# THE MULTI LAYERED CHERT SOURCING APPROACH (MLA) ANALYTICAL PROVENANCE STUDIES OF SILICITE RAW MATERIALS

# TÖBBRÉTEGŰ STRATÉGIA KOVAKŐZETEK PROVENIENCIA VIZSGÁLATÁRA

MICHAEL BRANDL

Institute for Oriental and European Archaeology (OREA), Austrian Academy of Sciences

Hollandstraße 11-13, 1020 Vienna, Austria

E-mail: michael.brandl@oeaw.ac.at

## Abstract

*Provenance studies of chert and flint raw materials (silicites) are an important component of archaeological research. The identification of the sources of rocks used for the production of chipped stone tools is the gateway to any further investigations concerning prehistoric resource management strategies. Chert source provenance studies thus play a significant role in the interpretation of lithic assemblages concerning the procurement, processing and distribution of lithic raw materials, e.g., revealing routes of migration, intercultural exchange and circulation networks.*

*A transdisciplinary concept (the Multi Layered Chert Sourcing Approach, short MLA) presents a possibility for successfully sourcing chert and flint. The proposed method consists of a tripartite analytical system: Visual (macroscopic), microscopic and petrological/geochemical. For geochemical analysis, Laser Ablation-Inductively Coupled-Mass Spectrometry (LA-ICP-MS) is applied. LA-ICP-MS allows for the detection of main-, trace- and ultra-trace element concentrations (-0.1 ppm) in rock materials and has been well established in lithic raw material research. The multivariate geochemical datasets are subsequently evaluated by applying Compositional Data Analysis (CODA). Since CODA is concerned with the ratios between values, raw composition data (i.e. the absolute measured values) need to be transformed into the Euclidean geometry system where statistical methods can operate. After transformation, discriminant analysis (DA) is applied for classification. Several successful studies demonstrate the potential of the MLA illustrating that it is not sufficient to rely on a single analysis method for chert sourcing. A combination of the proposed techniques produces the most robust data base for a secure characterisation and source separation, including the possibility to lay weight on the performed method(s) that produced the best results.*

## Kivonat

*A kovakőzetek származási helyének vizsgálata fontos eleme a régészeti kutatásnak. A pattintott kőeszközök nyersanyagforrásainak azonosítása elsődleges feltétele minden további, az őskori nyersanyagforgalom és gazdálkodás kérdéseit vizsgáló kutatásnak. A kovakőzetek proveniencia vizsgálata ennél fogva lényeges szerepet játszik a nyersanyag beszerzés, feldolgozás és elterjedés kérdéseinek kutatásában, így a vándorlási útvonalak, a kultúrák közti cserekapcsolatok és hálózatok feltárásában. A sikeres nyersanyag-lelőhely azonosítás lehetőségét egy multidiszciplináris stratégia jelentheti, amit rövidítve MLA-nak nevezhetünk (Multi Layered Chert Sourcing Approach, több rétegű kova nyersanyag azonosítás). A javasolt módszer három szintes vizsgálatot feltételez: vizuális (makroszkópos), mikroszkópos és kőzettani/geokémiai szemléletű vizsgálat. Ez utóbbira, lézer ablációs tömegspektrometriát (LA-ICP-MS) alkalmaztam. Ez a módszer lehetővé teszi a főalkotók, nyomelemek és nagyon kis mennyiségben jelen lévő ultra-nyomelemek (-0.1 ppm) vizsgálatát is, jól ismert és elfogadott a kő-nyersanyag vizsgálatokban. A sokváltozós geokémiai adathalmazt ezután statisztikai összetétel-elemzéssel (Compositional Data Analysis, CODA) vizsgáltam. Miután a CODA nem az abszolút értéket, hanem az értékek közötti arányokat vizsgálja, a nyers adatokat ennek megfelelően alakítottam át. Az átalakítás után diszkriminancia analízist végeztem (DA) a csoportok elkülönítésére. A módszer hatékonyságát több sikeres esettanulmány támasztja alá. A különböző technikák együttes alkalmazása lehetővé teszi a nyersanyagforrások megfelelő jellemzését és a régészeti lelőhelyek anyagának azonosítását.*

KEYWORDS: CHERT SOURCING, MLA, MICROSCOPY, GEOCHEMISTRY, LA-ICP-MS, COMPOSITIONAL DATA ANALYSIS

KULCSSZAVAK: KOVA NYERSANYAG AZONOSÍTÁS, TÖBBRÉTEGŰ ELEMZÉS, MIKROSZKÓPOS VIZSGÁLAT, GEOKÉMIA, LA-ICP-MS, ÖSSZETÉTEL VIZSGÁLAT

## Introduction

The scientific study of raw materials used for the production of chipped stone tools can be condensed into two main questions: (1) What kind of materials were used, and (2) where did they originate from.

(1) The initial step when analysing chipped stone tool assemblages is the proper determination of the materials present, i.e., silicites (chert, flint), jasper, chalcedony, opal, quartz, etc. There exist well established analytical methods that can be employed for achieving this task, since this question is situated within the field of classical petrology and mineralogy. However, some terminological disagreements do still exist amongst geo-scientists especially when addressing members of the silicite group, thus hampering comparisons on an international level. Hence, a brief discussion concerning this issue will also be provided in this paper.

(2) The second issue is more complex and concerns the provenance of lithic raw materials. The Multi Layered Chert Sourcing Approach (MLA) is specifically designed to investigate the origin of biogenically formed siliceous rocks (i.e. silicites), which is the main focus of this contribution.

Although there was a rapid progress in provenance studies during the last decade, a standard method for assigning members of the Chert Group as defined by Brandl (2014) to their original source or source region was never established. This goal could be achieved with the MLA, which was developed and further refined in the course of various international case studies. The method does of course not make the claim to be the only functioning system for chert sourcing, but it is a solid analytical approach that can be individually adapted to the geological conditions which determine the possibilities for a source separation.

