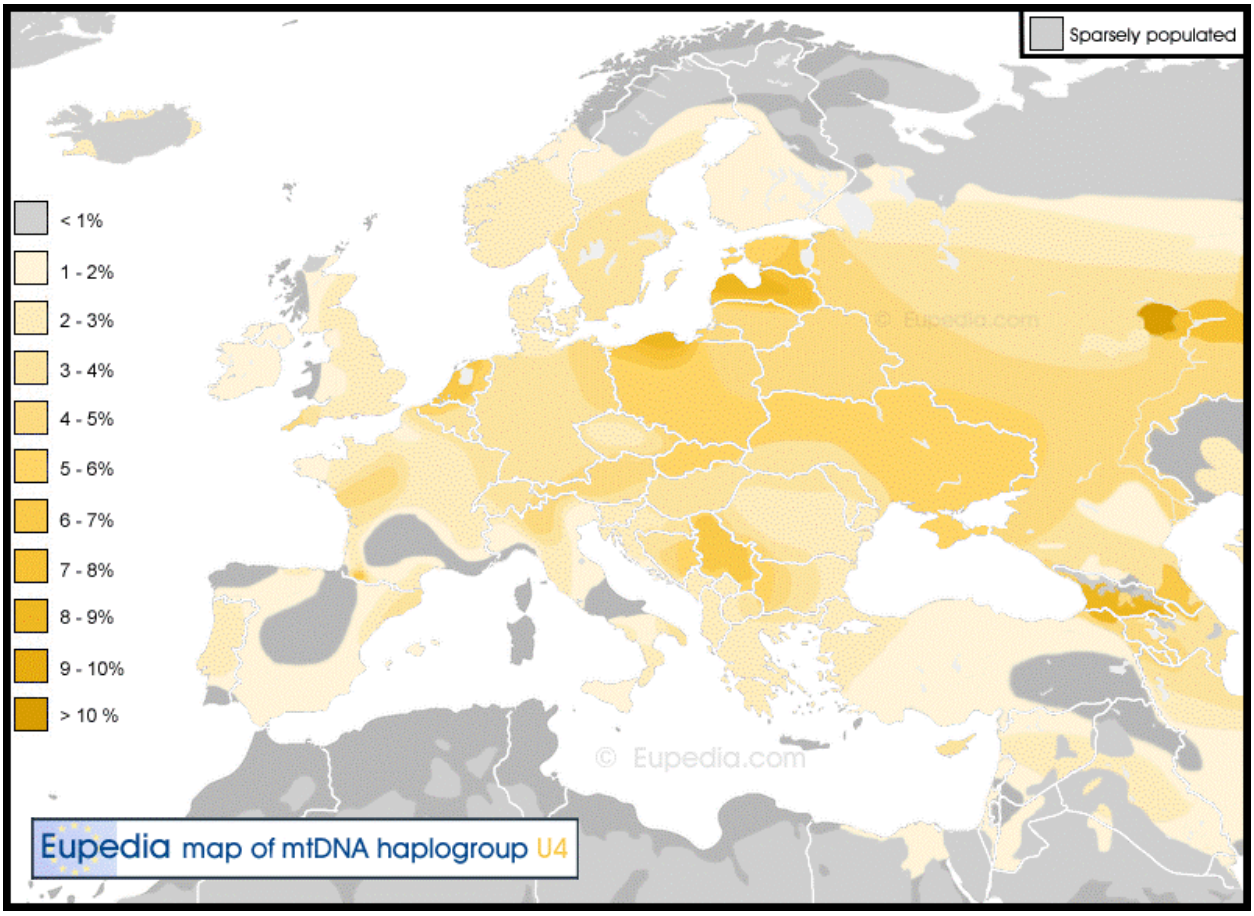

Figure 3. Identified U4 haplogroup distribution in Europe and their relative frequency (http://www.eupedia.com/europe/Haplogroup_U4_mtDNA.shtml).

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The Boyadzhik Concession Area: the Use of GIS Technology in the Protection of Cultural Heritage

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Abstract

This paper presents the results of a field survey carried out in the Boyadzhik concession area involving the use of PDAs (personal data assistants), GPS points, relation databases and GIS technologies adapted to field conditions. The results consisted in the identification of ten archaeological sites (eight settlements, one burial mound and a more detailed documentation of the St. George Monastery) dating from various periods beginning with the Bronze Age and ending with the Middle Ages. This is one of the few cases where present-day technologies have been used in the identification of archaeological sites, with the main advantage of these new technologies, in comparison with the traditional field walk, being that they allow us to establish a precise location for the sites in question.

Keywords: field survey, GIS technologies, settlement map, prediction models.

Introduction

In the autumn of 2011, a team from the Regional Historical Museum in Yambol set about investigating a number of archaeological sites in the Boyadzhik concession area. This area covers of 8.5 square kilometers and is situated near the villages of Boyadzhik, Galabintsi and Zlatari within Municipality of Yambol, Bulgaria (Бакърджиев и Вълчев 2012: 555).

The team from the Regional Historical Museum were among the first Bulgarian researchers to make use of information technology in the field of archaeology, having previously used various technologies during archaeological field surveys undertaken in 2008 as part of the Tundzha Regional Archaeological Project (TRAP). The international project based in the Yambol region was led by Shawn Ross, Adela Sobotkova, Iliya Iliev and Stefan Bakardzhiev. The project aimed to document cultural heritage using non-destructive field methods, such as intensive field surveys aided by satellite remote sensing, mobile computing, relational databases and Geographic Information Systems (Iliev *et al.* 2012; Ross *et al.* 2018).

Methodology

The methods used during these field surveys varied according to the environmental conditions. The team used both intensive and extensive surveys (Figure 1). The former is employed when the visibility of the surface is estimated at being over 50% and consists of walking at a steady rate, with a 20m spacing between team members. This results in units of 20x20m. Artifacts found on the surface are counted and recorded when each unit is completed. Significant pottery pieces are collected and processed, while insignificant pieces are left on the field. One polygon comprises between 4x4 and 6x6 units, depending on the number of participants. In contrast, during an extensive survey the spacing between walkers is increased to 25m – as this is the maximum distance that still allows for easy communication during the walking process (Iliev *et al.* 2012: 14-19; Ross *et al.* 2018: 24-30).

The areas of all sites were covered by GPS points, which were used to show the approximate size of the archaeological site and its correct position on the geographical map.

Analysis of the results helps to identify clusters of pottery concentrations, which may be interpreted as being indicative of archaeological structures.

Archaeological sites without pottery concentrations, such as burial mounds, were recorded using GPS points, photographs and basic descriptions of the condition of the site (Figure 2).

Different information about the survey area was collected using record sheets. These include information about land use and agricultural condition, the topography of the area and other aspects (Figures 1 and 2). This varied information is helpful in the creation of settlement maps for different chronological periods and predictive models for potential archaeological sites (Iliev *et al.* 2012: 68-72; Ross *et al.* 2018: 28-29).

Results

The field survey carried out in the Boyadzhik concession area identified ten archaeological sites: eight settlements,

Бояджик 2011 Boyadzhik 2011	Дата: Date:	Време: Weather:	СВ? RP?
Обходен участък: Survey unit:	Разстояние между обхождащите: 15м Walk interval: 15m		Друго: Other:

Тип на броене на фрагментите: Гъстота на м²/брой
Shard count type: Density per m²/Raw count

Обработка на земята: ☐Годишна ☐Перманентна ☐Пасище ☐Гора ☐Смесена ☐Друго
Land use: Annual Per Pasture Forest Disturbed Other

Земеделие: ☐Орница ☐Бранувана ☐Покарала ☐Узряла ☐Ожъната ☐Угар ☐Друго
Agr C: Plow Harrow Seedling Mature Harvest Fallow Other

Топография: Topography:	Наклон: Slope:	Видимост: Visibility:	Проходимост: Pass:	Л 2 3 4 Н Е 2 3 4 Im
○ Долина Valley btm	○ Равен (<2%) Level	○ >80%	Дренираност Drain	С 2 3 4 М D 2 3 4 W
○ Склон Hillside	○ Слаб (2-15) Gentle	○ 60-80%	Растителност Veg	Н 2 3 4 М N 2 3 4 М
○ Вододел Ridgeline	○ Стръмен (15-30) Steep	○ 40-60%	Камъни Stone	Н 2 3 4 М N 2 3 4 М
○ Речна тераса Riv terrace	○ Много стръмен (30-45) Vr st	○ 20-40%		
Образец? ☐ Sample?	○ Невъзможно (> 45) Imp	○ <20%	Сянка Shade	Н 2 3 4 М N 2 3 4 М

Бележки:
Notes:
Фрагментираност =
Frag =

Същото като по-долу? ☐
Same as below?

Figure 1. Survey record sheet.

Бояджик 2011 Boyadzhik 2011	Дата: Date:	Обект №: Object №:	Главен обект №: Parent Object №:
Име/Описание: Name/Desc:			
Полигони: Units:		Образци: Sample Nos:	
Дължина (макс.): Lenght (max): Дължина (мин.): Lenght (min):	Ширина (макс.): Wight (max): Ширина (мин.): Wight (min):	Височина (макс.): Height (max): Височина (мин.): Height (min):	Други размери: Other Dim:
Тип: Type: ○ Могила Mound ○ Повърхн. конц. Surf Conc ○ Некропол Necropolis ○ Многосл. конц. Mult Conc ○ Други Other:	Админ: Slope: Регион: Ямбол Region: Yambol Община: Municip: Местност: Locale: Кадастр. № Kadastre №	Околна среда: Environment: Употреба: LU: З. условия: Ag. Cond.: Видимост: Vis.: Наклон/Разположение: Slope/Aspect:	Състояние: 1-2-3-4-5 CRM urgency: Иманярски изкопи/ активност Robbers, trenches/ activity;
Тип на източника: Source type: ○ Информатор Informant ○ Библиография Bibliography ○ Обхождане Survey ○ Други Other:	Информация от източника: Source info:	GPS точки GPS pts: Снимки: Photo Nos:	Бележки/Скица: Notes/Sketch:

Figure 2. Object record sheet.

a monastery and a burial mound (Figure 3) (Бакърджиев and Вълчев 2012). The settlements will be presented from north-west to south-east (Figures 4-7).

Settlement 1 has an area of 0.4ha (Figure 4.1). The finds consisted of pottery fragments from vessels covered with green or brown glaze typical of the Ottoman period (15th-16th centuries) (Плетньов 2004).

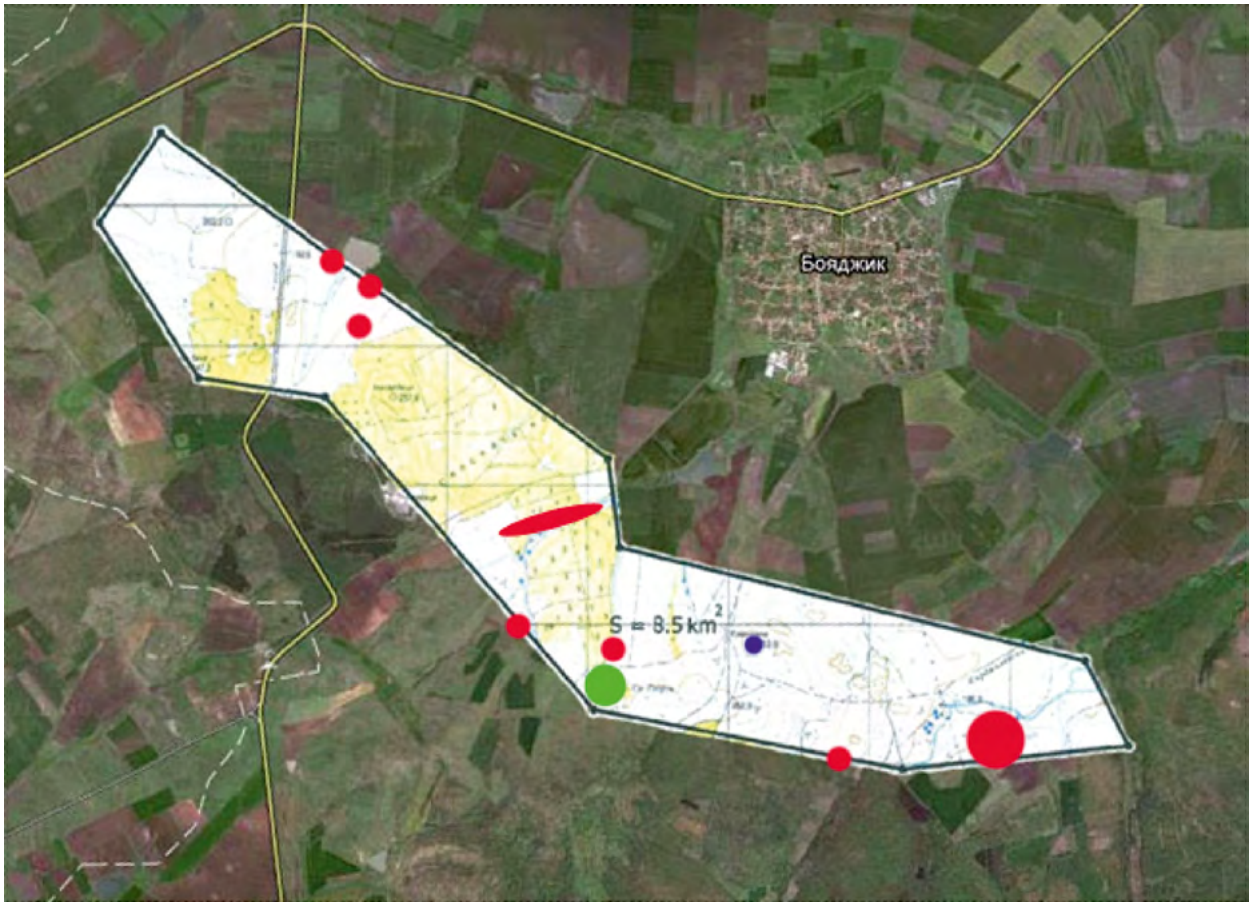

Figure 3. The Boyadzhik concession area showing all archaeological sites: open-air settlements in red, monastery in green and burial mound in blue.

