PGAA Analysis of Szeletian Felsitic Porphyry – Non-destructive Analysis of an Important Hungarian Palaeolithic Raw Material

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Abstract. Szeletian felsitic quartz porphyry is one of the most specific prehistoric raw materials in Hungary. This raw material was used mostly in the Middle and Upper Palaeolithic bifacial industries with a decreasing importance to the more recent periods. Artefacts from five archaeological sites from the territory of the Cserhát Mts. (Acsa, Galgagyőr, Azsidő, Vanaróc, Hort) and two from the Danube Bend (Szob, Verőce) were compared to tools from the classical sites with Szeletian raw material (Szeleta Cave and Puskaporos Rock Shelter) lying in the vicinity of the sole outcrop of the stone at Bükkszentszlászló / Miskolc. The examinations were carried out by Prompt Gamma Activation Analyses (PGAA) method. This non-destructive method is useful for the simultaneous determination of a wide range of elements. The results were studied in a series of charts. Two well-marked cluster stand out for most of the plots. One comprising the typical siliceous raw materials (radiolarite and hornstone) and the other containing the archaeological pieces assumed to be felsitic quartz porphyry and the geological samples. PGAA seems to be an easy and non-destructive method for the investigation of this special problem, but at the current state of observations, the method is not suitable for making fine distinction between the siliceous raw material sources. From an archaeological point of view, our studies confirmed clear relations between the territory of Cserhát and the Bük Mountains.

Introduction
Szeletian felsitic porphyry is one of the most famous raw materials used in the Hungarian Palaeolithic. At present only one restricted area is known, in the south eastern part of the Bük Mountains near Bükkszentszlászló, where raw material suitable for producing chipped stone can be collected from natural outcrops (http://www.ace.hu/litot/186-024c.html; cf. Balogh, 1964, 422-425). Due to its high silica content and homogeneity it was erroneously first identified as hornstone (Herman 1893: 9, 17-18, 1906: 10, 8, Kadić 1907: 343), later as ash-grey chaledony (Kadić 1909: 527, 536 1915: 212, Kadić and Kormos 1911: 112), even in petrographical descriptions based on thin sections (Vendl 1930: 468, 1935: 229-230). With the advance of new analytical methods and their application to archaeology, Lajos Tóth and László Vétes undertook a classic study (Vétes & Tóth 1963) to fingerprint this material with the help of X-ray diffraction analysis (XRD), which can be considered the first Hungarian effort to apply high-tech analytical methods to study of lithic materials. Moreover it is an early application of an archaeometrical approach in archaeology altogether.

In the 1970s and 1980s during general investigation of Hungarian lithic raw materials, archaeological (Dobosi 1978: 16) and geological (Biró & Pálosi 1986) samples of Szeletian felsitic porphyry were examined by thin sectioning, chemical analyses of the main components, OES and IR spectra, as well as X-ray diffractograms.

The detailed analysis of the rock by several authors and various methods clarified the lithology and petrographical character of this special rock type. This is a relatively old volcano (from the Triassic period) with rhylotic composition. The newly formed rock must have had a lot of rock glass in the matrix. There are scattered porphyric grains (in the size range of mm), basically quartz and feldspars in the fine-grained matrix. Over the course of time, the matrix became devitrified, felsitic; as for an exact petrographical category, this rock should be classified a
meta-rhyolite (see results of Ravasz-Baranyai in Dobosi 1978).

All of the above mentioned analytical methods, however, were destructive, which is problematic in the case of unique archaeological artefacts (Map 1.). In this study, new aspects were added to the analysis, i.e. the non-destructive character of the analytical method because some of the study pieces were irreplaceable gems of the collection. The method selected for the analysis was Prompt Gamma Activation Analysis, which seemed to be suitable for the task.

