

IN SEARCH OF HUMAN REMAINS IN THE LAYERS OF A PASSAGE TOMB: THE COMBINATION OF ICP-MS, FLUORESCENCE (XRF) AND SEM METHODS AT THE COBERTORIA DOLMEN (SALAS, ASTURIAS, SPAIN)

EN BUSCA DE RESTOS HUMANOS EN LOS NIVELES DE UN DOLMEN DE CORREDOR: USO COMBINADO DEL ICP-MS, FLUORESCENCIA DE RAYOS X (FRX) Y MICROSCOPIO ELECTRÓNICO (SEM) EN LA COBERTORIA (SALAS, ASTURIAS, ESPAÑA)

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Abstract

This paper summarises the results of the first analytical investigation of the soil chemistry of Asturian Megalithism, an approach which is essential, due to the scarcity of materials conserved in the burial areas. The combination of three analytical techniques enabled this study of the soils from the Cobertoria dolmen (Salas, Spain), a megalithic monument dated at around 3500 BC. The text describes the techniques and results of the analyses made on the corridor, and their relationship with their archaeological contexts. The peaks of some elements closely correspond with the geology of the site while others, especially the phosphorous components, are not common in the natural soils of this area. XRF and ICP-MS analysis showed peaks of this element indicating phosphorus concentrations that cannot be understood without the anthropogenic influence of the use of the corridor. The decomposition

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of bodies or the organic elements buried here is the most probable reason for these high peaks.

Keywords

Soil chemistry; Neolithic; Calcolithic; Megalithism; Cantabrian area

Resumen

Este artículo resume los resultados de la primera investigación dentro del megalitismo asturiano sobre composiciones químicas de los horizontes funerarios. La combinación de tres técnicas analíticas permitió una caracterización detallada de los niveles del dolmen de la Cobertoria (Salas, Asturias), monumento datado sobre el 3500 a.C. En el texto se describen las técnicas utilizadas para analizar estos niveles, así como los resultados obtenidos y su relación con el contexto arqueológico. La presencia de algunos componentes corresponde a la naturaleza geológica del sitio mientras que otros, como el fósforo, deben ser explicados por otros motivos. El uso de FRX y de ICP-MS mostró cifras elevadas de este componente que no pueden ser entendidas sin tener en cuenta el uso funerario que tuvo esta entrada. La descomposición de cadáveres, o de elementos orgánicos asociados a estos, es aquí la razón más probable para explicar estos altos índices de fósforo.

Palabras clave

Química del suelo; Neolítico; Calcolítico; Megalitismo; área cantábrica

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1. INTRODUCTION

Although the megalithic type known as the passage tomb is widely represented throughout Prehistoric Europe, in the Cantabrian area this megalithic design is not so common. Furthermore, it is always less monumental than the big megalithic sites, besides being a very unorthodox interpretation of the original megalithic label (De Blas 1983; Arias *et al.* 2006). Therefore, in this northern coastal region of Spain, the term passage tomb hides a «surprising diversity», as it does in most of Europe (Flanagan 1998). In northern Iberia, Asturias, Galicia and the Basque Country possess a long tradition of research into these monuments which has entailed considerable effort in gathering data from excavations and field work. Thanks to these data it is possible to define the main characteristics of the architecture, as well as the chronology of some archaeological zones (De Blas 2008; Fábregas and Vilaseco 2004; Fernández-Eraso and Mujika-Alustiza 2013).

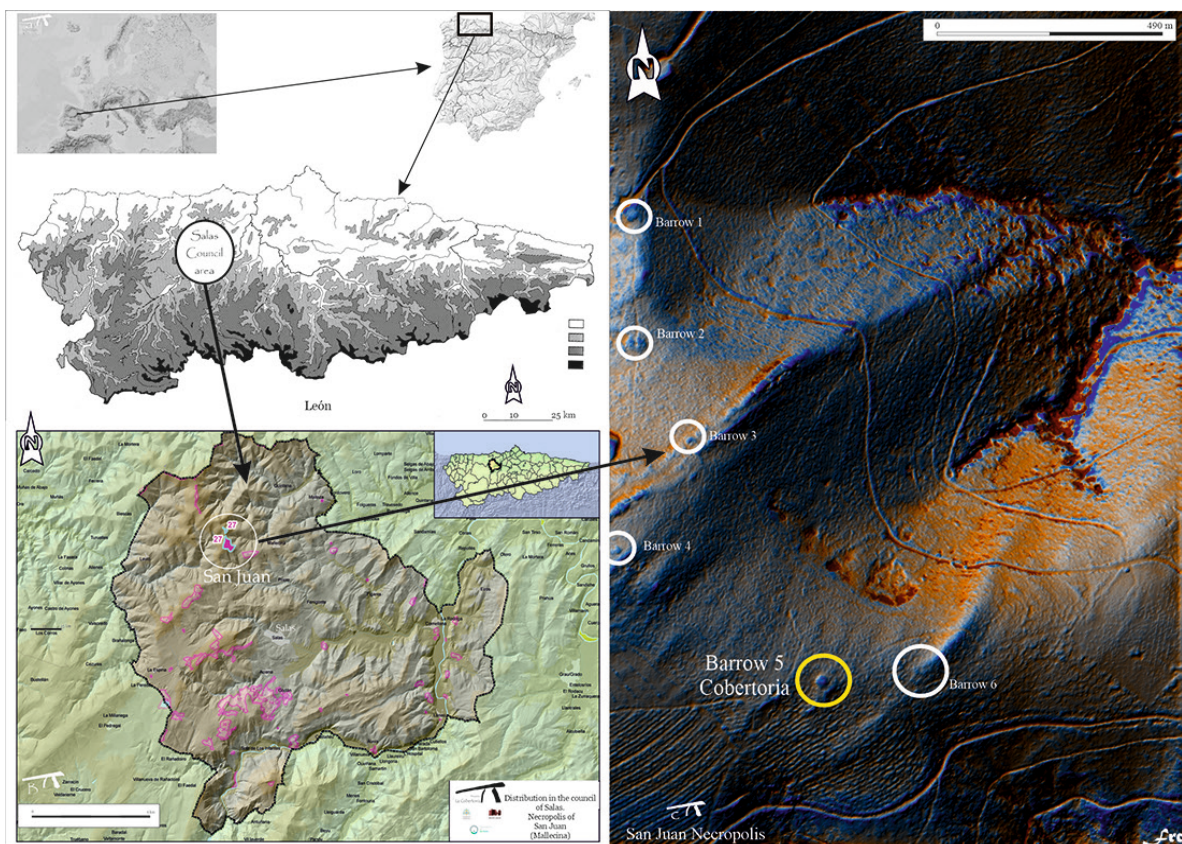


FIGURE 1. A) MAP OF ASTURIAS. B) MAP OF THE ADMINISTRATIVE AREA OF SALAS. C) SAN JUAN NECROPOLIS FROM THE LIDAR DATA

In all these megalithic areas archaeologists are confronted by the problem of highly acidic soils which implies that, even in historical burials, only a few elements of human bodies are conserved after a few centuries. Obviously, this is a general concern for megalithic funerary studies in most of the Cantabrian and north-western geological areas. However, in some territories there are fewer problems and,



FIGURE 2. AREA EXCAVATED AND THE MEGALITHIC REMAINS IN THE MIDDLE OF THE BARROW, OVER A DRONE PHOTOGRAPH OF THE SITE

certainly, some interesting collections of bodies have been recovered (Fernández-Crespo and de la Rúa 2015). Unfortunately, there are no studies focused on the geochemical definition of the levels excavated in the burial areas of the northern zone, although there have been notable efforts in the field of edaphology (Fábregas and Vilaseco 2003). Despite this lack of data, the environmental information is very complete in the Cantabrian region, thanks to the additional information provided by peatbogs or caves (Fábregas *et al.* 2003; Iriarte 2009; López-Merino *et al.* 2010; Uzquiano 2018; Pérez-Díaz *et al.* 2018). The information provided for other Iberian cases is more extensive, especially during recent decades, thanks to the edaphic analysis conducted in regions such as Galicia and Valencia⁵. These recent trends are based on previous papers derived from initial considerations of this discipline (Moreno and Ruiz Galvez 1989; Díaz 1993: 251-255); or, more commonly, from the

5. As a result of the research conducted by A. Cortizas in Galicia, and from the group of the researchers led by A. Pastor in Valencia (several references to the work of both researchers are included in the text and in the bibliography).

study of particular and regional cases. The latter present some interesting examples such as the analysis carried out in the Bronze Age necropolis of La Traviesa, in Sevilla⁶ (Valdés 1995), or in the rooms of the Iberian sanctuary of «Cerro Pajarillo» in Jaen (Sánchez and Cañabate 1999).

Between 2016 and 2019 several excavations were carried out in the Cobertoria dolmen (R. del Cueto and de Blas 2018), one of the most important megaliths in the Asturian region (Figure 1). The main phases of the monument were described, defining three main periods of use during Prehistoric times, between 4000 BC and 3500 BC (R. del Cueto and Busto 2020). The aim of this paper is to continue this research by adding a very specific characterization of the main levels of the only element that offers testimony of the burial gesture: a two-meter-long corridor in which the levels are completely intact (Figure 2). Three different kinds of analysis were performed during the years 2020 and 2021: inductively coupled plasma mass spectrometry (ICP-MS), X-ray fluorescence (XRF) and scanning electron microscopy (SEM). All the techniques were always applied to each of the selected layers in order to compare the results obtained in each case. The main conclusions of this cross-check test are a key part of this paper.

2. SOIL CHEMISTRY AND ITS APPLICATION IN THE PREHISTORIC ARCHAEOLOGY OF THE CANTABRIAN AREA

Soil chemistry has a long tradition of defining its own methods and opening several sublines of research in order to gather more information about archaeological levels. For this reason, summarizing all the trends and challenges that must be addressed by soil chemistry studies is no easy task. Soils are the result of the sum of natural and anthropogenic processes, which entails difficulties for their characterization. Many different compounds are found in soils and those considered «artificial» may originate from a wide range of human activities. The large number of journals publishing in this field gives a clue to the complexity of the research and the necessity for an interdisciplinary perspective. Authors still emphasize the potential of the available tools, always highlighting the need to combine different analytical techniques for greater accuracy (Wilson *et al.* 2008).

