Black adzes in the Early Neolithic of Belgium: Contribution of the Raman microspectrometry and petrography in characterization and sourcing

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Abstract:

Early Neolithic (Linear Pottery Culture) adzes originate from settlements and workshops accompany the neolithization of Belgium. They are made from a wide range of extraregional lithic raw materials such as metamorphic green rocks (amphibolite) and black volcanic rocks ("basalt') beside more local or regional raw material as flints, light-coloured (sedimentary and lightly metamorphic) quartzites, black lydites (Cambrian nodular phtanite of Céroux-Mousty and Lower Namurian banded phtanites) and dark grey Lower Namurian silicified sandstones previously called "Micaceous sandstones of Horion-Hozémont'. The discovery of the workshop of Noirfontaine near the city of Liège in the 1970s and 1980s provides exceptional assemblage available for updating analytical studies. This research focuses on the multi-scale characterization, the discrimination and sourcing both Cambrian and Namurian black sedimentary rocks rich in secondary silica composing Early Neolithic adzes found in Belgium. Their black colour results from finely dispersed organic matter, but the absence of palynomorphs does not allow a biostratigraphic ascription. Additional petrographical analyses (Optical Petrography, Scanning Electron Microscope), X-ray diffraction, chemical analyses (Energy Dispersive Spectroscopy) and measuring the degree of graphitization of the organic matter through Raman microspectrometry have been decisive in identifying the geological and geographical

Journal of Lithic Studies (2023) vol. 10, nr. 1, 34 p. DOI: https://doi.org/10.2218/jls.6772

Published by the School of History, Classics and Archaeology, University of Edinburgh
ISSN: 2055-0472. URL: http://journals.ed.ac.uk/lithicstudies/

provenances by comparing the acquired results with geological reference samples collected in the field or through reference collections. Cambrian lydites are coming from a very restricted area and were preferred to other more local rock sources.

Keywords: adze; lydites; silicified sandstones; Raman microspectrometry; physical and chemical analyses; Early Neolithic

1. Introduction

During the 6th millennium B.C.E., sedentariness associated with plan cultivation and cattle farming became the dominant lifestyle of the North-western European population, replacing the more mobile lifestyle of the Palaeolithic and Mesolithic hunter-gatherers. Sedentarization was also associated with ceramics production and exploitation of the woodlands as a timber resource on a large scale to build their houses (Tegel *et al.* 2012). This transformation marked the onset of the Neolithic period and human societies accentuates the transformation of the natural environment already outlined in the Upper Palaeolithic and even more in the Mesolithic into a cultural landscape mainly devoted for living and storage around their settlements. Consequently, innovations in tool manufacture and woodworking techniques were crucial for setting up the required settlement infrastructure. The first Central European farmers, who likely immigrated from the Balkan Peninsula and the Carpathian Basin ~7,500 (cal. B.C.E.) years ago, left a uniform archaeological record of settlement structures with longhouses, pottery and stone tools, called the Linear Pottery Culture (LPC, also called LBK for *Linearbandkeramik* in the German literature) (Tegel *et al.* 2012). LPC settlements rapidly spread across the continent's fertile loess regions. Hafted polished stone adzes (we will use the shortcut “adze” to speak about the head or blade of the full tool) were introduced from East to West (“great migration”) by the LPC farmers in the loess zone of the German Rhineland, southern Limburg (NL-BE) and in turn to Belgium where Early Neolithic settlements are located on the Hesbaye plateau (from East Limburg to West Hesbaye) and then the Dendre River springs loessic areas (figures 1A, B). Stone adzes (Early Neolithic) then axes (Middle and Late Neolithic) occurred in the woodworking toolkit of the Neolithic farmers to perform carpentry tasks. We will focus only on adzes called “herminettes” in French. They are distinct from axes on several bases: the working edge of an adze is set to be perpendicular to the handle while axes are set in a handle such that the working edge is parallel to the handle (Hirst 2018).

Evidence for a sophisticated level of carpentry at Neolithic sites was reported by Tegel *et al.* (2012). Early Neolithic carpenters built sophisticated corner joints and log constructions, using a series of stone adzes to cut and trim the timber required for their infrastructures (houses, protection walls, wooden-walled water wells…). Hafted polished stone adzes were introduced in the Lower Rhine Basin by the LPC farmers, who settled the loess zone of the German Rhineland, southern Limburg and the Belgian Hesbaye around 5,300 cal. B.C.E. Stone adzes were not known in the preceding Late Mesolithic, during which period all heavy chopping equipment was made from bone and antler (Verhart 2012). Two main cultural groups settled in Belgium during the Early Neolithic: the Linear Pottery Culture and the Blicquy-Villeneuve-Saint-Germain culture (BQY-VSG). Stone adzes were only found in the LPC cultural group, and not later. In regard to the typology, the Early Neolithic adzes are divided in six types according to C.C. Bakels (Modderman *et al.* 1970: 186-187). The basic two main types are: the flat adzes (*Flachhacke - herminette plate*) for which the width exceeds the thickness (Figure 1C) and the shoe-last adzes (*Schuhleistenkeile* - *herminette en forme de bottier*) also referred as the high adzes for which the thickness exceeds the width

(Figure 1D). The selected adzes have been treated as a whole in this study, belonging to the same culture.

Some archaeological studies of the LPC adzes in Belgium have focused on the origins of raw materials used for these implements (Toussaint & Toussaint 1982). These are green "amphibolites" (actinolite-hornblende schists metamorphic rocks), black grey "basalts" (volcanic rocks) and fine, high-silica rocks (sedimentary rocks) as the light grey quartzites and black lydites. Adzes made from lydites, quartzites and sandstones are considered to have been extracted in or close to the region where they were found because the presence of similar raw material and sometimes the occurrence of workshop wastes nearby the settlements (Bakels 1987; Hauzeur *et al.* 2011; Jadin & Hauzeur 2003). "Basalt" adzes found from Belgian settled areas are considered by some authors to have their source in Germany (Eifel, Siebengebirge), while "amphibolites" were probably imported from countries east of the Rhine River (Western Carpathians in Slovakia; High Balkan in Bulgaria; Bohemia in Czech Republic (Arps 1978: 202-228; Ramminger 2009; Verhart 2012). In the Mosel area, amphibolites and basalt families are supposed to come from Middle Rhine (Westerwald, Siebengebirge, Odenwald, Spessart), but also locally from the Hunsrück (Hauzeur & Errera 2016; Schmidgen-Hager 1993).

Local (from Hesbaye itself and the Meuse basin) as well as exogenous raw material sources coexist for the Neolithic adzes discovered in Belgian LPC settlements but detailed archaeometric and sourcing studies are either lacking, old or incomplete. It is why we gathered our selected samples of adzes in black and grey rocks under the generic term of "black" ones as they included different kind of raw materials. Other local/regional raw materials such as oolitic haematites for the production of red powders, different types of sandstones for the production of grinding stones, as well as pottery clays were extracted and used during the LPC period in Hesbaye. Local and regional resources suitable for the production of adzes were used extensively, but it is unclear whether these quarried rocks met specific needs for local populations and different from those provided by imported materials. The coexistence of adzes made of local and imported rocks may be due to the fact that the more local raw materials are less easy to manufacture due to the mechanical properties of the rock itself. Prospective tests will be planned in the future to look in that direction like in Central Europe for axes (Monik *et al.* 2021). As rocks of good quality like phtanite seem to be exported over rather long distances (Mosel area, work in progress), others like silicified sandstone from Horion-Hozémont rarely leave their regional territory probably because of their complex manufacturing process, difficulty of collecting, *etc*. as recent studies concerning Western European axes tend to demonstrate (Delgado-Raack *et al.* 2020). The aims are: a) to obtain a multiscale description and characterization of the black materials constitutive of the Early Neolithic adzes by means of appropriate analytical methods, b) to characterize and differentiate the black fine-grained silica-rich raw materials, c) to source the black adzes, d) to propose a non-destructive instrumental technique and d) to propose trade routes to achieve our aims.

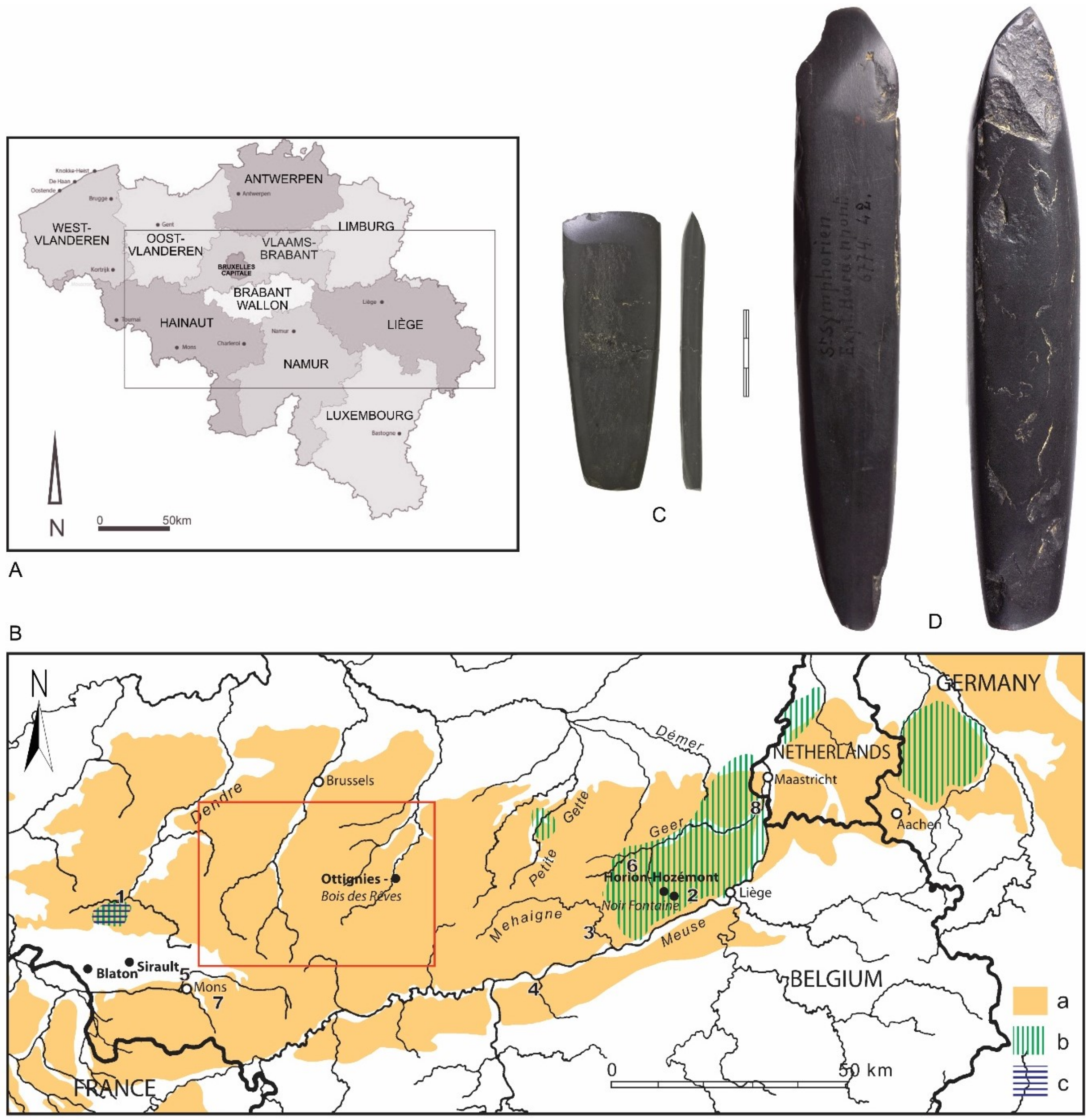

Figure 1. A. Belgian provinces map. B. The LPC settlements in Belgium's most fertile soils: (a) the loessic belt in Belgium and adjacent countries; (b) LPC settlements in Hesbaye (Liège and Limburg Provinces, BE and NL), the Petite Gette River area (Vlaams Brabant) and Dendre springs (Hainaut), (c) BQY-VSG settlements from the Dendre springs in the Hainaut Province. Orographic network drawn by Fr. Laurent (ADIA-RBINS); loessic soils repartition by Jadin & Langohr, after the Soil Map of the European Communities. Red rectangle: area covered by figure 3. C. Flat black adze in phtanite, from Oleye "Al Zèpe" (Liège province). RBINS collection, Id: OZ87-100-F2-10-20. Photography: Éric Dewamme (Patrimoine Dept., RBINS). D. Shoe-last black adze in phtanite from Saint-Symphorien (Hainaut Province). RBINS collection, Id: IG-6774-42. Photography: Pierre Cattelain (Musée du Malgré-Tout, BE). Localities cited in the paper: 1. Ath; 2. Bierset (Grâce-Hollogne); 3. Huccorgne (Wanze); 4. Namêche (Andenne); 5. Nimy (Mons); 6. Oleye (Waremme); 7. Saint-Symphorien (Mons); 8. Visé. Basemap : Fr. Laurent, ADIA. a. Loess; b. LPC; c. Blicquy/VSG Group. Infography: A. Hauzeur.

