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Multi-method study of a Pyrenean lithological tracer and its presence in the Magdalenian of Cova del Parco and Forcas I rock shelter (NE Iberia)

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Abstract

The multi-method study of a Pyrenean lithological tracer, the Montgaillard-Montsaunès chert type, is presented in this paper. These cherts outcrop in the northern Pyrenees, in three outcrops belonging to two Upper Cretaceous formations: the marly flysch cherts from the Campanian-Maastrichtian (Buala and Montsaunès outcrops) and the grey flysch cherts from the Turonian-Santonian (Montgaillard outcrop).

After macroscopic and petrographic characterization, geochemical analyses by ED-XRF, LA-ICP-MS and PIXE were conducted to establish chemical differences between outcrops and formations. Then, archaeological cherts potentially associated to this tracer were included in the study. These cherts were recovered from the Magdalenian levels of Cova del Parco and Forcas I rock shelter, in the southern Pyrenees. Results demonstrate the presence of this lithological tracer in the archaeological series studied, highlighting wide mobility of these materials through Pyrenean hunter-gatherers at the end of the Upper Palaeolithic.

Keywords: Geochemistry; lithic provenance studies; Chert, Magdalenian; NE Iberia

Résumé

L'approche multi-méthode sur un traceur lithologique pyrénéen, les silex du type Montgaillard-Montsaunès, est présenté dans cet article. Ces silex affleurent dans le versant nord des Pyrénées centrales, en trois gîtes appartenant à deux formations du Crétacé supérieur : les flysch marneux du Campanien-Maastrichtien (gîtes de Buala et Montsaunès) et les flysch gris du Turonien-Santonien (gîte de Montgaillard).

Après une caractérisation macroscopique et pétrographique, des analyses géochimiques par ED-XRF, LA-ICP-MS et PIXE ont été menés afin d'établir des différences entre gîtes et formations. Ensuite, des silex archéologiques potentiellement associés avec ce traceur ont été soumis au même protocole analytique. Ce sont des artefacts provenant des niveaux magdaléniens de la Cova del Parco et l'Abri de Forcas I, en versant sud pyrénéen. Les résultats ont permis de constater la présence de ces traceurs dans les séries archéologiques étudiés, mettant en évidence une mobilité importante de ceux matériaux à travers des chasseurs-cueilleurs pyrénéens à la fin du Paléolithique supérieur.

Mots-clés : Géochimie ; étude de provenance lithique ; silex ; Magdalénien ; NE Péninsule Ibérique

1. Introduction

Chert provenance studies provide valuable data about past human groups, specifically regarding their mobility and procurement strategies. The chert outcrops exploited as sources of tool-making raw materials are generally well documented for the Paleolithic communities of Europe. Their geological products have been characterized mainly at the macroscopic and petrographic scale, based on textural and micropaleontological descriptions. In some cases, if a chert source is well delimited geographically and possesses specific textural or micropaleontological traits, recognizing its archaeological use is possible just using macroscopic or microscopic methods. Nevertheless, in other cases, cherts exhibit identical macroscopic and petrographic features, also when they belong to different geological formations. In these cases, geochemical methods are required to distinguish between different sources.

In this paper a multi-method study concerning a lithological tracer outcropping in the Pyrenees is concerned. The Pyrenean mountain range is located in south-western Europe and separates the Iberian Peninsula to its south from the rest of continental Europe to the north. It extends for almost 500 km from the Bay of Biscay to the Mediterranean Sea. Archaeological work in this region, carried on especially since the last century (Mangado *et al.* 2010, Utrilla *et al.* 2010) has confirmed that this natural barrier was occupied, at least at the eastern margins, since the Lower Palaeolithic (Falgüeres *et al.* 2015, de Lumley *et al.* 2004). Moreover, some studies have demonstrated that certain connections existed, at least during the Upper Palaeolithic, between both Pyrenean slopes, specifically considering lithic productions (Langlais 2011, Langlais *et al.* 2016, Sánchez de la Torre 2015).

