

FIRST GEOCHEMICAL ‘FINGERPRINTING’ OF BALKAN AND PRUT FLINT FROM PALAEOOLITHIC ROMANIA: POTENTIALS, LIMITATIONS AND FUTURE DIRECTIONS*

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Long-distance raw material transfers across Romania prior to the Last Glacial Maximum have previously been inferred from either visual and/or petrographic observations of East Carpathian sites. We investigated the potential to ‘fingerprint’ flint from archaeological sites at Mitoc-Malu Galben and Bistricioara–Lutărie III in Eastern Romania, using in situ high-precision analyses of 28 major, minor and trace elements determined by laser ablation – inductively coupled plasma – mass spectrometry (LA–ICP–MS) in combination with multivariate statistical analysis. Our results suggest that geochemical analyses have the ability to distinguish between different geographical sources but are unable to positively associate flint artefacts from archaeological contexts to these geochemical groups. The mismatches of signatures between artefacts and geological materials, however, raise new questions and open unforeseen perspectives.

KEYWORDS: LA–ICP–MS, FLINT OR CHERT, GEOCHEMICAL SOURCING, UPPER PALAEOOLITHIC, ROMANIA, MOBILITY

INTRODUCTION

In Europe, the period between 32 and 27 ka uncal BP (36 000 and 30 000 years ago) witnessed a series of profound behavioural changes in human evolutionary history. This roughly coincides with the socio-economic change from the Aurignacian to Gravettian periods of the Early Upper Palaeolithic. The timing and nature of this behavioural change, during a period characterized by pronounced climatic variability, are debated due to the scarcity of Aurignacian and Gravettian

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assemblages with secure chronostratigraphic and environmental contexts (Haesaerts *et al.* 2003; Moreau 2016).

One of the most significant behavioural shifts from the Aurignacian to Gravettian periods concerns the organization of lithic raw material economies in association with variable blank production strategies. During both periods, hunter-gatherers implemented lithic raw material provisioning strategies according to anticipated future needs. However, an increased reliance on high-quality, more distant raw materials in lithic assemblages is claimed to be absent until the Gravettian period (Svoboda *et al.* 2000). This has been interpreted as the result of climatic deterioration leading towards the Last Glacial Maximum (LGM), which may have triggered greater mobility and more extended social networks to mitigate the risk of resource failure than among previous hominin populations (Gamble 1999; Svoboda *et al.* 2000).

The premise underlying chemistry-based provenance determination posits that the raw material source of an artefact can be successfully determined as long as between-source chemical differences exceed within-source differences (Weigand *et al.* 1977; Wilson and Pollard 2001; Glascock and Neff 2003). This ‘provenance postulate’ and its relevance for answering archaeological questions has been demonstrated with variable success since the 1970s, using a range of instrumental technologies (e.g., Sieveking *et al.* 1972; Luedtke 1978; Stockmans *et al.* 1981; Pollard and Heron 2008). Most of the techniques that have proven helpful in deriving useful chemical data for chert or flint are typically destructive and/or expensive (Shackley 2008). As a result, archaeologists frequently differentiate between raw material types based on visually observable properties (e.g., colour, cortex, texture and inclusions). However, cryptocrystalline quartz-rich lithic materials, such as chert or flint, are particularly prone to misidentification, given their low compositional variation and low trace element concentrations, as well as the possibility of strong visual similarities across geographically dispersed sources, or, alternatively, high heterogeneity within a single outcrop (e.g., Luedtke 1992; Speer 2014).

In Romania, research concerned with the characterization and provenance of siliceous raw materials from prehistoric sites is mostly petrographic in scope. Until 2000, only a handful of disparate and isolated studies have been published (Protopopescu-Pache and Mateescu 1959; Păunescu 1970; Comșa 1976; Muraru 1987, 1990; Bobo and Avram 1990; Marinescu-Bîlcu *et al.* 1997; Păunescu 1998; Cârciumaru *et al.* 2000). In contrast, the past two decades have seen a substantial increase in petrographic analyses of lithic raw materials (e.g., Bălțean *et al.* 2008; Crandell 2008, 2013, 2014a, 2014b; Alexandrescu and Soare 2009; Cârciumaru *et al.* 2010; Crandell *et al.* 2013; Ciornei 2014, 2015a, 2015b, 2017; Ciornei *et al.* 2014; Crandell and Vornicu 2015; Niță *et al.* 2015). As far as geochemical analyses are concerned, the vast majority of studies conducted in Romanian prehistoric archaeology are mostly concerned with obsidian (Păunescu 1970; Cârciumaru *et al.* 1985; Constantinescu *et al.* 2002; Bugoi *et al.* 2004; Biagi *et al.* 2007; Culicov *et al.* 2012; Dobrescu *et al.* 2018). Only a handful of studies, however, directly address the characterization and sourcing of siliceous materials, such as chert or flint (Muraru 1990; Astaloș and Kasztovszk 2009; Crandell 2012). This study aims to contribute to the small but growing literature on flint and chert by analysing major, minor and trace element concentrations in lithic material from two archaeological sites in Eastern Romania, Mitoc-Malu Galben (MMG) and Bistricioara-Lutărie III (BL III).

THE RESEARCH OBJECTIVES

Building on the few previous studies to geochemically characterize flint artefacts from Romania and Bulgaria (Muraru 1990; Bonsall *et al.* 2010; Gurova *et al.* 2016), this study evaluates the

potential to 'fingerprint' flint from two archaeological sites in Eastern Romania—Mîtoc-Malu Galben (MMG) and Bistricioara–Lutărie III (BL III)—using major, minor and trace elements determined by LA–ICP–MS in combination with multivariate statistical analysis (Fig. 1). This paper has three main objectives:

- To assess the geochemical signatures and variability of Upper Cretaceous 'Prut' flint and Lower Danube chert in order to test the starting hypotheses, established based on visual criteria: (1) that Palaeolithic foragers at MMG and BL III supplied themselves with 'Prut' flint available on the banks of the Middle Prut river; and (2) the potential long-distance transfer of raw 'Balkan' flint between their source and MMG and BL III during the Upper Palaeolithic.
- To ascertain the degree of suitability for geochemical analyses to test on their own either visual or petrographic similarities between chert or flint from different geological formations and, further, to evaluate how geochemically defined groups of raw materials relate to geographical locations in Romania.
- Ultimately, to reveal patterns in raw material procurement and mobility ranges in Upper Palaeolithic Aurignacian, Gravettian and Epigravettian hunter–gatherer societies prior to and after the LGM.

