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Geochemical Sourcing of Lithic Raw Materials from Secondary Deposits in South Serbia. Implications for Early Neolithic Resource Management Strategies

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Abstract
The valleys of the South Morava River and its tributaries in the region of Pusta Reka around the cities of Leskovac and Lebane in southern Serbia are notable for the high density of early prehistoric settlements identified archaeologically. The area represents a link between the Mediterranean and the (northern) Balkans and is therefore of key importance for understanding the processes of Neolithisation in south-eastern and central Europe, which commenced at the beginning of the 6^{th} millennium BC. The current study is part of a larger project which aims to address issues concerning Early Neolithic resource management and production strategies, and specifically the use of the prehistoric landscape, through the characterisation of lithic materials in archaeological assemblages from this region. Lithic raw materials used for chipped stone tool production in the Pusta Reka region include a wide range of cryptocrystalline SiO_2 modifications of volcanic and perivolcanic origin. These materials are found abundantly in secondary alluvial deposits in the extensive Neogene basin complexes of southern Serbia. The current pilot study was undertaken to test the viability of sourcing such lithic materials from secondary deposits to their primary origin using the Multi-Layered Chert Sourcing Approach (MLA), a method developed by the first author of this study, which combines visual, microscopic, and geochemical techniques using Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). In the light of the encouraging results, it is planned to extend the analytical work and to apply this method of provenance study to archaeological materials in order to reconstruct the economic behaviour of the Early Neolithic communities in this region.

Keywords
Neolithic resource management, lithic raw materials, secondary deposits, geochemistry, provenance studies, Multi-Layered Chert Sourcing Approach (MLA), southern Serbia.

Zusammenfassung – *Geochemische Herkunftsbestimmung von Rohstoffen aus sekundären Lagerstätten Südserbiens. Bedeutung für Ressourcenmanagement und Produktionsstrategien im Frühneolithikum*
Die Pusta Reka Region, die sich um Leskovac und Lebane in Südserbien erstreckt, weist eine hohe Dichte prähistorischer Siedlungen in den Flusstälern der Südmorava und ihrer Zuflüsse auf. Diese Region stellt ein Bindeglied zwischen dem mediterranen Raum und dem (nördlichen) Balkan dar, weshalb ihr eine Schlüsselfunktion für das Verständnis der um 6000 v. Chr. beginnenden Neolithisierung von Südost- und Zentraleuropa zukommt. Die aktuelle Studie ist Teil eines größeren Projekts, welches die Rekonstruktion von Ressourcenmanagement und Produktionsstrategien im Frühneolithikum durch die Charakterisierung lithischer Materialien in archäologischen Fundinventaren der Pusta Reka Region zum Ziel hat. Die zur Herstellung geschlagener Steingeräte verwendeten Gesteinsrohmaterialien dieser Region umfassen eine große Vielfalt von kryptokristallinen SiO_2-Modifikationen vulkanischen und perivulkanischen Ursprungs. Diese Rohmaterialien treten häufig in alluvialen Kontexten in den ausgedehnten neogenen Beckensystemen Südserbiens auf. Diese Pilotstudie testet Möglichkeiten zur Herkunftsbestimmung solch lithischer Rohstoffe aus sekundären Lagerstätten im Hinblick auf ihre primäre Herkunft mithilfe des *Multi-Layered Chert Sourcing Approach (MLA)*, in welchem makroskopische, stereomikroskopische und geochemische Methoden zum Einsatz kommen. Im Lichte der ermutigenden Resultate soll diese Studie unter Anwendung der gewonnenen Erkenntnisse auf archäologische Materialien ausgedehnt werden, um das ökonomische Verhalten frühneolithischer Gemeinschaften in dieser Region zu rekonstruieren.

Schlüsselbegriffe
Neolithisches Ressourcenmanagement, Gesteinsrohstoffe, Sekundärlagerstätten, Geochemie, Herkunftsanalysen, *Multi-Layered Chert Sourcing Approach* (MLA), Südserbien.

1. Introduction

Neolithisation represents a profound change in all aspects of human lifeways. The transition from hunting and gathering to sedentary herding and farming with all its economic, social and cultural consequences has shaped human mind and behaviour and can be regarded as the foundation of deeply rooted patterns of behaviour which are still active today.[1] The complex processes which underlie the spread of the Neolithic from Anatolia to central Europe, a development which commenced around 6000 BC, are still poorly understood, especially with regard to economic strategies, networks of contact, trade and exchange, and the use of the landscape. Most recently, the research focus has shifted towards aDNA and isotope studies, which have convincingly demonstrated that the main Neolithic trajectory runs from south-east to north-west.[2] Although the results from these studies form an invaluable basis for our understanding of the spread of Neolithic lifeways, complementary methods of scientific investigation are required to tackle the nature of these processes.

One powerful line of inquiry is the investigation of lithic 'resource management', which can be used to gain deeper insights into the socio-economic processes underlying Neolithisation. Since stone tools are among the most ubiquitous of finds on Neolithic sites, they can make an important contribution to reconstructing the economy and economic behaviour. Significant contributions to the reconstruction of the lithic economy in the context of the Neolithisation of the Balkans and central Europe have been made by Inna Mateiciucová and Maria Gurova,[3] who have focussed mainly on aspects of tool technology and raw material economy in the Balkan region. While Gurova stresses the significance of the so-called 'Balkan Flint' for tracing the spread of the Neolithic in the Balkan region,[4] Mateiciucová's results[5] indicate that the local Mesolithic groups had a significant impact on the formation of early Neolithic 'cultural' complexes such as Starčevo and Körös. Specific raw materials, which were distributed through pre-existing contact networks, established the direction for ensuing developments and facilitated the spread of the Neolithic.

Currently, there is an ongoing debate which is centred around three Neolithisation scenarios: (1) the migration hypothesis, which assumes that Neolithic lifeways arrived along with the first farmers from the east;[6] (2) the acculturation or adaptation theory, which suggests that the local population adopted Neolithic lifeways through contacts and the transfer of knowledge;[7] (3) and most recently, a set of models that propose integrationist scenarios, in which both local Mesolithic populations and neighbouring Neolithic groups co-operated.[8] The results of the geochemical investigations presented in this paper and the future extension and application of the results to archaeological materials will make a significant contribution to this discussion. This paper considers the first results from in-depth investigations into the raw materials used for chipped stone tool production in southern Serbia. Geographically and culturally, southern Serbia is a 'missing link' between Asia Minor, the core area of Neolithic expansion, and the (northern) Balkans and is of critical importance for understanding the spread of the Neolithic way of life into south-eastern and central Europe.

The primary goals of this study were the characterisation and determination of the provenance of siliceous rocks using the Multi-Layered Chert Sourcing Approach (MLA). In this pilot study the potential for using this technique to trace geological materials from secondary deposits back to their primary source areas was tested. Identifying and defining lithic resource management, which entails the procurement, use, and distribution of resources for stone tool production, is primarily dependent on our ability to trace lithic raw materials back to their original source and to differentiate local from non-local raw materials.[9]

In order to gain an overview of the raw material varieties present in the region, Neolithic assemblages containing lithic finds from throughout the study area stored at the National Museum in Leskovac and finds from archaeological field surveys undertaken during the summer of 2017 were studied. Based on these investigations, geoarchaeological surveys were then conducted to locate potential raw material sources and to collect geological samples for the analytical work.