**Distribution of Szeletian felsitic porphyry on archaeological sites**

According to our present knowledge Szeletian felsitic porphyry was mainly used in the Palaeolithic period, preferentially in the Middle Palaeolithic and Early Upper Palaeolithic of the North-Hungarian Mid-Mountain Range. It is definitely closely related to the EUP Szeletian culture. Sporadical, often secondary use occurrences of the material can be found during the Neolithic and the Copper Age. Its maximum extent and quantity could be observed in the Middle and Early Upper Palaeolithic leaf shaped industries in the territory of Hungary, Slovakia, Ukrainian Transcarpathia and even in Moravia (Map 2. – for the details see: Markó et al., in press).

Recently, during the revision of the chipped stone finds from the Danube Bend (Markó 2002) and the intensive field surveys in the Cserhát Mountains, more than 30 new surface sites were discovered which yielded several hundreds of artefacts macroscopically identified as Szeletian felsitic porphyry. On typological grounds, the assemblages could be connected mainly with the Middle and Early Upper Palaeolithic bifacial industries, while some pieces Neolithic in character also came to light. The new sites are lying about 100-135 km away from the geological source as the crow flies. Interestingly, this territory yielded not only finished tools but also a large quantity of waste, flakes, and raw material fragments made from this exotic raw material. At some collecting points in the territory of Vanyarc, 25 to 30 per cent of the several hundred flakes and tools collected were made of this raw material, that so was similar in the case of the current excavation (July 2003), where 25.96% of the artefacts were made of Szeletian felsitic porphyry.

Earlier, it was generally supposed that Middle Palaeolithic people mainly used local raw materials when the distance of the source is less than one day’s walking. On the other hand it seemed that Szeletian felsitic porphyry was intensively used only in a limited territory of 35-50 km radius (Vértes and Tóth 1963: 8, Vértes 1965, Dobosi 1978, Simán 1986). However some isolated leaf shaped implements made of Szeletian felsitic porphyry beyond the local supply area has been known for a long time.

Because of the relatively large distance of the studied area from the geological source and the limitations of macroscopic inspection alone, it was necessary to consider some other similar siliceous raw materials (hornstone, radiolarite, limnic quartzite) which may be mistaken for felsitic porphyry. We had to be aware of possible interaction of other grey siliceous materials because during the studies of the 1960’s some items macroscopically identified as felsitic porphyry proved to be a kind of hornstone after the XRD examination (Vértes and Tóth 1963: 4, 6). Therefore we tried to test our judgement with analytic instrumental methods. The principles were the same as in the 1960s: fingerprinting differences between the siliceous raw materials (hornstone, radiolarite, limnic quartzite) and the silicified volcanic rock (Szeletian felsitic porphyry). The below described PGAA was applied, as non-destructive analytical method.

**Experimental**

The prompt gamma activation analysis facility at the Budapest Neutron Centre has been operational since September 1995. Though the system has been described elsewhere (Révay et al. in press), here we recall a few
Element identification and determination of chemical composition

The chemical elements are identified in a PGAA spectrum according to the energies of their characteristic gamma-ray peaks, while the quantitative analysis is based on the exact determination of gamma peak intensities. During the spectrum evaluation the effects of overlapping peaks and background originated from the natural gamma radiation and the \((n,\gamma)\) reactions on surrounding materials have to be considered.

The detected gamma-ray intensity is directly proportional to the mass of a given element, the analytical sensitivity for that element and the measurement time:

\[ A_k = m \cdot S \cdot t \tag{1} \]

where

\[ S = \frac{N_A \cdot \theta \cdot \sigma_0 \cdot I_\gamma \cdot \Phi_0 \cdot \varepsilon(E_\gamma)}{M} \tag{2} \]

is the analytical sensitivity, expressed in units of counts \(s^{-1} \text{mg}^{-1}\). It is proportional to the neutron capture cross-section of the nucleus \(\sigma_0\), the isotopic abundance \(\theta\) and the gamma yield per neutron capture \(I_\gamma\), which are nuclear constants, as well as to the neutron flux \(\Phi_0\) and the detector efficiency \(\varepsilon(E_\gamma)\), which are characteristics of the measuring system.

