Obsidian provenance studies of Transylvania's Neolithic tools using PIXE, micro-PIXE and XRF

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Abstract

Obsidian is a natural volcanic glass, which was widely used for prehistoric stone tools and traded over long distances. In the case of Transylvania (the North-Western part of Romania), the sources of the prehistoric tools are supposed to be Tokaj Mountains, Greek islands, Armenia and Turkish-Asia Minor. We used PIXE and XRF to analyse various obsidian tools from the above sources. The two-dimensional scatter plots of Ti/Mn versus Rb/Zr and Ba/Ce versus Y/Zr were considered as source indicators. On the basis of these classifications, the majority of the Transylvania's obsidian prehistoric tools were determined as coming from either Hungarian or Slovakian Tokaj Mountains.

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1. Introduction

Obsidian is a natural volcanic glass whose chemical composition is similar to that of granite. The similar chemical composition of samples within individual obsidian sources and the restricted number of potentially exploitable sources almost always permits the confident assignment of an archaeological artefact to a single geological source. Obsidian – usually in the form of rather large cores – was a widely traded raw material in prehistoric times, the final purchaser working the cores into objects. Typical composition of an obsidian sample is the following: 35% Si, 47% O, 8% Al, 4% K, 3% Na, 1%Fe, 1% Ca, 0.3% Ti, 0.3% Mg [1]. Geochemical studies have shown that obsidian flows are usually uniform in chemical composition. It follows, therefore, that to identify obsidian with a particular geological source, two assumptions should first be made: 1) different flows are distinguishable from one another by their chemical composition and 2) the chemical composition of a single obsidian flow is uniform throughout. If these assumptions hold, it is possible to assign tools, which have been distributed by trade over wide areas, to their sources. The most unambiguous identification of an obsidian can be obtained by determining the trace-element composition.

In the Near East and the Mediterranean Sea area, obsidian flows are found only around Italy, in some islands in the Aegean Sea and in certain localities in Turkey, Iran and Armenia. In Central Europe, the most important source is the Tokaj Mts. (Hungary and Slovakia) [2, 3, 4, 5].

In Transylvania (the North-Western part of Romania, a region surrounded by Carpathian Mountains), Neolithic (6000-2000 BC period) obsidian tools were discovered mainly in three regions: North-West – Oradea (near the border with Hungary, Slovakia and Ukraine), centre – Cluj and Southwest - Banat (near the border with Serbia). Three long-distance trade routes could be considered: from Caucasus Mountains (Armenia) via north of the Black Sea (the classical historical Indo-European route, e.g. Greek-Achaic invasion against Minoic civilisation in the Xth Century BC or later “barbarian” invasion of Roman Empire starting form the IVth Century A. D.), from Greek islands or Asia Minor via Ilyria – now Albania – Serbia (the Balkan route used for the first time during the VIth Millennium BC to expand the first known European civilisation called Vinca) or from Central Europe similar to the Celtic expansion in the VI-Vth centuries BC [6].

The provenance studies could help the archaeologists to distinguish between these routes and to solve important historical problems connected to the relationships between the ancient Central-Eastern European populations.

2. Experimental

Eighteen archaeological samples (Neolithic obsidian tools): five from Oradea region (Seleuş, Beiuş, Salca, Taşad), ten from Cluj area (Iclod, Ţaga, Cheile Turzii, Bucin) and three from Banat (Silagiu – Buziaş) were obtained from “Tara Crişurilor” Museum and Transylvania’s History National Museum.

Obsidian samples were analysed in vacuum with a 3 MeV proton beam from the Bucharest accelerator impinging at 45° to the surface. A Canberra GL0110P – Low Energy Germanium Detector (100 mm^2 area, 10 mm thickness, 0.075 mm Be window thickness, energy resolution 160 eV FWHM at 5.9 keV, 500 eV FWHM at 122 keV), oriented perpendicularly to the proton beam direction recorded the X-ray spectrum emitted by the trace elements. We routinely used a 0.8 mm diameter beam and a constant proton dose, each acquisition taking roughly 20 min.