## Silicite terminology

Silica occurs in at least 15 crystalline and amorphous modifications in the Earth's crust, with the identical chemical formula $SiO_2$ but differing crystal structure (Götze 2010, 164). Petrologically, $SiO_2$ rocks are best classified according to their magmatic, metamorphic or sedimentary origin, with the vast majority belonging to the latter group. Siliceous sediments are typically formed through chemical, biochemical and diagenetic $SiO_2$ precipitation and can be neutrally grouped under the term "silicites". They belong to the group of non-detrital chemical sedimentary rocks, of which members of the Chert Group form the most important component (Götze 2010; Přichystal 2013).

Silicites occur since the Precambrian period, e.g. on the East European Platform, and chronologically extend into the Neogene (see **Table 1**.). These siliceous rocks can form in marine or lacustrine environments.

Within this broadly defined Chert Group one specific material has to be specifically addressed due to the oftentimes erroneous use of the term: Flint. The term "flint" is widely used in archaeological literature referring to a wide range of $SiO_2$ raw materials. The definition of a silicite raw material as "flint" is typically related to one of the following attributes: 1. the macroscopic appearance (e.g. Black flint), 2. the geographic region (e.g. Baltic flint) or 3. the geological age (e.g. Danian flint). A fourth aspect may be added here, i.e. quality (typically referring to granularity). Oftentimes archaeologists classify poor quality material as "chert" and high quality $SiO_2$ varieties, which are in most cases cryptocrystalline, as "flint".

Regarding the frequent and oftentimes confusing (i.e. random) use of the term flint, this material deserves further attention. The following parameters may help to decide on the proper use of the term:

*Geographic occurrence:* Sensu stricto flint exclusively occurs in Europe north of the Alps and most commonly in Northern Europe (Scandinavia). Flint bearing geological formations roughly extend from England to the Ukraine and western Russia.

*Geological age:* According to Přichystal (2010, 179) the term "flint" should only be used for nodular siliceous rocks of Upper Cretaceous (Maastrichtian) and Lowermost Palaeocene (Danian) age. However, an expansion of the geological timeframe to the entire Upper Cretaceous stage including all geological stages from the Cenomanian to the Danian seems appropriate in order to avoid a too narrow definition which would again lead to misconceptions.

*Genesis environment:* Flint of Upper Cretaceous age is bound to chalk formations, and Danian flint in marine limestone, which is reflected by characteristic (micro-)fossil inclusions.

Hence, in the true sense, flint is of Upper Cretaceous (including Early Paleocene) age and exclusively bound to northern European chalk and limestone formations displaying comparable fossil inclusions and formation environments (Brandl 2014, 42).

**Table 1.:** Terminological system for members of the Chert Group.

**1. táblázat:** Kovakőzetek megnevezésére javasolt terminológiai rendszer

| **Material** | **Index fossils** | **Terminology** | **Type** | **Petrological genesis** | **Structure** |
|---|---|---|---|---|---|
| ***Chert*** | radiolarians | radiolarite | rock | biochemical sedimentary<br>**Precambrian - Neogene**<br>ca. 3.5 Myr – 10 Ma | (crypto-) microcrystalline |
| | sponge spicules | spiculite | | | |
| | sponge remains | spongiolite | | | |
| | forams, echinoderms, others | *chert* | | | |
| ***Flint*** | Cretaceous marine organisms | (Baltic/ Scandinavian) *flint* | rock | biochemical sedimentary<br>**Upper Cretaceous**<br>**including Danian**<br>100.5 – 61.6 Ma | crypto- microcrystalline |

## *Silicite genesis*

For provenance studies, the most important questions concern the origin of the silica and the genetic conditions under which silicites were formed (i.e. the host rock facies and diagenesis).

As previously stated, chert formation can take place in marine or lacustrine environments. Within marine genetic environments the source of silica in cherts is commonly assigned to bioactivity or volcanic processes, with the former prevailing. Involving biogenetic factors, four controlling factors for chert formation can be distinguished: Temperature, burial depth, age and host rock facies. Diagenesis of biogenic sediments as displayed in **Fig. 1.** is initiated by pressure causing the dissolution of organic remains. Increasing temperature leads to reduction of water over time triggering recrystallisation processes forming opal-A, so-called “skeletal opal”.

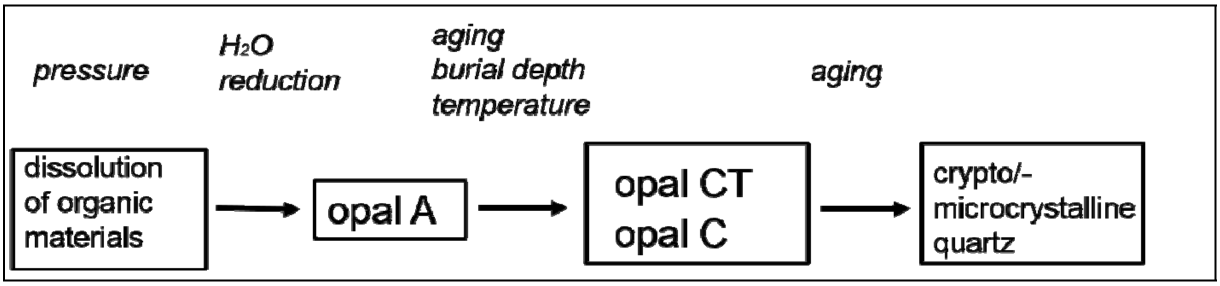


**Fig. 1.:** Diagenesis of biogenic sediments

**1. ábra:** A biogén eredetű üledékek diagenezise

Transformation of the amorphous opal-A phase into microcrystalline opal-C and opal-CT depends on time, burial depth and temperature. With aging the coarseness of microcrystalline $SiO_2$ modifications increases resulting in the recrystallisation into macro-quartz with aged cherts (Calvert 1974; Graetsch, Grünberg 2012, 20).

If microfossils are not present (e.g. in Precambrian cherts), the impregnation or replacement of sediments by siliceous solutions is also possible. In such cases, volcanic activities producing saturated solutions or, if the host rock environment does not indicate sufficient volcanic activity for silification, silica dissolved from continental chemical weathering are the main sources of silica (e.g. Laschet 1984).