The geological setting of the sample sites

The Middle Prut and Middle Bistrița Valleys in Moldavia (Fig. 1) represent the areas with the highest degree of human occupation during the Upper Palaeolithic in Romania. It has long been claimed that local Upper Cretaceous flint represents the main raw material used in all Upper Palaeolithic sites along the Middle Prut Valley (Moroșan 1938). Even amongst the siliceous raw materials used in the Upper Palaeolithic sites along the Middle Bistrița Valley, an imported component of the raw material economy was identified as 'Prut flint' by the excavators (Nicolăescu-Plopșor and Petrescu-Dîmbovița 1959; Nicolăescu-Plopșor *et al.* 1966). The name 'Prut flint' has also been used by Comșa (1968, 29–30; 1975; 1976, 244) to describe the main raw material used at the Neolithic sites of Moldavia.

Prut flint is a very fine-grained siliceous material, mainly composed of authigenic micro- to cryptocrystalline quartz and silicified planktonic foraminifera and/or sponge spicules. Varieties range in colour from blackish to light grey or light brown with rare whitish spots; they have a vitreous to waxy lustre and are generally translucent (with the exception of one opaque black variety and one blackish to dark brownish very translucent variety) (Comșa 1975; Muraru 1990; Crandell 2013; Crandell *et al.* 2013; Ciornei 2015a). Prut flint is found in primary position in the Upper Cretaceous chalky limestone deposits of the Middle Prut Valley, along the 30 km stretch between the towns of Rădăuți and Liveni (Fig. 2). In secondary position (i.e., reworked), Prut flint occurs in the Badenian conglomerates found on top of the Upper Cretaceous 'flint horizon' (Fig. S1), as well as in the Prut terrace gravels further to the south of the Rădăuți–Liveni sector (Muraru 1990; Crandell 2013; Văleanu 2015).

Balkan flint encompasses the following varieties: (1) Upper Cretaceous K2 flint or *Moesian flint*; and (2) Lower Cretaceous K1 flint or *Ludogorie flint* (Gurova and Nachev 2008; Bonsall *et al.* 2010; Andreeva *et al.* 2014). The latter corresponds to intraclastic–bioclastic grain-supported cherts. Gurova and Nachev (2008) distinguished two variants of Ludogorie flint based on petrographic observations: the Ravno and Kriva Reka types. *Moesian flint* corresponds to nodular flint from chalky limestones occurring in Upper Cretaceous Coniacian, Campanian and Maastrichtian deposits in three distinct areas of northern Bulgaria (Gurova and Nachev 2008; Gurova *et al.* 2016). As a further variety of Moesian flint, *Murfatlar flint* occurs in the

