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A new Cambrian black pigment used during the late Middle Palaeolithic discovered at Scladina Cave (Andenne, Belgium)

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ABSTRACT

Sedimentary Unit 1A at Scladina Cave, Belgium has yielded archaeological material from a Middle Palaeolithic occupation dating to between 40,210 + 400/−350 BP and 37,300 + 370/−320 BP. Fifty-one fragments of a black, friable rock with a black streak were found in association with 194 burned bone fragments and several thousand lithic artefacts. This black material is interpreted as a pigment brought to the site by Neandertals.

The pigment was analysed by petrography, XRD, Raman microspectroscopy, and other geochemical methods. It was identified as a highly siliceous graphitic siltstone. This is a very unique discovery, as European archaeological research has so far only recorded black pigments comprised of manganese oxides from the Middle Palaeolithic. Raman microspectroscopy is a non-destructive method able to distinguish the attributes of black siliceous materials that originate from different tectono-sedimentary contexts. By measuring the degree of alteration of the carbonaceous material, this method allowed for the determination of its geographical and geological origins: a Cambrian formation of very limited extent located near Ottignies, about 40 kilometres north-west of Scladina Cave. The absence of a drainage network connecting the two locations eliminates the possibility of natural transport, and supports its anthropogenic origin.

1. Introduction

Not only did Neandertals produce domestic and hunting tools, they also likely practiced symbolic and spiritual activities (Chase and Dibble, 1987; Otte, 1996, 1997, 2001; Soressi and D'Errico, 2007; Vandermeersch and Maureille, 2007; d'Errico et al., 2010; Caron et al., 2011; Salomon et al., 2012; Bodu et al., 2013). This has been documented through the discovery of burials, sometimes organised into funerary areas such as those at La Ferrassie (France), Shanidar (Iraq), or Spy (Belgium, Maureille and Vandermeersch, 2007), and also through the collection of geological curiosities, such as fossils, that were transported and sometimes roughly manufactured (Otte, 1996). These activities reflect symbolic behaviour and/or aesthetic interest. Neandertal symbolism is further supported by evidence of use of shells (Zilhão et al., 2010; Peresani et al., 2013), bird feathers and claws (Peresani et al., 2011; Morin and Laroulandie, 2012), engravings, and organized cuts on bones and stone fragments (Soressi and D'Errico, 2007; Peresani et al., 2014).

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Neandertals also collected red and black mineral pigments (Leroi-Gourhan, 1971; Mellars, 1996; Soressi et al., 2002; Soressi and D'Errico, 2007; Roebroeks et al., 2012; Bodu et al., 2013; Dayet et al., 2014). At archaeological sites such as Arcy-sur-Cure (Baffier, 1999; Soressi and D'Errico, 2007), Pech de l'Azé I (Soressi and D'Errico, 2007), and Maastricht-Belvédère (Roebroeks et al., 2012) discoveries of manganese and iron oxides often have been interpreted as pigments even though their exact use is largely unknown (Roebroeks et al., 2012). The functional or symbolic application of the pigments has been hypothesised in detail by some researchers (e.g. Soressi and D'Errico, 2007; Wadley et al., 2009). This paper characterises a new type of black pigment that has been discovered at Scladina Cave (Sclayn/Andenne, Belgium; Fig. 1), including its geological and geographical provenance.

In Europe, more than 70 archaeological occurences (*sensu* Depaepe, 2010) dating to the Lower and Middle Palaeolithic have yielded pigments, which are sometimes associated with objects that may have been used to process them. Most of these sites are dated to the late Middle Palaeolithic, between 60,000 and 40,000 BP (Soressi and D'Errico, 2007). Overall, black pigment is the most abundant type; it is commonly found in the form of small fragments of manganese oxides. Red and yellow ochre are rarer. The largest collection of black pigment known to date was discovered at the Pech de l'Azé I (Dordogne), where more than 500 small pieces of manganese oxides were found, 250 of which exhibited clear traces of use (Soressi and D'Errico, 2007).

In Belgium, black pigment associated with archaeological material has been found at Spy Cave. Manganese oxides were recorded there at the end of the 19th century by A. Rucquoy (1886-1887: 323). Unfortunately, the anthropogenic origin the material cannot be proven due to a lack of precise archaeostratigraphic provenance and evidence for their association with other artefacts, as recent re-examinations of the available data demonstrate (Di Modica et al., 2013; Pirson et al., 2013).

At Scladina Cave 51 fragments of millimetre to centimetre scale, black, poorly-lithified, and friable siltstone (Fig. 2a and b) have been found. This material is associated with a homogeneous Middle Palaeolithic archaeological assemblage rich in lithic artefacts (Loodts and Bonjean, 2004; Bonjean et al., 2009; Di Modica, 2010). Herein, this previously undefined black, friable material found at Scladina will be referred to as the Black Pigment of Sclayn (BPS). In Europe, the discoveries at Scladina are the northernmost known examples of black pigment used by Neandertals.

We interpret the BPS as having been imported to Scladina Cave by Neandertals. This was determined by examining the material's archaeological context and finding its geological/geographical source. Several BPS samples were analysed in order to determine the nature of the material, as well as to verify the homogeneity of the samples. This study focuses on the Raman response for the carbonaceous matter (CM) component of the BPS, more specifically the crystallinity degree of CM and the application of geothermometer proxies. This provides evidence for the material's geological/geographical origin by comparing the BPS with geological reference samples from known locations.

2. Scladina Cave

Scladina Cave (50°29′03″N and 5°01′30″E; elevation = 137.7 m AMSL) was discovered in 1971. It is situated in the village of Sclayn (Fig. 3), in a small valley adjacent to the Meuse River, 7 m below a plateau and 30 m above the alluvial plain of the Ri de Pontainne. Filled with sediment at the time of discovery, Scladina has been the subject of scientific excavation since 1978 (Otte, 1992). In its current state, the cave appears as a cylindrical karstic cavity that extends eastwards more than 39 m into the limestone bedrock (Fig. 4A). At about 35 m from the porch, an aven connects the cave and the plateau (Bonjean et al., 2002), on which a sinkhole of approximately 60 m^2 developed. Evidence of the opening of the aven was discovered in sedimentary Unit 1B-TAB (Pirson, 2007). As soon as the aven opened, two independent sedimentary sequences began accumulating in the cave: the classic entrance sequence continued

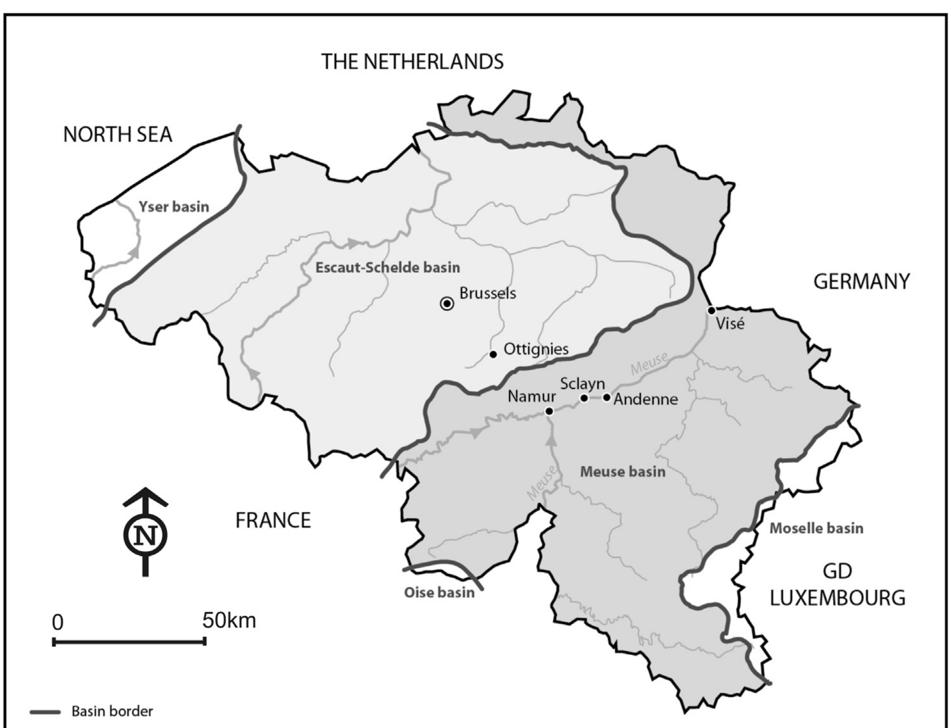

Fig. 1. Map of Belgium. Sclayn and Ottignies, separated by a distance of 40 km, are located in different hydrogeological basins.

