



## Using ZooMS to assess archaeozoological insights and unravel human subsistence behaviour at La Viña rock shelter (northern Iberia)

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### ABSTRACT

The highly fragmented nature of Palaeolithic faunal assemblages is a regular limitation in archaeozoological analyses as it prevents a precise taxonomic identification following comparative anatomy criteria. In this paper, we integrate Zooarchaeology by Mass Spectrometry (ZooMS) analysis of unidentifiable bone fragments within archaeozoological and taphonomic data to overcome this limitation and disentangle the subsistence strategies of Solutrean and Magdalenian human groups of the La Viña rock shelter (northern Iberia). The ZooMS results are consistent with the archaeozoological data showing preferential exploitation of red deer complemented by horses and caprids, whereas large bovinds and reindeer are a minor component. This study also reveals significant species variability in classifying unidentifiable bones to mammal-size classes. The combination of biomolecular methods and traditional archaeozoology and taphonomy provides a higher resolution of faunal diversity in Palaeolithic assemblages and hominin subsistence behaviour related to carcass transport and seasonality.

### 1. Introduction

Iberia, particularly the Cantabrian region on the North Atlantic coast, plays a significant role in the European Palaeolithic. This northern Spain area has a long research tradition of more than 150 years due to the notably rich archaeological assemblages preserved in the numerous regional cavities. The study of faunal remains consumed by human groups is key for understanding past human behaviour broadly, including subsistence strategies and other socio-economic aspects such as hunting tactics, transport decisions and carcasses processing, site functionality and mobility patterns.

Since the 1970s, by the pioneer work of palaeontologist J. Altuna (1972) and North American archaeologists L.G. Freeman (1973) and L. G. Straus (Straus, 1977, 1992), archaeozoological studies and paleo-economic interpretations of Middle and Upper Palaeolithic sites of the Cantabrian Region are abundant, especially those focused on the Solutrean and Magdalenian cultures (e.g. Castaños, 1992; Altuna, 1995; Quesada, 1997; Yravedra, 2002; Mateos, 2005; Marín-Arroyo, 2010; Marín-Arroyo and Geiling, 2015; Portero et al., 2019). From the 2000s onwards, applying taphonomy to regional faunal assemblages has also allowed assessing aspects previously disregarded such as deciphering

carcasses exploitation, site formation processes and identification of bone accumulator agents, primarily when carnivores and birds of prey used the same cavities throughout time (Marín-Arroyo et al., 2009; Sanchis et al., 2019; Sánchez-Romero et al., 2020).

As in other Eurasian regions, the Cantabrian Palaeolithic faunal record is generally highly fragmented due to different taphonomic processes, including activity by humans and other non-human biological accumulating agents and post-depositional processes. As a result, around 70–80% of the faunal assemblages correspond to unidentifiable remains. Despite the abundance of archaeozoological studies, these generally focused on the analysis of identifiable bone fragments, therefore losing valuable information to infer past human subsistence behaviour and determine the role of other biological agents in the archaeological deposit formation. When non-identifiable bones are included in faunal analyses, archaeozoologists usually approach their study by classifying those remains into mammal-size classes. However, these classifications differ among archaeozoologists lacking standard categorizations, which is problematic for inter-site comparisons.

In recent years, the study of the unidentifiable bone fraction has also been approached through Zooarchaeology by Mass Spectrometry (ZooMS), a minimally destructive proteomic method for taxonomic

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identification based on collagen peptide mass fingerprinting (Buckley et al., 2009). This biomolecular method overcomes the issues associated with high bone fragmentation rates by allowing the taxonomic identification of those remains on a broader scale. In previous studies, ZooMS has identified new animal species previously unknown in those sites (Welker et al., 2015, 2017; Buckley et al., 2017; Sinet-Mathiot et al., 2019; Buckley and Cheylan, 2020; Ruebens et al., 2023) as well as hominins (Brown et al., 2016; Welker et al., 2016; Devièse et al., 2017; Hublin et al., 2020). In parallel, ZooMS data and morphologically identified faunal assemblages from the same sites have been compared in terms of taxonomic diversity and abundance to evaluate the global faunal composition (Silvestrini et al., 2022). In conjunction with the growing use of ZooMS, its integration with archaeozoology and taphonomy to assess the relationship between faunal composition and Palaeolithic human subsistence behaviour is also increasingly addressed (Sinet-Mathiot et al., 2019, 2023; Pothier Bouchard et al., 2020; Ruebens et al., 2023) but so far has not been explored in the archaeological record of the Iberian Peninsula.

In this paper, we explore the potential of using ZooMS to enhance the archaeozoological methodology and, therefore, to better understand past human subsistence strategies during the Upper Palaeolithic. For this goal, we present the integration of taxonomic identification through ZooMS and traditional archaeozoology combined with the taphonomic analysis of the Solutrean and Magdalenian macrofaunal remains of the La Viña rock shelter (northern Iberia) as a case study. Moreover, this study aims to examine the degree of Pleistocene collagen preservation based on protein concentration measurements and glutamine deamidation and how these values are connected.

## 2. Materials

La Viña rock shelter (La Manzaneda, Asturias) is located in the western part of the Cantabrian Region (northern Spain) within the Nalón Valley. This large limestone cavity was excavated during the 80s and 90s of the last century by a team led by J. Fortea (University of Oviedo) (Fortea, 1981, 1990, 1992, 1995, 1999). The excavations carried out in two areas of the rock shelter (western and central sector) revealed a long archaeological sequence dating from the late Mousterian to the Magdalenian cultural techno-complexes, as well as a set of pre-Magdalenian parietal engravings (Fortea and Rodríguez, 2007; González-Pumariega et al., 2017). AMS and conventional radiocarbon dates provide a chronological framework for the entire stratigraphy extending from >62 to 16 kyr cal BP (Fortea, 1990, 1999; Santamaría, 2012; Wood et al., 2014; Marín-Arroyo et al., 2018; Torres-Iglesias et al., 2022).

The numerous lithic and bone industry, faunal remains, portable art and combustion structures found in the archaeological levels reveal an almost continuous human occupation of the rock shelter from the late Middle Palaeolithic to the end of the Upper Palaeolithic (Fernández de la Vega and Rasilla, 2012; Santamaría, 2012; Martínez, 2015; Duarte and Rasilla, 2020; López-Tascón et al., 2020; Rasilla et al., 2020; Torres-Iglesias et al., 2022). The faunal assemblage analysed in this study comprised a total of 11,818 remains found in levels VI, V, IV and III of the western sector. The first two, dated between 25.3 and 24.9 kyr cal BP, are culturally attributed to the Middle and Upper Solutrean, respectively, and the latter (16.4–16.7 kyr cal BP) to the Middle Magdalenian.

## 3. Methods

### 3.1. Archaeozoology and taphonomy

Taxonomic and anatomical identification was based on a comparison with the reference osteological collections at the Grupo I + D + i EvoAdapta and the Cantabrian Maritime Museum (Santander) and animal anatomy atlases (Pales and Lambert, 1971; Schmid, 1972; Barone,

1987; Hillson, 2005). The remains that could not be identified taxonomically due to the absence of distinctive landmarks were grouped into five mammal-size classes based on the classification proposed by Bunn (1986): size 1, animals weighing <2 kg (small mustelids); size 2, animals weighing <20 kg (Lagomorphs and small carnivores such as *Vulpes*); size 3, small-sized animals weighing between 20 and 30 kg (e.g. *Rupicapra*, *Capreolus* and *Canis lupus*); size 4, medium-sized animals weighing between 30 and 160 kg (e.g. *Cervus elaphus* and *Capra pyrenaica*) and size 5, large-sized animals weighing >300 kg (e.g. *Bos primigenius*/*Bison priscus* and *Equus ferus*). The small bone fraction was also analysed following the sorting process proposed by Geiling et al. (2018).