Since we directly analyse hard rock fragments, it is not recommended to use ordinary international geological standards available as powders. Instead, we used obsidian pieces previously analysed by Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) at Centre de Recherches Ernest Babelon, Orléans, France [7] and by micro-PIXE [2] and micro-PIGE [3, 8] at the Institute of Nuclear Research of the Hungarian Academy of Sciences (ATOMKI), Debrecen, Hungary. These samples were seven pieces from Tokaj Mountains – Hungary (Tolcsva, Erdőbénye, Sima, Mád), six from Melos (Greek island – Aegean Sea), two from Yali (Greek island), two from Turkey (Kömörcü közü and Karaçaören), two from Armenia (Aragats and Jerevan), one from Tokaj Mountains – Slovakia (Vinicki), one from Mexico (Teotihuacan) and one from Iceland (Hrafutinnusker).

Reproducibility of our data was checked by duplicate measurements on a particular sample (Silagiu obsidian tool no. 3).

Our archaeological samples are frequently waste flakes remaining after stone tool production or, sometimes, genuine tools of typically 2-3 centimetres in the largest dimension and a thickness less than 0.5-1 cm. For these samples, non-destructive analysis is absolutely needed due to their archaeological importance. Because of the conchoidal fracture of obsidians it is always possible to find a flat surface at the scale of the beam spot for an analysis on natural cleaned surfaces. In order to account for possible local heterogeneity, the composition of three very different samples was measured in three points, obtaining compositional differences less than 10% for the interesting elements.

For XRF we used a 30 mCi ^{241}Am annular source and a Hungarian ATOMKI Si(Li) detector (energy resolution 190 eV FWHM at 5.9 keV) [9].

Some archaeological samples coming from Oradea region sites were also analysed by micro-PIXE at ATOMKI Debrecen [10, 11, 12]. The radiation was detected by two Si(Li) detectors: (a) a common Be-windowed detector with a 98.8 μm aluminium filter (higher than 5 keV), (b) a special detector with an ultra thin polymer window (light elements, $Z>5$ but quantitative results for $Z>10$). The monitoring of the beam current was carried out by using a recently developed beam chopper which was calibrated before the measurements and had a 1-1.5 % precision. The testing of the reliability of our set-up was also done by means of obsidian standards. For the determination of major and minor elements, the proton beam of 2 MeV was focused to 2 × 2 μm^2 size with a beam current of 50 pA. The integrated charge on the samples varied in the range of 200-400 nC. The trace element analyses were carried out by using 10 × 10 μm^2 size beam of about 1 nA current collecting 3-4 μC charges. The scan size of the beam was about 1.5 mm × 1.5 mm.