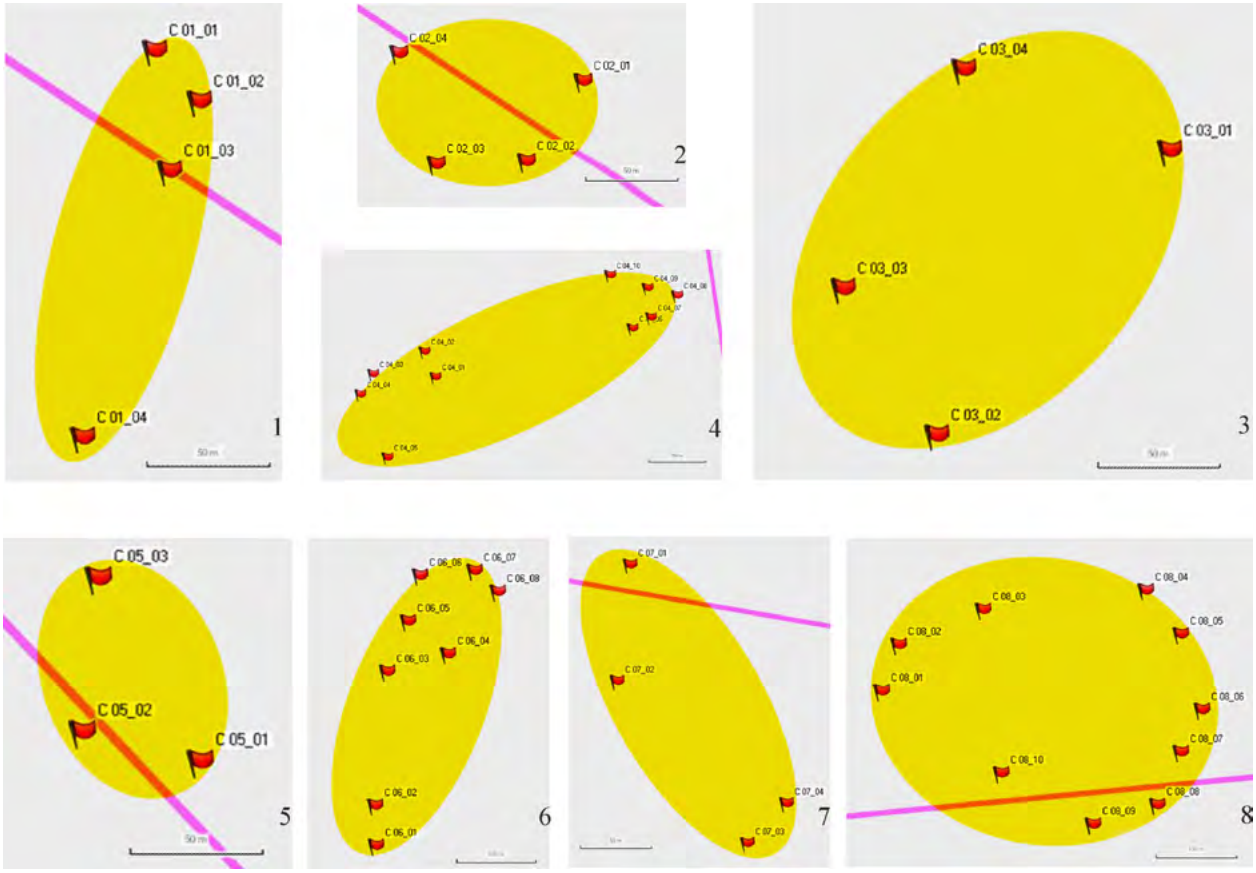

Figure 4. Areas of open-air settlements.

Settlement 2 has an area of 0.17ha (Figure 4.2). The ceramic finds include pieces from plates and amphorae dating to Late Antiquity (4th-6th centuries) (Figure 5.1-4) (Кузманов 1985). Two flint tools were also retrieved during the survey (Figure 5.5-6).

Settlement 3 has an area of 0.4ha (Figure 4.3). Finds include fragments of handmade pottery (Figure 5.7-11) and wheel-made pottery (Figure 5.12-15), mostly from pots, plates and storage vessels. Some of these were decorated with incised lines (Figure 5.9-11). The site is dated to the Early Iron Age and Roman period (Кабакчиева 1986; Нехризов 2008).

Settlement 4 has an area of 19ha (Figure 4.4) and is situated on the south-west bank of a small river. It was inhabited during the Bronze Age and Roman period. The hand-made pottery from the Bronze Age includes fragments of pots and storage vessels (Figure 6.1-4) (Лещаков 2006). The ceramic material from the Roman period predominantly comprises fragments of amphorae, pots and plates (Кабакчиева 1986).

Settlement 5 has an area of 0.17ha (Figure 4.5). The survey uncovered fragments of wheel-made pottery, such as pots, plates, bowls and amphorae dating to Late Antiquity (Figure 6.5-8) (Кабакчиева 1986; Кузманов 1985).

Settlement 6 has an area of 1.64ha (Figure 4.6). Late Bronze Age hand-made pottery decorated with incised lines, small shallow pits and circle stamps were found during the survey (Лещаков 2006). Flint and stone tools were also found. The settlement was re-inhabited during the Roman period, as shown by the wheel-made pottery, such as pots, jugs and amphorae fragments, found on the surface (Figure 6.9-12) (Кабакчиева 1986). The spatial distribution of the pottery fragments shows that later materials dominated in the western part of the site.

Settlement 7 has an area of 0.7ha (Figure 4.7). It was inhabited during Late Antiquity (4th-6th centuries), as shown by the fragments of wheel-made amphorae and storage vessels found during the survey (Figure 7.1-4) (Кузманов 1985). Some fragments of metal slag were also found.

Settlement 8 has an area of 6.75ha (Figure 4.8). It is situated to the south-east of the local dam. Fragments of hand-made and wheel-made pottery, such as pots, plates, bowls and storage vessels, were found during the survey (Figure 7.5-11). Some of these were decorated with channels, incised lines and stamped circles and lines (Figure 7.12-14). The ceramic material dates to the Early and Late Iron Ages (Нехризов 2008).

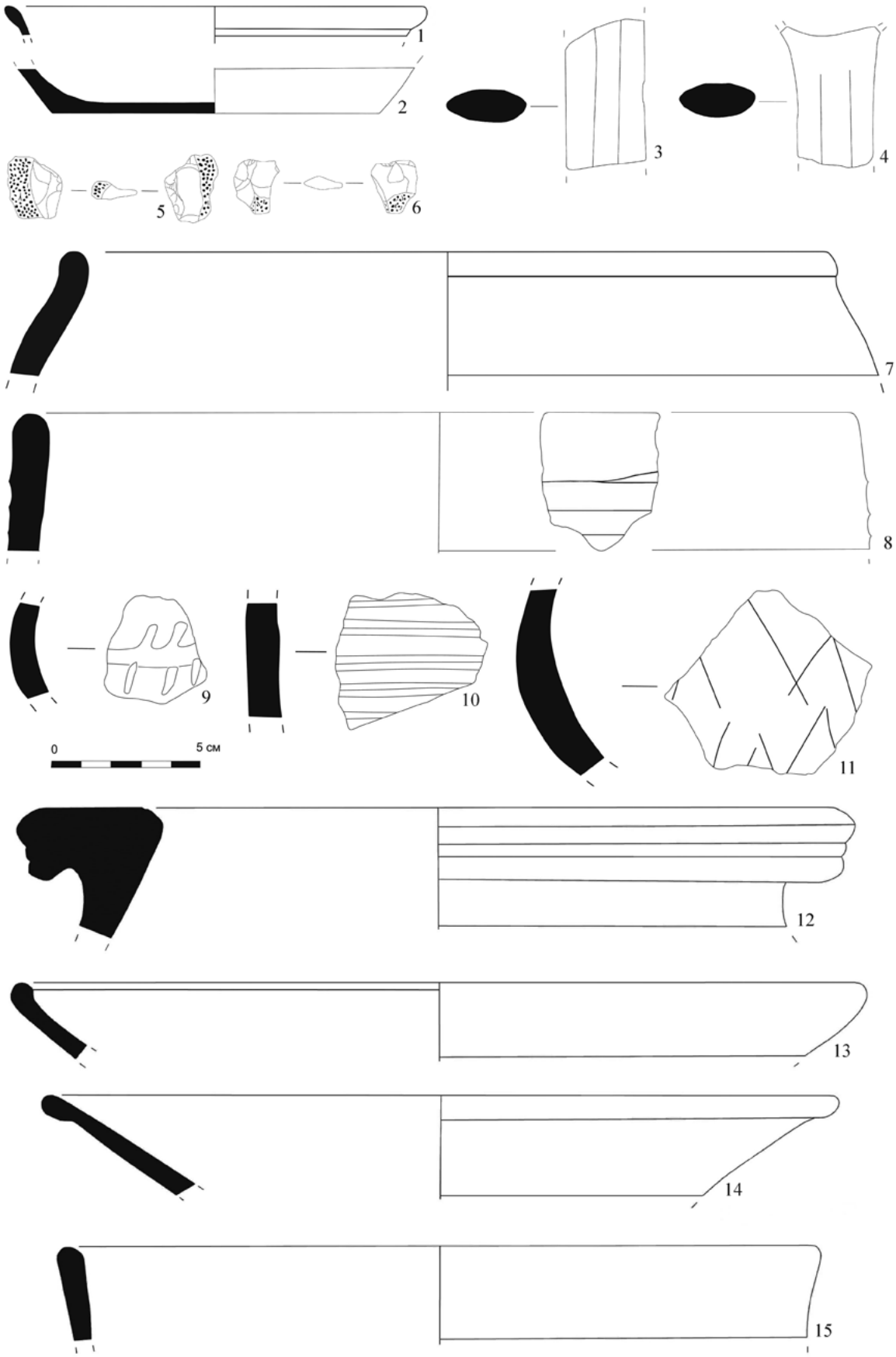

Figure 5. Pottery fragments: Settlement 2 (1, 2, 3 and 4), Settlement 3 (7, 8, 9, 10, 11, 12, 13, 14 and 15); flint tools from Settlement 2 (5 and 6).

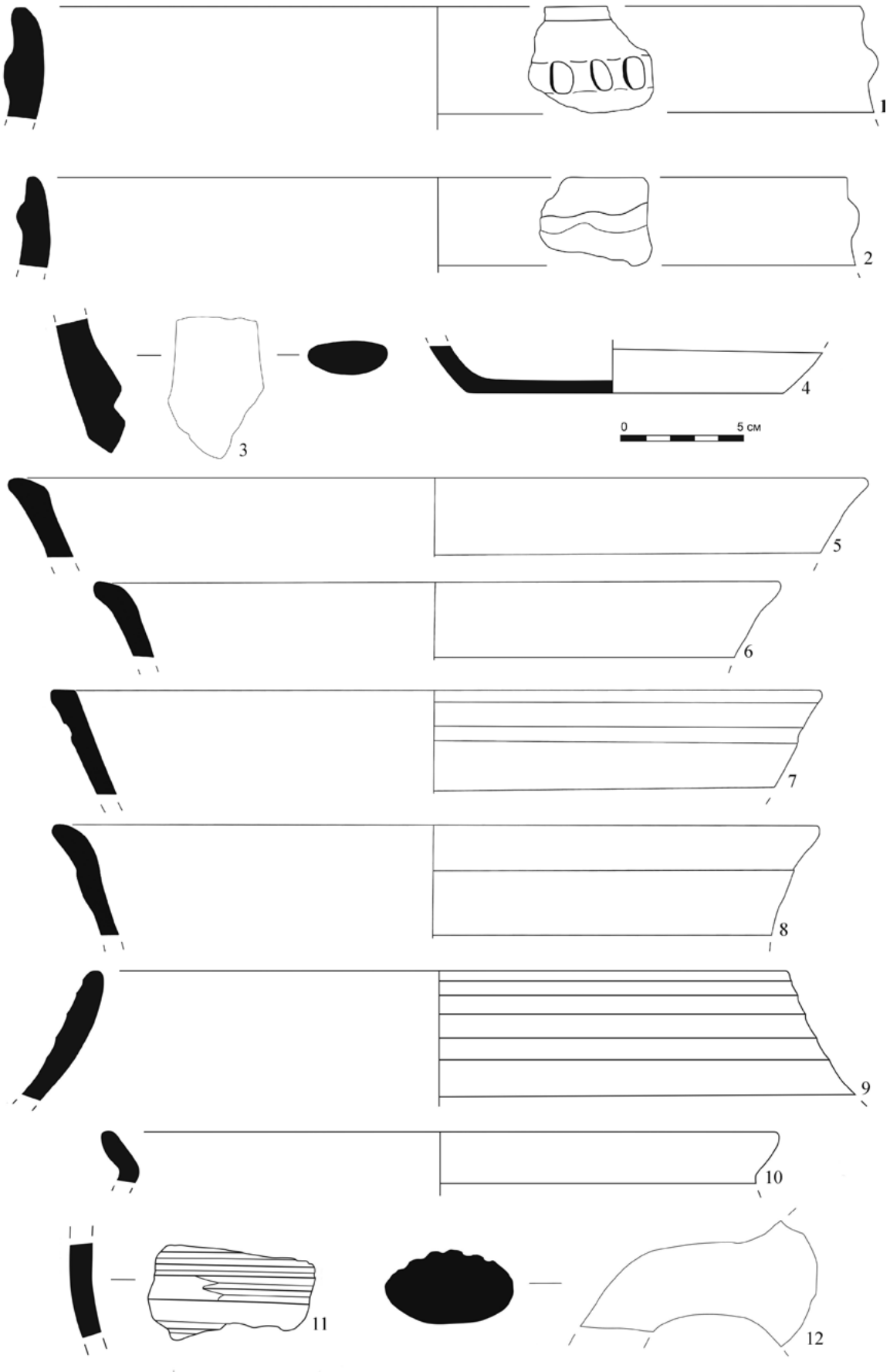

Figure 6. Pottery fragments: Settlement 4 (1, 2, 3 and 4), Settlement 5 (5, 6, 7 and 8), Settlement 6 (9, 10, 11 and 12).