In lacustrine environments diagenesis and chert formation is assigned to very similar processes, however, due to the highly diverse geological settings of non-marine chert deposits lacustrine chert formation is still not entirely understood.

## Microstructure of silicites and trace elements

According to Greatsch and Grünberg (2012) chalcedony is the dominating rock constituent of most microcrystalline $SiO_2$ modifications. Additionally, moganite can be present up to ca. 20 wt.% in cherts. Hence, most silicites display a fibrous microstructure (exceptions are e.g. lacustrine cherts like Styrian Rein Basin chert which displays a microgranular structure; see in Brandl et al. 2014b, 264). Planar structural defects, moganite content, crystalline domain size and microstrain are anisotropic and correlated with each other. Structural elements in chert and flint as described by Micheelsen (1966) could not in all cases be reproduced (Flörke et al. 1991; Greatsch, Grünberg 2012).

Due to the fact that micro- and cryptocrystalline modifications of quartz are typically very pure materials and can consist of nearly 100 wt% $SiO_2$ the concentration of additional components useful for the characterisation of a source is limited to trace elements which typically range between 200-500 ppm in silicites.

The trace element content in siliceous rocks can be attributed to the following geochemical processes:

Silica can be substituted by other cations in the crystal lattice of $SiO_2$ modifications, however, this is not very common. Substitution of $Si^{4+}$ is limited to ions with a similar ion radius and charge, such as $Al^{3+}$, $Ti^{4+}$, $Ge^{4+}$, $Fe^{3+}$ and $P^{5+}$ (high field strength elements). A charge difference of 1 is also possible, but requires additional cations or crystal defects to achieve neutrality (Faure 1998, 99-111).

Deposition of chemical elements in pore spaces is another possibility. If $Al^{3+}$ and $Fe^{3+}$ are present, additional cations such as $Li^+$, $Na^+$, $H^+$, and $K^+$ (low field strength or large ion lithophile elements) can occupy interstitial positions in the crystal lattice. There are two possibilities for trace elements to be deposited in pore spaces, co-genetically during the sedimentation processes or secondary in the course of diagenesis (Milliken 2003, 214-218). Additionally, the chemical composition can be altered in the course of weathering effects causing enrichment or depletion of trace elements on rock surfaces.

A third scenario involves synsedimentary inclusion of foreign minerals in the rock matrix. These are typically feldspar, carbonates, clay minerals and heavy-minerals. The presence of e.g. Ba, Ca, Al, Fe, Mn, Ni and Cr in silicites can be attributed to such foreign inclusion minerals.

## The Multi Layered Chert Sourcing Approach (MLA)

Quantitative methods have been applied in the past, however previous studies were not able to produce satisfying and conclusive results (e.g., Roll et al. 2005; Speakman & Neff 2005; Morgenstein 2006; Rafferty et al. 2007; Hughes 2010; Cheben & Cheben 2010). Due to the numerous constraints and limitations inherent in every analytical method, a concept including several layers of investigation promises the most reliable outcome. As a result the MLA was developed, combining visual (macroscopic), microscopic, and mineralogical / geochemical aspects (**Fig. 2.**). Geological formations do not display highly standardised patterns. They are comparable, however, they are not uniform. Hence, all analytical levels of the MLA adhere to the principle: Standardise when possible and individualise when necessary. This makes the analysis flexible and allows researchers to lay weight on the individual components of the method most suitable for raw material characterisation and source differentiation.