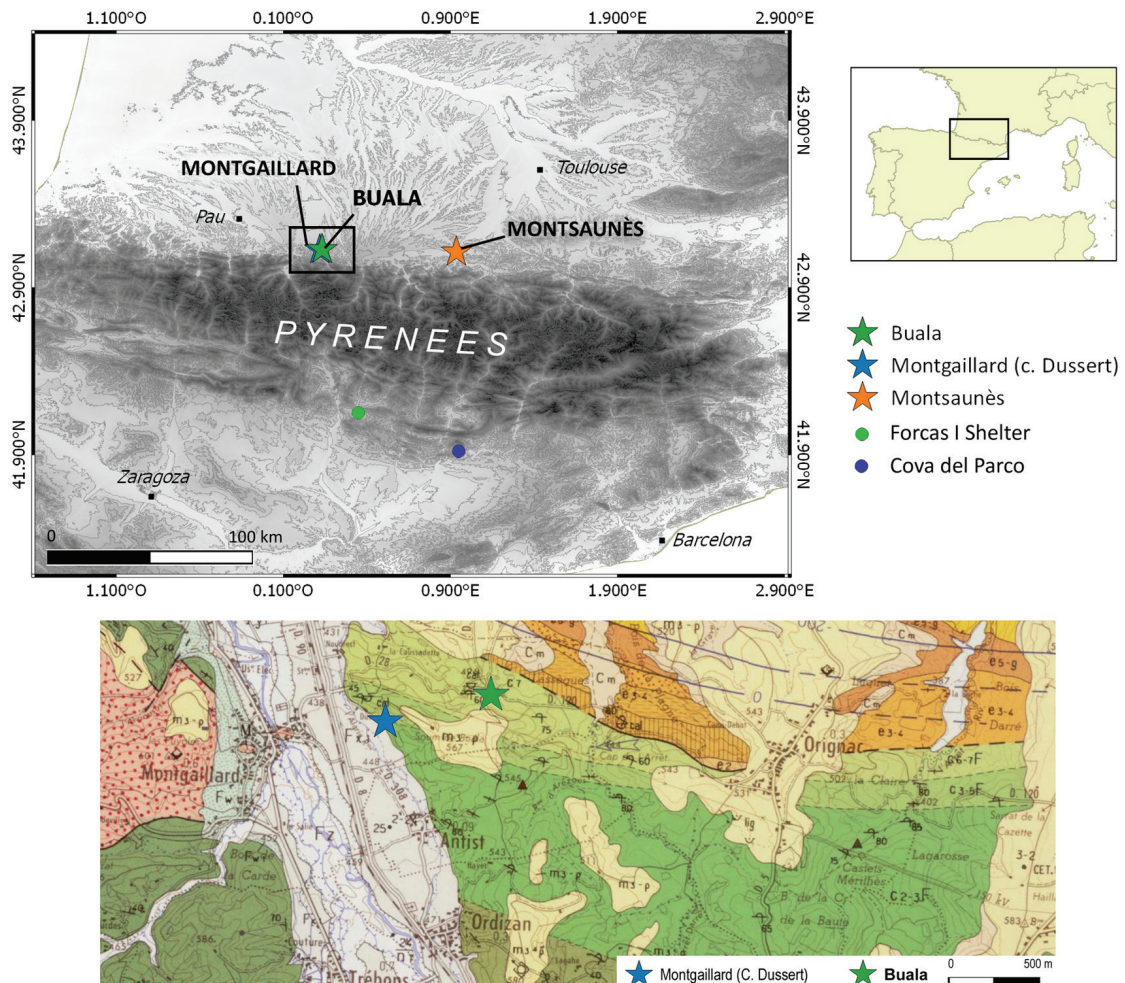


Figure 1. Location of the chert outcrops and the archaeological sites studied in this paper.

Considering its value as a promising lithic tracer potentially used by Palaeolithic groups of both Pyrenean slopes, a marine chert type outcropping in the northern slope of the Central Pyrenees was selected for this study: the Montgaillard-Montsaunès cherts. It is a marine chert type that already at the macroscopic scale presents parallels with cherts found at several Palaeolithic sites from both Pyrenean slopes (Sánchez de la Torre 2015). Three outcrops of this chert type have been recognized in the northern slopes of the Central Pyrenees. They belong to two Upper Cretaceous formations: the marl flysch cherts from the Campanian-Maastrichtian (Buala and Montsaunès outcrops) and the grey flysch cherts from the Turonian-Santonian (Montgaillard outcrop).

The first formation is comprised of the Montgaillard flysch cherts. This silicification originates from the flysch limestone from the Turonian to the Santonian outcropping in primary position near the Montgaillard village (Hautes-Pyrénées, France), and in secondary position near Hibarette, Bénac, Saint Martin and Visker (Hautes-Pyrénées, France), where lithic remains of ancient knapping were found (Barragué *et al.* 2001; Foucher *et al.* 2016). Cherts possess identical features in primary and secondary outcrops. Cortex are regulars, with variable thicknesses and colors from grey to brown with a high internal variability. The micropaleontological content is composed of sponge spicules and some small benthic foraminifera. In thin section, a cryptoquartz mosaic is the main silica texture. Length-fast chalcedony is identified in few average. Siliceous sponge spicules are also observed. Carbonate components include micrite and some bioclastic skeletal remains partially transforming into silica. Metal oxides are abundant and detrital quartz crystals are also observed (Sánchez de la Torre 2015).

