Applying ED-XRF and LA-ICP-MS to geochemically characterize chert. The case of the Central-Eastern Pre-Pyrenean lacustrine cherts and their presence in the Magdalenian of NE Iberia

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Abstract

The geochemical characterization of several lacustrine chert formations outcropping in the Central-Eastern Pre-Pyrenean area is presented. Four geological formations were considered: one Upper Cretaceous (Tremp formation), two Oligocene (Castelltallat and Tartareu-Alberola formations) and one Miocene (Aragonian limestones formation). Furthermore, lacustrine cherts appearing in the Magdalenian levels of Forcas I and Cova Alonsé (Huesca, Spain) were also considered. Analyses were done using energy-dispersive X-ray fluorescence (ED-XRF) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Results show different geochemical features between formations, in some cases also between outcrops, concerning major, minor and trace elements. Archaeological samples from Cova Alonsé and Forcas I fit in some of the established groups, being the dispersion area slightly different between sites. Consequently, results determine the presence of diversified lithic procurement strategies.

Keywords

Magdalenian, lithic procurement, human mobility, geochemistry, chert
1. Introduction

Chert was one of the most used lithic raw materials by Palaeolithic human groups to make their tools. When present in the region, hunter-gatherer groups usually preferred chert resources to other rock types to make knapped lithic tools due to their physical and mechanic properties. The characterization of chert tools found in the archaeological record of prehistoric sites is essential for determining their provenance and thus, inferring mobility and lithic procurement strategies. Whereas characterizations of chert tools first basically concerned textural, micropalaeontological and petrographic features, in the last two decades we are attending to the development of geochemical analyses to better redefine the characterization of chert artefacts. However, it has sometimes been difficult to develop systematic geochemical chert studies as basically destructive techniques have been used, requiring the partial or total destruction of the sample (Milne, Hamilton, and Fayek 2009; Hughes, Baltrunas, and Kulbickas 2011; Olofsson and Rodushkin 2011; Ekshtain et al. 2014; Vallejo Rodríguez, Urtiaga Greaves, and Navazo Ruiz 2015; Bruggencate et al. 2016). In this way, there is a lack of systematic analyses concerning chert artefacts by the use of non-destructive techniques, with only a few published examples until now (Blet, Binder, and Gratuze 2000; Hawkins et al. 2008; Olivares et al. 2009; Gauthier and Burke 2011; Gauthier, Burke, and Leclerc 2012; Hogberg, Olausson, and Hughes 2012; Hughes, Hogberg, and Olausson 2012; Hassler et al. 2013; Speer 2014; Roldan et al. 2015; Gurova et al. 2016; Moreau et al. 2016; Parish 2016).

This paper presents a systematic study based on two geochemical techniques: energy-dispersive X-ray fluorescence (ED-XRF) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). The aim of the paper is to prove the validity of two new analytical protocols developed for the analysis of chert tools by using non-destructive techniques. Lacustrine cherts outcropping in the Central-Eastern Pre-Pyrenees were selected for analyses. In this region several formations possessing identical lacustrine cherts had been previously recognised from the textural, micropalaeontological and petrographic points of view, so a geochemical characterization was essential to find differences between formations. Moreover, being lacustrine cherts the most represented in the archaeological record of most of the Palaeolithic regional sites, the distinction between formations would help better defining human mobility and lithic procurement strategies.

The Central-Eastern Pre-Pyrenean area is placed in NE Iberia, immediately to the south of the Pyrenean mountain range, a mountain chain located in South-Western Europe, a natural boundary between the Iberian Peninsula and the rest of the continental Europe. The study area is delimited by the Pyrenees to the north, the Central Depression of the Ebro Basin to the south and west and the Segre River axis to the east (figure 1).
In the selected space four geological formations containing lacustrine cherts were identified: The Upper Cretaceous cherts from the Tremp formation, the Oligocene cherts from the Castelltallat formation and Tartareu-Alberola and the Miocene cherts from the Aragonian limestones (figure 1).

The Central-Eastern Pre-Pyrenean area is very interesting from the archaeological point of view, as several Palaeolithic sites have been identified. Our studies are chronologically focused in the Magdalenian period, being represented in the region by four archaeological sites containing one or several levels from this phase. These are from west to east: Cova Alonsé, near the Cinca River, Forcas I, in the intersection between the Ésera and Isábena Rivers, Cova Gran, near the Noguera Pallaresa River and Cova del Parco, in the middle Segre valley. The Lower Magdalenian is represented in Cova Alonsé (level m), in Forcas I (levels 15 and 15b) and in Cova Gran (levels 6P and 4P). The Middle Magdalenian has recently been discovered in Cova del Parco (level III), still under excavation, and a radiocarbon date from S4H level of Cova Gran is also attributed to the Middle Magdalenian (Mora et al. 2011). Upper Magdalenian and Upper Final Magdalenian occupations have been found in Cova del Parco (level II) and Forcas I (levels 13 and 14) (Mangado et al. 2010; Montes 2005; Mora et al. 2011; Utrilla and Mazo 2007) (table 1) (figure 2).