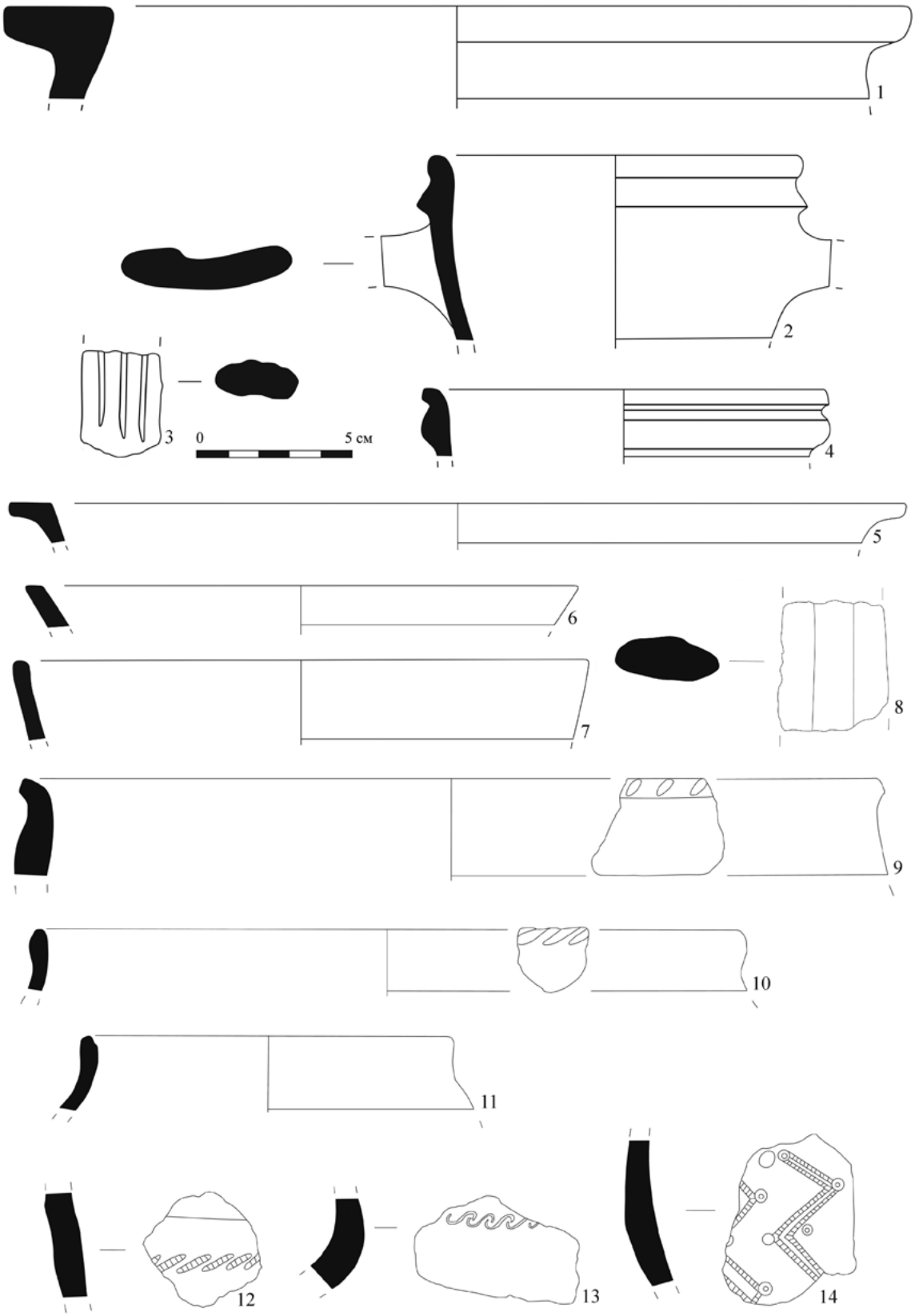

Figure 7. Pottery fragments: Settlement 7 (1, 2, 3 and 4), Settlement 8 (5, 6, 7, 8, 9, 10, 11, 12, 13 and 14).

The St. George Monastery covers an area of 4.64ha and is situated to the south-east of the village of Boyadzhik. It has a church dating from the end of the 19th century that was built on the site of an earlier temple. The monastery is situated at the foothill of the late antique and medieval fortress located near the present-day village of Boyadzhik. Settlement 6 lies to the north-east of the monastery. The following data relating to the fortification were recorded during the survey: it was built from small- and medium-size chopped stones and white mortar, and it was 1.2-1.4m high and 2.6m wide.

The last site recorded is a small burial mound measuring 0.8m in height and 18m in diameter. It is situated on top of a small hill.

Concluding remarks

The Boyadzhik concession area is an example of how, with the help of modern technologies such as mobile electronic devices like PDAs (personal data assistants), GPS points, relational databases and GIS technologies, we are able to determine the location of ancient settlements more precisely and accurately. The information thus collected is helpful in the creation of settlement maps for different chronological periods and predictive models for potential archaeological sites. The know-how and experience of the archaeological team from the Regional Historical Museum in Yambol makes it a leader in the area of field surveys in Bulgaria.

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Laser-Assisted Removal of Graffiti Paint on Stone: Potential Use in the Restoration of Cultural Heritage Monuments

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Abstract

Graffiti painting is a common component of contemporary street art in big cities, but very often, in being subjected to vandalism in this way, the aesthetics and integrity of the facades of the buildings and monuments, etc. on which this art form is practiced undergo certain damage. Moreover, it is difficult to extract the paints commonly used in graffiti from the stone surface. In light of this, graffiti has become a serious problem for restorers.
This paper describes the use of lasers in the removal of graffiti from stone as a potential restoration technique. In seeking to achieve the best possible results, the efficiency of two laser systems was compared: a copper bromide vapour laser (CuBrVL) generating nanosecond pulses with a wavelength of 510.6nm; and a pulse repetition frequency 20kHz and Q-switched Nd:YAG laser, commonly used in restoration, generating nanosecond pulses at the fundamental wavelength of 1064nm and its second harmonic of 532nm with pulse repetition frequencies of 1Hz and 10Hz. The potential of the CuBrVL in graffiti removal was demonstrated here for the first time.
The cleaning tests were performed on samples of limestone, granite and marble covered in different coloured graffiti spray paints. Pre-assessment of the optical properties of the graffiti paints and the stones was performed by spectrophotometry. The evaluation of the results was performed by means of optical microscopy.

Keywords: Laser cleaning, Nd:YAG laser, CuBr vapour laser, graffiti removal, limestone, granite, marble, Cultural Heritage restoration and conservation.

Introduction

Restoration is a key act in prolonging the life of the material remains of the past. Its aim is to stabilise the condition of the object of interest, preventing its further degradation and giving it an aesthetically pleasing appearance. A significant component of the restoration procedure involves acquiring a complete understanding of the processes of decay and the nature of the building material in question, so that an appropriate restoration technique can be chosen. Environmental conditions have an important impact on the state of the object. Very often stone works are exposed to outdoor urban conditions in which air pollution, salt growth, biodeterioration, differential stress, climate change, vandalism, etc., all cause degradation and aesthetic damage to the object (Brimblecombe 2016; Doehne and Price 2010; Koh 2006).

An example of this is given by the painted graffiti found on monuments and historical buildings (Figure 1). This is a serious problem of the urban environment. As acts of vandalism, graffiti spread in an uncontrollable manner and thus pollute the urban environment. They endanger the aesthetic and economic value of built heritage (Brimblecombe 2016; Sanmartín *et al.* 2014). In this paper we look at graffiti spray paints. Their composition is very complex (Pozo-Antonio *et al.* 2016; Sanmartín *et al.* 2014). Conventional methods of removing graffiti paint, typically involving the use of chemicals and mechanical abrasion, can have unfavourable side-effects, for they are often difficult to control (Rivas *et al.* 2012). When choosing a suitable technique, it is important to bear in mind the significance and value of the historical site or object as a unique material remnant of the past and thus to handle it with great care (Koh 2006).

These considerations, as well as the diversity of historical materials in question, triggered the search for innovative restoration approaches able to overcome these issues. The invention of the laser tool has led to major advances in the field of cultural heritage conservation during the last several decades. The use of laser light to remove unwanted surface impurities from historical objects has many advantages, given that it offers selective, highly precise and controllable cleaning with minimal collateral damage. Once a suitable working practice is established, the process can be automated. The lack of mechanical contact allows for the handling of fragile objects (Koh 2006; Phipps 2007). The process of laser cleaning is based on the selective vaporisation of the optically absorbing layer or particles in a reflecting surface, which determines

Figure 1. Examples of graffiti application as an act of vandalism on monuments in the centre of Sofia, Bulgaria (photo by V. Atanassova).

its self-limiting nature. The corresponding physical phenomenon is called laser ablation, and this results in a non-linear, irreversible and intrusive laser-matter interaction. It involves highly complex processes (Schreiner *et al.* 2008). The parameters of the laser, such as wavelength, pulse duration, pulse repetition frequency and pulse energy, as well as the chemical and physical properties of the processed material itself (optical absorption, surface hardness, porosity, pore size distribution, mechanical strength, heat conductivity, and so forth) all contribute to this interaction. Ablation occurs when the laser energy deposited per surface area (laser fluence) exceeds a certain level called the ablation threshold, which is an intrinsic property of the material being cleaned. In order to achieve a desirable cleaning effect, the working laser parameters should be correctly chosen by tailoring them to the properties of the object's material and contamination (Fotakis 2007).

A wide range of laser sources have been tested in the cleaning of stone works. The most widely commercialised is the Nd:YAG laser, which generates nanosecond pulses at the fundamental and its different harmonic wavelengths. There are several articles available on how this laser has been employed to remove different graffiti paints (Costela *et al.* 2003; Pozo-Antonio *et al.* 2016; Sanjeevan *et al.* Klemm 2007). Other lasers have also been tested (Fiorucci *et al.* 2013; Gómez *et al.* 2006).

This paper demonstrates the potential of two different systems in the laser cleaning of different coloured graffiti spray paints on various types of stone: the Q-switched Nd:YAG laser generating ns pulses at 1064nm and 532nm at a low repetition frequency (1Hz and 10Hz), a laser conventionally used in restoration; and a Copper Bromide vapour laser (CuBrVL) generating ns pulses at 510.6nm at a high repetition frequency (20 kHz). To the best of our knowledge, the CuBrVL had not been tested before in this application. The unique characteristics of this latter laser, such as its high output power from a direct source of visible laser light, its near-diffraction limited beam, etc., offer several advantages over the lasers commonly used in conservation, and this could make it a reliable restoration tool.

Experiment

Sample preparation

Five commercial stone samples were prepared: two cut and polished granite slabs, two limestone slabs and one marble slab. Five colours of graffiti spray paint (Montana Colors® http://www.montanacolors.com) were selected and applied to separate areas of the stones. The commercial names of the colours are as follows: black (R-9011), divinity white (R-9010), light red (RV-3020) and electric blue (RV-30), all with a gloss finish; and Tasmania green (RV-294) with a matte finish. The exact chemical composition of these graffiti paints is a trade secret and thus not publicly available. One area of each sample was left unpainted so as to be able to reference the original surface.

Laser systems

The cleaning tests were performed using two different laser setups. One of the lasers was a low repetition frequency (max. 10Hz) Q-switched Nd:YAG laser (Quanta Ray GCR3) generating pulses with a duration of 8ns at the fundamental wavelength of 1064nm and with a maximum pulse energy of 500mJ and a second harmonic of 532nm with a maximum pulse energy of 60mJ. This laser was equipped with a gradual energy attenuator and a focusing lens with a 17cm focal length in order to control the laser fluence. The spot of the fundamental wavelength after the lens had a circular shape with a diameter of 3.3mm, while the spot of the second harmonic was rectangular, with dimensions of 3.3 x 1.3mm. The sample was placed on an X-Y stage (Figure 2.1). During the experiments, a different number of pulses with different energy levels were applied at 1Hz and 10Hz. The other laser was

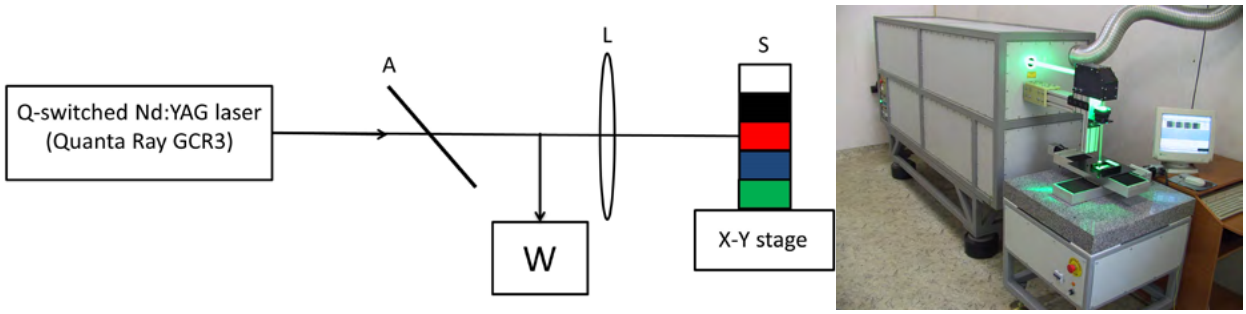

Figure 2. Experiment setups: Left: Nd:YAG system: A = attenuator;
W = power meter; L = focusing lens; S = sample. Right: Commercial CuBrVL system (Pulslight Ltd).

a high repetition frequency (max. 20kHz) industrial CuBrVL system (Pulslight Ltd.) generating pulses with a duration of 30ns at 510.6nm with an average output power of 5W and a maximum pulse energy of 250μJ. The CuBrVL system was equipped with a galvo-scanner, which moves the beam into different shapes, and an XYZ stage, which moves the sample into a different position (Figure 2.2). The lens of the scanner had a focal length of 256mm and the beam was focused on a spot of 60μm in diameter. The treatment with the CuBrVL was performed by placing the object at the focal point and then at 2mm, 3mm and 4mm from the focal point of the lens in order to change the laser spot size, hence the fluence at a single scan. The pulse repetition frequency of the laser was 20kHz and the scanning rate of the galvo-scanner 100mm/s. By keeping these two values constant, the uniformity of the laser irradiance was guaranteed, with every surface point being given the same exposure. Depending on the spot size, the beam overlap fell within the range of 90-99%.

Results and discussion

Limestone

The first stage in the laser cleaning procedure involved establishing the safe working range of the fluences, i.e. the damage threshold of the contamination should be lower than the damage threshold of the substrate (Fotakis 2007). The ablation thresholds of the stone and the contaminations were determined according to the criterion of the fluence level for which a visible destruction of each material was noticeable. The working range for the limestone-graffiti samples was found to be 1-2 J/cm^2 for 1064nm and 0.4-0.8 J/cm^2 for 532nm. Although the limestone has a higher reflection level than the marble (Figures 4 and 8), it is less durable, which results in a lower damage threshold. Both of the stones are carbonate rocks, but the limestone exhibits higher porosity and lower hardness. It appears that upon irradiation with the CuBrVL there was no safe working range of fluences, since the damage thresholds of the paints and the limestone were too close in terms of values. Some of the results are presented in Figure 3.

To ensure maximum energy absorption, it is essential to choose a suitable wavelength so that the coupling with the optical absorption of the substrate is optimal. This condition increases the cleaning efficiency. In order to verify this, the full diffuse reflection from a semi-sphere for a wide spectral range (320-2000nm) of the graffiti paints and the stone surfaces was measured. The spectrophotometer used was a Perkin Elmer Lambda 1050. The measured reflection (R) determines the absorption (A) of the surface, since $A = 1 - R$, corresponding to the part of laser radiation effectively absorbed by the material. Figure 4 depicts the full diffuse reflection spectra of the five paints and the limestone.