The Montsaunès-Buala cherts are embedded within the Nankin limestone of the Middle Maastrichtian and outcrop at the ancient quarry of Montsaunès (Haute-Garonne, France) (Séronie-Vivien *et al.* 2006) and the ancient quarry of Buala, near the village of Montgaillard (Hautes-Pyrénées, France) (Sánchez de la Torre *et al.* 2017b). The micropaleontological content of this limestone is characterized by a rich assemblage of classical benthic Maastrichtian foraminifera (Bilotte and Andreu 2006). Cherts possess beige to brown colors with a micropaleontological content represented by sponge spicules and small foraminifera. In a few samples, some Maastrichtian benthic foraminifera were observed. In thin section, a cryptoquartz mosaic is the main silica texture and length-fast chalcedony appears in a few average. Siliceous sponge spicules are also visible. Carbonate components are represented by micrite and bioclastic remains in the process of being converted into silica.

Cherts showing similar macroscopic and petrographic features as the geological ones have been recognized in the archaeological record of the Magdalenian levels at Cova del Parco (Alòs de Balaguer, Spain) and Forcas I rock shelter (Graus, Spain), with radiocarbon dates ranging from 16,800 to 13,700 cal BP (Utrilla and Mazo 2007; Mangado *et al.* 2010).

Cova del Parco (Alòs de Balaguer, Spain) is an archeological site located in the southern Pyrenees, in the Segre river valley at 420 m asl, in a sheltered area. It features human occupation from the Paleolithic to the Bronze Age (Mangado *et al.* 2015; Fullola *et al.* 2012; Mangado *et al.* 2014). Fieldwork was started in the 1980s by a team from the University of Barcelona and is still in progress. The samples studied in this paper come from the Magdalenian levels. This period is well represented at the site, with several occupations going from the Middle to the Late Upper Magdalenian (Table 1).

Forcas I rock shelter (Graus, Spain) is located in the eastern province of Huesca, near the Ésera river, tributary of the Cinca river. Discovered by chance in 1990, the site was destroyed by 90% due to gravel exploitation in the area. Archaeological fieldwork was conducted by a team from the University of Zaragoza. Results demonstrated that the site was repeatedly occupied since the Magdalenian to the Early Mesolithic. Samples studied in this work come from the Magdalenian levels. This period is also well documented in the site, with some occupations from the Lower Magdalenian and the Upper Magdalenian (Utrilla and Mazo 2007; Utrilla and Mazo 2014).

Site	Data	Lab. Ref.	Met.	SN	Calendar 68% range Cal BP	Calendric Age Cal BC	Reference
Cova del Parco	12605±60 BP	OxA-10796	AMS	C	14662-15260	13011±299	Fullola <i>et al.</i> 2012
Cova del Parco	12460±60 BP	OxA-10797	AMS	C	14426-15055	12791±314	Mangado <i>et al.</i> 2006
Cova del Parco	12560±130 BP	OxA-10835	AMS	C	14535-15234	12935±349	Mangado <i>et al.</i> 2006
Cova del Parco	12995±50 BP	OxA-13597	AMS	C	15447-16245	13896±399	Mangado <i>et al.</i> 2006
Cova del Parco	13025±50 BP	OxA-13596	AMS	C	15503-16293	13948±395	Mangado <i>et al.</i> 2006
Cova del Parco	13095±55 BP	OxA-17730	AMS	C	15616-16387	14052±385	Mangado <i>et al.</i> 2010
Cova del Parco	13255±50 BP	OxA-29336	AMS	C	15778-16592	14235±407	Mangado <i>et al.</i> 2014
Cova del Parco	13475±50 BP	OxA-23650	AMS	C	16022-16839	14481±408	Mangado <i>et al.</i> 2014
Forcas I	12440±50 BP	GrA-32957	AMS	B	14378-15018	12748±320	Utrilla & Mazo 2007
Forcas I	12010±60 BP	GrA-33987	AMS	B	13783-14197	12040±207	Utrilla & Mazo 2007

Table 1. Radiocarbon dates concerning the Magdalenian levels of the two archaeological sites mentioned in the paper. The calendar age has been calculated by Online CalPal (quickal2007).

CalCurve: CalPal_2007_HULU. 68% range cal BP. SN: Sample Nature. C: Charcoal. B: Bone.