3. Discussion and Conclusion

Nuclear methods were already used in obsidian provenance studies for South America - by PIXE [13], Australia - by electron microprobe X-ray spectrometry [14, 15] and Tokaj Mountains - by microPIGE [3]. As provenance fingerprints, binary diagram plotting the Sr content versus Mn [13], bivariate plot of Al_2O_3 and CaO concentrations [18] and two-dimensional scatter plots of Li content versus B, Na content versus F and Nb/Zr versus Y/Zr [3] were used. In our case, K, Ca, Ti, Mn, Fe, Zn, Pb, Rb, Sr, Y, Zr contents from PIXE analysis (see figure 1), Na, Al, Si, Cl, K, Ca, Ti, V, Mn, Fe, Zn, Ga, As, Rb, Sr, Y, Zr constituents from micro-PIXE measurements and Ba, La, Ce elements from XRF runs were determined. As concerning the similarity of data obtained by different methods, to avoid complicated and time consuming intercomparison measurements between our laboratories, considering the good homogeneity of the obsidian samples (geological and petrographical reasons [16, 17]), we decided to use only the ratios of the content of some neighbouring elements. As significant for provenance determination, considering the experience of above mentioned provenance studies and the LA-ICP-MS determined composition of our standards, we chose the following seven elements: Ti, Mn, Rb, Y, Zr, Ba, Ce, especially because their value often strongly differ from one source to another. We represented them as two-dimensional scatter plots: Ti/Mn versus Rb/Zr and Ba/Ce versus Y/Zr (see figures 2, 3, and, as details from figure 2, figures 4, 5, 6). It can be seen that three main groups could be considered. One is similar in composition to Tokaj Mountains – Hungary Tolcsva, Sima sources (figure 4) – archaeological samples from Cluj area , the 'heart' of Transylvania, linked to Danube – Tisza region and further down to Tokaj Mountains through Someş river. Another one is similar in composition to Tokaj Mountains - Hungary Erdőbénye, Mád sources (figure 5) – archaeological samples from Banat, close not only to Pannonian Plane, but also to Serbia (e.g. the famous Neolithic site of Vinca, with important links to the Mediterranean world). The third group is similar to Tokaj Mountains –Slovakia Vinicki source (figure 6) – archaeological samples from Oradea and Cluj areas, also along Someş river. This grouping indicates strong commercial contacts of the local populations with the ones from Central Europe. Our samples are completely different in composition comparing them with specimens from Iceland and/or Mexico (evidently), relatively different from obsidians of Turkey, Armenia and Melos (Greek island) [18] sources, but some of them – see figure 6 - are not far from Yali (Greek island) sources. We intend to increase the number of the analysed samples (especially from Banat area – the closest region to the Balkan route) to see if it is possible to find conclusive evidences for a Greek islands provenance of some samples. We also intend to enlarge the analysed areas, including Oltenia, Muntenia (South of Romania, near the Danube river) and Moldova (North – East of Romania).

In conclusion, our findings demonstrate that long-distance trade networks existed between Central and East-Europe by the late 5th millennium BC (the climax of Neolithic period in Transylvania). This suggests that some of the most important characteristics of Transylvania's Neolithic culture may have had their origins in the famous Tiszapolgár and

Bodrogkeresztúr cultures from the Danube – Tisza region [6]. The archaeological presence in Cluj of obsidian coming from more than 1500 km is the surviving evidence of what was almost certainly the longest stone-age trade route in this part of Europe.

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Figure Captions

Figure 1 PIXE spectrum for Silagiu – Buziaş (Banat) Neolithic obsidian tool no. 5.

Figure 2 Two-dimensional scatter plot of Ti/Mn versus Rb/Zr ratios.

Figure 3 Two-dimensional scatter plot of Ba/Ce versus Y/Zr ratios.

Figure 4 Detail of figure 2: Tokaj Mountains (Tolcsva, Sima) Hungarian area.

Figure 5 Detail of figure 2: Tokaj Mountains (Erdőbénye, Mád) Hungarian area.

Figure 6 Detail of figure 2: Tokaj Mountains (Vinicki) Slovakian area.

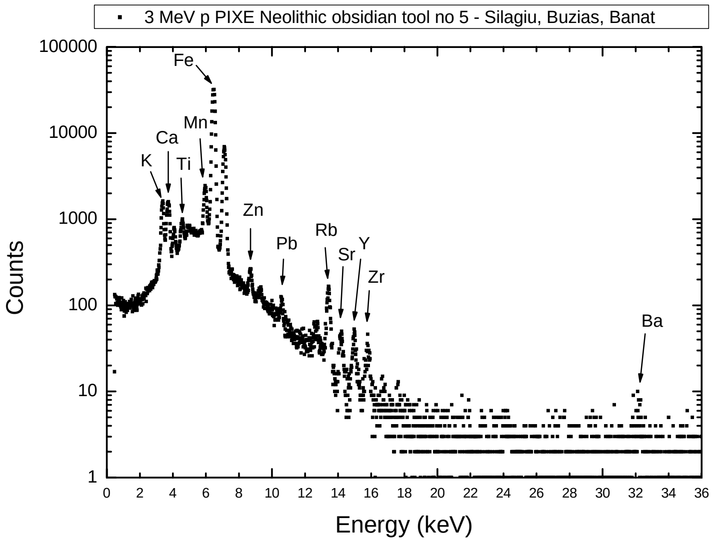

▪ 3 MeV p PIXE Neolithic obsidian tool no 5 - Silagiu, Buzias, Banat
Counts
Energy (keV)
100000
10000
1000
100
10
1
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
Fe
Mn
Ca
K
Ti
Zn
Pb
Rb
Sr
Y
Zr
Ba