1.1. Black LPC adzes in Belgium: context

Typical LPC adzes occur as stray finds all over the sandy plain to the North of the LPC settlement clusters of the loess belt (Brandt 1967). But in the Dutch and Belgian areas numerous adzes were also found outside the loess belt (Bakels 1987: 78; Lodewijckx & Bakels 2009; Verhart 2012). Among all the adze series, the black ones fit with the general distribution of adzes. They were found in the entire area of LPC, in the Hesbaye (Jadin 2003; Toussaint & Toussaint 1982) as well as in the Dendre River springs and the Petite Gette River valley (Lodewijck & Bakels 2009). Around the settlements themselves, isolated adzes were mainly found in the Hainaut Province, but also, in small quantities, in the Ardennes (Jadin 2003). They have been considered as lost tools, on the way to look for Upper Cretaceous good quality flint (Hallsworth & Knox, 1999: 22) outcrops (case of those collected in Hainaut) or to cross the Ardennes to go in the Mosel Valley for example, where LPC populations also settled and where finished black adzes were found (Hauzeur 2006).

Most of the black adzes in Belgium are finished products found in the waste pits of the domestic areas. They were used and reused, sometimes reshaped and repolished, partly because the outcrops are not in the vicinity of the settlements. As imported finished products they revealed circulation networks. Besides those finished products, some settlements provided roughouts and workshop wastes. Outcrops of Cambrian lydites (called phtanites in Belgium and in France) located in the Brabant Province and outside the LPC territory are disconnected from domestic settlements. In Hesbaye, roughouts and workshop wastes occur in domestic pits closed to potential outcrops of "micaceous sandstones of Horion-Hozémont" (MSHH). Archaeological finds excavated in domestic pits of LPC settlements in the Gette valley are far from the lydite outcrops as well as the MSHH outcrops. None of them occur in Mesolithic context like the phtanites of the Armorican Massif. They are interbedded in numerous Late Proterozoic (Brioverian) sedimentary formations, and were widely exploited in Western France during the Mesolithic, principally during its final phase (Tsobgou & Dabard 2010).

Beside fine-grained silica-rich rocks, some adzes made of black basalt-like lavas occur in places in Hesbaye and Dendre River springs areas. Macroscopically they could be confused. A basalt is an aphanitic (fine-grained) extrusive igneous black rock with crystals indistinguishable to the human eye. Any larger crystals visible to the human eye, called phenocrysts, form earlier while slowly cooling in the magma reservoir. The IUGS classification of aphanitic extrusive igneous rocks is complex and require petrographic studies in thin-section and geochemical analyses (wt% (Na_2O+K_2O) vs wt% SiO_2) to confirm that the rock is a basalt. In the absence of petrographic and geochemical analyses of this type of adze, it's better to used "basalt-like lavas". One example is the Eifel volcanic field (Germany) showing a wide variety of extrusive rocks and needing geochemical analyses to source the millstones from the Gallo-Roman and Medieval periods (*e.g.*, Gluhak and Hofmeister, 2011).

1.1.1. Cambrian lydites and workshop places

The use of Cambrian lydites collected from the Ri Angon valley (Bois des Etoiles, Ottignies - Louvain-la-Neuve, Province of Walloon Brabant) is attested since the Middle Palaeolithic at Franquenies, with a series of artefacts collected at less than one kilometre from the Ri Angon river (Michel & Haesaerts 1975). On the top of "Bois des Etoiles" is an open-air site dated to the Final Palaeolithic (Federmesser) containing debitage products (flakes, blades and bladelets, and cores) and tools made from lydite (Caspar & Cahen 1981).

A workshop place with blade debitage was discovered in the same area and is attributed to the Neolithic. On the right riverbank of the Ri Angon a huge Neolithic workshop was discovered, excavated by an amateur J. Soetens (1964). He collected roughouts of massive tools, tools and debitage wastes. The aim of these roughouts production remains a question mark (Caspar 1982), with nevertheless a hypothesis for adzes roughouts (Caspar 1984).

Other debitage products and roughouts belonging to adzes "chaîne opératoire" have been discovered far from the lydite outcrops. They are mixed with domestic wastes in pits of LPC settlements in the Petite Gette valley (Lodewijckx 1990) and represent up to 25% of the lithic assemblage or more. None of the Hesbaye sites gives such a high percentage of lydite wastes (Caspar 1984).

1.1.2. Horion-Hozémont and Noirfontaine

Discovered close to the current village of Horion-Hozémont (city of Grâce-Hollogne, Province of Liège) in the 1970s and 1980s (Dradon 1967a; 1967b; Tromme and Haeck 1974-1976), the archaeological site of Noirfontaine provides different types of adzes. Beside adzes made from the well-known classical black lydites, hundreds roughouts and semi-finished adzes in stone firstly described as “grey black phtanites” were discovered close to a workshop. After identification on sight by Bourguignon (mineralogist at the Liège University), Dradon renamed and attributed this material as a “variety of sandstones with micas probably coming from the Carboniferous”. However, Dradon did not write as such that it was a “local” sandstone in the vicinity of the site. This author mentions his unsuccessful searches for phtanite sites in the Chokier stratigraphical unit (Carboniferous), especially in the vicinity of Chokier, a locality near Horion-Hozémont in the Meuse valley. Toussaint and Toussaint (1982) give a comparative macroscopic and the first petrographic description of the adzes and coal measures sandstones found at a short distance from the Omalian sites of Noirfontaine and Lexhy (commune of Horion-Hozémont) accrediting the sandstone nature of the archaeological material and the close origin of the raw material. The authors conclude by “Although similar coal measures sandstones must outcrop throughout the Meuse basin, almost from the French border to that of the Netherlands, they seem to have been exploited only in Horion-Hozémont”. In the following papers (Toussaint 2011), the name was changed to “Micaceous sandstones of Horion-Hozémont”. Both flat and shoe-last adzes were produced in this workshop. The exceptional amount of waste, half-products, roughouts in MSHH gives the opportunity to undertake deeper analyses. A spatial distribution of the adzes in MSHH is given by Toussaint & Toussaint (1982) and Toussaint *et al.* (1983) followed by Toussaint (2011). New excavations close to the workshop are conducted since April 2021 by the AWaP (Walloon Cultural Heritage Agency, part of the Public Service of Wallonia, department Spatial and Urban Planning) with the discovery of roughouts.

1.1.3. Black adzes from the Dendre River springs

Sixty-six pieces of black material (entire adzes, fragments and roughouts) were collected in excavations conducted since the seventies, eighties and in 2015 (Constantin *et al.* 2009, Denis *et al.* 2021, 2024 (submitted and accepted); Livingstone Smith & Goemaere 2012; Livingstone Smith & Teheux 1994) and preserved both in the AWaP’s collections and in the collections of the “*Cercle de Tourisme et de Recherches archéologiques*” (Blicquy Aubechies association). Fifty-height pieces made of silica-rich detrital rocks were discovered in four of the height registered settlements: Ath (Les Haleurs), Ormeignies (Au Pilori, Bois de la Bonne Fortune et Moulbaix), Beloeil (Aubechies CoronMaton), and Leuze-en-Hainaut (Blicquy, Couture du Couvent, La Petite Rosière, Ville d’Anderlecht). The four archaeological sites with black silica-rich adzes are: Ath (Les Haleurs), Blicquy (La Petite Rosière, Couture du Couvent) and Aubechies (Coron Maton)) located at the Dendre River springs area (tributary of the Scheldt River, Province of Hainaut). Three sites included adzes and fragments from weathered basalt ($n = 8$) exhibiting a grey-coloured surface and pyroxene phenocrysts in relief. At Aubechies - Coron Maton, part of the adzes was made from a raw material described as close to MSHH (Arps & Bakels 1980). Beside settlements isolated finds have been gathered in the regional area, where the most spectacular piece is the long, thick and narrow shoe-last adze in lydite coming from Hardenpont quarry at Saint-Symphorien (Jadin & Hauzeur 2003: 85).

1.2. Black lydites in the Belgian geological record

The National Commission for Stratigraphy in Belgium (NCS) has the task to organize the stratigraphic nomenclature of the Belgian geology according to international standards and conventions. It works in strong collaboration with the mapping teams, the universities and the geological surveys. Geological maps, leaf notes, litho- and chronostratigraphical information are available online for readers wishing to receive more comprehensive geological data (Website of the NCS: https://ncs.naturalsciences.be/cretaceous/lithostratigraphy. Guide to a revised lithostratigraphic scale of Belgium (edited by Bultynck & Dejonghe, 2011): https://popups.uliege.be/1374-8505/index.php?id=1896. Consultation of the geological maps of Wallonia (in French): https://geologie.wallonie.be/home/acquisition-de-donnees/applications-en-ligne/carte-geologique.html).

Four main levels of black rocks very rich in silica (called “silicites” by A. Přichystal 2010, referring to all silicified rocks of chemical, biochemical or diagenetic origin in Eastern and Central Europe) occur in the Belgian stratigraphical record in the Palaeozoic: the Lower Cambrian lydites, the Dinantian nodular (rarely black) lydites (called *cherts* in French), the Lower Namurian banded lydites and the Lower Namurian dark grey micaceous sandstones (Figure 2). Additionally, some nodular or tabular Cretaceous flints have a black colour (Figure 2). Since no adze was made from Dinantian lydites nor in black flint, the raw material is just described to have a complete overview on black sedimentary rocks rich in secondary silica (Hallsworth & Knox, 1999: 22) available in the country.

In Belgium, lydites are named “phtanites”. All of these sedimentary rocks rich in secondary silica are very fine-grained, opaque, grey to black due to finely disseminated organic compounds, with a (sub)conchoidal fracture, showing rare and undetermined microfossils. Phtanites are stratified in cm-thick layers and interbedded with C-rich and pyritic shales (called “ampélites” in Belgium). Topped by a Mesozoic-Cenozoic cover these Palaeozoic levels do not outcrop in their French and Dutch geological extensions.

