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The unique laurel-leaf points of Volgu document long-distance transport of raw materials in the Solutrean

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Abstract

The Upper Palaeolithic Solutrean culture that coincided with the last glacial maximum has become famous for documenting an increasing investment of time and effort in the production of tools. However, Solutrean lithic assemblages predominantly document local procurement of flint and only in rare cases, stones were transported over distances above 100 km. The perhaps most remarkable Solutrean artefacts are the large bifacial laurel-leaf points of Volgu. Some studies on the points suggested long-distance transport, proposing multiple raw material locations in the > 170 km distant Paris Basin. These findings were not based on physical or chemical measurements but rather on evaluations of macro- and microscopically visible features at the surface of the flint. In this study, we aim to verify previously made propositions on the Volgu points' origin with an archaeometric technique. For this, we apply reflectance infrared spectroscopy, a method that relies on identifying differences in the crystallographic properties of flint. We compare eight of the Volgu laurel-leaf points with five regions of Upper Cretaceous flint deposits in France and Belgium. We found that the Volgu points' flint is most similar to flint from the south-eastern Paris Basin in terms of its crystallography (identifying a region between 170 and 250 km from Volgu). Our findings provide a reproducible line of evidence for the long-distance procurement of flint to produce exceptional artefacts in the Solutrean. Our study is the first application of this method to flint sourcing in a European context. It has therefore also implications for future provenance studies on other archaeological sites in France.

Keywords *Feuilles de laurier* · Raw material procurement · Hunter-gatherer mobility · Lithic technology · Provenance analysis

Introduction

The western European Solutrean culture (~ 25 to 23 ka cal. BP) was contemporary with the last glacial maximum. It has become famous among archaeologists for its new lithic industries, documenting an increasing investment of time and effort in the production of tools (Smith 1966; Thevenot 2019b). Heat treatment of stone raw materials (see: Schmidt et al. 2018; Schmidt and Morala 2018) and pressure flaking (Walter et al. 2013) are two examples of the willingness to put more effort into tool making in the Solutrean. The stone tool type best illustrating this comprises thinly crafted foliate points, called laurel-leaf points, or *feuilles de laurier* (see for example Aubry et al. 2009). Laurel-leaf points are bifacial points of varying size, mostly crafted from flint or chert, with symmetrical leaf shape. The perhaps most impressive laurel-leaf points are those discovered in 1874 in a cache near the township of Volgu (Chabas 1874). During the excavation of the cache, no stratigraphic sequence was recorded, but the artefacts (their exact number is debated but 16 points are known today) have been associated with the Solutrean techno-complex based on technological arguments (Cabrol 1940; Chabas 1874; Thevenot 2019a), i.e. after comparisons with laurel-leaf points found at other Solutrean sites such as Solutré or Laugerie-Haute (Chabas 1874; Smith 1966). Fifteen artefacts are curated in museums today: two of the points are made from a dark black-greyish flint and the other points are

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of a lighter brown-yellowish colour. The size and quality of these artefacts, together with the a priori intentional deposition of the cache, have put the Volgu laurel-leaf points into the spotlight of archaeological research for over a decade.

For example, several hypotheses on the provenance of the flint raw materials used to make the Volgu points have been proposed (Cabrol 1940; Chabas 1874; Jost 1927; Mortillet 1921). In the initial report on the Volgu discovery, Chabas (1874) noted that although secondary deposits of flint nodules can be found in the proximity of Volgu, these local flints are different from the Volgu points in colour, texture and composition. Jost (1927) found that the flint of the Volgu points formed in chalk deposits, leading to subsequent suggestions that the Volgu raw materials can be matched with flint from the Upper Cretaceous strata of the Paris Basin (Aubry et al. 2009) or with flint that can be found in the surroundings of Digoin (Cabrol 1940). Later, Aubry et al. (2003) analysed 15 of the Volgu points microscopically to investigate their microfacies and microfossil content. They argued that twelve of the lighter yellow–brown points bear strong resemblance with flint nodules from near the town Gien (in the south-eastern Paris Basin). The two darker specimens were described to resemble flint samples originating from an outcrop in La Celle-Saint-Cyr (~ 60 km to the northeast of Gien). In a more recent study, Affölter (2019) re-analysed 13 Volgu points (all curated at the Musée Denon in Chalon-sur-Saône) microscopically. She found that the microfossils in all points are characteristic of Upper Cretaceous flint. It was further proposed that all analysed Volgu points were made from flint that originated from different locales in the southern to eastern Paris Basin (with two exceptions: points N°2 and N°13 and points N°7 and N°12 were proposed to come from the same locals, accession numbers as in Affolter (2019), i.e. points curated at the Musée Denon are numbered from N°1–13). The proposed raw material locations are scattered over a distance of ~ 250 km. One potential problem arising from this (rather precise) assignment of the Volgu points' origin is that it was based on the comparison of features in the Volgu flints and reference pieces from the personal reference collection of the analyst. Quantitative microscopic criteria leading to the assignment of the flint's geographical origin were not published along with the results (Affolter 2019).

In this study, we aim to verify the hypotheses proposed on grounds of the Volgu points' microscopic analyses. For this, we use reflectance infrared spectroscopy, and a method similar to the one proposed by Parish (2013), to investigate whether eight of the Volgu points curated at the Musée Denon in Chalon-sur-Saône are more similar to flint from the Paris Basin than to other flint types that can be found in the surroundings of Volgu. We do this because we hope to verify and perhaps refine the currently available provenance model of the Volgu points, using a more transparent and reproducible method.

Similar approaches to the origin of flint and chert, using infrared spectroscopy, have become popular in archaeological science over the past two decades (e.g. Hawkins et al. 2008; Long et al. 2001; Parish 2013, 2016; Parish et al. 2013). The method has not been explained in terms of the underlying mechanisms that allow to discriminate different flint and chert types, but several studies (Parish 2011; e.g. Parish 2013, 2016; Parish and Finn 2016; Parish et al. 2013) have yielded promising results allowing the identification of specific chert types among other regional outcrops in North America. In this paper, we therefore first attempt to provide a comprehensive explanation of the principle of provenance analyses using reflectance (mid-)infrared spectroscopy. In the second step, we apply the method to the provenance analysis of the Volgu points.