Figure 1

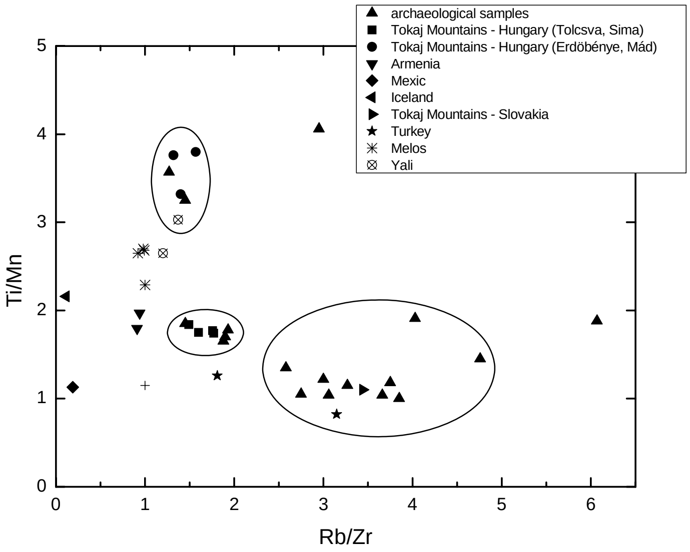

▲ archaeological samples
■ Tokaj Mountains - Hungary (Tolcsva, Sima)
● Tokaj Mountains - Hungary (Erdöbénye, Mád)
▼ Armenia
◆ Mexic
◀ Iceland
▶ Tokaj Mountains - Slovakia
★ Turkey
✳ Melos
⊗ Yali
Ti/Mn
Rb/Zr
0
1
2
3
4
5
6

Figure 2

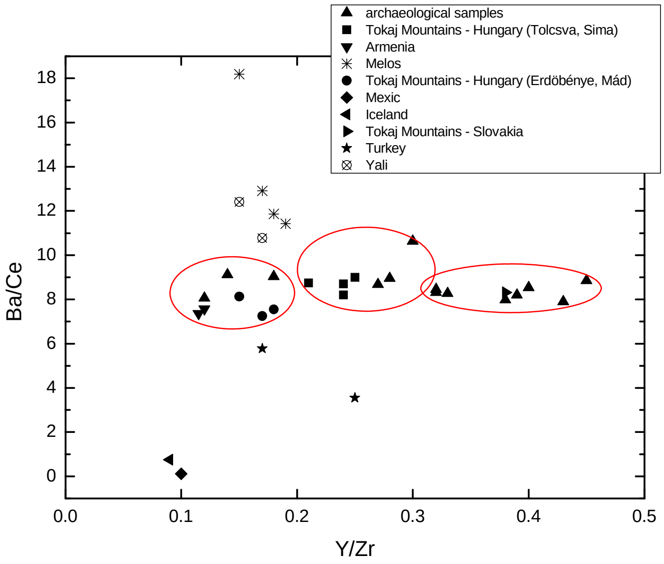

archaeological samples
Tokaj Mountains - Hungary (Tolcsva, Sima)
Armenia
Melos
Tokaj Mountains - Hungary (Erdöbénye, Mád)
Mexic
Iceland
Tokaj Mountains - Slovakia
Turkey
Yali
Ba/Ce
Y/Zr
0
2
4
6
8
10
12
14
16
18
0.0
0.1
0.2
0.3
0.4
0.5

