

Chemical fingerprinting of Hungarian and Slovakian obsidian sources using three complementary analytical techniques

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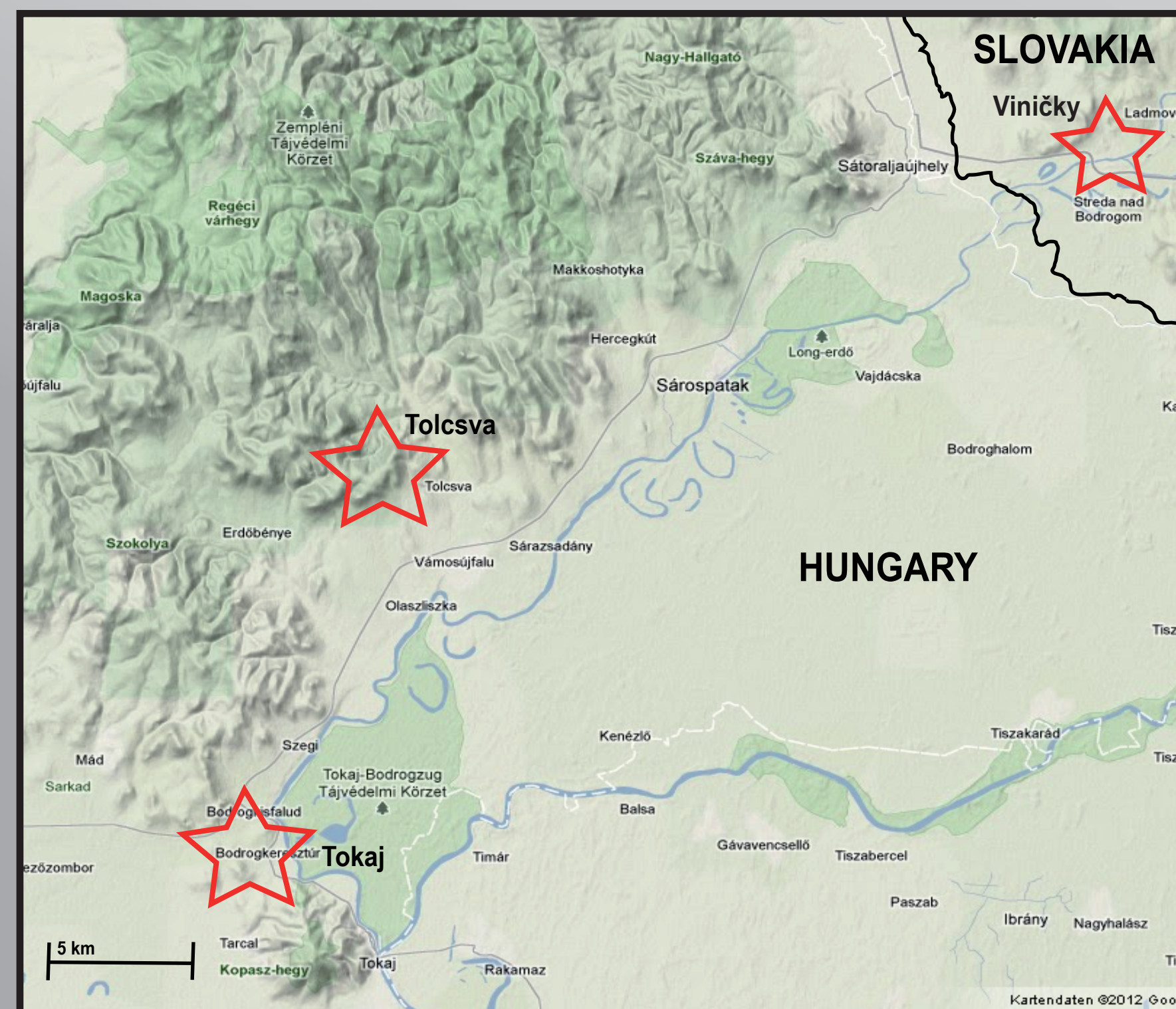
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Introduction

Obsidian from Hungary and Slovakia was one of the most appreciated raw materials of prehistoric man in central parts of Europe. It was traded south to Macedonia, north to Poland and west to Moravia, Austria and to the Adriatic near Trieste [1].