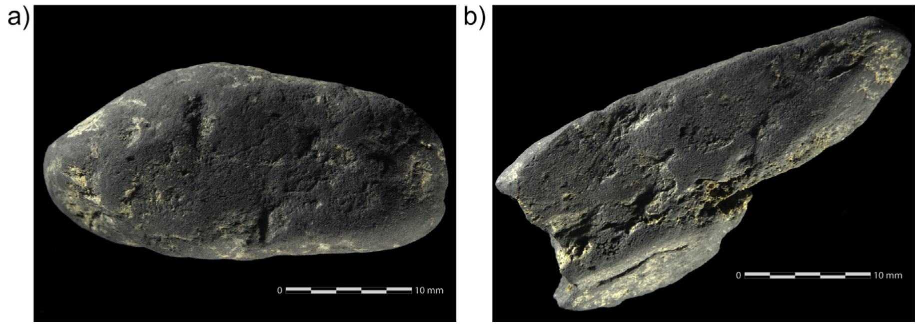

Fig. 2. Pictures of two BPS samples: a) sample Sc-1983-152-1; b) sample Sc-1983-152-3.

to develop (Fig. 5A), while a new, contemporaneous (although spatially separate) sequence began under the aven (Fig. 5B).

Scladina Cave is a major occupation site of the Middle Palaeolithic in north-west Europe and was classified as a *Site exceptionnel de Wallonie* ('Exceptional site of Wallonia', protected by regional laws) in 1996. The cave's stratigraphy records an exceptional sequence of the Upper Pleistocene (Pirson, 2007; Pirson et al., 2008). The permanent, multidisciplinary research that takes place at Scladina closely respects stratigraphy and combines both horizontal and vertical excavation techniques (Bonjean, 2009). A stratigraphic reappraisal led to the establishment of a new stratigraphic record encompassing 120 layers, categorized into 28 sedimentary units (Pirson, 2007; Pirson et al., 2008, Fig. 5A and B). Two main Middle Palaeolithic lithic assemblages have been identified (Fig. 5). The age of the older assemblage (from Sedimentary Unit 5) has been estimated at ~110,000 BP. The upper assemblage, from Sedimentary Unit 1A (Fig. 5A) and its lateral equivalent under the aven, Unit Z-INF (Fig. 5B), has been dated between 37,000 and 40,000 BP. Both assemblages have been analysed from stratigraphic, faunal, palynological, typological, technological, petrological, spatial, calibrational, and statistical perspectives (Otte, 1990; Otte, 1992; Otte et al., 1998; Pirson, 2007; Pirson et al., 2008; Bonjean et al., 2009; Di Modica, 2011; Abrams et al., 2014). In addition, in Sedimentary Complex 4A (Fig. 5), the mandible and fragments of the maxilla from an 8 year-old (Smith et al., 2007) Neanderthal child were discovered along with 16 isolated teeth (Toussaint et al., 1998; Toussaint and Bonjean, 2014; Toussaint and Pirson, 2006). Dated to approximately 86–88,000 BP (Toussaint and Bonjean, 2014), this individual produced the oldest Neandertal DNA yet retrieved (Orlando et al., 2006).

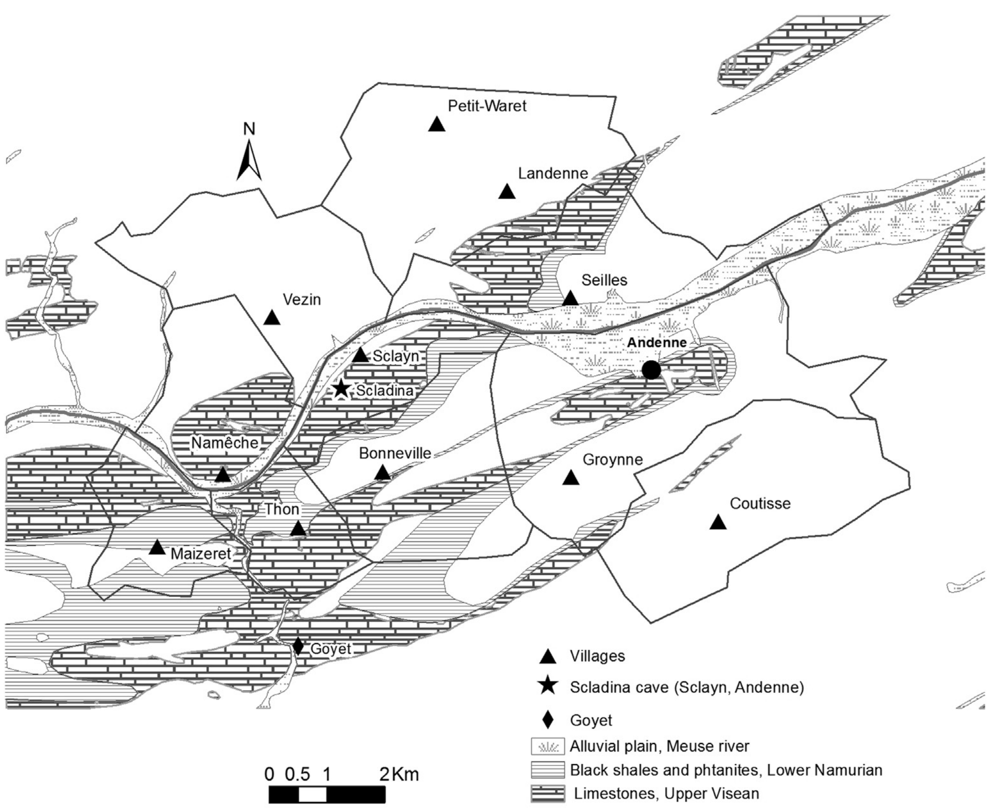

Fig. 3. Geological map of the surroundings of Scladina Cave with Upper Visean and Lower Namurian outcrops shown.