The number of identified specimens (NISP) and its percentage were used to evaluate species abundance in the assemblage and to compare archaeozoological and ZooMS data, as other common archaeozoological quantification indexes, such as the minimum number of elements (MNE) and the minimum number of individuals (MNI) cannot be compared equally with ZooMS results.

Bone surface modifications were characterised using a stereomicroscope Leica S8APO (10x–80x magnification range). The determination of biostratigraphic and diagenetic alterations and the identification of bone collector agents was made following the criteria established in the taphonomic literature. For each faunal remain, taphonomic alterations were systematically recorded, including those made by natural agents (weathering stages, manganese coating, root etching, water dissolution, concretion, and trampling) (Behrensmeier, 1978; Lyman, 1994; Fisher, 1995; Fernández-Jalvo and Andrews, 2016) as well as by carnivores and birds of prey (tooth marks, furrowing and digestion) (Haynes, 1983; Marín-Arroyo and Margalida, 2012; Sala et al., 2014; Lloveras et al., 2017). The anthropogenic modifications include different types of butchering marks (incisions, scraping marks, and chop marks) (Shipman, 1981; Shipman and Rose, 1983; Olsen and Shipman, 1988; Domínguez-Rodrigo et al., 2009) and their associated activity (Binford, 1981; Nilssen, 2000; Costamagno et al., 2019), percussion marks (percussion pits, grooves, and notches) (Capaldo and Blumenshine, 1994; Pickering and Egeland, 2006; Vettese et al., 2020), burning stages (Shipman et al., 1984), fresh fractures for bone marrow extraction, and bone flakes derived from this activity (Villa and Mahieu, 1991; Fisher, 1995; Coil et al., 2020).

### 3.2. ZooMS

162 faunal remains (bone and dentine) out of the total specimens analysed were selected for ZooMS analysis. Sample selection was focused on the faunal remains that had already been part of the archaeozoological and taphonomic analysis (carried out by one of us, LTI). Samples are mostly morphologically unidentifiable long bone shafts attributed to one of the mammal-size classes established in the archaeozoological methods. Priority was given to remains, first, identified at the anatomical level; second, to all those that showed evidence of anthropogenic modification (cut marks, percussion marks and fresh fractures) and third, to those that belonged to a category including two mammal sizes (e.g. mammal size 4–5). Sample selection also attempted to represent various bone types (cancellous and cortical). Remains identified as foetal or infant individuals, whose taxonomic identification is generally problematic due to fragmentation and the absence of typical morphological characteristics, were also selected. Sample selection excluded remains smaller than 2 cm and bones showing signs of burning or high sedimentary concretions. Cortical thickness (in mm) was systematically recorded for each long bone shaft and mandible fragment (n = 101) for comparison with the mammal-size class classification.

Extraction and digestion of collagen type I (COL1) were carried out following published protocols. First, each sample (~10–30 mg) was incubated in 100 µL of 50 mM ammonium-bicarbonate (NH<sub>3</sub>CO<sub>3</sub>, AmBic) buffer at 65 °C for 1 h to extract the collagen, following the AmBic method (van Doorn et al., 2011). The resulting soluble collagen supernatant was removed from the bone sample and stored at –20 °C in

case a second analysis was required. Then, all samples were demineralised in 150  $\mu\text{L}$  of 0.6 M HCl at 4 °C for 18 h, according to the acid-insoluble collagen method (Buckley et al., 2009). After neutralising the samples to a pH of around 8, bone collagen was extracted by incubating at 65 °C for 1 h in 100  $\mu\text{L}$  of AmBic buffer. Subsequently, the protein concentration of each extraction was quantified by BCA (bicinchoninic acid) assay (ThermoFisher Scientific) and the volume of gelatinised protein required to achieve a ratio of 20  $\mu\text{g}$  of digested protein to 0.4  $\mu\text{g}$  of trypsin in each sample was transferred to a new tube. Buffer volumes containing soluble protein were enlarged to 50  $\mu\text{L}$  of AmBic buffer and digested using trypsin (Promega) between 12 and 18 h at 37 °C and acidified by adding 1  $\mu\text{L}$  of 10% trifluoroacetic acid (TFA) to stop digestion. BCA assay was performed on 148 of the 162 samples. The collagen peptides were concentrated and cleaned using C18 Ziptips (ThermoFisher Scientific) and eluted in a 50  $\mu\text{L}$  solution of 50% ACN/0.1% TFA. Eluted peptides were then spotted in triplicate on a MALDI Bruker plate and mixed with a matrix solution of  $\alpha$ -cyano-4-hydroxycinnamic acid (CHCA).

MALDI-TOF MS analysis was conducted at the University of Cambridge on a Bruker ultrafleXtreme MALDI TOF/TOF, except for 14 samples analysed at the University of York on a Bruker Ultraflex III, in the mass range 800–4000 Da. Spectral triplicates for each sample were merged in R (R Core Team, 2021) using the MALDIquant package (Gibb and Strimmer, 2012) with the settings as previously described (Ruebens et al., 2023). Taxonomic identification was made manually in mMass v. 5.5.0 (Strohalm et al., 2008) by comparing the spectra against a reference library of known peptide markers for the medium and large-sized mammalian species occurring in Europe during the Late Pleistocene (Buckley et al., 2009, 2014; Kirby et al., 2013; Welker et al., 2016; Jensen et al., 2020).

The taxonomic identity of 26 samples was verified through the digestion and analysis of the first soluble collagen extracted (AmBic). The bone collagen digestion and peptides analysis for these samples followed the above-mentioned steps.

In order to assess the level of collagen degradation and preservation, the glutamine (Gln) deamidation ratio was calculated using the Q2E package (van Doorn et al., 2012; Wilson et al., 2012) for the peptide COL1 $\alpha$ 1 508–519 (1105.6  $m/z$ ), as it is one of the most stable peptides and the predominant one in the samples analysed. This peptide also has an identical amino acid sequence for the taxa encountered in this study. The rate of Gln deamidation is expressed as a range from 0% (complete deamidation, when all the glutamine has been converted to glutamic acid) to 1% (no deamidation, and all glutamines are unmodified).

Peptide markers may be similar or identical for phylogenetically close species such as *Bos primigenius* and *Bison priscus* or cervids, except for *Rangifer tarandus* and *Capreolus*. Therefore, the resolution of ZooMS taxonomic identifications is often at the family or subfamily level. To allow easier comparison between ZooMS results and archaeozoological data, some taxonomic groups were linked to a particular species identified in the archaeological record at La Viña and other contemporary sites in the Cantabrian region based on currently available information. The Cervus/Saiga category includes, among other taxa, several cervids species (Table S1). However, only red deer (*Cervus elaphus*) has been identified at La Viña, and the evidence of the rest of the species in the archaeozoological record of the Cantabrian Region during the Solutrean and Magdalenian is exceptional or even absent (Mariezkurrena, 2011). Equidae also includes several species from the genera *Equus*, although they belong most likely to *Equus ferus*. Finally, the Caprinae category (not *Capra* sp.) includes those specimens in which the marker COL1 $\alpha$ 2 978–990 could not be identified. When observed, this peptide marker allows distinguishing between chamois (*Rupicapra*) and musk ox (*Ovibos moschatus*). In La Viña, an attribution to chamois is more likely. In the ZooMS and archaeozoological data comparison, only ungulate and carnivore data have been used, excluding small vertebrates (e.g. leporids, amphibia and rodents) and birds, as they have a low representation and do not seem to be directly linked to human subsistence strategies or

carnivore occupation of the rock shelter.

## 4. Results

### 4.1. Faunal composition

The analysed assemblage (including data from both morphological and ZooMS components) comprises 11,818 faunal remains. Of those, 2099 are mammal remains, 28 bird remains, and one fish vertebra, while 1898 fragments were classified to mammal-size classes and 7778 remained indeterminate after ZooMS analysis. The extraction blank processed alongside the samples to monitor possible protein contamination was empty of COL1. Moreover, the 26 samples analysed following AmBic and acid-insoluble methods resulted in the same taxonomic identifications for both collagen extraction methods. Therefore, the results can hardly be explained as the result of protein contamination in the laboratory.