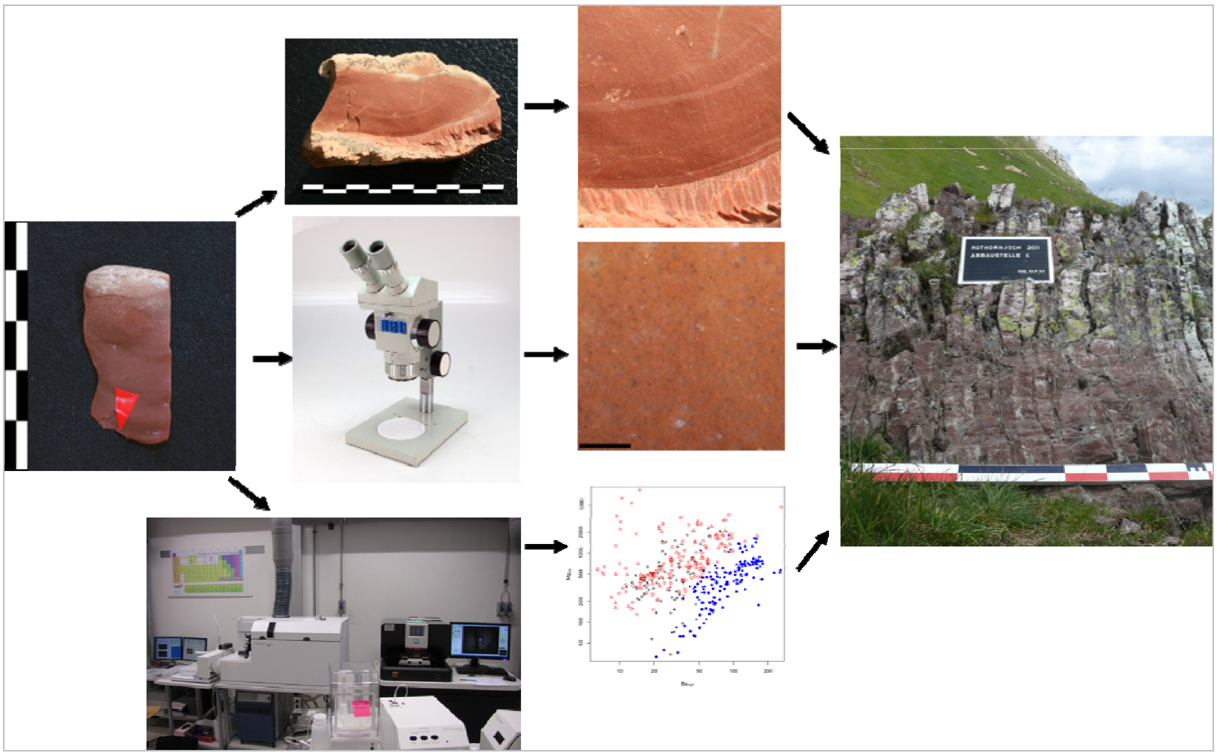


**Fig. 2.:** The Multi Layered Chert Sourcing Approach (MLA)

**2. ábra:** MLA modell: többrétegű stratégia kovakőzetek nyersanyag azonosítására

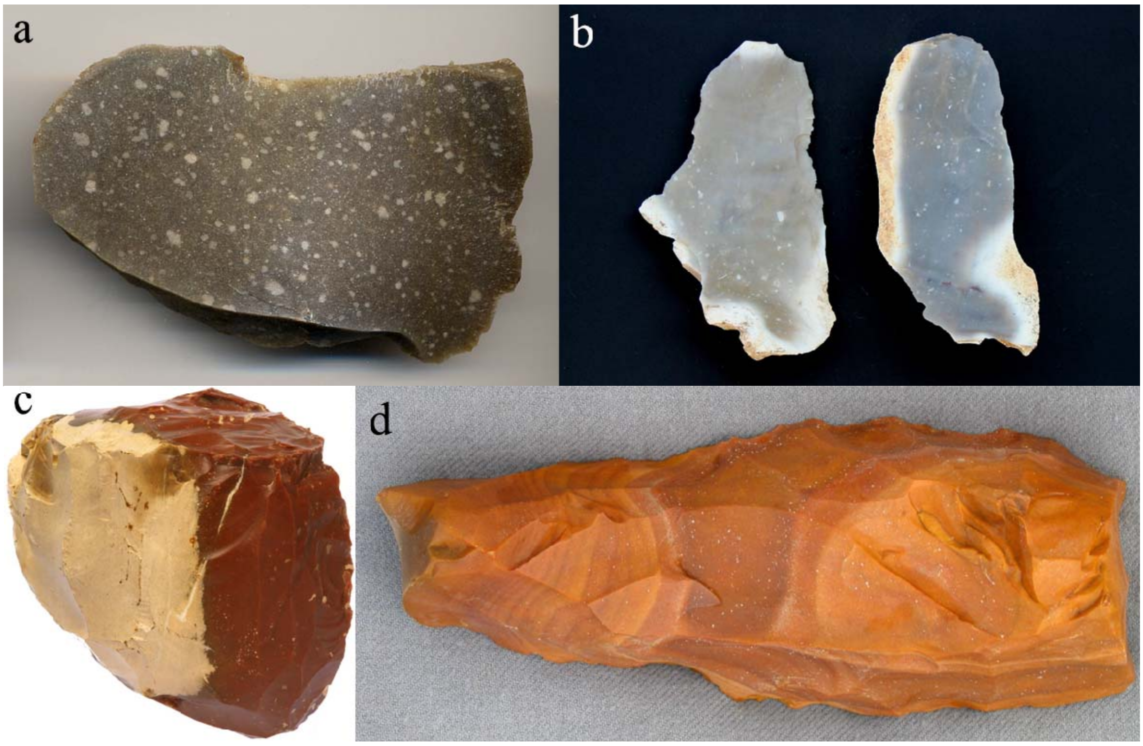
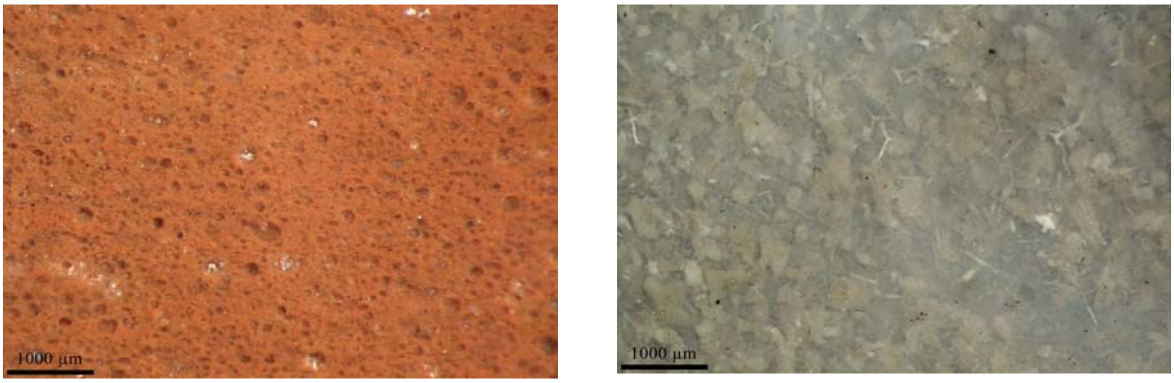


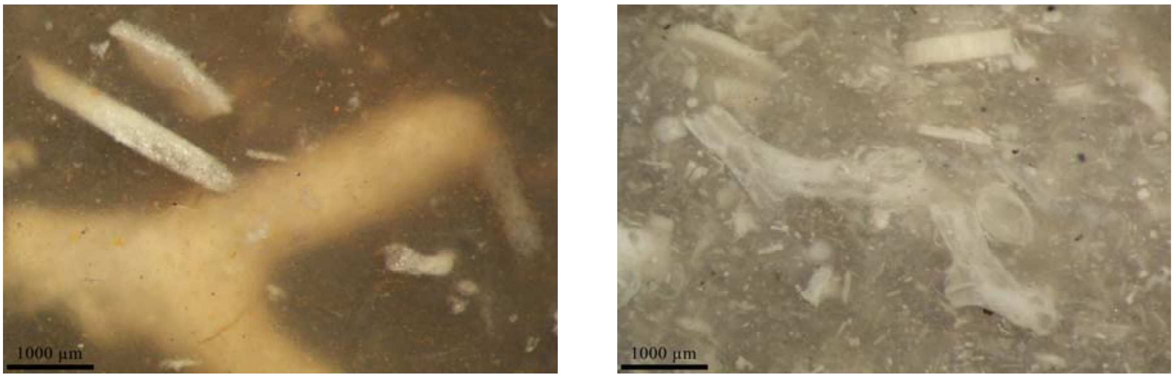
**Fig. 3.:** Comparison between high quality silicite varieties displaying characteristic features. 3a) Świeciechów, Poland; 3b) Monti Lessini, northern Italy; 3c) Szentgál-Tűzköveshegy, Hungary; 3d) Le Grand Pressigny, France. Photo courtesy G. Trnka.