As expected, the black paint proved to be a good absorber over the entire spectral range. Good extraction for both the 1064nm and 532nm wavelengths was noticed on the micrographs (Figure 3.1-2), but discoloration of the original surface was also observed. Good extraction of the white paint was achieved when cleaned at 1064nm (Figure 3.3), but it was more resistant to irradiation at 532nm (Figure 3.4). The other paints were more difficult to clean. As can be seen from Figure 4, the blue and the green paints exhibited similar optical properties (absorption/reflection). The extraction level for those paints for all the applied wavelengths of the Nd:YAG laser was not so good (Figure 3.5-8). Increasing the pulse repetition rate at the green wavelength to 10Hz resulted in better extraction for all the paints, but it was also harmful to the stone. In order to achieve better results at 1064nm, a thin water film was applied successively between the sets of pulses for some of the paints (Figure 3.5-7) – it is known that the presence of water enhances the removal of persistent dirt from a surface owing to its penetration into the pores and facilitation of the ejection of particles (Koh 2006). That being said, the paints were still not fully extracted. The red paint had a similar optical reflection in the green spectral region as the black paint. That made its extraction easier upon irradiation with the second harmonic of the Nd:YAG laser (Figure 3.2). The removal of the paints with the CuBrVL system was not successful, as the original surface appeared to be damaged and remnants of the

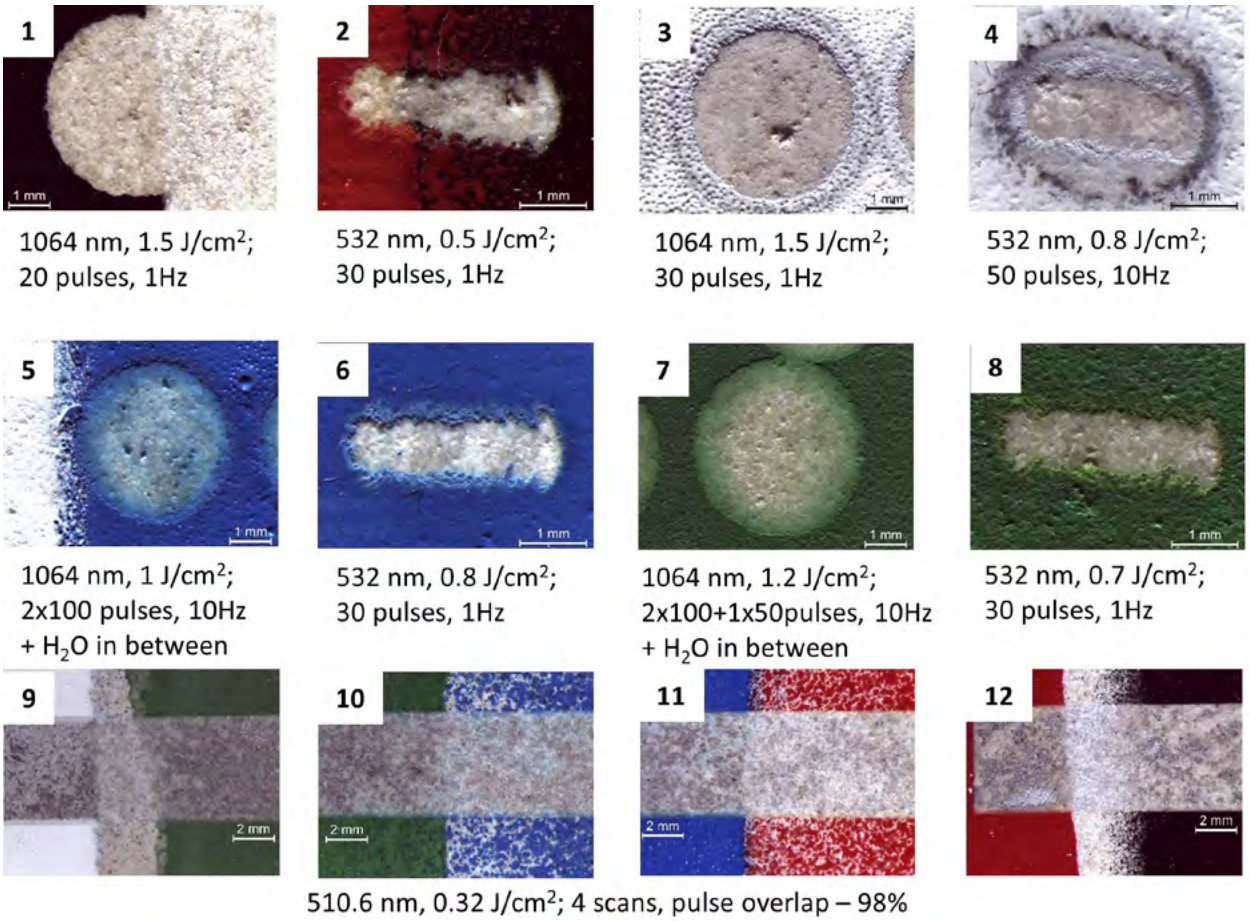

Figure 3. Micrographs of the laser cleaning of graffiti paints on limestone.

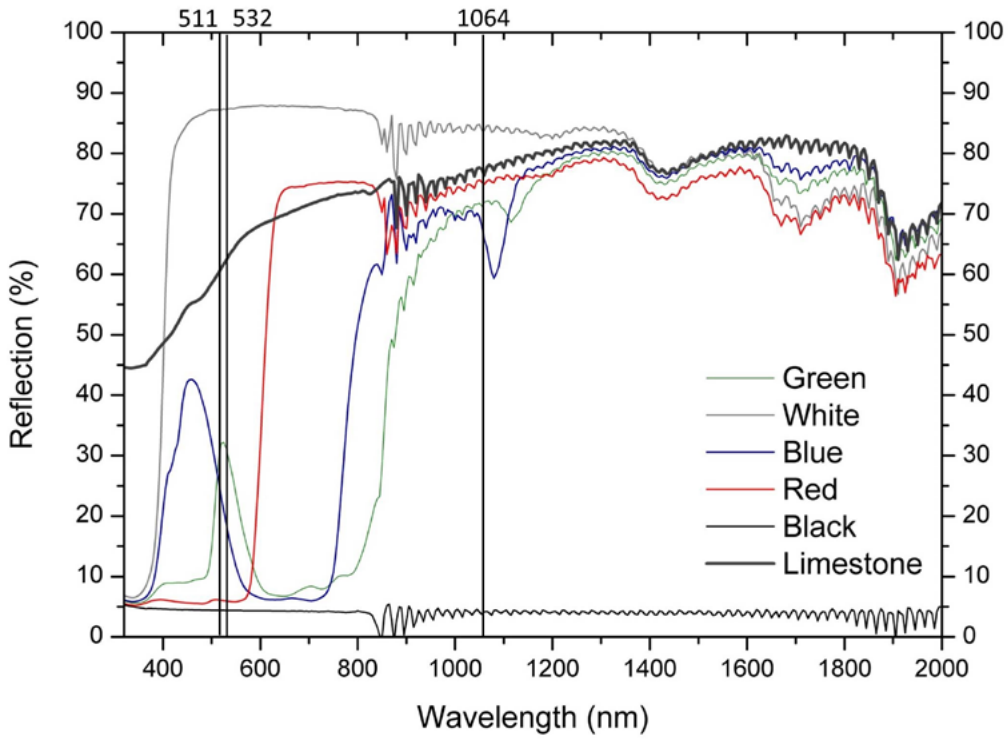

Figure 4. Reflection spectra for the different paints and the limestone.

paint were still present (Figure 3.9-12). This might have been caused by the high repetition frequency of the laser, the high percentage of the pulse overlap and the close damage thresholds of the limestone and the graffiti paints for the green wavelength.

The results are summarised in Table 1. The difficulties encountered in removing the paints from the limestone might be due to the stone's high porosity. The paint penetrated into the stone pores making it hard to extract without causing damage to the surface of the stone.

Laser	Black	White	Blue	Green	Red
Nd:YAG 1064 nm	G	G	M	M	D
Nd:YAG 532 nm	G	M	M	M	M
CuBrVL 510.6 nm	D	D	D	D	D

Table 1. Extraction levels for the graffiti paints on limestone. Legend: G = good; M = medium; D = damage to the surface.

Granite

Granite contains various compounds with different surface tensions, optical absorption rates, grain sizes, etc. This made it difficult to establish a safe working range of laser fluences. However, it is expected that the granite would suffer higher fluences than the limestone because it has a greater hardness (http://www.mineralszone.com/stones/). Some of the results are depicted in Figure 5. The full related diffuse reflection spectra are shown in Figure 6. Although the reflection of the granite is lower compared with the limestone (Figures 4 and 6), it shows higher resistance to the irradiation due to the higher hardness of the material. It can be seen that the reflection of the graffiti paints is different depending on the type of stone they are applied to. This might be due to the differences in surface roughness of the stones, which may influence the diffuse reflection.

The best results were attained with the CuBrVL system (Figures 5.3, 6, 9 and 12). Thanks to its high pulse repetition frequency and constant scan speed, the affected areas were cleaned homogeneously. This is the main advantage offered by this type of laser over the low repetition frequency laser. And while some of the paints required a higher number of scans, still no damage to the original surface was observed. On first sight, the black paint appeared to have been fully extracted at all wavelengths, but upon irradiation with the NdYAG laser, the stone surface was seen to have lost its gloss (Figure 5.1-2). This problem was resolved with one of the working practices of the CuBrVL (Figures 5.3, 5). The other graffiti paints interacted with the different wavelengths in a similar way as in the case of the limestone. After the treatment with both of the lasers, colour remnants were observed that could have been caused by the high degree of adhesion of the paint to the stone surface. The results are summarised in Table 2.

Laser	Black	White	Green	Blue	Red
Nd:YAG 1064 nm	D	G	M	M	M
Nd:YAG 532 nm	D	G	M	M	G
CuBrVL 510.6 nm	G	M	M	M	G

Table 2. Extraction levels for the graffiti paints on granite. Legend: G = good; M = medium; D= damage to the surface.

Marble

The marble showed the widest safe working range of fluences: 1-3J/cm^2 for 1064nm and 0.5-1J/cm^2 for 532nm. For the CuBrVL system, the damage threshold of the marble was found to be lower due to the high repetition frequency and the pulse accumulation. Some of the results are shown in Figure 7. The full diffuse reflection spectra are shown in Figure 8.

Again, the different graffiti paints exhibited similar optical properties when interacting with the three wavelengths, as in the case of the limestone and granite. The micrographs show that the level of extraction of the black paint was good for all wavelengths (Figure 7.1-3). The red paint was well extracted when irradiated with the green wavelengths (Figure 7.11-12). The green and blue paints were not easy to extract fully (Figure 7.4-9). This might be due to the level of adhesion of the paint to the stone surface. In terms of a more uniform cleaning of the surface, the CuBrVL produced good results (Figures 7.3, 6, 9, 12, 15). The cleaning was smooth and gradual. Keeping the fluence constant, it was able to remove the paint layer by layer through supplementary scans. The exception was the white paint. Even when applying higher fluence, the damage threshold of the marble was exceeded and the paint layer was not removed at all (Figure 6.15). The results are summarised in Table 3.

Laser	Black	White	Green	Blue	Red
Nd:YAG 1064 nm	G	G	M	M	M
Nd:YAG 532 nm	G	G	M	M	G
CuBrVL 510.6 nm	G	D	M	M	G

Table 3. Extraction levels for the graffiti paints on marble. Legend: G = good; M = medium; D = damage to the surface.

Conclusions

The potential of two systems for the laser cleaning of graffiti paint on various stone surfaces was demonstrated. For different stones and paints, different wavelengths and working practices should be applied where appropriate. For the first time, the potential of the CuBrVL for graffiti removal was demonstrated. The main advantage of the CuBrVL over the conventionally

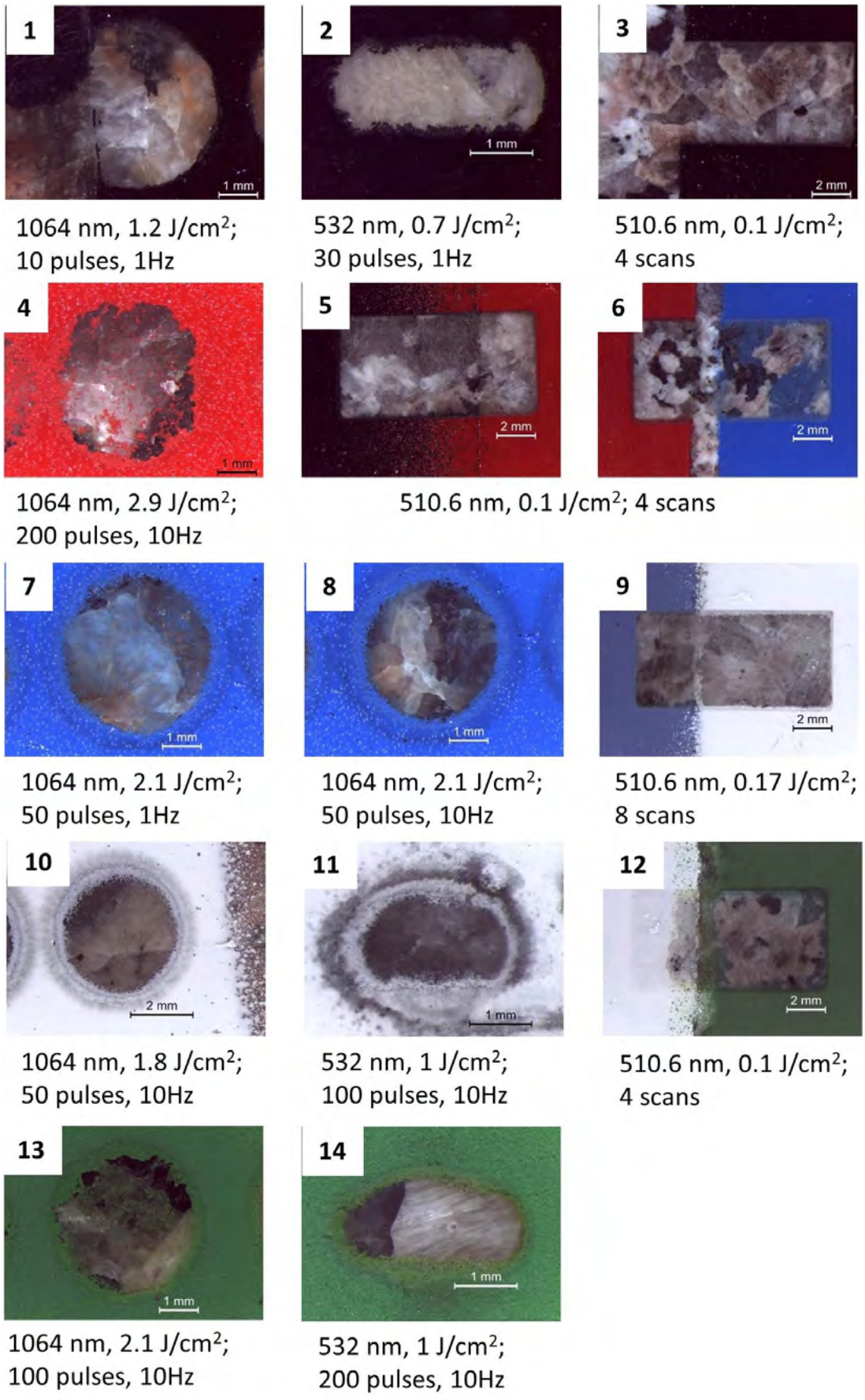

Figure 5. Micrographs of the laser cleaning of graffiti paints on granite.