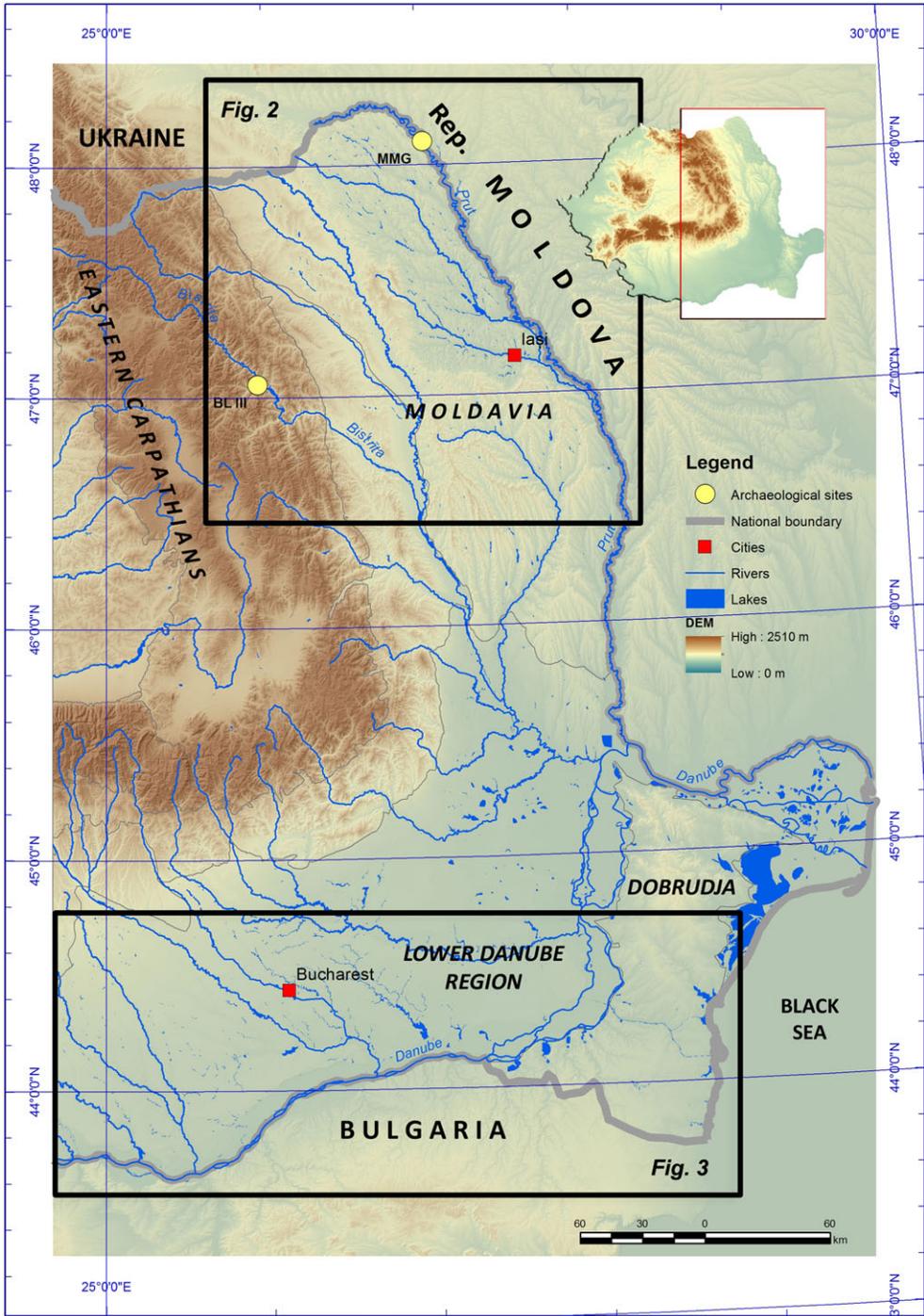


Figure 1 A map of eastern Romania, showing the location of Mitoc-Malu Galben (MMG) and Bistricioara-Lutărie III (BL III). [Colour figure can be viewed at wileyonlinelibrary.com]

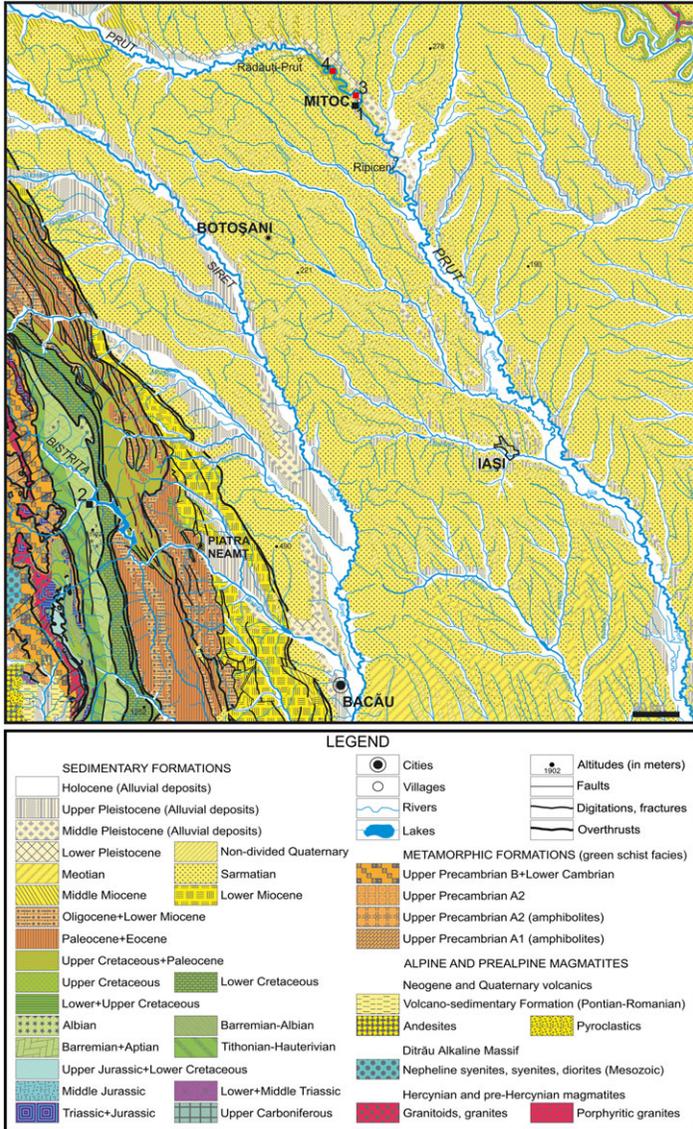


Figure 2 A geological map of the study area between the Middle Bistrița Valley and the Middle Prut Valley. Black squares denote Upper Palaeolithic sites: 1, Mitoc-Malu Galben; 2, Bistricioara–Lutărie III. Red squares denote sampling locations of Prut flint: 3, Cotul Mic; 4, Cotu Miculiși. The base map has been redrawn and modified after a part of the Geological Map of Romania 1:1 000 000 (Săndulescu et al. 1978). [Colour figure can be viewed at wileyonlinelibrary.com]

white chinks of the Murfatlar Formation, ranging in age from Santonian to lowermost Upper Campanian. The latter covers the north-eastern part of southern Dobruđja region (Avram et al. 1993, 302). Crandell (2013) and Crandell and Vornicu (2015) use the term 'Balkan flint' in the same way as Comșă, who saw the Upper Cretaceous *Murfatlar flint* from Dobruđja as a variety of Balkan flint (Comșă, 1973–75).

The term *Balkan flint* has recently been conflated with the northern Bulgarian *Moesian flint* (Gurova 2012; Gurova *et al.* 2016), despite clear similarities between southern Romanian flint from Ciuperceni and Bulgarian *Moesian flint* from Nikopol (Păunescu 1966; Ciornei *et al.* 2014). This misleading oversimplification obfuscates the fact that the *Moesian flint* occurs in gravel deposits along the Romanian Lower Danube Valley and was used by the Upper Palaeolithic people living along this valley.

MATERIALS AND METHODS

Geological flint samples

In September 2016, a programmed survey was initiated by one of us (L.M.) to investigate the variability and compositional signature of Prut flint outcropping along the Middle Prut Valley (Fig. S1). We collected nodules of ‘black’ flint from the horizontal seams at the summit of the Cenomanian chalky limestone, in addition to samples of ‘grey’ flint from the redeposited Badenian conglomerates on top of the Cenomanian chalky limestone. We deliberately refrained from collecting samples from the loose river gravel deposits devoid of stratigraphic association with one of the aforementioned formations.