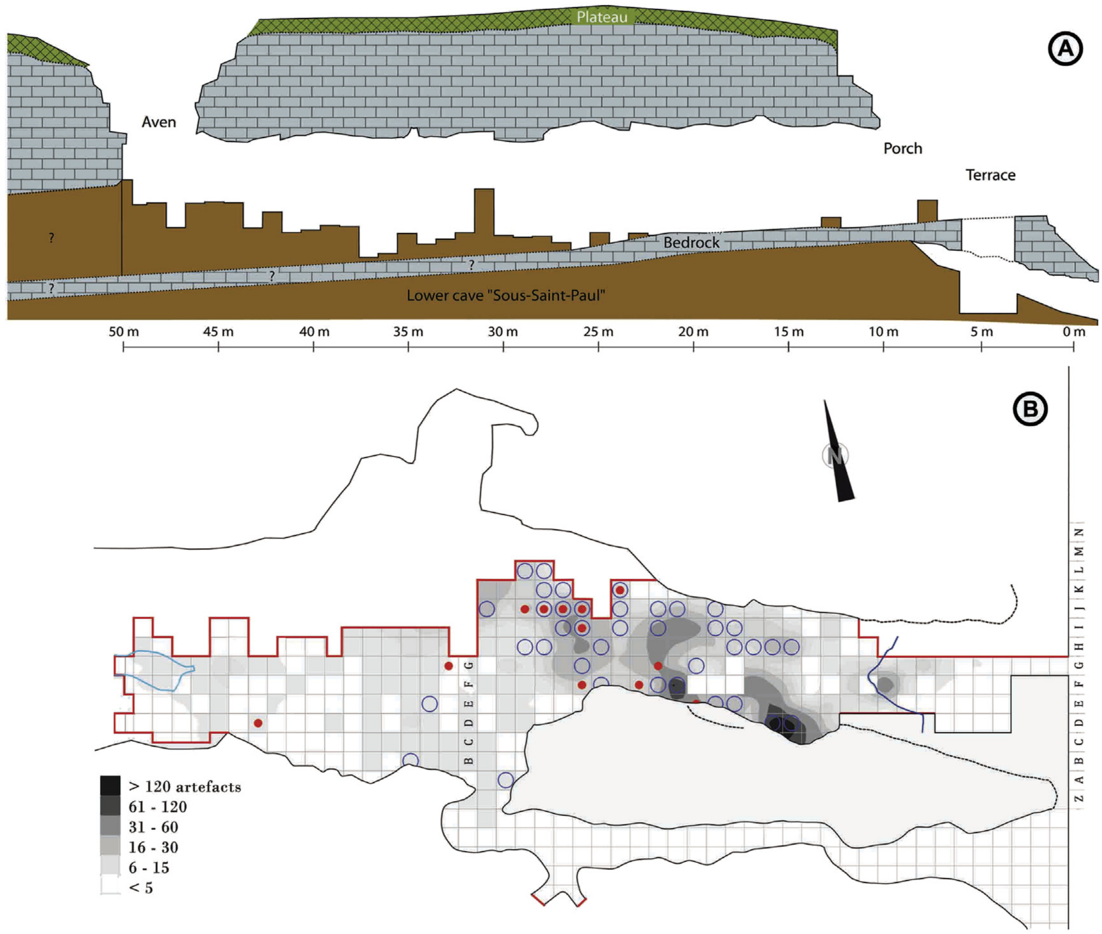

Fig. 4. Scladina Cave. A) Longitudinal cross section. Blue: limestones; green: superficial deposits; brown: Quaternary cave infill sediments. B) Distribution map of BPS fragments (red dots), burned bones (blue circles) and lithic artefact concentrations (grey zones) in units 1A, T and Z-INF. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3. Macroscopic to microscopic description of the BPS

At Scladina, a total of 51 fragments of the BPS have been uncovered, their stratigraphic provenance within the cave recorded, and their characteristics described (Table 1). All samples of BPS have the same macro- and meso-scopic properties: a fine porous siltstone, dark grey (N3 on the Munsell rock colour chart) for dry samples, and greyish black (N2) for wet samples. The fragments were primarily found in the form of planar fragments (nearly parallelepipedic overall shape), and more rarely as prisms that are triangular in cross-section (Fig. 6). Macrofossils, microfossils, and mica flakes are not present. No stratification is visible and schistosity is only very weakly expressed. Pores are circular to elliptical, ranging between 0.01 and 0.30 mm in diameter, with irregular edges. Rare millimetre-scale areas correspond to the coalescence of adjacent pores. Pores and friability result from outcrop weathering. No macroscopic differences can be observed between different samples. The homogeneity of the material suggests a single source for all fragments. The samples were weighed and measured with the exception of those that were partially destroyed during analysis (Table 1). The size of the pieces varies between a few millimetres to slightly less than 5 cm, and they weigh between 0.1 gr and 15 gr.

When the pigments were discovered, no diffusion between the pigment and the sediment was observed, and the pigment appeared unaltered by its sedimentary context. This suggests that the material did not become friable during its contact within the sediments in Scladina but was incorporated into the site in a state similar to its present form. The material has an earthy appearance (Fig. 2a and b) and produces a black streak - it easily leaves black marks on ceramic as well as on paper. Each laboratory manipulation was accompanied by the abrasion of the outside of the black pigment. Cleaning the objects of their brown clay matrix generated a loss of material and prevented the search for traces of anthropogenic alteration, as well as any possibility of refitting between different objects. Due to its high porosity the material sticks to one's tongue. When submersed in water (empiric test), the material becomes completely saturated very quickly, while maintaining its shape and cohesiveness. It does not react with HCl.

Although the fine black matrix was a major obstacle for good microscopic observations, the different techniques used allowed for the characterisation of the BPS. It is a porous and highly siliceous rock composed mainly of quartz. The matrix appears isotropic and contains xenomorphic clay-sized quartz grains and sub-automorphic silt-sized quartz grains. The material exhibits micro- and macroporosity. Macropores (>50 μm in diameter) generally have an elliptical shape. Some pores are partially filled by quartz grains displaying undulouse extinction. The abundance of these pores implies prior dissolution of one or more mineral phases such as carbonate cement or sulfides. Stratification planes, bioturbation, as well as fossils or trace fossils were not observed.

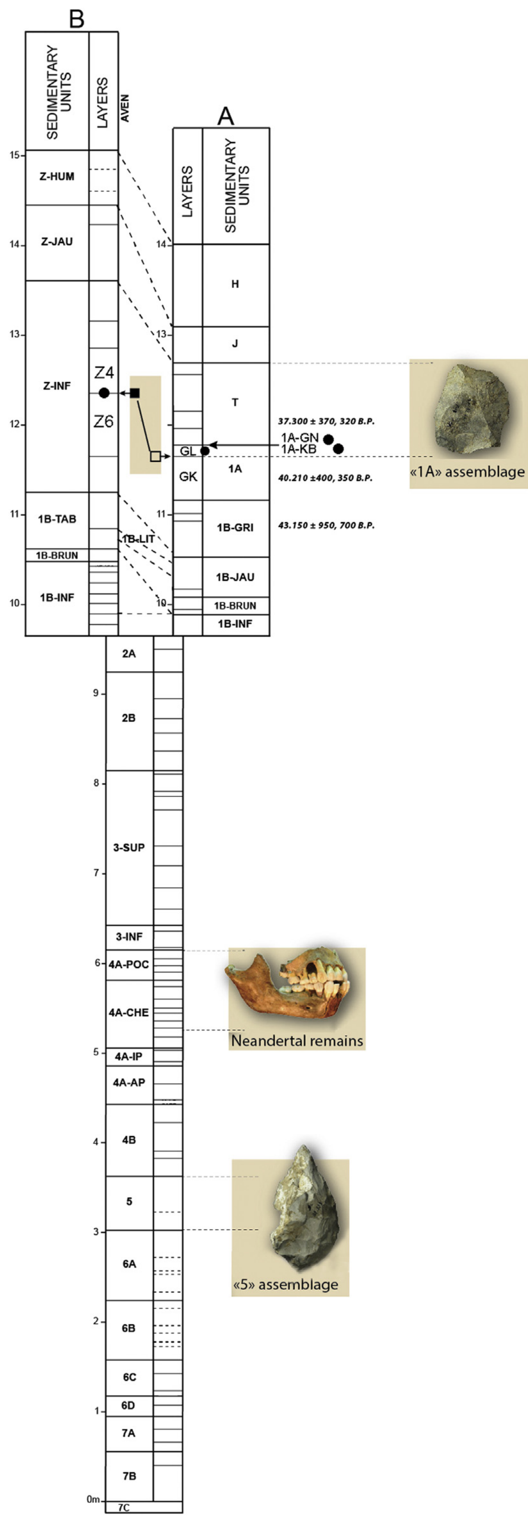

Fig. 5. Stratigraphic profile of Scladina Cave composed of the entrance-sequence (lower and upper portions of A) and the aven sequence (upper portion of B). The "1A" lithic assemblage is linked to that at the boundary between layers Z6 and Z4 by refitting of two artefacts. Black dots: BPS samples (modified after Pirson, 2007).