2. Materials and methods

We selected 131 pieces of chert for analysis. Of these, 66 were geological products from Montsaunès (n=23), Montgaillard (n=23) and Buala (n=20), whereas 65 were artifacts from the sites of Cova del Parco (n=50) and Forcas I rock shelter (n=15). All of them have been characterized according to their texture and micropaleontological content, which revealed that they formed in a marine environment. These samples exhibit features identical to those observed in the geological cherts from the French Central Pyrenees.

To avoid the influence of surface alterations/geochemical weathering, geological samples were prepared in squares of 5 x 5 mm by removing the cortical surface and subsequent polishing. However, as it was our aim to compare the results here obtained with archaeological samples in a non-destructive mode, some of the geological samples were analyzed without any prior surface preparation. Results were similar to those obtained for the other geological samples.

To analyze major and minor elements, ED-XRF (Energy-Dispersive X-ray Fluorescence) was applied. Analyses were done at the Research Centre for Applied Physics in Archaeology, IRAMAT, Bordeaux, France. Nine elements were quantified (Na, Mg, Al, Si, P, K, Ca, Ti, Fe) using an X-ray fluorescence spectrometer SEIKO SEA 6000 VX (Orange *et al.* 2017). Fundamental parameters corrected by the granodiorite GSP2 from the U.S. Geological Survey (USGS) international standard (Wilson 1998) were used. A 3 x 3 mm collimator was used and analysis time was set to 400 seconds for each of the three measurement conditions (with air or He environment and Cr or Pb filter). To check instrument calibration and accuracy a JCh-1 chert standard from the Geological Survey of Japan (GSJ) was employed (Imai *et al.* 1996). To prove and validate the used formula and to check instrument accuracy a measurement with the JCh-1 chert standard was established, with an obtained standard deviation always lower than 0.08 wt%, validating the accuracy of the used formula (Sánchez de la Torre *et al.* 2017a).

To analyze trace elements, LA-ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry) was performed at the Ernest Babelon laboratory, IRAMAT, Orleans, France. Elements were quantified using a Thermo Fisher Scientific Element XR mass spectrometer associated with a Resonetics RESolution M50e ablation device. The ablation device is an excimer laser (ArF, 193

nm), which was operated at 7-8 mJ and 20 Hz. 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: 10 s pre-ablation to let the ablated material reach the spectrometer and 30 s collection time. Laser spot size was set to 100 μm and line mode acquisition was chosen to enhance sensitivity. Background measurements were run every 10 to 20 samples. Calibration was performed using standard reference glass NIST610 which was run periodically (every 10 to 20 samples) to correct for drift. NIST610 was used to calculate the response coefficient (k) of each element (Gratuzé 1999, 2014) and the measured values of each element were normalized against ^{28}Si , the internal standard, to produce a final percentage. Glass Standard NIST612 was analyzed 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, Ca, Ti, V, Cr, Fe, Ga, Ge, As, Rb, Sr, Y, Zr, Nb, Cs, Ba, La, Ce, Pr, Nd, Sm, W, Bi, Th, U).

After quantifying major, minor and trace elements by ED-XRF and LA-ICP-MS, PIXE (Particle Induced X-Ray Emission) was applied for developing trace element mapping. PIXE analyses tried to determine the place where trace elements appeared in cherts, identifying by mapping the surface if specific trace elements were related with the main Si matrix or with some inclusions. The PIXE measurements were performed at the scanning nuclear microprobe installed on the 0° beamline of the 5 MV Van de Graaff accelerator of MTA Atomki (Debrecen, Hungary) (Rajta *et al.* 1996). A proton beam of 3.2 MeV energy was focused down to $\sim 4 \times 4 \mu\text{m}$ with a current kept between 50-100 pA in order to avoid the charging up of the samples over these values. The scan size was 1 mm x 1 mm. On each sample 2-4 areas of 1 mm² were measured. At first, elemental maps and summed up X-ray spectra on the full 1 mm x 1 mm area were recorded. If inhomogeneities were present, e.g. microfossils or mineral inclusions, the scan size and thus the scan area were reduced in order to better see these patterns, and additional measurements were made on the inclusion itself using the selected raster mode. For the light-element PIXE-PIXE measurements, two X-ray detectors placed at 135° geometry relative to the incident beam were applied to collect the emitted characteristic X-rays. An SDD detector with AP3.3 ultra-thin polymer window (SGX Sensortech) with 30 mm² active surface area was used to measure low and medium energy X-rays (0.2-12 keV, $Z > 5$). A Gresham type Be windowed Si(Li) X-ray detector with 30 mm² active surface area equipped with an additional kapton filter of 125 μm thickness was applied to detect the medium and high energy X-rays (3-30 keV, $Z > 19$). The accumulated charge was monitored with a beam chopper. Detailed description of the measurement setup can be found elsewhere (Kertész *et al.* 2009). Signals from all detectors (two PIXE and the particle detector of the chopper) were recorded event by event in list mode by the Oxford type OMDAQ2007 data acquisition system (Grime and Dawson 1995). PIXE spectra with better resolution and lower dead time were recorded parallel to this with an independent Canberra data acquisition system and with the SGX DX200 digital DPP. The obtained PIXE spectra were evaluated with the GUPIXWIN software (Campbell *et al.* 2010) to determine the elemental composition of the samples. Analyses of reference materials were carried out at the beginning and at the end of the measurement campaign in order to check the accuracy of the dose measurement and of the precision of the PIXE-PIXE system.