2. Terminology of Siliceous Rocks in Southern Serbia

Various schemes for classifying siliceous rocks are used in Europe and North America and the system applied here follows Antonín Přichystal's[10] terminology for SiO_2 rocks with refinements proposed by the author,[11] focussing on lithic materials from central Europe. In this system, raw materials

1 Spolaore, Wacziarg 2013.

2 E.g. Haak et al. 2010. – Skoglund et al. 2012. – Lipson et al. 2017.

3 Mateiciucová 2004. – Mateiciucová 2008. – Gurova 2012. – Gurova 2016. – Gurova et al. 2016.

4 Gurova 2012. – Gurova 2016.

5 Mateiciucová 2004, 91–96. – Mateiciucová 2008, 57–110, 165–166.

6 E.g. Hofmanová et al. 2016.

7 E.g. Tringham 2000.

8 E.g. Zvelebil 2002.

9 Brandl et al. 2016.

10 Přichystal 2010.

11 Brandl 2014.

are generally defined according to their geological origins, since this is the most important factor in considering the provenance of lithic materials. Only if the lithogenetic processes cannot be established are mineralogical classifications (e.g. 'chalcedony', 'opal', etc.) used. Raw materials detected in the course of the current study, which can collectively be termed 'Neogene Volcanic Siliceous Rocks' (NVS), can be separated into two major groups: primary volcanic material and materials secondarily silicified in a volcanic context.

2.1. Primary Volcanic Material

Such materials can be securely classified as jasper (colourful) or chalcedony (pale bluish to bluish-grey). There exist two possible formation processes for such materials: (a) primarily volcanic as in the case of hydrothermal cleft fillings or sinters or (b) siliceous weathering products of host rocks such as serpentinite and andesite.

2.2. Silicification in a Volcanic Context

Raw materials resulting from silicification in a volcanic context are defined in different ways in the literature. In eastern European countries they are generally referred to as 'limnic quartzite' or 'hydroquartzite' on account of their origin in freshwater environments (i.e. limnic or lacustrine).[12] This terminology is, however, misleading since the term 'quartzite' should be used exclusively for clastic (ortho-) or metamorphic (metaquartzite) rocks.[13] One solution, which would result in a more neutral classification, would be to use the term 'perivolcanic limnic silcrete' (silcrete = silica-cemented sediment).[14] Given the fact that this specific sedimentary siliceous rock type frequently contains microfossil inclusions, it can also be classified as 'silicite'.[15] Since these materials are typically of the Neogene age, we propose the innocuous and encompassing term 'Neogene Lacustrine Silicites' (NLS). NLS can be subdivided into (a) clearly fossiliferous and (b) unclear NLS (containing heavily dissolved fossil inclusions or totally lacking fossils).

3. Scientific Questions

The following research questions were addressed during the initial phase of the project: (1) Which raw material varieties are present in the study area? (2) Which of those materials were used for the production of chipped stone tools?

The investigation of the archaeological materials housed in the National Museum in Leskovac and from the archaeological field surveys revealed that, with the exception of a very small number of lithic implements, the majority were produced from NLS displaying a wide range of visual variability. Other materials such as chalcedonies and jaspers seem to have been of far less significance for stone tool production. Hence, the focus of this study was on NLS varieties. From the examination of natural surface remains on lithic artefacts, it became apparent that practically all raw materials (except for a very few 'exotic' specimens corresponding to the enigmatic 'Balkan flint'[16]) were derived from secondary deposits. Consequently, the primary goal of this pilot study was to find ways to reliably source these materials from secondary contexts.

4. Geology of the Study Area

The study region is situated in the Neogene Niš-Dobrič and Leskovac basin complexes. Geotectonically, the basins are located within the border area with the elevated morphostructures of the Carpatho-Balkanides to the east and the Serbo-Macedonian Massif to the west and south, underlain by rocks of both geological units (Fig. 1).[17]

The Carpatho-Balkanides display a complex geological structure, composed of green schists, flysch, sandstones, limestones, metamorphic rocks, volcanic-sedimentary rocks, ultramafic rocks, and gabbros.[18] The Serbo-Macedonian Massif is comprised of crystalline schists, amphibolites, gneisses, micaschists, greenschists, marbles, and quartzites.[19] On a more regional scale, siliceous rocks are – in addition to the widespread carbonate complexes – predominantly bound to the Diabase-Chert-Formation linked to the ophiolitic belt of the Inner Dinarides and the Vardar zone west of the Serbo-Macedonian Massif, and the Porphyrite-Chert-Assemblage, which occurs in two NW–SE trending belts in western Serbia.[20]

The Niš-Dobrič Basin is directly connected to the Leskovac Basin in the south and both basins display a similarly complex tectonic history related to Neoalpine shaping. The basin system was formed during the Ottnangian-Carpathian period and inverted in the Early Badenian. It shows signs of subsidence in some parts during the Late-/Epipleistocene period and this probably continued up to the present day.

The Niš-Dobrič Basin is rhomboid in contour and the thickness of Neogene deposits reaches 1750 m in its central part. In the course of subsidence, several minor basins and elevated geomorphological structures were created.

12 E.g. Biró 2010.
13 Přichystal 2010, 178.
14 E.g. Ulyott et al. 2004.
15 Přichystal 2010.
16 Gurova 2012. – Gurova 2016.
17 Marović et al. 2007.
18 Dimitrijević 1997.
19 Pavlović et al. 2012, 349–350.
20 Obradović, Goričan 1988.