Furthermore, a substantial number of geological samples of Romanian K1-Ludogorie and K2-Moesian flint have been analysed for 28 major, minor and trace elements by LA-ICP-MS (Table 1). They all derive from seven locations of secondary alluvial and colluvial Pleistocene deposits considered to represent possible supply sources for Palaeolithic foragers (Ciornei 2017). Spread over 200 km in southern Romania along the Lower Danube and Dobrudja regions (Fig. 3), the sampled locations are as follows: Ciuperceni – *La Carieră* ($N=22$), Ghizdaru –

Table 1 *Archaeological and geological samples analysed by LA-ICP-MS*

Prut flint	
<i>Cotul Mic</i> (black flint)	16
<i>Cotul Mic</i> (grey flint)	3
<i>Cotu Miculinți</i> (black flint)	18
Balkan flint	
K1-Ludogorie flint, Lower Danube	
Ghizdaru – <i>Cariera de la Haltă</i> (Gh-CH)	9
Giurgiu – <i>Cariera de la Sud-Vest</i> (Giur-Ca)	1
K1-Ludogorie flint, Dobrudja	
Pe tera – <i>Dealul Peșterica</i> (P-DP)	2
K2-Moesian flint, Lower Danube	
Ghizdaru – <i>Cariera de la Haltă</i> (Gh-CH)	9
Giurgiu – <i>Cariera Malu Roșu</i> (GMR-Ca)	3
Ciuperceni – <i>La Carieră</i> (Ciup-Ca)	22
Căscioarele – <i>Malul Estic al Lacului</i> (Căs-Lac)	6
Cetatea – <i>Cariera Bălănoaia</i> (Ct-CaB1)	8
Giurgiu – <i>Cariera de la Sud-Vest</i> (Giur-Ca)	2
K2-Moesian flint, Dobrudja	
Pe tera – <i>Dealul Peșterica</i> (P-DP)	5
Total	104

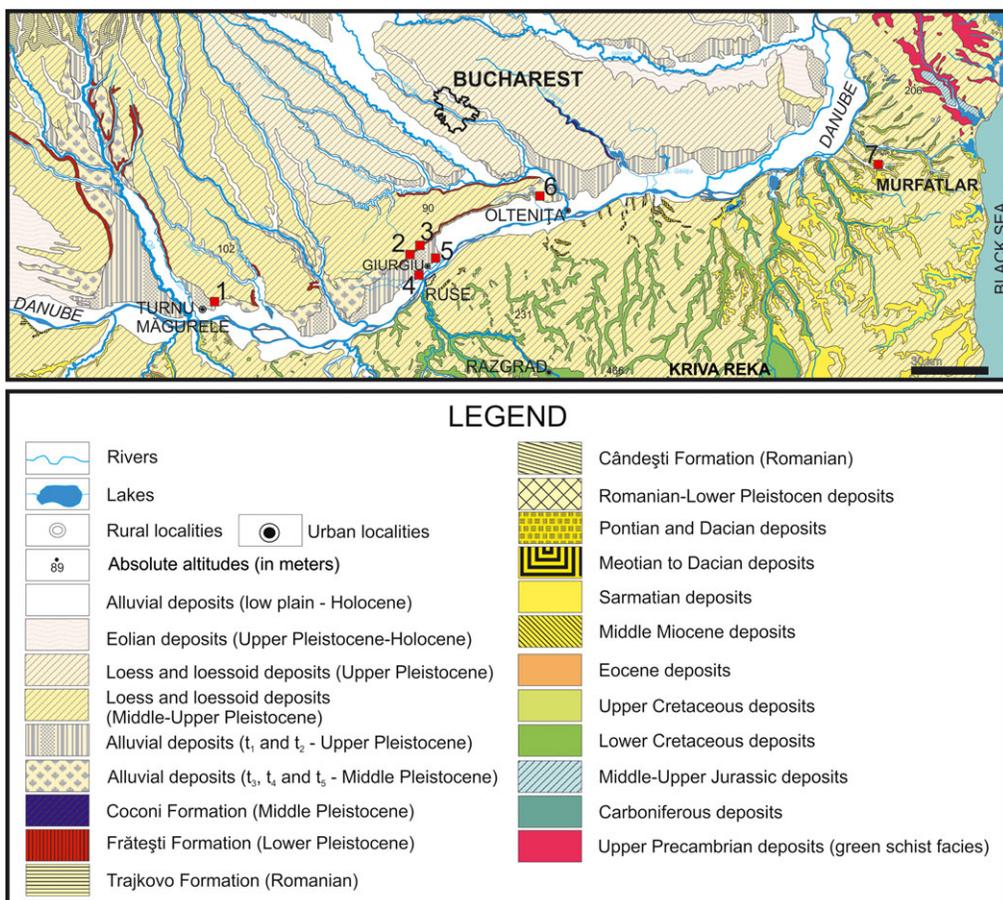


Figure 3 A geological map of the Lower Danube region. Red squares denote the sampling locations of Lower Danube flint: 1, Ciupercești – La Carieră; 2, Ghizdaru – Cariera de la Haltă; 3, Cetatea – Cariera Bălănoaia; 4, Giurgiu – Cariera de la Sud-Vest; 5, Giurgiu – Cariera Malu Roșu; 6, Căscioarele – Malul Estic al Lacului; 7, Peștera – Dealu Peșterica. The base map has been redrawn and modified after a part of the Geological Map of Romania 1:1 000 000 (Săndulescu et al. 1978). [Colour figure can be viewed at wileyonlinelibrary.com]

Cariera de la Haltă (N=18), Cetatea – Cariera Bălănoaia (N=8), Căscioarele – Malul Estic al Lacului (N=6), Peștera – Dealu Peșterica (N=7), Giurgiu – Cariera de la Sud-Vest (N=3) and Giurgiu – Cariera Malu Roșu (N=3) (for details on the geological contexts of the cherts from the gravel deposits, see Cioinei 2014, 2017; Cioinei et al. 2014). The data on Romanian flint were complemented by additional LA-ICP-MS elemental data for nine samples of K2-Moesian flint from the Moesian platform in northern Bulgaria, analysed according to similar instrumentation parameters (Gurova et al. 2016).