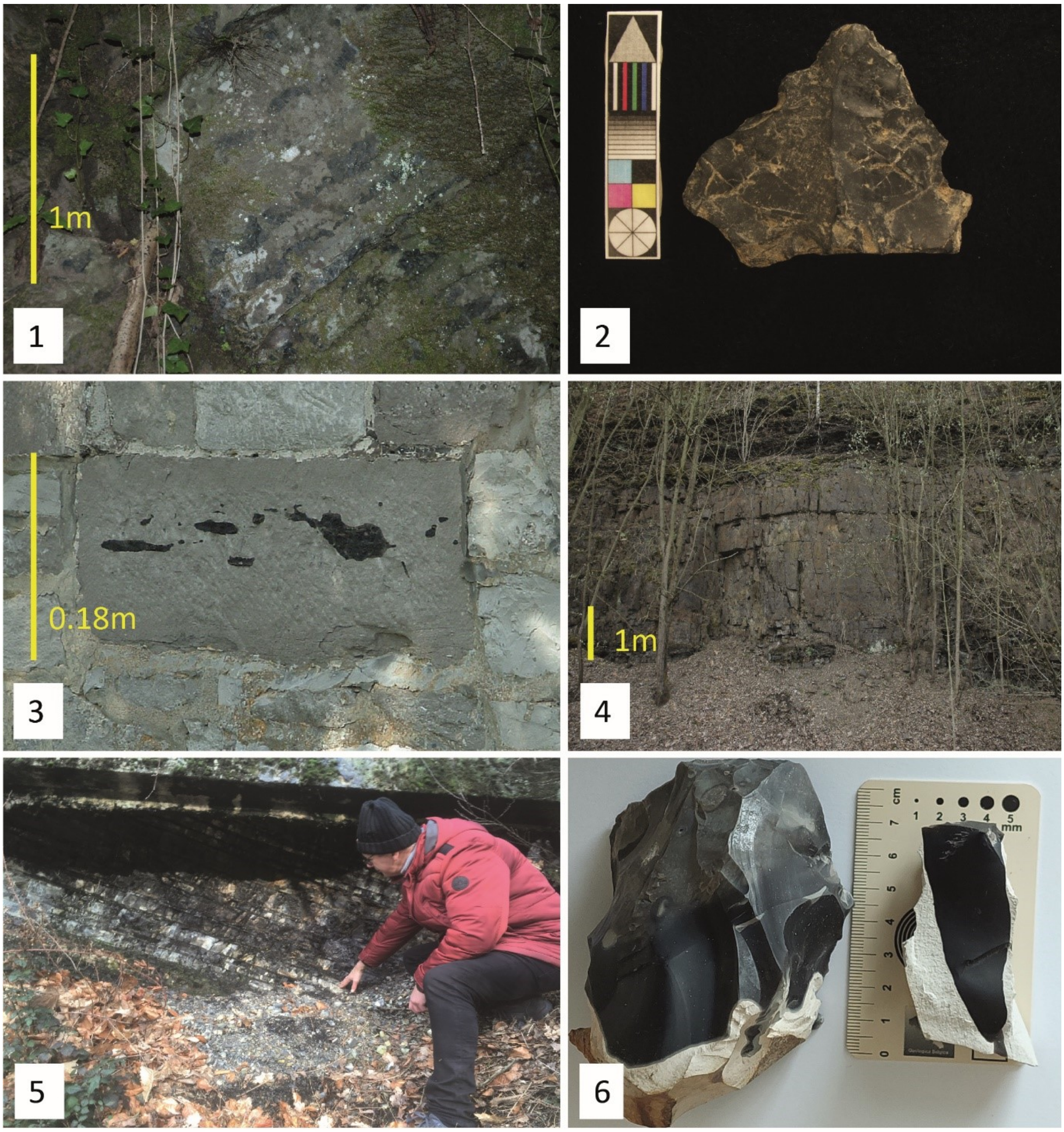

Figure 2. Illustration of raw black sedimentary rocks rich in secondary silica from Belgium. 1. Outcrop of light blue Tournaisian limestones (Yvoir Formation) including dark blue to black (after polishing) nodular cherts. Disused railway along the wooded Hoyoux valley (Marchin, Province of Liège). 2. Broken piece from a Dinantian deep blue nodular chert showing a conchoidal fracturation and an irregular shape. Archaeological artefact. RBINS collection (43_P9248227). 3. Limestone block with black Dinantian nodular chert. These nodules are released when limestone dissolved. These nodules are called "*clous"* in French due to the challenge of cutting this rock, here used as a building stone. Nineteenth-century mansion, Seilles (Andenne, Province of Namur). Picture by EG. 4. Outcrop of Lower Namurian black phtanites (banded sedimentary rocks rich in secondary silica and also called *phtanites* in French), top of the disused limestone quarry of Maizeret (Andenne, Province of Namur). Picture by EG. 5. Outcrop showing layers of Lower Namurian black phtanites, along the Nimy-Blaton Canal, Mont des Groseillers, Blaton (Bernissart, Province of Hainaut). A geologist is shown to give the scale. Picture EG. 6. Broken surfaces in black flints sampled from the Formation of Obourg (Campanien, Upper Cretaceous, Mons Basin unit). It typically exhibits a core with a black glassy appearance, conchoidal fracture and a white crust due to the transformation of opal into chalcedony. Obourg quarry (Mons, Province of Hainaut). Lithostratigraphic collection of the RBINS. Picture by EG.

1.2.1. Black lydites of Céroux-Mousty

The Franquenies Member (lower part of the Mousty Formation, Upper Cambrian, Caledonian Brabant Massif) is characterized by decimetric siliceous beds or lenses of lydite embedded in typical black shales (NCSB 2009; Verniers *et al.* 2001). These lydites are known as “phtanites d’Ottignies-Mousty” or “phtanites de Céroux-Mousty”. Small outcrops of the Franquenies Member only occur in the Dyle valley, south of Ottignies (Mousty and Franquenies, Bois des Etoiles, Ri d’Angon, (Figure 3). The Brabant Massif has been folded and faulted during the Caledonian orogeny (Verniers *et al.* 2001) but was not or little affected by Variscan deformation.

Geological samples were newly collected from the disused quarry of Franquenies (Bonjean *et al.* 2015) and from the Ry Angon stream (Bois des Etoiles, Ottignies) Supplementary raw material was selected from the RBINS (Royal Belgian Institute of Natural Sciences, Brussels) prehistoric rock collection.

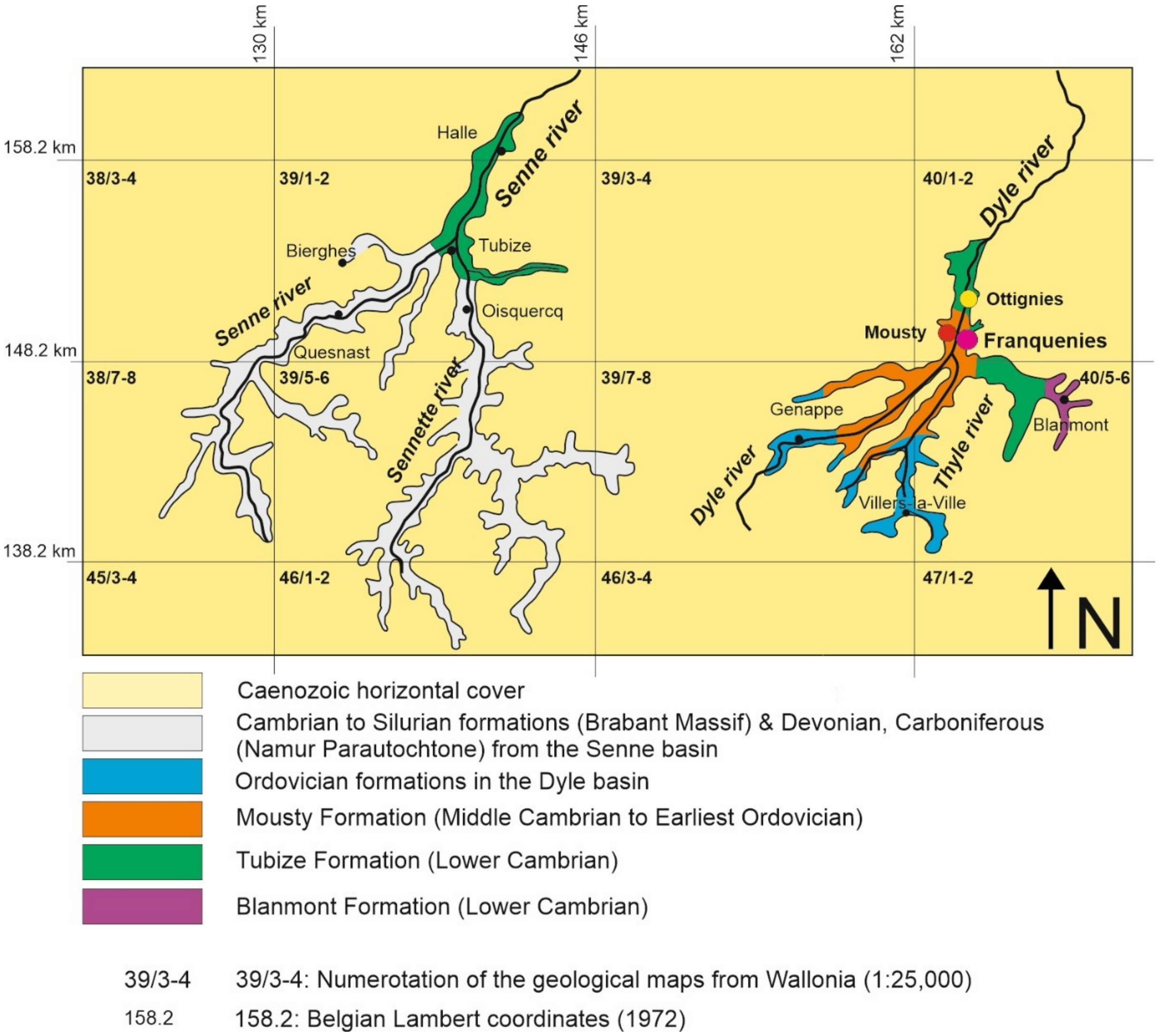

Figure 3. Simplified geological map locating the Cambrian lydites of Céroux-Mousty. Modified after Bonjean *et al*. (2015).

1.2.2. Lower Namurian banded lydites

The Upper Carboniferous system (Namurian and Westphalian) in Belgium forms part of the Variscan Foredeep in north-western Europe. The Belgium Coal Measures Group includes all Carboniferous coal-bearing siliciclastic sediments. It is characterised by a thick siliciclastic continental sedimentation succeeding the Dinantian marine carbonate sedimentation. More geological and stratigraphical data is given by Delmer *et al.* (2001). The basal layers of the Carboniferous system contain layers of black lydites occurring in three formations. Cartographically, Lower Namurian series are in a long and narrow geographic area (figures 1B, 3) extending from the France-Belgium border to the Belgium-Netherlands border and corresponding to the south flank of the Brabant Parautochthone (formerly known as the Namur Syncline). Outcrops of Lower Namurian phtanite beds are very rare, restricted to the deep incised valleys of the Sambre and the Meuse rivers, and their tributaries. Nevertheless, anthropic outcrops occur to the top of limestone quarries. The LPC settlements of the Dendre springs are located 10-15 kilometres northward of the outcrops of the Gottignies Formation while the Hesbaye LPC sites are located all around Horion-Hozémont.

The basal layers of the Upper Carboniferous system contain layers of black lydites occurring in three formations. 1. The Gottignies Formation (Visean - Serpukhovian transition). It contains finely bedded completely silicified limestone beds and siliceous radiolarian shales, transitional between Dinantian limestones and Namurian siliciclastics (“*Phtanites tachetés de Gottignies”*). This unit occurs in the western part of the north of the Brabant Parautochthonous (“Auge hennuyère”, Blaton - Saint Ghislain area). These phtanites are black-coloured with thin white quartz veins and sometimes rare Fe-phosphates and a radioactive anomaly; these last features only occurring in the small area near Blaton (Hainaut Province). 2. The Souvré Formation (Visean - Serpukhovian transition) in the Visé area, close to the Belgium-Netherlands border, is made of thin-bedded, grey to black, silicified laminar shales and limestones. The formation is present in the Visé-Maastricht sedimentation area, but very poorly exposed. 3. The Chokier Formation (Serpukhovian; Arnsbergian and Chokierian). It is composed of calcareous shales, pyrite-rich aluniferous shales and phtanites at the base of the unit. It occurs in all Carboniferous basins (Campine basin, Namur, Dinant and Vesdre synclinoria) in Belgium. Delcambre (on-line map) attributes the basal Namurian deposits around Horion-Hozémont, eastern part of the north of the Brabant Parautochthonous, to the Chokier Formation but without precise stratigraphic attribution. He found lydite scattered pieces in the gardens of the Lexhy castle (Horion-Hozémont) previously assigned by the archeologists to a possible neolithic workshop. Unfortunately, new excavations are not possible in this private property.