Chemical fingerprinting of Hungarian and Slovakian sources is of great interest especially for Central European sites where obsidian has been used widely [1-3].

Reliable provenancing of archaeological obsidian artefacts can provide evidence of prehistoric exchange systems and can give information about the mobility of prehistoric people.



Aim of the study

- Application of three complementary analytical techniques on 25 raw material samples from three Hungarian and Slovakian sources [Fig. 1]
- Determination of a maximum element spectrum for obsidian source characterisation
- Reveal the most characteristic “chemical fingerprint”
- Help to decide which least invasive analytical method should be chosen for the reliable identification of an archaeological artefact

Fig. 1: Map of three Hungarian and Slovakian obsidian sources characterized in this study.

Methods

Instrumental Neutron Activation Analysis (INAA)

- Irradiation with neutrons in the TRIGA Mark II research reactor of the Atom-Institut in Vienna
- Detection of emitted γ -rays
- Analysed sample mass >10 mg
- At least 10 mg of crushed and homogenised sample is required
- Detection limit: $\mu\text{g/kg}$
- 25 major, minor and trace elements measured [Fig. 2]

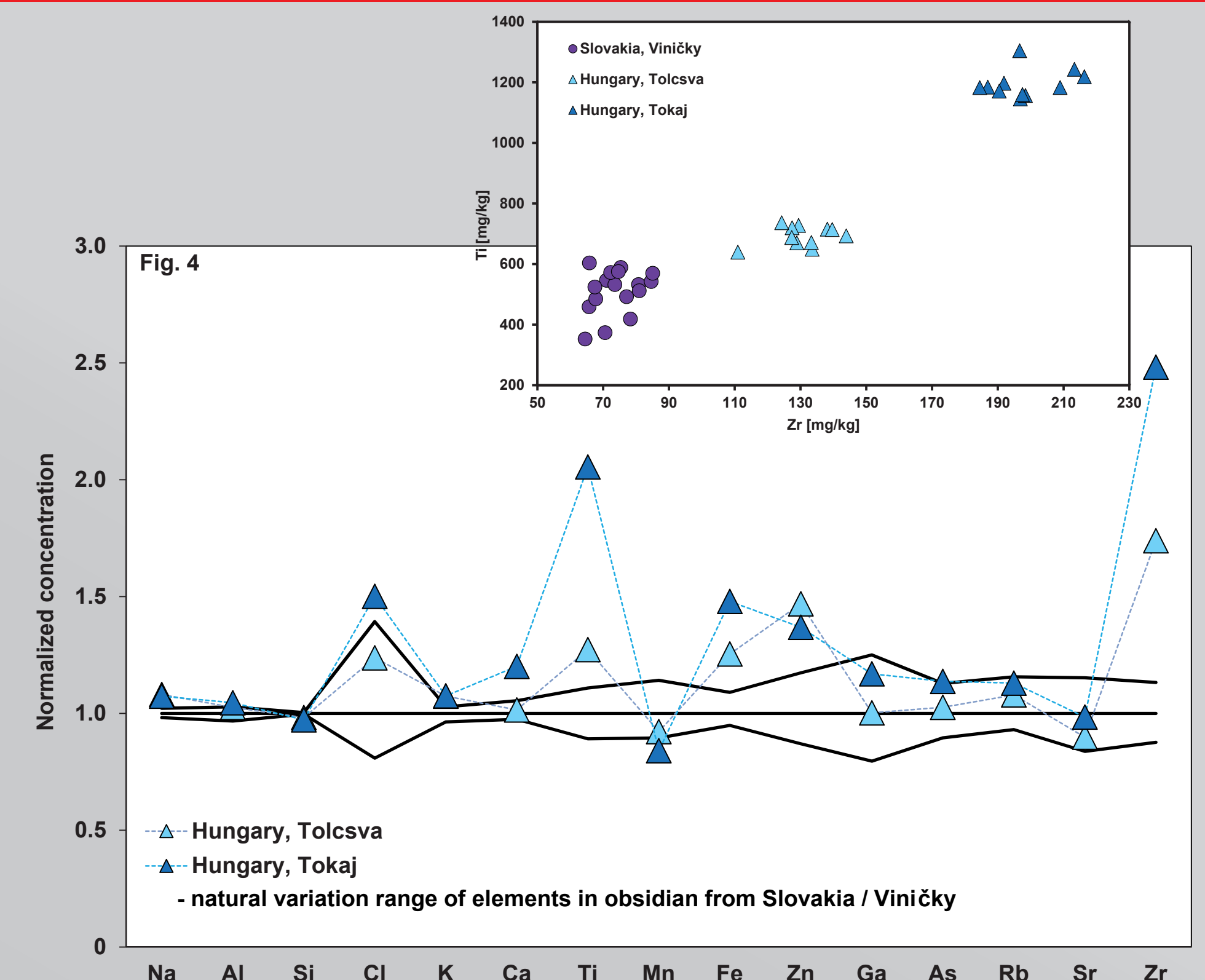
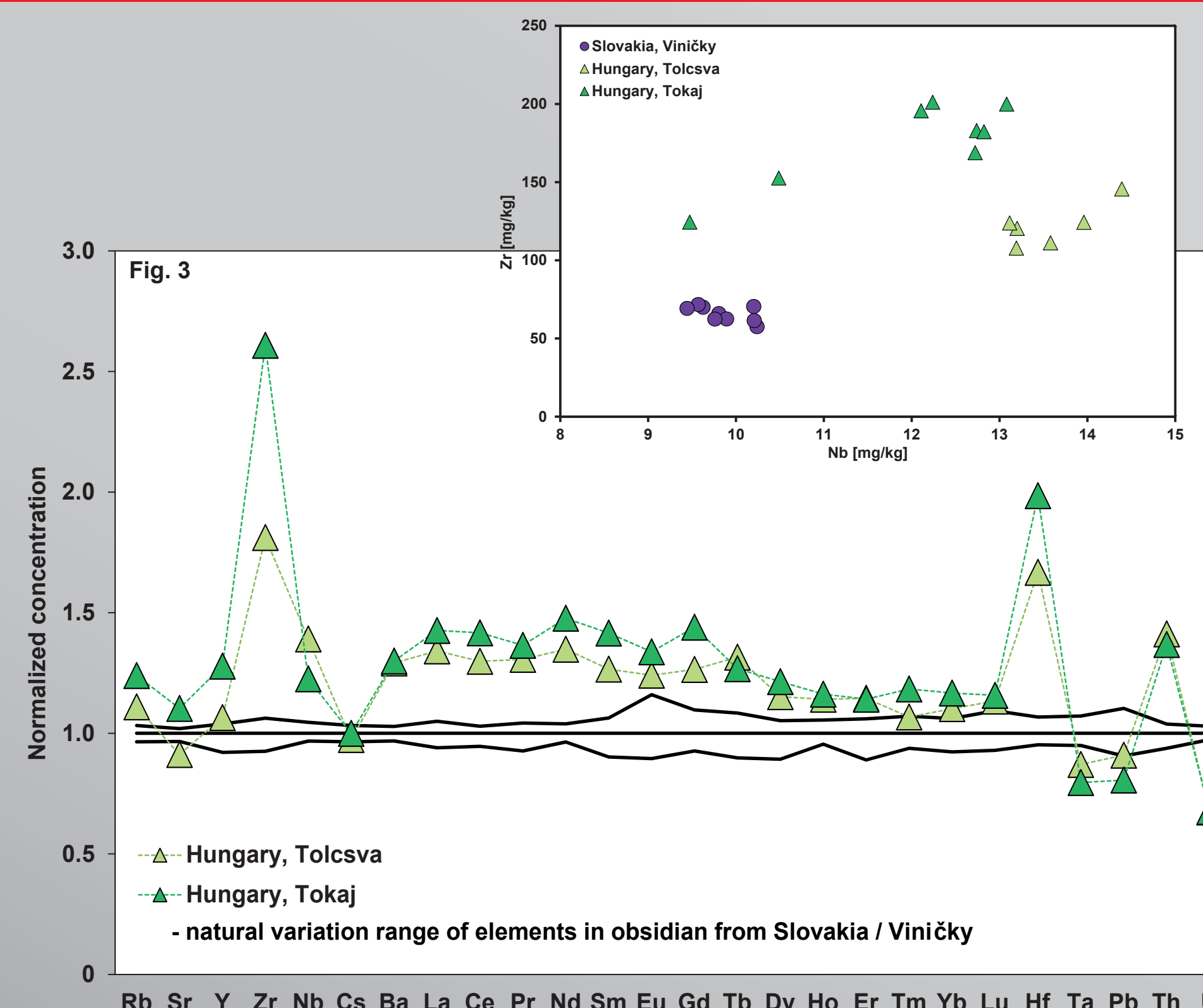
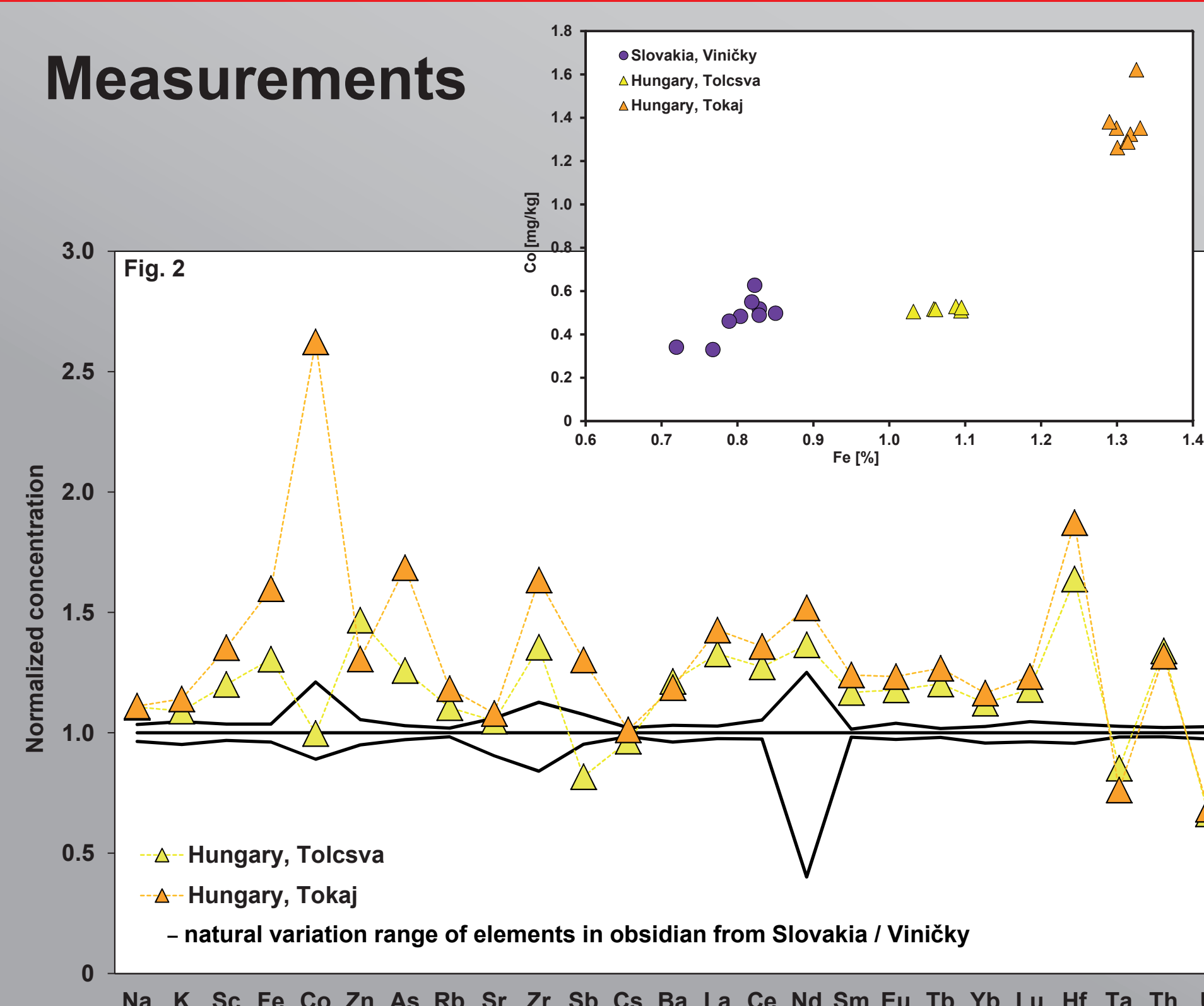
Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS)