3. Results

Results obtained by energy-dispersive X-ray fluorescence show slight differences between the three analyzed geological cherts concerning major and minor elements (Table 2). Nine elements were chosen for analysis (Na, Mg, Al, Si, P, K, Ca, Ti, Fe) but only five were present above the detection limit of the spectrometer. SiO_2 represents at least 98 wt% of the samples' composition. Minor components are Al_2O_3 , CaO, Fe_2O_3 and K_2O . NaO, MgO, P_2O_5 and TiO_2 results were not considered, as they were mostly below the detection limit. Thus, the major and minor general composition obtained after ED-XRF do not enable us to distinguish between the Montgaillard flysch cherts and the Montsaunès cherts. However, the Buala flysch cherts differ slightly from the other geological

	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃
Buala	<LD	0.002	0.558	98.955	<LD	0.022	0.350	0.004	0.111
Montgaillard	<LD	0.006	0.354	99.294	<LD	0.016	0.288	0.003	0.038
Montsaunès	<LD	<LD	0.347	99.473	<LD	0.020	0.128	0.005	0.027

Table 2. ED-XRF analytical median values (in wt%) of each analysed geological outcrop.

formations in their major and minor components. Thus, scatterplots combining the Al₂O₃, SiO₂ and Fe₂O₃ percentages show a differential distribution for the Buala flysch cherts. Nevertheless, archaeological samples mostly fit with the overlapping area of Montsaunès and Montgaillard cherts, so no relevant results were obtained after ED-XRF analyses (Figure 2).

LA-ICP-MS analyses have shown several differences between the three formations and some interesting results regarding the association of some archaeological samples, in terms of some trace elements (Table 3). In this case, discrimination is possible between the three types of chert, giving a different dispersion area for each source. This discrimination is essentially based on the amounts of Ti, V, Sr and Th. Thus, the scatterplot concerning Ln [Th/Sr] vs Ln [Ti/Sr] shows three different dispersion areas for the three analyzed chert types (Figures 3 & 4). When introducing the archaeological samples of Cova del Parco (Figure 3, top), most of them are placed in the dispersion area of the Montgaillard geological cherts. Only one sample is clearly placed in the dispersion area of the Buala cherts, while none appears in the Montsaunès main geochemical dispersion. When introducing archaeological samples from Forcas I rock shelter (Figure 3, bottom), they are again mostly related with the main dispersion area of Montgaillard geological cherts. Nevertheless, some samples seem to be located at the boundary between the dispersion area of Montgaillard and Montsaunès cherts, given that one of them is clearly inside the Montsaunès dispersion area. However, any sample fits in the main dispersion area of the Buala cherts.