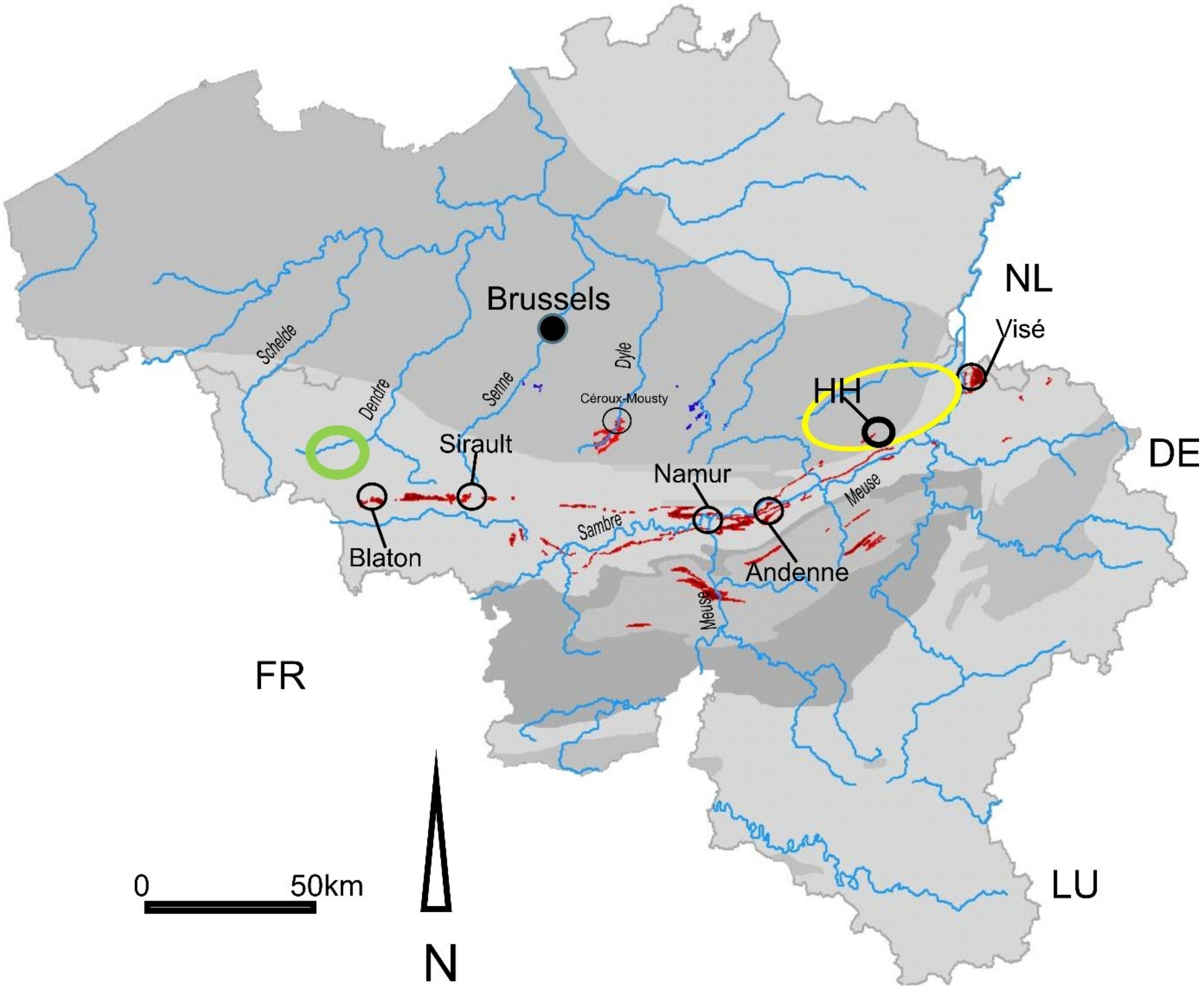

Figure 4. Simplified geological Palaeozoic basement map of Belgium locating the Namurian outcrops (deep red). The yellow and green circles indicate the locations of the Hesbaye and Dendre River LPC settlements respectively. HH: Horion-Hozémont. The main river system is in blue. Names of some rivers (in small black italics) as well as some localities cited in the paper have been indicated.

1.2.3. Micaceous sandstones of Horion-Hozémont (MSHH)

The current village of Horion-Hozémont (Figures 1B, 4) is rural entity composed of stone houses which are made from Visean limestones, Namurian sandstones and MSHH blocs locally extracted in small-sized disused open-pit quarries. Only the ancient geological literature (Anten & Bellière 1919) and archives preserved at the Geological Survey of Belgium (Stainier 1899) describe the rocks occurring in the northern flank of the Brabant Parautochthon. Rocks there are both rarely and very badly exposed because they are usually buried under a Cretaceous and Cenozoic horizontal cover (especially a thick mantle of Quaternary loess) and the weak erosion by the rivers. In Horion-Hozémont, less than three meters-thick layers of microconglomerates and sandstones lies in unconformity on Upper Visean marine limestones. One outcrop in the centre of the village shows layers gently dipping to the south.

1.2.4. Black flints

Nodules of light grey, greyish brown and black Upper Cretaceous flint pebbles are found in a wide band along the northern ridge of the Sambre-Meuse fluvial basin. Black flints are exposed in primary exposures across the Mons Basin (Western Belgium, Spiennes, Nouvelles and Obourg Formations, Campanian in age, *e.g.*, Collin 2016; 2019) and the Liège-Limbourg area (Oriental Belgium, Lixhe Member, Gulpen Formation, Campanian in age). A full archaeometric study of regional black flints has been performed by Moreau *et al.* (2016), mainly for the study of Upper Palaeolithic lithic assemblages. Until now, no adzes were made in this kind of raw material in Belgian Early Neolithic set of tools.

1.2.5. "Basalt" lavas

In Belgium magmatic rocks outcrops less than 0.1% of the country and they are concealed under the Upper Palaeozoic, Mesozoic and Cenozoic covers. The magmatic activity is restricted to the Ordovician-Silurian from the Condroz ridge and the Brabant, Stavelot-Venn and Rocroi inliers. The primary mineralogical composition and the texture have been thoroughly obliterated by greenschist facies recrystallization. It corresponds to a north-western calc-alkaline province in the Brabant Massif and a south-eastern back-ark tholeiitic province in the Brabant and Ardenne massifs (André *et al.* 1991). The Voroux-Goreux volcanic complex (including the Hozémont sill) comprises basaltic pillow lavas associated with gabbroic hypabyssal intrusions, acidic pyroclastic rocks and rhyolites (Herbosch *et al.* 2020).

Early Neolithic "basalt" (in the absence of the chemical signatures, the name "basalt" is put into brackets) adzes show olivine and pyroxene phenocrysts in a very fine-grained, black-coloured matrix, these features are incompatible with the magmatic-volcanic rocks occurring in the Belgian geological record. Furthermore, the surface of the adzes turned light grey after weathering with a grainy surface putting in evidence the phenocrysts. Only a fresh break shows the internal black colouration of the matrix. Toussaint & Toussaint (1982) observed theses rocks in thin section, but no geochemical study has been performed to determine the source of this material attributed to the Eifel area in Germany. Although located close to the outcrops of the "*Grès micacés de Horion-Hozémont*", the magmatic rock from the sill of Horion-Hozémont (see the location of Horion-Hozémont on the Figure 1) has never been found on Hesbayan Neolithic sites and appears not to have been used as a raw material to produce lithic tools.

2. Material and methods

The abundant archaeological material is provided by the collections of scientific or museal institutions as the RBINS, the Préhistomuseum (Flémalle), the *Archéosite et Musée d'Aubechies* (Beloeil), the *Musée des Celtes* (Libramont-Chevigny), the Leiden University and from private collections (Supporting Information 1, Figure 1). Artefacts range from old (1960s) to more recent excavations linked to infrastructure works (high-speed train line Brussels-Liège, Bierset airport extension and in Ath Les Haleurs), scheduled excavations and occasional surface discoveries. The majority of adzes originate from waste pits associated with settlements. The workshop of Noirfontaine provides thousands of roughouts in MSHH, available for analytical studies and the reconstruction of the "*chaîne opératoire*". More than forty geological samples were analysed, coming from rock collections and recent field work (Nimy-Blaton canal section, the disused quarry of Sirault, chalk quarries in the Mons and Visé areas, old Upper Visean limestone quarries of Namêche (Andenne) and Visé, outcrops at Horion-Hozémont) to cover the main outcropping area in Belgium (Supporting Information 1, Figure 1).

Archaeological and geological samples were studied using four complementary methods of characterization available in the laboratories of the Geological Survey of Belgium. For optical petrography (OP), samples were thin sectioned using standard techniques. Petrographic thin sections (45 × 35 mm) were made from 15 adzes (new thin sections and from public and C. Constantin's collection) and from 20 geological references. The sections were examined using a Nikon Optiphot-Pol polarizing light microscope. Sawed fragments were embedded in epoxy resin and silicon carbide-polished (1200 mesh). Fabric observations on uncoated polished sections and uncovered thin sections were made by Scanning Electron Microscopy (SEM FEI Quanta 200, 23 kV, spot size 6-7, backscatter electron (BSE) detector) while chemical analyses were performed by Energy Dispersive X-ray spectroscopy (EDS EDAX: Apollo 10 SDD silicon drift detector). X-ray diffraction (XRD) analyses were performed on bulk powder using a PANanalytical Empyrean diffractometer (Cu anode, Ni filter, 40 mA and 45 KV, 6 to 70°2Θ). Samples were coarsely reduced in size using a hammer and steel plate then further reduced and homogenized using a Fritsch Laboratory Planetary mill equipped with agate grinding balls. The powder was passed through a 75 µm sieve, then loaded and disoriented into stainless steel sample holders using back loading. Semi-quantitative interpretation was performed in Visual Crystal 6 software. The percentages of the minerals obtained through the XRD analyses should be considered as estimates as there was no use of internal standards. They are based on the relative proportions of the area under the curve combined with the RIR (Reference Intensity Ratio) value of the minerals. Raman spectra on both unweathered (fresh break) archaeological and fresh geological samples were acquired with the green and the red lasers on the Senterra Raman microspectrometer. This technology was applied here with a focus on the Raman response of the carbonaceous material (CM) and especially the progressive graphitization of CM with the peak temperature recorded by the material during the metamorphism history. The equipment and the acquisition parameters are summarized in Table 1. Usually, two spectra were acquired per sample, but in some cases more tests were required, especially in case of high fluorescence until a clear carbonaceous material signature could be interpreted without a doubt. Hence a total of > 250 spectra were acquired on 60 analysed archaeological and geological samples.

Table 1. Raman microspectrometer settings.

Equipment	SENTERRA manufactured by Brucker
Detector	1024x512 pixels cooled CCD, Raman signal acquired on a 60 pixels vertical binning
Grating	400 groves/mm reflective grating (dispersive power of 2.48 nm/mrad)
Laser wavelength	532 nm (green); 789 nm (red)
Green laser power	2 mW (at the exit of laser box) ~1.2 mW at the sample surface
Red laser power	10 mW
Acquisition time	3 X 10 s
Spectrometer slit	50x1000 mm
Spectral window	114 -> 4450 cm-1
Objective	50x (long-distance)
Environmental conditions	Room temperature and atmospheric pressure

3. Results

3.1. Petrographical results

3.1.1. Lydites of Céroux-Mousty

Rocks and adzes made in Cambrian lydite of Céroux-Mousty show crosscutting thin vitreous dark black Si-rich veins and white spots of microcrystalline quartz grains plus rare small-sized muscovite flakes. In thin section, the very-fine grained matrix is almost completely obliterated by a finely disseminated black carbonaceous pigment. Only some subrounded spots (100-200 µm) made of microquartz grains and rutile needle crystals are distinguished through the uniform black background (Bonjean *et al.* 2015). The spots have the size of radiolarians, but no ornamentation could be observed in thin section nor under the SEM and the circular shape is also absent. Radiolarian presence is yet to be confirmed by specialists (Herbosch & Blockmans 2012; Herbosch *et al.* 2002). A banded texture is observable under the SEM, showing an alternation of pure vitreous silica bands without any pores and cryptocrystalline (<5 µm) silica bands with numerous micropores and rutile crystals (Figure 5). On the polished adzes, these bands correspond respectively to a glossy intense black finish and a matt black finish, visible in raking light. While diagenetic micrometric (2-8 µm) acicular crystals of rutile sometimes grouped in bundles are observed in the more porous layers, micrometric rounded detrital zircons are very rare while pyrite crystals are absent (Figure 5). The mineralogical assemblage is restricted to quartz, rutile and micas (Table 2). The main petrographic characteristics of the lydites of Céroux-Mousty are listed in the Table 3. This table put in evidence the differences with other (raw and archaeological) material studied.