In this study lacustrine cherts from the Magdalenian levels of Cova Alonsé and Forcas I were considered for analysis. This election is due to the fact that both sites had already been texturally, micropalaeontologically and petrographically characterized (Sánchez de la Torre and Mangado 2013; Sánchez de la Torre 2014, 2015) and they represent two different hunter-gatherer’s occupations. Having identified four geological formations containing lacustrine cherts, the establishment of the precise origin of the archaeological cherts from Cova Alonsé and Forcas I by geochemical analyses was essential for better determining prehistoric lithic procurement in the region.

Cova Alonsé (Estadilla, Huesca, Spain) is a small campsite with only one preserved archaeological level (m) dated to the Lower Magdalenian. It occupies a strategic position in a ravine that communicates the wide Cinca River basin with a small fertile valley that could have been frequented by herds of animals looking for food and water. The archaeological remains found during the excavation works reveal the human presence in the area basically for gathering strategies (Montes and Domingo 2013). Lithic industry is strictly composed by chert remains and only two types have been recognised, both probably coming from local and/or regional sources; exogenous cherts were not found in the assemblage (Sánchez de la Torre and Mangado 2013).

Forcas I (Graus, Huesca, Spain) is placed in a large conglomerate rockshelter and possesses a recurrent occupation, with an archaeological sequence that spans from the Lower Magdalenian to the Epipaleolithic; from the Denticulate Mesolithic onwards, prehistoric dwellers moved to a neighbouring rockshelter, located barely 400 m upstream in the same conglomeratic formation, where they dwelled during visits that lasted until the Ancient Neolithic. The last prehistoric employment of the site is linked
to funerary activities that date to the Chalcolithic (Utrilla and Mazo 2014). The Magdalenian lithic industry is composed basically by chert, but other rock types as fine limestone, quartzite, jasper and lydite were also knapped. The first textural and micropalaeontological characterization revealed the existence of several chert types. Between them, in addition to the local and/or regional chert types also present in Cova Alonsé, extra-regional and exogenous cherts were identified, whose origin has to be searched in the Northern Pyrenees slopes (Sánchez de la Torre 2015).

2. Material and methods

2.1 Geological samples: survey and previous analyses

As previously exposed, four geological formations containing lacustrine cherts from the Central-Eastern Pre-Pyrenees were considered. In order to collect chert samples and to characterize its outcrops, some field surveys were systematically done. During these works several outcrops were localised and analysed. From each identified outcrop a new file was opened in a database, describing its main characteristics. Samples were collected trying to obtain a major representation of the outcrop internal variability. After macroscopic observations and petrographic characterizations (figure 3), a total of 158 samples from 18 different outcrops were selected for geochemical analyses (table 2). With the aim to improve analysis time and avoid surface alterations, geological samples were prepared in squares of 5 x 5 mm without cortex surfaces.

The Tremp Formation (Maastrichtian, Upper Cretaceous) possesses a level of laminated micritic limestones with Charophyte algae and gastropods moulds filled with sparite (IGME e.p.). This package, that also contains nodular chert levels, outcrops in the Carrodilla mountain range, a Pre-Pyrenean foothill located between the Cinca River Basin to the west and the Noguera Ribagorzana River to the east. Outcrops identified (MENT & ZURI) possess chert with a macroscopic heterogeneous texture with impurities of mineral oxides, carbonate residues and probably organic matter. Charophyte algae, gastropods and ostracods form the micropalaeontological content. At a microscopic scale, a microquartz mosaic is the main texture. Length-fast chalcedony was identified filling pores, as well as macroquartz. Sub-angular detrital quartz rarely appears. A total of 22 samples from two different outcrops (ZURI and MENT) were selected for geochemical analyses.

The Castelltallat formation (Rupelian, Oligocene) largely outcrops in Serra Llarga (IGME 1998b), a mountain range located between Castelló de Farfanya and Alfarràs towns (Lleida, Spain), in the contact among the Pre-Pyrenees and the Central Depression (Anadón et al. 1989, 213). Nodular cherts appear within the stratified limestone, having been identified more than 40 primary outcrops along the Serra Llarga (Mangado 2005). The presence of chert nodules from the Castelltallat formation was also noticed near the village of Peraltilla (Huesca, Spain), some km to the west of Serra Llarga and close to the Cinca
River (Sáez 1987). Cherts from the Castelltallat formation are quite homogeneous, possessing similar
textural, micropalaeontological and petrographic features in nodules collected within Serra Llarga
outcrops (CDF) and Peraltilla outcrop (PERAL). A macroscopic heterogeneous texture, with metal
oxides, carbonate remains, detrital quartz and probable organic matter is observed during the textural
characterization. Charophyte algae and lacustrine gastropods are the representative
micropalaeontological content. Concerning the petrographic description, the primary silica texture is a
microquartz mosaic, in some cases appearing length-fast chalcedony. Nevertheless, a variability was
detected in cherts outcropping near Alfaràs town (ALF), possessing an inhomogeneous texture and
orange to reddish colours. However, the micropalaeontological content and the petrographic
characteristics were mostly similar to the samples collected in the other outcrops. For the geochemical
analyses, 80 samples from the Castelltallat formation were selected: 51 came from 11 different outcrops
from Serra Llarga (CDF), 8 were selected within the Alfaràs outcrop (ALF) and 21 from the Peraltilla
outcrop (PERAL).

