HYALOPHANE- AND TOURMALINE-BEARING K-METASOMATISED POLISHED STONE IMPLEMENT FROM NORTHERN HUNGARY

HIALOFÁN- ÉS TURMALIN TARTALMÚ KÁLIMETASZOMATISZÁLT VULKANIT NYERSANYAGÚ CSISZOLT KŐESZKÖZ ÉSZAK-MAGYARORSZÁGRÓL•

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A 65 éves Szakmány György tiszteletére,
a hazai archeometriai kutatásokban végzett
kiemelkedő munkásságáért,
aki nélkül ez a cikk sem születhetett volna meg.

Abstract

A late Neolithic flat adze, originated from Szerencs-Taktaföldvár locality, North Hungary, was studied from archaeometric aspect. The adze suffered an alkali metasomatism which was revealed by the strikingly high alkali content and a large amount of potassic feldspars. Ba-rich and Ba-free potassic feldspars, and tourmaline, as characteristic minerals, were recorded from the adze. Despite of the several unique features, the precise provenance cannot be established. According to the mineral assemblage, one of the most possible provenances of raw material is Slovak Ore Mountains, near Tisovec; but due to the archaeological background of the Tisza-culture, the regions south of the Carpathian basin (Balkan, Banat) should be considered as well.

Kivonat

Szerencs-Taktaföldvár régészeti lelőhelyről származó késő neolit csiszolt kőeszköz archeometriai vizsgálatát végeztük el. A kőeszközt kálimetaszomatózis érte, melyet alátámaszt a nagyon magas alkália-tartalom és a nagyméretű káliföldpátok jelenléte. A káliföldpátok között Ba-dús és Ba-mentes változatok is kimutatásra kerültek, ezen kívül turmalint is tartalmaz a kőbalta. A számos egyedi jegy ellenére, a nyersanyag származási helye nem állapítható meg biztosan. Az ásványi összetevők alapján a Szepes-Gömöri-érchegység Tiszolc melletti területe tekinthető a legvalószínűbbnek. Ugyanakkor a Tisza kultúra régészeti hátterét tekintve, a Kárpát-medencétől délre eső vidékek (Balkán, Bánság) is megfontolandók.

KEYWORDS: POLISHED STONE IMPLEMENT, PROVENANCE, K-METASOMATISED VOLCANITE, HYALOPHANE, TOURMALINE, SZERENCS-TAKTAFÖLDVÁR

KULCSSZAVAK: CSISZOLT KŐESZKÖZ, FORRÁSTERÜLET, KÁLIMETASZOMATIZÁLT VULKANIT, HIALOFÁN, TURMALIN, SZERENCS-TAKTAFÖLDVÁR

Abbreviations: Ap: apatite; Bt: biotite; Chl: chlorite; Ep: epidote; Ep-REE: epidote with rare earth element content; En: enstatite; Kfs: potassic feldspar; Kfs-Ba: Ba-rich potassic feldspar; Mgt: magnetite; Olg: oligoclase; Ph: phengite; Ti-mgt: titanomagnetite; Tur: tourmaline

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Introduction

The largest archaeological collection of Northern Hungary can be found in the Herman Ottó Museum, Miskolc, which contains cc. 500 polished stone tools including metabasites in high proportion. A detailed archaeometric research was performed on them, resulting in a doctoral thesis, also (Kereskényi 2021).

Szerencs-Taktaföldvár is a well-known late Neolithic, Tisza culture related archaeological site (Seljan 2005) from which 12 polished stone implements were excavated in a particular position (Hellebrandt 1979). Several pieces of them were examined in petrological and mineralogical aspect but the stone implement No. 74.44. was significantly different from the other polished stone tools in terms of all characteristics.

In this study our aim is the archaeometric investigation of the tool and detecting its possible provenances.

Methods

As the implement is intact, only non-destructive mineralogical and petrological analytical methods were allowed to carry out.

Macroscopical description took place and magnetic susceptibility was measured with KT-5 Kappameter, applying thickness correction (Bradák et al. 2009).

The chemical analyses (EDS-SEM) were performed by a JEOL JXA 8600 Superprobe electron-microprobe with backs-scattered image recording and energy-dispersive X-ray spectrometry, using the original surface method (Bendő et al. 2013). The accelerating voltage was set to 20 kV and the beam current was 20 nA.

Non-destructive X-ray diffraction (XRD) analysis was accomplished with a Bruker D8 Advance X-ray diffractometer with CuKα source, 40 kV and 20 mA generator settings, parallel beam geometry (Göbel-mirror), Vantec1 position detector (1° window opening degree), 0.1 mm air-scatter collimator.

A 10x5 mm slice of aluminium foil (Al), 0.05 mm thick, was placed on the area to be measured to detect and correct for possible sample plane errors. The absorption of the aluminium foil and the sensitivity of the sample centering to sample plane position were tested by Kristály (2014) using NIST 1976a corundum standard.

After the measurement, the crystallographic phase identification was performed with Bruker DiffracPlus EVA software based on ICDD PDF2 and COD (Crystallography Open Database) database, using Search/Match algorithm (Kristály & Kereskényi 2016).

EDS-SEM and XRD measurements were carried out at the Institute of Exploration Geosciences, University of Miskolc.

The bulk elemental composition of the polished stone tool has been determined by prompt-gamma activation analysis (PGAA) at the Budapest Neutron Centre. The Budapest PGAA facility was described by Szentmiklósi et al. (2010). The method is applicable to determine the major geochemical components (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O), some specific trace elements and water phase with relatively high neutron absorption cross-sections (B, Cl, Sc, V, Cr, Ni, Sm and Gd).