Table S1 shows the identified taxa in the studied levels according to the morphological and ZooMS identification and the total NISP combining both methods. Although MNI and MNE were also calculated during the archaeozoological analysis (Torres-Iglesias, 2023), only NISP has been included in this study as the other quantification units cannot be compared with ZooMS results.

ZooMS identification was successful in 97.5% of the 162 sampled specimens, of which 66.7% ( $n = 108$ ) could be identified as a specific ZooMS taxon (Equidae, *Capra* sp., *Rupicapra*, *Cervus* – Cervidae/Saiga, *Rangifer* and *Bos/Bison*), whereas 16.7% ( $n = 27$ ) were classified into subfamilies (Caprinae/Cervidae, Caprinae, Caprinae not *Capra* sp. and *Rangifer/Capra*) and 14.2% ( $n = 23$ ) could only be assigned to family or order level (Bovidae/Cervidae, Elephantidae, Cetacea and Cervidae/Saiga/Capreolus) as some of the peptide markers were missing.

The ZooMS species representation is coherent with the results offered by the archaeozoological identification (Fig. 1). However, ZooMS has identified species not present in the morphological component in some archaeological levels (Table S2), as well as corrected the taxonomic identification of two specimens. In the Middle Solutrean level VI, the presence of a cetacean has been confirmed. It is one of the two teeth previously identified as belonging to a phocid (Torres-Iglesias et al., 2022). The remaining tooth, not analysed through ZooMS, has also been identified as a cetacean due to its morphological similarity. Based on the observed peptide markers (COL1 $\alpha$ 2 484–498: 1453.7  $m/z$  and COL1 $\alpha$ 2 793–816: 2119.1  $m/z$ ), this specimen could correspond to the Delphinidae or Phocoenidae family. The comparison with the collections of the Cantabrian Maritime Museum in Santander showed that these teeth correspond to a bottlenose dolphin (*Tursiops truncatus*). In level V (Upper Solutrean), *Bos/Bison* and Elephantidae were also added to the faunal spectrum identified. Regarding the latter, due to the low quality of the spectrum, only the markers COL1 $\alpha$ 2 484–498 (1453.7  $m/z$ ) and COL1 $\alpha$ 2 793–816 (2115.1  $m/z$ ) have been observed, so the specimen has been attributed to the Elephantidae family. However, considering the regional archaeological context, this dental fragment likely belongs to *Mammuthus primigenius*, a species also identified in level VI. No terrestrial carnivore species have been identified, which is consistent with the low representation of these taxa (total NISP = 9) in the morphological component of the analysed levels (Table S2).

Red deer is the main prey in all levels for the ZooMS and morphology components, although with varying representation. The Solutrean Level V shows the major difference in the representation of this species between both components (Fig. 1). In this level, combining both taxonomic identification methods produces a slight decrease in red deer and caprids (*Capra pyrenaica* and *Rupicapra*). At the same time, the percentage of *Equus ferus* increases (Table S2). ZooMS has also augmented the representation of *Equus ferus* and enabled its differentiation from other large ungulates (*Bos/Bison*), especially in the Solutrean levels V and VI (Table S2). In levels III + IV (Magdalenian), a six-fold increase in the reindeer representation in the ZooMS component (9.3%) is observed

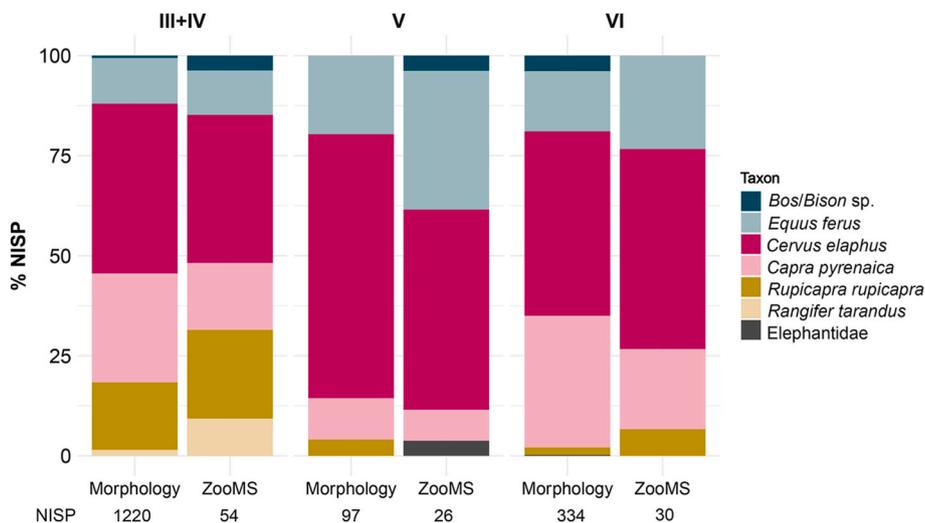


Fig. 1. Comparison of herbivore species identified by archaeozoology (morphology) and by proteomics (ZooMS) for each level of La Viña.

compared to the morphologic component (1.5%). The Magdalenian levels also show an increase of *Rupicapra* in the ZooMS component, while *Cervus elaphus* and *Capra pyrenaica* representation decreases compared to the morphological component (Fig. 1).

We also analysed 12 remains of foetal and newborn individuals (one from level V and level VI and ten from level IV) through ZooMS to improve the seasonality information and precise the hunting strategies. The taxonomic identification was successful for 11 out of 12 studied remains, demonstrating that Late Pleistocene foetal and newborn

remains are generally suitable for proteomic analysis. Most were identified at a subfamily level (Bovidae/Cervidae, Cervidae/Saiga/Capreolus and Rangifer/Capra sp.). Two specimens were identified as red deer (Cervidae/Saiga) and one as Equidae. ZooMS identification has provided helpful information to estimate or confirm the seasonality of human occupations at La Viña. In level V, a non-erupted tooth of red deer indicates the occupation of the rock shelter during autumn (Torres-Iglesias et al., 2022). Meanwhile, the ZooMS identification of a long bone shaft of the same level corresponding to a red deer foetal or