Table 2. Mineralogical composition of black lydites acquired by X-ray diffraction. MSHH: Namurian micaceous sandstones of Horion-Hozémont; CLCM: Cambrian lydites of Céroux-Mousty; NPV: Namurian phtanites of Visé, NPB: Namurian phtanites of Blaton and Sirault; < LD: below the detection limit.

Id.	**MSHH**	**CLCM**	**NPV**	**NPB**
Minerals (%)	n = 9	n = 4	n = 2	n = 2
Quartz	80-94	93-97	100	100
Muscovite/illite	4-16	2-5	Traces or < LD	< LD
Feldspars	< LD-7	-	-	-
Fe-Chlorite	1-2	-	-	-
Pyrite	1-2	-	-	< LD
Rutile	< LD	1-1.5	< LD	Traces
Calcite	-	-	-	-
Fe-Phosphate, Crandallite	-	-	-	on joints

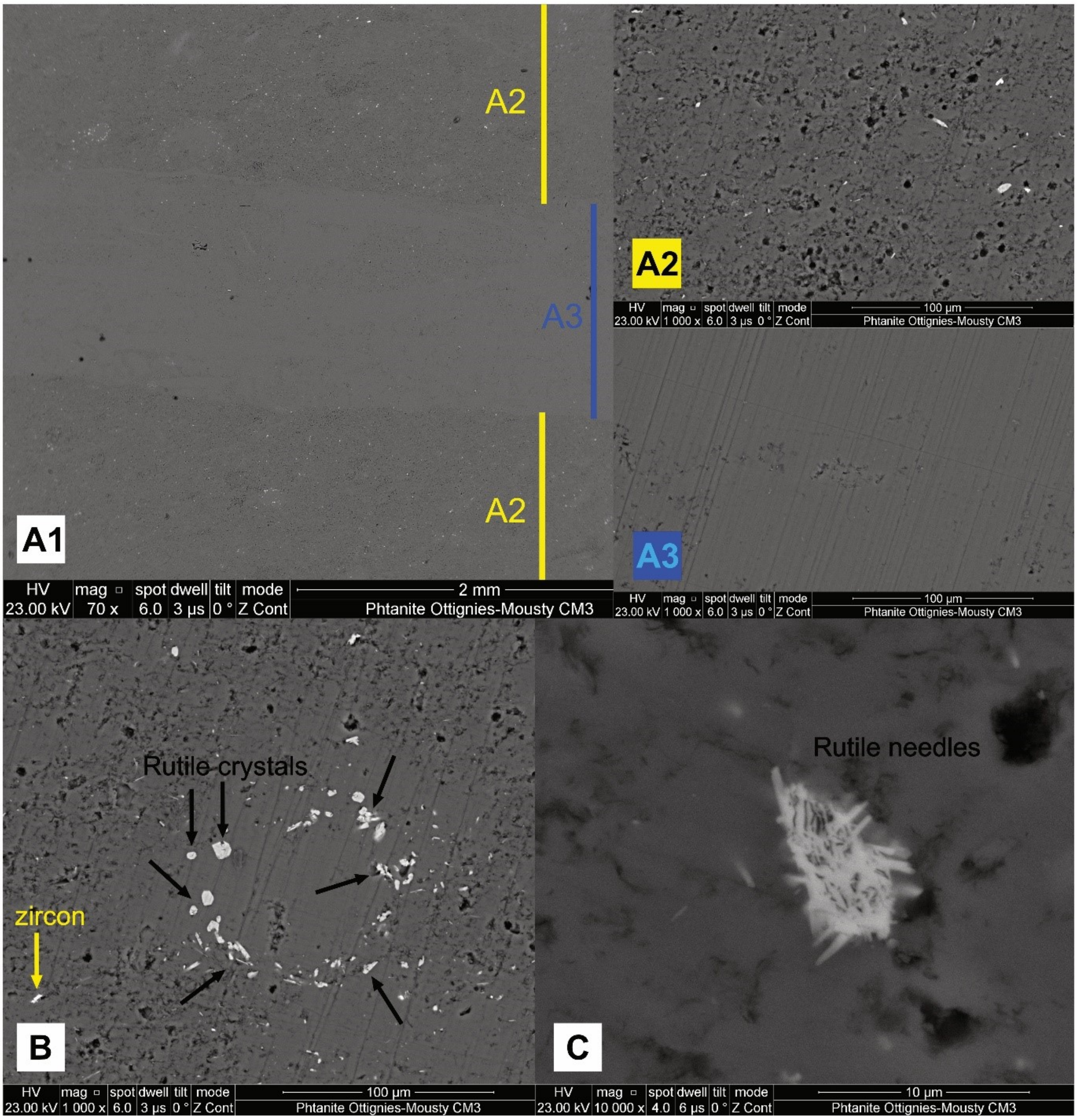

Figure 5. SEM (BSE mode) pictures on a geological sample from the Bois des Rêves (Ottignies). Oblique lines on the right-hand side of the picture are polishing stripes. A1. Polished surface showing the alternation of bands of variable microporosity. A2: Cryptocrystalline silica band with rutile and microporosity giving a matt black finished polished surface; A3: Pure vitreous silica band without any porosity producing a glossy intense black polished surface. B. Micrometric crystals of pure neoformed rutile, rare detrital zircon, C-graphite finely disseminated and no pyrite crystals. C. Bundle with acicular crystals of rutile. (See the supplementary files for a higher resolution version of this figure.)

3.1.2. The micaceous sandstones of Horion-Hozémont

Adzes in MSHH and geological samples collected in Horion-Hozémont are macroscopically and microscopically similar. They range between dark grey to black pyriteous siltstones (2-63 µm) to medium grey pyriteous sandstones (>63 µm). Rocks are stratified (parallel to cross-bedded or even bioturbated) with alternating thin layers of variable granulometry and colour intensity. No flakes of micas or chlorite can be observed by the naked eye but the faces (< 1 mm) of cubic crystals of pyrite reflecting the light can be erroneously interpreted as mica flakes. The qualifier “micaceous” is therefore not adapted to describe the material although thin and short flakes of phyllosilicates (muscovite and Fe-chlorite, Figure 6a) are observed in thin sections. The designation of "sandstones" is also not suitable since the majority of archaeological material are siltstones. All the samples contain pyrite in different shapes and habits and in a variable amount based on their lithology, especially frequent in the coarsest laminae (Figures 6a, b, c, d). The diagenetic pyrite occurs as framboids and sub-millimetric isolated cubes and penetration twins with summit truncations. Iron hydroxides covering the fracture surfaces of geological material and archaeological roughouts are due to pyrite weathering. No rutile needles are observed but detrital ilmenites and their weathering products (leucoxene grains) have been determined. The matrix consists of microcrystalline quartz as well as detrital grains of quartz and phyllosilicates (micas muscovite-phengite and chlorite). Tiny lithic fragments characteristic of the Namurian and Westphalian sandstones are observed in all materials but grains of lydite rich in radiolarians, feldspars and Fe-carbonates are lacking. Rare detrital heavy minerals as rounded zircon, tourmaline, rutile and ilmenite grains occur. Transversal fractures and white quartz veins found both on raw material and manufacturing wastes make them unsuitable for the production of adzes.

Petrographically, the most prominent features are the secondary silica cement (chalcedony) and the richness in sponge spicules as described first by Anten & Bellière (1919). Siliceous sponge spicules can be observed in light-coloured coarse layers (figures 7b, d). Preserved are monaxone spicules (oxeas) of various length (until 1600 µm) and diameter (until 160 µm). Transversal sections sometimes show a wall with a thickness of < 20 µm. Most of the spicules are completely filled by radiate chalcedony fibres. Tubes are straight and get thinner towards the end of the spicule. The flow direction is underlined by a strong alignment of the spicules. Due to their high content in spicules, some layers can be called spiculites. Gemmoscleres have not been found. The dissolution of sponge spicules is the leading cause of silicification inducing a subconchoidal fracture. Although siliceous sponges are occasionally found in freshwater, they are usually found in the marine ecosystem. Upper Carboniferous freshwater siliceous sponges are reported in the French Massif Central (Stefanian B) and the Saar-Nahe Basin (Stefanian C and Autunian) in south-west Germany. All Permo-Carboniferous finds originate from freshwater lake deposits (Schindler et al. 2008). A taxonomic classification on family level is not possible especially because of the silicification process. Stratification and lenses of fine-grained sandstones rich in spicules of sponges are better observable after HF-attack (Figure 7). In some layers, the matrix is cemented by radiate chalcedony fibres from the detrital quartz grains and pyrite crystals (syntaxial overgrowth on grain substrates). The silicification process preserves the sedimentological features but the stratification plane is no longer a surface of mechanical weakness. The polishing gives to the adzes their dark grey colour (due to the finely divided black organic matter) and a mirror finish allowed by the fine-grained silicified matrix. Some ornamental limestones show the same result after polishing. For exemple "*Petit Granit*" is a Belgian Carboniferous grey-bluish crinoidal limestone containing a very small amount of organic matter and pyrite that becomes shiny black when polished. Polishing is brightening its appearance and enhance its black colour. Other inclusions are lithic fragments, organic matter, and detrital grains of ilmenite. The main petrographic characteristics of the pyritic sponge-rich silicified siltstones (to fine-grained sandstones) are listed in the Table 3 allowing the comparison with other material studied.

Table 3. Comparative table of the various black sedimentary fine-grained rocks used to produce adzes during the Early Neolithic.

Id.	**MSHH**	**CLCM**	**NPV**
Geological location (this study)	Horion-Hozémont	Visé, Namêche, Blaton, Sirault	
Formation	Chokier	Gottignies	Céroux-Mousty
Belgian designation	Phtanite or "*Grès micacé de Horion-Hozémont*"	Phtanite	Phtanite
Acronyms (his paper)	MSHH	NPB	CLCM
Designation (this paper)	Pyritic sponge-rich silicified siltstones to fine-grained sandstones	Banded lydite	Nodular lydite
Tectonostratigraphic unit	Namur Syncline north border	Namur Syncline south border	Brabant Massif
Colour	Middle grey to black	Dark grey to black	Dark grey to black
Thermal evolution	High diagenesis	High diagenesis	Metamorphic (greenschist facies)
C (organic matter)	Finely disseminated	Finely disseminated	Finely disseminated graphite
Granulometry	Siltstones to fine-grained sandstones	Amorphous to microcrystalline	Amorphous to microcrystalline
Microfossils	Sponge spicules	Not seen	Not seen (radiolarian?)
Macrofossils	No	No	No
Pyrite	Framboids to diagenetic cubes	No	No
Titanium	Detrital ilmenite/leucoxenes	Detrital ilmenite/leucoxene	Needles of rutile
Phyllosilicates	Muscovite, (Chlorite) flakes	?	(muscovite)
Barite	Yes	No	No
Fracture	sub-conchoidal	Sub- to conchoidal	Conchoidal
Shape	Tabular, layered	Tabular	Nodular to tabular
Stratification	Yes, banded	Banded	(yes)
Bioturbation	(yes)	No	No
Cross-stratification	(yes)	No	No
Black veins	No	No	Yes
Lithological uniformity	No	Yes	Yes
Quartz veins or geodes	No	No	Yes
Fe-phosphates	No	(Yes)	No