The adze No. 74.44.5 was placed in an external horizontal cold neutron beam, which was guided away from the Budapest Research Reactor. The $7.7 \cdot 10^7$ n/cm$^2 \cdot$s thermal equivalent intensity beam was collimated to 24 mm^2 cross-section to achieve the optimal count-rate. The acquisition time was chosen to 2000 s. The prompt-gamma spectrum was collected in parallel with the irradiation. The composition was calculated using the prompt-k_0 method (Révay 2009).

Archaeological background, previous research

In 1974, during a road construction, ruins of a Neolithic house and fishnet weights came to surface at Szerencs-Taktaföldvár. 152 cm far from these findings, in a broken vessel, 12 polished stone implements were excavated (Hellebrandt 1979). Previous archaeometric studies were performed on 11 tools; five of them were identified as metabasite (Kereskényi et al. 2020, Kereskényi 2021), and there were five more volcanites, one sandstone and one white stone (kaolin?) rock-typed adzes.

The archaeological context of the adzes, whereby being hidden in a vessel, may also be related to the folk belief that the adzes have magical powers to ward off evil and trouble (Hellebrandt 1979). According to their archaeological typology most of them are flat adzes and three of them are broken implement-pieces.

Results

Macroscopic description and magnetic susceptibility

The colour of the flat polished stone implement is black (**Fig. 1.**) with red patches on its surface, observable by naked eye. White narrow bands can be observed on the lateral surface, which might be originated from the soil interaction, carbonate precipitation during the burial process. The size of the implement is 12.5 x 6.8 x 2.4 cm and the weight of the tool is strikingly heavy. The magnetic susceptibility is extremely high 76.57 x 10^{-3} SI.

Fig. 1.: Archaeological site of the polished stone implement No. 74.44.5 and its macroscopic image

1. ábra: A 74.44.5 leltári számú kőeszköz régészeti lelőhelye és makroszkópos felvétele

Bulk chemistry

Non-destructive PGAA analysis was applied for the determination of the bulk chemistry. According to the SiO_2-content, the studied implement has a composition typical of intermediate volcanic rocks. The total alkali oxide content is exceedingly high, 11.10 wt%, and the Al_2O_3 content is also elevated (23.20 wt%), while the CaO-content is very low (0.60 wt%). Based on the high alkalis, the rock was affected by alkali metasomatism. Focusing on the trace elements, enrichment of boron, vanadium and chromium can be recognized (**Table 1.**).

Table 1: PGAA results of the polished stone implement No. 74.44.5. The major components are given in wt%, the trace elements are in ppm. The amount of oxides is calculated from the elemental concentration, based on the oxidation numbers. The number of digits indicates the uncertainties of concentration values. "<D.L." stands for "less than the Detection Limit".

1. táblázat: A 74.44.5 leltári számú kőeszköz PGAA eredményei. A főelemek tömeg%-ban, a nyomelemek ppm-ben vannak megadva. (Rövidítés: <D.L.: detektálási határ alatt.).

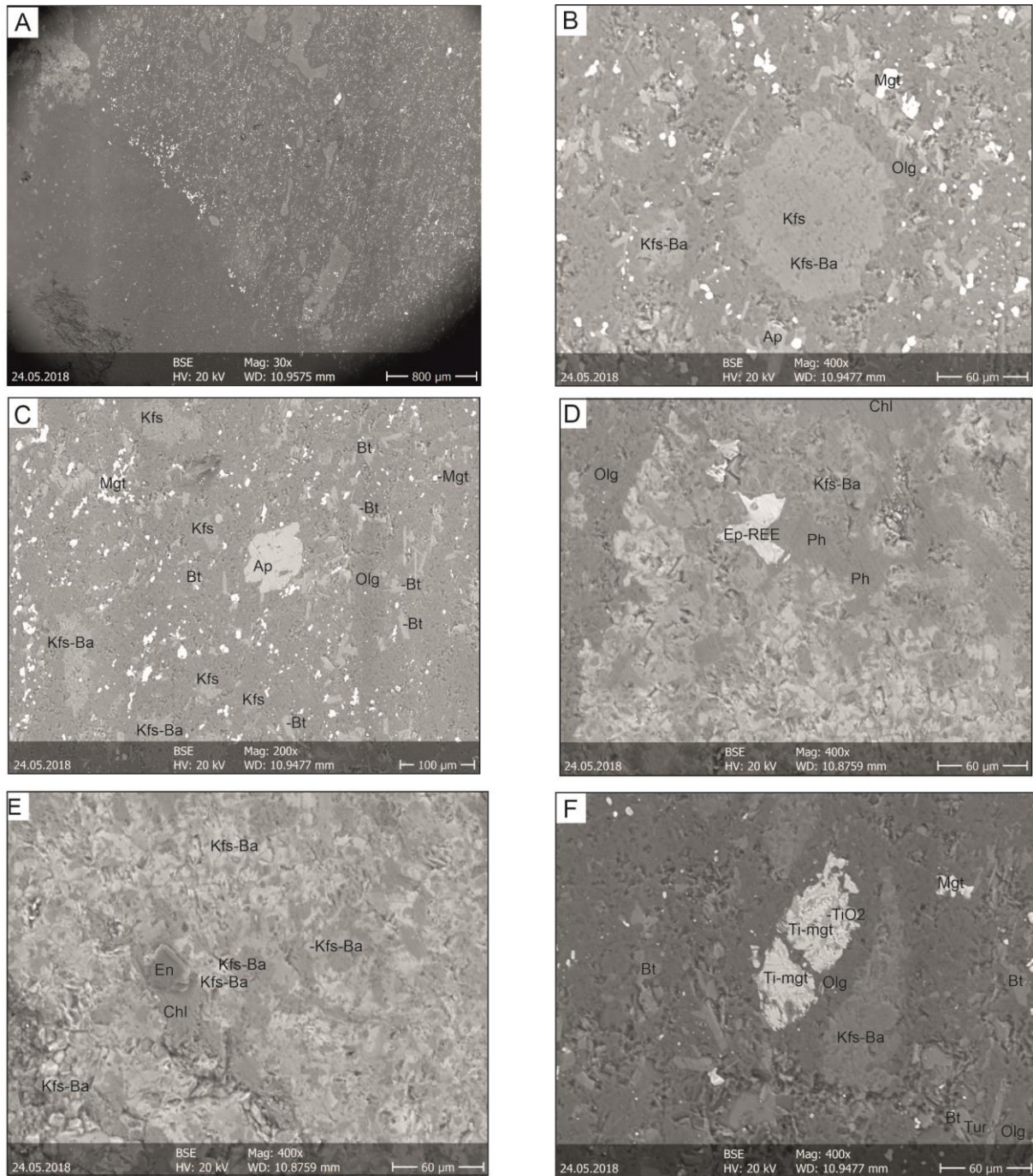| Oxide/Element	Concentration
SiO_2	52.20
TiO_2	0.78
Al_2O_3	23.20
Fe_2O_3*	9.94
MnO	<D.L
MgO	<D.L
CaO	0.60
Na_2O	3.67
K_2O	7.43
H_2O	1.94
Total	**99.76**
B	178
Cl	39
V	158
Cr	515
Nd	41
Sm	6
Gd	6