The sampled archaeological sites

Mitoc – Malu Galben (MMG) The site represents one of the few Early Upper Palaeolithic sites that yielded a succession of Aurignacian and Gravettian horizons in high-resolution

chronostratigraphic and palaeoenvironmental contexts in the time window 32–20 ka uncal BP (34 000–22 000 years ago). MMG is an open-air site located east of the Carpathian Mountains in the Prut valley of Romania (48°05'52"N; 27°01'23" E). The site is situated on the northern bank of a small tributary to the middle Prut valley, in the immediate vicinity of high-quality flint outcropping along the river shore (Chirica 2001; Otte *et al.* 2007). MMG is characterized by an approximately 12-m-thick loess–palaeosol sequence with a semi-continuous record spanning more than 10 000 years (Haesaerts *et al.* 2003; Haesaerts 2007). The archaeological sequence includes five Aurignacian and four Gravettian horizons within a succession of 13 lithostratigraphic units. The chronology is based on more than 40 radiocarbon dates. The chronostratigraphic position of the climatic events and archaeological horizons has been inferred by a climatostratigraphic approach (Haesaerts *et al.* 2003; Haesaerts 2007). MMG has been excavated since 1978 by the Archaeological Institute of the Romanian Academy of Sciences in Iași (PI: Professor V. Chirica) (Chirica 2001; Otte *et al.* 2007), most recently in the framework of a joint Romanian–Belgian–UK project (Chirica *et al.* 2014, 2015, 2016; Noiret *et al.* 2016).

A total of 46 black, grey and brown flint artefacts, mostly unretouched flakes, have been selected for *in situ* major, minor and trace geochemical analysis (Table 1), regardless of typological and technological criteria. They derive from two Aurignacian and at least two Gravettian layers labelled according to the system of archaeological layers by V. Chirica (Otte *et al.* 2007).

Bistricioara–Lutărie III (BL III) Research in the Bistrița Valley in the Eastern Carpathians (as part of the broader region of Moldavia), has revealed a high density of Upper Palaeolithic (UP) sites, variously attributed to the Aurignacian, Gravettian and Epigravettian technocomplexes, with numerical dates ranging between 35 and 15 ka cal BP (Nicolăescu-Plopșor *et al.* 1966; Păunescu 1998; Anghelinu *et al.* 2012, 2018). Most of these settlements were identified in the river's middle sector, roughly corresponding to the Ceahlău Basin (Fig. 1).

BL III (47°3'22"N; 25°57'2"E, ~500 m ALT) was identified in 2006 on the right bank lower terrace of the Bistrița River, close to the extensively excavated sites BL I and II (Nicolăescu-Plopșor *et al.* 1966; Păunescu 1998). Small-scale excavations took place in 2007 and revealed two Epigravettian layers, the oldest of which has been dated to 23 ka cal BP (Anghelinu *et al.* 2012). Further research, including a full chronometric assessment, palaeoclimatic sampling and archaeological excavations, revealed 12 major litho-stratigraphical units covering most of the Last Glacial (Trandafir *et al.* 2015) and six UP cultural layers. Two of these layers, a Late Gravettian with shouldered points dated at 27 cal BP and an undifferentiated UP (Aurignacian?) dated at 35 ka cal BP, were deposited before the LGM, while the other four provide C14 and TL burnt flint ages ranging between 20 and 15 ka cal BP (Anghelinu *et al.* 2018).

Previous studies have pointed out fluctuating percentages of Upper Cretaceous flint in the sites of the Bistrița Valley (Nicolăescu-Plopșor *et al.* 1966; Păunescu 1998; Anghelinu *et al.* 2012, 2018). At BL III, Upper Cretaceous 'black' flint accounts for the highest amount of non-local siliceous raw materials in all archaeological horizons. While the high frequency of Upper Cretaceous flint items in the assemblages derived from the old excavations might have been biased towards retouched artefacts made of high-quality flint (Niță-Bălășescu 2008), in the recently excavated Late Gravettian at BL III (426 items), black flint accounts for 93% of lithic artefacts based strictly on visual observations. Upper Cretaceous formations are known in the Eastern Carpathians. However, the nearest identified source of high-quality 'black' flint is the ~30-km-long stretch of the Prut River at a distance of ~150 km to the north-east.

A total of 23 lithic artefacts of BL III have been selected for analysis. They all derive from the most recent excavations in 2015, from three distinct archaeological layers pertaining to the

Gravettian, the Epigravettian and even to a possible Aurignacian occupation of the site (Table 1). While black (Prut) flint artefacts have been documented throughout the stratigraphy, brown (Balkan) flint samples derive exclusively from two post-LGM Epigravettian assemblages.

Analytical techniques

In situ high-precision geochemical analyses of major, minor and trace elements were conducted in the Department of Earth Sciences at the University of Cambridge, using an ESI NWR193 excimer laser ablation system interfaced to a PerkinElmer NexION 350D ICP-MS. The full set of geochemical analyses is available as Supplementary files (Table S1).

Statistical methods

The major goal of the statistical methods used in this research is to identify groupings in the major, minor and trace element data and to evaluate how geochemical groups relate to geographical locations. Here, we demonstrate a multivariate approach combining principal component analysis (PCA) and discriminant analysis (DA) that highlights the benefits of DA in the classification of elemental concentration data (Filzmoser *et al.* 2012). The combination of these approaches encourages a two-stage analysis starting with an unsupervised exploration of the data using PCA and working towards a more supervised, model-based approach (DA). All statistical methods used in this research were executed in the R computing environment (R Core Team 2017), with additional packages including rrcovHD (Todorov 2016) and robCompositions (Templ *et al.* 2011).

The analysis of compositional data starts with the aggregation of raw compositional data produced from LA-ICP-MS. As highlighted above, three or four separate ablations were performed on each flint sample and the median concentration value between these ablations is used to characterize each individual sample. The initial exploration of the data structure used an unsupervised PCA to identify compositional groups using all 28 chemical elements. The basis for this statistical analysis is not the raw concentration data, but the (log-)ratios between the element concentrations (see, e.g., Pawlowsky-Glahn *et al.* 2015).

Unsupervised methods, such as PCA, are useful in detecting broad patterns in elemental data; however, in order to increase the resolution of our analysis, we implemented sparse linear discriminant analysis (SDA). DA stands apart from other multivariate methods, as it presumes that the group to which an individual sample belongs is known (Baxter 1994). The assumption that a grouping 'model' for the data exists changes our expectation from explaining elemental variability in the data (i.e., PCA) to identifying the set of elements that best discriminate between the groupings provided by the analyst. In other words, DA aims to find the combination of elements that maximizes the difference between the presumed groups.