4. Physical and chemical characterization of the BPS

Scanning electron microscope (SEM – FEI Quanta 200) observations combined with energy-dispersive X-ray spectroscopy (EDS) analyses on a broken surface of a BPS sample show that the material is composed of three phases (Fig. 7): 1- quartz grains of different sizes, either with μm-scale grains or automorphous crystal of few tens of μm; 2- rutile needles with μm-scale width; and 3- a matrix composed of carbon. Quartz and rutile are also identified on the XRD powder diffractograms and with Raman microspectrometry. All samples discoloured after they were heated to 1050 °C under oxidized conditions.

The samples are sterile and contain no palynomorphs. Dissolution residue only shows small glitters or (isolated or agglomerated) xenorphic grains of a carbonaceous material, micrometric crystalline needles of rutile (isolated or grouped in bundles), as well as rare subautomorphic crystals of zircon.

The chemical analysis results (X-ray fluorescence, LA-ICP-MS) indicate a high silica content and a very low percentage of alumina (low clay minerals content) corresponding to very fine (hyper) siliceous rocks. The BPS is also Mn-poor, but especially Ti-rich. The carbon (3.3%) content of the BPS was determined by graphite furnace atomic absorption spectrometry.

In summary, all analysed BPS samples are strongly similar in composition, texture, and fabric, suggesting a single geological and geographical source. The black pigment of Sclayn can be defined as a highly siliceous friable graphitic siltstone. Its carbon content combined with its friable character endows this material with black colouring properties that were likely attractive to prehistoric humans.

5. The carbonaceous material characterization by Raman microspectrometry and geothermometry

Carbonaceous material (CM) is a frequent component of sedimentary rocks resulting from the chemical and physical transformation of natural organic content, which is modified from a disordered structure into well-ordered pure graphite (graphitization; Wopenka and Pasteris, 1993). Temperature is commonly referred to as a key parameter, especially for controlling the graphitization in metamorphic rocks, but pressure, organic precursors, stress, and time can also control the process, especially in low-grade metamorphic rocks (Wopenka and Pasteris, 1993; Beyssac et al., 2003; Lahfid et al., 2010). Wopenka and Pasteris (1993) have cited and compared different techniques (vitrinite reflectance, IR spectroscopy, XRD, HRTEM) of CM characterization, and it is now recognized that Raman microspectrometry is the most straightforward technique to quantify the degree of CM organization, since *in situ* measurements can be conducted in thin sections without the physical and/or chemical removal, reducing the risk of perturbing CM structures. Other advantages of the Raman analysis are its speed (spectra are now acquired usually in few minutes) and the micrometre scale of investigation allowing for the assessment of sample heterogeneity.

Therefore, CM characterisation by Raman microspectrometry (RMS) represents a valuable tool for geologists to evaluate the geodynamic evolution of rock formations/basins, and consequently to establish discrimination criteria between potential sources of raw material with a CM component. The main conditions that govern applicability are the content of CM in archaeological and geological material and the potential sources of raw materials that must have undergone different peak temperatures during their geological evolution.

This method was applied both on BPS samples and the geological samples described below.

5.1. Description of the RMS method

Raman spectra on carbonaceous material (CM) of archaeological and geological samples mounted on uncovered thin sections were

Table 1
The 51 black pigment samples from Scladina Cave: identification numbers, locations in the cave and in the stratigraphic sequence, measurements, and analyses performed on each sample. Sedimentary Unit Z-INF is the lateral equivalent under the aven of Sedimentary Unit 1A. XRF: X-ray fluorescence; LA-ICP-MS: Laser Ablation Inductively Coupled Plasma Mass Spectrometry; TS: thin section; XRD: X-ray diffraction; N–C–H: dosing of Nitrogen–Carbon–Hydrogen by the "graphite oven" technique.

N°		Square	Unit	Layer	X	Y	Z	L	l	h	gr	Analyses
					cm	cm	cm	mm	mm	mm		
Sc-1982-219-1		E20	1A				224–256	45.4	22.9	13.3	13.4	Raman
Sc-1982-219-2		E20	1A				224–256					XRF, LA-ICP-MS, TS
Sc-1982-219-3		E20	1A				224–256	30.6	25.4	8.9	4.7	
Sc-1982-345-1		G22	1A				225–244	19.5	15.5	8.1	1.8	
Sc-1983-152-1		F23	1A				200–240	32.1	16.7	15.3	6.5	
Sc-1983-152-2		F23	1A				200–240	33.6	21.8	12.2	4.6	
Sc-1983-152-3	1/2	F23	1A				200–240	33.4	16.1	10.3	4.2	LA-ICP-MS, TS
	2/2											Palynology
Sc-1987-25-1		I26	1A				240–250	38	33.8	12.3	14.4	
Sc-1987-85-1		F26	T				238–251	22.6	16.2	8.9	2.6	
Sc-1989-107-1		J28	1A				248–260	16	12.6	6.4	0.6	
Sc-1989-123-1		F29	Bioturb.				282–295	20	14.3	7.4	1.3	
Sc-1999-27-1		D43	Z INF	Z6/Z4			254					XRD, N–C–H, TS, Raman
Sc-1999-27-2		D43	Z INF	Z6/Z4			254					
Sc-1999-27-3		D43	Z INF	Z6/Z4			254					XRF
Sc-1999-27-4		D43	Z INF	Z6/Z4			254					Palynology
Sc-1999-27-5		D43	Z INF	Z6/Z4			254	14.1	10.9	4.9	0.5	
Sc-1999-27-6		D43	Z INF	Z6/Z4			254	10.1	5.8	5.2	0.2	
Sc-1999-27-7		D43	Z INF	Z6/Z4			254	8.1	6.1	5	<0.1	
Sc-1999-27-8		D43	Z INF	Z6/Z4			254	15.5	8.6	8.4	0.8	
Sc-1999-27-9		D43	Z INF	Z6/Z4			254	10	6.4	2.6	0.1	
Sc-1999-27-10		D43	Z INF	Z6/Z4			254	7.4	4.1	3.1	<0.1	Raman
Sc-1999-27-11		D43	Z INF	Z6/Z4			254				0.1	LA-ICP-MS
Sc-1999-27-12		D43	Z INF	Z6/Z4			254	12.1	8.1	6	0.2	
Sc-1999-27-13		D43	Z INF	Z6/Z4			254	20.5	13.3	7.4	1.2	
Sc-1999-27-14		D43	Z INF	Z6/Z4			254	19.1	14.8	5.3	1.2	
Sc-1999-27-15		D43	Z INF	Z6/Z4			254	20.8	10.3	7.5	1.1	
Sc-1999-27-16		D43	Z INF	Z6/Z4			254	17.9	11	4.4	0.7	
Sc-1999-27-17		D43	Z INF	Z6/Z4			254	16.9	15.6	5.2	0.9	
Sc-1999-27-18		D43	Z INF	Z6/Z4			254	7.3	5.9	2.4	<0.1	
Sc-1999-27-19		D43	Z INF	Z6/Z4			254	15.6	8.6	5.1	0.7	
Sc-1999-27-20		D43	Z INF	Z6/Z4			254	10.7	8.6	4.9	0.2	
Sc-1999-27-21		D43	Z INF	Z6/Z4			254	15.5	11.3	6.4	0.6	
Sc-1999-27-22		D43	Z INF	Z6/Z4			254	9	7.6	4.7	0.1	
Sc-2000-101-1		G33	1A				262–264	11.6	11.4	6.1	0.8	Raman
Sc-2007-458-2		J27	1A	1A-GL			251	4.9	3.7	2.5	<0.1	
Sc-2008-179-1		J26	1A	1A-GL	25	50	252	6.9	5.4	4.5	<0.1	
Sc-2008-202-12-1		J26	1A	1A-GL			246–264	6.6	3.6	3.4	<0.1	
Sc-2008-202-12-2		J26	1A	1A-GL			246–264	4.3	4.2	1.9	<0.1	
Sc-2008-202-13		J26	1A	1A-GL	35	25	246	14.5	9.5	7	0.6	Raman
Sc-2008-202-14		J26	1A	1A-GL	38	33	252	3.6	3.5	3	<0.1	
Sc-2008-202-15		J26	1A	1A-GL	39	19	250	9	7.7	5.7	0.2	
Sc-2008-224-1		J26	1A	1A-GN	30	40	246	8.2	7.9	4.4	0.2	Raman
Sc-2009-18-3		J26	1A	1A-GL	45	63	253	20	13.1	6	1.1	
Sc-2009-338-16-1		J26	1A	1A-KB	69	91	241	7.6	6.1	3.6	<0.1	
Sc-2009-338-16-2		J26	1A	1A-KB	69	91	241	8.8	5.3	2.4	<0.1	Raman
Sc-2009-359-9		K24	1A or T		20	60	244	2.7	1.6	1	<0.1	
Sc-2009-362-1		J26	1A	1A-GL	57	28	248	9.8	6	5.8	0.1	
Sc-2009-362-2		J26	1A	1A-GL	58	30	249	12.4	8.6	5.3	0.2	
Sc-2009-362-9		J26	1A	1A-GL	70	28	247	3.5	2	1.3	<0.1	
Sc-2009-362-16-1		J26	1A	1A-GL	58	82	247	12.8	10.7	9.2	0.7	
Sc-2009-362-16-2		J26	1A	1A-GL	58	82	247	9.3	6.2	4.3	0.1	