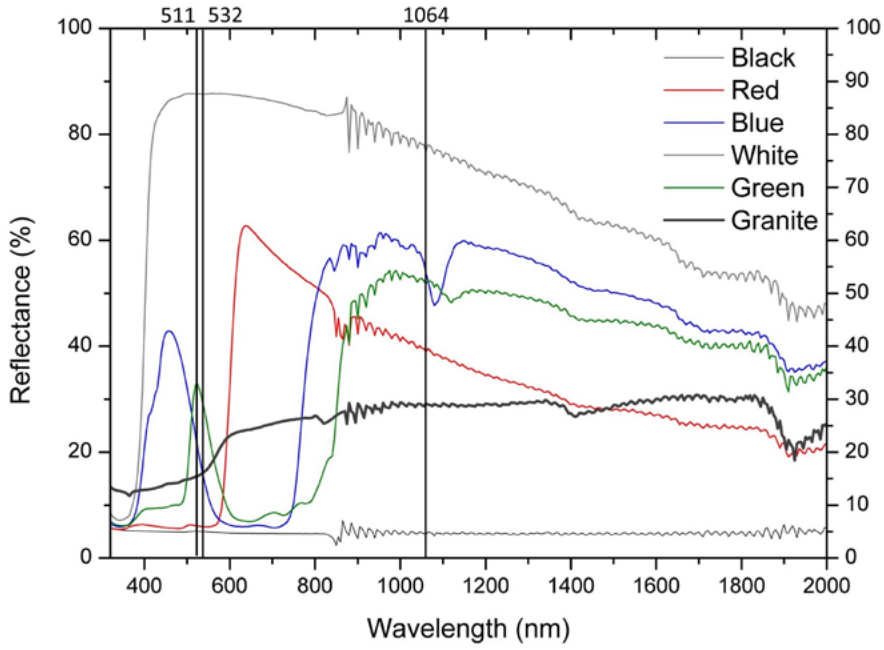

Figure 6. Reflection spectra for the different paints and the granite.

used Nd:YAG laser is the high repetition frequency of the pulse and the possibility of scanning the beam over the treated surface at a constant velocity. This guarantees the fast and uniform removal of impurities from large areas. The process is controllable as it provides smooth removal (layer by layer) of the unwanted material. This is a prerequisite for the optimal and safe restoration of cultural heritage objects.

The difficulty of removing paint is caused by the properties of both the stone and the paint. Some paints exhibit a high level of adhesion to the stone surface, while others are able to penetrate the surface of the stone if its porosity is very high, as in the case of the limestone.

Acknowledgments

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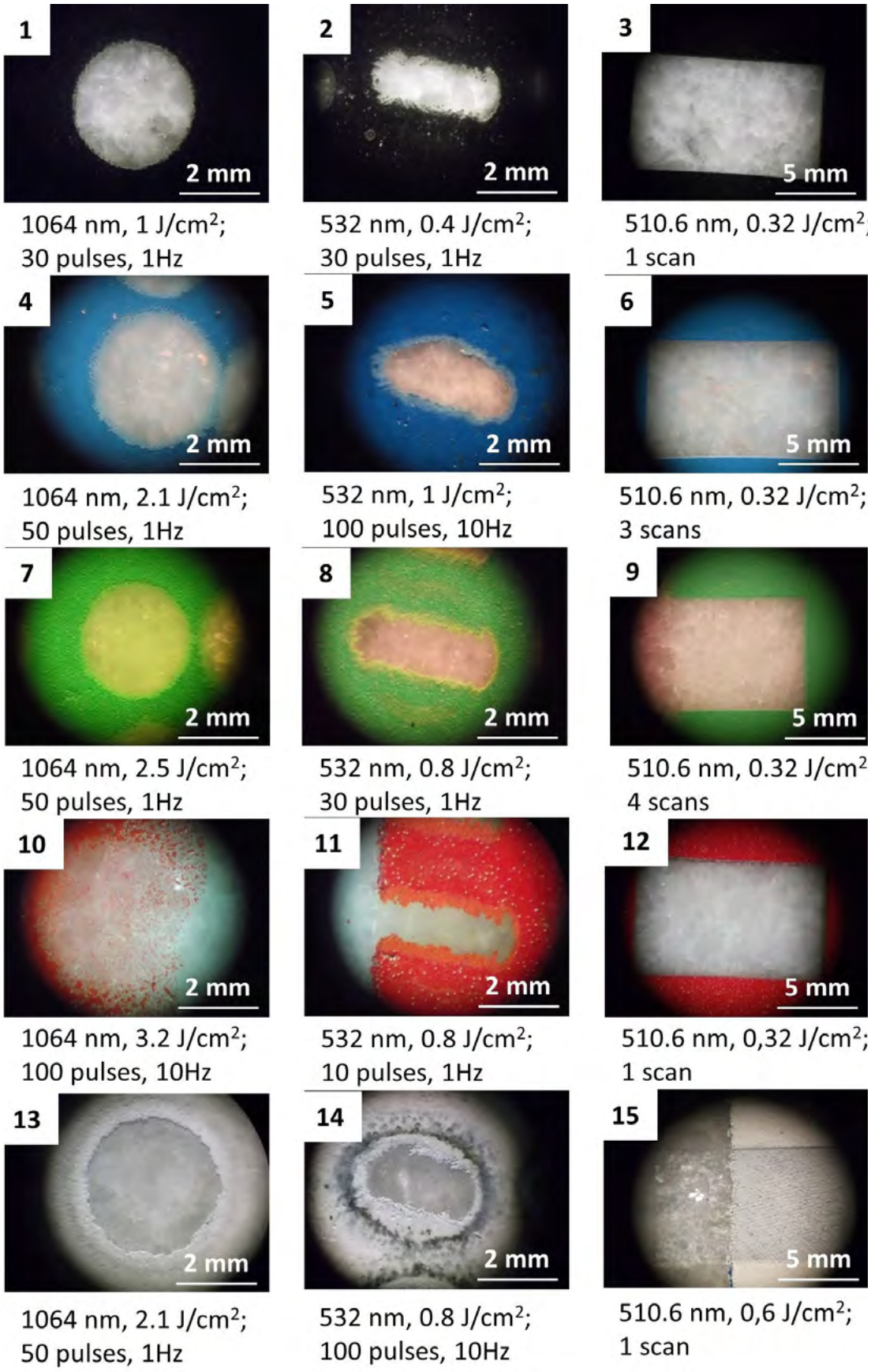
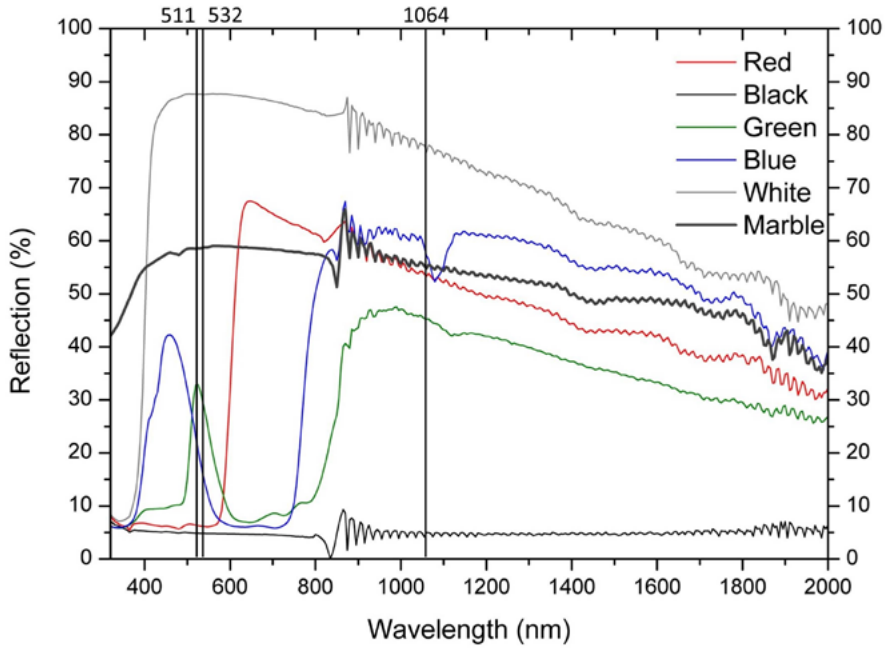


Figure 7. Micrographs of the laser cleaning of graffiti paints on marble.



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Cultural Heritage Disinfection by Irradiation

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Abstract

Throughout its hundred-year history, the applications of radioactivity have undergone constant development and consolidation. The biocide effect of radiation is today used in the sterilisation of medical devices and the disinfection of food at an industrial level. The disinfection of cultural artifacts is an extension of this industrial application and one that exploits all the advantages of this mature procedure. The reluctance to use this treatment among conservators was in the past based on an insufficient knowledge of the side effects of irradiation, as well as the lack of a unified and critical view of this field as a whole and a language that was comprehensible by all actors involved in the application of this interdisciplinary approach. These shortcomings now belong to the past thanks to a recently published book by the International Atomic Energy Agency – Vienna (IAEA) (IAEA 2017). This paper places irradiation disinfection among other well-known applications of radioactivity, explaining the biological effects, listing its pros and cons, and providing treatment examples.

Keywords: cultural heritage (CH) irradiation treatment, CH mass disinfection, IAEA publication on CH.

Radioactivity – a milestone in basic and applied physics

At the end of a romantic 19th century, by which time science had already proved itself to be the development engine of society, the world took note of two sensational discoveries: *X-ray* (Roentgen, 1895) and *Uranium spontaneous decay* (Becquerel, 1896). In both cases, invisible rays were involved, and these mysterious energy-bearing entities were able to pass through opaque material barriers, revealing the hidden structures within. These highly stimulating findings almost instantaneously found applications in medical imaging and as a means of providing a new perspective on the structure of matter. The scientific and technical effervescence in the years to come was unprecedented. *Science* published 23 new papers on medical imaging in 1896 alone (Natale 2011). Spontaneous decay was also observed in other chemical elements. This phenomenon was called *radioactivity* (Berkley Lab, https://en.wikipedia.org/wiki/Marie_Curie#cite_note-5).

The discovery of radioactivity had huge theoretical and practical consequences.

However, in order to be able to understand the applications of radioactivity, it is first necessary to explain the meaning of certain terms and phenomena.

- *Radiation* is the name given to the energy that is emitted and which travels in waveform. The same name is sometimes used to described the emission phenomenon itself
- *Ionizing radiation* is radiation with a higher energy than the energy of chemical bonds, which is a few eV. X-ray, gamma radiation and accelerated electrons (commonly termed EB – electronic beam) are examples of ionizing radiation. Radiation with an energy level greater than 10eV is conventionally considered to be ionizing radiation
- *Irradiation* is the name given to the interaction between radiation and a substance. The primary result of irradiation is an *energy transfer*
- What happens to the irradiated substance after the transfer of energy depends on the type of substance, more precisely on the nature of its chemical bonds
- *Inorganic substances* dissipate energy transferred by irradiation through heat and without any structural consequences. This is the case with metals, stones, ceramics, glass and inorganic pigments. In these materials the chemical bonds are electrostatic or metallic in nature. However, the irradiation of gems or glass is accompanied by a reversible color modification
- Many cultural artifacts are made out of organic substances, e.g. wood, leather, paper, textile etc. In *organic substances*, the predominant chemical bonds are covalent in nature. These bond types may be irreversibly broken by irradiation. By exceeding a certain dose, irreversible modifications to the structure take place, followed by modifications of the physical and chemical properties
- Radiation has a *biocide effect* on living creatures. This gives rise to various important applications

- The magnitude of all types of effect (physical, chemical or biological) depends mostly on the quantity of energy transferred during irradiation. This energy transfer is (correctly) called *absorbed dose* (D), but also *irradiation dose* or simply *dose*. The absorbed dose is the energy absorbed by the mass unit during irradiation or that transferred from the radiation to the mass unit of the irradiated substance. The unit used to measure dose, called a Gray (Gy), is defined as: $[D]^{SI} = 1Gy = 1Joule/kg$.

Applications

Irradiation has many important applications of the widest social interest. The best known of these and those with the greatest impact are briefly described below.

It is today impossible to imagine the field of medical diagnosis without the use of *medical imaging* in almost all areas. The benefits consist of both highlighting discontinuities (broken bones, tumors, etc.) and measuring metabolic processes (thyroid functionality, early cancers, etc.). Advances during its hundred-year history have seen the field of radiography develop complex applications such as the NMR, CT scanning, angiography and PET-CT technologies we see in use today.

The use of ionizing radiation in cancer therapy began in 1909 with the foundation of the Institut du Radium in Paris. This method is used extensively today under the generic name of *radiation therapy*. It makes use of different types of radiation, including X-ray, electron beam and proton beam, and, most widely, gamma radiation produced by Cobalt 60 radioisotope.

The ability of ionizing radiation to modify chemical structures and suppress contaminating microorganisms has extensive economic applications today. Indeed, industrial processes involving radiation crosslinking, grafting, polymerisation and chain scission are in use all over the world. Irradiation sterilisation, recommended by the European Pharmacopoeia (Council of Europe 2014), is used for more than 50% of the medical devices on the market. The microbiological control of foodstuffs is also used extensively in some parts of the world. *All these treatments are applied on a large scale in industrial facilities.* The generic name for all of these applications is *radiation processing*.

The most commonly used radiation types for the above applications are gamma radiation, accelerated electrons (electron beam) and X-ray. Medicine and industry are some of its better-known end users.

It should be noted that *nuclear analytical techniques* (NAT) are also based on irradiation. These techniques, which make up a complex scientific area of the greatest importance for archaeometry, are not discussed in this paper. A comprehensive review can be found in (Bradley and Creagh 2006; Creagh and Bradley 2000; Mackova *et al.* 2016).