Theoretical background of the method

Chemically and bio-chemically formed silica rocks like flint or chert (henceforth called only flint for simplicity; all samples analysed in this study are flint) are mainly composed of quartz crystals present as chalcedony and micro-quartz (Cayeux 1929). Chalcedony appears to be fibrous in thin sections (Michel-Levy and Munier-Chalmas 1892) because it is composed of ~ 50–100 nm large quartz crystals (Rios et al. 2001) that maintain the orientation of their crystallographic c-axes along the fibre axes (Flörke et al. 1991). The two most common orientations of quartz crystals in chalcedony are length-fast, where the crystals' c-axes are perpendicular to the fibre axes, and length-slow, where the c-axes lie parallel to the fibre axes (see for example Cady et al. 1998). A schematic representation of length-fast chalcedony, the most common form of chalcedony in flint, is shown in Fig. 1a. From this illustration, it can be seen that the crystals' c-axes are twisted around the fibre axes (for an explanation of this phenomenon see for example: Heaney 1993). Figure 1b shows that a typical sample of flint may contain chalcedony fibres of different lengths. The micrograph also shows darker zones where fibres cannot be recognised. It has been shown (Dejoie et al. 2015) that quartz crystals are not oriented preferentially in zones where fibres cannot be recognised (like in the darker zones in Fig. 1b). Thus, the nanometre-sized quartz crystals of flint may be oriented either preferentially in chalcedony fibres or randomly in zones outside of chalcedony fibres. Additionally, some flint samples contain quartz clasts or zones where randomly oriented quartz crystals are large enough to be seen with a petrographic microscope. What are the implications of this for reflectance infrared spectroscopy? Fig. 1c shows three reflectance spectra acquired on a
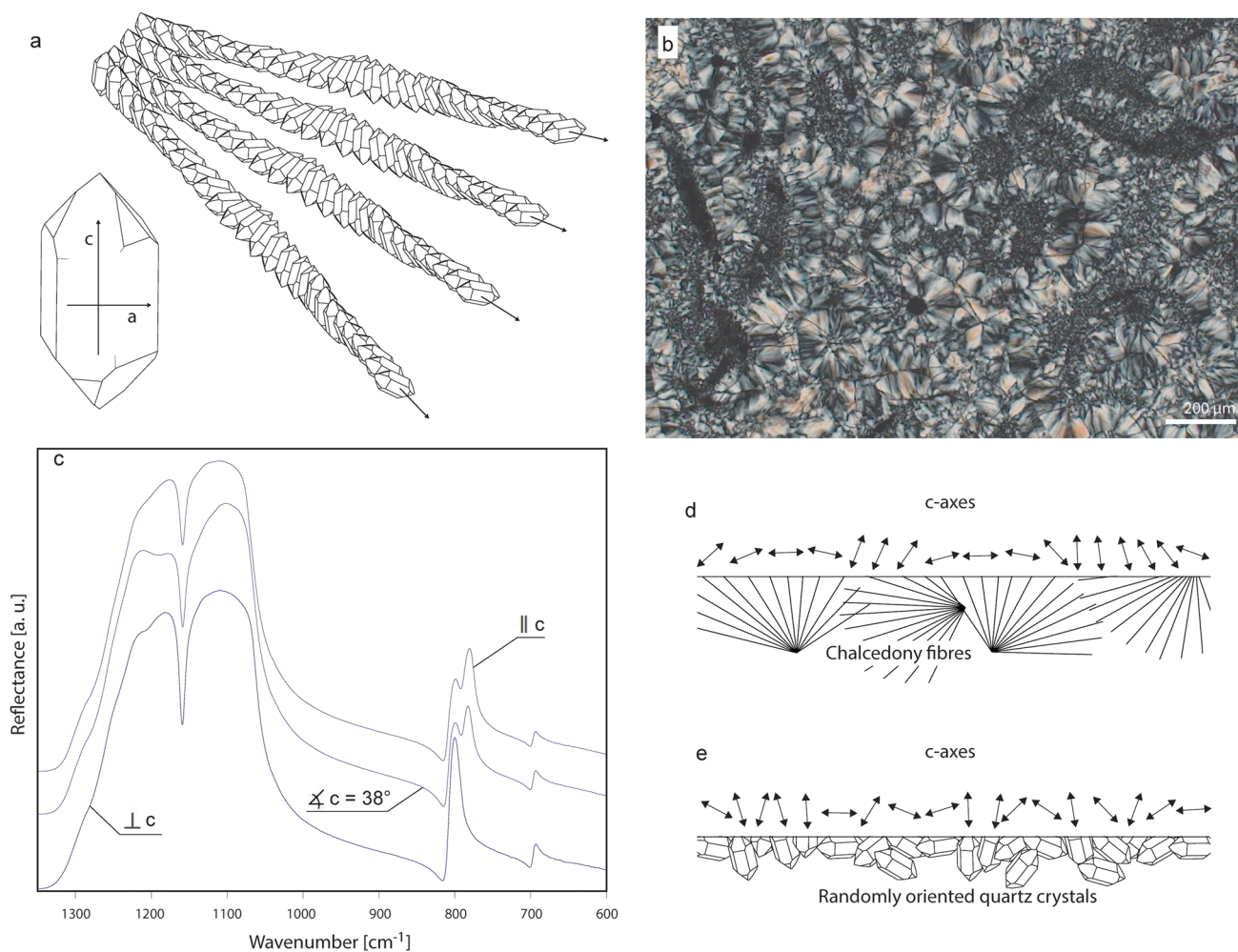
Fig. 1 Crystallographic properties of flint leading to differences in infrared reflectance spectra. **a** Schematic illustration of the crystal orientation in length-fast chalcedony. Note that crystals are oriented on fibre axes with their *c*-axes perpendicular to the fibre axes. The idealised quartz crystal in the lower left of **a** is shown with two pyramids to better visualise the orientations of *c*-axes. **b** Thin section micrograph of a typical flint sample (in this case from the Aquitaine Basin), showing the presence of fibrous chalcedony and zones where crystal orientation is random (darker zones). **c** Unpolarised near-normal incidence reflectance spectra of a quartz single crystal acquired with three different inclination angles to the crystal's *c*-axis. Note that all three spectra show differences in terms of their reflectance bands. **d** Schematic representation of a section cut perpendicular to the surface of a flint sample made of chalcedony fibres. **e** Schematic representation of a section cut perpendicular to the surface of a flint sample made of micro-quartz grains. Double-headed arrows schematically show the orientation of the quartz *c*-axes with respect to the sample surfaces

quartz single crystal (showing the spectral range analysed in this paper). All three spectra were acquired on the same crystal but on different surfaces that have varying inclinations to the crystal's *c*-axis. These spectra show differences in the number of bands present, the relative band heights and the shape of the reflection bands. These differences are a function of the inclination angle of the surface, on which the spectra were acquired, relative to the quartz crystal's *c*-axis (these phenomena are explained in detail in Sato 1965; Spitzer and Kleinman 1961). The implications of this are that infrared reflectance spectra acquired on flint samples in which quartz crystals are oriented in a particular way may be different from spectra

recorded on flint samples in which crystal orientation is completely random. This is so because specific crystal orientations, as in chalcedony fibres for example, cause certain alignments of the quartz *c*-axes (with respect to a surface on which reflectance spectra are acquired) to occur more or less often. Figure 1d, e show two schematic representations of quartz crystals in two different flint samples. The upper sample is made of chalcedony fibres that are arranged in fans (corresponding to spherulites in a 3D model). The lower sample is made of micro-quartz crystals that are oriented randomly with respect to the surface (the crystals are not drawn to scale for better readability). Double-headed arrows schematically show

the *c*-axis inclination at specific places on the surfaces. From this comparison, it can be appreciated that similar *c*-axis orientations are present across larger areas on the surface of chalcedony, as compared with the surface of randomly oriented quartz. The exact orientation pattern is a function of the type of chalcedony and the mean fibre length. Thus, infrared reflectance spectra acquired on flint can be expected to be slightly different, depending on whether there are more or fewer zones with chalcedony fibres and longer or shorter fibres. Other factors that may influence the shape of reflection bands are the presence or absence of different types of chalcedony (length-fast or length-slow), hydroxylation (for the resulting spectral differences see: Schmidt and Fröhlich 2011) and crystal size. In other words, the varying crystallographic properties of quartz in different flint samples cause different features in the fingerprint region of the quartz infrared spectrum. The presence of phases other than quartz (that have a different reflectance spectrum) can be expected to cause further differences in the spectra acquired on flint but, even if only quartz in present, infrared spectra can be used to differentiate between flint samples based on differences in their crystallography. Thus, the method we use here is based on making statements on the similarity or difference of flint samples in terms of their crystallographic and mineralogical properties (note that this is not the case for near-infrared spectra, as used in Parish (2011), but only for the mid-infrared range of the spectra as used here).