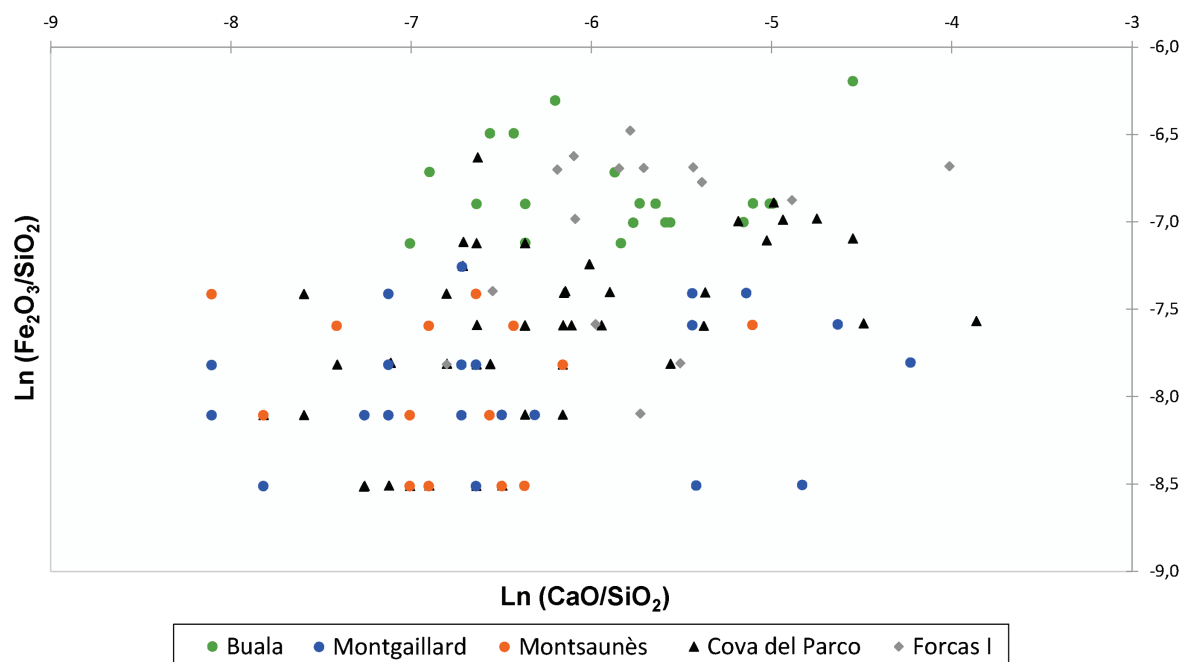


Figure 2. Scatterplot with the three analysed chert outcrops (Buala, Montgaillard and Montsaunès) and the archaeological artefacts from Cova del Parco and Forcas I rock-shelter concerning Ln Fe₂O₃/SiO₂ vs Ln CaO/SiO₂.

	Mg	Al	Si	Ti	V	Cr	As	Rb	Sr	Y	Zr
Buala	72.54	1071.7	460541	125.31	7.051	22.75	8.91	1.29	13.51	0.77	4.195
Montgaillard	147.88	2003.4	463833	160.08	5.481	12.87	4.19	3.28	30.10	1.29	2.192
Montsaunès	111.71	1692.4	464412	254.25	11.79	16.97	7.39	3.68	7.952	1.09	5.741

	Nb	Cs	Ba	La	Ce	Pr	Nd	Sm	W	Bi	Th
Buala	0.41	0.09	30.06	0.74	1.65	0.23	0.85	0.21	3.58	0.16	1.30
Montgaillard	0.43	0.23	44.84	1.14	2.31	0.28	1.13	0.26	1.06	0.29	0.44
Montsaunès	0.85	0.28	16.22	2.35	2.49	0.49	1.88	0.34	2.45	0.22	0.87

Table 3. LA-ICP-MS analytical median values (in ppm) for each analysed geological outcrop.

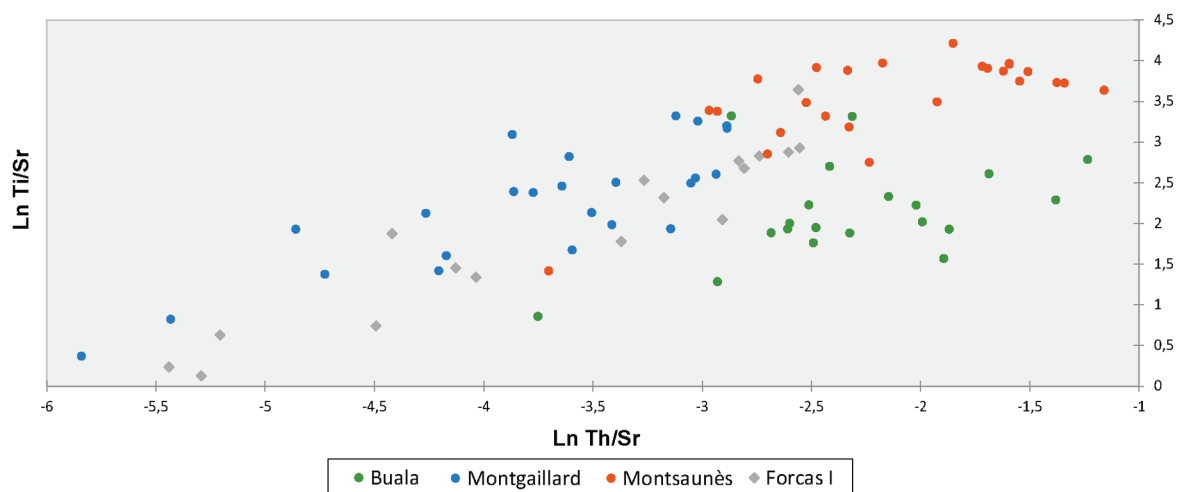


Figure 3. Scatterplot with the three analysed chert outcrops (Buala, Montgaillard and Montsaunès) and the archaeological artefacts from Cova del Parco concerning Ln Th/Sr vs Ln Ti/Sr.