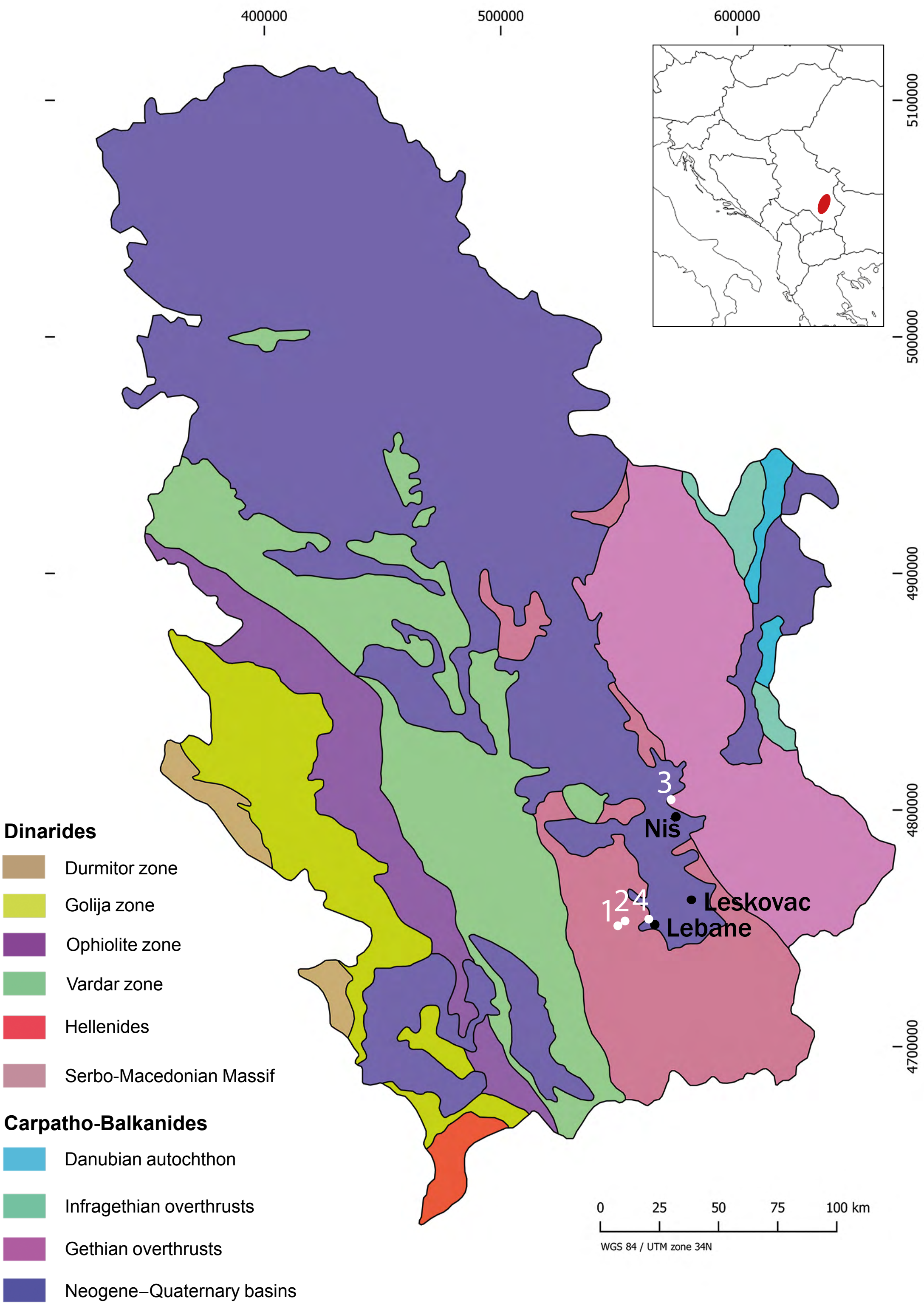

Fig. 1. Simplified geological map with the principle tectonic units in Serbia and location of the sampled localities in southern Serbia. – 1. Rasovača. – 2. Bučumet/Kameno Rebro. – 3. Kremenac. – 4. Lebane test sample (adapted from Marović et al. 2007, 6 and Fig. 2) (Graphics: M. Börner, OREA).

The Leskovac Basin comprises three large neostructural units: the Donja Toplica and Leskovac depressions and the relatively elevated Pečenjevac Block which separates the two. The Leskovac depression is the deepest with sediments reaching a depth of over 1300 m. The Oligocene history of this area resulted in the formation of the Lece volcanic complex (or Lece-Chalkidiki Metallogenic province), which is of importance for the formation of chemical sedimentary cryptocrystalline SiO_2 modifications, i.e. chalcedonies and jaspers.

During the Early to Middle Miocene period a series of long-lived lakes developed in the Dinarides and Serbian regions, with the so-called Serbian Lake System (SLS) in the latter region. The SLS was established around 14.5 Ma, and must have ended before 13.8 Ma as indicated by overlying Paratethyan sediments, which succeeded the Serbian Lake cycle.[21] In the study area, the SLS covered the afore-mentioned basins and initiated lacustrine sedimentation. Geoarchaeological surveys indicate that elements of this lacustrine environment (most likely freshwater limestones) were silicified due to continuing volcanic (i.e. hydrothermal) activity in the larger catchment area.[22] These are the birthplaces of the widespread Neogene Lacustrine Silicites (NLS), which occur in residual deposits at the basin rims and are contained in the alluvial basin fills, which consist of variegated sand-gravel series.

5. Previous Studies

There exist only a few studies of the raw materials which were used for prehistoric chipped stone tool production in present-day Serbia. Jelena Obradović and Špela Goričan [23] provided a general overview of siliceous raw materials on Serbian territory, but this compilation is of a summary character and is therefore of limited use in the present context. Provenance studies pertaining to chipped stone tools, chiefly related to specific lithic assemblages from Neolithic Serbian sites, were conducted by Vera Bogosavljević Petrović, but the results are only available in the Serbian language. These studies are referenced by Vera Bogosavljević Petrović and Jelena Marković[24] and provide an initial overview of raw material diversity at specific sites in Serbia.

Another contributor to Serbian raw material studies is Josip Šarić who investigated Early and Middle Neolithic chipped stone tool assemblages[25] and is currently working on Palaeolithic finds from the site of Kremenac, an important raw material source in the study area of the current project.[26] The most relevant published sources for the present study are the comprehensive investigations conducted by Zoran Miladinović who has discussed potential gemstone deposits (i.e. chiefly jaspers, agates, and chalcedonies) throughout present-day Serbia in great detail, including the provision of specific geological background information pertaining to all of the source areas.[27] The region of interest for the current undertaking is also included in this work and much preliminary information regarding local raw materials used on the archaeological sites under investigation can be found in these papers.

6. Hypotheses and Sampling Strategy

In order to tackle the nature and potential 'theoretical indicator centres' (TIC) of the SiO_2 gravels interspersed into the Neogene Leskovac Basin fill mélange, three distinct primary and sub-primary sources representing the most frequent NVS varieties (i.e. NLS, chalcedony, and jasper) were selected for geochemical analysis. Bučumet/Kameno Rebro and Rasovača are located west of the study area in the foothills of the Radan Mountain with Kremenac located further to the north, close to the city of Niš. Subsequently, the analytical results were compared with a sample of NLS from an alluvial gravel-sand deposit north of Lebane (Fig. 1).

The working hypothesis for the geochemical investigations was based on the assumption that the pattern of trace element distribution in lithic materials from primary deposits is reflected in materials in a secondary position from the same lithogenetic environment. In the case of NLS the following scenario can be proposed: NLS represent the silicified components of a specific host rock environment, in this specific case lacustrine sediments. Silicon (Si), which was dissolved under hydrothermal conditions in volcanic environments in the vicinity of these lacustrine formations, impregnated and silicified those sediments. Together with Si, trace elements were transferred into the lacustrine sediments, creating a source specific 'fingerprint'. Consequently, the trace element content in the products of the silicification processes, the NLS, reflects the larger geological environment. In the current study it was expected that the trace element distribution in the geological test sample from Lebane would display the closest affinity to the comparative geological samples coming from the same volcanic host environment, allowing the area from which the material originated to be identified.

21 Sant et al. 2017.
22 Hesse 1990.
23 Obradović, Goričan 1988.
24 Bogosavljević Petrović, Marković 2014.
25 Šarić 2002.
26 Šarić 2011. – Šarić 2013.
27 Miladinović 2012. – Miladinović et al. 2016.

7. Materials and Methods

For the provenance studies samples from primary deposits and secondary contexts were collected during geological field surveys. The source locations were chosen using previous studies conducted by Miladinović and colleagues[28] and Josip Šarić[29], with detailed geo-prospection of secondary deposits in the Leskovac Basin.

7.1. Primary Deposits

Rasovača (RA) and Bučumet/Kameno Rebro (KA)

According to Miladinović et al.[30], these deposits are lithogenetically linked to andesites of the Lece volcanic complex and were formed in the course of hydro- and telethermal activities. At Rasovača, Byzantine gemstone quarries primarily linked to Iustiniana Prima (Caričin Grad)[31] were established and gemstone extraction continued until recent times. The variation in SiO_2 rocks at Rasovača includes amethyst, agate, and subordinate red jasper. The geological sample consisted of iron-rich red jasper since this was the only material suitable for chipped stone tool production (Fig. 2). This material displayed partly significant heterogeneity, which had to be taken into account for the geochemical analyses.

Residual and sub-primary deposits of inorganically formed chalcedony and multi-coloured jaspers are found at Kameno Rebro, part of the small village of Gornji Bučumet (Fig. 3). For this study, samples from large chalcedony boulders (up to 3 m long and 1 m wide) were collected for petrographic and geochemical analyses.