Even the sampling process for this type of analysis has been under consideration in recent papers (Christian 2010; Pastor *et al.* 2016; Lubos *et al.* 2016) and while it is necessary to stress the texts focussing on current lines of research, the key challenges for the future must also be addressed (Oonk *et al.* 2009; Walkington 2010)⁷. Clearly, the first two decades of the twenty-first century saw great advances with respect to the number of papers published; sufficient to underline the strengths and weaknesses of this particular field (Pastor *et al.* 2016; Shahack-Gross 2017).

6. Based on the archaeological records recovered during 1992 and 1993 by L. García San Juan and M. A. Vargas Durán (Valdés 1995: 330).

7. It is necessary to add the thesis of Linderholm (2010).

Much interest has focused on burial environments, which have received attention from three directions: either from the archaeological point of view (Di Pietro *et al.* 2018; Pickering *et al.* 2018), or from a medical (Turner-Walker 2008) or forensic (Zangarini *et al.* 2016) analysis. The importance and ubiquity of some minerals such as phosphorous, deeply linked with human activity, make them of great interest in this field (Maritan and Mazzoli 2004; Holliday and Gartner 2007).

Chemical soil analysis relies on key analytical techniques, each having its own historical pathway that can be discerned from the bibliography, as is the case of XRF (Theden-Ringl and Gadd 2017; Ginau *et al.* 2020; Williams *et al.* 2021) or ICP (Zaeem *et al.* 2021). Both are techniques of long-standing importance in the field and may sometimes be employed on the same site (Lubos *et al.* 2016). Many analytical lines of interest are now available, depending on the chronology of the archaeological site or its geology and the particular phenomenon under consideration. Although they will require more time and effort, other approaches may have great importance in soil chemistry, as is true of the rare earth elements and their research (Gallelo *et al.* 2013).

This historical background shows that there is a long tradition of identifying the links between the different soil processes (human or natural) and the chemistry features of an archaeological site (Walkington 2010). At this point, it is always necessary to bear in mind the difficulties in quantifying this relation between the pedogenic, the diagenetic and the anthropogenic elements that can always make both analysis and interpretation of the results more complex (Walkington 2010: 125). The former author's study, based on Carter and Davison (1998), also summarised the three main problems for establishing a group of diagnostic properties for a site (Carter and Davison 1998; Walkington 2010:125). Apart from these preliminary considerations, accumulated research experience makes it possible to search in the soil for specific components that could be the key to evaluating the repercussions of human activity in a specific terrain.

Taking into account these previous recommendations and with the aim of better understanding the processes involved in the burial areas of the megaliths, it is necessary to conduct cross-tab analysis on the recovered soil. Although apparently simple, this represents a novel experimental approach in the megaliths of the Cantabrian areas. Despite this, the long series of studies which comprises the historical background emphasizes the key challenges. For Holliday and Gartner (2007), for instance, the most common chemical elements affected by human activity are carbon, nitrogen, sodium, phosphorus and calcium (2007: 32). All research into this issue should consider these basic elements, although several authors have emphasized that soil chemistry is not only based on making a general chemical characterisation. In fact, identifying components is the easiest part of the process and the doubts, as Middleton *et al.* states, arise when the ancient behaviours that have created this chemical fingerprint have to be explained (2010:186). Even when the key element in a soil is clear, there must be, necessarily, a serious consideration of the geochemical actions that lie behind the presence of this material in certain soil levels.

Another very important variable is the type of analysis that should be performed in each particular case. ICP-MS has been used in many papers about soil chemistry

and, more specifically, the statistical analysis carried out by Pastor et al. reported that this technique was employed in 32% of the papers reviewed by this author (2016: 50). Its greater sensitivity and its effectiveness in detecting some elements (RRE and trace elements, for example) are crucial reasons for selecting the ICP-MS, excluding other options (2016:56).

Another possibility is using ICP, but the Optical Emission Spectrometry Analysis variant (OES; ICP-OES). It is considered by Pastor *et al.* (2016) in their statistical evaluation as one of the most frequently used techniques. Middleton *et al.* (2010) states that ICP-OES is a very precise quantitative analytical technique that provides copious data amenable to evaluation by a powerful inferential statistical analysis (2010: 188). Although it is capable of identifying some components such as phosphorus, it is probably not so precise for detecting other organic components (Middleton *et al.* 2010:190).

Given all these constraints, it is fortunate that our research is based on a limited archaeological context, where the identification of a chemical fingerprint can only be in connection with burial processes. This means that there is no need to deal with a broad landscape or with different stratigraphic or environmental contexts, in which it would certainly be necessary to use other methods for identifying and characterising the archaeological context as Walkington states (2010: 128). For our research the techniques used were the ICP-MS and XRF. The former for its special relevance for analysing in detail the chemical fingerprint of a level and the latter for its general approach to the sediment, giving a comprehensive idea of the composition of the soil. The last technique used was the SEM, although this represented a secondary analysis to complement both ICP and XRF. The three of them were applied to the same archaeological levels, those recovered inside the corridor of the dolmen, which was the only part where testimony of the burial was conserved.

3. THE ARCHAEOLOGICAL RECORD: THE CORRIDOR DURING THE THIRD PHASE OF THE COBERTORIA DOLMEN

This paper focusses on the third phase of the Cobertoria tumulus. The initial moment of the megalithic site was around 4000 BC, when a large fire was lit and subsequently covered with a 6-meter-diameter barrow. Over this first structure, a ring of clay was built around 3800-3700 BC and most of the top part of the ring showed signs of having been burned by fire. Thermoluminescence and radiocarbon samples provide the chronological framework for these two initial phases (table 1).

During the third and final prehistoric period, dated around 3500 BC, the tumulus was expanded to 18 meters diameter. A dolmen chamber was identified in the centre of the barrow by the historical looters who plundered the monument and it was their intervention that made the chamber accessible. The area designed for burials is one of the most remarkable megalithic features in Asturias, and even in the Cantabrian area, where the megalithic structures do not possess the monumental character seen in other regions (R. del Cueto and Busto 2020). The 5 square metre area of its interior

makes it outstanding in Asturias in terms of dimensions, only comparable with the Dolmen of Santa Cruz, which has a similar size (De Blas 1983: 47). Excavations carried out up to 2019 led to increased interest in the Cobertoria, because they revealed other parts of the megalithic monument that were below ground level. For instance, the originally exposed structure had only seven orthostats in the burial chamber: six as pillars and a huge rock covering the burial area, although this capstone was broken in the 20th century. After further excavation, the structure was found to be more complex due to the discovery of five more orthostats. This change required a reconsideration of the megalithic tag of the Cobertoria site: the term simple chamber was replaced with the more appropriate description of passage tomb. In fact, the two metres of the corridor make it the longest structure of this type in Asturias (De Blas 2008).

TABLA 1

METHODS	LABORATORY REFERENCE	RESULT BP	RESULT B.C.	ARCHITECTURAL PHASE AND STRATIGRAPHIC CONTEXT
Radiocarbon. Wood (indeterminate)	Ua-59945	5179±35 BP	Between 4050 and 3940 B.C. (94.4% probability)	Phase I. Fires below a stone barrow (R. del Cueto y Busto, 2020: 58-60)
Thermoluminescence. Clay of a very concentrated and intense fire	MADN6627bb	4955±336 BP 68% range calBP: 5266 - 6070	Between 4120 and 3316 B.C. (68% probability)	Phase II. Fires at the top part of the ring of clay (R. del Cueto y Busto, 2020: 60-63)
Thermoluminescence. Clay of a very concentrated and intense fire	MADN6629bb	5304±329 BP 68% range calBP: 5723 - 6431	Between 4481 and 3773 B.C. (68% probability)	Phase II. Fires at the top part of the ring of clay
Radiocarbon. Wood (indeterminate)	Ua-57657	4785±34 BP	Between 3650 and 3510 B.C. (94.3% probability)	Phase III. Wood inside the corridor. Levels of use of the entrance (R. del Cueto y Busto, 2020: 63-69)

The design of the corridor, two meters long and 60 centimetres wide, included two stones on the right side, and one on the left (Fig. 2). In the megalithic monuments of Galicia there are at least four examples with a similar arrangement of the entrance (Vilaseco, 1997-98: 137) and, for this reason, it would seem to be a deliberate architectural proposal, rather than an incomplete structure (R. del Cueto and Busto 2020: 65). However, the most interesting aspect of the corridor is the archaeological deposits conserved inside. They are of great importance in the Cantabrian context, because they were not affected by the looting that the prehistoric remains in other parts of the monument suffered. The looters focussed, mainly, on the burial chamber, whose contents were completely removed, reaching in their action the geological deposits below, where there are no traces of human remains. The rocks of the burial chamber underwent a last prehistoric intervention:

an intentional closure of the entry as well as the movement of some stones (probably the cover rocks) to the surroundings of the entrance.