* Total Fe as Fe_2O_3.

Fig. 2.: BSE images of polished stone implement No. 74.44.5. (a) Dual texture of the tool: porphyritic inequigranular and fine-grained (in small magnification). (b) Large potassic feldspar grains, the Ba-content increases from core to rim., (c) Ba-rich and Ba-free potassic feldspars are often appear in the sample. (d) REE-rich epidote. (e) Small relict enstatite grain next to Ba-rich potassic feldspar. (f) Ti-magnetite with TiO_2 inclusion and small tourmaline (dravite) grain can be observed in the sample.

2. ábra: A 74.44.5 leltári számú kőeszköz BSE felvételei. (a) A kőeszköz kettős szöveti képe: porfíros inekvigranuláris és finom szemcsés (kis nagyításban). (b) Nagyméretű káliföldpátok, melyekben a bárium-tartalom a magtól a szegély felé növekszik. (c) Báriumos és báriummentes káliföldpátok rendre jelen vannak a mintában. (d) Ritkaföldfém-tartalmú epidot. (e) Bárium-tartalmú káliföldpát (hialofán) mellett relikt ensztatit szemcse mutatkozik. (f) Ti-magnetit TiO_2-zárványokat tartalmaz és egy turmalin szemcse (drávit) is megfigyelhető.
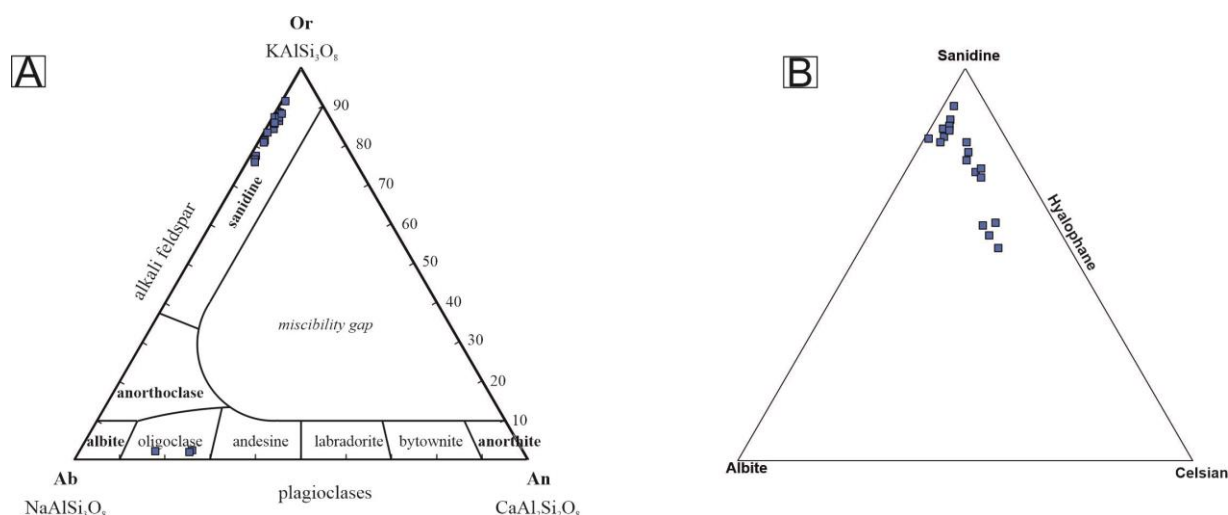
Fig. 3: Mineral chemistry data on polished stone implement No. 74.44.5 by SEM-EDS. (a) Feldspars in the Ab-An-Or diagram. (b) Ba-rich feldspars (hyalophane) plotted in the Albite-Celsian-Sanidine diagram

3. ábra: A 74.44.5 leltári számú kőeszköz SEM-EDS-sel mért ásványkémiai adatai. (a) Földpátok az Ab-An-Or diagramban ábrázolva. (b) Bárium-dús káliföldpátok (hialofán) az Albit-Celsián-Szanidin diagramban bemutatva.

Mineral chemistry

Studying the BSE image of the polished stone implement, the duality of the texture is striking. One half of the studied surface is in equigranular and porphyritic with large potassium feldspar crystals, while the other half of the section is fine-grained (**Fig. 2.a**).