**3. ábra:** Jellegzetes, jó minőségű kovakőzetek makroszkópos összehasonlítása. 3a) Świeciechów kova, Lengyelország; 3b) Lessini kova, Észak-Olaszország; 3c) Szentgál-Tűzköveshegy, radiolarit, Magyarország; 3d) Le Grand Pressigny kova, Franciaország. Fotók: G. Trnka.



4a) Radiolarians (Vienna Mauer, A)

4b) Various microscleres (sponge spicules) of demosponges (Krumlovský les, CZ)



4c) Bryozoa, spines and shell remains (Kraków, PL)

4d) Bryozoan colonies (Rømø, DK)

4e) Foraminifera (Val di Non, IT)

4f) Shells of *Planorbis* (Rein, A)

**Fig. 4.:** Examples for microfossil inclusions in chert and flint.

4a) Radiolarite; 4b) South Moravian chert; 4c) Kraków Jurassic chert; 4d) Silicite of Danian age (flint); 4e) South Alpine chert; 4f) Lacustrine Miocene chert

**4. ábra:** Mikrofosszília zárványok kovakőzetekben

4a) radiolarit; 4b) dél-morva kova; 4c) krakkói jura tűzkő; 4d) Harmadidőszaki (Danian) kovakőzet (tűzkő); 4e) dél-alpi kovakőzet; 4f) miocén korú tavi üledékes kovakőzet

### Layer 1: Macroscopic analysis

Visual group separation is an initial and valid analytical step towards source determination. It is however not sufficient to stop at this level of investigation due to the high macroscopic similarity of many silicite varieties.

Parameters that can securely be determined in the course of visual analysis are the hardness of the material by applying the scratch test using a steel nail which will help to evaluate if the rock is a silicite with the hardness of 7 according to Mohs (Brandl 2014, 39). Additionally, color information, rock texture, degree of internal fissuring and granularity can be recorded (compare **Fig. 3 a-d**). The latter two are the principal determinants when evaluating raw material quality for knapping.

### Layer 2: Microscopic analysis

There exist different microscopic methods that can be applied to silicite raw materials. Commonly thin sections and polished rock surfaces are investigated, however, when working with archaeological materials one principal requirement is non-destructive analysis. Hence, microscopy within the MLA concept is solely conducted on unpolished specimens. The purpose of microscopy is to detect fossil and non-fossil inclusions in silicites. Microfossil inclusions can be utilised to identify the age and origin of siliceous rocks based on characteristic individuals or entire fauna communities (e.g., Přichystal 1984; Brooks 1989) **(Fig. 4/a-f)**.

A method that helps to increase the optical effects for reflected light microscopy is known as water immersion. A drop of liquid on the rock surface enhances the optical resolution and compensates effects of the refractive index at air-water or air-material borders. As a result inclusions are better visible and can be determined with a higher security (Přichystal 1984).

### Layer 3: Geochemistry

Geochemical analyses in the framework of the MLA chert sourcing method are performed using Laser Ablation-Inductively Coupled-Mass Spectrometry (LA-ICP-MS). In the case of geological samples small chips (ca. 1x1 mm in size) are placed in resin mounts and polished prior to analysis in order to avoid analysing chemically altered rock surfaces ("patination effects") **(Fig. 5.)**. For geochemical investigations of archaeological materials non-destructive analysis is required. Because unpolished rock surfaces always bear the risk being chemically altered, even if they appear unpatinated, the solution for geochemically testing archaeological samples is to discard all data collected during the first ten seconds of the ablation process drilling through the surface area of the sample. The suitability of this procedure was successfully demonstrated in the course of previous studies applying the MLA for chert sourcing (Moreau et al. 2016, 233-234).

Each sample, geological and archaeological, is analysed at minimal three and up to ten discrete locations to control and minimise effects of heterogeneity naturally occurring in siliceous sedimentary rocks. The designated spots are selected according to rigid standards avoiding areas with apparent impurities, caused by e.g. microfossils or foreign mineral inclusions. Once the spots are defined a pulsed wavelength laser typically operated between 75 and 100 µm spot size vaporises (ablates) material from the surface. The ablated material is transported via helium gas stream into the argon plasma torch section of the mass spectrometer, where it is ionised and passed into the ICP-MS unit.

The standard reference glass NIST SRM 612 is used for standardisation and drift correction. Additionally, geological samples from the radiolarite source at Szentgál-Tűzköveshegy are used to define a "chert standard" at the University of Graz, Austria, where all LA-ICP-MS analyses were conducted to date. The standard glass NIST SRM 614 is analysed as unknown element due to its compositional similarity to most silicites. Only data that allow reproduction within 10 % relative error are accepted for our geochemical studies. Silicon (Si) is used as internal standard to control ablation efficiency and instrumental drift. The detection limit of LA-ICP-MS is typically 0.1 ppm for most elements, however the analytical error increases significantly with values below 1 ppm.

LA-ICP-MS is a quasi-non-destructive analysis method which allows for the rapid simultaneous detection of main- (1-100%), side- (0.1-1%), trace- (1-1000 ppm) and ultra-trace elements (< 1 ppm). In our case studies ca. 50 elements are regularly recorded. Disadvantages of the method can be the small sample size (typically 75-100 µm spots) and possible distortion of the results in the case of inclusions (e.g. fossils, foreign minerals…), however, a strict analytical protocol guarantees "data hygiene".