Biocide effects

When living entities are irradiated, *biological consequences* may appear.

The study of the irradiation effects on living organisms began during the same effervescent pioneering period mentioned above. The ability of radiation to treat skin diseases caused by bacteria and fungi was noticed at the same time as the hair loss and the skin and eye damage resulting from its careless use (Kathren and Ziemer 1980). Today, the scientific basis has been established and correlated with the progress made in biology, where new notions, like DNA, statistics, stochastic processes, etc., have appeared.

The *biocide effect* of the irradiation of living entities is complex in nature and governed by statistics. Even a brief overview of the biocide effect must take into account the internal structure and the organisational levels of the living organism.

Cellular level

Although all cell components are affected by the transfer of energy, the irradiation effect that matters most at the cellular level is DNA breakage. This modification impedes cell division. This explains the irradiation biocide effect in mono-cellular organisms like bacteria and fungi.

System level

More evolved living creatures contain specialised groups of cells organised into tissues and organs. In a complex living system there are many complex interactions at work on the inside, as described by physiology, and the irradiation of complex organisms produces not only the aforementioned cellular-level effects (DNA breakage), but also certain physiological modifications. These changes may lead to the ruin and death of the organism.

Finally, while some entities (cells, tissues, organisms) are irreversibly damaged, others are able to recover thanks to healing mechanisms.

As in engineering, the more complex a device is, the less reliable it is. This can be seen below by comparing irradiation doses at which the biocide effect is obtained on different living entities.

Taking into account the variability of living organisms, the biocide effect cannot be defined quantitatively

using a threshold value of the radiation dose, but, rather, statistically. For microorganisms, D_{10} – the dose at which 10% of the microorganisms survive – is used. Obviously, by using a dose equal to two D_{10} only 1% will survive, by using three D_{10} only 0.1% will survive, and so on, in a logarithmic dependence. For more complex organisms (where it is not possible to use statistics) LD50% – i.e. a Lethal Dose 50% – is used, this being that dose that provokes death in 50% of the irradiated subjects. The same concept is used to define the poisonous power of chemicals.

Most types of fungi and bacteria have D_{10} values of less than 1kGy. It is important to know these values when it comes to the radiation sterilisation of medical devices.

Human radio-sensitivity is a topic of great interest to medicine. When performing any intervention on human subjects, the key principle is *primum non nocere*. In imaging, for instance, where a certain dose is applied to identify an anomaly, it is important to know the effects that dose will have on the irradiated organ, on nearby organs and on the organism as a whole. When fighting tumors, it is important to apply the necessary dose locally and in several stages, so that the tumor cells are eradicated in stages and the organism as a whole is able to recover after each intervention. There is a great difference between full body irradiation and local irradiation. Different organs have very different levels of radiosensitivity. And irradiated subjects may react very differently, depending on age, sex and other factors. Moreover, some crucial information, especially in relation to limits, is obtained in the wake of accidents, which are of course rare. This is why procedures and regulations are constantly improving. For all these reasons, the corpus of knowledge in radiology is huge and any LD50% value has to be defined.

However, in any comparison of the biocide effect between less complex and more complex living creatures (for example, microorganisms and humans), it is necessary to use a LD50% value. So for this reason alone, we should note here that in cases of irradiation accidents, 4-6 Gy as a whole body irradiation could be a fatal dose for humans.The results of the studies performed on humans can be extended to all mammals.

There are not many studies of other complex living creatures – the exception being a few older global studies on insect radiosensitivity and a great number of practical interventions in the field of cultural heritage preservation. All of these established a treatment dose of max. 2kGy when the unique biodeteriogens are insects. This dose has stood the test of time and proved to be efficient.

In practice, conservators/restorers have to deal with many biodeteriogens, mostly insects and fungi, at the same time. The treatment dose for fungi is 8+/-2kGy. In terms of efficiency, knowing that for fungi D_{10} = 1kGy, the treatment dose of 6 kGy (minimum value of the recommended interval) leads to a reduction of at least one million (10^6) in surving fungi. At a treatment dose of 8+/-2kGy, side effects are negligible for most of the organic materials artifacts are made of. Ancient DNA is not compromised.

Two large-scale industrial applications make use of the biocide effect: *sterilisation* and *biological control.*

Sterilisation is the process of completely eradicating all microorganisms present on and inside an object. Sterility is necessary for the medical devices or pharmaceuticals used in direct contact with bodily fluids (syringes, catheters, perfusion sets, surgical tools, implants, some bandages drugs applied on nasal mucosa or directly to the eyes, etc.). Sterile objects are kept in sealed packaging.

Biological control is the process of reducing the level of microorganisms on and inside an object. Also called disinfection, it is mostly applied to certain foodstuffs, pharmaceutical raw materials and cosmetics. We live in a state of cohabitation with microorganisms. They are present in our environment and even in our digestive systems. But the presence of too many microorganisms in our body is dangerous. Some specific microorganisms can lead to illness or even death. That's why their presence needs to be controlled.

There are some minor differences between the industrial applications described: technically, the applied dose and packaging requirements are different; and from a procedural point of view, the validation stage is much more elaborate for sterilisation.

Radiation processing in industry and cultural heritage preservation

The manufacturing processes adopted in medicine and the food industry come with great responsibility. These processes are studied extensively to identify the right steps and proper equipment, to evaluate the consequences of any modifications to the process parameters, and to control risk. As a matter of necessity, these processes must be 'validated', even if in some cases (such as sterilisation) validation is very complicated. All of these provisions form part of special international standards. Compliance with the applicable standards for each manufacturer is verified by third party organisations. Without certification by one of these organisations, the manufacturer is not allowed to operate on the market.

It should be noted that while the biocide effect of irradiation was discovered more than 120 years ago,

its use in industrial applications began only around 60 years ago. Other applications, like medical imaging, became almost instantaneously widespread after the discovery of ionizing radiation. With *radiation processing* there was a long accumulation period. This maturation period gave rise to a field with very solid scientific and technical foundations in keeping with the responsibilities that came with it. This had the following consequences:

- The radiation sensitivity of microorganisms gave birth to a new scientific field called radiobiology
- Knowledge of irradiation effects and the testing of different materials has developed significantly, with cellulose and cellulose-based materials like paper having been studied extensively, given that herbs, spices and cotton are among most irradiated materials, both in the sterilisation of medical devices and the biological control of foodstuffs
- Specific standards and guidelines have been developed covering facility design, process reliability, safety, installation and exploitation, quality assurance and quality control
- All applications of radiation processing use industrial equipment that has been carefully designed, constructed, managed, surveyed and certified by a third party body
- The quality management system involves the keeping of written documents to demonstrate good manufacturing practice. It involves working according to approved technical procedures, the proper training of people, the calibration of measuring instrumentation, risk assessment, etc.
- Special care is paid to the measurement and verification of the dose. The dosimetry system used must have traceability to an international reference laboratory and be subject to frequent international inter-comparison exercises.

In the case of sterilisation and microbial control, irradiation is inevitably applied at the same time to *the contaminant microorganisms* and *the object*. The aim of irradiation is to achieve the biocide effect without any or with acceptable induced physical or chemical changes in the product. The applicable standards take both these aspects into account.

We find the same situation in the case of contaminated cultural heritage (CH) artifacts: the same association – between object and biodeteriogen – which cannot be separated; and the same rigor in respect of the chosen treatment, i.e. to eradicate the biodeteriogens without any physical or chemical modification of the objects.

- There exist similarities between irradiation sterilisation and CH decontamination in terms of *treatment purpose*, i.e. annihilation of bio-contaminants, and *additional requirements*, i.e. not to damage the treated objects. In both treatments, the same technology is used in terms of *equipment*, *rationale*, *control methods* and *management system*

All of this qualifies irradiation as a trustworthy and valuable CH disinfection method. Minor adaptations are required at the level of technical procedures. Adopting an industrial technology means adopting its values. In other words, by using irradiation for CH disinfection, the intervention process will be *safe*, *controlled*, *reliable* and *efficient*.

The particularities of cultural heritage disinfection by irradiation

The *advantages* of disinfection by irradiation, based on good practice in industrial facilities, are listed below. The radiation disinfection of CH artifacts is *safe* in every sense of the word.

- There is no risk for the artifact if the treatment is performed using proper equipment with proper credentials and using the correct treatment dose. Very few materials are sensitive to the treatment doses
- The artifacts do not become radioactive. This technology does not leave any residue in the treated artifact or cause any damage to the environment. There is no risk to the restorer, curator, museum visitor or the environment
- There is no risk to the facility operator. Radiation decontamination is performed in a confined and protected area called an irradiation room in which humans are not allowed to be present during irradiation. Radiation processing uses equipment that can only be used under strict safety conditions. Its design, construction and operation are all regulated

The reliability and total control of the radiation treatment are among its most important advantages. These are consequences of the fact that decontamination is controlled by a unique process parameter, i.e. the absorbed dose, which can be calculated, delivered, measured and certified with confidence.

- The dose is calculated using simple mathematical formulae based on the installed radioactivity, the distance between source and object, and object density. There are no other dependent factors. In alternative decontamination techniques based on gas or temperature diffusion, the effectiveness is determined by the type of material and the degradation level of the artifact's inner structure. Industrial irradiators

are obliged to dose-map the irradiation room. This is very useful in the treatment of oversized artifacts. In some facilities dedicated to cultural heritage, the whole treatment is designed using refined dose calculations
- In industrial facilities cultural heritage artifacts are properly treated. Here the dose is delivered in a very simple, unequivocal and repetitive manner
- Dose measurement is performed using trustworthy dosimetry systems. Specific ISO standards are used in their creation and utilisation. Establishment of the traceability of the dosimetry system in use to an international reference laboratory is mandatory for any industrial irradiator. It is also mandatory for an industrial facility to perform a dose-mapping of the irradiation room. Dose in air is measured in various 3D positions used as working places. It is also known how the density and shape of the irradiated object modifies the irradiation field
- All of the above actions and proven knowledge form key parts in the certification of the QMS (quality management system). The QMS certification of an irradiator is public information. The certificate is issued by a third party body following an audit.

In practice, calculations/estimates/evaluations help in establishing the radiation geometry and other details. To improve the homogeneity of the applied dose, the irradiation process may be interrupted to allow for modification of the irradiation geometry and then restarted. The applied dose is cumulative.

Finally, verification by measurement is performed. This involves measuring the doses actually applied to the artifact using dosimeters attached at selected spots.

The treatment *efficiency* is extended to the entire inner volume of the artifact. This is possible because of the excellent and predictable penetration of gamma radiation. Alternatively, any gas efficiency (including anoxic treatment) is limited by diffusion.

With the irradiation parameters being inherently the same, efficiency remains constant in time.

Other *advantages*:

- The treatment is performed at room temperature
- The artifacts can be treated without being removed from their transport packaging, reducing the risk and inconvenience of manipulation
- The method is suitable for mass treatment. It acts on all biological aggressors simultaneously. Oversized objects, composite items and large amounts of artifacts can be treated at the same time
- Treatment duration is short in industrial facilities, i.e. days or hours.

The *disadvantages* of the irradiation disinfection of CH artifacts must also be mentioned, even if they are not necessarily intrinsic or specific:

- Irradiators cannot be moved
- Access to industrial irradiators is sometimes difficult to obtain. Non-standard orders are not welcomed, especially those requiring careful handling. A compromise must be found to ensure that artifacts are properly manipulated inside the facility. End-user involvement could be such a compromise.
- Access to industrial irradiation facilities generally requires forward planning. This stands in contradiction to the needs of the artifact, especially when emergency interventions are required.

We should note a type of malpractice that results from well-intentioned efforts to overcome these disadvantages – the use of inappropriate equipment. Medical and industrial imaging facilities and those used in medical (cancer) treatment are totally inappropriate for CH disinfection. By using such facilities, all of the aforementioned advantages can turn into disadvantages, i.e. the treatment will be inefficient because it is not possible to obtain a sufficiently high dose; safety will not be ensured at the aforementioned high levels; the difference between the minimum and maximum applied dose may be huge and impossible to improve, and, worst of all, the treatment cannot be controlled because these irradiators do not use a dosimetry system.

As a rule, only facilities meant for radiation processing are properly designed for use in CH disinfection. These are called *panoramic irradiators.* The overwhelming majority are industrial facilities with a certified quality system including a trustworthy dosimetry system.

Side effects

Given its so many advantages and so few disadvantages, it is strange that irradiation disinfection is not used to its full potential. The most important concern among CH stake holders, especially conservators/restorers, is the irradiation side effects that can affect integrity and aging speed of the treated artifacts.

The scope of this paper does not allow us to discuss such issues, which anyway are dealt with elsewhere (IAEA 2017: 61-91). However, the conclusions in this respect are rather favorable. Correctly applied, this treatment has no serious side effects on most artifacts.

Caution is a natural and ethical response where there is a lack of information concerning the pros and cons. For various reasons, there was not an abundance of scientific research into the side effects of CH irradiation. And while recently the situation has improved, it must be noted that most of these papers are published in journals or by publishing houses less frequented by CH stake holders.

Reluctance among conservators versus worldwide applications

Over time, conservators have also shown reluctance on grounds other than those relating to side effects. There has been a lack of a critical overview of the field as a whole as well as a language that is comprehensible by all actors involved in this interdisciplinary approach. Subjective perceptions, in terms of subliminal associations with nuclear accidents and radioactive contaminations, must also be taken into account.

In spite of all this, there are certain circumstances where, when it comes to cultural artifacts, disinfection by irradiation is the method of choice and its true practical value comes to the fore.

Some circumstances that led to the use of disinfection by radiation are presented below.

- *Emergency intervention/mass treatment*; examples: Romania – flooding of the National Film Archive (IAEA 2017: 131-135); Brazil – flood-damaged books (IAEA 2017: 197-201); Croatia – artifacts salvaged from bombed buildings (IAEA 2017: 191-196); Poland – shoes from the Majdanek concentration camp (IAEA 2017: 159-162); USA – the medical archives of the Johns Hopkins University (Wellheiser 1992; Alan Mason Chesney Medical Archives 1984)
- *Interventions on objects with complex structures;* examples: France – Ramses mummy (IAEA 2017: 117-119), Chroma baby mammoth (IAEA 2017: 137-140)
- *Interventions on large objects/assemblages;* examples: Romania – church iconostases (IAEA 2017: 141-147; Figure 1), giant wooden statues (IAEA 2017: 179-189; Figure 2); Holland – Peace Palace Library (IAEA 2017: 113-115); Tunisia – ethnographic collection (IAEA 2017: 203-206)
- *When traditional methods cannot be applied;* example: when a gas chamber for use in CH is not available, Romania;
- *When the cost/benefit ratio must be low;* examples: Romania – wooden icons from parish churches, wooden iconostases, raw materials (IAEA 2017: 179-189).