conducted with a SENTERRA (Brucker) Raman microspectrometer (mineralogical laboratory of the Geological Survey of Belgium). The main analytical parameters are presented in Table 2. The incident laser beam was focused on CM located below transparent crystals, usually quartz grains, in order to acquire the signal on non-perturbated material during the polishing procedure. Our approach followed the requirements proposed by Beyssac et al. (2003) in order to obtain quantitative results. Between 10 and 15 spectra on each sample were acquired to get a representative assessment of the natural variability of CM. Three different BPS samples, representative of the spatial distribution within Scladina Cave, were made into polished thin sections (no cover) for petrographic observation and Raman microspectrometry analysis. Five reference geological samples were also studied with the same techniques as the archaeological samples. Four of these were collected as hand samples from near Scladina Cave, namely in the Namur Synclinorium tectonostratigraphic unit, while the fifth sample was taken in the former Franquenies quarry (Mousty Formation, Cambrian). Out of the first four samples, one corresponds to the Dinantian limestone from an outcrop below the Scladina Cave entrance, while the three other samples were collected from Namurian formations within a radius of 10 km around Scladina Cave. All geological samples were petrographically analysed.

5.2. Reference geological material

Within a radius of eighty kilometres around Scladina Cave, the possible source materials that display similar macroscopic facies

Fig. 6. The BPS fragments have the same macro- and mesoscopic properties: a fine grained, dark grey, and porous siltstone.

belong to two distinct tectono-sedimentary units, the Namur Synclinorium and the Brabant Massif. They both include geological formations containing siliceous black materials that have black streaks. These are observed at the base of the Upper Carboniferous 'Coal Measures' (Namurian) from the Namur Synclinorium, where Scladina Cave is located (Figs. 1 and 3) and from the Cambrian of Franquenies, near Mousty (Fig. 8).

Dissolution of the calcite cement in Namurian siliceous shale or phtanites makes the material slightly powdery, so that it leaves a black streak when abraded. Lower Namurian rocks are composed of finely bedded black siliceous radiolarian shales from the Chokier Formation (Serpukhovian, Namurian A, Belgian Coal Measures Group, Upper Palaeozoic (Verniers et al., 2001)). The geographical distribution of these 1 to 15 m-thick black siliceous shales is large, crossing Belgian territory from the French border to the Dutch border (Fig. 1). As these Namurian rocks are rapidly weathered, their outcrops are currently limited to river benches and open pits (Fig. 3), and therefore access to the material is very limited. Due to

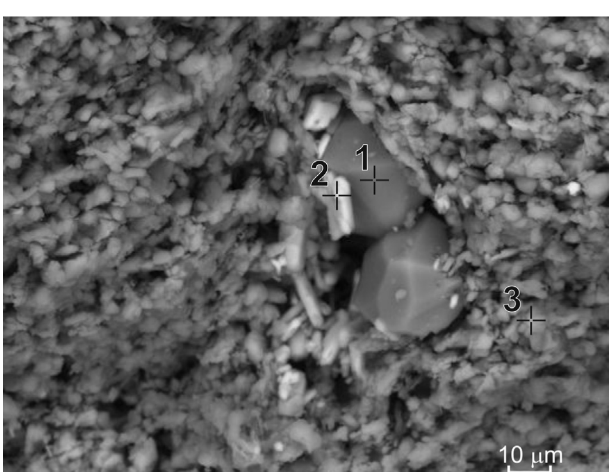

Fig. 7. SEM image of archaeological sample (Sc 1999-27-3) with locations of EDS analyses indicated. Quartz grains of different sizes (points 1 and 3) and a needle of rutile (points 2) are observed.

Table 2
Raman microspectrometer settings.

Laser wavelength	532 nm
Laser power	Between 5 and 20 mW
Acquisition time	Between 30 and 60 s with 10 co-additions
Objective lens	100×
Aperture	50 μm (pinhole)

the geographical proximity of these deposits with the Scladina Cave, assessing the possibility of natural importation into the cave is important.

Black graphitic shales/siltstones and hypersiliceous horizons from the Mousty Formation (Upper Cambrian, Lower Palaeozoic, Caledonian Brabant inlier, see Verniers et al., 2001) represent the second potential source of the BPS. This formation outcrops poorly in the Dyle valley between Court-Saint-Etienne and Ottignies (Herbosch and Lemonne, 2000; Verniers et al., 2001). Only the old Franquenies quarry exposes siliceous beds and lenses of lydite, found within the black graphitic shales. These rocks belong to the Franquenies Member (Fig. 9), the lower part of the Mousty Formation (Verniers et al., 2001; see Linnemann et al., 2012 for a review of the geological history of the Brabant inlier). Outcrops of silicified material are restricted to this quarry and the surrounding area (Fig. 8).

5.3. Results

The mineralogical paragenesis indicates that rocks of the Brabant Massif (deformed by the Brabantian orogeny) underwent very low-to low-grade metamorphism with temperatures that could have exceeded 350 °C (André and Deutsch, 1985; Fielitz and Mansy, 1999). Illite crystallinity data in the central part of the Brabant Massif also corroborate the epizonal conditions (>300 °C) for the Cambrian rocks in the central axis of the Brabant Massif, which is where the Franquenies-Mousty area is located. Mn-garnet, ilmenite, biotite, andalousite, and magnetite are metamorphic minerals occurring in appropriate facies. By contrast, the area near Scladina Cave has another thermal story; illite crystallinity data from the Namur Synclinorium shows that these rocks underwent only diagenetic conditions (<200 °C) (Fielitz and Mansy, 1999).

Raman spectra of CM can be subdivided into 2 main regions: first-order peaks (bands) are observed between 1100 and 1620 cm^{-1} and second-order bands between 2400 and 3200 cm^{-1}. These bands reflect different discrete forms of molecular vibrations, but can also be related to structural defects as is the case for CM. Well-crystallized graphite and slightly or strongly disordered CM can be distinguished on the presence/absence of specific vibrations, but also on the relative amplitude and area of bands in both spectral regions. For the sake of conciseness, comparisons were conducted only on first-order peaks in this study. Analysis of second order bands during this study followed Wopenka and Pasteris, 1993 and Sadezky et al., 2005.