One potential drawback to using DA with high-dimensional elemental data is the inclusion of uninformative elements, which contain little or no explanatory power about group membership and add uncertainty to the grouping model (Hoffman *et al.* 2016). These issues are countered in this research through the use of sparse modelling, which penalizes uninformative variables, effectively excluding their influence on the overall model and the classification of samples (Hoffman *et al.* 2016). In this work, we determine the appropriate number of elements to be used for each set of data through a K -fold cross-validation method (described by Hoffman *et al.* 2016, 156). This procedure begins by randomly dividing the samples into K subsets, with each subset used as test data, while all other samples considered the training data. For each combination of

elements and linear discriminants, a model is estimated from the training data and class membership is predicted for the test data. The lowest misclassification rate serves as the criterion to compare between different models and the number of informative elements to be used in the linear discriminant analysis. The discrimination ability of each element is identified by examining the absolute value of their coefficient, with larger values indicating a greater capability to maximize differences between groups, which is referred to here as the beta coefficient. These methods also provide a direct indication for how well our grouping model is classifying our data by producing a misclassification rate (Tables S2 and S3).

RESULTS AND DISCUSSION

Prut flint

It is generally taken for granted, based on visual criteria, that prehistoric foragers from MMG supplied themselves with high-quality local Prut flint readily available on the terraces of the Middle Prut valley (Văleanu 2015). In this study, the compositional ‘fingerprint’ of Prut flint has been assessed by conducting a comparative analysis of 37 geological flint samples of Upper Cretaceous ‘Cenomanian’ black flint from two sources located 12 km apart along the Middle Prut valley: *Cotul Mic* and *Cotu Miculinți* (Fig. 2). Our results strongly support the uniform signature of ‘black’ Prut flint, which holds independently of the adopted statistical approach (i.e., ‘unsupervised’ PCA or ‘supervised’ SDA) (Fig. 4). As expected, the elemental signature of ‘grey’ Prut flint derived from redeposited Badenian conglomerates on top of the Cenomanian chalky limestone corresponds to a separate compositional group.

The distinctness of ‘grey’ Prut flint artefacts from MMG is uncertain when plotted with principal components (Fig. 4 (a)). However, when plotted using the SDA model it becomes apparent that black and grey flint artefacts from MMG represent distinct compositional groups, in compliance with the distinct signatures of the geological reference group (Fig. 4 (b)).

Contrary to our expectations, our results do not support the common narrative of a local provisioning of Prut flint by MMG occupants (*Cotul Mic* and *Cotu Miculinți*) (Fig. 4). In fact, the elemental signature of lithic artefacts made of black and grey flint from MMG and BL III does not match any of the compositional groups determined from geological reference samples, regardless of the cultural attribution of the artefacts.

The most parsimonious explanation to account for the mismatch between archaeological specimens from MMG and BL III and geological reference groups is that the latter do not represent the full initial geochemical variability of Upper Cretaceous flint of the Middle Prut valley. In other words, artefacts from MMG and BL III might derive from a geographical source of ‘black’ flint not sampled in the framework of this study. In fact, it is likely that the exposure of the initial Upper Cretaceous chalk with flint had a greater extension and thus a greater chemical variability to start with, independently of subsequent erosion and redeposition processes, which led to the formation of Badenian conglomerates with flint and Prut terrace gravel deposits. The black flint artefacts from MMG analysed here have, with one exception, not been secondarily modified. However, there is no reason to assume that our results might be biased by having tested unretouched blanks instead of modified tools, since there is no quality difference between modified and non-modified blanks.

External macroscopic features of cortical surfaces on MMG and BL III artefacts further indicate that the nodular black flint, with which hunter–gatherers at these sites supplied themselves, was collected in nearby terrace deposits and not extracted directly from the primary chalk. As