Methods and materials

Volgu laurel-leaf points

We selected eight of the Volgu laurel-leaf points curated at the Musée Denon in Chalon-sur-Saône. The selection included the two darker points (N°5 and N°10) and a random selection of six of the lighter yellowish-brown points (N°1–4, N°9, N°12). Five of these samples are shown in Fig. 2. During Affolter's (2019) study, these artefacts were washed with water. No additional sample preparation was therefore necessary.

Geological reference samples

We conducted four sampling campaigns in different regions, yielding Upper Cretaceous flint deposits, which surround Volgu geographically: the French Paris Basin, the Aquitaine Basin, the French Jura and the Mons Basin (Belgium) (see Fig. 3). The choice to include these four regions in our study was driven by Affolter's (2019) finding that micro-fossils in the Volgu points indicated an Upper Cretaceous origin of the raw materials. Sampling locations were identified based on geological maps issued by the *Bureau de recherches géologiques et minières* (BRGM) for outcrops in France and by the *Service géologique de Wallonie* for outcrops in Belgium. Within the Paris Basin, we sampled flint nodules from 14 outcrops, including all 9 localities previously proposed by Affolter (2019) to be the origins of the Volgu points'

Fig. 2 Photographs of five of the eight Volgu laurel-leaf points chosen for the analysis (left to right: 2011.0.12.4, 2011.0.12.5, 2011.0.12.9, 2011.0.12.10 and 2011.0.12.12). The labels in the figure refer to the short artefact ID, as referred to in this study for each point
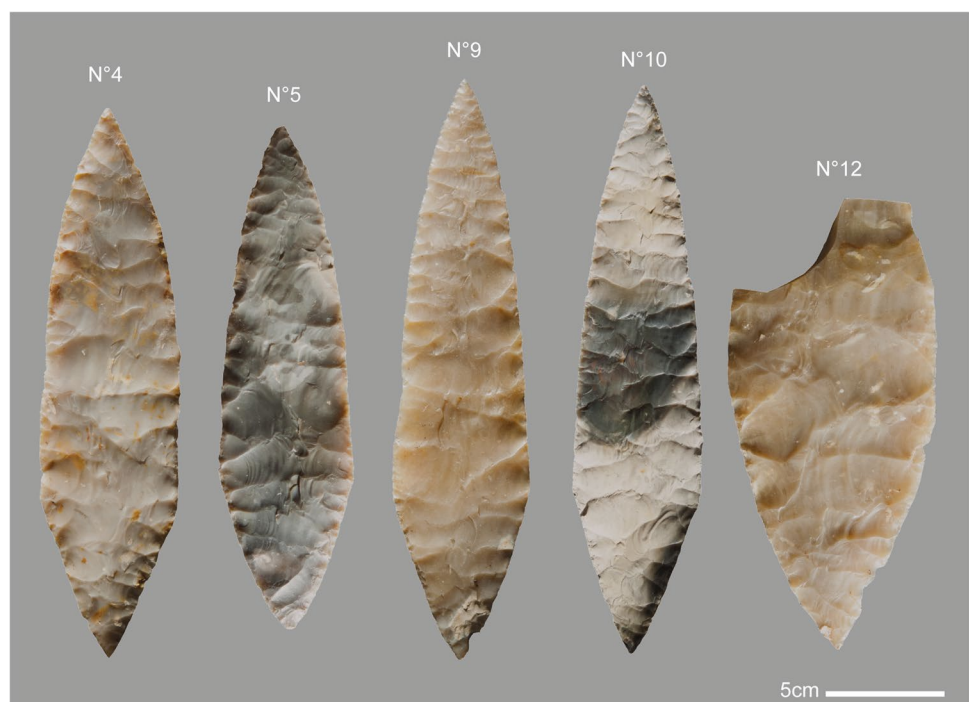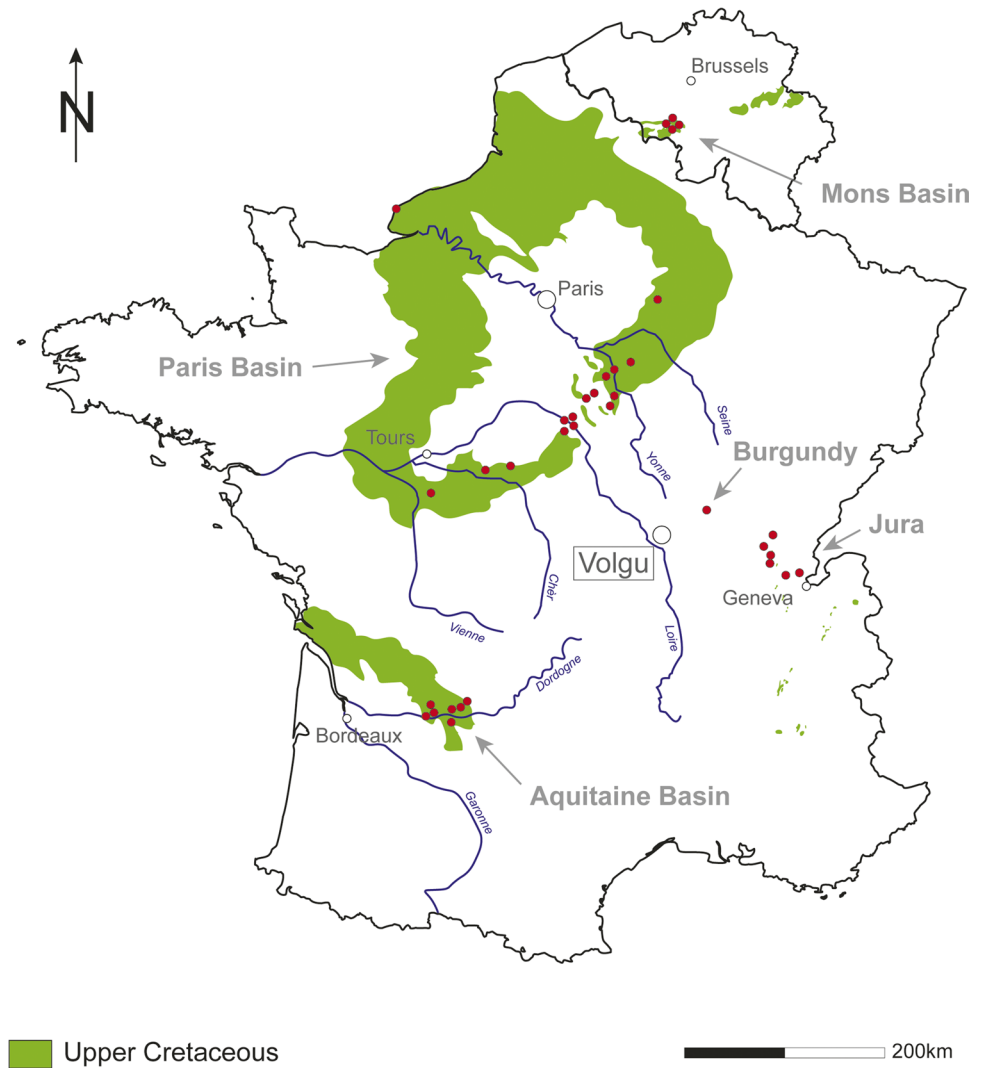
Fig. 3 Map of France and Belgium indicating the sampling regions with Upper Cretaceous deposits and the outcrop locations sampled for this study. Some of the outcrops are located very close to each other and are therefore summarised in one marker