Kremenac (KR)

Kremenac is located within the Carpatho-Balkan metallogenic province close to the village of Rujnik. The raw material deposit is situated on a gentle, elongated slope at the northern margin of the Niš Basin, measuring approximately 1.5 km from north to south and 200–270 m in width. The raw material at Kremenac corresponds to semi-translucent NLS varieties, predominantly of a greyish-blue colour (Fig. 4). At Kremenac, artefacts of Palaeolithic and later date were recovered, attesting to raw material extraction and on-site workshop activities.[32]

28 Miladinović et al. 2016.
29 Šarić 2011.
30 Miladinović et al. 2016.
31 Birk et al. 2014.
32 Šarić 2011.

7.2. Secondary Deposits in the Leskovac Basin

Secondary lithic deposits in the Leskovac Basin are associated with the Lece volcanic complex, which was formed as a result of Neogene volcanic activity and covers an area of over 700 km² in southern Serbia. It is part of the Serbo-Macedonian metallogenic province, also referred to as Lece-Chalkidiki metallogenic zone. Dominating lithologies are andesite, (biotitic) gneiss, granite, mica schist, amphibolite and quartzite. Volcanic activity commenced during the Upper Oligocene and continued during most of the Miocene period. Deposits of siliceous rocks were formed in the Lece volcanic complex as a result of hydro-/epithermal (producing quartz-brecciated zones and quartz/agate veins) and telethermal (producing siliceous sinters and volcanic agates) activity. Deposits of mechanical sediments (predominantly alluvial placers with gravels) resulted from the erosion of the primary endogenic formations and cryptocrystalline SiO_2 modifications were introduced into Neogene sediments of the Leskovac Basin.[33] These Neogene sediments are characterised by clay-sand series in the west and gravel-sand series in the east of the study area, and contain cryptocrystalline SiO_2 modifications.

Geoarchaeological surveys produced more detailed information concerning deposits of cryptocrystalline SiO_2 modifications in the site catchment area:

(1) Geological profiles produced by road cuts or (more or less recent) sand and gravel quarries reveal that the SiO_2 gravels are irregularly interspersed into the sandy matrix and do not form distinct layers.

(2) Rivers that cut through the Neogene sediments expose and accumulate siliceous rocks of up to 30 cm diameter but these are generally of very poor quality due to internal fissures and cracks which are the result of frost-cracking since the temperature frequently drops below -10°C during the winter.

(3) In certain places accumulations of siliceous rocks (and specifically of cryptocrystalline SiO_2 modifications, placer deposits) outcrop in agricultural fields and are exposed during ploughing. It appears that such surface accumulations represent spatially restricted deposits, as indicated by Miladinović.[34]

7.3. Analytical Strategy

Provenance studies follow the MLA chert sourcing concept.[35] In order to achieve conclusive results, a systematic

33 Miladinović et al. 2016.
34 Miladinović 2012.
35 Brandl 2016.

multi-layered technique combining three analytical steps was applied. Macroscopic/visual inspection for the initial grouping and stereo-microscopic investigation for micro-facies analyses[36] were coupled with geochemical analyses using Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS). This turned out to be one of the most promising approaches for the sourcing of chert. One important advantage of LA-ICP-MS is its (relatively) non-destructive character, which is consistent with the requirements of conservation when investigating archaeological finds. Additionally, this method allows for the detection of major- (1–100 %), minor- (0.1–1 %), trace- (1–1000 ppm), and ultra-trace elements (<1 ppm) and the rapid simultaneous analysis of c. 50 elements. Prior to LA-ICP-MS analyses, the mineralogy and major element composition of each sample was detected with an electron probe micro-analyser (EPMA). EPMA allows documenting the structure and texture of the sample by means of secondary and back scattered electron images and the quantitative analysis of singular minerals on a µm-scale. Five spots per sample were analysed to cover the compositional variability.

Trace elements were determined by LA-ICP-MS (Agilent 7500ce quadrupole ICP-MS unit) located at the Central Laboratory for Water, Minerals and Rocks, NAWI Graz Geocenter (University of Graz and Graz University of Technology, Austria), with sample introduction through an ESI NWR-193 laser ablation system. The spot size of the 193 nm wavelength laser was 75 µm, operated at 8 Hz pulse frequency corresponding to an energy of ~7 mJ cm-1. Ablated material was transported via a helium gas stream (0.7 1 min-1) into the argon plasma torch of the mass spectrometer and passed into the ICP-MS unit. Standard reference glass NIST SRM 612 was routinely analysed for standardisation and drift correction.[37] NIST SRM 614 was analysed as unknown and reproduced within 10 % relative error. Silicon (Si) was used as internal standard. For data reduction in GLITTER, a SiO_2 value of 99 wt% was established for the investigated samples, except for the Rasovača samples (RA) where values determined by microprobe in the range of 70 to 95 wt% were used. The detection limit of LA-ICP-MS is typically 0.1 ppm for most elements. In order to control natural heterogeneities in SiO_2 rocks (e.g. silicites), three individual spots were ablated per sample. From each geological comparative deposit, fifteen samples were analysed. The test sample from Lebane consisted of seven specimens.

8. Results and Discussion

8.1. Characterisation of Raw Materials from the Leskovac Basin

Rocks suitable for chipped stone tool production in the Leskovac Basin consist of multi-coloured cryptocrystalline SiO_2 modifications with chalcedony as main constituent (entire sections of the rock or veins and cleft fillings). Pale bluish/pinkish varieties consist of chalcedonies and intensely coloured jaspers (red/yellow/multi-coloured), which is in accordance with previous studies in this region (Fig. 5).[38] However, the vast majority of siliceous rocks consists of Neogene Lacustrine Silicites (NLS), sometimes displaying fossil inclusions. Although the poor preservation of the micro fossils only allows imprecise identification, the presence of fossil remains indicates an origin in a lacustrine environment. Algae remains (stems of charophyta) and gastropod shells were detected in the samples from Lebane under reflected light stereo-microscopy (Fig. 6). It appears that hydrothermal activity silicified components of this lacustrine environment, most probably including limestones, which were entirely eroded and eventually merged into the gravel-clay-sand series west of Lebane. The NLS components in the basin fill are associated with the Miocene Serbian Lake System.

8.2. Geochemical Results, Discussion, and Conclusion

Altogether, 40 trace elements were effectively determined through geochemical analyses using LA-ICP-MS (see Appendix 1): Li7, Be9, B11, Mg24, Al27, P31, K39, Ca43, Ti49, V51, Cr53, Mn55, Fe56, Co59, Ni60, Cu63, Zn66, Ga71, Ge74, As75, Rb85, Sr88, Y89, Zr90, Nb93, Cs133, Ba137, La139, Ce140, Pr141, Nd146, Sm147, Eu153, Gd157, Dy163, Er166, Yb172, Pb208, Th232, U238.

Bivariate statistical analysis contrasting trace elemental couples in scatter plot diagrams revealed that boron (B), aluminium (Al), germanium (Ge), lead (Pb), and barium (Ba) are suitable for the differentiation of the geological sources and the allocation of test samples to a specific source region. A separation between Kameno Rebro (KA), Rasovača (RA), and Kremenac (KR) can be achieved with only minimal overlapping effects by contrasting boron against aluminium (Fig. 7), and germanium against lead (Fig. 8) and barium (Fig. 9). Using the same elemental couples, the test sample from Lebane (LEB) corresponds best with the KA and RA clusters, with only a few outliers falling into the KR data field (Figs. 10–12). It seems therefore that a lithogenetic correlation between the KA/RA source area (= Lece

36 Affolter 2002.

37 Concentrations from Jochum et al. 2011.

38 E.g. Miladinović 2012. – Miladinović et al. 2016.

Fig. 2. Red jasper samples from Rasovača (Photo: M. Brandl).