Figure 1. Iconostasis of the church in Izvoarele (Prahova County, Romania) disinfected by irradiation (courtesy of IFIN-HH)

Figure 2. Giant wooden statue disinfected by irradiation (Nicăpetre Cultural Center, Brăila Museum, Romania; courtesy of Brăila Museum and IRASM, IFIN-HH).

Conclusions

The irradiation disinfection of heritage artifacts represents an extension into the cultural field of mature technologies that have already been used in the medical industry for the last half century. It is safe to use for all involved actors, offering total control and efficiency. If access to a proper facility is obtained, irradiation treatments can be applied without restriction.

Irradiation disinfection was for a long time considered exotic, if not also disregarded as dangerous and possibly associated with nuclear accidents. Several factors contributed to this erroneous perception: insufficient knowledge of the possible side effects, a lack of critical overview of its application, a lack of understanding of its physical, biological and ethical bases by all participants, and a subliminal fear of the nuclear field. There are hopes that the recent publication entitled *Uses of Ionizing Radiation for Tangible Cultural Conservation* (IAEA 2017) will help fill the knowledge gap and encourage acceptance and use of this promising radiation processing technique.

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Nuclear Techniques in Preservation Treatments of Archaeological Organic Materials and How to Take Archaeological Studies into Account When Applying Them

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Abstract

In Grenoble, France, nuclear techniques used in the preservation of cultural heritage artefacts have been in development since the early 1970s. Radio-curable resins were first used in the consolidation of dry porous degraded material before going on to be used to save waterlogged archaeological wooden artefacts. Another application was to use ionizing radiation to destroy insect and fungus attack. Both gamma ray biocidal treatments and radiochemical consolidation (the latter known as the 'Nucléart technique') are still in use today. These regularly offer appropriate solutions in the conservation of historical artefacts and archaeological items. But one question still remains: are there any consequences of applying these 'nuclear' treatments for further analytical studies? This paper provides a review of these techniques, discussing some older and more recent examples in which they are applied in conservation projects, being also compatible with and improving analytical study programs.

Keywords: cultural heritage (CH), irradiation and DNA information, CH irradiation side effects, CH irradiation disinfection and consolidation.

Introduction

The preservation of heritage is a duty to future generations. It involves the compilation of knowledge about heritage in its different forms, tangible and intangible, and the preservation of the physical items themselves.

Ancient remains can convey a lot of interesting information, thus increasing our knowledge of heritage. Archaeologists and historians collect this information through studies. From time to time, they are helped by specialists in one specific field of investigation or another. For instance, through an analysis of their chemistry and their biology, organic materials are able to provide a lot of interesting and detailed information for use by archaeologists.

On the other hand, when it comes to tangible cultural components, physical preservation is mainly taken care of by conservators/restorers. But as some heritage materials are very unstable, this may require the use of powerful methods, including non-traditional ones like nuclear treatments in which conservators have not been trained. Like archaeologists, they may require the help of specialists. Owing to their chemical and biological sensitivity, organic materials are among those items that call for the use of such techniques.

Gamma radiation has been used by ARC-Nucléart as a tool in the preservation of cultural heritage since the 1970s (Coeuré *et al.* 2000). This pioneering treatment, the so-called Nucléart technique, used radio-curable resins to consolidate wooden elements – first, a historic mosaic parquet, and then polychromed or uncoloured sculptures (Detanger *et al.* 1976b). This provided evidence that the biocide treatment of a heritage item could be achieved by direct exposure to ionizing radiation. This treatment was then proposed and applied in respect of the most modest to the most prestigious collections, including the famous mummy of Ramses II (de Tassigny and Brouqui 1978; Balout and Roubet 1985). At the same time, the systematic excavation of a medieval site near Grenoble provided a very large collection of waterlogged wooden items that required treatment in order to avoid collapse during drying. Nuclear techniques using radio-curable resins were similarly proposed as an original and efficient solution in the treatment of such unstable materials (Detanger *et al.*1976a). It should be noted that in all these pioneering works, organic materials were used.

However, these 'nuclear' techniques often raise concerns. Beyond any irrational fears or rejection as a matter of principle, legitimate concerns about the side-effects of the ionisation of irradiated material have been expressed. In fact, from this procedure as from any other active process, it is impossible to expect total harmlessness. Changes caused by gamma radiation are always possible, even if experience has shown these not to be particularly significant in practice. However, organic substances often include fragile molecules,

sensitive to ionizing effects. Any possible secondary effects are usually described in terms of the integrity or appearance of the material. But it is also useful to speculate as to whether the radiation can affect the informational content of an artefact that may be studied further after treatment.

This paper will focus on the conservation of organic material using nuclear techniques. It will present the main aspects of treatments using gamma rays, their advantages and limitations. But it will also address the question of how to manage the twin objectives of conservation, i.e. the material conservation of the item and the study of said item in order to increase our knowledge of it.

Biocide treatments using gamma rays

A tool for the biocidal preservation of cultural heritage

Gamma irradiation is widely used for its biocidal effect in sanitary applications, including the sterilisation of medical devices (IAEA 2008) and in the pharmaceutical and cosmetics (Katusin-Razem *et al.* 2003) and even the food industry (International Consultative Group on Food Irradiation 1999). Its many advantages, such as high efficiency and excellent reliability, not to mention the very few secondary effects on artificial or natural (biological) organic material in terms of the efficiency of the biocide effect (Alcaraz *et al.* 2016), often makes gamma irradiation the first choice when it comes to sanitary applications. The principle, sometimes called 'cold sterilisation' (Głuszewski *et al.* 2011), can also be used for insect eradication in cultural heritage. The biodegradation of the natural organic material found in heritage objects is one of the most important factors in their decay. The biocidal effect of gamma radiation is well suited to containing biodegradation: thanks to its penetrative abilities, particularly dangerous pests such as insects and fungi are easily eradicated from the entire volume through simple exposure to gamma rays. The dose used depends on the target organism. While 4-5Gy will cause death in humans in a deterministic way and 25kGy is the regulation minimum dose for medical sterilisation, 500Gy is required to kill insects whatever their life stage (Bletchy and Fisher 1957; Bakri *et al.* 2005), and between 3 and 10kGy will statistically reduce the more resistant fungi and their spores to at least a blank level (Moise *et al.* 2012; Michaelsen *et al.* 2013).

This contactless technology complies very well with the deontological concept of minimum intervention, being able to achieve the required conservation for a very low impact. The ability to treat *en masse*, even through packaging, and the absence of an associated thermic effect are two other desirable qualities. But once again, as in its sanitary applications, it is clearly its reliability, together with its efficiency, that distinguishes gamma irradiation from other techniques. Its reliability derives from the ability of gamma rays to penetrate the entire volume, but also from the ability to ensure, by means of measurement and calculation, that biocidal conditions are effectively achieved throughout the entire volume.

Of course, gamma rays do not produce any radioactivation or other residues in the processed material. Consequently, it is only curative and does not have any preventive effects. For this reason special care must be taken to ensure the item does not become re-infested (this is the aim of preventative conservation and this should immediately follow any treatment).

The compatibility of gamma irradiation with materials encountered in cultural heritage conservation

Compatibility is of course a matter of dose, but few materials come with contraindications regarding irradiation at disinfestation doses. The integrity of the cultural heritage artefacts is the first thing that should be checked before undertaking irradiation treatment. Its external appearance is the second.

There is an a priori risk of radiolysis effects in some materials. For example, it has been observed that with high doses, resulting in the breaking of bonds and molecules, this can cause the materials to become more brittle, as can also happen with excessive exposure to light or UV. Cellulose, which is surely the most widespread natural polymer, has long been known as one of the most chemically sensitive compounds to radiation (Charlesby 1955), leading to measurable depolymerisation at doses of just a few kGy, even if this does not directly affect its firmness at these doses. Furthermore, there is a lot of interest in the use of this method in the treatment of archives as an alternative to oxide ethylene fumigation, the use of which tends to be prohibited or severely limited by law because of its side effects on human health and the environment. Finally, in terms of the conservation issue, treatment by ionizing radiation at last appears to have been accepted in many cases (Bratu *et al.* 2009; Choi *et al.* 2012; Magaudda 2004), being less invasive than alternative chemical or physical methods, or less dangerous (for the items in question) than simply 'doing nothing' (Havermans 2011).

Other natural organic cultural heritage materials include wood, leather, parchment and textile fibres. Most of these would appear to be less sensitive to ionizing radiation than pure cellulosic material. Wood has been reported to handle doses of irradiation of up to 100kGy with no significant loss of integrity (Divos and Bejo 2006; Severiano *et al.* 2010). In the case of leather, hide, fur and parchment, doses of around 20-30kGy appear to be broadly sustainable (Chahine and

Vilmont 1988; Numes *et al.* 2012), even if the properties of hydrated collagen, such as shrinkage temperature and reduced viscosity, are known to be sensible to such doses (Cooper and Russel 1969; Rooney *et al.* 2008). While there is no much data available for textiles, cotton (Blouin and Arthus 1958), a cellulosic material, is thought to be more sensitive than wool (Millington 2000; Geba *et al.* 2014) or silk protein material.

Surprisingly, the only true category of incompatible materials is given not by organic materials, but transparent materials. Indeed, due to the modification of optical absorption after the creation of colour centers, glass and gemstones (Enokihara *et al.* 2007; Nunes and Lameiras 2005) can change colour in a more or less partially reversible way, even at low insecticide doses. This well-known phenomenon allows for the manufacturing of optical dosimeters from some transparent or dyed plastics after linking the optical density to the dose (Faraha *et al.* 2004).

It is only natural to wonder whether this behaviour can also occur in varnishes or binders whose function is to be transparent. However, in practice, the layers are thin enough that the superposition of colour centres is not sufficient to affect the optical properties and so transparency is preserved. This is one of the reasons why, according to numerous studies, the appearance of classic polychromic layers proves quite stable under irradiation (Negut *et al.* 2010; Rizzo *et al.* 2009; Yoon *et al.* 2015). As far as we know, at biocidal doses, no changes in the colour or any other features of cultural heritage artefacts involving the use of binders and varnishes have ever been detected, the same also being true of painted materials.

For a more complete review of the so-called 'secondary effects', and how these could result in contraindications, see the IAEA reference book (IAEA 2017).

Combining gamma biocide treatments and analytical studies of heritage

Biocide treatment, and more explicitly insect eradication, is the most popular application of gamma rays. Since the 1970s, thousands of cubic metres of cultural heritage artefacts have been treated, including furniture, wooden sculptures, ethnological objects, musical instruments, taxidermy specimens and modern art. In our workshop, in order to protect other collections we are working on from contamination, the insect eradication of any dry wooden artefacts requiring restoration is always the first step to be taken. This is very often followed by other actions, such as polychromic studies including pigment and binder identification performed by scanning electron microscopy and infrared spectrometry (Champdavoine 2006). No issues were ever encountered during analysis that had to do with the irradiation treatment undertaken previously.

Moreover, the fact of an item requiring treatment for pests has often been used as a pretext to carry out various studies. When the mummy of Ramses II arrived in France in 1976 to be treated for fungi, a long series of analyses and studies were undertaken to increase our knowledge of the mummy, including, for instance, neutron activation analysis to identify elemental traces of pigment in a sample of the mummy's red hair (Balout and Roubet 1985). All of these studies were performed before the treatment and before the gamma irradiation was proposed. Of course, after it was decided to apply this treatment, and in order to aid selection of the most appropriate technique, a second series of measurements were taken to verify the effects of irradiation on the constituent elements of the mummy (Balout and Roubet 1985), in particular the potential for any unwanted artificial aging. The gamma fungicide treatment of the mummy was then conducted in 1977 (de Tassigny and Brouqui 1978). In fact, as the treatment was only curative, it was decided to display the mummy in a transparent sterile box immediately after treatment in order to limit further contamination. It is clear that these sterility conditions cannot be compromised, even when undertaking subsequent analysis, something which will surely place a limit on further studies.

More recently, one notable treatment was that applied to a frozen baby mammoth named Khroma. From the outset, the idea was to perform not a conservation but a sanitary treatment, in order to protect those coming into contact with the item from any potentially dangerous bacteria. To this end, the frozen specimen was exposed to 20kGy dose of radiation, allowing for a reduction in any possible traces of *Bacillus anthracis* by a factor of at least 10^4. But the sanitary improvement of the item was not the only consequence of the treatment. Among other things, the treatment helped the scientists and conservators stop the very well preserved flesh of the specimen from decaying during the subsequent thawing periods required as part of an international scientific study (Lacombat *et al.* 2015a: Lacombat *et al.* 2015b). Indeed, the flesh was in such good condition that it was possible to conduct many other subsequent investigations. For example, the tracing and analysis of milk from the mother at different stages in the digestive system.

These examples, like the mummy and the ancient natural specimens, naturally raise the question as to the effects on ancient DNA analysis, which recently has become a very important source of knowledge for archaeologists and palaeologists. Since the desired biological effect is mainly the result of the action of the radiation on the DNA, the question of the behaviour of the DNA information is legitimate. However, from

a theoretical point of view, the number of lesions resulting from the treatment at the chosen doses should be relatively low (Cadet *et al.* 2002), i.e. in the order of one in one thousand base pairs for 1kGy, and even less for non-hydrated DNA. This will not, or only slightly, affect the quality of the ancient DNA information, with the fragment barely exceeding a few hundred base pairs. For example, it has been demonstrated in forensic studies that small fragments of DNA of around one hundred base pairs were clearly analysable after exposure to up to 100kGy and that in all the larger fragments investigated it was always possible to obtain a full DNA profile even at doses of up to 10kGy (Abbondante 2009). This is not so surprising if we consider that, unlike ethylene oxide, gamma irradiation at sterilisation doses as high as 25kGy is well known to be inefficient in cleaning materials used in DNA analysis, such as cotton swabs and micro-centrifuge tubes, so as to prevent contamination with extraneous DNA (Shaw *et al.* 2008). A case in point is given by the Qilakitsoq Inuit mummies, who were treated at 20-25kGy during the 1980s (Johansson 1989). Even if some were quick to say that the irradiation of these mummies will have irreparably damaged their DNA (Nielsen *et al.* 1994), the authors of interrelatedness mtDNA analysis undertaken 20 years after the irradiation treatment did not cite any difficulties potentially resulting from the prior exposure to gamma radiation (Gilbert *et al.* 2007). Finally, it is no longer surprising that the paleogeneticist in charge of the study of Khroma found a clean DNA even after irradiation (Lacombat *et al.* 2015b). Similarly, it can be assumed that the irradiation of the Ramses II mummy, at a time when DNA analysis was still not imaginable, did not reduce the chances of accessing the DNA information, as is so commonly believed. It should be noted that in many items commonly treated with ethylene oxide, the DNA was irreversibly damaged and rendered inaccessible to further DNA analysis (Michaelsen *et al.* 2013).