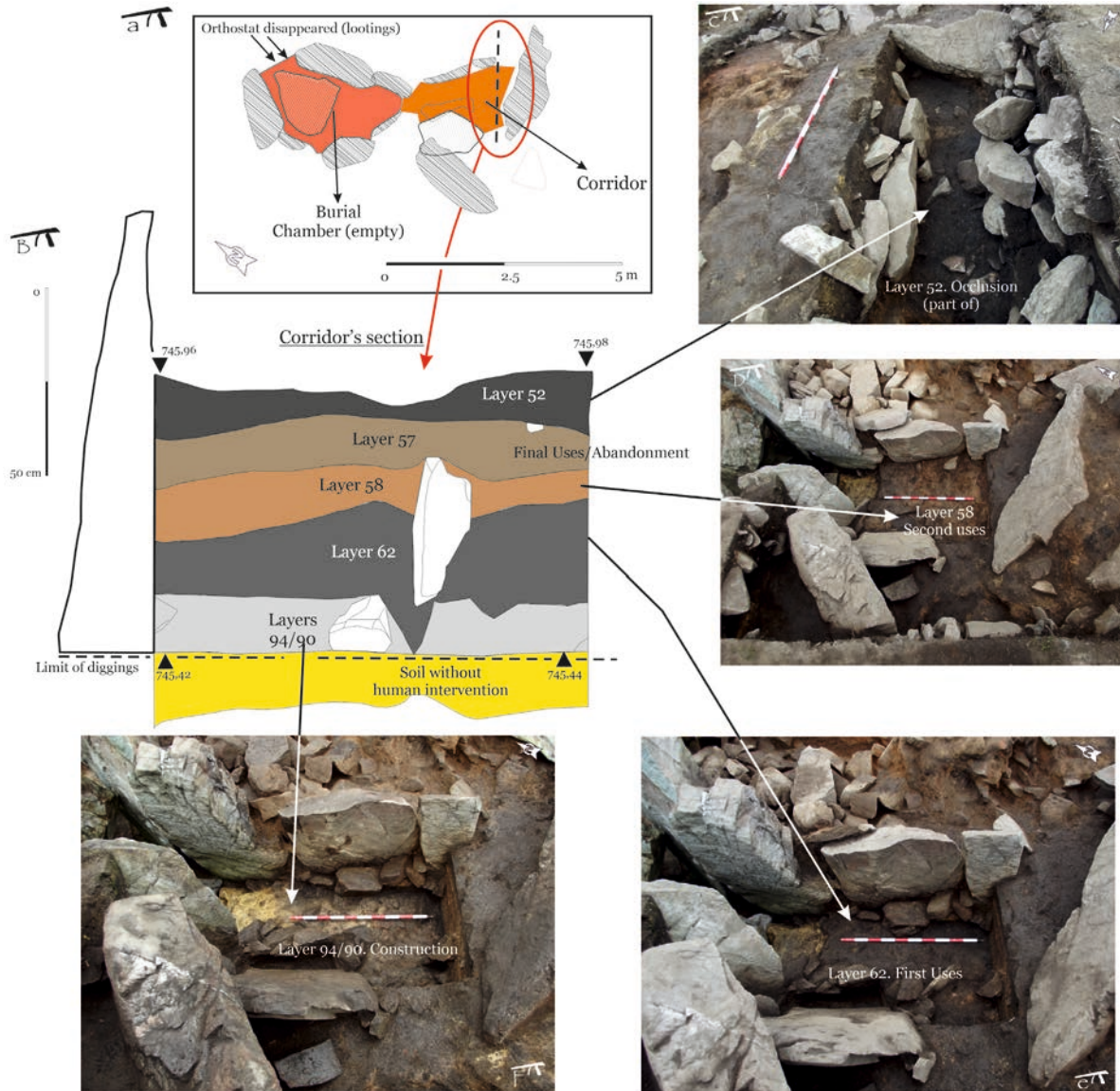


FIGURE 3. A) BURIAL CHAMBER AND PASSAGE OF ENTRANCE. B) SECTION OF THE PASSAGE. C) LAYER 52 (OCCLUSION) D) LAYER 58 (SECOND USES) E) LAYER 62 (FIRST USES) F) FINAL POINT OF THE DIGGINGS WITH THE AREA EMPTY

Unfortunately, it was impossible to find archaeological materials or suitable samples for radiocarbon analysis to date the construction of the dolmen more precisely. The small ditches for both corridor and burial chamber did not provide suitable material for dating. The only data available here was the radiocarbon samples recovered in the levels of use of the corridor (Figure 3). Regarding the sequence detected in the excavations, three main periods can be proposed as a synthesis of the main phases here. First, the construction levels close to the foundations of the three rocks that make up the corridor. In reality, evidence of some human activity previous to the

construction of the corridor was identified, but this consisted of only small holes opened in the geological surface, which did not provide carbon or any materials for dating. These holes were covered by level 94. Both this layer and the holes may be connected with the two initial phases, but must predate the construction of the corridor of the dolmen. It seems clear that the foundations of the structure for the entrance were opened by cutting into unit 94 as well as part of the geological surface below. A thin level (unit 90) covered the whole of the corridor but, due to its thickness of only 5-8 cm, it seems to represent a construction surface, made to level the entrance. It extends along almost the entire length of the access, but it is more difficult to identify in the southern section. Another step in building the corridor was the placement inside the foundation ditches of a group of stone blocks to provide stability to the corridor's orthostats.

From this point, we have a second group of units linked with the use of the corridor. Unit 62 condenses the human activities during the use of this space as an access and maybe for burial. It has a grey colouration and is composed of a lightly compacted mixture of clay with organic materials. The level extended throughout the corridor, completely covering the rocks of the foundations. For this reason, it occupies the whole available width between the orthostats, a key point in this narrow access. A small piece of charcoal was found inside this layer, giving the reference for dating the third phase of the monument at around 3,500 BC⁸. This age is considered in Asturias the summit of the megalithic evolution and it is the time of the development of the most complex structures in all the Cantabrian megalithic catalogue: the passage tombs. Apart from the radiocarbon dating, a small flint blade was found in this level, connecting the corridor with a probable funerary use. Due to the closed context of the corridor, as we will see below, there were no possibilities of recent access to it and, for this reason, the charcoal must be related to the prehistoric funerary gestures and the offerings associated with them⁹. Other possibilities, like the deposition by chance of the carbon in more recent times should be clearly rejected. Furthermore, the result of the radiocarbon dating fits very well with the two previous phases identified in the corridor, both linked in addition with a very clear overlap of architectural moments already described (R. del Cueto y Busto 2020). Finally, these long «life cycles» of such monuments are not unusual in the Iberian context, as recent research has shown (Mañana 2003; Tejedor 2014).

Lastly, in the top part of the entrance were found two different layers, 57 and 58, very similar to one another. These two units were defined not only by containing less compact soils, but by the lack of any kind of archaeological material. That does not mean that access would not have been possible during these final moments of use. The final covering, unit 41, was a mass of quartzite stones blocking any kind of access to the interior of the burial chamber (Figure 4). These rocks are part of the

8. Ua-57657 (charcoal): 4785±34 BP. Between 3650 and 3510 B.C. (94.3% probability). The sample was recovered in unit 62 (level of use). The type of food and other studies of the pollen recovered in all the levels of the corridor are under preparation now for publishing by the Botanic Department of Oviedo university.

9. The level of archaeological evidence that can leave both gestures, thanks to a historic example, can be seen in Martín (2018).

last prehistoric action in the monument: an intentional collapse of the entry, as well as the movement of some stones (probably the cover rocks) to the surroundings of the entrance. This part of the tumulus was kept safe thanks both to this cover and the big stones that were part of the corridor that probably dissuaded the people of the 18th and 20th century who were looking for old treasures at these sites (R. del Cueto and Busto 2020: 69). This cover could have protected the underlying layers of the passage very efficiently, making recent chemical enrichments, a possibility that must always be considered, more difficult (Weihrauch and Söder 2021).



FIGURE 4. A) PASSAGE-CORRIDOR STRATIGRAPHIC UNITS B) TWO POSSIBLE SECTIONS OF THE ENTRANCE, BOTH BLOCKED BY STONES. C) LAYER 41, IN SECTION 1 D) THE ENTRANCE WITH THE POSSIBLE PATH FOR ENTRY E) SECTION 2, BLOCKED BY STONES.

4. MATERIALS AND METHODS

4.1. MATERIALS: SAMPLING

The most important advantage of the sequence described is that it consists of a very close group of stratigraphic units that remained undisturbed from prehistoric times until the excavations here described. This is always very positive, especially for later analysis, as was pointed out by Shahack- Gross (2017: 41). The importance of dealing with a whole and intact passage sequence meant that during the excavation work an extensive bank of soil samples were recovered for further analysis. Gathering as much soil as possible was part of an attempt to reduce the invasive effects of any archaeological excavation, following the recommendations of soil researchers. Linderholm, for instance, states that, «Not taking the soil information into account is like throwing out the baby with the bath water, along with the bathtub»¹⁰.

This extensive group of samples was used for different lines of research, namely, this investigation of the soil chemistry and botanical studies (awaiting publication). For each group, 10 grammes of soil were obtained by sifting the samples manually to remove unwanted elements (stones), always including the three main phases of the corridor: construction, use and use-abandonment¹¹.

Samples and analyses taken during the PhD studies of one of the team serve here as control samples¹². They analysed the Cambrian geological units of the area¹³ from a geological perspective using the XRF method, allowing us to compare them with samples connected with the human (burial) actions of the Cobertoria. Obviously, a wider consideration, in geographical and statistical terms, will be necessary in the future in order to determine the distribution of P in this particular landscape more precisely (as recommended by Weihrauch and Söder 2021). But the proximity of the geological samples to the dolmen (around 1 km) and the fact that they belong to the same «soil region» (using the term of Weihrauch and Söder 2021) make them suitable for our comparisons. Even the recent changes seen at both points in the landscape are similar, because both were converted into forested areas during the 1990's. For this reason, and because of their mountainous nature, both are inside the same «land use segment», an aspect very important for Weihrauch and Söder (2021).

4.2. ICP ANALYSIS

Before the determination of Mn, P and Ca content, soil samples were dried in an oven at 60°C overnight and, after that, they were sieved. The homogenous fraction

10. 2010: 12.

11. For this reason, the analysis gathered information about the abandonment phase of the corridor, the funerary levels and about layers below the burial area (the construction level).

12. Rubio 2010.

13. Samples were taken in the area of Malleza and Mallecina.

under 250 µm was then digested at 230 °C for 10 min in an ETHOS™UP microwave system (Milestone), employing reverse aqua regia (3 HNO₃ to 1 HCl) as solvent (250 mg of sample and 8 mL of solvent). Once digested, samples were analysed in a 7700 Series ICP-MS (Agilent), using rhodium as internal standard. Analyses were carried out at least in duplicate¹⁴.