The main observations related to the graphitization of CM in rocks show that one single peak (named G for graphite) is observed in the first-order region at about 1580 cm^{-1} for highly ordered graphite. Such results are expected for high-grade metamorphic rocks. Additional bands related to different forms of graphite lattice disorder (see Wopenka and Pasteris, 1993; Beyssac et al., 2002; Sadezky et al., 2005) are observed for slightly disordered CM at 1352 cm^{-1} (D1) and 1620 cm^{-1} (D2). The latter appears as a G-band shoulder. These types of responses are recorded in low-grade metamorphic rocks, such as greenschist facies. A wide and low-amplitude vibration (D3) can also be observed around 1510 cm^{-1} for CM that is more disordered. Finally, Raman responses of samples from very low-grade regions (diagenetic conditions) are

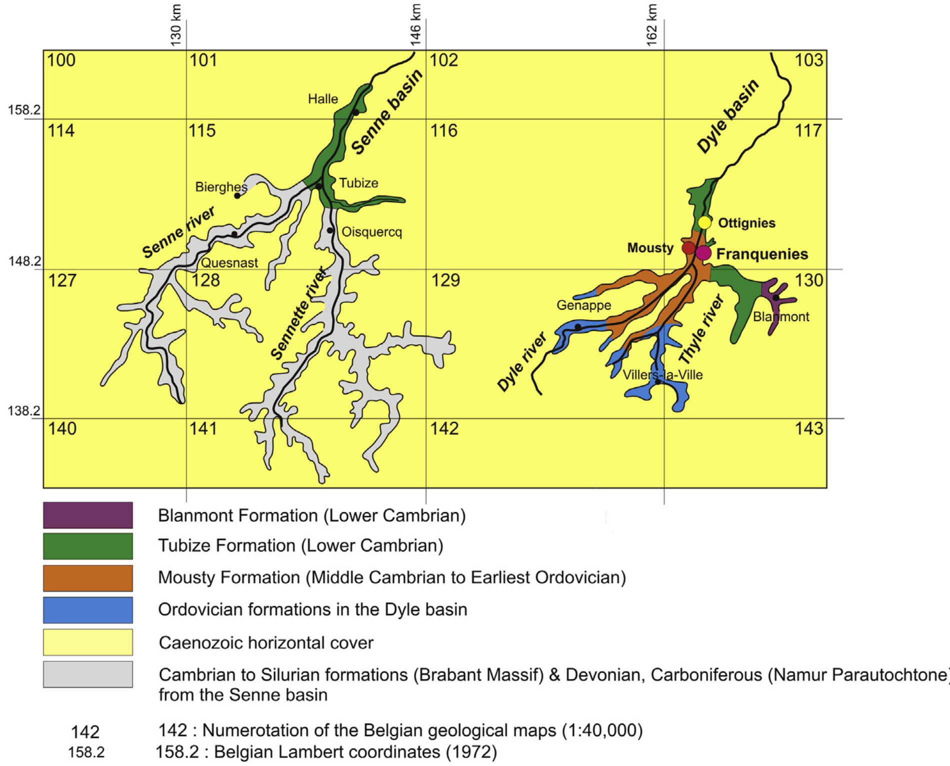

Fig. 8. Geological map of the Dyle basin with the location of the Cambrian Formation near Franquenies (Ottignies) shown (modified after Herbosch and Lemonne, 2000).

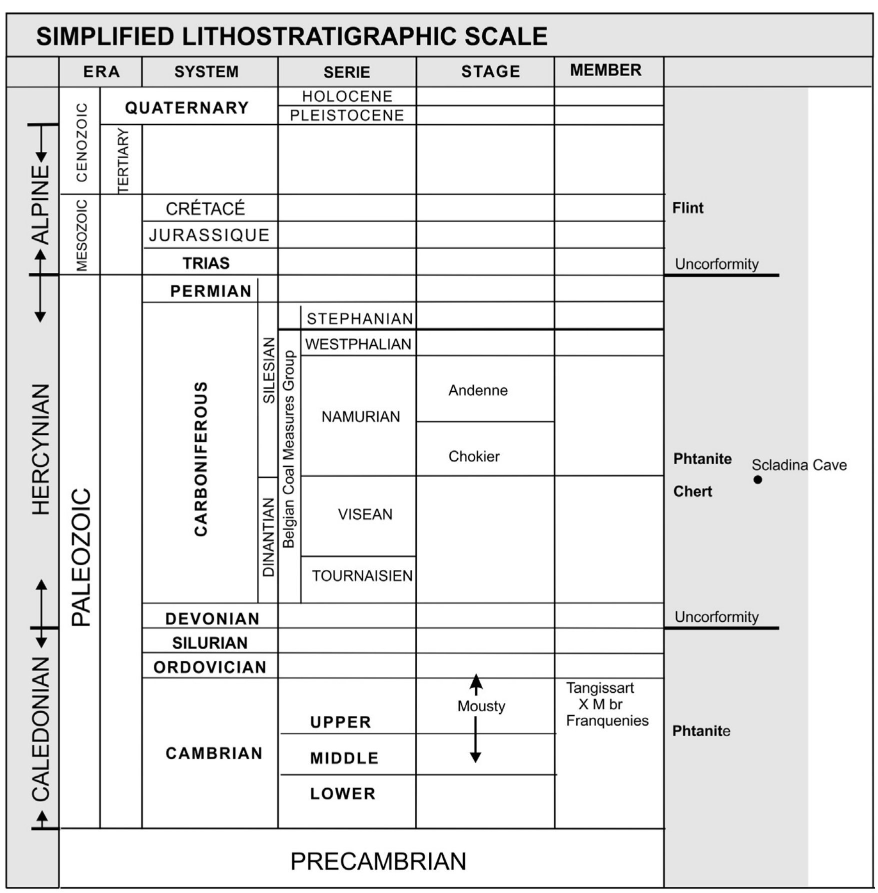

Fig. 9. Geological position of Cambrian siltstones and phtanites in the Mousty formation, lower Namurian phtanites, and Scladina Cave in the Upper Visean limestones (Eric Goemaere).

characterized by the strong asymmetry of D1, which also becomes very wide (FWHM 200–100 cm^{-1}). An additional peak (D4) observed for soot can explain this asymmetry (Sadezky et al., 2005). Rahl et al. (2005) show similar spectra with asymmetric D1 bands in rocks that were subject to very low temperature conditions (<150 °C).

Considering these observations, it appears that the Raman responses of the CM content of BPS samples and the Cambrian geological sample both show all the characteristics of partially ordered graphite as observed in greenschist facies (Fig. 10a). The recorded spectra show a narrow G peak located at about 1580 cm^{-1} with two additional defect peaks at about 1350 cm^{-1} (D1) and at about 1620 cm^{-1} (D2). Additional qualitative observations (Fig. 10b) include the higher amplitude of the G band with respect to the D1 and the lack of the D3 band that is observed between the D1 and G bands for less ordered CM. By contrast, all geological samples collected in the vicinity of Scladina Cave are characterized by a Raman signature of poorly-ordered CM as observed in rocks that were only subject to diagenetic conditions. Their Raman spectra include a broader G band centred at about 1600 cm^{-1}, which results from the merging of the G (*s.s.*) and D2 bands. Additional bands are observed on both sides of the D1 band, especially on the lower wavenumber side where the D4 band is clearly observed at about 1240 cm^{-1}. Two additional peaks are probably present at ~1380 cm^{-1} as already described by Lahfid et al. (2010), and also near ~1200 cm^{-1}. The last feature is not yet described in any literature. These bands were not integrated in the curve fitting procedure. Finally, a broad and low-amplitude D3 band located around 1510 cm^{-1} is required for convergence during the curve fitting procedure for such very-poorly organized CM.

A more quantitative approach can also be conducted on the recorded spectra by the analysis of the curve fitting results. The method is based on published geothermometric proxies from low-grade rocks (between ~200 and ~320 °C; Lahfid et al., 2010) and higher-grade rocks (between 330 and 650 °C; Beyssac et al., 2002). Both methods are based on the computation of different ratios of band areas. Beyssac et al. (2002) found a linear relationship for moderate-to high-grade metamorphic rocks between the peak temperatures recorded by CM content in rocks during their geological evolution with the so-called R2 parameter. The latter is equal to the D1/(D1+G + D2) area ratio. The published equation is: T [°C] = −445 R2 + 641 (Beyssac et al., 2002).

Table 3 shows the results of the curve fitting on the acquired spectra and the derived peak metamorphic temperature for the three studied thin sections of BPS and for the geological sample from the Mousty Formation (Cambrian). It is clear from this analysis that the BPS and the Cambrian geological samples underwent an identical peak metamorphic temperature of ~440 °C, which corresponds to a greenschist facies.