Figure 1. Gamma biocidal treatment of Khroma, a frozen baby mammoth. (a) as it was discovered in Yakutia in 2009 before being cleaned of permafrost residues (© P. Lazarev; reproduced with permission); (b) and (c) the taking of biological samples in an irradiation cell at ARC-Nucléart just before irradiation (© Avavian/ARC-Nucléart; reproduced with permission); (d) On display in a frozen showcase at the Musée Crozatier in Puy-en-Velay © Musée Crozatier; reproduced with permission).

Other issues relate to dating analysis. As there is no way in which irradiation can cause morphologic change, the wooden rings remain clearly accessible and the dendrochronology is obviously not an issue. The same is true of radiocarbon or other types of radioactive decay analysis, as irradiation does not induce any nuclear change. On the contrary, techniques such as radio-luminescence dating based on natural cumulative doses are completely distorted, as the dose in kGy is the equivalent to a natural dose of about one million years.

Finally, one area that is clearly affected is that of the 'living bio-information', given that the entire purpose is to achieve a biocidal effect. This was anticipated, for instance, before the baby mammoth Khroma was irradiated, by collecting samples in which old bacteria may have survived (Figure 1). These samples were passed onto to the Institut Pasteur, which collects such biological material.

Gamma radio-curing

A tool for the consolidation of cultural heritage artefacts

While biocidal power is the first property of ionizing radiation to be used in large-scale processing, there are many other applications in various processes (Ferry *et al.* 2016). For instance, the radiochemical power of gamma radiation is used to increase mechanical properties in some application on plastics.

In some cases, 'radio-curable' resins can also be used to consolidate a cultural heritage artefact in order to achieve effective and 'in the bulk' strengthening. This is usually referred to as the 'Nucléart treatment'. Indeed, ionising radiation can be used advantageously to control the polymer curing process, ensuring that this irreversible phenomenon does not begin before the objects have been properly cleaned of excess resin on the surface, as would be the case if chemical initiators were used. Styrene-unsaturated polyester resins are generally used. Both double bounds (C=C) from styrene and polyester open and react to crosslink, forming a stable 3-D solid inside the porosity of the material previously impregnated with the resin. Gamma radiation, thanks to its high penetrative power, allows for a homogeneous consolidation. It also facilitates, depending on the dose rate, the control of the crosslinking reaction kinetics and therefore the related exothermic phenomena (Tran *et al.* 1990).

To consolidate a dry and porous artefact, e.g. an artefact made of wood, impregnation is commonly conducted through a classic vacuum/pressure process to facilitate penetration, after which its surface can be wiped and irradiation used to harden the resin filling the micro-pores. This technique is known as consolidation by densification, as opposed to traditional consolidation techniques that use solvent to 'convey' a polymer into the material, leaving only a thin film of solid resin after evaporation. In fact, in the case of 'densification', all of the impregnated resin filling the porosity stays inside and becomes hard, participating in the reinforcement of the mechanical properties and allowing for a very effective consolidation.

If cleaning is properly conducted before the hardening stage, the resin will not be visible on the surface. However, depending on the wetting properties, the colours may be enhanced, as happens with a surface wetted by water. If not, the appearance of the object remains predominantly unchanged, but the physical and chemical properties obviously do not. Moreover, these changes are irreversible, meaning that the technique should be limited to cases in which a huge reinforcement of the mechanical properties is required, for instance to preserve the practical function of an object or when it is so degraded that other conventional treatments cannot be performed (the 'last chance' treatment).

This treatment can also be used to treat archaeological waterlogged wood. In immersion, or in a water-saturated environment, organic matter is protected from major aerobic biodegradation like fungus and insect attack. But a combination of anaerobic bioactivity and a hydrolysis phenomenon will cause loss of cellulose, such that the cell wall will no longer support the surface tensions arising during normal drying in air or in the vacuum pressure techniques used in impregnation. This results in irreversible collapse. It is for this reason that for decades double osmotic exchanges were used in order to impregnate the archaeological wood: as the resin cannot be dissolved in water, the water is gradually replaced in successive baths by acetone, and then the acetone replaced by resin before hardening by irradiation (Tran *et al.* 1990; Tran and Guinard 2009). Although still irreversible, this technique has noticeable advantages, particularly in terms of mechanical behaviour. It was also known to be one of the best methods whereby to conserve the initial volume. Moreover, it was very stable and to a large extent avoided the problems encountered in traditional alternative uses of a soluble but hydrophilic polymer like polyethylene glycol (PEG), including metal corrosion when associated with wood. But it was a complex, lengthy, dangerous and expensive technique. It is now preferred to treat waterlogged archaeological wood by classic freeze drying with a very low content of soluble polymer, and only then, if needed, to add a radio-curable resin, as in the case of a dry porous artefact (Chaumat *et al.* 2011). While we cannot claim that this process, sometimes called 'combined Nucléart treatment', comes with the full range of advantages in terms of conservation offered by double osmotic impregnation, it nonetheless clearly represents a

good compromise. It is very quick, lasting less than six months, sufficiently stable as long as the PEG content does not exceed around 20%, entirely safe and cheaper.

Combining radio-curing and analytical studies of heritage objects

As a first evidence, after applying this treatment, radiocarbon dating will clearly become impossible due to the irreversible presence of fossil carbon in the resin. It should be noted that chemical analysis can become very difficult and even impossible to perform in various cases. Firstly, some of the molecules may dissolve in the styrene-base resin. It is for this reason that, before performing this treatment on polychromed artefacts, it should first be checked that the styrene is not a solvent of some polychromic layer. The same applies in the case of archaeological organic remains, such as caulking on a shipwreck. If it is not, i.e. the matter being analysed presents no problems of compatibility, a consolidating resin may nonetheless mask some of the organic compounds that are trying to be identified. For example, with vibrational spectroscopy (infrared, ^{13}C nuclear magnetic resonance).

However, we can also raise doubts about many other techniques of consolidation, even if they are said to be 'reversible'. Is it really possible to clean samples treated with exogenous products including fossil carbon sufficiently such that the results of the radiocarbon analysis are not distorted or that no problems arise during spectroscopy measurement?

Conversely, it must be said that mineral matter will scarcely be affected by this treatment, meaning that it could still be possible to analyse it. Moreover, embedding media, including polyester resins very similar to our styrene-polyester resin, are often used to prepare samples for their characterisation. In such cases, samples from already impregnated items will not be a problem. This kind of embedding is usually done for MEB polychromic layer analysis.

However, where possible, it is always better to conduct the analysis, of whatever kind, before adding any given component, irrespective of whether or not it is considered reversible. In turn this could help us choose the best way to preserve a given item. For instance, before a conservation treatment was performed, a gun carriage from the 17th century Stirling Castle shipwreck (UK) was subject to an important characterisation program in order to assess the degree of wood degradation and the amount and nature of the corrosion compound inclusions, after which the Nucléart process was chosen to treat this problematic artefact (Tran *et al.* 2011).

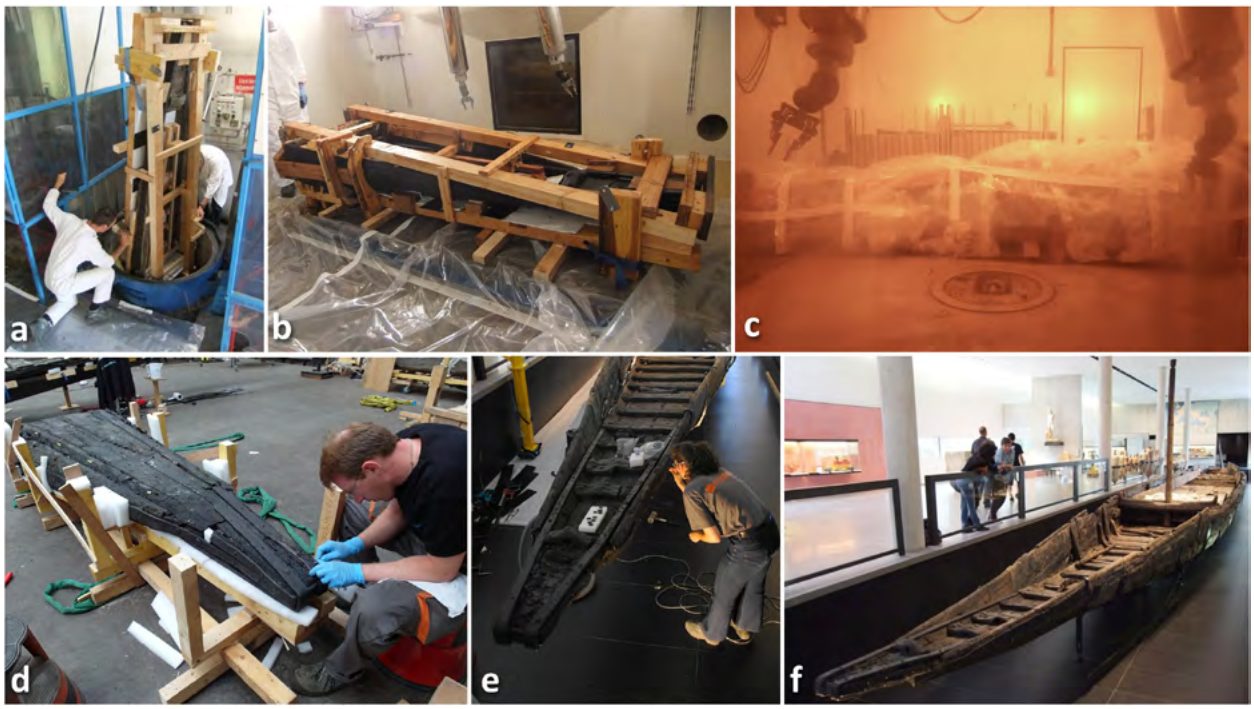

Figure 2. The Nucléart treatment of the prow of a Gallo-Roman barge excavated in Arles from the Rhone river. (a) the impregnation with styrene-polyester resin; (b) and (c) wrapping with tissues to absorb the excess resin prior to irradiation; (d) inspection of the back of the prow after consolidation; (e) and (f) restoration and assembly of the prow with the other elements of the ship in Musée de l'Arles Antique (© ARC-Nucléart; reproduced with permission).

On the other hand, given the effectiveness of consolidation, the Nucléart treatment is recommended as a safe means of obtaining micro- as well as macro-morphological information. In this sense, dendrochronology could prove easier thanks to the ability to make clean cuts using tools adapted for use on hard materials.

When archaeologists requested that radio-curing be adapted for use on waterlogged wood in the early 1970s, it was to treat items from a medieval site known as the 'Farmer-knights in the year one thousand', at Lake Paladru, near Grenoble. The aim was not only to perform an act of conservation, but also that the items would remain strong enough to undergo observation and study by archaeologists, including systematic measurement for statistical analysis. Consequently, the entire collection, including thousands and thousands of different items of waterlogged wood, had to be treated. This systematic excavation and study is today considered a landmark case (Colardelle and Verdel 1993).

Another very interesting case is that of the treatment of an almost complete Gallo-Roman boat, a 30m long barge found in Arles, in the Rhône River (Bernard-Maugiron and Viviès 2014). Given its size, it had to be divided into ten large pieces so it could be extracted from the river, after which it was further dismantled into even smaller pieces, allowing it to be studied by the team of archaeologists. The chosen treatment was a traditional PEG and freeze drying, piece by piece, prior to complete restoration. However, the presence of large metal components on the prow posed a problem, and it was decided to treat this 2.5m long element without dismantling it anymore, using the combined Nucléart method (Figure 2). As a welcome consequence, thanks to the consolidation power of this technique, it was possible to turn the element after treatment, making it available to be observed on his back. This of course was very interesting for archaeologist who were able for the first time to observe from that side how the different elements were assembled, while it was only possible to discover small part of the back face of the sole for the other sections, because the conventional PEG treatment was not sufficiently consolidating to allow to hold the elements without supporting this face... (It is noteworthy that previously to the treatment, the natural resin used for caulking that was present on the prow had to be removed because it could have been solved in styrene. It was replaced after the treatment.)

Conclusion

Increasing its knowledge and ensuring physical conservation are the two fundamental aims of heritage interventions. In many cases, these can be achieved either simultaneously, or one after the other in the correct order. The best conservation method is often a complex and sometimes difficult compromise. Nuclear techniques count among the suitable techniques available to us, and, contrary to what is often said, they are not necessarily any more 'damaging' than many other, more conventional techniques. To take just one example, we recall that DNA analysis was shown to be still possible after irradiation at up to relatively high biocidal doses, whereas this becomes completely impossible after treatment using the alternative conventional method, i.e. fumigation with ethylene oxide.

However, these nuclear techniques, like other competing active techniques, cannot claim absolute harmlessness. Whatever the situation, the appropriateness of using one technique or another in the preservation of heritage items must always be studied carefully. And we must not forget that we do not know what analysis techniques will be used in the future. How effective will they be after nuclear or conventional techniques have been applied? In the lack of any evidence, it could be that the best available conservation techniques today turn out to be the worst tomorrow. But given that we are unable to foresee the problems that could emerge in future, our responsibility is to do the best we can with our current knowledge.

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In a period when, particularly in the West, the study of archaeological remains is enriched through new methods derived from the natural sciences and when there is general agreement on the need for more investment in the study, restoration and conservation of the tangible cultural heritage, this book presents contributions to these fields from South-Eastern Europe. This region is characterised by a contrast between the rather limited development of the above scientific methods and the particularly rich and diverse material remains of its past societies, as well as by an obvious need to bring closer together traditionally-trained archaeologists with specialists in natural sciences interested in the research and conservation of ancient material remains. The title 'Bridging Science and Heritage in the Balkans' intends to show that the volume is part of this effort.

The departing point of *Bridging Science and Heritage in the Balkans: Studies in archaeometry, cultural heritage restoration and conservation* is the *5th Balkan Symposium of Archaeometry* (25–29 September 2016, Sinaia, Romania), where most of the papers published here were presented in preliminary form. The contributors are specialists from South-Eastern Europe as well as from other European countries working there. Some chapters focus on methods (in the research of glass, restoration of stone monuments affected by contemporary graffiti, conservation by irradiation of organic materials such as wood and human and animal body remains); most chapters present case studies (analyses of ceramics, metals, soils, wood anatomy, isotope-based reconstruction of human diet, ancient DNA, radiocarbon dating, technology assisted field survey, as well as restoration of paper and pigments); sometimes several methods are combined. The volume covers nearly all aspects of heritage sciences employed in this part of Europe.

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