The size of the *potassium feldspar* is over 1 mm (**Fig. 2.a**). Its composition varies, the Ba-content increases from core to rim (0.03 to 0.10 apfu) but this trend does not appear in each crystal. So, the rock includes Ba-rich (hyalophane) and almost Ba-free potassium feldspars, as well (**Fig. 2.c**, **Table 2.**), with the associated Na-content plotting in the high-temperature sanidine zone of the feldspar compositional plot (**Fig. 3.a-b**). The observed plagioclase in the implement is *oligoclase* (An_{17-25}) (**Table 2.**).

A cc. 20 µm *enstatite* grain in relict position was detected next to Ba-rich potassic feldspar and clinochlore (**Fig. 2.e**).

Epidote (**Fig. 2.d**) contains rare-earth elements: Ce = 0.18–0.27; La = 0.06–0.07; Nd = 0.0.8–0.12; Sm = 0.01–0.02; Gd = 0.01 apfu.

The size of the *biotite*-lamellae is 50 µm (**Figs. 2.c-f**) and the Fe/(Fe+Mg) ratio is in a narrow range, 0.35-0.42. The Al content, both in the octahedral- and tetrahedral sites, is relatively high (Al_{tot} = 1.78–1.88 apfu) (**Table 3.**), so the composition of the mineral shifts towards eastonite.

Among white micas, *phengite* was also observed with cc. 50 µm next to epidote (**Fig. 2.d, Table 4.**).

Chlorite was detected in large amount in the polished stone tool (**Figs. 2.d-e**), its composition reveals to be clinochlore (**Table 5.**).

From the implement a 10–20 µm-sized dravitic *tourmaline* grain was also perceived (**Table 6., Fig. 2.f**).

Magnetite and *titanomagnetite* are in even distribution and in large amount (**Fig. 2.**). The largest magnetite/titanomagnetite grain reaches 100 µm but the average size is 5–20 µm, respectively. TiO_2 phase as inclusions (**Fig. 2.f**) can be observed.

Table 2: Chemical composition of feldspars in wt%. (Stone adze, HOM, Inv. nr: 74.44.5)
2. táblázat: Földpátok kémiai összetétele tömeg%-ban megadva. (74.44.5 leltári számú kőeszköz, HOM).

	Olg	Kfs (Ba)	Kfs (Ba)	Kfs	Kfs (Ba)	Kfs (Ba)
SiO_2	63.48	62.13	62.03	63.76	58.53	57.21
Al_2O_3	23.96	19.66	19.53	19.78	20.83	21.00
FeO*	0.26	0.35	0.49	0.24	0.19	0.17
CaO	3.16	0.15	0.13	0.20	0.12	0.15
Na_2O	8.50	1.04	1.15	1.80	1.21	1.14
K_2O	0.34	14.07	13.90	13.13	12.39	11.83
BaO	0.00	1.67	2.04	0.41	6.23	8.05
Total	**99.70**	**99.07**	**99.27**	**99.32**	**99.50**	**99.55**
Cation numbers based on 8 oxygens						
Si	2.80	2.92	2.92	2.95	2.83	2.80
Al	1.25	1.09	1.08	1.08	1.19	1.21
Fe^{2+}	0.01	0.01	0.02	0.01	0.01	0.01
Ca	0.15	0.01	0.01	0.01	0.01	0.01
Na	0.73	0.09	0.10	0.16	0.11	0.11
K	0.02	0.84	0.83	0.77	0.76	0.74
Ba	0.00	0.03	0.04	0.01	0.12	0.15
Total	**4.95**	**5.00**	**5.01**	**4.98**	**5.02**	**5.02**
Feldspars molecule in mol%.						
An	16.68	0.80	0.69	1.05	0.70	0.92
Ab	81.18	9.78	10.74	17.11	11.39	10.80
Or	2.14	87.05	85.41	82.11	76.75	73.77
Ce	0.00	3.17	3.85	0.79	11.86	15.42

	Kfs (Ba)	Kfs (Ba)	Kfs (Ba)	Kfs (Ba)	Kfs (Ba)	Kfs (Ba)	Kfs (Ba)
SiO_2	56.69	52.85	54.39	52.99	59.60	56.66	51.81
Al_2O_3	21.05	22.26	22.46	22.32	20.44	21.46	22.52
FeO*	0.19	0.19	0.12	0.17	0.27	0.29	0.15
CaO	0.16	0.13	0.13	0.18	0.19	0.13	0.19
Na_2O	0.99	1.34	1.60	1.65	0.94	1.05	1.59
K_2O	12.08	9.49	9.04	8.92	12.83	11.10	8.36
BaO	8.48	13.39	11.69	13.38	4.97	8.68	15.11
Total	**99.64**	**99.65**	**99.43**	**99.61**	**99.24**	**99.37**	**99.73**
Cation numbers based on 8 oxygens							
Si	2.78	2.68	2.71	2.68	2.86	2.78	2.65
Al	1.22	1.33	1.32	1.33	1.16	1.24	1.36
Fe^{2+}	0.01	0.01	0.00	0.01	0.01	0.01	0.01
Ca	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Na	0.09	0.13	0.15	0.16	0.09	0.10	0.16
K	0.76	0.61	0.57	0.58	0.78	0.69	0.54
Ba	0.16	0.27	0.23	0.26	0.09	0.17	0.30
Total	**5.03**	**5.03**	**5.00**	**5.03**	**5.00**	**5.00**	**5.03**
Feldspars molecule in mol%							
An	0.98	0.94	0.94	1.31	1.11	0.85	1.46
Ab	9.29	13.02	16.14	16.14	9.05	10.39	15.67
Or	74.62	60.68	60.02	57.41	81.28	72.26	54.22
Ce	16.09	26.30	23.84	26.45	9.67	17.36	30.10

* Total iron was measured as FeO.