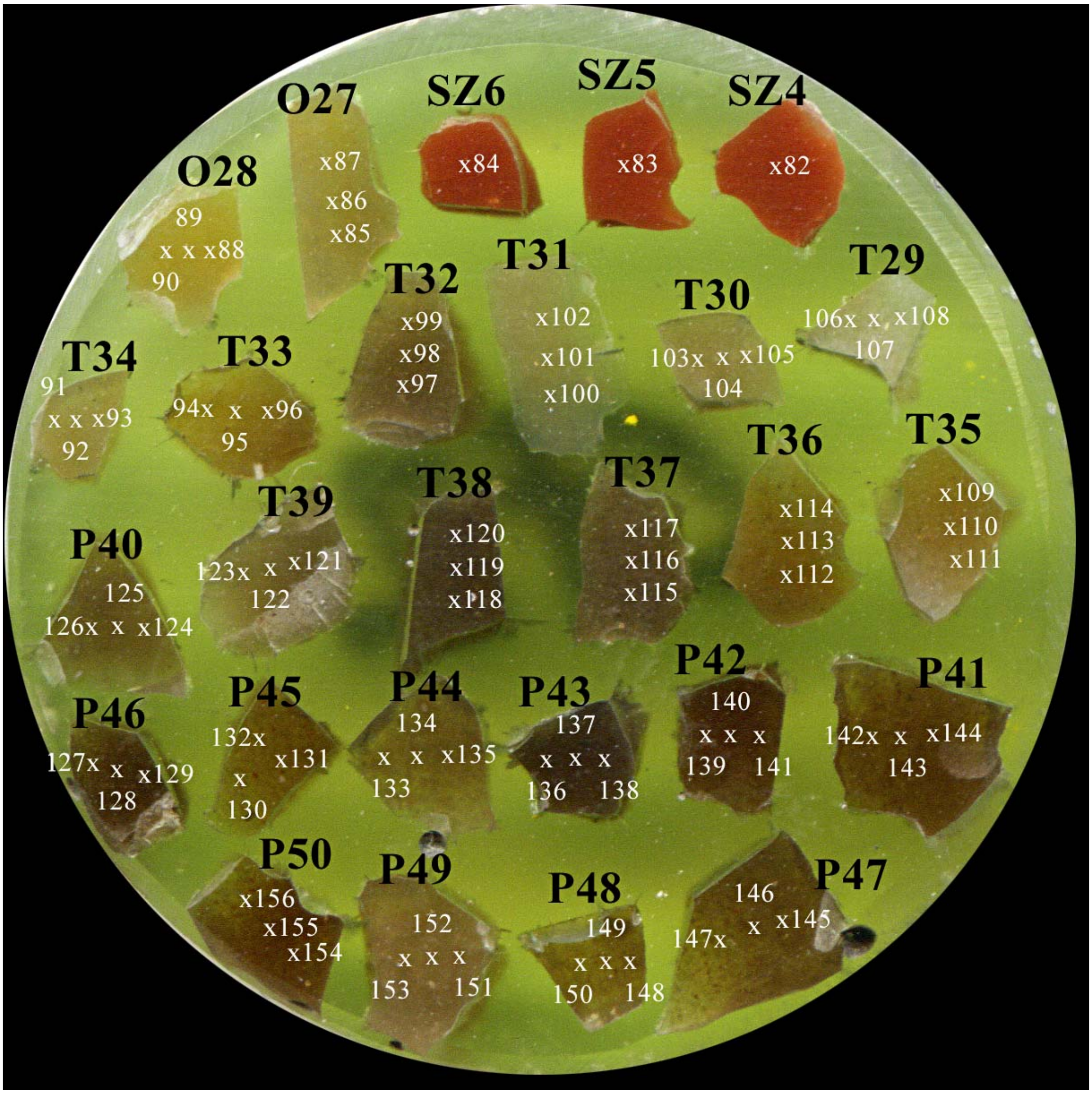


**Fig. 5.:** Resin mount of the “chocolate-silicite” analysis series, Holy Cross Mts., Poland (Brandl et al. 2016, *in press*). Analysed spots on the geological samples are individually indicated. SZ: Szentgál radiolarite standards. O: Samples from Orónsko. T: Samples from Tomaszów. P: Samples from Prędocin.

**5. ábra:** Műgyantába ágyazott preparátumok egy “csokoládé kova” vizsgálati sorozathoz (Szent Kereszt hegység, Lengyelország; Brandl et al. 2016, *in press*). A vizsgálati pontokat egyenként megjelöltük a geológiai mintákon. SZ: Szentgál radiolarit standardok. O: Orónsko-ból származó minták. T: Tomaszów-ból származó minták. P: Prędocin-ból származó minták.

## *The analytical protocol*

In order to collect data of the highest possible quality for source characterisation and differentiation one needs to follow a meticulous protocol to ensure that:

- the samples are properly selected and prepared prior to analysis.
- the spots for LA-ICP-MS analysis are selected according to strict criteria (e.g., avoiding visible fossil and non-fossil inclusions).
- the laser unit is specifically calibrated for $SiO_2$ materials (otherwise the Si will overwrite other signals). This includes the selection of the proper internal standards to guarantee that the results can be reproduced within 10 % relative error.

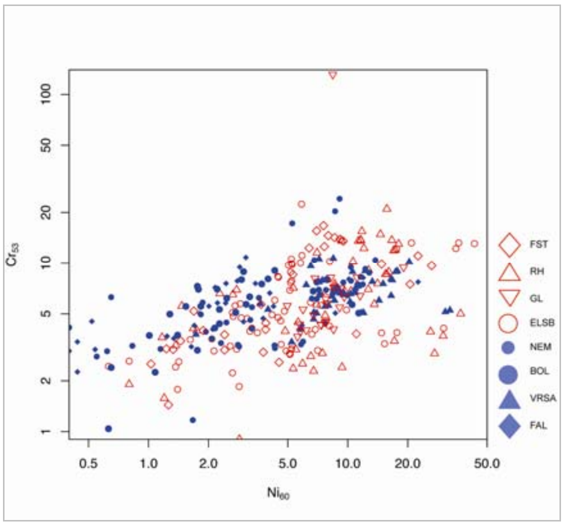


**Fig. 6.:** Nickel (Ni) versus chromium (Cr) concentration plot of Northern Alpine (red symbols) and Carpathian radiolarites (blue symbols). Data from Brandl et al. 2014a.