The use of ICP-MS has been outlined by some authors such as Walkington (2010) and Entwistle and Abrahams (1997), who remarked that alternative techniques should also be used if the focus was on analysing phosphate components. As ICP-MS is a quantitative method, the so called «levels of magnitude» and the combination of several methods for analysing the chemical composition of the soil are necessary to follow this recommendation.

4.3. FLUORESCENCE (XRF)

XRF samples were dried at 105 °C for 4 hours, and later were crushed and milled using wida components for 20s. The measurements of the geochemical composition of samples by X-ray Fluorescence (XRF), were performed using a Phillips PW 2404 spectrometer, with a 4 Kw Rh X-ray tube, 5 analyser crystals (Fli 200, Fli 220, Pe, Ge y Pxi) and a PR 10 scintillation gas detector. The relative precision of the XRF technique was better than ±1%. Major element analyses were performed using glass beads of powdered samples after fusion with lithium tetraborate. Raw data were processed using Pro-Trace-XRF PANalytical software.

4.4. SEM

Scanning Electron Microscopy (SEM) is one of the key techniques in soil chemistry studies (Pastor *et al.* 2016). Indeed, these analyses are considered an important part of detailed soil microscopy and geochemistry exercises, since they allow the characterisation of the morphology of soil samples (Di Pietro *et al.* 2018).

In addition, energy-dispersive X-ray spectroscopy (EDX) is a chemical microanalysis technique used in combination with scanning electron microscopy (SEM). The EDX technique provides semi-quantitative elemental composition information. In this study, EDX analyses were performed to determine the composition of the soil samples. A JEOL JMS-6610LV scanning electron microscope (SEM), operating at 0.3-30 kV, was employed. Prior to the EDX analysis, samples were dried in an oven at 60 °C overnight and then sieved. The homogenous fractions under 250 µm were mounted on aluminium SEM stubs and were sputter-coated with gold to make them electrically conductive (García Álvarez-Busto *et al.* 2019).

14. This methodology has several references that confirm its scientific accuracy (Melaku *et al.*, 2005; Toller *et al.*, 2022; Rogers *et al.*, 2022).

5. RESULTS

5.1. MOST INTERESTING RESULTS FROM ICP AND XRF

As Holliday and Gartner state, the most common chemical elements affected by human activity are carbon, nitrogen, sodium, phosphorus, and calcium (2007: 302). Based on this idea, it was initially thought that the trace of Ca in this burial structure might be relatively high. However, results did not corroborate this assumption, at least in the levels of use, the most likely to have an important amount of calcium. A possible reason for this is the quicker leaching of this mineral in acidic soils, widely perceived in other contexts (Cannell *et al.* 2020: 763; Holliday and Gartner 2007: 16). The only significant peak in the Ca levels was identified in the construction levels, according to the ICP results (Figure 5).

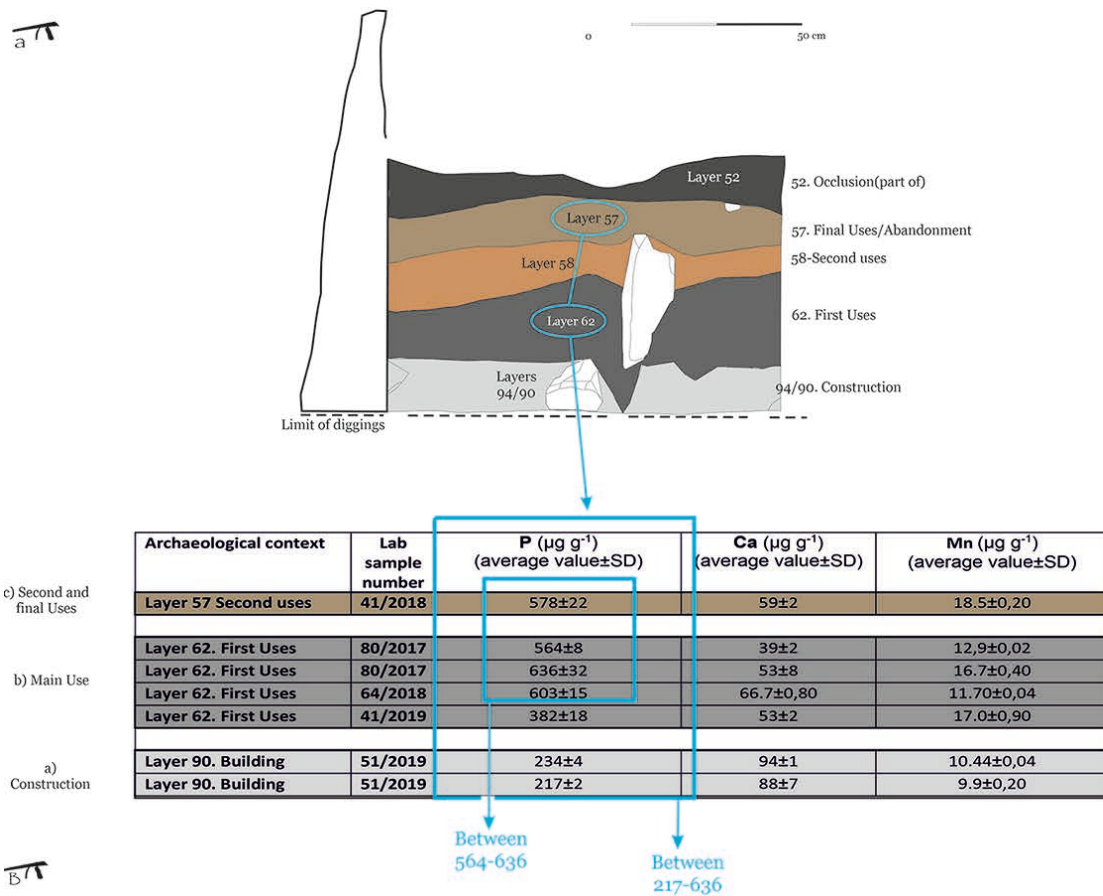


FIGURE 5. A) PROFILE OF THE MEGALITHIC ENTRANCE B) ICP RESULTS LINKED WITH THE STRATIGRAPHY. IN BLUE SQUARE THE HIGH FIGURES OF THE P

Also noteworthy was the regularity of the content of silicon, aluminium, iron, magnesium, manganese, calcium, sodium and titanium, which showed only small differences between the three main phases of construction, use and abandonment,

according to the XRF analysis (Figure 6)¹⁵. Thus, the results remained relatively homogeneous in all the main phases of the corridor, with general agreement between the techniques employed. The only element that did show recognisable differences is the phosphorus (Figs. 5, 6). A very interesting component, because it is usually linked with human activities due to its long persistence in the soils (Holliday and Gartner 2007: 303). According to these two authors, since phosphorus is not found by itself in elemental form in nature, a more accurate term for considering the phosphorus in soils is «phosphorous» (2007: 302).

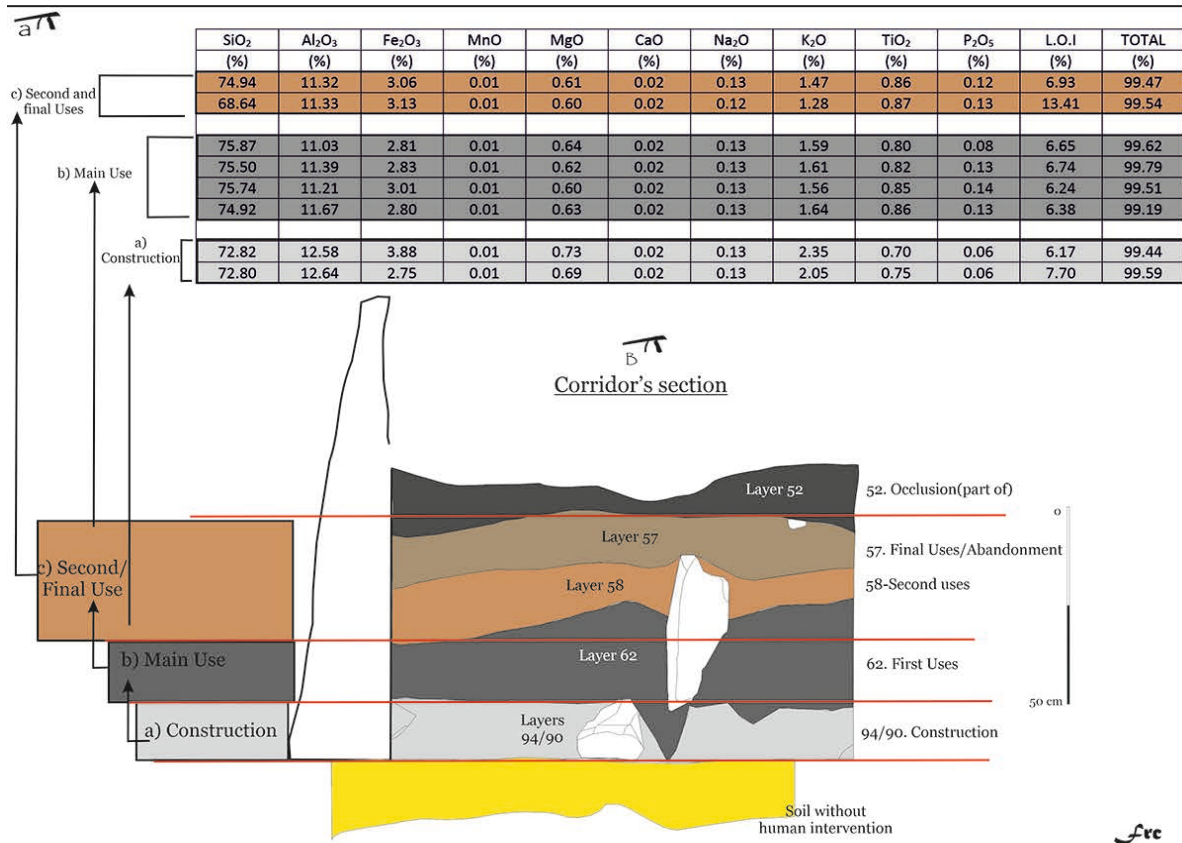


FIGURE 6. A) XRF RESULTS LINKED WITH THE STRATIGRAPHY. B) PROFILE OF THE MEGALITHIC ENTRANCE WITH THE LAYERS AND A COLOUR KEY FOR A BETTER UNDERSTANDING OF THE TABLE

5.2. SEM RESULTS

In the SEM images of the three phases under consideration, high levels of silica (between 21 and 22%) and aluminium (9.73-9.96%) were identified (Figure 7), which is to be expected since quartz is one of the main sedimentary rocks detected in the

15. Some recent studies emphasize the importance of Aluminium and Silicium as lithogenic elements of Salas (Martínez *et al.* 2016: 398).