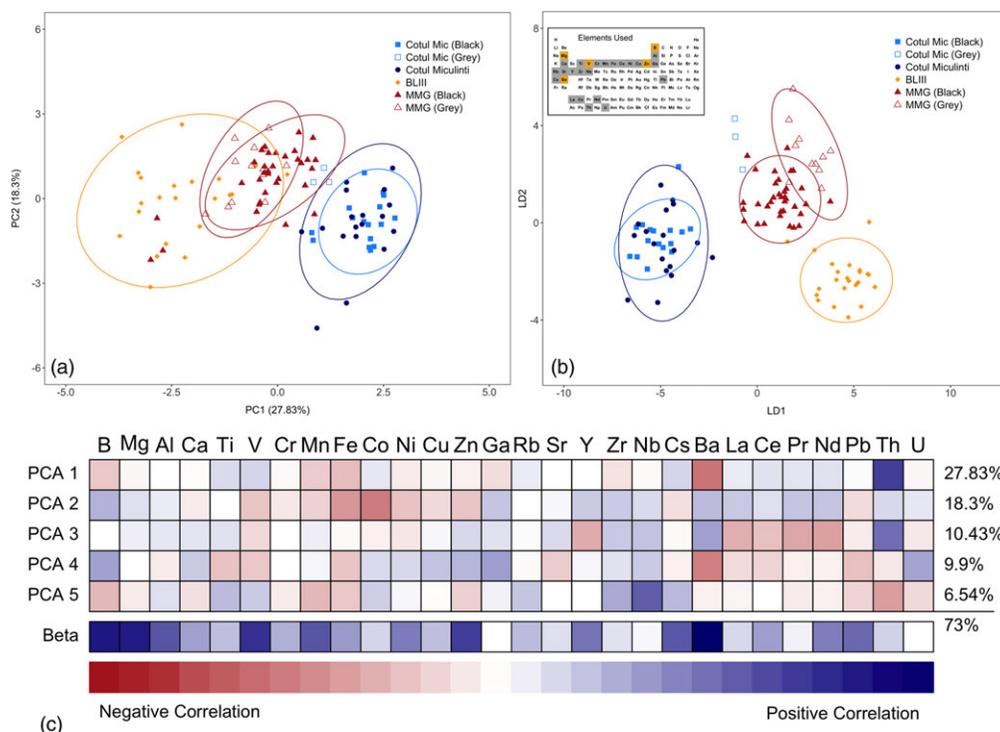


Figure 4 (a) A plot of the principal component analysis (PCA) scores and 95% confidence ellipses for flint artefacts from MMG and BLIII archaeological sites as well as geological samples of Prut Flint (Cotul Mic Upper Cretaceous 'black' flint, $N=16$; Cotul Mic Upper Cretaceous 'grey' flint from Badenian conglomerates, $N=3$; Cotul Miculinti Upper Cretaceous 'black' flint, $N=18$). (b) A sparse discriminant analysis (SDA) plot with 95% confidence ellipses for five groups. Informative elements to the SDA model are coloured in grey, with those elements that contribute the most to discriminating groups highlighted in gold (i.e., Mg, Mn, Ba, Cs and Ba). (c) A plot of element loadings for each of the first five principal components as well as the beta coefficients associated with the sparse discriminant analysis. The darker the colour, the greater is the correlation of the element with the principal component or the contribution of the element discriminate grouping model. [Colour figure can be viewed at wileyonlinelibrary.com]

such, we cannot exclude the possibility that 'Prut flint' has not been affected by secondary transformations undergone in the context of variable geomorphological environments before collection and use by prehistoric foragers (Fernandes and Raynal 2006; Fernandes *et al.* 2007). Since this study does not directly assess the geochemical variability of flint from the Pleistocene Prut terraces in secondary colluvial and alluvial deposits, we cannot exclude *a priori* that at least part of the distinct fingerprints of MMG and BL III samples is the result of geochemical diagenesis during reworking. However, microquartz is one of the most stable low-pressure silica polymorphs (α -quartz) and requires specific burial conditions in order to undergo profound diagenetic changes (Graetsch 1994; Heaney 1994). Accordingly, we consider it unlikely that the chemical composition of flint from recent geological stages found in secondary position was substantially affected by chemical alteration, except perhaps the surface and endocortical areas. Instead, we favour the hypothesis which highlights that the chemical dissimilarity between sampled sources and artefacts from MMG and BL III is due to the fact that the current exposure of the Cenomanian chalk with flint represents only a fraction of the initial chemical variability (before erosion and redeposition) characterizing the genetic Cenomanian flint type. The secondary

sources may, in fact, reflect some of the initial chemical variability of eroded parts that are longer accessible in primary position and require further investigation.

Balkan flint

The rationale for expected geochemical groupings according to their geographical position and geological origin closely follows the petrographic reality (Ciornei *et al.* 2014). Accordingly, K1-Ludogorie and K2-Moesian flint samples have been treated as distinct compositional groups both within and between the Romanian Lower Danube (*RoLoDan*) and Dobrudja (*RoDob*) regions. However, due to the limited sample size, K1 flint samples from the Giurgiu area in the Lower Danube region ($N=8$) and from Pestera in the Dobrudja region ($N=2$) have been treated as one compositional group in the SDA model (Fig. 5 (b)).

The results of our study only partly conform to the aforementioned rationale. Bearing in mind that K2-Moesian flint from Bulgaria is represented by only nine samples, the fact that the emerging geographical pattern is independent of the chosen statistical approach suggests the validity of LA-ICP-MS analyses to discriminate Romanian or northern Bulgarian origins of artefacts made of Balkan flint (Fig. 5).

The PCA approach has little interpretative value to distinguish compositional groups of Romanian K1 and K2 flint, apart from suggesting that discrimination between geographical and geological sources of Balkan flint from Romania cannot be conclusive without complementary petrographic observations (Fig. 5 (a)). In contrast, the SDA model mirrors the geographical structure of the Romanian and Bulgarian K1 and K2 flint sources on the landscape (Fig. 5 (b)). In fact, none of the Bulgarian K2 samples could be assigned to any of the control groups of K2 flint from Romania (Table S3). As there is no justifiable reason to treat Balkan flint artefacts from MMG and BL III as a single petrographic group, these samples were not included in the discriminant analysis.

BROADER IMPLICATIONS

Although a broad diversity of questions may be answered with raw material sourcing data, the principal aims of any archaeological provenance study are to infer the movement of people across the landscape and, ultimately, to assess the economic and social factors that underlie the movement of materials (Pollard and Heron 2008). Long-distance raw material transfers across Romania prior to the LGM have previously been inferred solely on the basis of visual similarities and, more rarely, on petrographic investigations of Eastern Carpathian sites (Crandell *et al.* 2013; Ciornei 2015a). The presence of artefacts made of Balkan flint from the Lower Danube region at MMG and BL III suggests an extensive provisioning area for the human communities involved. As no empirical occupational break of Moldavia has been noted during the LGM (Haesaerts *et al.* 2003; Anghelinu *et al.* 2018), and given the presence of Balkan flint artefacts in both Gravettian and Epigravettian assemblages in Moldavian sites, our observations suggest diachronically stable raw material procurement patterns prior to and after the LGM. However, given the pronounced diversity of local and regional sources with similar macroscopic features but different geological origin and geographical occurrence (Ciornei 2015a), this inference begs for additional support. Whether the appearance of Balkan flint in assemblages of Moldavia during the later Gravettian period is indicative of an increase in long-distance mobility or of a geographical switch of circulation patterns in connection to the deteriorating climate towards the LGM is currently unclear.