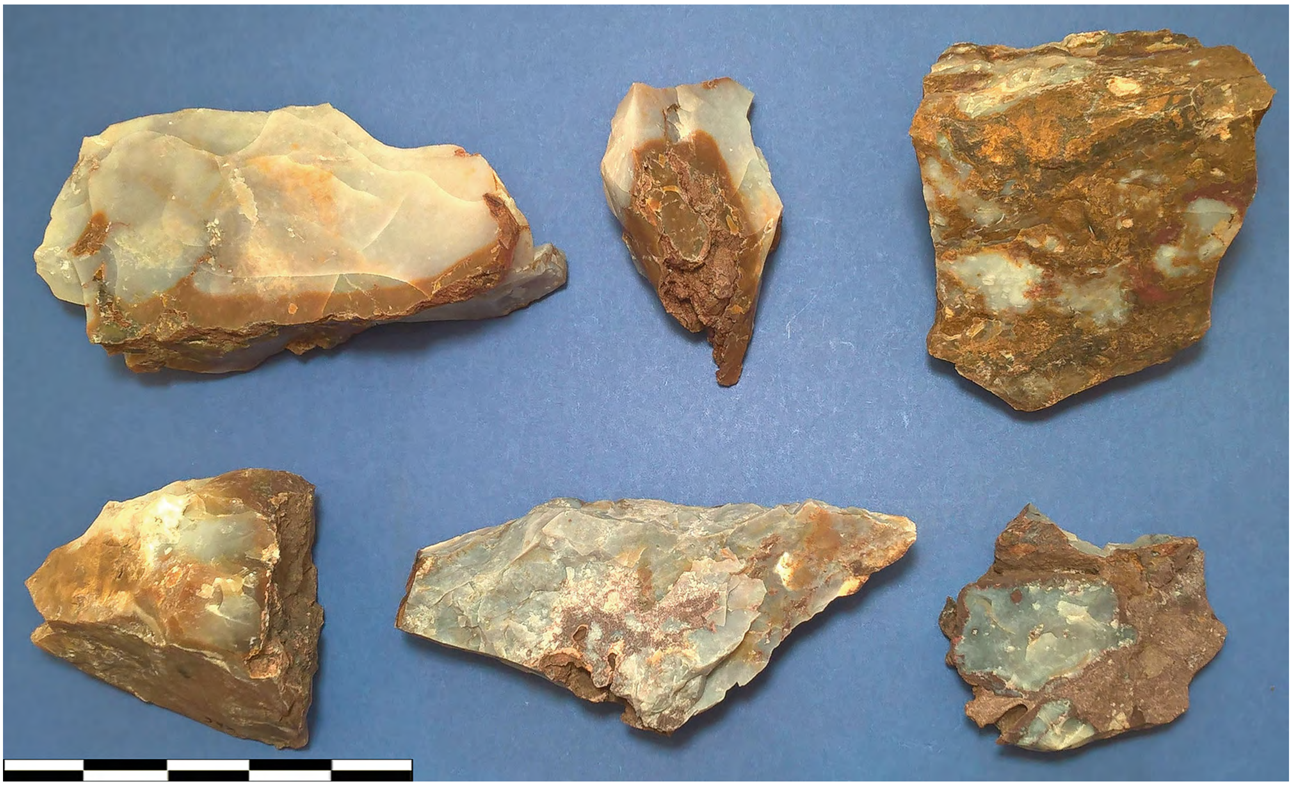

Fig. 3. Chalcedony samples from Kameno Rebro (Photo: M. Brandl).

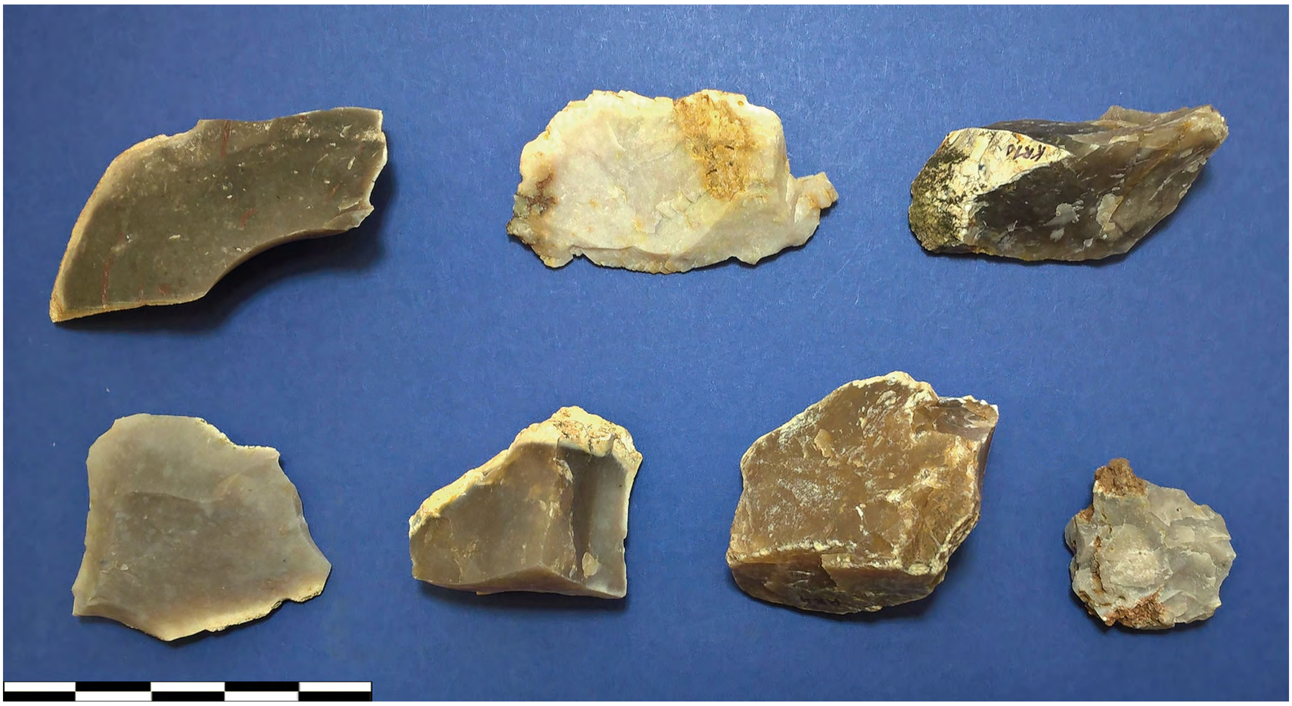

Fig. 4. Sample of Neogene Lacustrine Silicites (NLS) from Kremenac (Photo: M. Brandl).

Fig. 5. NVS type varieties from the Neogene clay-sand series in the Leskovac Basin from a river bed close to Lebane. Ch = chalcedony (Photo: F. Ostmann, OREA).