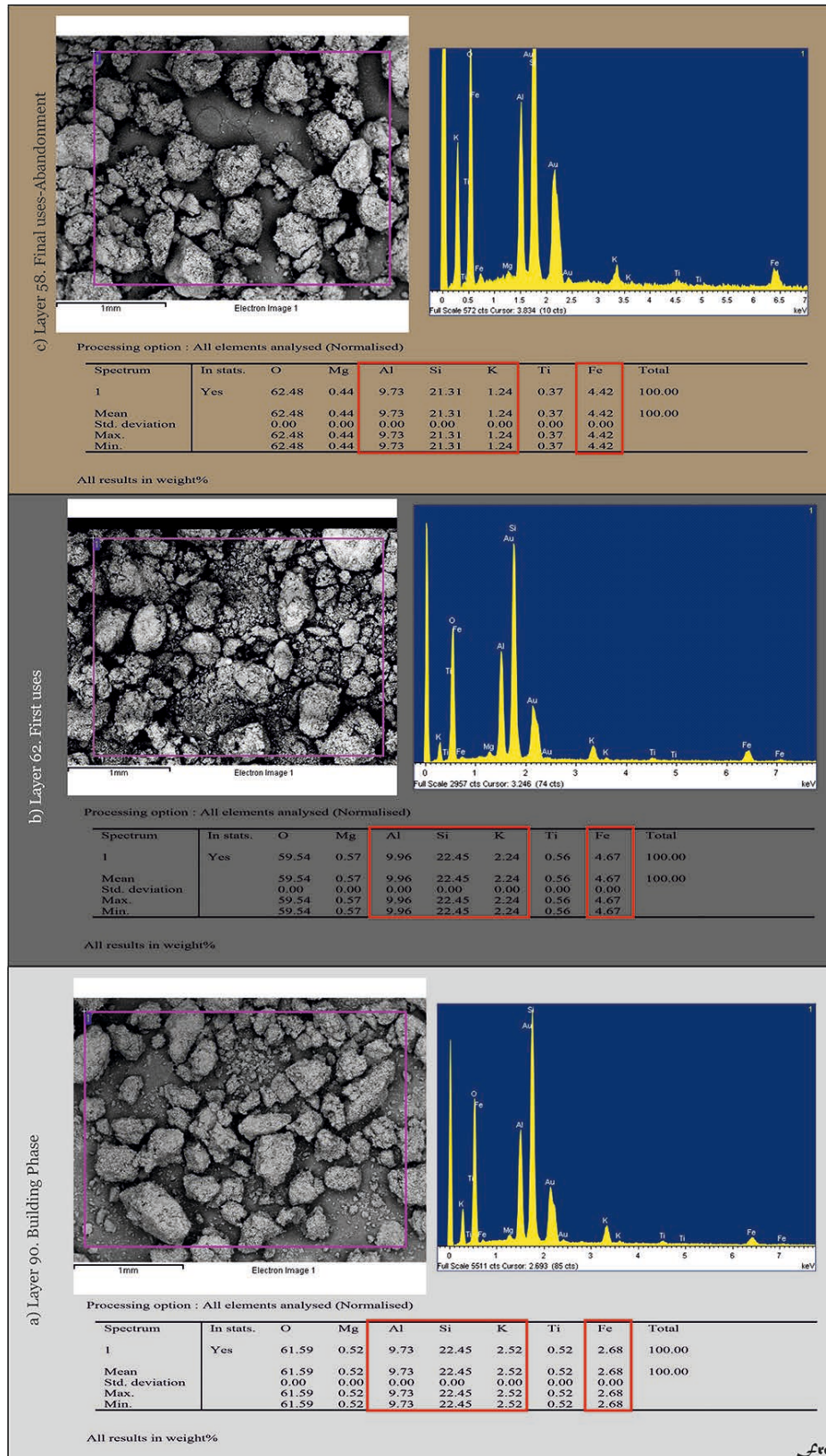


FIGURE 7. SEM RESULTS IN DIFFERENT PHASES: A) BUILDING LAYERS. B) FIRST USES. C) FINAL USES-ABANDONMENT

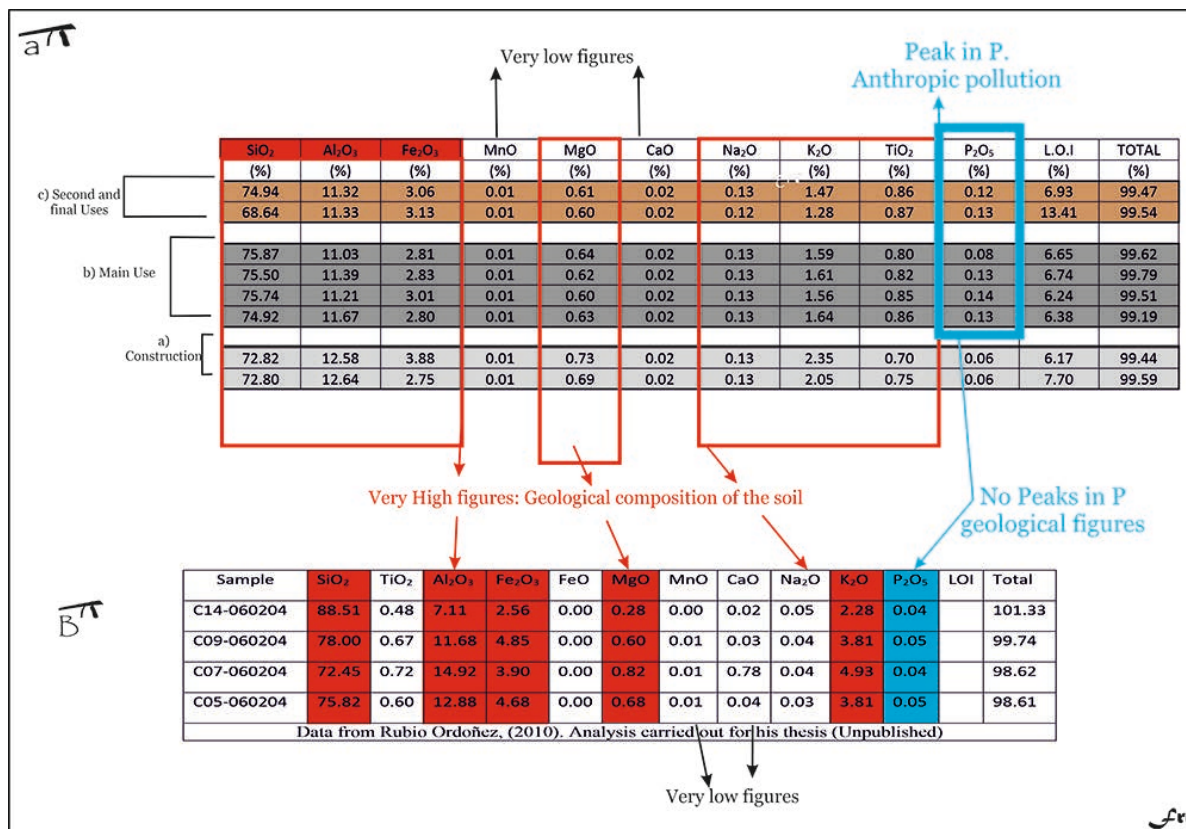


FIGURE 8. A) XRF RESULTS, CONNECTED WITH THE ARCHAEOLOGICAL CONTEXT B) GEOLOGICAL ANALYSIS CARRIED OUT BY RUBIO ORDOÑEZ FOR HIS PHD. IN RED, THE MAIN COMPONENTS OF THE LOCAL GEOLOGICAL SUBSTRATE. IN BLUE, THE PEAKS IN PHOSPHOROUS ELEMENTS, AS WELL AS THE LOW LEVELS SEEN IN THE GEOLOGICAL ANALYSIS

area, according to geological studies (Rubio, 2010). The high levels of aluminium can be explained by the presence of muscovite in the area of Malleza and Mallecina, villages very close to the dolmen (2010). Iron is the third component, with figures between 4.67 and 2.68%, also coherent with the rock types identified in the area by Rubio¹⁶. Other materials show small peaks in the three samples analysed by SEM, as is the case of K (the fourth element in importance after Si, Al and Fe). The figures are also in agreement with the geological samples analysed in the area of Malleza for geological purposes¹⁷ (Figure 8). In all the cases, SEM and geological analysis, it is necessary to stress the low levels of P in all the tables. It was practically non-existent according to the SEM and at very low levels in all the geological tests done.

16. 2010.