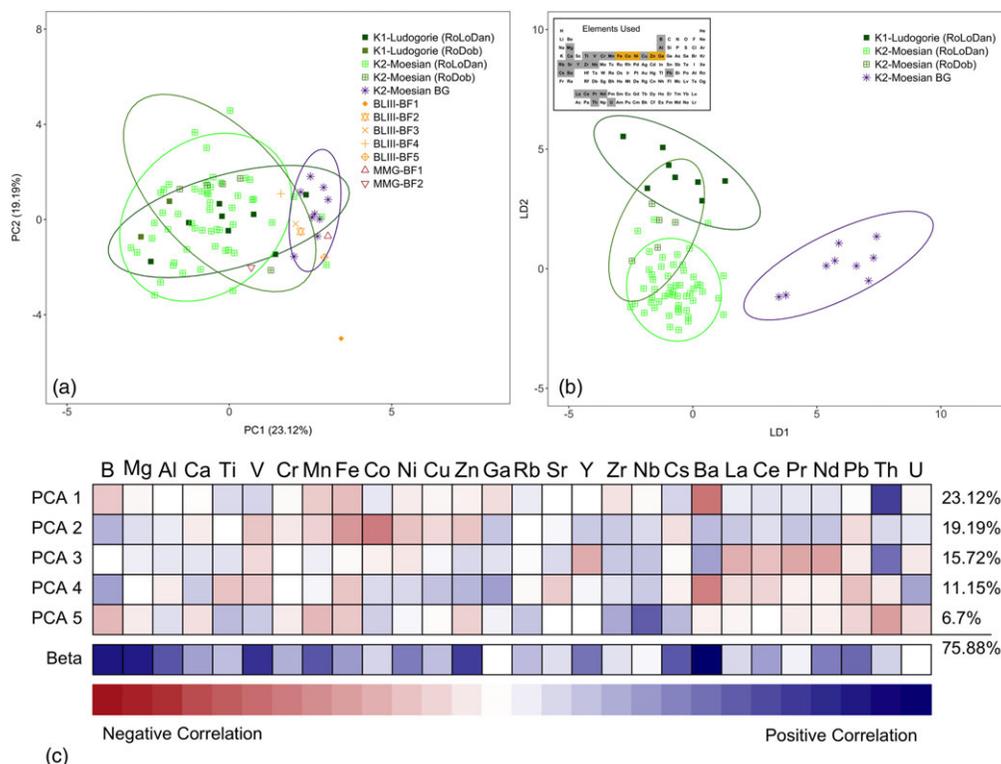


Figure 5 (a) A plot of the PCA scores and 95% confidence ellipses for flint artefacts from the MMG and BLIII archaeological sites as well as geological samples of Balkan flint (Lower Cretaceous K1-Ludogorie flint from the Romanian Lower Danube (RoLoDan) and Dobrudja (RoDob) regions; Upper Cretaceous K2-Moesian flint from Romania and Bulgaria (BG). (b) An SDA plot with 95% confidence ellipses of Bulgarian and Romanian geological flint from the Lower Danube and Dobrudja regions. Informative elements to the SDA model are coloured in grey, with those elements that contribute the most to discriminating groups highlighted in gold (i.e., Fe, Co, Ni, Ga and Th). (c) A plot of the element loadings for each of the first five principal components as well as the beta coefficients associated with the sparse discriminant analysis. The darker the colour, the greater is the correlation of the element with the principal component or the contribution of the element discriminate grouping model. [Colour figure can be viewed at wileyonlinelibrary.com]

By assessing the geochemical signatures and variability of Cretaceous Prut and Balkan flint, one of the aims of this study was to further test the assumption, established on the basis of visual criteria, that Palaeolithic foragers in the Middle Prut valley and the Eastern Carpathians supplied themselves with flint available on the banks of the Middle Prut river. The mismatch between archaeological samples of black flint used at BL III and visually similar geological samples of Prut flint raises new questions and opens unforeseen perspectives. Bearing in mind that chemical provenance studies proceed by systematic elimination of possible sources rather than by positive attribution, the most parsimonious explanation to account for the mismatch between artefacts and geological samples made of 'black' flint is that our sampling strategy did not encompass the initial compositional variability of Prut flint: initial exposures might have been eroded and are no longer accessible in primary position. Since we did not assess the geochemical signature of flint from the secondary Prut gravels, this question remains open. Either way, our results imply that our geological groups are not representative enough of the initial variability of Prut flint. Further controlled geological sampling is required.

We have seen that, in the context of Romania and Bulgaria, geochemical analyses do not have the level of resolution required to test on their own either visual or petrographic similarities between flint or chert from different geological facies and to assign single artefacts to specific geographical locations. Nevertheless, this study has prepared the ground for further sourcing studies to come. The systematic combination of petrographic and geochemical approaches in future research will significantly strengthen the behavioural inferences on Palaeolithic mobility and social networks under changing environmental constraints. Moreover, the methodological advances and results obtained in the framework of this study will benefit and inform future sampling strategies in the wider region of south-eastern Europe (including the Western Ukraine, Hungary and Bulgaria) and will orient future research questions. In particular, the mismatches of signatures between training and test data will have to be investigated further regarding their behavioural significance.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

Figure S1. Left: Schematic geological section of the Prut shore (after Muraru, 1990); Right: Sampling of Upper Cretaceous “Prut flint” at Cotul Mic in September 2016. 1: glauconitic sands and sandstones; 2: Upper Cretaceous ‘Cenomanian’ chalky limestone with nodular flint; 3: Badenian conglomerates with Upper Cretaceous flints; 4: limestone; 5: bentonite; 6: sandstone; 7: gravels with flints and sand; 8: loess; 9: Holocene soil.

Table S1. Element list and dwell times from Syngistix Software.

Table S2. Misclassification rates for raw flint samples from the Prut Region and for archaeological flint samples from the sites of MMG and BLIII. Table shows that only 5 out of 106 samples are misclassified (i.e., classified in a different group than what was presumed from geography). This model provides an overall misclassification rate of 3.8% (0.038).

Table S3. Misclassification rates for raw flint samples from the Lower Danube and Dobrudja regions without archaeological samples. Table shows that only one out of 74 samples is misclassified (i.e., classified in a different group than what was presumed from geography). This model provides an overall misclassification rate of 1.4% (0.014).

Table S4. Mitoc-Malu Galben. Artefacts analysed by LA-ICP-MS.

Table S5. Bistricioara-Lutărie III. Artefacts analysed by LA-ICP-MS.

Table S6 Correlation matrix for Prut flint.

Table S7 Correlation matrix for Balkan flint.

Table S8 Compositional data of geological and archaeological samples of Romania analysed in this study.