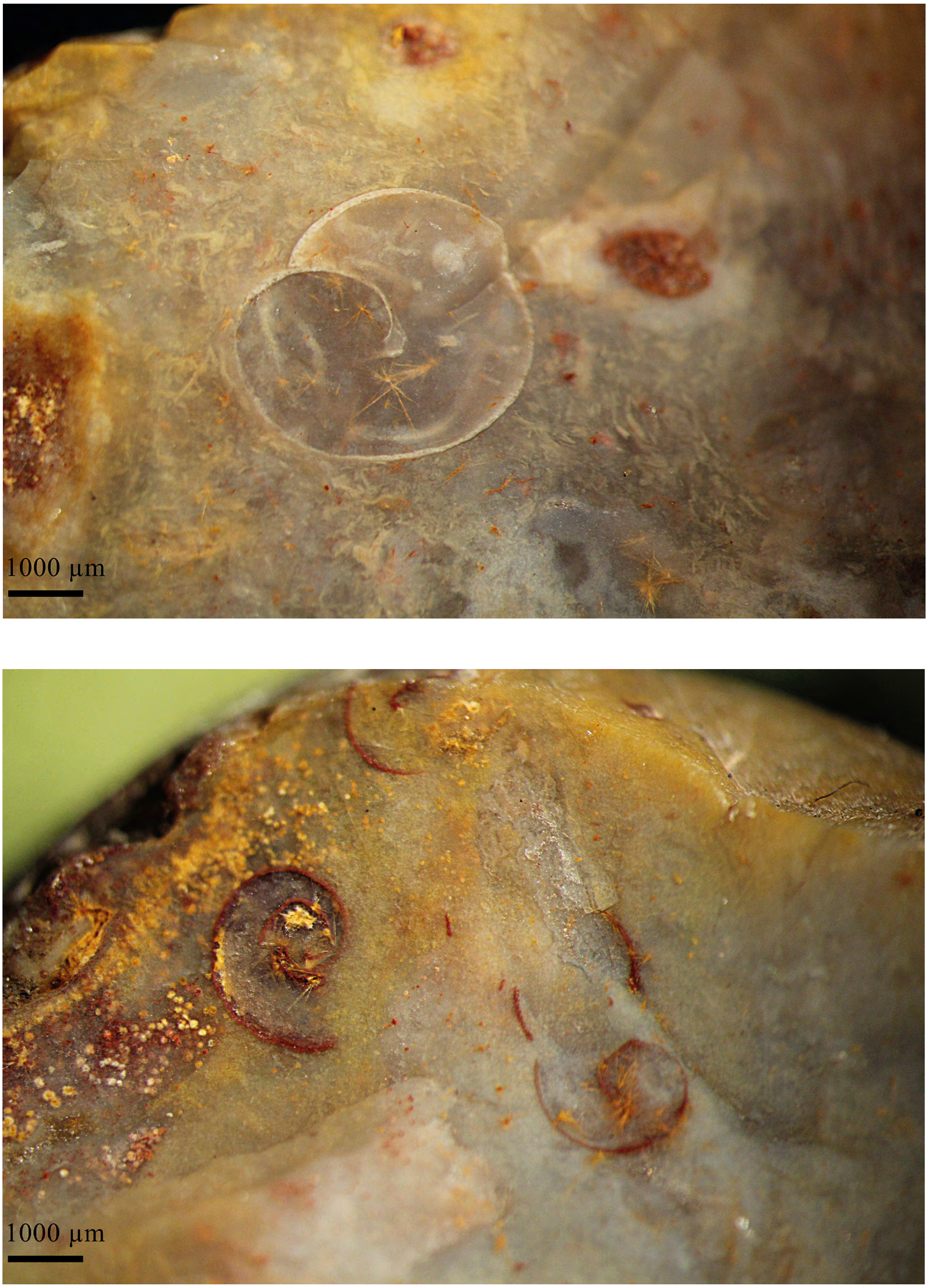

Fig. 6. Micrographs of gastropod inclusions in NLS from Lebane (Photos: M. Brandl).

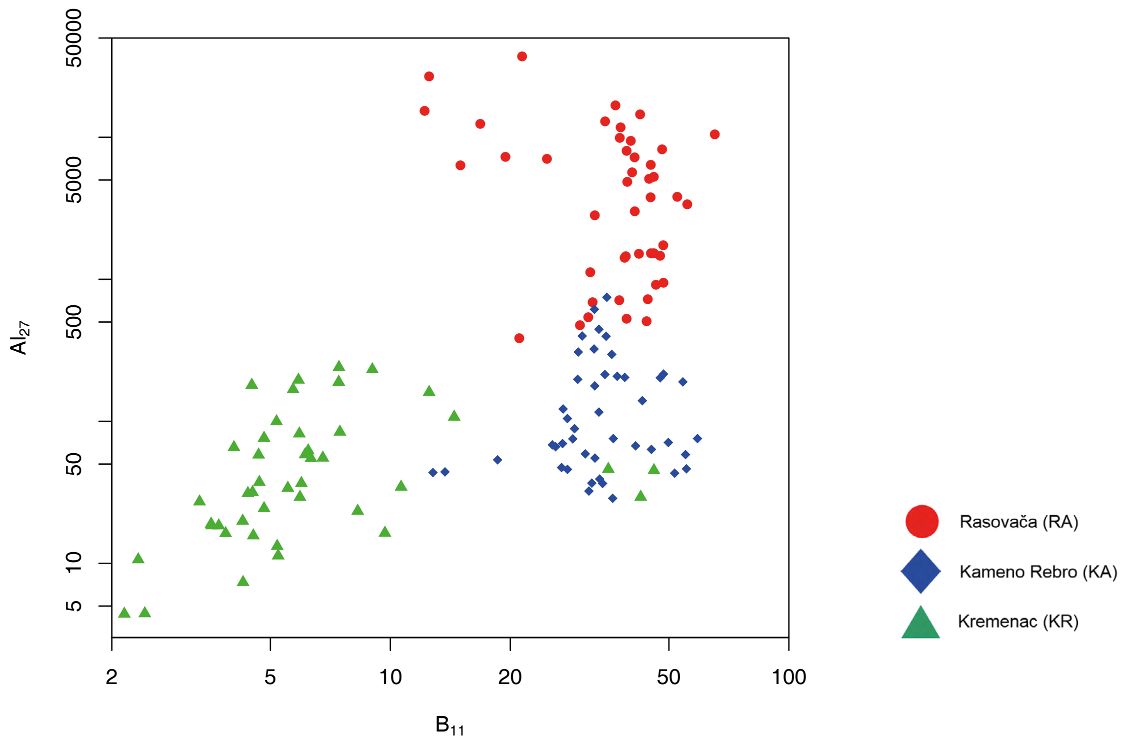

Fig. 7. Boron (B) versus aluminium (Al) concentration plots of data from the primary geological sources.