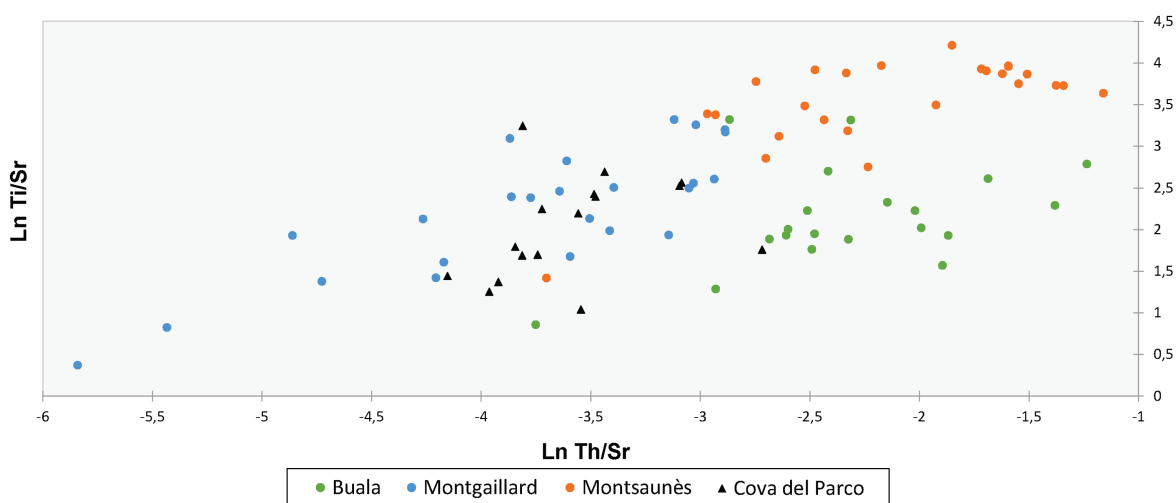


Figure 4. Scatterplot with the three analysed chert outcrops (Buala, Montgaillard and Montsaunès) and the archaeological artefacts from Forcas I rock-shelter concerning Ln Th/Sr vs Ln Ti/Sr.

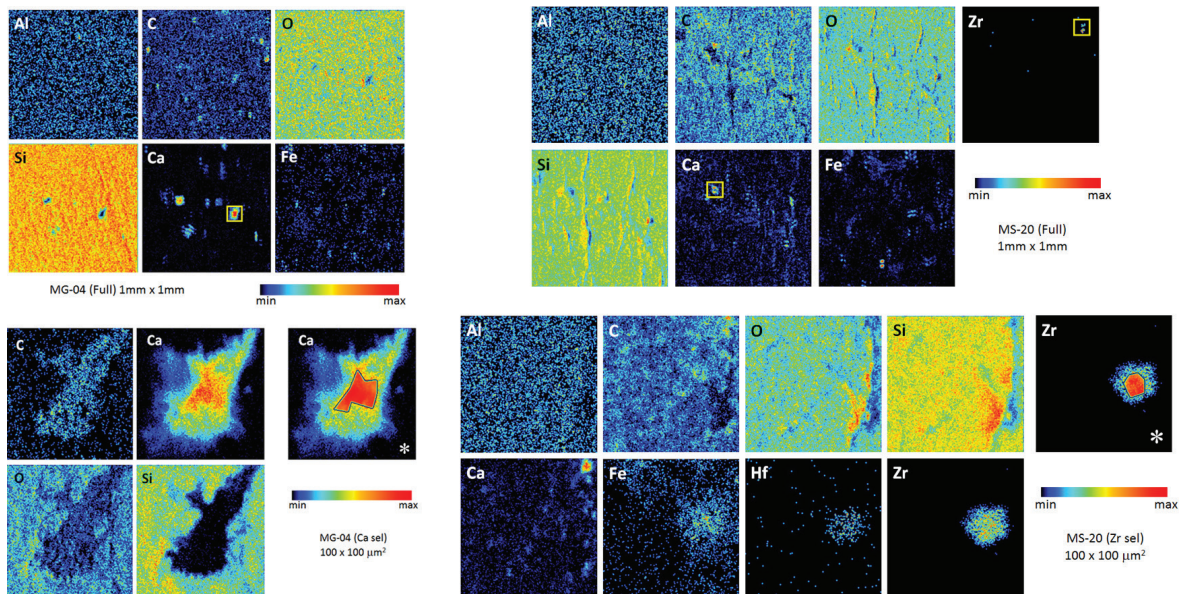


Figure 5. PIXE elemental mapping for Montgaillard MG-07 (left) and Montsaunès MS-20 samples (right) with a full 1 mm² area (top) and a Ca (bottom left) a Zr (bottom left) selected 100 μm² area. In full Ca and Zr areas, the yellow squares indicate the zoom selected area. *Selected raster on Ca and Zr maps.