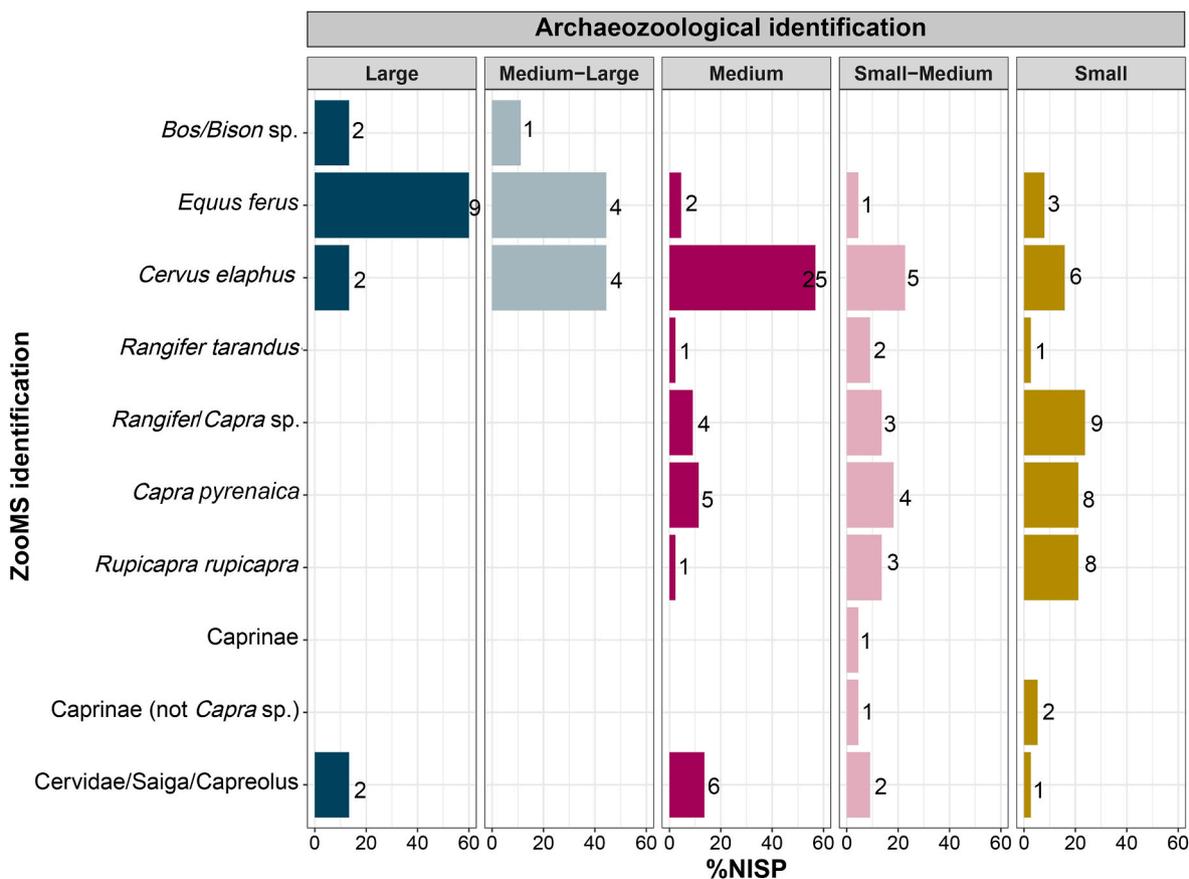


Fig. 2. Comparison of the ZooMS taxa with their previous attribution to one of the mammal size classes. Numbers in each bar indicate NISP. Correlation of the mammal-size classes established in the methodology: Large = size 5; Medium-Large = size 4–5; Medium: size 4; Small-Medium = size 3–4; Small = size 3.

newborn suggests that the rock shelter was also occupied during spring, coinciding with the calving season of hinds. In level IV, a fragment of a foetal humerus was identified as Equidae. According to the morphology and size of this bone, the foetus was probably no more than seven months gestation, indicating that the pregnant mare was captured during the late winter-early spring months. While in level V ZooMS results complement the seasonality data derived from the morphological assemblage, in level IV the species identification of the foetus by ZooMS allowed us to estimate the seasonality of human occupations, as the archaeozoological results prevented information in this sense.

#### 4.2. Mammal-size classification

In this work, non-identifiable bones were classified into mammal-size classes based on the cortical thickness for long bone shafts and body size in the case of axial skeletal elements and epiphyses, considering the comparison with the reference osteological collection and the archaeozoologist's (LTI) own experience. The cross-checking between the ZooMS identification and the previous attribution to one of the size classes shows that classifications are consistent with the ZooMS identification, except in the case of red deer and horse, which are present in all mammal-size categories (Fig. 2). 67.5% of the specimens were correctly attributed to the corresponding size, while 32.5% had been attributed to a larger or smaller size (e.g. red deer classified as a small mammal). The horse specimens previously attributed to small or small-medium size are fragments of vertebrae and ribs and a fragment of a humerus epiphysis, while the specimens attributed to large or medium-large mammal size are long bone shafts and a cranial element. Therefore, the misclassification appears to be related to the skeletal part considered. In contrast, the variability in the red deer body size classification does not seem to be associated with skeletal elements since part of the red deer remains classified as small or medium-small mammals are long bone shafts. Among the caprids, size attribution tends to classify them as small and small-medium mammals. The same happens with reindeer. Although a few reindeer remains were identified in the current study ( $n = 4$ ), only one was classified as a medium mammal, the size to which the reindeer would theoretically correspond based on its body weight.

Fig. 3 shows the cortical thickness (mm) of the species identified by ZooMS. Only measurements of the long bone shafts and mandible

(excluding ribs and vertebrae) of adult specimens have been selected. Horse is the species showing the greatest variability and range of dimensions (variance = 6.02 mm). Most of the bone elements of this taxon are grouped between 10.9 and 8 mm. However, there are bones with higher and lower measurements, which overlap with other large ungulates such as bison and auroch as well as the dimensions of red deer. The variance of the red deer measurements is lower (2.07 mm), although it overlaps with most of the other taxa (horse, ibex, reindeer and chamois).

#### 4.3. Skeletal representation

Sample selection was also focused on anatomically identifiable skeletal elements to increase the taxonomic data available for evaluating prey skeletal profiles. Studied long bones have been unidentified diaphysis fragments from the mid-shaft or near the metaphysis. Epiphysis fragments were categorised separately as they are mainly spongy bone fragments, usually taxonomically categorised as indeterminate. Within the anatomical units, long bone shafts, forelimb and hindlimb remains are the most abundant, as preference was given to these skeletal elements during sampling (Fig. 4). All taxa were identified in those categories, although with different abundances.

Cranial and axial elements mainly belong to red deer and chamois, although reindeer and horses are also present. Despite the cranial and axial sample being smaller than the limbs one, their taxonomic identification by ZooMS is relevant. These anatomical parts, especially ribs and cranial fragments (excluding teeth), are generally difficult to attribute to a specific species. Therefore, they are usually under-represented in skeletal profiles. ZooMS has identified vertebra and cranium fragments of *Equus ferus* in level V (Upper Solutrean) previously not present in the skeletal representation.

#### 4.4. Taphonomic modifications

Anthropogenic modifications were recorded in almost all the taxa identified by ZooMS (Table 1), representing 49.4% of the 162 analysed bones. Fresh fractures for bone marrow extraction are the most common (31.5%), followed by percussion marks (9.9%). These two anthropogenic modifications were recorded in all the ungulates (excluding

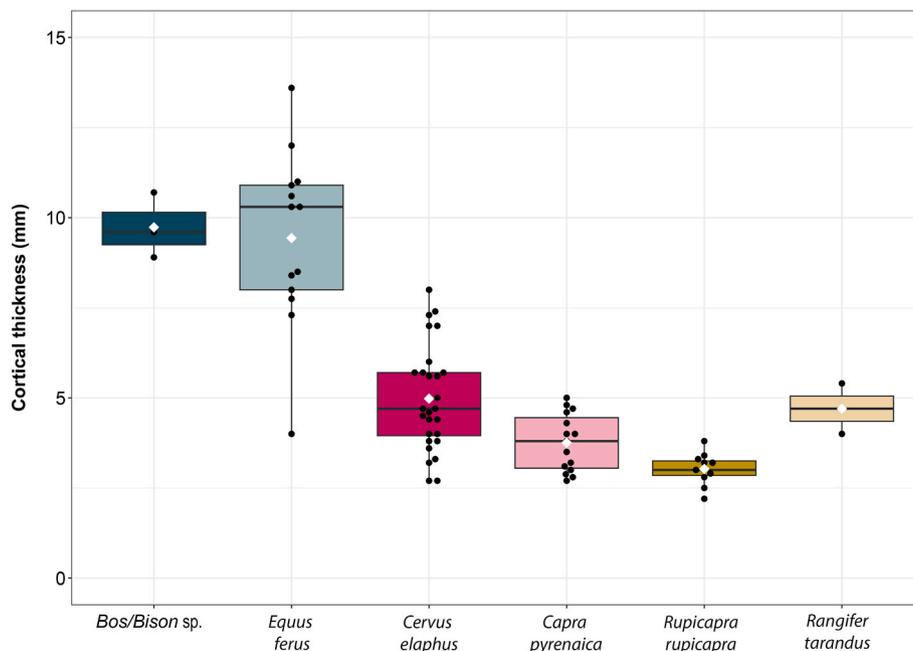


Fig. 3. Distribution of the cortical thickness (mm) in long bone shafts and mandible fragments (corpus) according to the species identified by ZooMS. The white rhombus indicates the mean.