**6. ábra:** Nikkel (Ni) és króm (Cr) koncentrációk az észak-alpi (vörös jelek) és a kárpáti radiolaritok (kék jelek) esetében. Brandl et al. 2014a adatai.

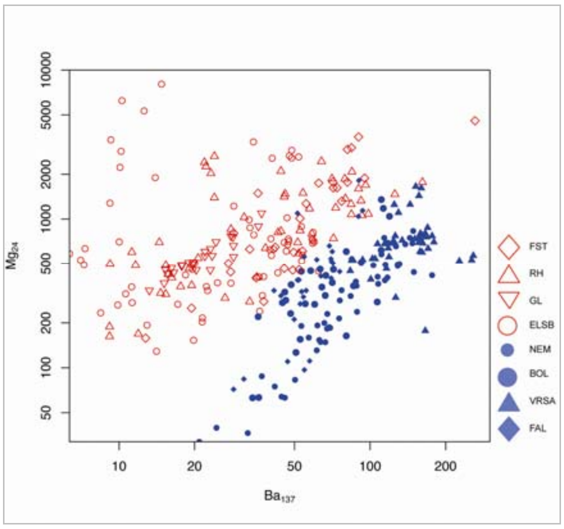


**Fig. 7.:** Barium (Ba) versus magnesium (Mg) concentration plot of Northern Alpine (red symbols) and Carpathian radiolarites (blue symbols). Data from Brandl et al. 2014a.

**7. ábra:** Bárium (Ba) és magnézium (Mg) koncentrációk az észak-alpi (vörös jelek) és a kárpáti radiolaritok (kék jelek) esetében. Brandl et al. 2014a adatai.

A number of pilot projects have been conducted and the results of our LA-ICP-MS chert source provenance studies (Brandl et al. 2011; Brandl et al. 2014a and b; Brandl et al. 2016; Moreau et al. 2016) can be summarised as follows:

Coloring cations, e.g. Fe, Mn, Ni, Cr, etc., do not allow for a source differentiation, since such trace elements are enriched in darker rock parts and occur in lower amounts in lighter areas **(Fig. 6.)**.
A certain differentiation is possible utilising poorly soluble cations able to replace Si in the lattice such as Al, Ti, Cu and Zn.

The highest possibilities for a differentiation between chert sources are provided by using soluble cations deposited in the lattice interstitials or in pore spaces, e.g. Sr, V, Rb and Ba **(Fig. 7.)**.

### Layer 4: Statistics

In order to achieve optimal group assignment and at the same time best group separation statistical methods can be applied to multivariate geochemical data sets. Within the framework of the MLA we use Compositional Data Analysis (CODA) for statistical evaluation. CODA is concerned with ratios between values. By definition, compositional data represent *"quantitative descriptions of the parts of some whole, conveying exclusively relative information"* (Aitchison 1986). Typical units are parts per unit, percentages, ppm, ppb, etc. In 1982 John Aitchison introduced the log-ratio approach for compositional data analysis in the structure of their sample space, the so-called D-part simplex. This means that raw composition data (i.e. the absolute measured values) are transformed into the Euclidean geometry system where statistical methods can operate (the simplex lies outside the Euclidean geometry).

After transformation, discriminant analysis (DA) can be applied for classification.

Fisher's linear discriminant analysis is best suitable to achieve optimal group separation of so-called training data derived from known geological sources. This analytical step generates pre-defined groups from the training data. The resulting discriminant rules are used for classifying and assigning the test data (i.e. the investigated archaeological specimens) to these pre-defined groups **(Fig. 8.;** for further information on the method see Filzmoser et al. 2012**)**.

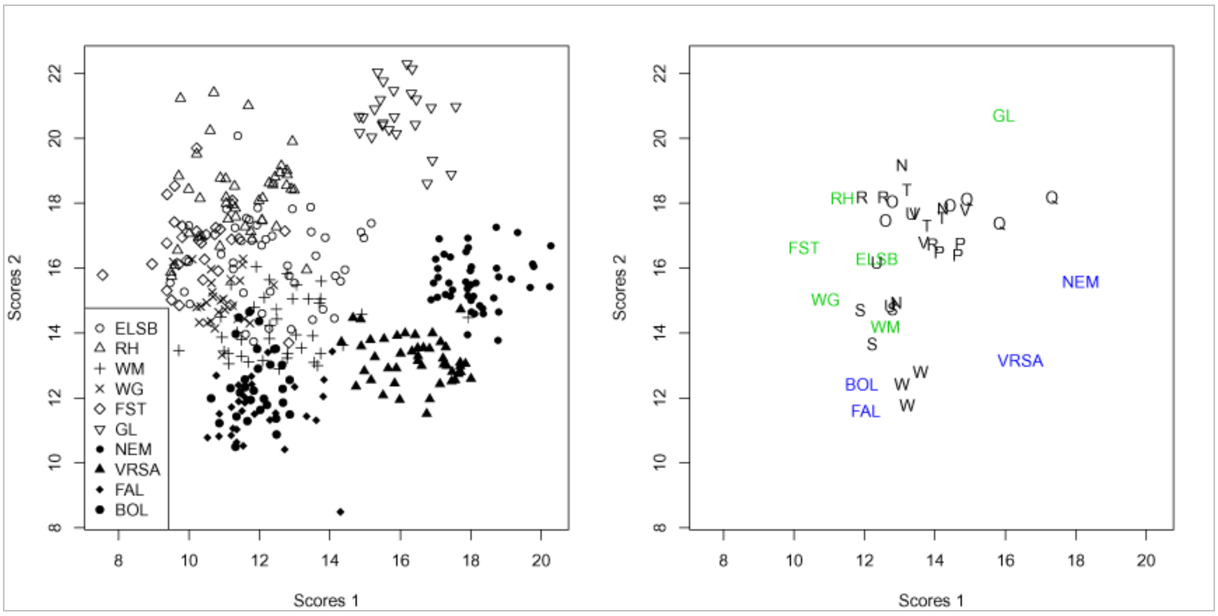


**Fig. 8:** Results applying CODA to radiolarite samples: The left plot displays the optimal group separation of geological radiolarite samples (ELSB, RH, WM, WG FST and GL are Northern Alpine sources and NEM, FAL and BOL Carpathian deposits). These are the trainings data. The right plot illustrates the assignment of archaeological artefacts (i.e. the test data N, O, P, Q, R, S, T, U, V, and W) to the source areas. The plot reveals the closest affiliation of the "W"-artefact to the Carpathian cluster, whereas the rest of the archaeological samples belong to the Northern Alpine group. Data from Brandl et al. 2014a.