17. Rubio, 2010

6. DISCUSSION OF THE RESULTS OBTAINED

The results obtained allow us to make deeper deliberations about the chemical compositions identified using the three techniques. For instance, and regarding the low results in calcium, some explanations can be suggested. One of them is the possibility of some movement of calcium and potassium from the levels of use to the lower parts of the corridor. But here this explanation does not seem coherent, at least bearing in mind that phosphorous is not affected by the same phenomenon. Percolation and the resulting leaching of soil components is more common in more complex archaeological contexts, and, in our case, it is difficult to understand, due to the closed nature of the corridor. Although some examples of this percolation process are known of in the Iberian context (Valdés 1995: 339), the analyses from the Cobertoria are not consistent with this natural process. Neither would it be correct to state that the occurrence in one site means that the same process happens in other sites, due to the different circumstances of each case (geology, archaeological context, etc.), which provide special singularity to each archaeological site. In fact, the Bronze Age cists studied by Valdés show important differences with the Cantabrian Context. In the former there are some examples of tombs with human remains inside. On the contrary, in the latter there is no bone evidence in the tumuli studies in Galicia, Asturias, Cantabria and most of the Basque Country. For this reason, the geological context cannot be compared, and neither can the relevance of soil analyses like these in such diverse archaeological regions. Particularly, because in the northern area evidence proving the funerary uses of these chambers is very scarce and additional information is always welcome. Although the architecture seems clearly focused on this action, and the offerings can also be explained as part of burial activity, the lack of bones is crucial here. At this moment, the only way to recognize human depositions is the soil chemistry and there were no previous attempts at doing these analyses, although it is an old problem in Europe as emphasized Valdés (1995: 330), based on previous publications in the European context (Christie 1960; Coles 1965).

Valdés had previously also shown some limitations of soil chemistry: for instance, its reduced capacity for establishing chronological inferences about the buried people (Valdés 1995: 342). Another example is the number of individuals buried in one specific area, information that current soil chemistry analysis is simply unable to provide. The main reason for this limitation, as Valdés stressed, is that the total mass of phosphorus equivalent to a human body can never be recovered from the archaeological site. At least at La Traviesa the loss and diagenesis of this element was clear (1995: 344) and it makes sense that similar problems could happen in other settlements. Moreover, this process of loss of phosphorus could be even more intense in archaeological sites older than La Traviesa, as is the case with the Cobertoria.

In regard to the high levels of phosphorus in the Cobertoria corridor, it is necessary to stress that our results coincide with levels of phosphorus that have been previously linked with human activities in a soil (Sánchez and Cañabate 1999: 55). In other archaeological sites the peaks in the phosphorous components, using similar techniques, were also linked with the presence of burials (Aston *et al.* 1998: 467; Oonk *et al.* 2009: 40) and thus, the association between burial contexts and high

levels of phosphorous components is not unusual. However, the levels indicated by some authors for a burial phenomenon (over 2%) (Williams *et al.* 2021: 3) are not totally coherent with the percentages obtained in our XRF analysis. In fact, the amounts of phosphorous found here are more in accordance with the levels indicated by these authors for «dwellings and manufacturing areas», which tend to leave moderate phosphorous percentages (between 0.02-0.20%) (2021: 3). Pastor, for instance, states that 250 mg/kg would be a notable proportion of phosphorous after human occupation (2016: 50).

Here, however, we should consider the archaeological context, because there is no other human activity in the dolmen: only burials. The lapse in time between the analysis and the creation of the soil, around 5,500 years, should not be ignored either. Some papers have remarked that biogenic (from animal and fish bones, mainly) Ca-P levels disappear ten times faster than geogenic Ca-P in some archaeological levels (Sato *et al.* 2009). Weihrauch and Söder stated that long and constant permanence of P only happens in soils that «regularly receive inputs of P-containing matter» (2021).

It can be certainly discarded that the pH of the soils in this area affected this peak in the phosphorous components. This kind of alteration is more common in soils with a more neutral pH (Holliday and Gartner 2007: 306), but that is not the case of the Asturian soils, that show higher levels (between 4.5 and 6%; in the western part of Asturias for instance (Oliveira-Prendes *et al.* 2014). The high levels of acidity in the soil are clearly the main characteristic for understanding the quick degradation of bones and teeth, a process that is, however, not only due to pH and that can be tracked in other parts of the world (Tuner-Walker 2008: 22). The post-mortem alterations in some tropical Savannah grasslands of Kenya occur in a period of between 15 and 40 years, being accelerated by other factors that favour the final dissolution of bones (Trueman *et al.* 2004: 736).

In other cases, high phosphorous levels are the result of materials such as pottery that can load the composition of a level with P (Maritan and Mazzoli 2004: 681). That is not the case in the Cobertoria, due the scarcity of pottery in all the Asturian neolithic period (De Blas 2008). Several types of fungi were identified in the corridor, after an analysis performed by the botany department of Oviedo University (awaiting publication). Other authors recommend considering possible fungal contamination to explain some high levels in the analysis (Holliday and Gartner 2007: 305). But in this study, we must establish a difference between the appearance of some evidence of fungi, and a mass contamination due to these organic materials. In fact, in the level of use (which has the most notable levels of phosphorous materials) only one fungus (one spore) was found, while in the top part of the entrance 4/5 different types appeared (*Coprinus* sp., *Venturia* sp., *Helminthosporium* sp. and *Leptosphaeria* sp.).

Considering other factors of adulteration, it has been suggested that soils with a high clay content can affect the results (Holliday and Gartner 2007: 305). However, in this site the corridor levels have a low presence of clay in the soil composition. Finally, although the effects of soil fauna must always be considered (Pickering *et al.* 2018: 94), the very closed nature of the structure here studied reduces the possibilities of it having undergone contamination due to soil fauna. It seems clear that our context is very different from peatbogs, places with a rich organic activity. These

factors considerably reduce the possible repercussion of soil fauna here. Although in previous excavations this team has identified intrusions (krotovinas), as in the case of the excavation of the prehistoric camp of the miners of el Aramo (De Blas and R. del Cueto 2015; the krotovinas aspect is unpublished), which were very similar to those described by Butzer (1982: 113), here there is no such evidence of small tunnels due to animal intervention. Besides, the tumulus of the dolmen is formed by organic black sediments, richer and probably more attractive for the soil fauna due to their lower hardness (compared with the more compacted layers of the corridor). In conclusion, after considering these key points, the evidence seems to indicate that people buried here (or their belongings) could be the origin of the high levels of phosphorus. Especially, because it is detected mainly in the levels of use and use/abandonment. If the soil fauna had been the principal cause of the deposition of phosphorous, it would have to be asked how the animals had been responsible for a very selective impact: only in the layers of use and abandonment, leaving the construction levels relatively unaffected.

Finally, as regards the third technique, the SEM results agree with those of the XRF tests corresponding to the layers of the corridor: the highest levels are of Si (68-75%) and Al (11-12%); followed by iron (2.80-3.88%), K (1-2%), Ti (0.70-0.87%), Mg (0.60-0.73%) and Na (0.12-0.13%). All of them were very well characterized in the geological tables relating to the XRF analysis (both geological and archaeological results). The low figures of Ca (0.02%) and Mn (0.01%) are not important for our considerations now. However, it is remarkable that, in contrast to the very low or insignificant levels of P measured by geological analysis (XRF) and SEM, the XRF of the Cobertoria indicated significant values of P_2O_5 in certain samples. The most important peaks, between 0.12 and 0.14%, (Fig. 8), appeared in the use and use/abandonment levels. The results are different to those from the construction levels, which are more similar to the geological analyses carried out by Rubio¹⁸, who analysed the evolution and nature of the geological units of this area of Asturias. As we previously remarked, his study, carried out in the same Cambrian geological unit of the excavation area, indicates the common or natural figures for the P_2O_5 : (between 0.04 and 0.05), similar to those from the construction levels (0.06). However, the use layers of the corridor have double or more than double (between 0.12 and 0.14) these concentrations. This comparison of soil samples from inside and outside the burial context is critical as the latter provide a base line to assess the results obtained. In the corridor, as we previously remarked, the possibility of anthropogenic activities that can disturb the analysis is very low, in particular because the corridor it is a structure that was buried during most of its existence. Furthermore, it was used very occasionally through this time and, underwent a final collapse in Prehistoric times, thus creating a closed context ideal for the analysis. Although the interior levels of water can have some influence in all archaeological sites (Valdés 1995: 338), it does not seem here to be the main reason for the peaks detected in key elements such as phosphorus.

18. 2010.

Regarding the scarcity of P in the SEM analysis we must insist on the different approaches of the three techniques used here. Among them the SEM is the most superficial for understanding the composition. This idea is confirmed considering that the SEM measured the content of six elements, whereas XRF was able to quantify ten minerals. For this reason, the disappearance of some minerals in the SEM results are not due to the scarcity of these elements. It is more closely related to the capacity of SEM to identify them within the soil, as the cross-checking analyses have demonstrated.

CONCLUSIONS

Although further research with both similar and different approaches will be necessary to tackle the problems and analyse the results under discussion here, the «purely archaeological evidence» presented here allows us, as in other similar studies (Sánchez and Cabañate 1999: 48)¹⁹, an «adequate interpretation by itself». As was stated by these two authors «the analysis of a high number of chemical markers become secondary» as is true in the Cobertoria. It is clear that the individual studies of these chemical markers in particular archaeological excavations are crucial, and sometimes may represent a milestone, but most of them are not able to resolve the main problems of the discipline. Each makes a contribution towards resolving a problem in the archaeological record, based on the most recent works published about this topic²⁰. A statement that is particularly significant in soil chemistry studies. Furthermore, this analysis is very important in this field because it is the first time that this kind of investigation has been carried out in northern Iberia (for the megalithic context), and our analysis can be applied to other archaeological contexts all over the world. In a more general context, the methods used here are part of diverse goals in archaeology and the forensic world: from the time frame of the decomposition of human bodies, to the chemical markers signalling the remains of this process. It seems clear that the current analysis carried out is only one alternative among the many options now available in the field of soil chemistry applied to archaeological contexts²¹. Although not performed in this study, testing for trace element content could also be done in future investigations for instance. This might contribute more information about the processes involved here, due to their key role during the dissolution of bones and the chemical track that is left in the soils (Trueman *et al.* 2004: 737).

The approach to the archaeological reality of burials without bodies is not easy in any region of the world, due to the challenging requirements of reliable soil research. This study followed a common recommendation of other authors in this field, namely,

19. Like the analysis carried out in the two rooms of the Iberian Sanctuary of «Cerro El Pajarillo».

20. Although there are very interesting papers from the 1990s included in our bibliography, the last two decades show an increasing number of references in soil chemistry (Holliday and Garner 2007; Oonk *et al.* 2009; Shahack-Gross 2017).