The Tartareu-Alberola cherts (Rupelian, Oligocene) appear within the lacustrine stratified limestones
outcropping in the San Miquel mountain range, a Pre-Pyrenean mountain chain located to the north of
Serra Llarga and being limited by the Noguera Ribagorzana River to the west and the Farfanya River to
the east, a tributary from the Segre River (IGC 2008). Two primary outcrops were identified during the
survey works. Chert possesses macroscopic heterogeneous textures with metal oxides and micrite
remains. The micropalaeontological content is formed by Charophyte algae and gastropod sections. A
microquartz mosaic is the main texture at a petrographic level, with some vestiges of length-fast
chalcedony. 36 samples from the two identified outcrops (ALB1 and ALB2) were selected for
geochemical analyses.

The Aragonian limestone formation containing chert nodules (Aquitanian-Vindobondian, Miocene)
outcrops near Candasnos, in the Central Depression of the Middle Ebro basin (IGME 1998a). Chert
possesses irregular nodular morphologies with homogeneous textures with metal oxides, carbonate
remains, probably organic matter and detrital quartz crystals. Charophyte algae and gastropods sections
configure the micropalaeontological content. At microscopic scale, a cryptoquartz mosaic is the main
texture, with some length-fast chalcedony and macroquartz cementations. 20 samples coming from the
same outcrop (PC) were selected for geochemical analyses.

2.2 Archaeological samples: sampling and previous analyses

Concerning archaeological samples, 99 chert artefacts from the Magdalenian levels of Cova Alonsé (n.
80) and Forcas I (n. 19) were analysed by ED-XRF. For LA-ICP-MS analyses, 26 artefacts from Cova
Alonsé and 19 from Forcas I were selected. All of them had been previously characterized by their
texture and micropalaeontological content and defined as originated in a lacustrine context. Due to the
absence of remarkable differences between the four geological formations containing lacustrine cherts in the Central-Eastern Pre-Pyrenean area, the relation between the archaeological samples and the geological formations could be established only by geochemical analyses.

### 2.3 ED-XRF and LA-ICP-MS: methods

To analyse major and minor elements, ED-XRF (energy-dispersive X-ray Fluorescence) was applied. Analyses were developed at the Research Centre for Applied Physics in Archaeology, IRAMAT, Bordeaux, France. 9 elements were quantified (Na, Mg, Al, Si, P, K, Ca, Ti, Fe) using an X-ray fluorescence spectrometer SEIKO SEA 6000VX (Orange et al. 2016). Fundamental parameters corrected by the granodiorite GSP2 from the U.S. Geological Survey (USGS) international standard (Wilson, 1998) were used. A 3x3 mm collimator was used and analysis time was set to 400 seconds for each measurement condition (3 conditions with air or He environment and Cr or Pb filter were established). To check machine calibration and accuracy JCh-1 chert standard from the Geological Survey of Japan (GSJ) international standard was used (Imai et al. 1996). To prove and validate the receipt and to check machine accuracy, a measurement with the JCh-1 chert standard was established. Two powder tablets were analysed in several points in routine mode. Results show that the average obtained for the 17 analysed points were close to the desired value, being the standard deviation always lower than 0.08 wt% and validating the accuracy of the receipt (table 3).

To analyse trace elements, LA-ICP-MS (laser ablation inductively coupled plasma mass spectrometry) at the Ernest-Babelon laboratory, IRAMAT, Orléans, France, was used. Elements were quantified using a Thermo Fisher Scientific Element XR mass spectrometer associated with a Resonetics RESOlution M50e ablation device. This spectrometer offers the advantage of being equipped with a dual mode (counting and analogue modes) secondary electron multiplier (SEM) with a linear dynamic range of over nine orders of magnitude, associated with a single Faraday collector which allows an increase of the linear dynamic range by an additional three orders of magnitude. This feature is particularly important for laser ablation analysis of lithic samples, as it is possible to analyse major, minor, and trace elements in a single run regardless of their concentrations and their isotopic abundance. The ablation device is an excimer laser (ArF, 193nm), which was operated at 6.5mJ and 20hz. A dual gas system with helium (0.65 l/min) released at the base of the chamber, and argon at the head of the chamber (1.1 l/min) carried the ablated material to the plasma torch. Ablation time was set to 40 seconds: 10s pre-ablation to let the ablated material reach the spectrometer and 30s collection time. Laser spot size was set to 100µm and line mode acquisition was chosen to enhance sensitivity. Background measurements were run every 10 to 20 samples. Fresh fractures were analysed on geological samples to reduce potential contamination. Priority was given to characterizing the largest number of samples for each site, thus - only one ablation line per sample was carried out. However, if during analysis element spikes due to the
presence of inclusions or heterogeneities were observed, results were discarded and a new ablation site selected. For archaeological samples three analyses of each artefact using the same line mode acquisition area were taken to measure the potential post-depositional alteration of surfaces.