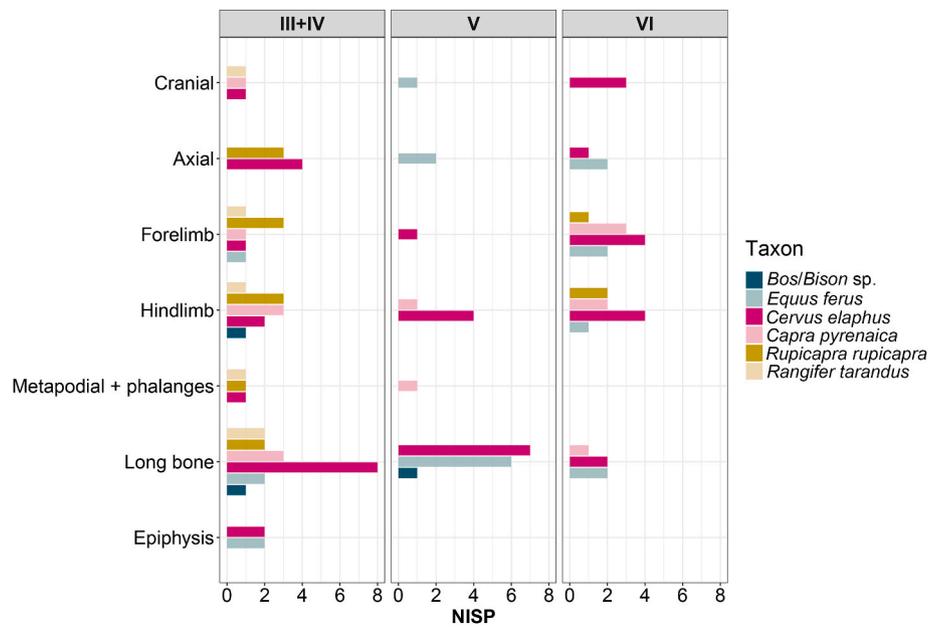


Fig. 4. Anatomical distribution of bone elements identified by ZooMS from levels III and IV (Middle Magdalenian), V (Upper Solutrean) and VI (Middle Solutrean) of La Viña.

Table 1  
Human and carnivore modifications recorded in bones of La Viña sampled for ZooMS.

Taxon	N	Anthropogenic modifications								Carnivore modifications			
		Cut marks		Fresh fracture		Percussion marks		Flakes		Pits		Crenulated edge	
	n	%	n	%	n	%	n	%	n	%	n	%	
Elephantidae	1												
<i>Bos/Bison</i> sp.	3			1	33.3	1	33.3						
<i>Equus ferus</i>	22	2	9.1	7	31.8	1	4.55	1	4.5		1	4.5	
<i>Cervus elaphus</i>	48	2	4.2	19	39.6	7	14.6	1	2.1				
<i>Rangifer tarandus</i>	5			1	20	1	20	1	20.0				
Rangifer/Capra sp.	18	3	16.7	4	22.2			1	5.6				
<i>Capra pyrenaica</i>	17	1	5.9	10	58.8	2	11.8						
<i>Rupicapra</i>	13			3	23.1	2	15.4						
Caprinae	1			1	100								
Caprinae (not <i>Capra</i> sp.)	4					1	25			1	25		
Caprinae/Cervidae	4			2	50								
Cervidae/Saiga/Capreolus	12			3	25			1	8.3				
Bovidae/Cervidae	9					1	11.1						
Cetacea	1												
Failed	4												
<b>Total</b>	<b>162</b>	<b>8</b>	<b>4.9</b>	<b>51</b>	<b>31.5</b>	<b>16</b>	<b>9.9</b>	<b>5</b>	<b>3.1</b>	<b>1</b>	<b>0.6</b>	<b>1</b>	<b>0.6</b>

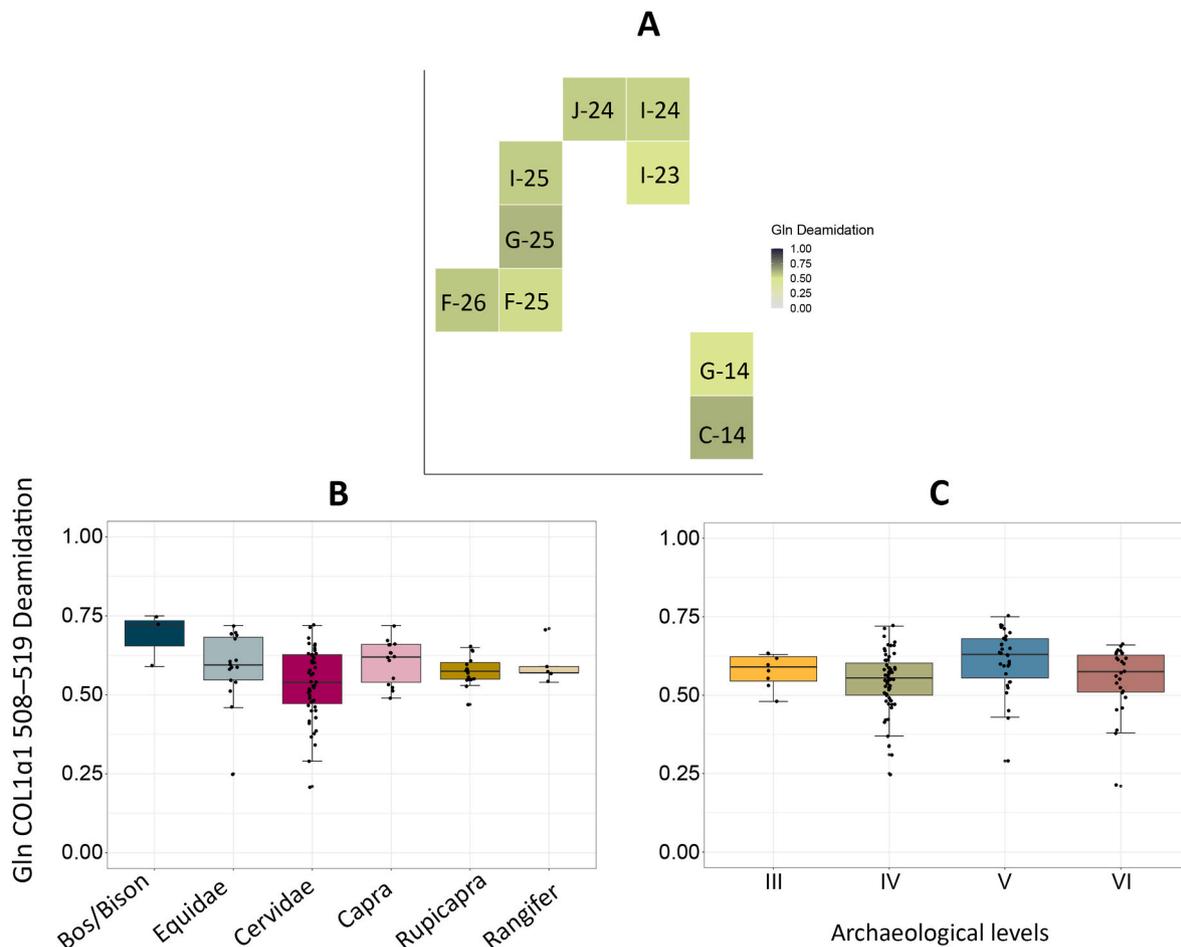
Elephantidae). Evidence of fresh breakage and impact points are more frequent in long bone elements with high marrow content, although it was also observed on a red deer phalanx and mandible. Cut marks resulting from different butchering activities were only recorded in horses, red deer, Spanish ibex and Rangifer/Capra. The butchering marks are mainly concentrated on long bone shafts and are probably related to meat extraction. Evidence of periosteum removal was observed on a humerus of ibex, and skinning activity was also registered on an intermediate phalanx of red deer. The latter species concentrates most of the human modifications (41.5% of the 80 bones with anthropogenic marks) located mainly on long bones of the limbs but also the mandible, ribs and phalanges.