▩ Upper Cretaceous   ▬▬▬▭▭▭ 200km

raw materials. The closest of these Paris Basin outcrops lies approximately 170 km from Volgu. Another 10 outcrops were sampled in the eastern part of the Aquitaine Basin. Our Aquitaine Basin outcrops lie approximately 300 km from Volgu. Another set of flint outcrops close to Volgu (~ 130 km) is located at the foot of the French Jura mountains. We collected flint from 9 outcrops in this area (our collection in this area was aided by works of: Affolter 2002; Affolter and Bressy 2008). We also collected flint from four localities in the Mons Basin in Belgium. Samples from eight additional locations were provided by one of us (PS). These include in situ samples from the north-western (near Étretat) and south-western extremities (in the Touraine region) of the Paris Basin, five localities with secondary flint deposits of the Aquitaine Basin as well as Upper Cretaceous flint samples from a secondary (ex situ) alterite horizon west of the town of Chalon-sur-Saône (our closest reference samples to Volgu at ~ 60 km). We included the former two groups in our Paris Basin sample and henceforth call the samples from

near Chalon-sur-Saône, the Burgundy sample (the Tertiary Burgundy formation was included in this study because it contains part of the insoluble part of altered Upper Cretaceous deposits, i.e. Upper Cretaceous flint nodules (Rué 2000). Thus, there are five sampling regions in total that are compared with the Volgu points: the Paris Basin, Jura, Aquitaine Basin, Mons Basin and Burgundy. Our sampling campaigns yielded flint samples from 45 locations in total (see Table 1; for a detailed list see Table S1 of the supplementary material) and include all major Upper Cretaceous flint bearing regions where in situ chalk deposits can be found and that geographically surround Volgu. There is another region in the northeast of the town of Dijon that may potentially contain Upper Cretaceous flint outcrops (near the towns of Magny-Saint-Médard and Velloreille-lès-Choye, approximately 140 km from Volgu). We systematically surveyed this region but were not able to locate flint samples. We also considered sampling flint from the surroundings of Digoin (~ 5 km south of Volgu) as initially proposed by

Table 1 List of analyses per region and the number of outcrops sampled in these regions. Note that the number of outcrops is not applicable to our Burgundy sample because these samples originate from a single secondary alterite deposit that stretches over an area of ~40 km

Region of Upper Cretaceous deposits	Number of outcrops sampled	Number of spectra
Paris Basin	16	362
Aquitaine Basin	15	268
Jura	9	202
Mons Basin	4	55
Burgundy	n/a	35
Total	45	922

Cabrol (1940) but found no Upper Cretaceous outcrops in the region indicated by the local geological maps. All flint nodules were knapped to produce > 20 flakes per outcrop if possible, so that fresh flake surfaces could be used for spectral measurement. This means that, in some cases, multiple flakes were knapped from the same flint nodule which allowed us to assess the variability within the same geological reference sample. This protocol resulted in a total number of 922 reference samples.

Reflectance infrared spectroscopy

We used a portable Agilent Cary 630 FTIR infrared spectrometer with an attachable reflectance module, allowing for 10° specular reflectance measurements, to record infrared spectra on archaeological and geological samples (see Fig. 4a). Spectra were recorded in the mid-infrared region between 4000 and 400 cm^{-1}, and resolution was set to 4 cm^{-1} (which actually resulted in a spectral point taken at every 3.73 cm^{-1} by the spectrometer). For each spectrum, 360 single scans were repeated and averaged to obtain spectra with a suitable signal-to-noise ratio. Reflectance values in percent were calibrated with a gold mirror and the instrument settings remained the same for the spectral measurement of all samples. The eight Volgu points were analysed at the Musée Denon in Chalon-sur-Saône. Spectra were measured at ten different locations on both sides of each Volgu point to account for possible heterogeneities within the artefacts. In total, 80 spectra were acquired from the Volgu points. We collected spectra on all 922 flakes produced from geological reference samples (the number of spectra per region is summarised in Table 1). We only measured freshly knapped surfaces on geological samples to avoid contamination by surface alteration or dirt.

Spectral processing

We included the spectral range between 1300 and 600 cm^{-1} in our study (this region lies in the fingerprint region of the quartz spectrum where quartz lattice stretching and bending vibrations occur, see Fig. 4b). The choice of this region was guided by two criteria: no lattice bands occur at higher wavenumbers than 1300 cm^{-1} and the signal/noise ratio produced by our spectrometer is generally very poor at wavenumbers lower than 600 cm^{-1}. To reduce background noise in the spectra, we applied spectral smoothing over five points on the spectra. After this, all spectra were normalised in the
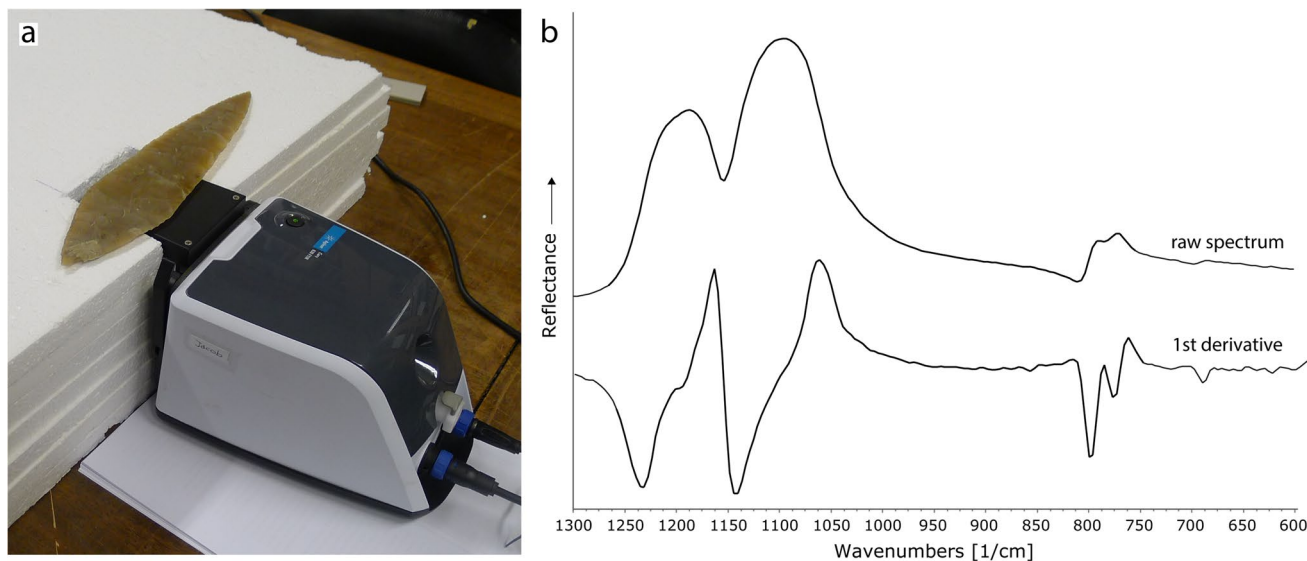