Calibration was performed using standards reference glass NIST610 which was run periodically (every 10 to 20 samples) to correct for drift. NIST 610 was used to calculate the response coefficient (k) of each element (Gratuze 1999, 2014) and the measured values of each element were normalised against 28Si, the internal standard, to produce a final percentage. Glass Standard NIST612 was analysed independently of calibration to provide comparative data. After doing some tests with 56 elements, a total of 30 were measured (Li, Be, B, Mg, Al, Si, Ti, V, Cr, Fe, Ga, Ge, As, Rb, Sr, Y, Zr, Nb, Cs, Ba, La, Ce, Pr, Nd, Sm, W, Bi, Th, U).

Raw data was interpreted with XLSTAT (Addinsoft 2007) and JMP (Inc. 1898-2017) softwares. Boxplots and scatterplots presented below were obtained by using XLSTAT and JMP devices. In boxplots, the width of the box shows the interquartile range. Quartiles have been calculated using exclusive median. Whiskers, when present, show the highest and lowest values, which are the existent variability outside the interquartile ranges.

3. Results

3.1 Geochemical characterization of major and minor elements by ED-XRF

9 elements were quantified (Na₂O, MgO, Al₂O₃, SiO₂, P₂O₅, K₂O, CaO, TiO₂, Fe₂O₃) by energy dispersive X-ray fluorescence. Nevertheless, only five of them were used for interpretation (Al₂O₃, SiO₂, K₂O, CaO, Fe₂O₃), as values obtained for Na₂O, MgO, P₂O₅ and TiO₂ were too low to be used for interpretation. After the analysis of the five measured elements with ED-XRF, only three of them (SiO₂, CaO and Fe₂O₃) provided enough data to establish differences between the four geological formations containing lacustrine cherts outcropping in the Central-Eastern Pre-Pyrenees. In addition, the concerned major and minor elements presented below contributed to link archaeological samples with some geological cherts. In the next boxplots are presented samples from the eight outcrops with lacustrine cherts and Cova Alonsé and Forcas I samples. It has to be taken into account that Cova Alonsé and Forcas I samples are expressed in the boxplots as a same unit, but they could come from separate outcrops. Consequently, outliers must also be taken into account because they could be expressing the existence of several sources in the archaeological record. For this reason, all measures coming from an archaeological sample have been considered.

In the CaO boxplot (figure 4), three outliers were discarded for making the graph: ALB1-08-B (CaO value: 10.85 wt%), ALB1-08-A (CaO value: 10.21 wt%) and ALB2-13 (CaO value: 10.16 wt%). Two main geological groups can be distinguished regarding CaO values. There is a first group possessing
lower CaO rates (0.02 – 0.9 wt%), which is composed by Castelló de Farfanya (CDF), Alfarràs (ALF), Puente Candasnos (PC), Zurita (ZURI) and Mentirosa (MENT) samples. The second group, having higher CaO rates (1 – 6.99 wt%), is formed by Peraltilla (PERAL), Alberola 1 (ALB1) and Alberola 2 (ALB2) samples.

Thus, regarding CaO values, the Oligocene cherts coming from the Tartareu-Alberola type are largely separated from the Maastrichtian cherts (ZURI and MENT) and the Miocene cherts (PC). Moreover, CaO values separate the Castelltallat formation cherts, being in the same group all the outcrops from Serra Llarga (CDF and ALF). However, cherts coming from the Peraltilla outcrop, which also is part of the Castelltallat formation but outcrops some km at the NW of Serra Llarga, possesses different CaO values, allowing a discrimination between outcrops from the same geological formation.

The archaeological samples of Cova Alonsé possess low CaO rates (0.04 to 0.9 wt%), so they would rather be associated to the Castelltallat formation samples outcropping in the Serra Llarga (CDF and ALF), the Maastrichtian cherts (ZURI and MENT) and the Miocene cherts (PC). Nevertheless, one sample possessed more than 0.9 wt% CaO (AL-60: 1.44 wt% CaO), so we cannot discard that some samples could be connected with the Tartareu-Alberola cherts or the Peraltilla cherts outcrop from the Castelltallat formation.

The archaeological samples from Forcas I also present low CaO rates (0.07 to 0.5 wt%), so they would also be connected with Castelltallat cherts outcropping in Serra Llarga (CDF and ALF), Maastrichtian cherts (ZURI and MENT) and Miocene cherts (PC). In this case, as any analysed sample possesses values higher than 0.5 wt% concerning CaO values, the lacustrine cherts from Forcas I would not be associated with the Tartareu-Alberola cherts or the Peraltilla outcrop from the Castelltallat formation.

In the Fe₂O₃ boxplot (figure 5) two outliers were discarded for making the graph: ALB1-09 (Fe₂O₃ value: 1.52 wt%) and ALB1-06 (Fe₂O₃ value: 1.08 wt%). Regarding the graph, three geological groups can be distinguished. There is a first group arranging geological samples with low Fe₂O₃ rates, mostly between 0 and 0.03 wt%, composed by the Miocene (PC) and the Maastrichtian cherts (ZURI and MENT). The second group, with mid Fe₂O₃ rates mostly between 0.03 and 0.11 wt% assembles the Castelltallat cherts outcropping in Peraltilla (PERAL) and Serra Llarga (CDF), except those from the Alfarràs outcrop (ALF), already different at the textural characterisation. The third group, with geological samples with higher Fe₂O₃ rates (between 0.12 and 0.6 wt%) is formed by samples from Alfarràs and from Tartareu-Alberola (ALB1 and ALB2).