Carnivore modifications were only observed on two bones from the ZooMS component identified as horse and Caprinae not *Capra* sp. (likely chamois). These specimens with gnawing marks represent barely 1% of the total analysed sample. Generally, the bone surface modifications recorded on ZooMS samples are consistent with those shown in the assemblage identified by archaeozoology, including their distribution among major taxa (Table S3).

The ZooMS assemblage is also affected by natural taphonomic modifications, mainly manganese coating (44%) and weathering (35%), although both alterations are recorded in low stages. Root etching (12%), concretion (6%) and trampling (4%) were also registered on bone surfaces.

#### 4.5. Molecular preservation

Glutamine deamidation values for peptide COL1α1 508–519 (1105.6 m/z) were obtained for 77.2% of the bone specimens analysed and range between 0.21 and 0.75 (Fig. 5). The median of deamidation values shows significant differences between stratigraphic levels (Kruskal-Wallis test: chi-square = 11.67, df = 3, p = 0.009). However, the only statistically significant levels are IV and V (Mann-Whitney pairwise Bonferroni correction: p = 0.01) with a medium effect size (Cohen's d = 0.67 95% CI [0.22, 1.11]). Nevertheless, the sample size should be increased to have more robust results. On the contrary, no differences are observed at the spatial level between the mean deamidation values for each square analysed in levels III, IV, V and VI of the



**Fig. 5.** Comparison of the glutamine deamidation values of the peptide COL1 $\alpha$ 1 508–519 obtained for the La Viña bone fragments. Data are compared in A by excavation spatial squares (F, G, I and J are western sector and G and C correspond to the central sector), B by main taxa and C by archaeological levels. Cervidae category corresponds to Cervidae/Saiga/Capreolus. NISP values for each group in B: Bos/Bison = 3, Equidae = 16, Cervidae = 50, Capra = 15, Rupicapra = 16, Rangifer = 5 and in C: III = 8, IV = 60, V = 31, VI = 26.

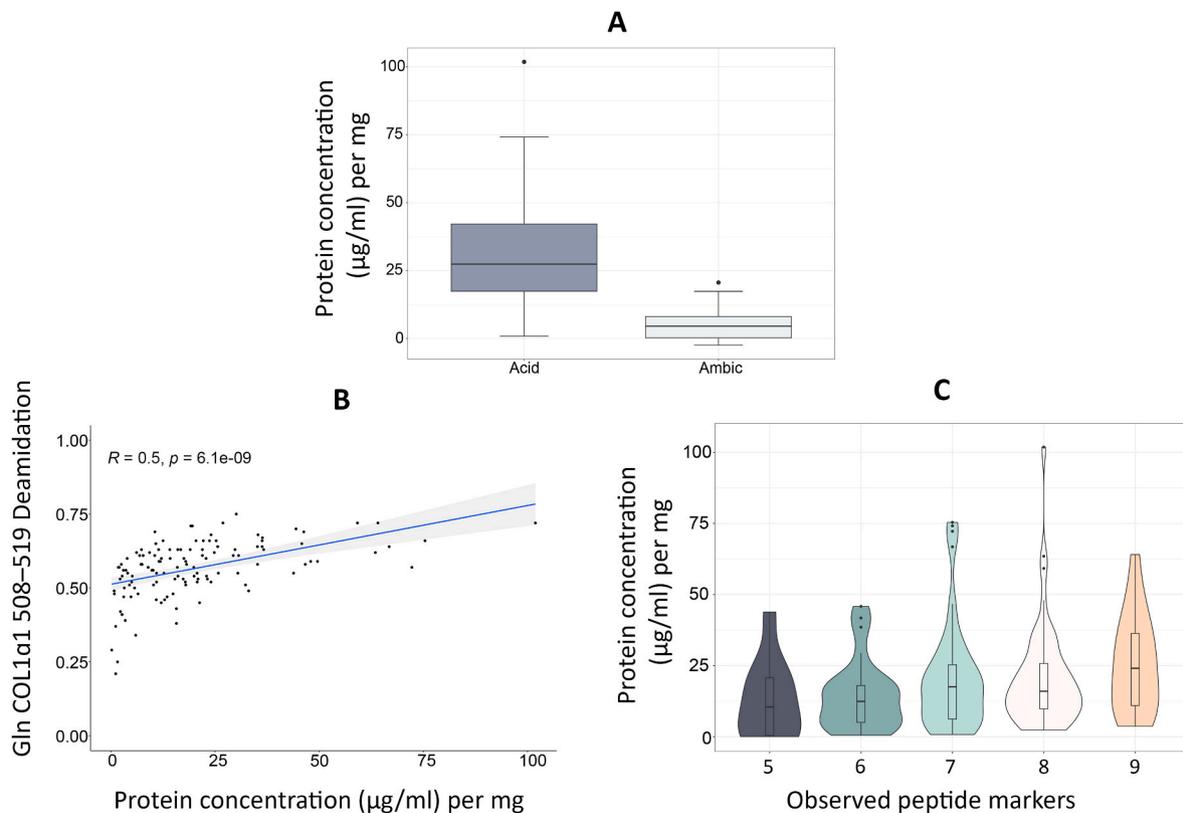
western sector or S.O. (Fig. 5a). We have also included the results of two squares from the central sector or S.C. (G-14 and C-14, analysed for a different study) to assess whether the differences in bone surface preservation between both sectors observed in the taphonomic analysis (Torres-Iglesias, 2023) are also reflected in the biomolecular preservation. Although the sample of the S.C. squares is small, there appear to be no spatial differences in the mean deamidation values per square (Fig. 5a).

No significant differences in deamidation between species were observed (Kruskal-Wallis test: chi-square = 7.37, df = 3,  $p = 0.06$ ). Therefore, all species appear to have undergone similar molecular diagenesis. Cervidae/Saiga/Capreolus and Equidae are the taxa with the highest range of values and the most significant variance (Cervidae/Saiga/Capreolus = 0.12 and Equidae = 0.01). The specimens more deamidated (0.21 and 0.25) also belong to these two taxa, although both specimens are outliers. No significant differences (Mann-Whitney  $U$  test:  $w = 935.5$ ,  $p = 0.27$ ) were observed in deamidation values between the different bone tissue (cortical and trabecular) sampled either.

A BCA assay was performed on the collagen extracted with the acid-insoluble protocol from 148 bone samples to quantify the protein concentration. Additionally, the protein concentration of the AmBic collagen extractions from 22 of those samples was also measured. Nine samples show negative protein concentration values which might be because the actual protein concentration of those samples is below the limit of the standard curve used. The comparison of the Acid protein concentration (per mg of each sample) yielded no significant differences

(Kruskal-Wallis test: chi-square = 4.23, df = 3,  $p = 0.24$ ) between the major species (*Equus*, *Capra*, *Cervus* and *Rupicapra*), thus suggesting similar protein preservation among different animal species. When comparing the protein concentration values between the different bone tissues sampled, no significant differences were registered either (Mann-Whitney  $U$  test:  $w = 1412.5$ ,  $p = 0.26$ ). However, a significant difference is observed (Mann-Whitney  $U$  test:  $w = 451$ ,  $p < 0.001$ ) when comparing the protein concentration datasets of the acid and AmBic collagen extractions from the same 22 samples. The protein concentration measurements of the AmBic extractions are much lower in all the samples, with a reduction of more than half in terms of the mean (Fig. 6a and Table S4).