21. For examples of post-Roman age in Galicia combining different techniques (elemental, spectroscopic, principal components, etc.), see García López *et al.*, 2022.

to use and integrate «different techniques for the chemical analysis of archaeological floors that will allow us to achieve as much information as possible» (Middleton *et al.* 2010: 205). The combination of quantitative concentration data, from ICP-MS, with other semiquantitative data from XRF and SEM, satisfy the investigative requirements and offer a method for analysing other neolithic sites in this area. Similar approaches in previous work have reported these same techniques to be powerful tools (Lubos *et al.* 2016: 52; Ginau *et al.* 2020: 3), although it is always necessary to consider the particularities of the sites under study. The combined use of ICP analysis with XRF has been highlighted for reaching meaningful interpretations of the sites in terms of abundance, concentration and interaction (Theden-Ringl and Gadd 2017: 247). In the end, the main goal is always to provide a reliable interpretation of the geo-chronological and archaeological history of the site.

The results were in agreement, especially those provided by XRF and ICP-MS, both showing increases in the phosphorous materials in the soil samples from the levels of use. Although P can be linked with other human activities, burials are one of the human actions that always increase this component. Here, the archaeological context established human burial as the explanation for the peaks detected. Either due to the dissolution of bones (more probable), or the interment of organic offerings (De Blas 2004: 77²²; 2006: 251) (less probable) the action of burial is always the main reason for prehistoric human soil contamination. Furthermore, the results are consistent with experimental burials carried out in the field of forensics, giving more support to the hypothesis of bones as the origin of the phosphorus. For instance, burying swine carcasses in an open site, with analysis before and after the burial (in bones and soil), identified the transfer of phosphorus from inhumated remains to the soil (Zangarini *et al.* 2016: 86).

Finally, the chemical fingerprints were in a very clear and encapsulated archaeological context with which they were closely linked. As was stated by Sánchez and Cañabate, this connection of the chemical patterns with the archaeological data is crucial for giving a «reasonable and more thorough interpretation» (1999: 54). In fact, the levels of P identified in their paper show many coincidences with our data (1999:55), thus emphasizing the funerary use of these megalithic sites. Although this usage can be inferred from the features of these sites held in common with others in the Atlantic and European context, in the Cantabrian cases only the funerary use can be suggested by the offerings. Such studies of the soil chemistry could be another element to certify these uses on a reliable empirical basis.

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22. Wood, fur, tree bark or basketry could be part of the offerings, for instance.

REFERENCES

- Arias, P., Armendariz, Á. and Teira, L. 2006: «The megalithic complex in Cantabrian Spain». In A. Rodríguez Casal (ed.): *Le Megalithisme Atlantique/The Atlantic Megaliths*. BAR. International series 1521, Archeopress. Oxford: 11-29.
- Aston, M.A., Martin, M. H. and Jackson, A.W. 1998: «The use of heavy metal soil analysis for archaeological surveying». *Chemosphere* 37: 465-477.
- Blas Cortina, M. Á. de 1983: *La Prehistoria reciente en Asturias*. Estudios de Arqueología asturiana, I, Fundación pública de cuevas y yacimientos prehistóricos de Asturias. Oviedo.
- Blas Cortina, M. Á. de 2004: «Túmulos enigmáticos sin ofrendas: a propósito de Monte Deva V (Gijón) y Berducedo (Allande), en Asturias». *Trabajos de Prehistoria*, 61(2): 63-83. <https://doi.org/10.3989/tp.2004.v61.i2.43>
- Blas Cortina, M. A. de 2008: «La plenitud de la arquitectura megalítica». In J. Rodríguez Muñoz, (ed.): *La Prehistoria en Asturias. Un legado artístico único*. La Nueva España. Oviedo: 525-528.
- Blas Cortina, M. Á. de and R. del Cueto, F. 2015: «La cuestión campaniforme en el Cantábrico Central y las minas de cobre prehistóricas del Aramo». *CuPAUAM* 41: 165-179. <http://dx.doi.org/10.15366/cupauam2015.41.011>
- Butzer, K.W. 1982: *Archaeology as human ecology: method and theory for a contextual approach*. Cambridge University Press. Cambridge.
- Cannell, R.J.S., Bill, J., Cheetham, P. and Welham, K. 2020: «Geochemical analysis of the truncated Viking Age trading settlement of Heimdalsjordet, Norway». *Geoarchaeology* 35: 748-771. <https://doi.org/10.1002/gea.21795>
- Carter, S.P. and Davison, D.A. 1998: «An evaluation of the contribution of soil micromorphology to the study of ancient arable agricultura». *Geoarchaeology* 13 (6): 535-547.
- Christian Wells, E. 2010: «Sampling Design and Inferential Bias in Archaeological Soil Chemistry». *Journal of Archaeological Method and Theory* 17: 209-230. <https://doi.org/10.1007/s>
- Christie, P.M. 1960: «A Bronze Age Barrow at Liskey, Perranzaboule, Cornwall». *Proceedings of the prehistoric society* 26: 76-98.
- Coles, J.M. 1965: «The excavation of a Neolithic round barrow at Pinacree, Perthshire, Scotland». *Proceedings of the prehistoric society* 31: 34-47.
- DiPietro, L.M., Driese, S.G. and Goebel, T. 2018: «Deposition and pedogenesis of periglacial sediments and buried soils at the Serpentine Hot Springs archaeological site, Seward Peninsula, AK». *Catena (Amst)* 170: 204-223. <https://doi.org/10.1016/j.catena.2018.04.036>
- Díaz Vázquez, M. 1993: «Aplicación de métodos físico-químicos en Arqueología». *Espacio, Tiempo y Forma, serie I, Prehistoria y Arqueología* 6: 249-262.
- Entwistle, J.A. and Abrahams, P.W. 1997: «Multi-Element Analysis of Soils and Sediments from Scottish Historical Sites. The Potential of Inductively Coupled Plasma-Mass Spectrometry for Rapid Site Investigation». *Journal of Archaeological Science* 24: 407-416.
- Fábregas Valcarce, R., Martínez Cortizas, A., Blanco Chao, R. and Chesworth, W. 2003: «Environmental change and social dynamics in the second-third millennium BC in NW Iberia». *Journal of Archaeological Science* 30: 859-871. [https://doi.org/10.1016/S0305-4403\(02\)00264-9](https://doi.org/10.1016/S0305-4403(02)00264-9)

- Fábregas Valcarce, R. and Vilaseco Vázquez, X. I. 2003: «El Neolítico y el Megalitismo en Galicia: problemas teórico metodológicos y estado de la cuestión». *Trabalhos de arqueologia* 25: 281-304.
- Fábregas Valcarce, R. and Vilaseco Vázquez, X. I. 2004: «El megalitismo gallego a inicios del siglo XXI». *Mainake* 26: 63-87.
- Fernández-Crespo, T. and de-la-Rúa, C. 2015: «Demographic evidence of selective burial in megalithic graves of northern Spain». *Journal of Archaeological Science* 53: 604-617. <https://doi.org/10.1016/j.jas.2014.11.015>
- Fernández-Eraso, J. and Mujika-Alustiza, J. A. 2013: «La estación megalítica de la rioja Alavesa: cronología, orígenes y ciclos de utilización». *Zephyrus* 71: 89-106.
- Flanagan, L. 1998: *Ancient Ireland. Life before the celts*. Gill & McMillan. Dublin.
- Gallelo, G., Pastor, A., Diez, A., la Roca, N. and Bernabeu, J. 2013: «Anthropogenic units fingerprinted by REE in archaeological stratigraphy: Mas d'Is (Spain) case». *Journal of Archaeological Science* 40: 799-809. <https://doi.org/10.1016/j.jas.2012.10.005>
- García Álvarez-Busto, A.; Laca, A. and Fernández González, A. 2019: »Revealing the Monastic Kitchen: Chemical Analysis of the Soil Inside the Monastery of Cornellana (North-West Spain)». *Archaeometry* 61: 145-160. <https://doi.org/10.1111/arc.12408>
- García-López, Z., Martínez Cortizas, A., Álvarez-Fernández, N. y López-Costas, O. 2022:»Understanding Necrosol pedogenetical processes in post-Roman burials developed on dunes sands». *Sci Rep* 12, 10619. <https://doi.org/10.1038/s41598-022-14750-5>
- Ginau, A., Steiniger, D., Hartmann, R., Hartung, U., Schiestl, R., Altmeyer, M., Seeliger, M. and Wunderlich, J. 2020: «What settlements leave behind — pXRF compositional data analysis of archaeological layers from Tell el-Fara'in (Buto, Egypt) using machine learning». *Palaeogeography, Palaeoclimatology, Palaeoecology* 546: 10966. <https://doi.org/10.1016/j.palaeo.2020.109666>
- Holliday, V.T. and Gartner, W.G. 2007: «Methods of soil P analysis in archaeology». *Journal of Archaeological Science* 34: 301-333. <https://doi.org/10.1016/j.jas.2006.05.004>
- Iriarte, M.J. 2009: «Vegetation landscape and the anthropization of the environment in the central sector of the Northern Iberian Peninsula: Current status». *Quaternary International* 200: 66-76. <https://doi.org/10.1016/j.quaint.2008.10.008>
- Linderholm, J. 2010: *The soil as a source material in archaeology, Theoretical considerations and pragmatic applications*. Doctoral thesis, Environmental Archaeology Lab, Umea Universitet, Umea.
- López-Merino, L., Cortizas, A.M. and López-Sáez, J.A. 2010: «Early agriculture and palaeoenvironmental history in the North of the Iberian Peninsula: a multi-proxy analysis of the Monte Areo mire (Asturias, Spain)». *Journal of Archaeological Science* 37: 1978-1988. <https://doi.org/10.1016/j.jas.2010.03.003>
- Lubos, C., Dreibrodt, S. and Bahr, A. 2016: «Analysing spatio-temporal patterns of archaeological soils and sediments by comparing pXRF and different ICP-OES extraction methods». *Journal of Archaeological Science: Reports* 9: 44-53. <https://doi.org/10.1016/j.jasrep.2016.06.037>
- Mañana Borrazás, P. 2003: «Vida y muerte de los megalitos. ¿Se abandonan los túmulos?». *Era-Arqueología. Revista de divulgação de estudos arqueológicos* 5: 164-177.
- Maritan, L. and Mazzoli, C. 2004: «Phosphates in archaeological finds: implications for environmental conditions of burial». *Archaeometry* 46 (4): 673-683.
- Martín Seijo, M., 2018: «Madera para acompañar la muerte: antracología en los contextos funerarios de el Caño (Coclé, Panamá)». In M. Alcántara, M., García Montero, F.