- Ablation using an ArF gas Excimer laser coupled to a Thermo Element 2 ICP-MS at the Aberystwyth University
- Mass analyzer sorts the ions by their masses
- Analysed sample mass ~30 ng (laser beam diameter of 30 μm , penetration depth ~15-20 μm) per spot
- Minimally destructive (crater size ~30 μm)
- Detection limit: $\mu\text{g/kg}$
- Spectrometer scanned across 26 minor and trace elements [Fig. 3]

External Ion Beam Analysis (IBA):

- Particle Induced X-ray Emission (PIXE) and Particle Induced Gamma-ray Emission (PIGE)
- Irradiation with a 3.85 MeV proton beam of the 6 MV Tandem accelerator of the Ion Beam Centre of HZDR
- Detection of emitted X- and γ -rays
- Analysed sample mass ~20 μg (proton beam diameter of 1 mm, penetration depth ~100 μm) per spot
- Non-destructive
- Detection limit: mg/kg
- Determination of 15 major and minor elements as well as some traces [Fig. 4]

Measurements



Figs. 2-4: Element distribution patterns of obsidian from Tolcsva and Tokaj (Tokaj Mountains, Hungary). Data obtained by INAA (Fig. 2), LA-ICP-MS (Fig.3) and ion beam techniques PIXE and PIGE (Fig.4). The black lines represent the natural variation range of the elements in obsidian from Viničky (Lower Zemplin, Slovakia). Values are normalized to the average element concentrations obtained by the respective methods in obsidian from Viničky. Binary plots of selected element pairs and ratios are superimposed.

Results

- Determination of a maximum set of **41 elements**
- Discrimination between the three Hungarian and Slovakian obsidian sources with each technique possible (Figs. 2-4)
- Most indicative elements for each technique:
 - INAA:** Sc, Fe, Co, Zn, As, Zr, Sb, Nd, Hf
 - LA-ICP-MS:** Zr, Nb, REE (Rare Earth Elements), Hf
 - IBA:** Ti, Fe, Zn, Zr

Conclusions

- Proof of complementarity of analytical methods in use
- Combination of IBA, LA-ICP-MS and INAA revealed a maximum of more than 12 indicative elements
- Recommended method of choice: **INAA**
INAA provides the largest number of characteristic elements to the chemical fingerprint

References

- [1] O. Williams-Thorpe et al. *J. Archaeol. Sci.* **11** (1984) 183–212.
- [2] Z. Kasztovszky et al. *J. Radioanal. Nucl. Chem.* **278** (2008) 293–298.
- [3] K.T. Biró *Lithic Materials and Paleolithic Societies* (1996) 47–53.

Acknowledgment

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