The archaeological samples from Cova Alonsé present low to medium Fe₂O₃ rates (0 to 0.1 wt%), being mostly associated with the Miocene and the Maastrichtian cherts, as well as with the Castelltallat cherts from Castelló de Farfanya (CDF) and Peraltilla (PERAL) outcrops. Concerning Fe₂O₃ values, the lacustrine cherts from Cova Alonsé would not directly be connected with the Tartareu-Alberola cherts neither the Alfarràs cherts from the Castelltallat formation.
The archaeological samples from Forcas I present medium Fe$_2$O$_3$ rates (0.02 to 0.07 wt%), better connecting with cherts from the Castelltallat formation outcropping in Castelló de Farfanya (CDF) and Peraltilla (PERAL). The Miocene and the Maastrichtian cherts for these samples with the lowest Fe$_2$O$_3$ rates (0.02 wt%) cannot be discarded. Nevertheless, the Tartareu-Alberola cherts, as well as the cherts from the Castelltallat formation outcropping in Alfarràs (ALF), could be discarded if Fe$_2$O$_3$ rates are considered.

For the SiO$_2$ boxplot (figure 6) all samples were considered. Two main geological groups can be distinguished. There is a first group possessing higher SiO$_2$ rates (96 to 99 wt%) composed by the Castelltallat formation cherts outcropping in Serra Llarga (CDF and ALF), the Maastrichtian cherts (ZURI and MENT) and the Miocene cherts (PC). The second group is formed by geological cherts possessing lower SiO$_2$ rates (88 to 95 wt%): the Castelltallat formation cherts outcropping in Peraltilla (PERAL) and the Tartareu-Alberola cherts (ALB1 and ALB2).

Archaeological samples from Cova Alonsé present high SiO$_2$ values (96 to 99 wt%), being mostly associated with the Castelltallat formation cherts outcropping in Serra Llarga (CDF and ALF), the Maastrichtian cherts (ZURI and MENT) and the Miocene cherts (CP). Taking into account SiO$_2$ rates, the lacustrine cherts of Cova Alonsé would not be connected with the Castelltallat formation cherts outcropping in Peraltilla (PERAL) and the Tartareu-Alberola cherts (ALB1 and ALB2).

Archaeological samples from Forcas I also possess high SiO$_2$ rates (96 to 99 wt%), being mostly connected with the Castelltallat formation cherts outcropping in Serra Llarga (CDF and ALF), the Maastrichtian cherts (ZURI and MENT) and the Miocene cherts (PC). As for Cova Alonsé samples, the lacustrine cherts from Forcas I would not directly be connected with the Oligocene cherts outcropping in Peraltilla (PERAL) and the Tartareu-Alberola chert type.

CaO, Fe$_2$O$_3$ and SiO$_2$ provided some interesting data considering the differentiation between geological formations and the identification of the archaeological samples with some of them, so the next step was to interconnect data with scatterplots. Several scatterplots were developed, being the Log CaO/SiO$_2$ vs Log Fe$_2$O$_3$/SiO$_2$ the most enlightening.

In relation to Cova Alonsé samples, the scatterplot concerning Log CaO/SiO$_2$ vs Log Fe$_2$O$_3$/SiO$_2$ showed the connection between the archaeological samples and several geological formations (figure 7 – right), being others totally discarded (figure 7 – left). Thus, the lacustrine cherts from Cova Alonsé were not related with the Oligocene cherts from the Castelltallat formation outcropping in Peraltilla (PERAL) and Alfarràs (ALF) neither with the Oligocene cherts from the Tartareu-Alberola (ALB1 and ALB2). However, the lacustrine cherts from Cova Alonsé seem to be partially related with the Oligocene cherts from the Castelltallat formation outcropping in Serra Llarga (CDF) and with the Maastrichtian cherts outcropping in Zurita (ZURI) and possibly the Miocene cherts (PC). Being overlapped the dispersion of the Maastrichtian cherts (ZURI and MENT) with the Miocene cherts (PC), it has not been possible to
determine by energy-dispersive X-ray fluorescence if the archaeological samples were related with one, the other or both overlapped formations. The scatterplot concerning Log CaO/SiO₂ vs Log Fe₂O₃/SiO₂ and relating geological and Forcas I archaeological samples also showed the connection between the archaeological samples and several geological formations (figure 8 – right), being others totally discarded (figure 8 – left). In this case, the lacustrine cherts from Forcas I are different from the Oligocene cherts of Tartareu-Alberola (ALB1 and ALB2), the Castelltallat formation cherts outcropping in Peraltilla (PERAL) and Alfarràs (ALF) and the Maastrichtian cherts outcropping in Mentirosa (MENT). On the contrary, they seem to be clearly related to the Castelltallat formation cherts outcropping in Serra Llarga (CDF). As part of the Castelló de Farfanya dispersion overlaps with the Zurita dispersion (Maastrichtian cherts) and Puente Candasnos dispersion (Miocene cherts), we cannot discard these two chert types as potentially used by Forcas I groups. Nevertheless, it clearly seems that in any case, some lacustrine chert used in Forcas I came from the Oligocene cherts from the Castelltallat formation outcropping in Serra Llarga (CDF).