Table 3.: Chemical composition of biotite in wt%. (Stone adze, HOM, Inv. nr. 74.44.5)
3. táblázat: Biotitok kémiai összetétele tömeg%-ban megadva. (74.44.5 leltári számú kőeszköz, HOM).

SiO_2	35.77	36.41	36.32	36.23	37.69	35.77
TiO_2	2.68	2.75	2.43	2.66	2.51	2.68
Al_2O_3	21.03	21.28	21.43	21.35	21.93	21.03
FeO*	15.14	13.83	13.57	13.58	12.29	15.14
MnO	0.18	0.20	0.08	0.12	0.20	0.18
MgO	11.56	11.64	12.62	12.47	10.87	11.56
CaO	0.00	0.10	0.00	0.00	0.12	0.00
Na_2O	0.20	0.21	0.38	0.38	0.36	0.20
K_2O	9.39	9.49	9.07	9.12	9.89	9.39
H_2O**	4.06	4.09	4.10	4.10	4.13	4.06
Total	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**
Cation numbers based on 11 oxygens						
Si	2.64	2.67	2.90	2.65	2.74	2.64
Al	1.36	1.33	1.10	1.35	1.26	1.36
ΣT	**4.00**	**4.00**	**4.00**	**4.00**	**4.00**	**4.00**
Al	0.47	0.51	0.33	0.50	0.62	0.47
Ti	0.15	0.15	0.08	0.13	0.14	0.15
Fe^{2+}	0.93	0.85	0.81	0.83	0.75	0.93
Mn	0.01	0.01	0.01	0.00	0.01	0.01
Mg	1.27	1.27	1.77	1.37	1.18	1.27
ΣM	**2.84**	**2.79**	**3.00**	**2.84**	**2.69**	**2.84**
Ca	0.00	0.01	0.01	0.00	0.01	0.00
Na	0.03	0.03	0.00	0.05	0.05	0.03
K	0.88	0.89	0.89	0.85	0.92	0.88
ΣI	**0.91**	**0.92**	**0.90**	**0.90**	**0.98**	**0.91**

* Total Fe was measured as FeO.

** H_2O based on stoichiometry: OH = 2 *apfu*.

XRD analysis

Non-destructive XRD analysis was carried out on the implement and confirmed the presence of sanidine, plagioclase, enstatite, titanomagnetite and magnetite (**Fig. 4.**). The presence of quartz is the result of soil-originated contamination on the surface. Even if the measured surface was selected to avoid the carbonate precipitation (macroscopic white spots), microscopic soil grains were attached into the pores. As anatase was detected, part of the TiO_2-content is present in this form, a usual product of metasomatic processes, however it does not mean that other TiO_2 species, or other Ti-bearing phases are not present. This agrees with the observation of titanomagnetite (in which case the chemical formula in **Fig. 4.** is not relevant, only indicates deviation from regular composition) structures, corroborated with the titanomagnetite identified by the EDS-SEM.

Table 4.: Chemical composition of white micas in wt% in the stone implement No. 74.44.5

4. táblázat: Fehér csillámok kémiai összetétele tömeg%-ban megadva. (74.44.5 leltári számú kőeszköz, HOM).

SiO$_2$	45.97	48.01
TiO$_2$	0.53	0.24
Al$_2$O$_3$	31.98	30.62
FeO*	3.34	3.51
MnO	0.11	0.08
MgO	3.39	2.77
CaO	0.12	0.10
Na$_2$O	0.43	0.21
K$_2$O	9.66	9.98
H$_2$O**	4.47	4.48
Total	**100.00**	**100.00**
Ion numbers based on 24 (O, OH)		
Si	6.17	6.43
Al^{IV}	1.83	1.57
ΣT	**8.00**	**8.00**
Al^{VI}	3.23	3.26
Ti	0.05	0.02
Fe	0.38	0.39
Mn	0.01	0.01
Mg	0.68	0.55
ΣO	**4.35**	**4.24**
Ca	0.02	0.01
Na	0.11	0.05
K	1.65	1.70
ΣI	**1.78**	**1.77**
OH	**4.00**	**4.00**

* Total Fe was measured as FeO.
** H$_2$O based on stoichiometry: OH = 2 *apfu*.

Table 5: Chemical composition of chlorite in wt% in the stone implement No. 74.44.5

5. táblázat: Kloritok kémiai összetétele tömeg%-ban megadva. (74.44.5 leltári számú kőeszköz, HOM).

SiO$_2$	28.71	28.50	28.00	28.33
TiO$_2$	0.13	0.00	0.04	0.05
Al$_2$O$_3$	21.19	21.86	21.12	21.09
FeO*	18.23	16.74	19.01	18.61
MnO	0.35	0.33	0.41	0.41
MgO	18.92	20.35	19.31	19.42
CaO	0.18	0.04	0.02	0.04
Na$_2$O	0.19	0.08	0.11	0.06
K$_2$O	0.16	0.07	0.10	0.07
H$_2$O**	11.93	12.03	11.88	11.91
Total	**100.00**	**100.00**	**100.00**	**100.00**
Ion numbers based on 18 (O,OH) anions.				
Si	2.88	2.84	2.83	2.85
Al^{IV}	1.12	1.16	1.17	1.15
Al^{VI}	1.39	1.41	1.34	1.36
Ti	0.01	0.00	0.00	0.00
Fe^{2+}	1.53	1.40	1.61	1.57
Mn	0.03	0.03	0.04	0.04
Mg	2.84	3.02	2.91	2.92
Ca	0.02	0.00	0.00	0.00
Na	0.04	0.02	0.02	0.01
K	0.02	0.01	0.01	0.01
sum X	**5.88**	**5.89**	**5.93**	**5.90**
O	10.00	10.00	10.00	10.00
OH	8.00	8.00	8.00	8.00
Fe/(Fe+Mg)	**0.35**	**0.32**	**0.36**	**0.35**

* Total Fe was measured as FeO.
** H$_2$O based on stoichiometry: OH = 8 *apfu*.