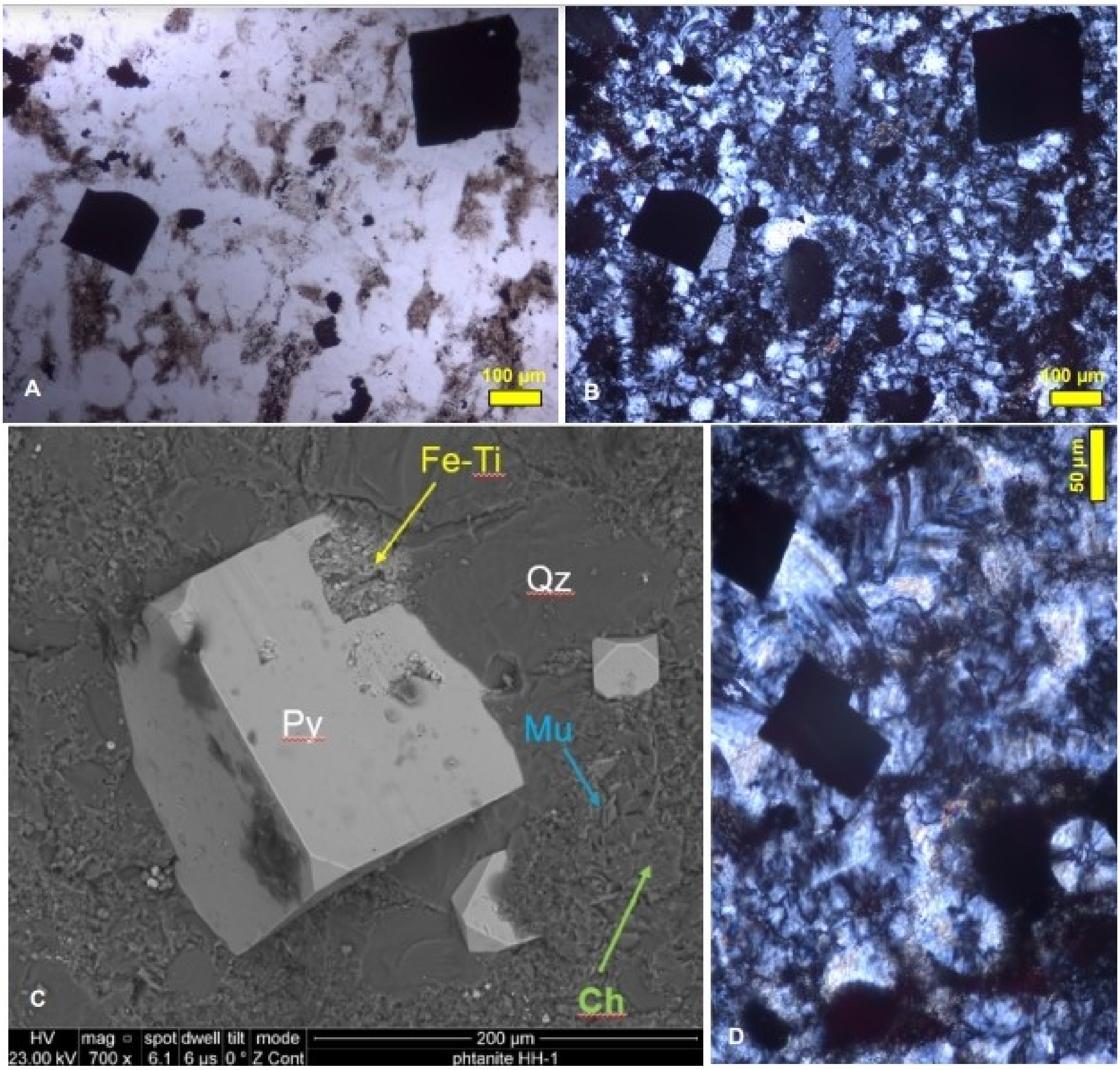

Figure 6. OP and SEM pictures. Geological samples, Horion-Hozémont outcrop. A & B. Petrographic facies of the silicified siltstone rich in sponge spicules (circular cross-sections), automorphic black crystals of pyrite and fine-grained matrix (grey), Plane Polarized Light (PPL & XPL). C. SEM micrograph showing a cubic automorphic crystal of pyrite (Py) crystallised from a detrital leucoxene (Fe-Ti) grain (BSE mode). The clay matrix contains rare muscovite (Mu) and chlorite flakes (Ch) and quartz grains (coarse silt (31-63 µm) to fine-grained quartz sand (63-250 µm). Silty-sandy light grey layer from a geological sample.

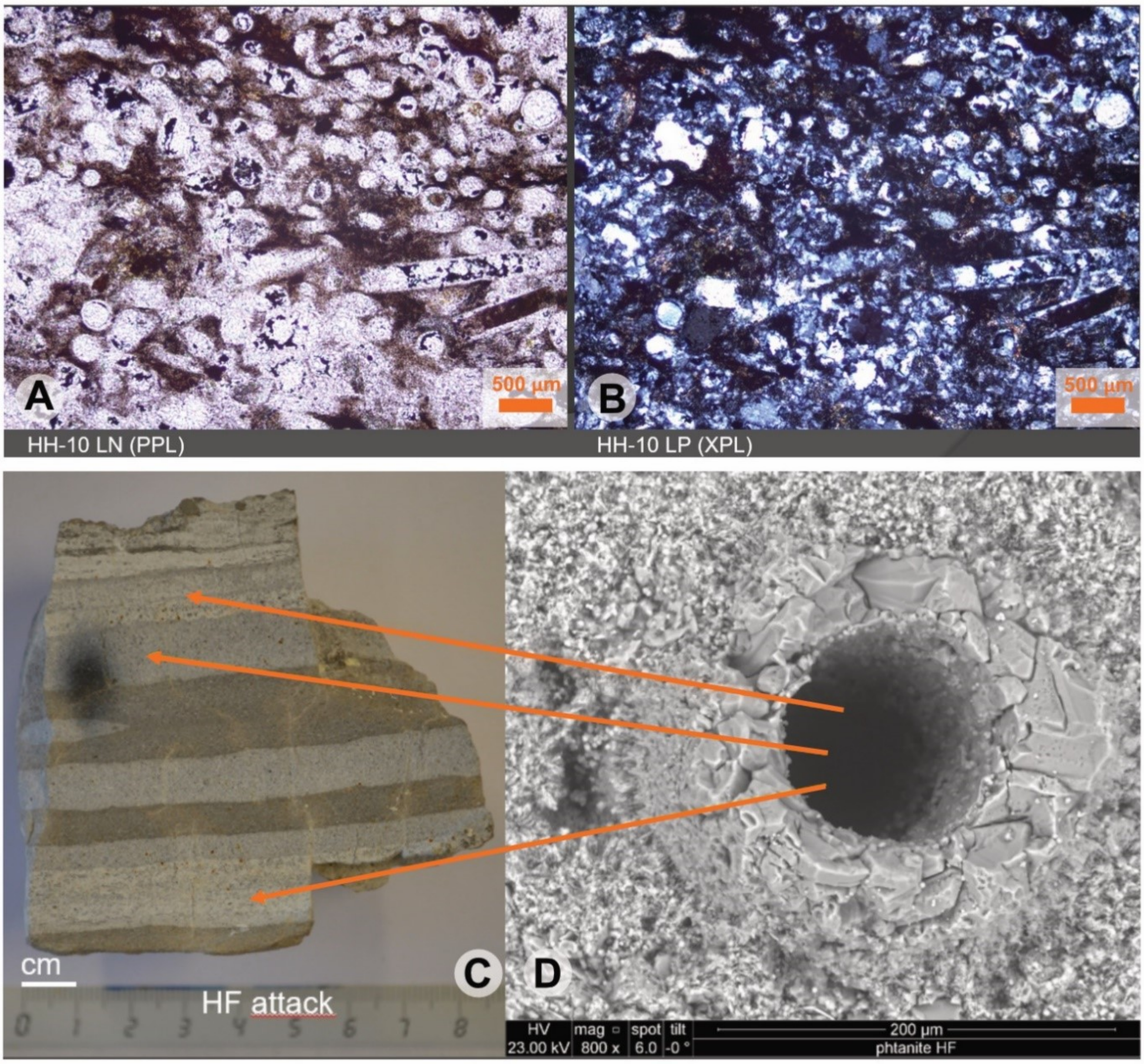

Figure 7. Pictures related to geological samples from Horion-Hozémont, RBINS. A & B. Petrographic images of the layers rich in siliceous sponge spicules (monoaxones): rounded (note the wall thickness and the infilling of the tubes) transversal and rectangular longitudinal cross-section (PPL & XPL). C. Cut transversal section after an HF-attack put in evidence middle grey-coloured siltstones poor in bioclasts and light-grey coloured layers and lenses very rich in spicules. D. some circular holes observed under the SEM represents the unfilled sections through sponge spicules. Note the fine-grained matrix and the wall made of blocky quartz crystals.

3.1.3. Lower Namurian banded lydites

Lower Namurian banded lydites (phtanites) exploited south of the Dendre springs have been shaped and used only in the Dendre spring area but the workshop's location is unknown? Roughouts have been found in Ath Les Haleurs. Due to their fine-grained nature and the black pigment camouflaging any sedimentological structure and petrofabric, the Lower Namurian banded lydites have never been subject to an exhaustive study in Belgium. These rocks are finely stratified and divided in cm-thick layers. They have a conchoidal fracture and these rocks are difficult to knap. In the outcrops, the phtanites are often cut by a close network of transversal joints. These fracture planes are often filled by Fe-Mn coatings. In the Nimy-Blaton canal section, joints are mineralized by very rare Fe-phosphates together with other minerals (Fiège 1967; Hatert *et al.* 2002; Scheere & Van Tassel 1968; Van Tassel 1966). Petrographically (OP, SEM), phtanites have a perfect thin-spaced planar stratification underlined by Carbonaceous elongated particles (50 to 300 µm). Rare grains of quartz

(< 60 µm), short (< 20 µm) and thin (< 5 µm) mica flakes and (fresh or weathered, framboids and crystals) pyrite grains (< 10 µm) are dispersed in the cryptocrystalline siliceous matrix (> 96% SiO_2, < 3% Al_2O_3; < 0.5% for other chemical elements detected by EDS as Fe, Mg, K and Ca). Ti-compounds and (micro)fossils were not observed. The mineral proportions slightly differ from one sample to another. In the phtanite of Sirault, diamond-shaped cavities (until 60 µm) are interpretated as dissolution cavities of dolomite crystals.

3.1.4. Dinantian nodular chert

Other silica-rich materials are the Visean and Tournaisian lydites (well-known as cherts in the Belgian and English literature) embedded in the limestone. This dark material (bleu, grey, black) was very scarcely used by the Middle Palaeolithic human groups of the Spy cave (Di Modica 2010; Goffin-Cabodi 1985: 170). Delvigne *et al.* described different types of sedimentary rocks rich in secondary silica from the Upper Palaeolithic societies (Gravettian) of the "*Station de l'Hermitage"* in Huccorgne (Delvigne *et al.* 2021). But use of Dinantian nodular lydites is not attested for the making of Neolithic adzes.

3.1.5. Black flint

Flints occur in Upper Cretaceous chalk formations outcropping in the Mons and Liège basins. Flint mining dates back to the Neolithic (*e.g.*, the Spiennes UNESCO World Heritage site). Petrographic observations in Cretaceous black flints (Collin 2019) are scarce for the reasons mentioned above, but ghosts of fossils (foraminiferous, bioclasts, belemnites, sponge spicules...) are recognizable within chalcedony-quartz fine-siltstone. There are local variations in the granulometry of the silica grains and sometimes small-size geodes. Carbonate bioclasts are completely to partially replaced by silica minerals. Organic matter is diffused in the groundmass.

3.2. X-ray diffractometric results

The XRD results generally support the petrographical observations. Aside from quartz obviously being the major phase in every sample there are clear differences in the minor and accessory phases. In the MSHH there is the presence of both muscovite-illite and chlorite as well as a small amount of pyrite and the occasional feldspar. In the Cambrian lydites of Céroux-Mousty (CLCM) the presence of rutile is observable in addition to a very small amount of K-mica. The Namurian phtanites of Blaton and Sirault (NPB) only show quartz with other phases being under the detection limit. Lastly the Namurian phtanites of Visé (NPV) consist solely of quartz with traces of mica.

3.3. Raman microspectrometry results

Black coloured adzes and raw material made in silica-rich rocks contain finely dispersed organic matter. Past research of palynomorphs by HF dissolution showed that the samples are sterile, without any palynomorphs. The residues of dissolution only show small glitters or (isolated or agglomerated) xenomorphic grains of a carbonaceous material, and insoluble heavy minerals without any possibility of attribution to a stratigraphic level (Bonjean *et al.* 2015). But carbonaceous Material (CM) results from the chemical and physical transformation (graphitization) of natural organic content, which is modified from a disordered structure into well-ordered pure carbon graphite (Wopenka & Pasteris 1993). Temperature is commonly referred as a key parameter controlling the graphitization especially in metamorphic rocks, but pressure, organic precursors, stress and time can also control the process, especially in low-grade rocks (Beyssac *et al.* 2003; Lahfid *et al.* 2010).