- Sánchez López, (Coords.): *56º Congreso Internacional de Americanistas. Aquilafuente*, 251, Arqueología. Ediciones Universidad de Salamanca. Salamanca: 566-574.
https://doi.org/10.14201/oAQ0251_2
- Martínez Cortizas, A., López-Merino, L., Bindler, R., Mighall, T. and Kylander, M.E. 2016: «Early atmospheric metal pollution provides evidence for Chalcolithic/Bronze Age mining and metallurgy in Southwestern Europe». *Science of total environment*, 545-546: 398-406. <http://dx.doi.org/10.1016/j.scitotenv.2015.12.078>
- Melaku, S., Dams, R. and Moens, L. 2005: «Determination of trace elements in agricultural soil samples by inductively coupled plasma-mass spectrometry: Microwave acid digestion versus aqua regia extraction». *Analytica Chimica Acta*, 543 (1-2): 117-123. <https://doi.org/10.1016/j.aca.2005.04.055>
- Middleton, W.D., Barba, L., Pecci, A., Burton, J.H., Ortiz, A., Salvini, L. and Rodriguez Suárez, R. 2010: «The Study of Archaeological Floors: Methodological Proposal for the Analysis of Anthropogenic Residues by Spot Tests, ICP-OES, and GC-MS». *Journal of Archaeological Method and Theory* 17 (3): 183-208.
- Moreno, F. and Ruiz-Gálvez, M. L. 1989: «Método de análisis de fosfatos». *Revista de Arqueología* 94: 39-48.
- Oliveira-Prendes, J.A., Afif-Khouri, E. and Palencia-García, P. 2014: «Producción, composición botánica y fertilidad del suelo en prados de riego del suroccidente de Asturias». *Pastos y Pac* 2014-2020 (53): 247-254.
- Oonk, S., Slomp, C.P. and Huisman, D.J. 2009: «Geochemistry as an aid in archaeological prospection and site interpretation: Current issues and research directions». *Archaeological Prospection* 16: 35-51. <https://doi.org/10.1002/arp.344>
- Pastor, A., Gallelo, G., Cervera, M.L. and de la Guardia, M. 2016: «Mineral soil composition interfacing archaeology and chemistry». *TrAC-Trends in Analytical Chemistry* 78: 48-59. <https://doi.org/10.1016/j.trac.2015.07.019>
- Pérez-Díaz, S., López-Sáez, J.A., Núñez de la Fuente, S. and Ruiz-Alonso, M. 2018: «Early farmers, megalithic builders and the shaping of the cultural landscapes during the Holocene in Northern Iberian mountains. A palaeoenvironmental perspective». *Journal of Archaeological Science: Reports* 18: 463-474. <https://doi.org/10.1016/j.jasrep.2018.01.043>
- Pickering, M.D., Ghislandi, S., Usai, M.R., Wilson, C., Connelly, P., Brothwell, D.R. and Keely, B.J. 2018: «Signatures of degraded body tissues and environmental conditions in grave soils from a Roman and an Anglo-Scandinavian age burial from Hungate, York». *Journal of Archaeological Science* 99: 87-98. <https://doi.org/10.1016/j.jas.2018.08.007>
- R. del Cueto, F. and Blas Cortina, M. Á. de 2018: «Investigaciones iniciales en el megalito de la Cobertoria, en el paraje de la Campa San Juan (Mallecina, Salas)». *Excavaciones Arqueológicas en Asturias 2013-2016* (7): 171-182.
- R. del Cueto, F. and Busto Zapico, M. 2020: «La construcción secular de un espacio funerario mediante distintas arquitecturas monumentales: primeras consideraciones tras las investigaciones en la Cobertoria (Salas, Asturias)». *Lucentum* XXXIX: 53-72. <https://doi.org/10.14198/LVCENTVM2020.39.03>
- Rogers, K. M., Martin, A. P., Pradel, G., Yuan, Y., Zhang, Y. and Turnbull, R.E. 2022: «Elemental and isotopic compositions of New Zealand regional soils identifies human and climate-induced effects». *Applied Geochemistry* 143: 105356. <https://doi.org/10.1016/j.apgeochem.2022.105356>
- Rubio Ordoñez, Á. 2010: *Magmatismo Neoproterozoico en el Antiforme del Narcea*. Doctoral thesis, Geology Department, University of Oviedo. Oviedo.

- Sánchez Vizcaino, A. and Cañabate, M. L. 1999: «Identification of activity areas by soil phosphorus and organic matter analysis in two rooms of the Iberian sanctuary 'Cerro El Pajarillo'». *Geoarchaeology* 6: 329-352.
- Sato, S., Neves, E.G., Solomon, D., Liang, B. and Lehmann, J. 2009: «Biogenic calcium phosphate transformation in soils over millennial time scales». *Journal Soils sediments* 9: 194-205.
- Shahack-Gross, R. 2017: «Archaeological formation theory and geoarchaeology: State-of-the-art in 2016». *Journal of Archaeological Science* 30: 439-459.
<https://doi.org/10.1016/j.jas.2017.01.004>
- Tejedor, C. 2014: «Reconstruyendo 'biografías megalíticas: algunos ejemplos de alteraciones estructurales en monumentos megalíticos del valle del Duero/Douro'». In J. Honrado; M. Brezmes; A. Tejeiro and O. Rodríguez (coords.): *Investigaciones Arqueológicas en el valle del Duero: Del Neolítico a la Antigüedad Tardía. II Jornadas de Jóvenes Investigadores del valle del Duero*. Ed. Glyphos. Valladolid: 67-86.
- Theden-Ringl, F. and Gadd, P. 2017: «The application of X-ray fluorescence core scanning in multi-element analyses of a stratified archaeological cave deposit at Wee Jasper, Australia». *Journal of Archaeological Science: Reports* 14: 241-251.
<https://doi.org/10.1016/j.jasrep.2017.05.038>
- Toller, S., Funari, V., Zannoni, D., Vasumini, I. and Dinelli, E. 2022: «Sediment quality of the Ridracoli fresh water reservoir in Italy: Insights from aqua regia digestion and sequential extractions». *Science of The Total Environment* 826: 154167.
<https://doi.org/10.1016/j.scitotenv.2022.154167>
- Trueman, C.N.G., Behrensmeyer, A.K., Tuross, N. and Weiner, S. 2004: «Mineralogical and compositional changes in bones exposed on soil surfaces in Amboseli National Park, Kenya: Diagenetic mechanisms and the role of sediment pore fluids». *Journal of Archaeological Science* 31: 721-739. <https://doi.org/10.1016/j.jas.2003.11.003>
- Turner-Walker, G. 2008: «The Chemical and Microbial Degradation of Bones and Teeth». In R. Pinhasi, and S. Mays (eds.): *Advances in human paleopathology*. Jon Wiley&sons. Chichester.
- Uzquiano, P. 2018: «Vegetation, firewood exploitation and human settlement in northern Spain in relation to Holocene climate and cultural dynamics». *Quaternary International* 463: 414-424. <https://doi.org/10.1016/j.quaint.2016.10.034>
- Valdés, V. M. 1995: «Cistas de la Edad del Bronce: el análisis de fosfatos como evidencia de la inhumación». *Complutum* 6: 329-352.
- Vilaseco Vázquez, X. I. 1997-1998: « Datos sobre la presencia de estructuras de acceso en túmulos megalíticos da provincial de Lugo». *Boletín do Museo Provincial de Lugo* 8(1): 125-158.
- Walkington, H. 2010: «Soil science applications in archaeological contexts: A review of key challenges». *Earth-Science Reviews* 103: 122-134. <https://doi.org/10.1016/j.earscirev.2010.09.002>
- Weihrauch, C. and Söder, U. 2021: «On the Challenges of Soil Phosphorus Prospections in Heterogeneous Environments—a Case Study on the Iron Age Altenburg Hillfort (Niedenstein, Hesse, Germany)». *Journal of Archaeological Method and Theory* 28: 470-511.
<https://doi.org/10.1007/s10816-020-09461-y>
- Wilson, C., Davidson, D. and Cresser, M. 2008: «Multi-element soil analysis: an assesment of its potential as an aid to archaeological interpretation». *Journal of Archaeological Science* 35(2): 412-424.

- Williams, R., Errickson, D. and Taylor, G. 2021: «Mapping an archaeological site: Interpreting portable X-ray fluorescence (pXRF) soil analysis at Boroughgate, Skelton, UK». *Journal of Archaeological Science: Reports* 38: 103109. <https://doi.org/10.1016/j.jasrep.2021.103109>
- Zaeem, M., Nadeem, M., Huong Pham, T., Ashiq, W., Ali, W., Shah Mohioudin Gillani, S. and Thomas, R. 2021: «Development of a hyperspectral imaging technique using LA-ICP-MS to show the spatial distribution of elements in soil cores». *Geoderma* 385: 114831. <https://doi.org/10.1016/j.geoderma.2020.114831>
- Zangarini, S., Trombino, L. and Cattaneo, C. 2016: «Micromorphological and ultramicroscopic aspects of buried remains: Time-dependent markers of decomposition and permanence in soil in experimental burial». *Forensic Science International* 263: 74–82. <https://doi.org/10.1016/j.forsciint.2016.03.052>