The sensitivity of the PGAA method strongly depends on the neutron capture cross-section of the considered nuclei; thus one expects a wide range of sensitivity values for the different elements. The best detectable elements are B, Cd, Sm and Gd with detection limits below 0.01 \(\mu\)g/g. The worst cases are C, N, O, F, Sn, Pb and Bi, with detection limits above 1000 \(\mu\)g/g. Knowing the exact values of the parameters in Eq. 2, one can directly calculate the absolute mass of different elements in the sample. However, using a comparator method, more precise values can be achieved. Introducing the flux-independent quantity

\[ k_{0,C}(X) = \frac{(\theta \cdot \sigma_0 \cdot I_\gamma / M)_X}{(\theta \cdot \sigma_0 \cdot I_\gamma / M)_C} \tag{3} \]

we can write

\[ m_X = \frac{A_X \cdot S_{r,\gamma}}{A_Y \cdot S_{r,\gamma}} = \frac{A_Y \cdot k_{0,C}(Y) \cdot \varepsilon_{r,\gamma}}{K_{0,C}(X) \cdot \varepsilon_{r,\gamma}} \tag{4} \]

which gives the mass ratio of any two elements. The \(k_\gamma\)-factors or equivalently the sensitivities for the most intensive prompt-gamma lines of most chemical elements were determined by internal standardisation measurements at the Budapest Research Reactor and are collected in a new gamma-ray spectrum catalogue for PGAA (Révay et al. 2000; Révay and Molnár 2003). The approximate calculated detection limits for elements of interest, assuming 5 \(\times\) 10^7 \(\text{cm}^{-2}\text{s}^{-1}\) thermal equivalent neutron flux, 3600 s irradiation time and 12 g sample mass are the following:

- for major elements, H 0.001 \(\mu\)g/g, Na 0.02 \(\mu\)g/g, Mg 0.2 \(\mu\)g/g, Al 0.3 \(\mu\)g/g, Si 0.1 \(\mu\)g/g, K 0.06 \(\mu\)g/g, Ca 0.2 \(\mu\)g/g, Ti 0.007 \(\mu\)g/g, Mn 0.002 \(\mu\)g/g, Fe 0.02 \(\mu\)g/g;
- for trace elements, B 0.1 \(\mu\)g/g, S 200 \(\mu\)g/g, Cl 15 \(\mu\)g/g, Sc 10 \(\mu\)g/g, V 100 \(\mu\)g/g, Cr 100 \(\mu\)g/g, Ba 1000 \(\mu\)g/g, Sm 0.5 \(\mu\)g/g, Eu 0.2 \(\mu\)g/g, Gd 0.03 \(\mu\)g/g, Dy 5 \(\mu\)g/g, respectively.

As all major elements contained in the sample are supposed to be observed, their individual masses should satisfy the equation:

\[ \sum m_i = m_{\text{total}} \tag{5} \]

Thus, according to Eq. (4) the obtained composition data can be expressed in mass% or \(\mu\)g/g units. The concentration data are usually processed further with Principal Component Analysis (PCA), a well-known multivariate method to find similarities and differences between the objects.

As all elements contained in the sample are expected to be observed, their amounts according to Eqs (1) and (2) can be summed to obtain the total detected mass. Thus, by renormalising the detected mass with the total mass, the element concentrations are obtained directly, without the need for separately measuring elemental standards. The obtained composition data, mostly expressed in mass% or \(\mu\)g/g units are processed further with Principal Component Analysis (PCA), a usual multivariate method to find similarities and differences between the objects.

Measurements

In the present experiments 13 archaeological and 6...
The third area of interest was the Danube Bend. The finely elaborated leaf-shaped point (Inv. no.: Pb. 21/1935
- :SZOB21) from Szob - Öregfelu-dülö (Torma 1993, Markó 2002: 82-83) was one of the first tools examined by petrographical methods in the 1960s (Vértes 1965: 162). The age of the typical blade segment with sickle shine from Verőce - Magyar mál (Inv. no.: Pb. 86/382. – VER383) can be placed in the Middle Neolithic (Lienenbandkeramik – Torn. 1993, Markó 2002: 117-118). These sites lie 125-135 km from the source of the raw material.