Figure 3

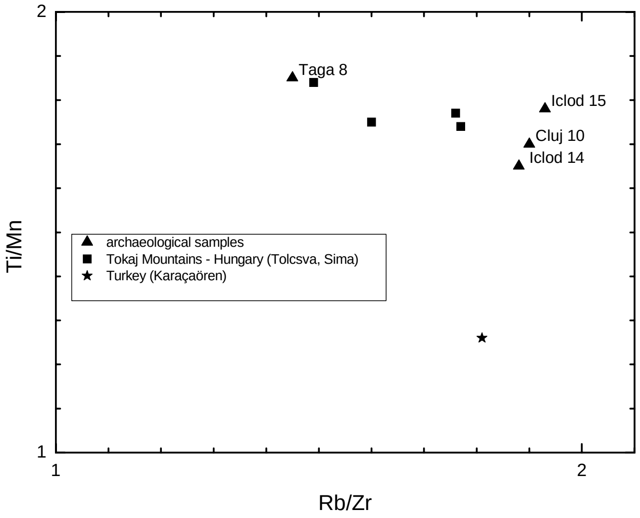

2
1
Ti/Mn
1
2
Rb/Zr
Taga 8
Iclod 15
Cluj 10
Iclod 14
▲ archaeological samples
■ Tokaj Mountains - Hungary (Tolcsva, Sima)
★ Turkey (Karaçaören)

Figure 4

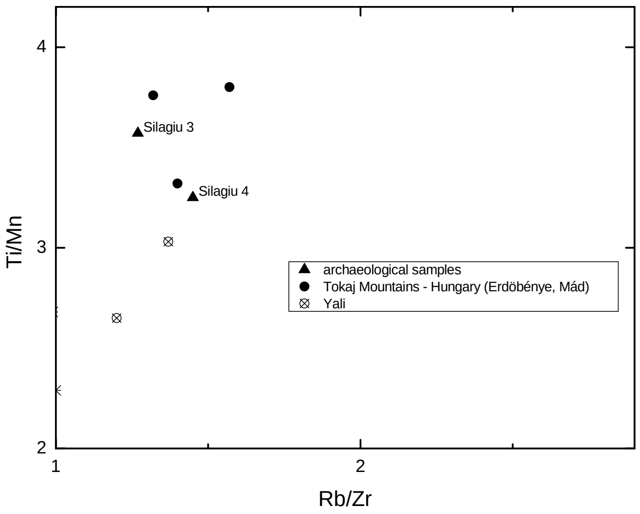
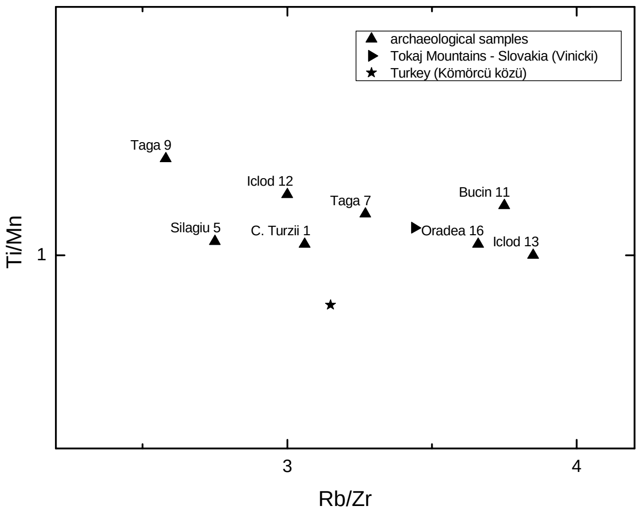

Ti/Mn
4
3
2
1
2
Rb/Zr
Silagiu 3
Silagiu 4
▲ archaeological samples
● Tokaj Mountains - Hungary (Erdöbénye, Mád)
⊠ Yali

Figure 5



archaeological samples
Tokaj Mountains - Slovakia (Vinicki)
Turkey (Kömörcü közü)
Taga 9
Iclod 12
Taga 7
Bucin 11
Silagiu 5
C. Turzii 1
Oradea 16
Iclod 13
Ti/Mn
1
3
4
Rb/Zr

Figure 6