During PIXE analyses, three types of inclusion were consistently detected within the geological cherts of Montgaillard, Montsaunès and Buala, of which surfaces of about 1000 x 1000 μm were selected for analysis and mapped. The most common inclusions were essentially composed of Ca, Fe and Zr. While Ca and Fe inclusions were detected in the three chert sources, Zr inclusions only appear in Montsaunès samples (Figure 5). Thus, mapping analysis combined with quantitative data show that there are correlations between certain elements. Therefore, Na, Mg, Al, Mn and Cu are elements regularly present in the Si matrix, while also occurring in some inclusions. Instead, K, Ca, Fe and Zr usually make up inclusions rather than occurring in the Si matrix. Concerning specific analyzed areas, some trace elements are frequently related with Ca or Fe inclusions, as S, V, Cr, Ni or Sr. As and Pb have only been identified in association with Fe inclusions, while W is present in Fe and Zr inclusions and Y, Hf, Th and U are always related to Zr inclusions.

4. Discussion

With this multi-method study, after developing macroscopic and petrographic analyses, three geochemical techniques have been used to examine the same types of chert. Once observed that for this case study macroscopic and petrographic analyses were not sufficient to distinguish between these so-close textural and micropalaeontological chert sources, ED-XRF, LA-ICP-MS and PIXE were applied to determine whether it is possible to identify differences in the main geochemical content. Once the variables were established, the three presented techniques have produced different results with the same types of chert, thus offering complementary data.

ED-XRF is a non-destructive technique that offers quantitative data and is good to measure major and minor elements. However, it is a limited technique for this archaeological case study due to the high Si rates present in this type of chert, always up to 98 wt%. Therefore, trace elements cannot be detected with ED-XRF, as they are always present in quantities below the instrument's detection limit.

LA-ICP-MS presents several advantages when analyzing chert. It is a good technique to quantify major, minor and trace elements, a result which could be achieved thanks to the facility in Orléans. Since it is a fast technique, LA-ICP-MS is characterized by good accuracy and precision. In addition,

given that the spectrometer is associated with an ablation device, there is no need to destroy the sample for analysis. The only inconvenient is that an ablation device is required. Nevertheless, due to the small ablation spot size – about 100 μm in diameter, the result is not visible to the naked eye. In the present case study, LA-ICP-MS proved a valuable technique to distinguish between the three chert sources, as some trace elements are present in different averages. It was thus possible to correlate the archaeological samples of Cova del Parco and Forcas I rock shelter with a specific geological source.

With regard to the PIXE potential and limitations, and its application to the study of the Montgaillard-Montsaunès cherts, while it is not the best technique to quantify elements due to the large acquisition time taken for quantification, it can analyze most of the elements. Furthermore, it is one of the few techniques able to determine the spatial distribution of elements in a sample thanks to mapping.

5. Conclusions

The three geochemical techniques used in this study have produced valuable data for the present archaeological case study. First, ED-XRF analyses have revealed that no differences exist between the Montgaillard and Montsaunès-Buala cherts in terms of major and minor elements, showing that both marine formations exhibit similar SiO_2 , K_2O , CaO and Fe_2O_3 values. Secondly, LA-ICP-MS has revealed that both formations and the three outcrops can be distinguished based on the occurrence of specific trace elements concentrations, i.e. V, Cr, Sr and Th. Moreover, it has also been possible to relate the archaeological cherts from Cova del Parco and Forcas I rock shelter particularly with the Montgaillard geological cherts, thus providing valuable data for the archaeological interpretation. Finally, PIXE analyses have determined whether the elements are associated with the Si matrix or with the inclusion content, showing differences between formations, as Zr inclusions were only observed in the Montsaunès cherts.

Using this multi-method approach, the present study has shown that geochemistry can be useful in solving some archaeological problems that routine macroscopic and petrographic analyses cannot tackle. In the specific case, differences between the two geological formations have been noticed after applying LA-ICP-MS. Further, after the analysis of specific trace elements, it appears clear that most of the archaeological cherts from Cova del Parco and Forcas I rock shelter are related to the Montgaillard flysch cherts, thus lending support to the hypothesis that these archaeological cherts derive from that geological formation. From the archaeological point of view, this data supports the idea that the Pyrenees were not a barrier for human groups at the end of the Upper Palaeolithic; rather, they are an example of long-distance procurement across a mountain range.

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