 DOI: https://doi.org/10.2218/jls.6772

The regular evolution of the Raman spectrum of graphitic carbon with increasing P and T° allow to consider the CM as a geothermometer and its use for tracing the source of archaeological artefacts. After comparisons of different techniques (vitrinite reflectance, IR spectroscopy, XRD, HRTEM) of CM characterization, it is recognized that Raman microspectrometry is the most straightforward technique to quantify the degree of organization of CM and differentiate between Cambrian and Lower Namurian Belgian rocks due to the Caledonian orogeny in between (end of Silurian). In addition, this method has been used to characterize the carbonaceous matter from black Cretaceous flints which were unaffected by an orogeny. The distinction of the different kinds of flints can be achieved by a microfacies characterisation with a high magnification binocular (Collin 2016, 2019). Geochemistry can help to source the flints in some favourable cases (Moreau *et al.* 2016).

Four types of Raman spectra can be distinguished: a) black cretaceous flints have a signal mainly composed of fluorescence; b) probably a profile of high-grade metamorphic rock, but the Raman response is strongly overwhelmed by the fluorescence; c) Lower Namurian phtanites and MSHH show profiles characteristic of diagenetic conditions and d) Cambrian lydites from Céroux-Mousty which have profiles linked with high-grade conditions (greenschist metamorphic facies) (Figure 8).

The sample C shows all the CM-signature characteristics of a low-grade rock, namely a single and intense peak centred at 1606 cm^{-1} associated with another important peak at 1353 cm^{-1}. These two peaks are referred as G and D1 bands, respectively (Bonjean *et al.* 2015; Buseck & Bessac 2014). On the low wavenumber side of peak D1, an important shoulder results from the presence of the D4 band. Spectral decomposition of similar spectra indicates the presence of another band D3 between D1 and G. This peak is probably present in the acquired spectra, but no deconvolutions were conducted yet. Finally, the Raman response of the CM-content of low-grade metamorphic rocks is also characterized by poorly resolved second-order bands in the wavenumber window between 2400 and 3300 cm^{-1}. By contrast, the G band of high-grade samples (d and b, Figure 8) is located at 1580 cm^{-1} and is associated with band D2 represented by a shoulder on the high wavenumber side. In such samples D4 and D3 bands disappear. The second-order bands are more well-defined especially the band near 2700 cm^{-1}. The bulk of the Raman spectra acquired during this study are associated with a fluorescence envelope with the green laser representing a very broad domed curve more or less centred near 2000 cm^{-1}. Raman responses of CM of b are associated with very minor peaks greatly hindering the interpretation. However, in some cases the characteristics of high-grade rocks similar to those of (d) can be observed. A bell-shape fluorescence signal centred c. 670 cm^{-1} is also another characteristic of (b). The type (a) shows only a fluorescence envelope centred at 2000 cm^{-1} and a very minor SiO_2 related peak at 460 cm^{-1}. Previous experiments have shown that such signatures are associated with flint samples.

The bulk of some samples characterized by a Raman signature of type (b) gives indications of high-grade signatures. For instance, one can detect the secondary band D2 appearing near 1620 cm^{-1}. In order to further investigate this assumption additional tests were conducted with the red laser (789 nm) clearly showing a high-grade signature (Figure 9). For the sake of completeness additional tests were also conducted with the red laser on the black flint and clearly the change of laser does not improve the response, which could therefore be a good criterion to discriminate such material (Figure 9).

The analyses on black adzes and geological material show that low-grade and high-grade rocks have clear CM Raman signatures allowing fast discrimination between two lithostratigraphic units: the high-grade rocks from the Brabant massif (Céroux-Mousty) and the diagenetic rocks from the Lower Carboniferous units. In additional, adze artefacts from the settlement of Ath exhibit a strong fluorescence with very low CM signal, while the tests were conducted on fresh conchoidal fractures. The reason for the signal alteration should be the object of an additional analysis. Finally, spectra acquired on black flint material are characterized by only fluorescence (response valid for both lasers).

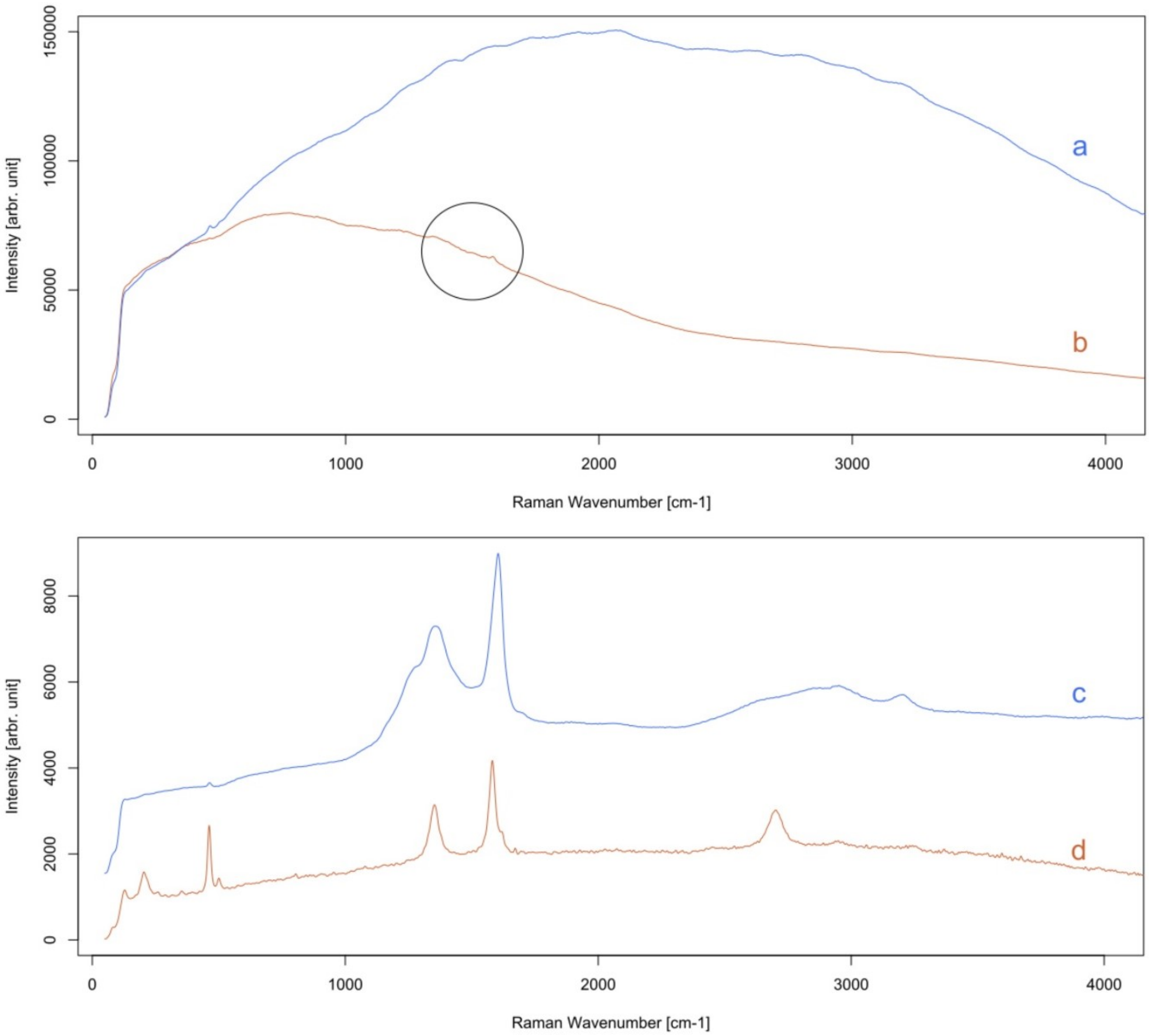

Figure 8. Selected spectra representing the four categories of Raman responses: a) black cretaceous flints; b) high-grade metamorphic rock; c) Lower Namurian phtanites and MSHH; d) Cambrian lydites.

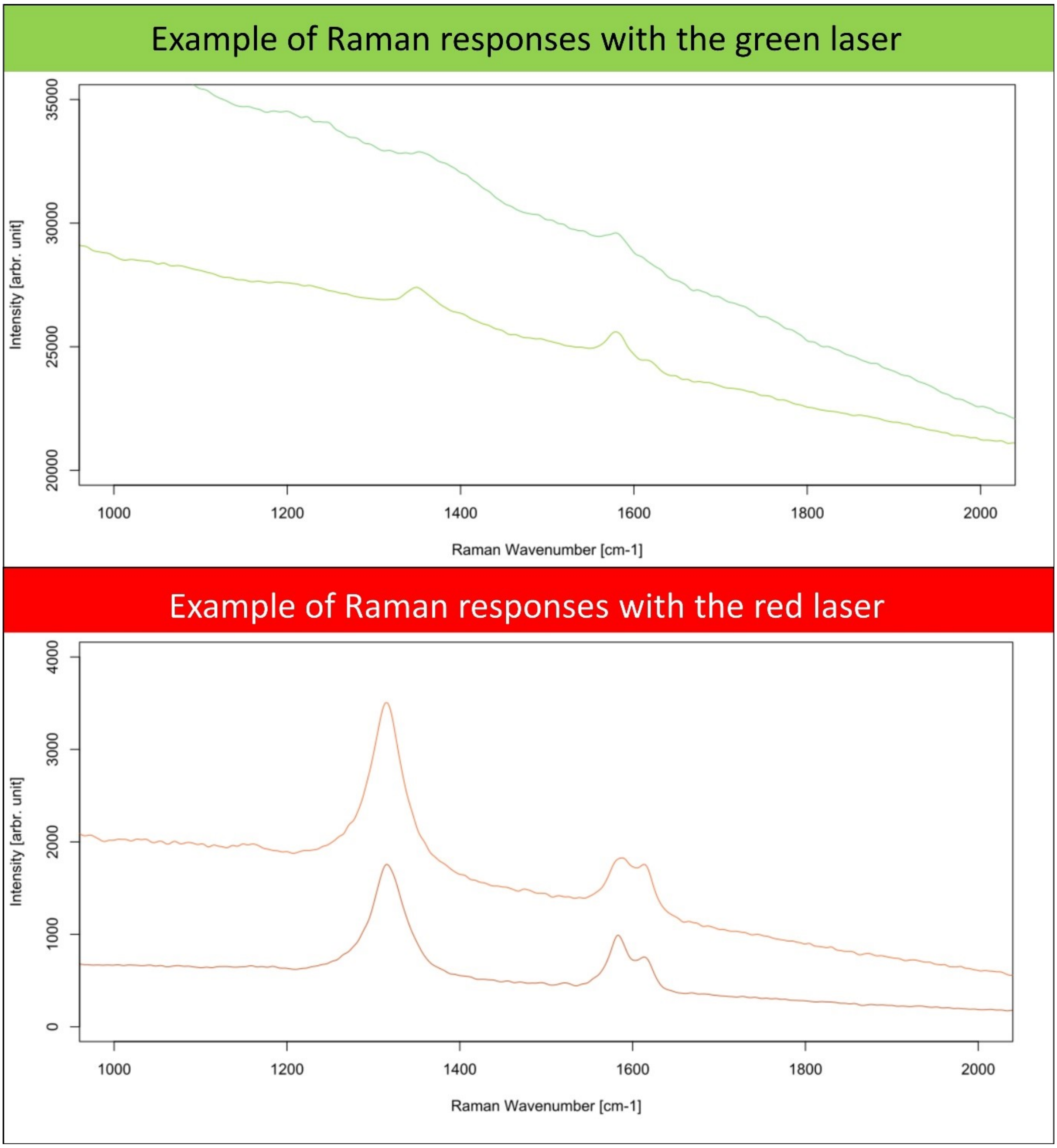

Figure 9. Selected spectra comparing the Raman responses between the green and the more energetic red laser on material showing a strong fluorescence masking peaks but finally corresponding to high-grade metamorphic rocks.