For comparative material we chose two flakes inferred to be made of local Buda hornstone from Bronze Age sites in the vicinity of Budapest, Albertfalva and Csepel: uninventioned items in the Budapest Historical Museum – ALB19, CSEP22. - Biró 2002).

Results

The concentrations of the components detected were expressed in weight percentage of oxides for major elements and in ppm for accessory and trace elements (Table 1).

Although the SiO$_2$ concentrations in the investigated samples were rather high (70 to 98%), we were able to identify other major components such as Na$_2$O, MgO, Al$_2$O$_3$, K$_2$O, CaO, TiO$_2$, MnO and Fe$_2$O$_3$ with great accuracy. In addition, some of the trace elements such as B, S, Cl, Sm, Eu and Gd were measured with acceptable precision, which may help to classify the objects.

According to the major components of SiO$_2$, Al$_2$O$_3$ and K$_2$O themselves, the investigated objects seemed to form two clear groups (See Fig.1-3). In order to clarify the similarities of the composition, the different element concentrations were normalised by the concentrations of SiO$_2$ and Al$_2$O$_3$ for each sample. The different ratios were investigated in detail, and almost all of them i.e. Na$_2$O/ SiO$_2$, (Na$_2$O+K$_2$O)/SiO$_2$, TiO$_2$/SiO$_2$, K$_2$O/SiO$_2$, Fe$_2$O$_3$/SiO$_2$, Al$_2$O$_3$/SiO$_2$, K$_2$O/Al$_2$O$_3$, TiO$_2$/Al$_2$O$_3$, (Na$_2$O+K$_2$O)/Al$_2$O$_3$ were found to show the same characteristic groupings of the objects. One of the significant element ratios is plotted on a chart (See Fig. 4). Note the logarithmic scale on this chart.

According to our data we can state the following: two well-marked clusters can be seen on most of the plots. One comprises the typical siliceous raw materials (radiolarite and hornstone), while the other contains the archaeological pieces assumed to be Szeletian felsitic porphyry and the geological samples. One particular sample (cherty dolomitic limestone from Csővár) shows significantly lower SiO$_2$ and higher CaO content, probably due to the presence of carbonatic grains in the irradiated volume. From the Lithotheca collection the most similar example to the Palaeolithic objects is the sample collected in Bükkszentlászló.
Conclusions

PGAA proved to be an easy and non-destructive method for making fine and clear distinctions between the Szeletian felsitic porphyry and other siliceous raw materials, although at the current state of development the method was not suitable for distinguishing among the different hornstone and radiolarite sources. The new results from PGAA confirmed our opinion made on the basis of macroscopic observation of field survey material and strengthened the observation made on the Szob leaf shaped point. In a recent series of examinations, further artefacts from the Cserhát Mountains and from the Transdanubian Middle Palaeolithic (Jankovichian) sites were examined, as well as some Epigravettian implements from the Great Hungarian Plain and the Danube Bend. All the studied samples proved to be made of felsitic porphyry, which verified our former suppositions and the results of the first series of the PGAA investigations.

From an archaeological point of view, our studies confirmed clear relations between the territories of the Cserhát and Bükk Mountains. This observation is supported by the results of the archaeological investigations as well, the typological connections of the small assemblages with the Middle and Early Upper Palaeolithic of the Bükk Mountains (Ringer 1983).

In the followings we would like to test further “long-distance” samples claimed to be made of Szeletian felsitic porphyry on the territory of the neighbouring countries, notably in Slovakia, Ukraine and the Czech Republic. The archaeometrical and archaeological analysis of these pieces will serve as invaluable information on the early history of the Carpathian Basin.

Acknowledgments

This study was performed with the financial support of Grant T 025086 from the Hungarian National Science Foundation (OTKA), “Atlas of prehistoric non-metallic raw materials in the Carpathian Basin”. Part of the archaeological material investigated has been supplied by Budapest Historical Museum. The base map used for the article was constructed by Holl, Balázs (Hungarian National Museum).

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<td>1.16</td>
</tr>
</tbody>
</table>

Table 1.