An attempt to determine the thermal conditions of the very-low grade rock formations located in the vicinity of Scladina Cave was also conducted with the geothermometer proxies determined by Lahfid et al. (2010). The published equations are related to other ratios (RA1 and RA2), relating different combinations of the area of five bands (D4, D1, D3, G, and D2). The thermal window for the applicability of this method extends between ~200 and ~320 °C and in this range RA1 varies between 0.54 and 0.63, while RA2 covers values between 1.17 and 1.71. The curve fitting conducted on the geological samples from the region of Scladina Cave systematically gives values below 0.54 for RA1 and below 1.17 for RA2. Therefore, these geological samples underwent thermal conditions below the thermal window (<200 °C). The results also show a strong variability of RA1 and RA2 ratios, which contrasts the small standard deviation observed by Lahfid et al. (2010). The presence of an additional peak at ~1380 cm^{-1} in the geological samples and the clear presence of the D4 band and the low-amplitude of the D1 peak with respect to the G-band reinforce the very low-thermal conditions (diagenetic) undergone by rocks near Scladina Cave. These results are also concordant with other geological data for the region (Namur Synclinorium), which also indicate diagenetic conditions.

6. Discussion

6.1. A strict association between the BPS and the archaeological material

In order to assess the anthropogenic origin of the BPS found in Scladina Cave, its spatial and stratigraphic distribution at the site

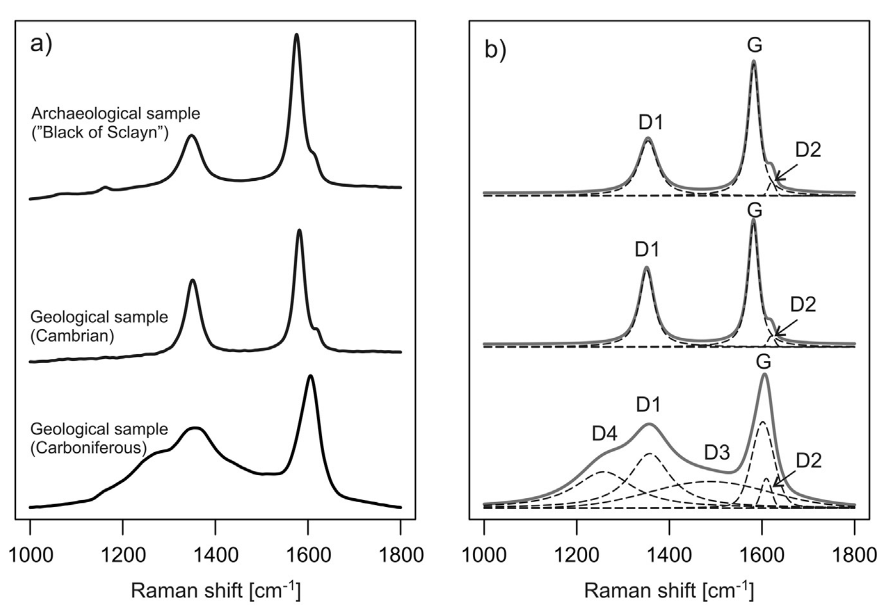

Fig. 10. a) Reference spectra of a BPS fragment compared to Cambrian and Carboniferous geological samples; b) curve fitting of the reference spectra (see (a)) with individual bands (dashed lines) and their respective assignments. The resulting envelope is represented by a grey line.

Table 3
Results of curve fitting procedure on archaeological thin sections and a Cambrian geological sample with geothermometer proxies.

Part I

Name	Nb. Spectra	D1 band				G band			
		Position	sd	FWHM	sd	Position	sd	FWHM	sd
Archaeological samples									
Sc 1982-219-2	4	1347.5	3.5	63.1	17.0	1576.0	3.9	32.9	3.4
Sc 1983-152-3-1	16	1351.6	1.0	57.7	9.6	1580.0	1.8	30.6	2.4
Sc 1999-27-1	11	1352.4	1.9	46.3	1.4	1582.2	1.3	27.6	1.2
Geological samples									
Franquenies	11	1351.8	0.8	39.7	1.9	1582.4	0.6	28.1	1.2

Part II

Name	D2 band				R1		R2		Temperature	
	Position	sd	FWHM	sd	Ratio	sd	Ratio	sd	Value (°C)	sd
Archaeological samples										
Sc 1982-219-2	1614.2	2.8	20.7	5.1	0.506	0.111	0.506	0.111	436	41
Sc 1983-152-3-1	1618.2	1.4	19.2	1.0	0.485	0.056	0.462	0.039	435	17
Sc 1999-27-1	1618.8	1.7	21.1	2.6	0.549	0.098	0.455	0.044	438	20
Geological samples										
Franquenies	1620.8	1.1	16.7	5.6	0.628	0.127	0.448	0.036	442	16

was examined and compared with those of other archaeological artefacts recovered from the cave.

Among the 51 Black Pigment of Sclayn (BPS) samples, 50 are stratigraphically associated with the archaeological material from sedimentary Unit 1A, Unit T, and their lateral equivalent under the aven, Unit Z-INF. The original stratigraphic position of the sample discovered in Square F29 (sample Sc-1989-123-1) is unknown since it was unearthed from a bioturbated area. Spatially, 48 BPS fragments (94.1%) were found in close proximity (the same square metre) to lithic artefacts. Fifteen of the BPS fragments (29.4%) are also in close proximity to the same square metre of burned bone fragments (Table 4 and Fig. 4B).

6.1.1. *Sedimentary Unit 1A*

Sedimentary Unit 1A has yielded 26 fragments of the BPS, approximately 4500 artefacts primarily made on flint, quartz, and quartzite (Otte et al., 1998; Di Modica, 2010, 2011), and several thousand animal teeth, bones, and bone fragments. 194 of these bone fragments are burned, sometimes calcined, suggesting their use as fuel (Abrams et al., 2010). Lithic artefacts, faunal remains, and BPS fragments were reworked a distance of approximately 20 metres into the karstic cavity from the entrance of the cave by various sedimentary depositional processes, mainly identified as debris flow and runoff (Pirson, 2007). Sedimentary Unit 1A is subdivided into 4 layers (Bonjean et al., 2009; Pirson et al., 2012): Layer 1A-GK, which is mostly archaeologically sterile; Layer 1A-GL, which represents the first sedimentary event that reworked the lithic artefacts, burned bones, and the BPS in the cave; and layers 1A-KB and 1A-GN, both of which have eroded and successively reworked lithics, burned bones, and BPS from Layer 1A-GL.

Ten fragments of BPS were uncovered from Sedimentary Unit 1A between metres 20 and 33 in the cave (Table 1 and Fig. 4B) in close proximity to five burned bone fragments and 180 lithic artefacts (Table 4). After stratigraphic reappraisal (2007), thirteen other fragments of BPS were recorded in Layer 1A-GL (Fig. 11), in squares J26 and J27 (Fig. 4B), adjacent to 43 burned bone fragments and 62 lithic artefacts (Table 4). Layers 1A-KB and 1A-GN, containing reworked objects from the subjacent Layer 1A-GL, also yielded (in Square J26) three fragments of BPS accompanied by 44 lithic artefacts (Table 4).

In this area of the cave (between meters 20 and 33), three more fragments of the BPS were found (Table 1). One (Sc-1987-85-1) was

Table 4
48 BPS fragments are in close proximity with 291 flint artefacts and 48 burned bone fragments.