Fig. 4 Portable infrared spectrometer used for our analyses and resulting spectra. **a** The portable Agilent Cary 630 spectrometer measuring one of the Volgu points in the Musée Denon. **b** One raw reflectance spectrum (top) in the spectral range included in our analyses and one first derivative spectrum calculated from the reflectance spectrum (bottom)

sense that their highest points were set to the same maximum value and their baseline to the same minimum value on an ordinate that now reports arbitrary units. This was done to correct for differences in signal strength that might result from the uneven and unstandardized sample surfaces. After this, the first derivative spectrum was calculated from all spectra (see Fig. 4b). This derivative spectrum reports the evolution of the reflectance spectra's slope as a function of wavenumber and allows to compare the relative shape differences between spectra. The same spectral processing protocol was applied to all spectra. Every ten spectra acquired one Volgu point were averaged to produce a single spectrum per artefact.

Statistical analysis

To treat our spectral data, we applied principal component analysis (PCA) and linear discriminant analysis (LDA) to all spectral points in the spectral region between 1300 and 600 cm^{-1} (189 spectral points; the intensity of each of these points on the derivative spectra's abscissa were set as variables). To verify the accuracy of the classification of our

dataset, we performed accuracy assessment tests on five predefined groups of samples from the four geological regions and Burgundy (for this, the Volgu points were excluded from the dataset). For these accuracy tests, three LDAs were performed with a 10%, 20% and 30% random sample subset for which the grouping assignment was removed, to see if the method would correctly assign them to their respective regional group.

Results

Can we differentiate between Volgu points based on their crystallography?

PCA may be able to investigate whether the eight analysed Volgu points are different in terms of their crystallographic properties. If ten respective spectral measurements cluster together for each artefact in a PCA plot, and if these clusters are separated in space, it may be concluded that each point is made from a different type of flint. Figure 5 shows such a PCA plot. In this plot, the ten measurements representing

Fig. 5 PCA score plot of the 80 spectral measurements taken on the Volgu laurel-leaf points (in the spectral region between 1300 and 600 cm^{-1}). Each artefact is represented by a distinct marker and their distribution highlighted in a different colour
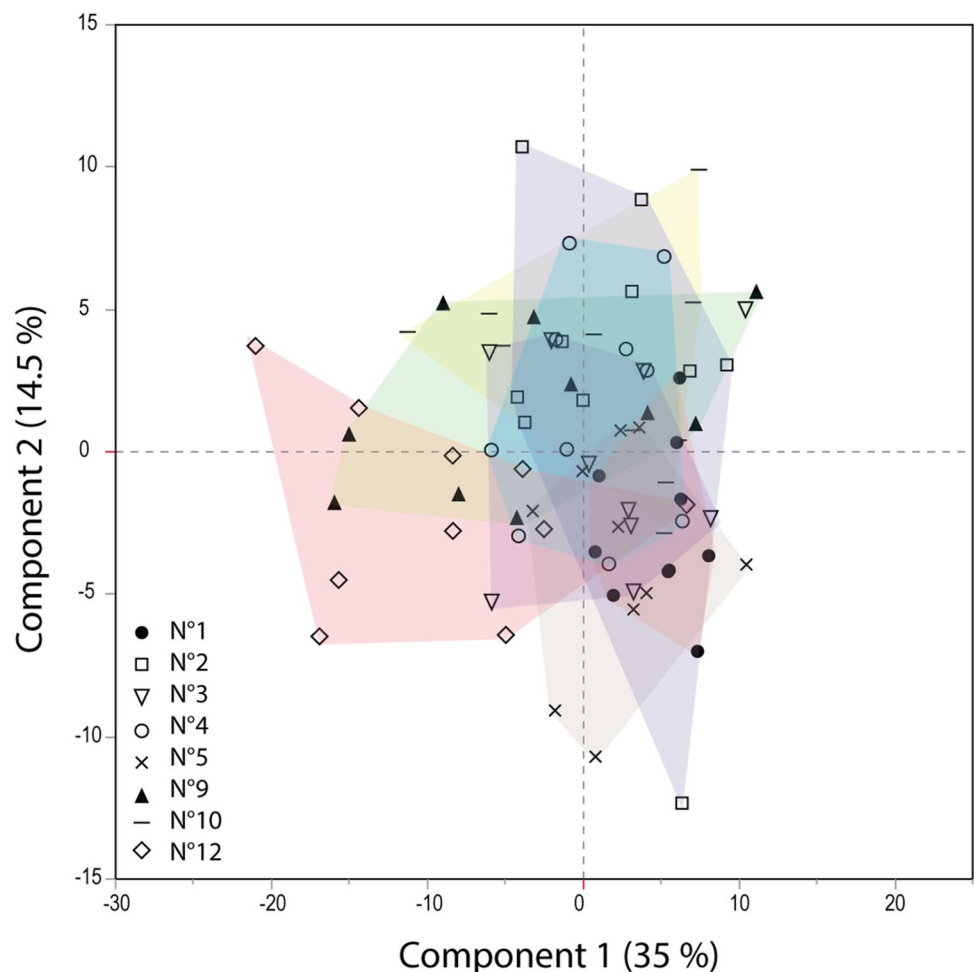
each Volgu point overlap with the measurements of the other points in all cases. There is no distinct cluster observable for any of the Volgu points, i.e. PCA is not capable of separating the artefacts based on differences in their reflectance spectra. Even a LDA performed on this dataset, i.e. defining every 10 measurements of a Volgu point as a group (thus, 8 predefined groups), and removing the grouping assignment for one measurement per Volgu point, cannot distinguish between different groups. There is a misclassification of seven out of the eight measurements for each group. Thus, no differentiation between Volgu points is possible based on their crystallographic properties. It remains unclear whether this is because the flint used to manufacture all eight Volgu points originates from the same source or because the points' raw materials originate from different sources that are similar to each other.