4. Discussion and conclusions

In this multidisciplinary study (associating prehistorians-archaeologists and mineralogists-geologists) the multitool and multiscale characterization of the black sedimentary rocks rich in secondary silica makes it possible to establish, for the first time a list of criteria (Table 3) and an analytical method to distinguish and differentiate them, a first step before discussion on the trades of finished products. This research completes the study published by Toussaint & Toussaint (1982). Non-destructive, reproductible, unexpensive, the Raman microspectrometry is the most effective method to distinguish between Namurian and Cambrian lydites, when the macro- and mesoscopic criteria leave an interpretative doubt, especially on whole and polished adzes. *In situ* measurements can be conducted in thin sections without the physical and chemical removal and probably perturbation of CM structure. Other advantages of the Raman approach are its speed (spectra are now acquired usually in few minutes) and the micrometre scale of the investigation allowing the sample heterogeneity assessment. The use of the red laser makes it possible to free oneself from the fluorescence that sometimes appears on the Raman spectra. The origin of the fluorescence must still be understood.

The issue of raw material provenance, transfer and use is crucial to formulate testable hypotheses concerning the socioeconomic organisation and mobility strategies of prehistoric societies (*e.g.*, Delage 2003; Féblot-Augustins 1997; Floss 1994; Freund 2013; Milne *et al.* 2011; Moreau *et al.* 2016; Pettitt *et al.* 2012; Shackley 2008). An examination of the raw geological material shows that the source of the adzes made in Ottignies-Mousty Cambrian lydites does indeed originate from this production area and is restricted to a short section of the Dyle valley, south of Ottignies. The location of the workshops has yet to be identified. They were used in the Dendre spring area as well as the Hesbayan plateau and the Petite Gette valley but also in the settlements in the Netherlands (Figure 10). It seems that it is the most appreciated raw material, probably due to its deep black colour, silky and shiny appearance, and its good knapping quality.

The MSHH has been mined in a restricted area close to the centre and around the actual village of Horion-Hozémont. The appellation of "micaceous sandstones of Horion-Hozémont" must be renamed to be identifiable by researchers working on extra-regional sites because they are poor in mica flakes and particularly rich in siliceous sponge spicules and vary lithologically between siltstones (the most frequent lithology) and fine-grained sandstones. We suggest to rename the rock "pyritic sponge-rich silicified siltstones" into "fine-grained sandstones of Horion-Hozémont" which could be abbreviate to SSHH. The partial dissolution of the sponge pieces provides silica cementing the detrital grains, giving a subconchoidal fracture and allowing to reach dark grey brilliant, polished surfaces and strength. New excavations should be scheduled in the Lexhy private ownership where traces of a Neolithic workshop were discovered by local collectors some decades ago but without any samples preserved in the collections. The workshops at Noirfontaine are located two kilometres southward of Horion-Hozémont (Archives Marcel Dradon, "*Centre de Conservation, d'Étude et de Documentation*" - CCED -, Préhistomuseum, Ramioul; Tromme & Haeck 1974-1976). Adzes from Noirfontaine are distributed throughout the Belgian Hesbaye but were not found in the Dendre springs settlement area (Figure 10).

Lower Namurian banded lydites (phtanites) exploited south of the Dendre springs have been shaped and used only in the Dendre spring area. The workshop's location is unknown but roughouts have been found in many settlements. What all these rocks have in common is that they are confined to very limited locations in space due to exceptional genetic conditions of formation and outcropping.

Cambrian and Namurian lydites are found in almost all Belgian LBK settlement places, including the Hainaut area. Finally, a third source of lydites, Lower Namurian in age, occurring some kilometres south of the Dendre springs settlements was collected by the Neolithics but the manufacturing tests do not seem to have been successful.

The next step of this research will consist in investigating their chronology and their mechanical properties regarding the importation of magmatic and metamorphic rocks from the east during the peopling of the loess fertile area, but also the distribution of these black adzes outside Belgium in order to cross a maximum length of time (the East to West migration) to try to understand causes of intensity of exploitation and distribution in the North-western part of Europe during the Early Neolithic. First observations in French Lorraine (in collaboration with Vincent Blouet) show that a limited number of finished adzes made both in SSHH and Cambrian lydites are found in some LPC settlements (Figure 10).

Franco-Belgian research is presently conducted to understand the circulation of products (ceramic, flint, adzes, haematite-rich material) between the Hesbaye and the Lorraine areas.

Archaeometric studies must be conducted on adzes made in "basalt" and actinolite-hornblende schists metamorphic rocks ("amphibolite" rocks) found in Belgium. These studies would require destructive methods (*e.g.*, OP, XRD and geochemical analyses).

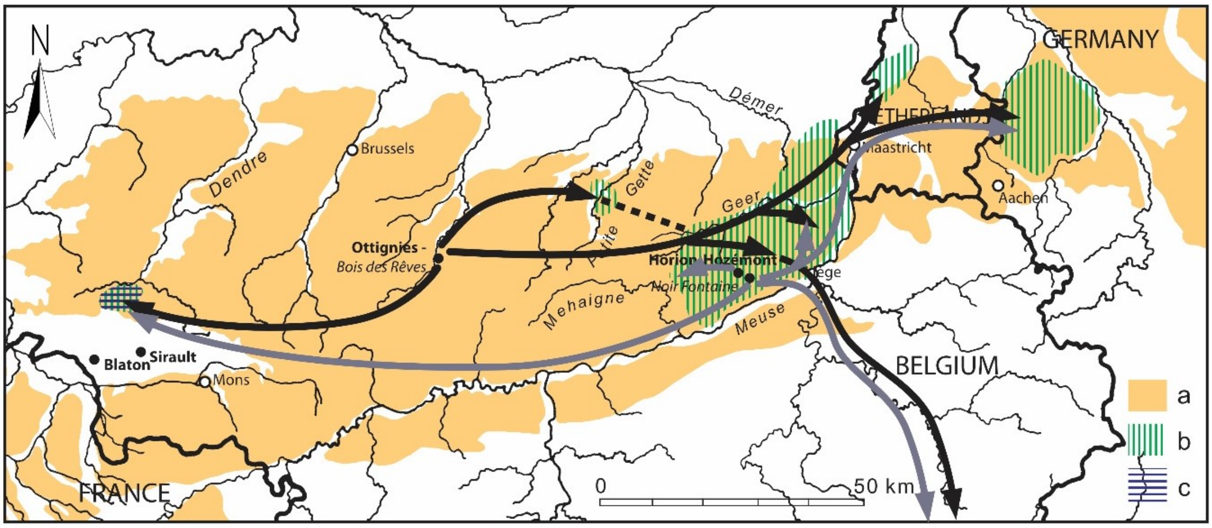

Figure 10: Indication of the 'road' followed by the two main raw materials (phtanite and SSHH) from their outcrops inside the '*Rubané du Nord-Ouest*' (according to Jeunesse 1995; 1996). The arrowed lines (black for phtanite and grey for SSHH) don't represent the physical road trip neither the way of how the pieces arrived in the different LPC countries. Indications are based on data registered by É. Goemaere (Belgium and towards the Mosel area outside the map) and literature (Bakels 1987). Infography: A. Hauzeur.

Acknowledgements

The authors thank Claude Demarez ("*Archéosite et musée d'Aubechies*"), Corrie C. Bakels (honory professor Leiden University, The Netherland), Vincent Blouet ("*Ministère de la Culture SRA Lorraine*", France) and Claude Constantin (honorary researcher, France), for provision of their reference material and Éric Dewamme, photographer at the RBINS. The authors would like to thank the two anonymous reviewers for their comments and discussions as well as the editors.

Data accessibility statement

The authors confirm that the data of this study are available within the article and its supplementary materials without any restriction.

List of supplementary files

If there are supplementary files, please list them here in the following format.

GOEMAERE - Supplementary file 1 - dataset.xlsx: dataset of LPC black adzes (fragments, roughouts) and geological samples.

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Les herminettes en roches noires du Néolithique ancien de Belgique. Contribution de la microspectrométrie Raman et de la pétrographie à la caractérisation des matières premières et à la recherche de leur origine.

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Abstract:

La présence d'herminettes du Néolithique ancien (culture rubanée) sur les sites d'habitats et d'ateliers en Belgique accompagne le processus de néolithisation. Ces herminettes sont fabriquées à partir d'une large variété de matières premières lithiques d'origine extrarégionale telles que des roches vertes métamorphiques (amphibolites) et des roches volcaniques noires ("basaltes") à côté de matériaux d'origine locale ou régionale comme des silex (gris ou noirs), des quartzites de teintes claires (roches sédimentaires ou légèrement métamorphiques) ainsi que des roches très riches en silice et de teintes gris foncé à noires. Ces dernières sont de plusieurs types comme les lydiennes nodulaires cambriennes noires de Céroux-Mousty (aire d'affleurement extrêmement limitée, Ottigines-Mousty en Province de Brabant), les phtanites en bancs stratifiés du Namurien inférieur (bande étroite mais de grande extension géographique traversant la Belgique d'ouest en est de la frontière française à Visé près de la frontière avec les Pays-Bas) ainsi que des grès gris foncé silicifiés riches en spicules siliceux d'éponges (visibles en lames-minces), datés du Namurien inférieur antérieurement appelés "Grès micacés de Horion-Hozémont" (affleurant dans la localité éponyme). L'article détaille les contextes géologiques des différentes occurrences de roches noires. En Belgique, les fosses liées aux sites d'habitats de la culture LBK renferme à la fois des fragments d'herminettes de production régionale et des herminettes importées. La découverte de l'atelier de Noirfontaine à proximité de la ville de Liège dans les années 1970 et 80 (complétée par de nouvelles fouilles menées en 2022) illustre toutes les étapes de fabrication des herminettes en grès gris foncé depuis la matière première jusqu'à l'herminette polie (article en cours d'écriture par les présents auteurs) et apporte un assemblage exceptionnel disponible pour des analyses. Cet atelier se trouve à faible distance des affleurements de Horion-Hozémont. L'étude archéométrique menée et présentée dans cet article utilise différentes méthodes analytiques visant à caractériser chaque type de roches siliceuses noires et à appréhender les origines géographiques et géologiques ainsi qu'à discriminer les roches silicifiées cambriennes et namuriennes constituant les herminettes du Néolithique ancien de Belgique. Si la couleur noire de ces dernières résulte de la présence de matière organique finement dispersée, l'absence de palynomorphes ne permet toutefois pas une attribution stratigraphique. Les analyses pétrographiques (microscopie optique polarisante et microscopie électronique à balayage), la diffraction des rayons X, les analyses chimiques (spectrographie par dispersion d'énergie) ainsi que la mesure du degré de graphitisation de la matière organique par microspectroscopie Raman ont été décisives pour l'identification des provenances géologiques et géographiques, en comparant les résultats acquis sur les échantillons archéologiques avec ceux des échantillons géologiques (silex, grès namuriens, phtanites namuriens, lydiennes cambriennes) collectés sur le terrain ou disponibles dans les collections de référence. La matière organique des roches cambriennes est nettement plus évoluée que celles des roches namuriennes. Les roches cambriennes sont riches en aiguilles plurimicrométriques de rutile (TiO_2) tandis que les roches namuriennes de Horion-Hozémont, granulométriquement mal classées, sont pauvres en paillettes de micas mais riches en spicules d'éponge orientés, qui par dissolution fournissent la silice qui va cimenter le grès et conférer ses propriétés de dureté. La matière organique finement disséminée confère la couleur noire et l'aspect luisant des surfaces après polissage. Un tableau synthétise les caractéristiques de chaque type de roches noires. Une étude archéométrique est encore à réaliser pour ce qui concerne les herminettes en roches importées comme les roches en "basalte" et les amphibolites. Les lydiennes cambriennes proviennent d'une zone géographique très restreinte et furent préférées aux autres ressources lithiques plus locales. Cette étude est importante dans le cadre de la compréhension de la circulation des matières premières lithiques et des produits finis accompagnant la « grande migration ».

Mots-clés: herminettes; lydiennes; grès silicifiés; microspectrométrie Raman; analyses physiques et chimiques; Néolithique ancien