Discussion – Possible provenance

The flat adze was studied from archaeometrical aspect, detailed petrological, mineralogical analyses were performed in order to define the rock-type and the provenance.

According to the high alkali content and the observed potassic feldspar crystals in large amount, an intermediate volcanic rock was affected by potassic metasomatism. Ba-rich and Ba-free potassic feldspars were recorded in the adze (**Fig. 2.**). In the early phase of crystallization of potassic feldspars Ba^{2+} can be captured in the feldspar having the same ion radius as K$^+$ (von Engelhardt 1936, Oftedal 1961, Heier 1962). In the studied adze Ba-content increases from core to rim (**Fig. 2.**) but this geochemical process can take place reversely (Němec 1975) as well.

Boron and chromium contents of the adze are showing elevated values. Enrichment of volatile (B) and metallic (Ba, Cr) component may be related to postmagmatic, metasomatic event (Pirajno 2013) which is confirmed by the presence of the significant amount of potassic feldspars.

A late magnetite-forming process took place which resulted the presence of large amount of magnetite and Ti-magnetite (**Figs. 2.b-c**) producing the high magnetic susceptibility value.

Table 6.: Chemical composition of tourmaline in wt%. (Stone adze, HOM, Inv. nr: 74.44.5)

6. táblázat: Turmalinok kémiai összetétele tömeg%-ban megadva. (74.44.5 leltári számú kőeszköz, HOM).

SiO_2	35.74	35.26
TiO_2	0.24	0.37
B_2O_3*	10.59	12.38
Al_2O_3	32.80	39.90
FeO**	6.68	7.63
MnO	0.00	0.00
MgO	7.45	7.74
CaO	0.52	0.49
Na_2O	2.18	2.65
K_2O	0.15	0.03
H_2O***	3.65	4.27
Total	**100.00**	**100.00**
Based on 31 (O, OH) anions		
Si	5.87	5.78
Al	0.13	0.22
ΣT	**6.00**	**6.00**
B	3.00	3.00
ΣB	**3.00**	**3.00**
Al	6.00	6.00
ΣZ	**6.00**	**6.00**
Al	0.21	0.38
Ti	0.03	0.05
Mg	1.82	1.62
Mn	0.00	0.00
Fe^{2+}	0.92	0.90
ΣY	**2.98**	**2.94**
Ca	0.09	0.07
Na	0.69	0.72
K	0.03	0.01
□	0.18	0.20
ΣX	**1.00**	**1.00**
OH	4.00	4.00

* B_2O_3 calculated from the stoichiometry: B = 3 apfu.
**Total Fe was measured as FeO.
***Based on the stoichiometry: OH = 4 apfu.

In the Carpathian Basin or its surroundings, similar rocks with SiO_2 content cc. 50 wt%, affected by alkali metasomatism, are known as potassic-trachyte from Mátra Mountains, Telkibánya, both in Hungary and Baia Mare (Nagybánya), Romania (Kubovics, 1966). However, they can be excluded as source areas, because of the much higher iron content of the stone tool.

In the Veporicum and the Gemericum (Slovakia), alkali metasomatism took place, but more acidic rocks, mainly dacite, were affected by the process (Šimurková et al. 2016), therefore these two units can be excluded as source areas.

Hyalophane-bearing, magnetite rich rocks were described from the Slovak Ore Mountains, near Tisovec (Tiszolc) (Hurai & Huraiová 2011),

furthermore dravite-bearing rock is mentioned from this area, too (Bačík et al. 2015). It can be a good match for provenance but differences occur in the described ore minerals, additionally the bulk chemistry data of these lithotypes were not published therefore no basis for comparison.

From Szerencs-Taktaföldvár the previously studied polished implements were amphibolite, contact metabasite, volcanites, sandstone and white stone (kaolin). The provenance of the amphibolite was Klátov, Gemericum (Slovakia) (Kereskényi et al. 2020) while the contact metabasite derived from the Czech Massif (Kereskényi 2021). Detailed mineralogical analysis were not performed on the other lithotypes, therefore provenance cannot be established.

Knowing the fact that the polished stone implement belongs to the Tisza culture, it is imaginable that the raw material came from southern areas (e.g. Balkan or Banat regions) to Szerencs-Taktaföldvár archaeological site (**Fig. 5.**). It is due to the fact that the Tisza culture spread over a wide area, covering the Danube-Tisza interfluve and Transtisza (Tiszántúl) areas, either (Kreiter et al. 2017). Furthermore, the Tisza culture appeared in the Banat region (Romania), too and showing many analogies with the Vinča culture, which spread in North Serbia (Raczky 1992).

Despite of the numerous unique signatures, the exact provenance field cannot be determined, and because of the special rock-type, remote source areas cannot be excluded either.

Conclusions

Considering the mineralogical assemblage, and the bulk chemistry of the stone adze, the implement suffered an alkali metasomatism. Despite of the characteristic, index minerals e.g. hyalophane (Ba-rich potassium feldspar) and dravite (tourmaline) and the extreme alkali content of the bulk chemistry, the provenance of the adze cannot be identified from these data for sure.