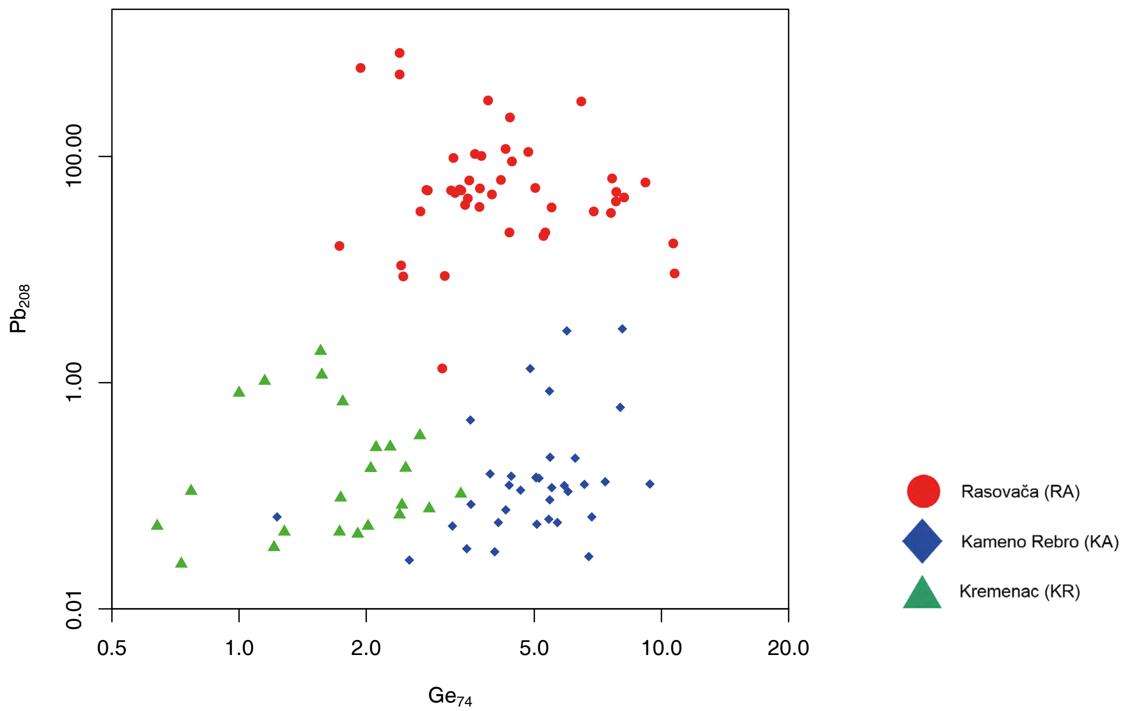

Fig. 8. Germanium (Ge) versus lead (Pb) concentration plots of data from the primary geological sources.

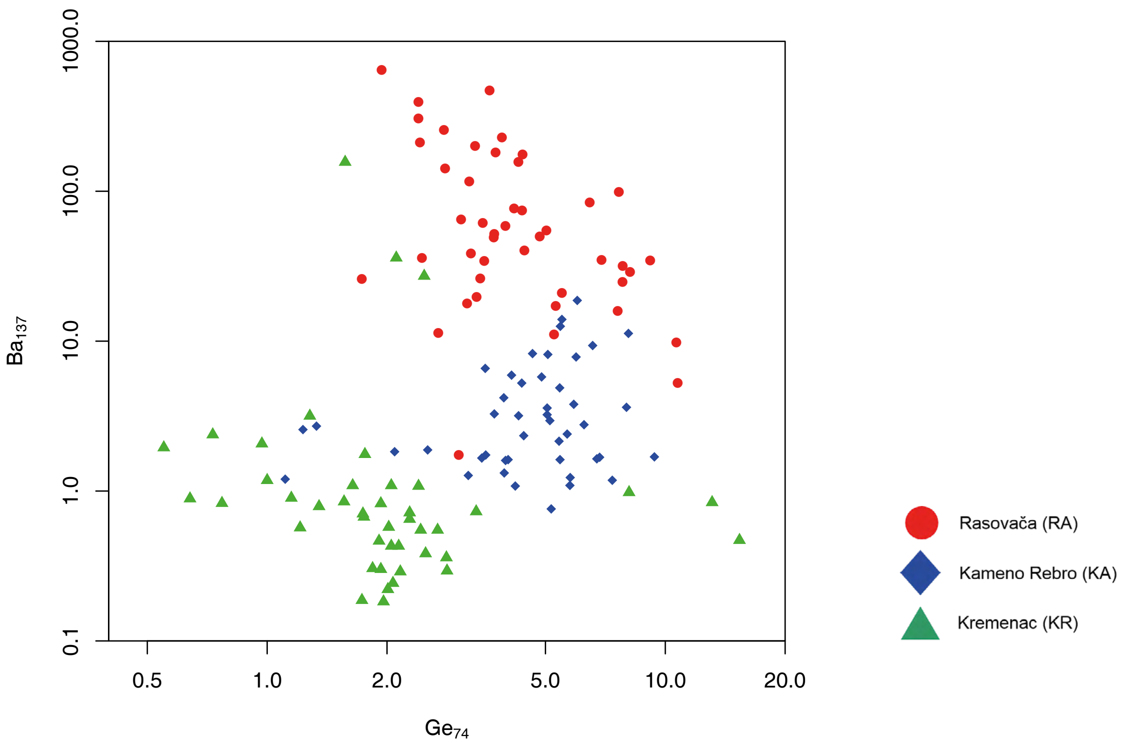

Fig. 9. Germanium (Ge) versus barium (Ba) concentration plots of data from the primary geological sources.

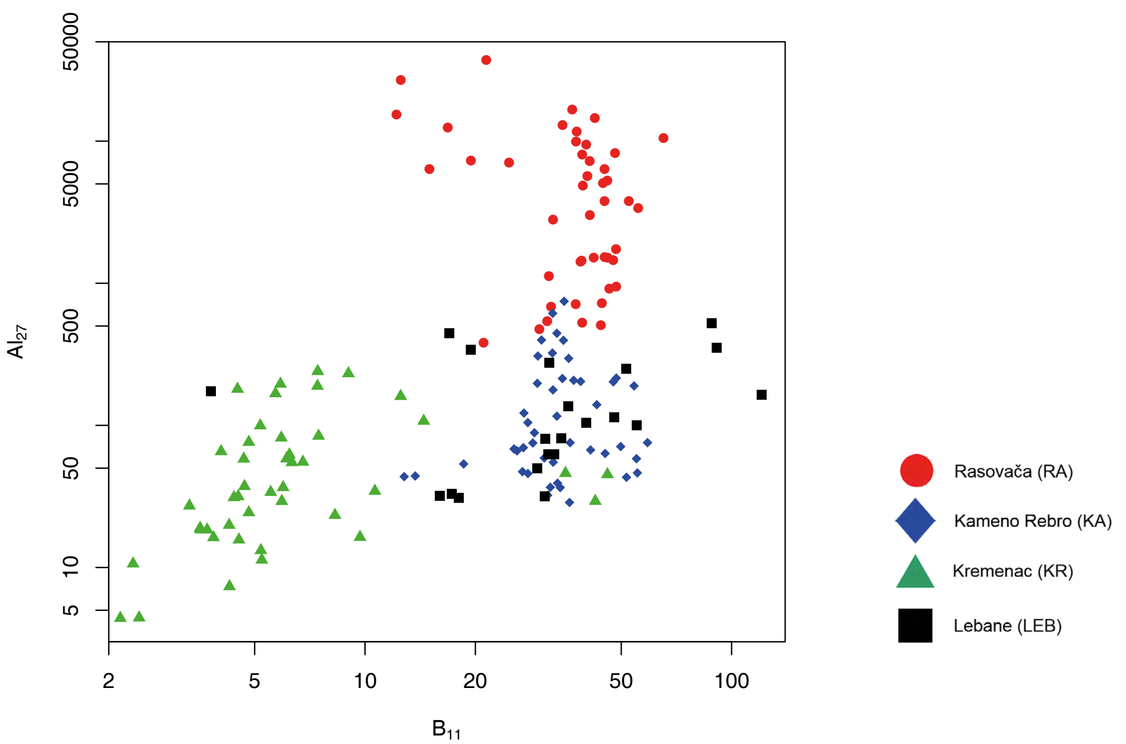

Fig. 10. Boron (B) versus aluminium (Al) concentration plots of data from the primary geological sources and the test sample from Lebane.