A multiple linear regression model was used to estimate the relationship between the protein concentration and the digested mass values with the glutamine deamidation after removing one outlier (LV35). Importantly, no significant relationship between the digested amount of protein ( $\mu$ g) and deamidation (estimate = 0.02, standard error = 0.02,  $t = 0.93$ ,  $p = 0.35$ ) was observed in the model. However, the analysis of the variance (ANOVA) indicates a statistically significant relationship between the independent variables and deamidation (f-statistic  $p < 0.001$ ), suggesting that the protein concentration per mg of bone sampled partly influences deamidation values. Adjusted R squared indicates that protein concentration explains 24.18% of the variability in deamidation. This significant and positive correlation between these two variables suggests that, at least partly, the more protein is preserved, the less it is deamidated (Fig. 6b). Although this appears intuitive and in



**Fig. 6.** A: Protein concentration values obtained for 22 samples following acid and Ambic collagen extraction protocols. B: Correlation between the protein concentration per mg and glutamine deamidation values for peptide COL1 $\alpha$ 1 508–519 (1105.6 m/z). C: Violin plot showing the distribution of protein concentration values by the number of observed peptide markers. Only samples with five or more peptide markers were selected as they are the majority (see Table S4). Data in B and C correspond to the 148 samples analysed following the acid protocol.

agreement with theoretical models, to our knowledge this is the first time this is shown quantitatively within a ZooMS proteomic dataset. In addition, a significant and positive correlation was also observed between the number of observed peptide markers and the measured protein concentration (Spearman's rank:  $\rho = 0.38$ ,  $p < 0.001$ ). When we analyse the distribution of protein concentration in relation to the number of peptide markers observed, a higher concentration of samples is visible between 0 and 25  $\mu\text{g/ml}$ , regardless of the number of peptide markers observed. Nevertheless, a slight increase in protein concentration is seen in some of the samples with seven, eight and nine peptide markers (Fig. 6c).

## 5. Discussion

### 5.1. Faunal exploitation patterns

Our study reveals a consistency of species composition between ZooMS results and morphologically identifiable fauna undertaken during the archaeozoological analysis. Although we are aware that a direct comparison in terms of taxonomic abundance between the ZooMS and the morphological datasets may be somewhat biased by the number of the ZooMS samples and their selection criteria, we believe it is important to point out the case of reindeer. This species has a six-fold increase in the percentage of specimens in the ZooMS component. The reindeer, although predominant in the Palaeolithic record of France, is a minor taxon in the faunal assemblages of the Iberian Peninsula. In the Cantabrian region, this species is mainly located in the eastern part, such as those archaeological and paleontological sites of the Basque Country, including Santa Catalina (Berganza et al., 2012) and Kiputz IX (Castaños, 2017), respectively. At La Viña, the difference in the representation of reindeer in both components is likely driven by a bias in this

species identification, partly caused by the anthropogenic bone fracture for marrow extraction. Its anatomical similarity to red deer, along with the high fragmentation of the assemblage, has only allowed us to identify through archaeozoology the skeletal elements with distinctive morphological characters such as the teeth, metapodials and sesamoids but it was limited in long bone shafts. At the same time, limbs or axial parts were classified in the mammal-size classes. Although we did not rule out that the presence of this cervid in the western area of Cantabrian Spain was probably more occasional than in the eastern part, the ZooMS approach to the unidentifiable component of archaeofaunal assemblages has shed further light on the under-representation of this species in Iberia.

Consequently, combining the ZooMS dataset with the archaeozoological and taphonomic evidence has provided a more comprehensive view of the faunal spectrum exploited by these Upper Palaeolithic societies. Solutrean and Magdalenian human groups were the main bone accumulators of the La Viña faunal assemblage as attested by the multiple anthropogenic modifications recorded, including fresh breakage, butchering marks, and percussion notches. Moreover, evidence of carnivore activity was very scarce. The subsistence strategies of La Viña Solutrean human groups were mainly focused on the exploitation of red deer complemented by other taxa, mostly caprids and horses. The Elephantidae and Cetacea remains identified in the Solutrean levels are probably related to the extraordinary bone industry and ornaments production at the site, as it has been recorded in other Cantabrian contemporary sites (Corchón, 1981; Álvarez-Fernández and Sánchez Chillón, 2002; Corchón et al., 2008; Álvarez-Fernández, 2011; Corchón and Ortega Martínez, 2017; Lefebvre et al., 2021). On the contrary, Magdalenian hunter-gatherers exploited more diversified animal resources, and caprids are the major component in the archaeozoological assemblage, followed by red deer. Therefore, we observe a preferential

exploitation of red deer although not as specialized as it is recorded in other Cantabrian contemporary sites such as Las Caldas, La Riera and El Juyo (Altuna, 1986; Klein and Cruz Uribe, 1987; Mateos, 2005; Altuna and Mariezkurrena, 2017a, 2017b) where red deer represents more than 70% of the MNI in some levels, and even more than 80% in the latter site. Dental eruption patterns and ZooMS identification of foetal/newborn specimens indicates that the Solutrean human groups occupied La Viña during spring and autumn (Torres-Iglesias et al., 2022), while the Magdalenian hunter-gatherers seem to have stayed at the site for longer periods, during autumn-winter and spring-summer.

Despite the small sample size, the taxonomic identification of anatomically unidentifiable bone fragments has allowed us to obtain a larger skeletal representation, especially of those taxa that are less represented, such as *Rangifer tarandus*. The reindeer skeletal profile before the ZooMS analysis was mainly composed of dental specimens, metapodial remains and a distal tibia epiphysis. ZooMS identified several reindeer mandible fragments, a lateral metapodium and a radius diaphysis, as well as a bone flake, produced during anthropogenic fracturing, thereby complementing the skeletal parts attributed to reindeer via morphological means of identification.

The data obtained for La Viña follows the pattern observed in other European Palaeolithic sites, where the results of ZooMS and archaeozoological identification do not differ significantly (Welker et al., 2015, 2016, 2017; Buckley et al., 2017; Berto et al., 2021; Ruebens et al., 2023). However, other ZooMS studies reveal a different species abundance between ZooMS identification of the non-identifiable fraction and the morphological component analysed through archaeozoology (Sinet-Mathiot et al., 2019, 2023; Pothier Bouchard et al., 2020; Brown et al., 2021b; Ruebens et al., 2022). These differences among sites are probably related to the different sampling strategies followed in each ZooMS study as well as the bad preservation of the faunal assemblages, as in Riparo Bombrini (Pothier Bouchard et al., 2020). However, it cannot be ruled out that human and carnivore behaviour during the Palaeolithic may also have played a role in contributing to those differences between ZooMS and morphological species abundance, as has been proposed previously (Sinet-Mathiot et al., 2019, 2023).

The absence of carnivore bones in the ZooMS component aligns with archaeozoological data showing a low proportion of these animals in the analysed levels. Carnivore activity is also relatively low, so it seems these predators occupied the rock shelter sporadically during MIS 2. ZooMS taxonomic identification of several bones with gnawing marks also reflects a diversity of prey targets by carnivores, confirming that their activity was focused not only on red deer and caprids but also on larger ungulates such as horses, likely corresponding with scavenging after human abandonment.

## 5.2. Integrating ZooMS within archaeozoology: advantages and challenges

The development of biomolecular methods such as aDNA and, more recently, SPIN (Rüther et al., 2022; Mylopotamitaki et al., 2023) have a great potential to enhance archaeofaunal information and overcome some of the limitations of traditional archaeozoology. On the other hand, ZooMS is a cost-effective tool compared to alternative biomolecular methods in terms of time, resources and costs, making it a more widespread option and a gateway to additional palaeoproteomic or genetic studies. However, properly integrating both types of data is essential to expand archaeozoological data and thus to obtain new information necessary to assess human behaviour. For this, it is important firstly to clearly define the key questions to be answered by combining these techniques. Another crucial factor to integrate ZooMS and archaeozoological data successfully is the type of sample under study. The research questions and, thus, the sampling strategy will be different in a site with little information about the animal remains than in a site with prior knowledge about the fauna and human subsistence patterns, as is the case of La Viña. In the first case, ZooMS can be useful for

obtaining an overview of the faunal spectrum. In contrast, in the second case, it can be used to focus on more specific issues, such as the assessment of skeletal profiles or identifying carnivore prey, for example.