Gemericum and Veporicum as possible provenances can be excluded except the outcrops near Tisovec in the Slovak Ore Mountains where partly similar mineral assemblage (Hurai & Huraiová 2011, Bačík et al. 2015) was recorded. South of the Carpathian Basin, e.g. Banat or Balkan outline (**Fig. 5.**) as possible provenances which can be justified by archaeological point of view even (Raczky 1992, Kreiter et al. 2017).

Concluding, hyalophane- and tourmaline-bearing alkali metasomatised volcanite as lithic raw material has not been mentioned from the earlier studied polished stone tools yet, therefore it can be handled as a unique lithotype with accurately not assured provenance.
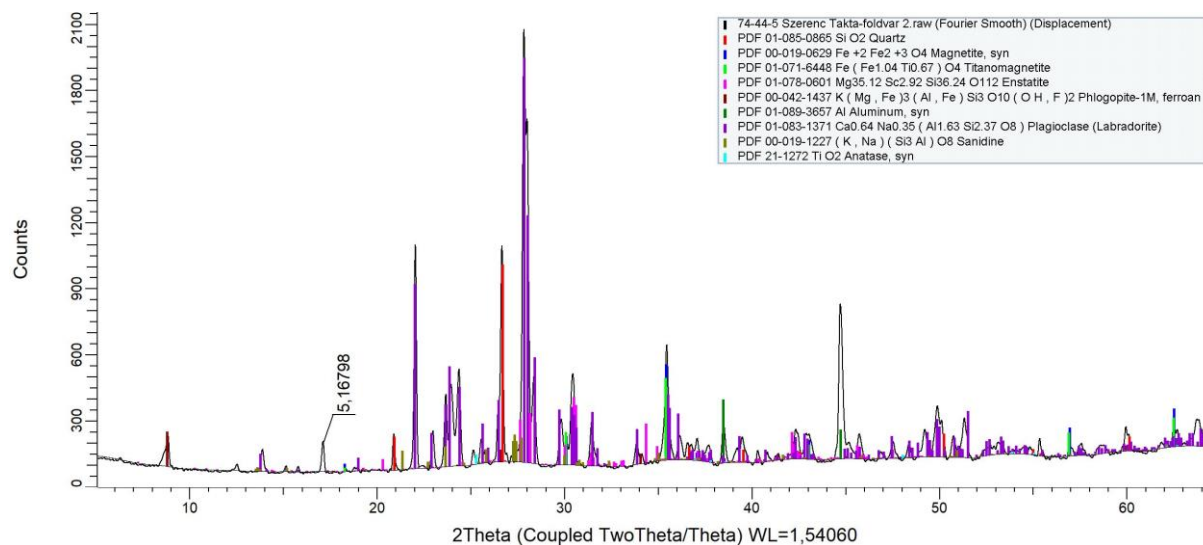
Fig. 4.: XRD pattern of stone tool No. 74.44.5
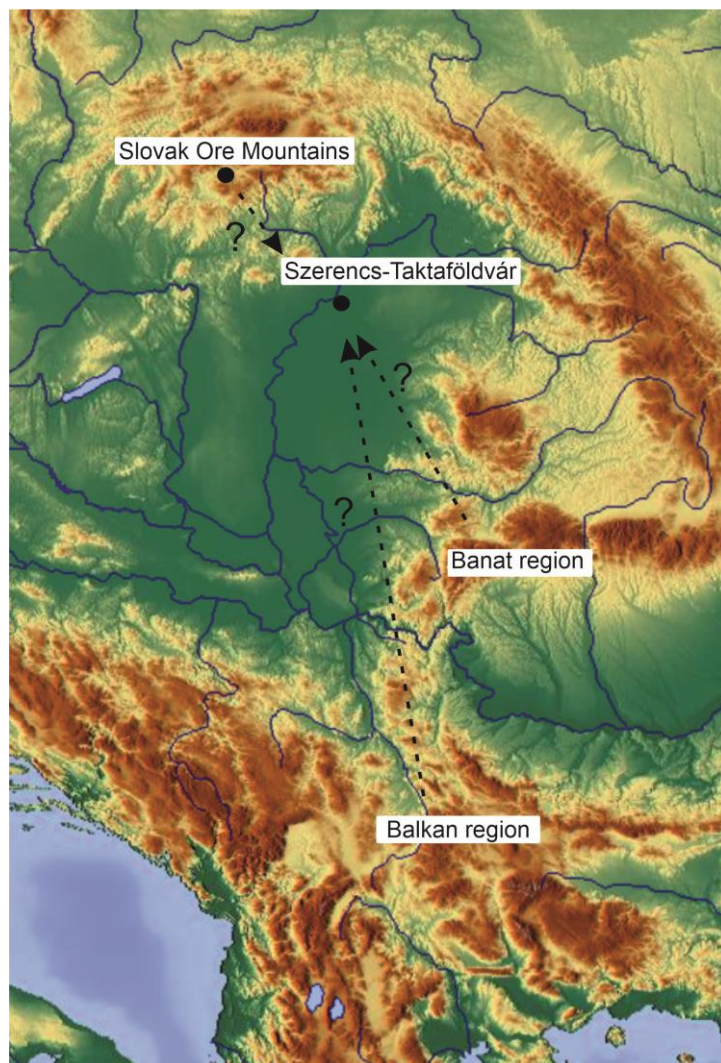**4. ábra:** A 74.44.5 leltári számú kőeszköz XRD felvétele

Fig. 5.: Possible provenances of the flat adze No. 74.44.5.

5. ábra: A 74.44.5 leltári számú kőeszköz lehetséges forrásterületei.