Provenance of the Volgu flint

This part of the analysis is based on a PCA plot of reference samples from all five sampling regions—Paris Basin ($n = 370$), Aquitaine Basin ($n = 293$), Mons Basin ($n = 55$), Jura ($n = 202$) and Burgundy ($n = 35$)—compared with the averaged measurements of the eight Volgu points. Figure 6a shows such a PCA plot. In this plot, most of the samples from the Aquitaine Basin, Mons Basin, Jura and Burgundy largely overlap, although some samples plot outside of this scatter. The Aquitaine Basin samples seem to scatter across a larger area than the Jura samples. Samples from the Paris Basin form a distinct cluster, only marginally overlapping with the samples from the other regions. The averaged measurements of the eight Volgu points overlap almost exclusively with the Paris Basin samples in this plot. The only exception is Volgu point N°12, which can visually not be associated with only one particular region. PCA, therefore, suggests that the majority of the Volgu points are more similar (in terms of their crystallography) to the Paris Basin reference samples than to samples from the other regions included in the analysis. LDA was performed on this dataset, including all five reference sample groups and the eight averaged Volgu points that were included without a grouping variable. The LDA plot (Fig. 6b) allows to distinguish three groups. The Paris Basin and the Jura samples are clearly separated from the Aquitaine, Burgundy and Mons Basins that all three cannot be separated (i.e. these three overlap almost entirely). All Volgu points cluster together with the Paris Basin samples and lie within the 50% confidence ellipse of the group cluster. Probabilities of predicted group membership, as calculated by the LDA, are summarised in Table 2. These percentages support the similarity of the Volgu points to the Paris Basin reference samples (the probability that the artefacts belong to the Paris Basin group lies between 91 and 98% for all eight artefacts). Thus, all eight Volgu points are most similar to reference samples coming from the Paris basin in terms of their crystallographic properties.
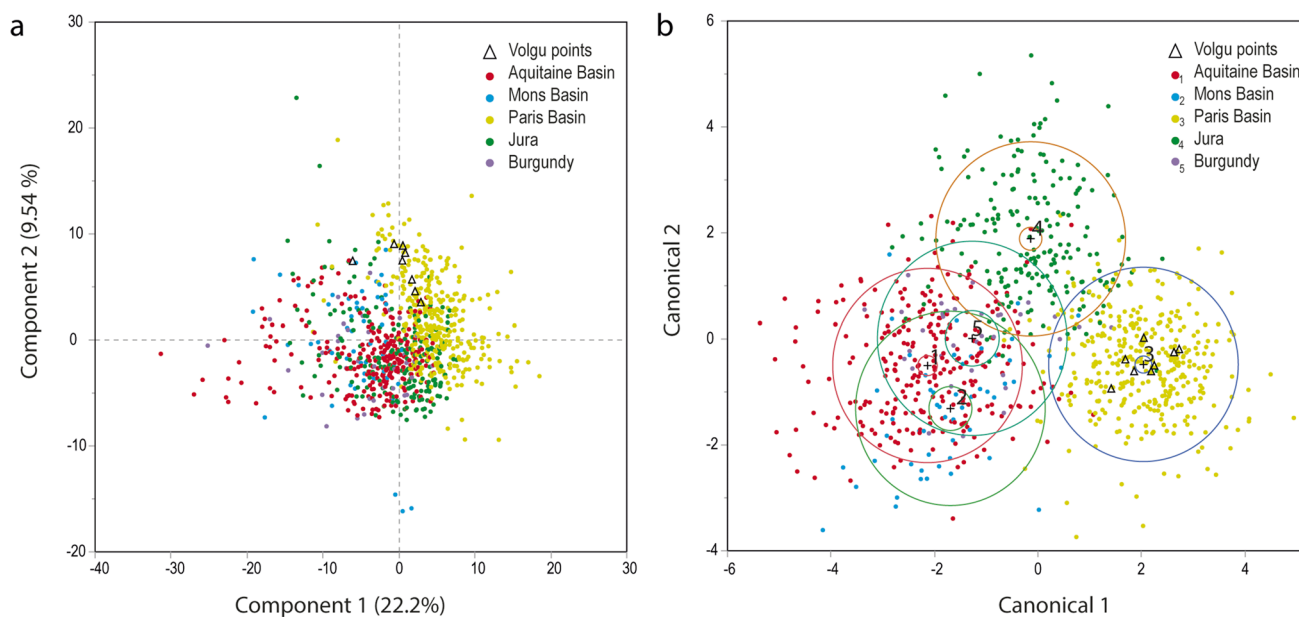

Fig. 6 Plots of the five sample groups and the Volgu points (in the spectral region between 1300 and 600 cm^{-1}). **a** PCA score plot of the sampling regions and the averaged measurements of the eight Volgu points. **b** Canonical plot of the sampling regions as predefined groups and the averaged measurements of the Volgu points included as unknown variables; the cross markers indicate the group mean, the small ellipses represent the 95% confidence interval for each group mean and the large ellipses encompass 50% of the samples in each group

Table 2 Group membership prediction for the LDA shown in Fig. 6b

Volgu point	Aquitaine Basin	Mons Basin	Paris Basin	Jura	Burgundy
1	0.01	0.00	0.91	0.08	0.00
2	0.00	0.00	0.97	0.02	0.00
3	0.00	0.00	0.92	0.08	0.00
4	0.00	0.00	0.94	0.05	0.00
5	0.00	0.00	0.95	0.04	0.00
9	0.00	0.00	0.98	0.02	0.00
10	0.00	0.00	0.95	0.05	0.00
12	0.00	0.00	0.92	0.08	0.00

Can we refine the Volgu points' provenance within the Paris Basin?

To refine our provenance analysis within the Paris Basin, we performed PCA to test whether flint from one of the 16 sampled outcrops is more similar to the Volgu flint than the others. However, the variation within and between flints from the sampled locations is too great to allow a differentiation between the 16 sampled locations of the Paris Basin (see Fig. S1 of the supplementary material). This variation between, and within, each outcrop is comparable

to the variation between the Volgu points, and within each of the artefacts.

Another way to approach this question is by grouping Paris Basin outcrops into three subregions based on their geographic distribution (southeast, southwest and north). Figure 7a shows these subgroups. Figure 7b is a PCA plot of the reference samples from these three subregions and the eight averaged Volgu points. In this plot, the Volgu points plot together with reference samples from the south-western and northern parts of the Paris Basin. Samples from the south-western part of the Paris Basin plot in a different area (most of the samples plot in the grey field in Fig. 7b). Thus, the Volgu flint is more similar to flint from the southeast and the north of the Paris Basin than to flint from the south-west. Based on these results, our three sampling locations in the south-western Paris Basin are unlikely to represent the source of the flint used to manufacture the Volgu laurel-leaf points.

LDA accuracy assessment

The accuracy of group membership prediction was assessed by performing LDA with a random selection of a 10%, 20% and 30% subsample of all geological reference samples. Five groups were predefined, corresponding to the four sampling regions and the samples from Burgundy. The group
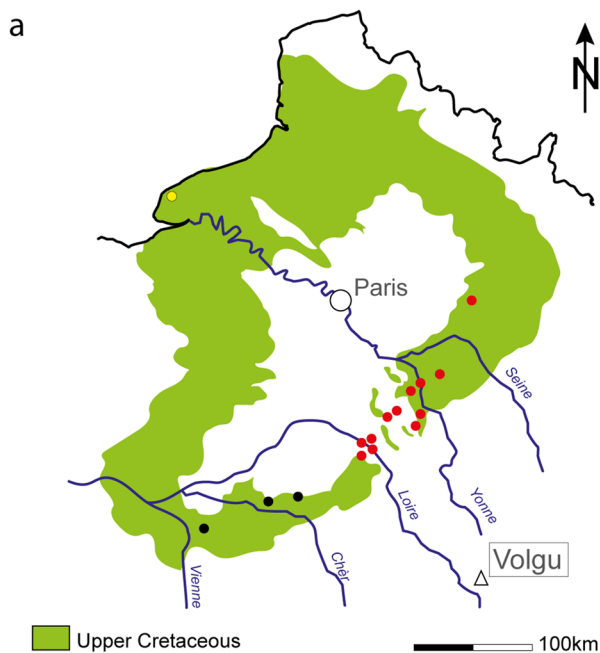