With this aim in mind, this research was designed to tackle three aspects of archaeozoological methodology: first, the assessment of mammal-size classification; second, the identification of perinatal specimens and third, the enhancement of skeletal profile data.

Comparing the taxonomic identification obtained through ZooMS and the mammal-size categories shows that more than half of the classifications were successful. However, it is essential to consider the high variability of horse and red deer, as their remains were initially classified into all mammal size classes. The horse bones classified as small or medium mammal are axial and epiphysis fragments, while the long bone shafts were attributed to the medium-large or large mammal category. Therefore, the misclassification of this species seems to be related to the skeletal representation. On the contrary, the variability in body size classification of red deer does not appear to be linked to particular skeletal elements, as some of the red deer remains previously classified as small or medium-small mammals are long bone shafts.

The thickness of the long bones cortical part shows a wide range in species, such as horse and red deer. This overlap, initially classified into several mammal size classes, may be due to the possible size coincidence between individuals of different species and sex, such as male ibex and female red deer or male red deer and female horses. Furthermore, it must be noted that the cortical thickness can also vary between skeletal elements of the same species or even within the same skeletal element depending on the bone region (e.g. central part of the diaphysis vs the metaphysis), without forgetting that the fracture angle can also influence this measurement.

Mammal-size classification is a well-established method in the archaeozoological methodology and has been proven helpful in numerous Palaeolithic studies. However, it is essential to remember that this classification may not reflect the expected body size class taxonomic composition, as illustrated in this research and in other ZooMS-based studies (Sinet-Mathiot et al., 2019, 2023; Brown et al., 2021b). This species variability is due to numerous factors that influence the classification such as the preservation of the assemblages and the different weight and size depending on the biological sex of animals. Therefore, it is important to be cautious with the information derived from these classifications, especially their interpretations of human behaviour or faunal diversity in a particular environment.

For the first time, ZooMS has been successfully used to identify taxonomically foetal and newborn bones. The study of foetal and perinatal animal bones informs about seasonality and hunting strategies as wild animal gestation processes and calving seasons are well-studied and the period of their occurrence established. Therefore, accurate taxonomic identification is essential to understand how past populations manage these animal resources. However, foetal and newborn bones are generally difficult to identify taxonomically depending on the stage of gestation and also due to the fragmentation of the assemblages. The taxonomic identification of these specimens combined with the archaeozoological data provide the seasonality of human occupation patterns of La Viña. The inclusion of foetal or newborn specimens in ZooMS analysis is significant because it also informs about the hunting strategies patterns, as in the case of La Viña, where hunter-gatherers captured herds including pregnant females or with early young individuals.

Archaeozoology, in combination with taphonomy and ZooMS taxonomical identification, has extended the information about animal carcass transport and exploitation strategies. Nevertheless, it is still necessary to develop a method that fully integrates ZooMS data with standard archaeozoological quantification units, such as the minimum number of individuals (MNI) and elements (MNE), and the derived from the latter, minimum number of animal units (MAU), as we carried out on this pilot study. Instead of conducting a massive sampling strategy of

unidentifiable bone fragments randomly selected, usually by size fragment, here for ZooMS analysis we established a sample selection which focuses preferentially on anatomically identified bone fragments in order to enlarge the skeletal representation profiles, especially in similar ungulate size classes (e.g. red deer, reindeer and ibex, all included in the medium mammal category). Despite the small size of the sample, this sampling method improved the available data to estimate the MNE and provided a better skeletal representation, especially of those taxa less represented, such as reindeer and large bovines. Although slightly addressed in this study, another relevant aspect for integrated archaeozoological and ZooMS studies is the taxonomic identification of axial elements. Identifying these skeletal elements is generally problematic in highly fragmented archaeological contexts (especially in the case of ribs); thus, they are usually underrepresented in skeletal profile representations, which may lead to misinterpretations of carcass transport decisions. Further investigation on this low density anatomical part is needed to address fully prey transport strategies.

### 5.3. Collagen preservation in a Late Pleistocene context

The measurement of protein concentration through BCA assay is a routinely employed method in palaeoproteomics studies. However, it has not been included in ZooMS protocols so far as it is not strictly necessary to perform peptide mass fingerprinting analysis, and it increases analytical costs. Nevertheless, this method may be useful for less preserved or more precious samples where knowing the protein concentration enables the optimisation of the trypsin digestion process to obtain better spectra. In our research, the BCA measurement results show that the acid-insoluble protocol extracts a higher concentration of proteins, which generally results in better taxonomic identification with the observation of more peptide markers. These data agree with the results of studies comparing the different ZooMS protocols (Naihui et al., 2021).

The glutamine deamidation values obtained for the La Viña samples (between 0.21 and 0.75) indicate a medium level of collagen degradation, with only two specimens heavily deamidated (values below 0.25). It has been demonstrated that protein diagenesis and deamidation rates are subjected, among multiple agents, to climatic and environmental factors such as temperature, pH of the sediment, presence of water and ionic strength (Robinson and Rudd, 1974; Scotchler and Robinson, 1974). La Viña level V shows slightly lower deamidation values (closer to 1) than the other levels, suggesting better collagen preservation. These small differences in deamidation observed between stratigraphical levels may be related to the different geological and environmental conditions under which the stratigraphic units were formed in this rock shelter, as it has also been attested in other studies addressing Pleistocene contexts (Schroeter and Cleland, 2016; Welker et al., 2017; Brown et al., 2021a; Silvestrini et al., 2022).

## 6. Conclusion

The combination of ZooMS with archaeozoology and taphonomy provides valuable data to increase our knowledge of Palaeolithic human behaviour, particularly hunting strategies, carcass exploitation and seasonality.

This study represents the first implementation of ZooMS and archaeozoology to address Palaeolithic subsistence strategies in Iberia. Integrating biomolecular and morphological data enabled us to increase the NISP statistical significance of ungulate species and distinguish horse specimens in the large mammal category. In this research, the sampling strategy followed has been useful in expanding data on skeletal profiles, seasonality of human occupations by targeting foetal remains, and carnivore activity. Regarding archaeozoological methodology, we demonstrate that mammal-size classifications based on size and cortical thickness may not reflect the actual taxonomic composition. Therefore, bone cortical thickness should not be a determining factor for taxonomic

classifications or ZooMS sampling.

Finally, we explored the correlation between collagen protein concentration and glutamine deamidation. Our data shows that the more protein is preserved, the better it is preserved, showing less deamidation. Moreover, this study also shows that the acid-based protocol extracts more protein than the AmBic protocol, which generally results in more accurate taxonomic identifications. These findings, therefore, also provide insights into future ZooMS studies as well as study design on the Iberian Peninsula.

### Author contributions statement

**Leire Torres-Iglesias:** Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Writing - Original Draft, Visualization. **Ana B. Marín-Arroyo:** Conceptualization, Methodology, Resources, Writing - Review & Editing, Visualization, Supervision, Project administration, Funding acquisition. **Frido Welker:** Conceptualization, Methodology, Investigation, Resources, Writing - Review & Editing, Visualization, Supervision. **Marco de la Rasilla:** Resources, Funding acquisition.

### Research data

A list of the observed peptide markers for each sample is presented in [Table S5](#). MALDI-TOF raw data and merged spectra are available at: <https://github.com/ERC-Subsiliencia/ZooMS-archaeozoology-at-La-Vina-rockshelter/blob/main/README.md>.

### Declaration of competing interest

The authors declare no competing interests.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jas.2023.105904>.

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