3.2 Geochemical characterization of trace elements by LA-ICP-MS

Despite having quantified 30 elements by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), six of them were discarded during interpretation (Li, Be, B, Ga, Ge, Bi), as values obtained were below the limits of detection. Raw data were interpreted with JMP software and scatterplots presented were also obtained using JMP software. For LA-ICP-MS analyses, 152 geological samples were analysed. Due to analysis chamber restrictions, samples from Mentirosa outcrop (Maastrichtian cherts) were not analysed. 45 archaeological samples (26 from Cova Alonsé and 19 from Forcas I) were selected for analysis. As presented before, during the analysis of archaeological artefacts three measures were taken of each sample, following the same acquisition line, to avoid surface alterations. To check the validity of the second and third measurement with two more analyses in the same acquisition line some tests were done (table 4). The observation of the measurements of each sample revealed some surface alterations affecting archaeological samples, being the first measurement the most altered. Consequently, we took the third measurement for interpretation analyses.

Having discarded the elements not useful for quantification (Li, Be, B, Ga, Ge, Bi), a spidergram with the median values obtained for each element concerning all the analysed outcrops was created (figure 9). The average obtained for each element in each analysed formation was divided by the JCh-1 international standard (Imai et al. 1996) to standardize the obtained data. Within all the quantified elements, only three of them (As, Sr, U) presented a large variability. Thus, several scatterplots were created to evaluate the dispersion of the geological samples and to observe where the archaeological samples were placed.
Results obtained by LA-ICP-MS supports the data previously obtained by ED-XRF. Thus, the Oligocene cherts from the Tartareu-Alberola (ALB1 and ALB2) as well as the Castelltallat formation cherts outcropping in Peraltilla (PERAL) and Alfarràs (ALF) are largely distant from the dispersion of Cova Alonsé and Forcas I samples. Moreover, with LA-ICP-MS analyses some differences were observed between the Miocene cherts (PC), the Oligocene cherts from the Castelltallat formation outcropping in Serra Llarga (CDF) and the Maastrichtian cherts (ZURI). The scatterplot concerning U and Sr dispersion (in Log scale) reveals that Miocene cherts of Puente Candasnos (PC) are largely distant to the Maastrichtian cherts of Zurita (ZURI), being solved the overlapping observed during ED-XRF analyses.

To analyse the dispersion of archaeological samples, the non-suitable geological cherts already discarded during ED-XRF and confirmed by LA-ICP-MS were removed. Thus, the Miocene cherts (PC), the Maastrichtian cherts (ZURI) and the Oligocene cherts from Castelló de Farfanya (CDF) were maintained. The scatterplot considering Log Sr/U vs Log As/U presented three types of chert, mostly separated between them, being specifically the dispersion area of the Miocene cherts (PC) well established and not overlapped with the other formations (figure 10).

Concerning the distribution of the archaeological samples, the lacustrine cherts of Cova Alonsé (figure 10 –left) properly fit within the Zurita dispersion group (Maastrichtian cherts) and the Castelló de Farfanya dispersion group (Oligocene cherts from the Castelltallat formation). Some samples are clearly placed inside the Castelló de Farfanya dispersion area, while others are located in the overlapped area between Castelló de Farfanya and Zurita. Nevertheless, it seems obvious that not a single sample fits within the Miocene cherts (PC). Regarding the archaeological samples of Forcas I (figure 10 -right), nine tools (53%) largely fit within the Zurita dispersion group. Seven artefacts (37%) are directly related with the Castelló de Farfanya group, as they are placed inside its dispersion range. The remaining three samples are placed in the overlapping area of Castelló de Farfanya and Zurita, not being possible to connect them to a specific group.

4. Discussion

The geochemical analysis of Central-Eastern Pre-Pyrenean lacustrine cherts has allowed differentiating four analysed formations that were almost identical from the textural, micropalaeontological and petrographic point of view. By determining the major and minor components with ED-XRF, it has been possible to differentiate between formations (the Oligocene cherts from the Tartareu-Alberola and the Oligocene cherts from the Castelltallat formation). Moreover, some differences have been established also in the bosom of one formation. In this way, the outcrops of Peraltilla and Alfarràs are largely separated from the other outcrops (Castelló de Farfanya) of the Castelltallat formation. Nevertheless, an overlapping has been observed within the dispersion area of the Miocene cherts and the Maastrichtian cherts, not being possible to establish differences by ED-XRF analyses.
The determination of trace element components by LA-ICP-MS has confirmed the dispersion already observed in ED-XRF analyses. Moreover, trace-element analyses have allowed establishing differences between the Miocene and the Maastrichtian cherts, overlapped in the ED-XRF researches.