Square	Sedimentary unit	Layer	BPS		Burned bones		Lithics artefacts	
E20	1A	1A	3	Total		Total	37	Total
G22	1A	1A	1	10		5	94	180
F23	1A	1A	3				11	
I26	1A	1A	1		3		29	
J28	1A	1A	1		2		9	
G33	1A	1A	1					
J26	1A	1A-GL	12	Total	37	Total	35	Total
J27	1A	1A-GL	1	13	6	43	27	62
J26	1A	1A-KB	2	Total			38	Total
J26	1A	1A-GN	1	3			6	44
F26	T		1	Total				Total
K24	1A or T	2009 us 61	1	3			4	4
F29	bioturbation		1					
D43	Z INF	Z6/Z4	22	22			1	1
		Total	51		48		291	

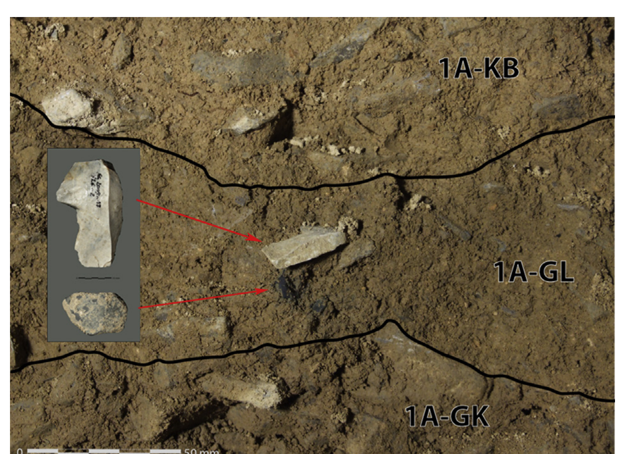

Fig. 11. Longitudinal sedimentary profile inside Square J26: a flint flake (Sc-2009-18-2) and a fragment of BPS (Sc-2009-18-3) are nearly in contact in the Layer 1A-GL. Inset shows the same objects after they were excavated.

found in the Sedimentary Unit T, which contains reworked lithic artefacts from the subjacent Layer 1A-GL. In Square K24, one fragment of BPS (Sc-2009-359-9) and four flint artefacts were found in a layer (not listed in Fig. 5) also containing reworked material from 1A-GL. Finally, one fragment of BPS (Sc-1989-123-1) was recovered from the bioturbated sediment of a burrow (Table 4).

6.1.2. Sedimentary Unit Z-INF

Towards the back of the cave, in the aven sequence approximately 100 flint, quartz, and quartzite artefacts have been found at the boundary between layers Z4 and Z6, as well as the base of Layer Z4 (Fig. 5B). In Square D43 (Fig. 4B), at the boundary between layers Z6 and Z4, a cluster of 22 new fragments of BPS were found adjacent to each other in a 0.25 m^2 area (Table 1), in close proximity to a single flint flake (Table 4). The ~100 lithic artefacts from that area of the cave are very similar petrographically and technologically to the lithic assemblage from Unit 1A.

Combined analysis of the assemblages from the entrance sequence (sedimentary units 1A and T) and the aven sequence (Sedimentary Unit Z-INF) yielded a refit between two quartzite flakes, demonstrating the contemporaneity of the two occupations. Therefore, the two groups of objects were deposited at the same time: one on the cave terrace (and/or at the entrance of the cave), where Neandertals produced lithic debitage, used bones as fuel, and manipulated the BPS; and another towards the back of the cave, where a small amount of debitage was also produced in association with the handling of the BPS (Bonjean et al., 2011).

With the exception of the sample exhumed from a bioturbated context (Sc-1989-123-1), all fragments of BPS were collected from well-understood sedimentary contexts that spatially relate them directly to lithic artefacts and often to burned bones. The archaeological evidence therefore indicates that all BPS samples are strictly associated with the lithic assemblage of sedimentary units 1A and Z-INF, which correspond to the second main Neandertal occupation of Scladina Cave. The chronology of this assemblage is understood with high precision (Pirson et al., 2012). The oldest layer in which the objects were found is 1A-GL (Fig. 5A), which dates between 40,210 + 400/−350 BP (Layer 1A-GK; Gr-32635; Pirson, 2007) and 37,300 + 370/-320 BP (Layer T-GV; GrA-32633; Pirson, 2007).

6.2. Evidence against natural transportation of the BPS to Scladina Cave

We have clearly demonstrated that the geological origins of this highly siliceous friable graphitic siltstone can be attributed to the Upper Cambrian formation at Franquenies. The absence of this formation near Scladina Cave excludes the possibility of the incorporation of the BPS through natural sedimentary processes during the site's formation.

The outcrop of Franquenies siltstone (at an elevation of 80 m above mean sea level: AMSL) is located in the basin of the Scheldt River (flowing north), while Scladina Cave (at an altitude of 137.7 m AMSL) is located in the Meuse Basin (flowing east). These two basins are separated by the Hesbaye plateau at an elevation between 150 and 210 m AMSL. As the crow flies, these two locations (Scladina and Franquenies) are separated by 40 km. From a hydrographical point of view, the absence of rivers connecting Franquenies and Scladina excludes the possibility of natural transport of the material. Furthermore, the fragility of the BPS means that it would likely not survive such a hydrological transport in any case.

6.3. Prehistoric interest in the BPS and intent of use

At Scladina Cave, the importation of raw lithic material from old fluviatile terraces and the alluvial plain of the Meuse River was documented by the flint, quartz, and quartzite tools and fragments uncovered from the sedimentary units 1A, T, and Z-INF. The lithic debitage is the best documented activity at the site. The presence of 194 burned bone fragments also illustrates another facet of the domestic activities that occurred at Scladina, which involved the complete exploitation of these osseous remains by Neandertals. The demonstration of an anthropogenic importation of the BPS from afar expands the range of Neandertal practices at the site. The transport of the pigments from the Franquenies area (over a distance of 40 km) suggests a clear intention by Neandertals to use this material, even if no evidence of use has yet been discovered at Scladina. Furthermore, it illustrates extensive use of the landscape and transportation of materials over long distances prior to the Upper Palaeolithic period (Feblot-Augustins, 1997).

The staining and colouring properties of the BPS make it very suitable as pigment. Even though their exact use is unknown in the Middle Palaeolithic context, pigments are often interpreted as having been used for personal decoration. The friability of the BPS would have allowed for it to be used without any preparation. Simply touching it is enough to obtain the colouring effect. Interestingly, use of the Cambrian black pigment of the Brabant Massif crosses the millennia: the quarry of Franquenies (presently L: 60 m; W: 30 m; H: 6 m) was exploited as black natural pigment before 1836 and until the beginning of the 20th century (unpublished archives of the Geological Survey of Belgium, Mourlon and Malaise, 1911) inducing the disappearance of the original outcrop.

7. Conclusions

In this work, the Black Pigment of Sclayn (BPS), recovered from Scladina Cave, was physically and chemically analysed. Combined petrographic, petrologic, and geochemical data identified this material as a highly siliceous and friable graphitic siltstone. Determining the degree of thermal maturation of organic matter by Raman spectroscopy proved to be the ideal tool for distinguishing between the different potential geological sources for BPS that have similar appearances and densities. This analysis unequivocally demonstrated the relationship between the BPS and geological material from Franquenies. The material from Franquenies is limited to a single geological unit with only rare outcrops. Given the homogeneity of the BPS, it is likely that all the fragments found in Scladina Cave are from the same outcrop.

The anthropogenic origin of the BPS recovered at Scladina is supported by three lines of evidence: lithologic, orohydrographic, and stratigraphic. This material is not naturally present in the immediate vicinity of Scladina - its only documented outcrop is situated approximately 40 km northwest of the cave. The absence of rivers connecting Scladina and Franquenies excludes the possibility of natural transport. The stratigraphic precision achieved during excavation at Scladina allows us to demonstrate that the recovered BPS fragments are clearly associated with lithic artefacts and burned bones linked with Neandertal occupation. It also indicates that the BPS is systematically absent from other sedimentary units.

Our results, therefore, document for the first time a type of black pigment collected by Neandertals around 40,000–37,000 BP that is not a manganese oxide, but carbonaceous material. The BPS illustrates the exploitation of a large geographical area by Neandertals with the transportation of materials across long distances. It also currently represents the most northwestern examples in Europe of the use of black pigment during the Middle Palaeolithic.

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