Fig. 7 Results of the analysis including the subregions within the Paris Basin. **a** Map indicating the outcrops samples within the Paris Basin; the outcrops are separated into three subregions based on their geographic location: the south-eastern Paris Basin, the south-western Paris Basin and the north-western Paris Basin (for legend, see
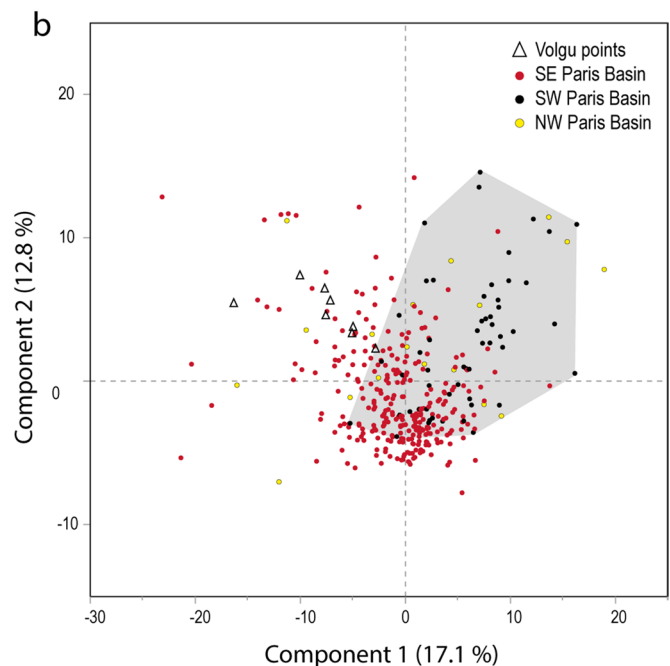
Fig. 6b). **b** PCA score plot of the three subregions shown in **a** and the averaged measurements of the eight Volgu points. The area highlighted in grey marks the distribution of the samples attributed to the south-western Paris Basin

assignment was deleted for the subsample to verify the group membership prediction. For the 10% subsample, 67 of the 92 unknown samples (~73%) were correctly classified to their actual group. For the 20% subsample, 125 out of 184 unknown samples (~87%) were correctly classified. For the 30% subsample, ~66% (182 out of 276) were correctly classified. Within each of the predefined groups, the accuracy of group membership prediction is highest for the Paris Basin samples with a correct classification between 82 and 97% for each of the three subsamples. The lowest accuracy of group membership prediction was noted for the Mons Basin samples (below 57% for all three subsamples) and the Burgundy samples (below 50% for all three subsamples). For the prediction percentages of all accuracy tests, see Table 3.

Discussion and conclusion

The quality and meaning of our data

Measurements acquired on the archaeological and geological reference samples show the typical fundamental vibrational bands of quartz. Although minor differences in these spectra occur that can be attributed to differences in quartz crystallite orientation (see the 'Theoretical background of the method' section), the spectra cannot be used to understand this phenomenon. To our knowledge, it is not possible to identify the nature of all crystallographic differences between samples that the used method relies on (for one example where this is possible, see: Schmidt and Fröhlich 2011). This is so because most minute changes in infrared spectra of different flint samples have never been the subject of dedicated spectral refinement or dispersion analysis. This was done for quartz single crystals (Sato 1965) but not for micro-quartz or silica rocks. Nonetheless, these differences are real and measurable in different flint spectra. While we acknowledge that such black box approaches bear the risk of not providing a thorough sample characterisation, we nonetheless stress that they allow to make statements on the similarities and differences between samples. For now, this statement on similarity and dissimilarity must remain the frame in which this method is used.

We acquired ten individual spectra on each of the Volgu artefacts. This was done to evaluate the variation within each

Volgu point in terms of its spectral signature. Averaging ten measurements made on each artefact can be expected to result in a spectrum that is representative of the whole point, eliminating intra-sample heterogeneity.

Our main arguments are based on PCA plots, which highlight that the Volgu points are similar to the sample from the southeast of the Paris Basin. LDA supports these results, providing group membership probabilities. For these PCA and LDA analyses, we used a set of 189 spectral points as variables. Over a total of 922 reference samples and 8 Volgu points, this corresponds to a subject to items ratio of 5:1 (samples/variables). Although our overall number of samples can be expected to produce robust results, the subject to items ratio may be considered as low (see for ex: Osborne and Costello 2004). The variance expressed by the principal components of the PCA plot that includes all reference samples and the eight Volgu points are 22.2% (PC1) and 9.54% (PC2), which is lower than the variance observed when only plotting the eighty measurements of the Volgu points (here PC1 represents 35% and PC2 represents 14.5% of the variance; compare Fig. 5 and Fig. 6a). To verify the reliability of our PCA analyses and the robustness of our LDA analyses, we therefore conducted a supplementary test reducing the number of variables. For this, we made a PCA plot with a smaller set of 132 variables (representing wavenumbers 1250–760 cm^{-1}) producing a subject to items ratio of 7:1. The resulting plots showed similar results as our plot in Fig. 6 (see Fig. S2 of the supplementary material). To further increase the robustness, we made another PCA plot from the sixteen wavenumbers that we found to be most influential, in the sense that they lie parallel to PC1 or PC2 (producing a subject to items ratio of 59:1). The principal components represent a higher percentage of variance (PC1 37.8% and PC2 30.7%) between the samples, and the plot shows a cluster grouping similar to the plots made with the larger sets of variables (see Fig. S3 in the supplementary material). Thus, our PCA analyses conducted with the larger set of variables can most likely be regarded as robust.

The likelihood that our LDA predicts correct group assignments was tested by conducting accuracy tests on all five groups (as listed in Table 3). This showed higher accuracy for the Paris Basin (>82%), Aquitaine Basin (>48%) and Jura samples (>56%), but lower accuracy for the Burgundy (33–50%) and Mons Basin samples (0–57%). Due to

Table 3 List summarising the LDA accuracy tests

Random subsample (%)	Percentage of correct group membership prediction (%)					
	Total	Paris Basin	Aquitaine Basin	Jura	Mons Basin	Burgundy
10	73	98	62	65	0	33
20	68	89	48	57	57	44
30	66	83	56	62	38	50

the small sample size, both the Mons Basin and the Burgundy samples cannot be accurately recognised by LDA. As it stands, the comparison of these groups with the other regions should be regarded with caution. Still, the PCA including all five sampling regions (Fig. 6) showed that the Mons Basin and Burgundy samples can be clearly distinguished from the Paris Basin. Our results can therefore be regarded as accurate in terms of the similarity between the Volgu points and the Paris Basin.

Our attempt to refine the provenance of the Volgu points' flint within the Paris Basin included one subregion in the northern extremity of the Paris Basin (see Fig. 7). Due to the small sample size for this subregion, the results from this outcrop must be considered an indication only and demand to be verified with a larger sample.