Contribution of authors

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References

BAČÍK, P., ERTL, A., ŠTEVKO, M., GIESTER, G. & SEČKÁR, P. (2015): Acicular zoned tourmaline (magnesio-foitite to foitite) from a quartz vein near Tisovec, Slovakia: The relationship between crystal chemistry and acicular habit. *The Canadian Mineralogist* **53** 221–234.

BENDŐ, Zs., OLÁH, I., PÉTERDI, B., SZAKMÁNY, Gy. & HORVÁTH, E. (2013): Csiszolt kőeszközök és ékkövek roncsolásmentes SEM-EDX vizsgálata: lehetőségek és korlátok. *Archeometriai Műhely* **10/1** 51–66.

BRADÁK, B., SZAKMÁNY, Gy., JÓZSA, S. & PŘICHYSTAL, A. (2009): Application of magnetic susceptibility on polished stone tools from Western Hungary and the Eastern part of Czech Republic (Central Europe). *Journal of Archaeological Science* **36** 2437–2444.
http://dx.doi.org/10.1016/j.jas.2009.07.001

ENGELHARDT, W. von (1936): Die Geochemie des Bariums. *Chemie der Erde* **10** 187–246.

HEIER, K., S. (1962): Trace elements in feldspars – a review. *Norsk Geologisk Tidsskrift* **42/2** 415–454.

HELLEBRANDT, M. (1979): A szerencs-taktaföldvári kőbalta lelet. In: SZABADFALVI, J., szerk., *A Herman Ottó Múzeum Évkönyve* **XVII-XVIII** Miskolc, 7–25.

HURAI, V. & HURAIOVÁ, M. (2011): Origin of ferroan alabandite and manganoan sphalerite from the Tisovec skarn, Slovakia. *Neues Jahrbuch für Mineralogie - Abhandlungen* **188/2** 119–134.

KERESKÉNYI, E., SZAKMÁNY, Gy., FEHÉR, B., HARSÁNYI, I., SZILÁGYI, V., KASZTOVSZKY, Zs. & M. TÓTH, T. (2020): Archaeometrical results related to Neolithic stone implements from Northeast Hungary. *Journal of Archaeological Science: Reports* **32** 102437 1–18.
https://doi.org/10.1016/j.jasrep.2020.102437

KERESKÉNYI E. (2021): *A Herman Ottó Múzeum neolit csiszolt kőeszközeinek vizsgálata, különös tekintettel a metabázitokra*. Doktori dolgozat, Debreceni Egyetem, 220 p.

KREITER, A., KALICZ, N., KOVÁCS, K., SIKLÓSI, Zs. & VIKTORIK, O. (2017): Entangled traditions: Lengyel and Tisza ceramic technology in a Late Neolithic settlement in northern Hungary. *Journal of Archaeological Science: Reports* **16** 589–603.
https://doi.org/10.1016/j.jasrep.2017.03.021

KRISTÁLY, F. (2014): Rapid non-destructive X-ray diffraction investigation of polished greenstone tools. *Archeometriai Műhely* **11/4** 223–242.

KRISTÁLY, F. & KERESKÉNYI, E. (2016): Non-destructive X-ray diffraction investigation of amphibole-rich stone implements: What precision should we expect for glaucophane-identification? *Archeometriai Műhely* **13/3** 191–202.

KUBOVICS, I. (1966): A kálimetaszomatózis szerepe a nyugat-mátrai kőzetképződésben. *Földtani Közlöny* **96/1** 13–26.

NĚMEC, D. (1975): Barium in K-feldspar Megacrysts from granitic and syenitic rocks of the Bohemian Massif. *Tschermaks Mineralogische und petrographische Mitteilungen* **22** 109–116.

OFTEDAL, I. (1961): Remarks on the variable contents of Ba and Sr in microdiorite from a single pegmatite body. *Norsk Geologisk Tidsskrift* **41** 271–277.

PIRAJNO, F. (2013): Effects of metasomatism on mineral systems and their host rocks: Alkali metasomatism, skarns, greisens, tourmalinites, rodingites, black-wall alteration and listvenites. In: HARLOV, D.E. & AUSTRHEIM, H., eds., *Metasomatism and the chemical transformation of rock.* Springer, Springer Nature, Berlin, Heidelberg, 203–251.

RACZKY, P. (1992): The Neolithic of the Great Hungarian Plain and the Vinča Complex (New archaeological evidences for the relations). In: SAMARDŽIĆ, R., ed., *Hommage á Nikola Tasić á l'occasion des ses soixante ans, Balcanica* **23** Beograd, 147–165.

RÉVAY, Zs. (2009): Determining elemental composition using prompt γ activation analysis, *Analytical Chemistry* **81** 6851-6859.

SELJÁN É. (2005): *A Tiszai kultúra települése Szerencs-Taktaföldváron a késő neolitikum időszakában*. Diplomadolgozat. Eötvös Loránd Tudományegyetem, Budapest, 105 p.

ŠIMURKOVÁ, M., IVAN, P. & GARGULÁK, M. (2016): Subsolidus alkali metasomatism in the metamorphosed Ordovician acid volcanics and volcaniclastics of the Gelnica Group (Gemeric Superunit, Western Carpathians). *Acta Geologica Slovaca* **8/1** 87–98.

SZENTMIKLÓSI, L., BELGYA, T., RÉVAY, Zs. & KIS, Z. (2010): Upgrade of the prompt gamma activation analysis and the neutron-induced prompt gamma spectroscopy facilities at the Budapest Research Reactor. *Journal of Radioanalytical and Nuclear Chemistry* **286** 501–505.
http://dx.doi.org/10.1007/s10967-010-0765-4