**8. ábra:** A CODA alkalmazásának hatása radiolarit minták esetén: A bal oldali ábrán az optimális csoportosítás látható geológiai (összehasonlító) radiolarit minták esetében (az ELSB, RH, WM, WG FST és GL jelű minták észak-alpi lelőhelyekről származnak, a NEM, FAL és BOL jelűek a kárpáti radiolaritokhoz tartozó minták). Ezek a „tanuló" adatok. A jobb oldali ábra a régészeti minták nyersanyagforráshoz rendelését mutatják be az N, O, P, Q, R, S, T, U, V és W teszt adatok esetében. Az ábra szerint a "W" minta legközelebb a kárpáti radiolaritok csoportjához áll, míg a többi régészeti minta az észak-alpi radiolaritokhoz köthető. (Brandl et al. 2014a adatai).

One frequently asked question concerns the additional use of binary concentration plots, particularly if statistics is able to reveal optimal group assignments. The reason is that multivariate statistical methods can produce clearer patterns by combining all information into a singular model, however, they obscure individual elements responsible for a source differentiation. Yet this information is crucial because such elements allow the reconstruction of geological formation processes and the reason why a separation can or cannot be achieved.

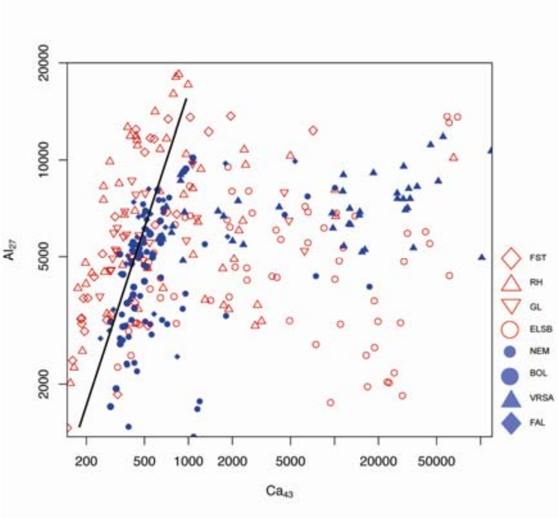


**Fig. 9.:** Ca (calcium) versus aluminum (Al) concentration plot of Northern Alpine (red symbols) and Carpathian radiolarites (blue symbols) displaying a steep tendency curve. Data from Brandl et al. 2014a.

**9. ábra:** Kalcium (Ca) és alumínium (Al) koncentrációk az észak-alpi (vörös jelek) és a kárpáti radiolaritok (kék jelek) esetében. Brandl et al. 2014a adatai.

Additionally they function as an initial "cluster analysis", revealing which samples cannot be included into statistical analyses based on inherent geological differences. When uncritically applying CODA to geochemical data sets every sample is treated as if it would belong to the investigated cluster, and only be considered as an outlier within the evaluation process. This can be avoided by plotting elemental couples prior to statistical analysis.

One example for the significance of binary plots revealing source specific genetic conditions and the origin of trace elements in silicites are correlations of the elements Al, Mg and Sr with Ca. In the case of Northern Alpine versus Carpathian radiolarites the Ca versus Al concentration plot displays values that can be assigned to the presence of Ca-rich plagioclase ($CaAl_2Si_2O_8$) in some of the samples (1:2 Ca:Al ratio), illustrated by a steep tendency curve **(Fig. 9.).**

## Conclusive remarks

To sum things up, what are the advantages of the MLA chert sourcing method? It is based on a flexible combination of analytical techniques which can be "weighed" according to the specific case. This may mean that geochemistry is not always the *ultima ratio*, but other components may be more revealing (e.g. microfossil inclusions).

Depending on the geological settings, sometimes only a source region can be established and a finer grained differentiation of geological deposits is not possible. This is especially true when deposits were formed under similar genetic conditions and in similar environments, resulting in sometimes indiscernible microfossil communities and identical trace element concentrations in silicites.

Most importantly, data collected from archaeological samples are only as valuable as the database they can be contrasted with. Currently our database contains information from over 50 sources in Western, Central and Eastern Europe, Central America and Anatolia, with ca. 4500 individual geochemical datasets of samples from these deposits.

Every successful sourcing approach has to be undertaken in a systematic manner and following a meticulous analytical protocol in order to ensure the highest possible data quality. This also implies constantly refining the method and adjusting the analytical steps according to the particular conditions, as we were able to demonstrate in our previous studies. We hope to be able to continue in this direction and achieve a characterisation of the most important prehistorically and historically used chert and flint sources in Europe based on the Multi Layered Chert Sourcing Approach.

## Acknowledgements

I want to express my deepest gratitude to the team that made the MLA chert sourcing approach a success, consisting of Christoph Hauzenberger (Department of Earth Sciences, University of Graz, Austria), Maria M. Martinez (The University of Texas at Austin, Department of Anthropology, Austin, TX, USA), Peter Filzmoser (Vienna University of Technology, Institute of Statistics and Mathematical Methods in Economics, Austria) and Gerhard Trnka (University of Vienna, Institute of Prehistoric and Historical Archaeology). The case studies mentioned in the paper would not have been possible without the generous support of the Austrian Academy of Sciences, formerly Prehistoric Commission, now OREA-Institute.

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