Another consideration is whether the outcrops we sampled could, at one point in time, have yielded large enough flint pieces to produce the Volgu points. These artefacts comprise the largest Solutrean laurel-leaf points found to date. The shortest is N°7, measuring ~ 23 cm in length and the longest is N°1, measuring 35 cm in length (Thevenot 2019b). Affolter (2019) stated that in her study she only included flint from outcrops where nodules of sufficient size can be found. She also claimed that these outcrops were already accessible during the Solutrean. During our field campaigns, we sampled part of the flint in primary position at outcrops that are accessible today due to modern construction works (road cuts, etc.). Other outcrops were secondary deposits made available by agricultural activity or erosional processes where nodules can be picked up on the ground (fields, forest floors, etc.). We cannot attest to whether any of these exact outcrops were accessible during prehistoric times. We believe that it is impossible to know which sources were accessible in the Solutrean, as there is no mechanism to test the correctness of such a proposition. With respect to nodule sizes, we further stress that even if no large nodules can be found at some of the outcrops today, this was not necessarily true 20 ka ago, when other parts of the outcrops might have been accessible (in the case of primary outcrops) or before ploughing and other actions of machinery lead to fracturing (in the case of secondary deposits). We therefore do not believe that nodule size and current accessibility of flint nodules can be seen as a strong argument for specific locations as a raw material source. Similarities between samples in terms of their crystallographic properties, on the other hand, are based on specific formation conditions and therefore constitute a promising alternative to macroscopic and microscopic approaches. Our finding that flint from geographically close but genetically different outcrops like the Paris and Mons Basins (compare Baele et al. 2012 and Pomerol 1980) can be separated based on crystallography strengthens our argument that

their mid-infrared spectroscopic signature can be used for provenance analyses.

Methodological implications of our results for future provenance studies

Previous studies (e.g. Parish 2013, 2016; Parish et al., 2013) successfully applied infrared spectroscopy to source archaeological artefacts in North America. In Europe, Parish and Werra (2018) conducted discriminant analyses on spectral data to distinguish between different flint outcrops in the Holy Cross mountains in Poland. They did not attempt to match archaeological artefacts to these sources. Thus, our results are the first application of an infrared spectroscopic method to make statements on the provenance of flint used to make artefacts in a European context. Our study has implications for future provenance analyses in the regions we sampled during our field campaigns. Because flint from some of these regions differs in terms of its crystallographic signature, it is possible to identify the approximate provenance of flint from sites that lie between these regions (e.g. the Jura and the Paris Basin). We also found that, even though the Upper Cretaceous formations of the Paris and Mons Basins lie at distances closer than 40 km from each other, we were able to separate their flints based on the differences in their crystallography. Future studies on flint provenance in areas between two such regions may benefit from this finding, as simple statements that raw materials came from either one or the other region will be easy to make. In the case of the Mons and Paris Basins, for example, promising candidates for such studies are the sites Biache-Saint-Vaast in France (Tuffreau 1978) or Mesvin IV (Cahen 1984) and Maisières-Canal (Miller 2014) in Belgium.

Our results in the light of previous provenance hypotheses on the Volgu points' flint

At the time of discovery of the Volgu points, Chabas (1874) had already noted that nodules from secondary flint deposits in proximity of Volgu differ in colour and texture compared to the artefacts. Our results confirm this statement, by attesting crystallographic differences between our reference samples from Burgundy and the Volgu points. Aubry et al. (2003) sourced the majority of the Volgu points to one single outcrop in the south-eastern Paris Basin (near the town of Gien). Affolter (2019) refined this provenance statement and proposed that the flint of thirteen Volgu points came from nine distinct locations in the south-eastern Paris Basin. Aubry et al.'s (2003) and Affolter's (2019) results are based on the comparison between microfossil inclusions and the distribution of visible elements (such as grains and other features visible at the surface with a microscope) in Volgu points and geological reference materials. Our results are in

partial agreement with these findings. They support that the Volgu flint is most similar to the flint from the Paris Basin in terms of its crystallography. However, our study also shows that there are crystallographic differences between the subregions of the Paris Basin. We were able to exclude the outcrops in the south-western Paris Basin as possible raw material origins, which includes one outcrop near the town of Meusnes that was proposed by Affolter (2019): this is the location proposed to be the source of Volgu point N°6. As N°6 is one of the artefacts not included in our analysis, we cannot make statements on the correctness of Affolter's (2019) proposition. For the eight analysed Volgu points, however, we exclude the three locations sampled in the south-western Paris Basin as their source. Samples from the south-eastern Paris Basin are crystallographically too similar to allow their separation, and so, it is not possible to make more precise provenance statements about the Volgu points based on their crystallography.

Implications for our understanding of long-distance raw material procurement during the Solutrean

Our results show that the Volgu points, or the raw materials used for their manufacture, were transported over distances between 170 and 250 km. This is the case even though closer sources (Burgundy and the French Jura) were available. Raw material procurement over such long distances has been shown to occur in a variety of other chronological and geographical contexts. For example, silcrete was shown to be transported over more than 200 km during the Middle Stone Age in southern Africa (Nash et al. 2013; Nash et al. 2016). On the African continent, there are other examples of early long-distance transport of obsidian, which was procured from sources at > 160 km distance during the MSA (e.g. Blegen 2017; Negash and Shackley 2006). Thus, compared to African MSA evidence, the Volgu points cannot be understood to document an exceptional behaviour. In the context of the Solutrean, long-distance procurement of flint was proposed for the Portuguese site Côa Valley, with some raw material sources at > 150 km distance (Aubry et al. 2015). Tarriño et al. (2013) found that some of the flint discovered at the Solutrean site Altamira (Spain) originates from sources over 100 km away. Stone tools found at Las Caldas (Spain) demonstrate the largest distance covered to access a specific flint source, with some flint originating from outcrops at a distance of 380 km from the site (Corchon et al. 2013). Thus, it may be argued that the Volgu points constitute no exception compared to transport distances documented on the Iberian Peninsula. The Solutrean occupation in southern-western France, however, appears to rely on flint sourcing on a smaller geographical scale.

Morala (2017) and Schmidt and Morala (2020) propose local flint sources (< 10 km from the site) for most of the laurel-leaf points discovered at Laugerie-Haute. Aubry (2013) describes flint sourcing of up to 100 km for some Solutrean sites in the Massif Central. However, he also notes that most flint used for making artefacts discovered at Les Maîtreaux was procured from an outcrop in immediate proximity. In the light of this comparison with other French Solutrean sites, the minimum distance between Volgu and the source of the points' flint would appear to be clearly above average. However, for this comparison, it seems important to note that the Volgu points represent exceptional pieces in terms of their particularly large size, and symmetrical shape, that to date remain unique in their kind. Procuring exceptionally good raw materials for these pieces is yet another argument for the willingness to invest more effort in these pieces than in other lithic reductions. Thus, the Volgu points fall well within the raw material provenience scheme proposed for other French Solutrean sites where most flint was procured locally and only some selected materials, perhaps for the manufacture of exceptional pieces, were transported over long distances. The Volgu points are among the best examples for such exceptional pieces that justified the additional investment in raw material procurement.

Declarations

Conflict of interest The authors declare no competing interests.

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