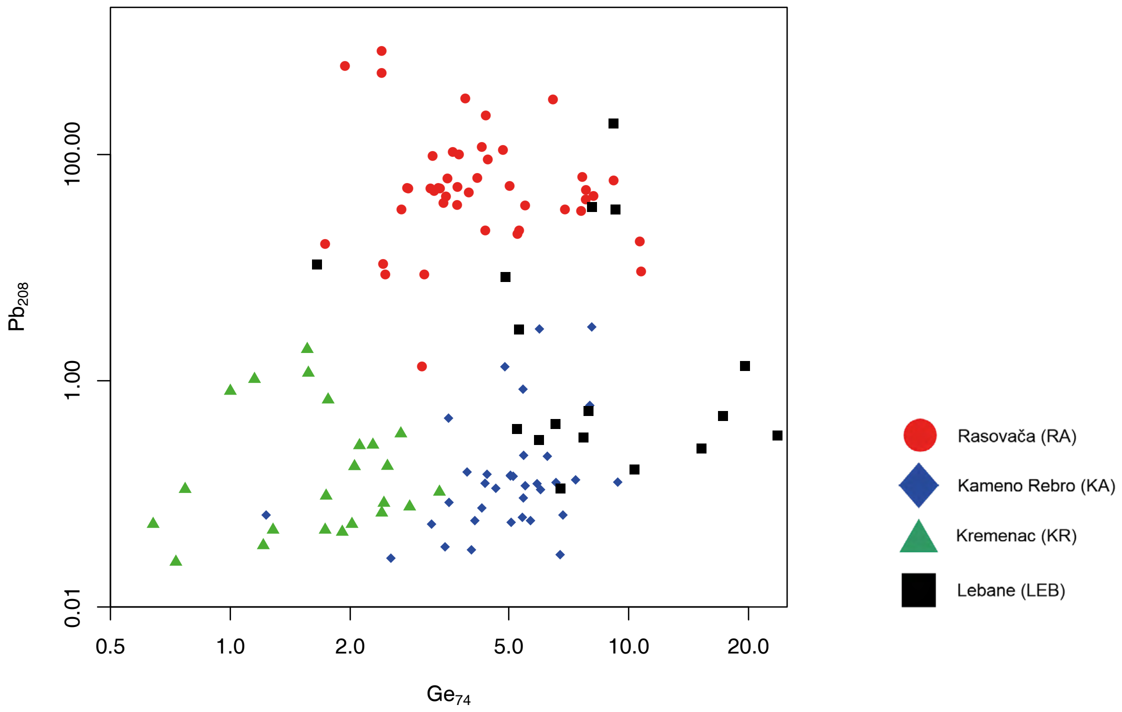

Fig. 11. Germanium (Ge) versus lead (Pb) concentration plots of data from the primary geological sources and the test sample from Lebane.

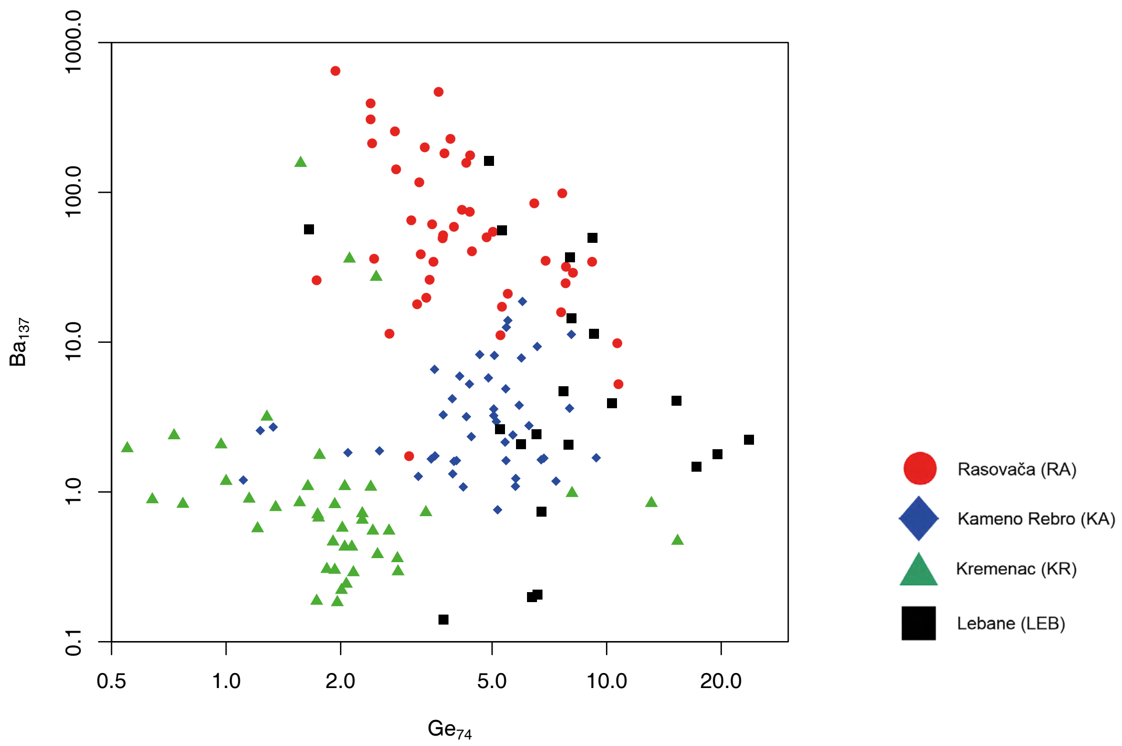

Fig. 12. Germanium (Ge) versus barium (Ba) concentration plots of data from the primary geological sources and the test sample from Lebane.

volcanic complex) and the LEB sample can be established and the KR source can be distinguished from the former deposits.

The presence of B, Al, Ge, Pb, and Ba in the siliceous rocks investigated is linked to localised volcanic activities[39] and therefore displays a distinctive distribution within the analysed samples. Trace element distribution appears to be source specific and thus confirmed our working hypothesis.

Although preliminary in nature, these results have significant implications for geochemical sourcing studies of lithic materials far beyond the study area. Several attempts have been undertaken with varying success,[40] but sourcing materials from secondary deposits is generally considered critical.[41] The current study demonstrates that through a systematic sampling strategy and asking the right questions of the materials under investigation, such an attempt can produce significant results. In the present case, it was possible to assign lithic materials from a secondary deposit to potential primary source areas.

One limitation is the question of whether the raw material for a specific archaeological artefact was actually obtained from a secondary source or from the primary source of the same material. In such cases, only the surviving traces of the natural surface (i.e. cortex in the case of silicites) can securely establish the provenance of an artefact, whether from a river, from a residual source, or from a primary deposit. This problem is minimised in lithic assemblages that contain several specimens of the same type of raw material procured from the same geological source, since traces of the original surface are normally present on at least some of the objects.

In the future, we hope to be able to trace archaeological material back to a secondary source area through the characterisation of primary deposits based on innovative strategies in gravel research, employing the MLA chert sourcing method. This scientific advance will significantly contribute to the inquiry into Neolithic 'resource management' on a broader scale.

Appendix 1

Supplementary LA-ICP-MS data related to this article can be found at:
https://epub.oeaw.ac.at/archaeologia102/Supplement_Brandl_Hauzenberger

39 Peccerillo, Taylor 1976. – Ryan, Langmuir 1993. – Winter 2001. – Gondal et al. 2009.

40 E.g. Luglièa 2006. – Milne et al. 2009.

41 E.g. Hughes et al. 2010, 19.

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