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Provenance studies of Central European Neolithic obsidians using external beam milli-PIXE spectroscopy

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ABSTRACT

External beam milli-PIXE technique was used for the determination of the elemental concentration ratios in some Prehistoric obsidian tools found in Transylvania, in the Iron Gates region near Danube, as well as on a few relevant geological obsidian samples from Slovak Tokaj Mountains, Lipari, Armenia. As provenance "fingerprints" the Ti to Mn and Rb to Zr ratios were used. The results confirm that the Transylvanian Neolithic samples have a Slovak Tokaj Mountains provenance. For Iron Gates samples, there are at least two different geological sources: for Late Neolithic tools, the origin is also the Slovak Tokaj Mountains but for Late Mesolithic–Early Neolithic samples, the sources are clearly different, possibly of the Hungarian Tokaj Mountains or the Balkan–Aegean origin.

1. Introduction

The natural volcanic glass called obsidian is one of the most important archaeological rocks used to make tools and weapons before the appearance of metal raw materials [1]. In Central Europe the geological sources are limited and concentrated in few geographical areas: Armenia, Eastern Anatolia, Italian Lipari and Sardinia, Greek Melos and Yali islands, Hungarian and Slovak Tokaj Mountains. A map displaying these areas is given in Fig. 1. In order to determine the geographical areas of origin of obsidian and to identify the prehistoric long-range trade routes and possible population migrations, the determination of the elemental concentration ratios can be of great help, since each geological source often present a specific chemical fingerprint. In Transylvania (the North–Western part of Romania, a region surrounded by Carpathian Mountains) Neolithic obsidian tools were discovered mainly in three regions: North–West – Oradea (near the border with Hungary, Slovakia and Ukraine), Centre – Cluj and Southwest – Banat. A previous analysis of some samples from these regions indicated the Slovak Tokaj Mountains source (Carpathian I) as predominant provenance [2]. Special cases are the Mesolithic and Early Neolithic sites from the Iron Gates (on river Danube, at the border with Serbia) [3] directly related to the appearance of agriculture replacing the Mesolithic economy based on hunting and fishing and the Teleorman (South of Romania) Early Neolithic sites. In the case of obsidians three long-distance trade routes could be considered: those starting from Caucasus Mountains via the North of the Black Sea, from Greek islands or Asia Minor via ex-Yugoslavia area or via Greece-Bulgaria or from Central Europe – Tokaj Mountains [4]. Our archaeological samples – i.e. Neolithic obsidian tools – from Oradea region (Seleuş, Bucin, Taşad), from Cluj area (Iclod, Ţzaga, Turda, Silagiu) and Mesolithic and Early Neolithic tools from Iron Gates on Danube area (opposite to famous Vinca site) – Cuina Turcului and from Teleorman – Magura were borrowed from the "Tara Crişurilor" Museum Oradea, Transylvania's History National Museum Cluj and Institute of Archaeology, Bucharest. A detailed description of all these archaeological sites can be found elsewhere [5].

In this work the argumentation of the previous paper [2] for using the ratios of the content of some neighbouring elements for provenance characterisation has been followed. For this strategy the external beam milli-PIXE spectroscopy [6] is a more convenient choice compared to some frequently used analytical techniques as ICP/MS, NAA, PGAA and so on. External beam milli-PIXE is fully non-destructive, there are not any mechanical or thermal damages at the proton currents used, and the analysed objects are not activated during the analysis. In contrast to in-vacuum milli-, or micro-PIXE methods where the objects should be put into a vacuum chamber raising serious size limitation, in the case of external-beam PIXE, objects of practically any sizes can be studied. In comparison to traditional XRF analysis the accurate location and the spatial limitations of the regions to be analysed are much easier. In addition, the generally lower background of more regular shape allows easier spectrum evaluation. These general merits of the external beam PIXE technique and the millimetre beam size

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Fig. 1. Geographical locations of the geological obsidian sources of interest.

allow to analyse flat areas of the multi-faceted mini-tools (blades and arrow heads) and verify the homogeneity of the samples (e.g. to avoid micro-inclusions of Ti rich soil) as well. Therefore in the present work this analytical technique was chosen.

The aim of the study was to identify obsidian geological sources used in Mesolithic and Early Neolithic Iron Gates and Teleorman sites and compare them with the Neolithic Oradea and Cluj sites. Neolithisation is the process of transition from hunting-fishing-based societies to agriculture, process related to an important populations migration. The most accepted theory is "Ex Oriente Lux" where the migration of the "Neolithic model" (and population) from Mesopotamia, Anatolia, Greece proceeds through Aegean Islands, Balkans, Central Europe – via Danube is considered [7]. Two main regions are presumed to be the obsidian sources for Romanian territory: Tokay Mountains (Carpathian I – now in Southern Slovakia and Carpathian II – in Northern Hungary) and Melos Island (Aegean Sea).

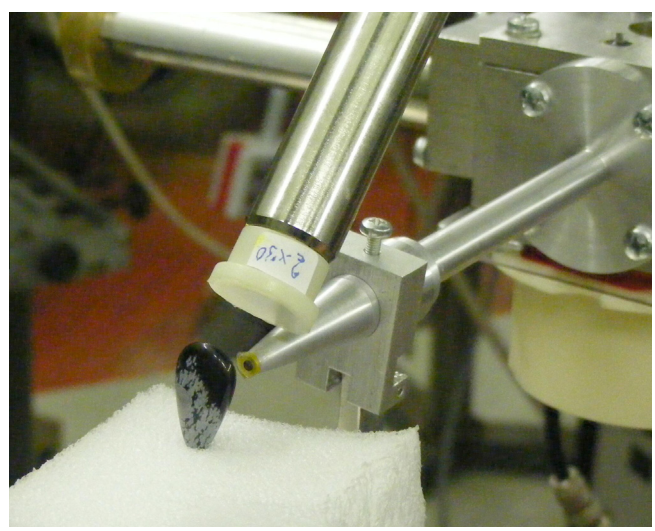

Fig. 2. The external milli-beam PIXE set-up.

2. Experimental

The measurements were performed at the 5 MV Van de Graaff accelerator of the Institute of Particle and Nuclear Physics, Wigner Research Centre of the Hungarian Academy of Sciences. The properly collimated proton beam of 3 MeV energy was extracted from the evacuated beam line to air through a 7.5 μm thick Kapton foil. The terminating tube was lined with pure carbon and its inner diameter of 0.5 mm determined the final beam size before it passed through the exit foil. For the actual measurements a target-window distance of 10 mm was chosen where the beam diameter was found to be about 1 mm. For the analyses the external beam intensity was varied from 1 to 10 nA depending on the actual total X-ray count rate. The last section of the beam line behaves as a Faraday cup and the entering beam current was continuously monitored. The above mentioned external beam current was estimated on the basis of the ratio of the diameter of the last collimating aperture in front of the Faraday cup section and that of the final exit collimator. Taking into account, however, that in the analysis elemental content ratios were considered, only, the accurate knowledge of the beam intensity had no specific importance. The obsidians were fixed to a micro-manipulator allowing for an accurate three-dimensional positioning. The final target positioning was achieved using a mechanical "aiming pin pointer". X-ray spectra were collected by using a computer controlled Amptek X-123 spectrometer with an SDD type detector of 25 $mm^2 \times 500$ μm active volume and 8 μm thick Be window. The detector with an energy resolution of 130 eV for the Mn Kα line was positioned at 135°