Concerning archaeological artefacts, after the determination of major and minor components, the majority of chert tools seemed to be connected to the overlapped Maastrichtian and Miocene cherts as well as with the Oligocene cherts from the Castelltallat formation outcropping in Serra Llarga (Castelló de Farfanya). By analysing trace-elements, it has been possible to discard the exploitation of the Miocene cherts by the Magdalenian groups settled in Cova Alonsé and Forcas I. Thus, archaeological cherts of Cova Alonsé are basically associated with the Maastrichtian cherts outcropping in the Carrodilla mountain range, being the outcrops less than 1 km from the site, and the Oligocene cherts outcropping in Serra Llarga, at more than 40 km to the southeast of Cova Alonsé. In Forcas I, Oligocene cherts from Castelló de Farfanya prevail –being the outcrops located 50 km SE of the site-, however some tools are directly connected with the Maastrichtian cherts outcropping in the Carrodilla mountain range, barely 15 km away. If differences between archaeological levels are considered, it has been observed that Oligocene cherts were slightly more exploited during the Upper Magdalenian (55%) and the Maastrichtian cherts preferred during the Lower Magdalenian (67%).

The geochemical analysis of lithic artefacts from Cova Alonsé has brought to light that hunter-gatherer groups settled in the Carrodilla mountain range not only operated in a local range. According to the supplementary analyses of lithic industry, that included techno-typological and use-wear studies, it was suggested that the site had been occupied basically for hunting reasons (Montes and Domingo 2013). Therefore, being the Carrodilla mountain range a good place for hunting and not having found in the archaeological record a copious ensemble of basic tools (as scrapers or denticulates), it seemed obvious that Cova Alonsé was not a main residential camp. The proved presence of Maastrichtian cherts in the archaeological record of Cova Alonsé, that are at the same time the closest chert outcrops in the region, suggest that these hunter-gatherer groups possessed a complete knowledge of the territory. The discovery of Oligocene cherts from Serra Llarga reveals the existence of clear lithic procurement strategies, with the selection of these materials, more distant from the site but with higher knappable properties according to the presence of impurities or fractures affecting the suitability for knapping. It must be highlighted that Castelló de Farfanya outcrops possess large chert nodules with great knapping properties and in some outcrops remains of ancient knapping were detected. In addition, the discovery of Serra Llarga cherts within the archaeological record of Cova Alonsé proves the existence of a frequented territory that exceeds the Carrodilla mountain range, opening towards the east in these first pre-Pyrenean foothills.

The geochemical analysis of lithic artefacts from the Magdalenian levels of Forcas I has proved the existence of two lacustrine chert types. On the one hand, the presence of the Maastrichtian cherts
outcropping in the Carrodilla mountain range has been attested. On the other hand, the exploitation of
the Oligocene cherts outcropping in Serra Llarga (Castelló de Farfanya outcrops) has been identified.
Even though some samples are placed in the overlapped dispersion area of the Maastrichtian and the
Oligocene cherts (Zurita and Castelló de Farfanya), at least seven of the analysed chert tools are perfectly
related with the dispersion area of Castelló de Farfanya. According to the analysed samples, it seems
that the Oligocene cherts from Castelló de Farfanya are preferred during the Upper Magdalenian, while
in the Lower Magdalenian cherts from the Maastrichtian outcropping in the Carrodilla mountain range
are more chosen. Nevertheless, as only a selection of samples has been analysed, this data must be
nuanced and only proved by the analysis of a larger number of artefacts.

The exploitation in Cova Alonsé and Forcas I of Castelló de Farfanya cherts confirms the existence of
regional procurement strategies and extends the acquisition operational range to the south-east of the
sites, proving human mobility within the Segre River path that could be related to other Magdalenian
occupations in the area (Cova del Parco and Cova Gran). But it is also interesting to note the absence of
Peraltailla cherts in the archaeological record of the two analysed sets. Peraltailla cherts belong to the
Oligocene Castelltallat formation cherts, largely outcropping in the Serra Llarga (Castelló de Farfanya
and Alfarràs) but also near the Cinca River. The Peraltailla cherts are the closest Castelltallat formation
cherts outcropping near both Cova Alonsé and Forcas I. Nevertheless, cherts from this outcrop are not
present in the archaeological record of any of these sites. While the no-exploitation of Alfarràs cherts
could be explained by knapping suitability (cherts are often cracked), the Peraltailla cherts possess the
same suitability as cherts from Castelló de Farfanya. Thus, maybe this outcrop was not well-known by
human groups that settled in Cova Alonsé and Forcas I. Could we suppose that the Cinca River was a
cultural barrier for this groups? If for the moment no evidence leads us to accept this hypothesis, we do
neither have evidences to discard it, as the rest of the chert types exploited in both sites do not seem to
come from outcrops located west of the Cinca River (Sánchez de la Torre 2015).

Finally, it has to be underlined that both archaeological sets have presented similar procurement
strategies concerning the acquisition of lacustrine cherts. The presence of the same chert types linked to
the absence of Peraltailla cherts in both sets lead us thinking that lithic procurement strategies concerning
lacustrine cherts remained stable without noticeable changes for groups occupying this part of the
Central-Eastern Pre-Pyrenees during the Magdalenian period.

5. Conclusion

In this study, a new analytical protocol has been established, being proved with the analysis of
international standards, among those the JCh-1. Results confirm the value of ED-XRF and LA-ICP-MS
techniques in chert characterization analyses. With the analysis of major and minor elements by ED-
XRF, a selection between some of the suitable geological formations has been done. After this, the
determination of trace elements with LA-ICP-MS has allowed distinguishing between the overlapping formations in ED-XRF analyses. Being ED-XRF a totally non-destructive technique and implying LA-ICP-MS only a limited ablation -not visible to the naked eye-, both techniques are suitable for working with archaeological remains, making possible the analysis of a large number of artefacts.

The determination of chert procurement areas for the Magdalenian settlements of Cova Alonsé and Forcas I gives valuable information to determine human mobility strategies in NE Iberia at the end of the Upper Palaeolithic. Thus, the forthcoming analysis of other chert types as well as the inclusion of the Magdalenian sets from Chaves Cave, Cova del Parco and Montlleó open-air-site to this topic research, will increase our knowledge about hunter-gatherer populations that settled the NE Iberia at the end of the Late Glacial Maximum.

Acknowledgements

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References


Figures & Captions
Fig. 1. The Central-Eastern Pre-Pyrenees with the geological formations and the archaeological sites studied in this paper.

Fig. 2. Calibrated dates vs probability density for the radiocarbon dates from Table 1.
Fig. 4. Boxplot with CaO values.

Fig. 5. Boxplot with Fe$_2$O$_3$ values.

Fig. 6. Boxplot with SiO$_2$ values.
Fig. 7. Scatterplots with Cova Alonsé dispersion with the non-related formations (left) and the related formations (right) concerning Log CaO/SiO₂ vs Log Fe₂O₃/SiO₂.

Fig. 8. Scatterplots with Forcas I dispersion with the non-related formations (left) and the related formations (right) concerning Log CaO/SiO₂ vs Log Fe₂O₃/SiO₂.

Fig. 9. Scatterplot concerning Log Sr/U vs Log As/U with the dispersion of the three most suitable geological formations.
Fig. 10. Scatterplots concerning Log Sr/U vs Log As/U with the dispersion of the three most suitable geological formations and the archaeological samples of Cova Alonsé (left) and Forcas I (right).

Tables

<table>
<thead>
<tr>
<th>Site</th>
<th>L</th>
<th>Period</th>
<th>Date</th>
<th>Lab. ref.</th>
<th>Met.</th>
<th>S.</th>
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<th>Author</th>
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<td>6P</td>
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<td>AMS</td>
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<td>C</td>
<td>18,034–18,523</td>
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<td>14</td>
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<td>B</td>
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<td>14,426–15,055</td>
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<td>B</td>
<td>13,783–14,197</td>
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Table 1. Radiocarbon dates concerning the Magdalenian levels of the four archaeological sites located in the Central-Eastern Pre-Pyrenees.
Table 2. Outcrops selected for the study with the number of samples analysed.

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Table 3. ED-XRF analytical data (in %w) for the JCh-1 test analysis to check machine accuracy.

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<th>Name</th>
<th>Na₂O</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>P₂O₅</th>
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<td>1</td>
<td>JCh-1 (A1)</td>
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<td>0.92</td>
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<tr>
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<tr>
<td>7</td>
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<td>JCh-1 (A3)</td>
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</tr>
<tr>
<td>11</td>
<td>JCh-1 (B1)</td>
<td>&lt; LD</td>
<td>0.59</td>
<td>0.99</td>
<td>97.97</td>
<td>&lt; LD</td>
<td>0.16</td>
<td>0.02</td>
<td>0.01</td>
</tr>
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<td>12</td>
<td>JCh-1 (B1)</td>
<td>&lt; LD</td>
<td>0.08</td>
<td>1.01</td>
<td>98.44</td>
<td>&lt; LD</td>
<td>0.15</td>
<td>0.03</td>
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</tr>
<tr>
<td>13</td>
<td>JCh-1 (B2)</td>
<td>&lt; LD</td>
<td>0.05</td>
<td>0.56</td>
<td>99.14</td>
<td>&lt; LD</td>
<td>0.08</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>14</td>
<td>JCh-1 (B2)</td>
<td>&lt; LD</td>
<td>0.05</td>
<td>0.57</td>
<td>99.11</td>
<td>&lt; LD</td>
<td>0.09</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>15</td>
<td>JCh-1 (B2)</td>
<td>&lt; LD</td>
<td>0.06</td>
<td>0.56</td>
<td>99.13</td>
<td>&lt; LD</td>
<td>0.09</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>16</td>
<td>JCh-1 (B2)</td>
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<td>1.02</td>
<td>98.42</td>
<td>&lt; LD</td>
<td>0.16</td>
<td>0.03</td>
<td>0.04</td>
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<tr>
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<td>JCh-1 (A2)</td>
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<td>0.75</td>
<td>98.86</td>
<td>&lt; LD</td>
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<tr>
<td>Average</td>
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<td>0.02</td>
<td>0.01</td>
<td>0.74</td>
<td>&lt; LD</td>
<td>0.07</td>
<td>0.01</td>
<td>0.00</td>
<td>0.12</td>
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<tr>
<td>Std. Dev.</td>
<td>&lt; LD</td>
<td>0.03</td>
<td>0.08</td>
<td>0.73</td>
<td>97.81</td>
<td>0.02</td>
<td>0.22</td>
<td>0.04</td>
<td>0.36</td>
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</table>

| Exp. value | 0.03 | 0.08 | 0.73 | 97.81 | 0.02 | 0.22 | 0.04 | 0.36 |