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Neutron activation analysis of archaeometallurgical ancient artifacts found in Uzbekistan

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Abstract

The current work presents the results of neutron activation analysis applied to determine the elemental composition of ancient metallurgical slags found by archaeologists in the medieval settlement "Eski Khovos" in Uzbekistan. In Uzbekistan, archaeological artifacts, including products of archaeometallurgy, are predominantly studied using traditional descriptive techniques. Two slag-like object samples and three fragments of clay furnace walls were irradiated by thermal neutrons at the research reactor of the Institute of Nuclear Physics of Uzbekistan. The comparative analysis method enabled the identification of up to 34 different chemical elements in these samples (As, Au, Ba, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Ga, Hf, K, La, Lu, Mn, Mo, Na, Nd, Rb, Re, Sb, Sc, Sm, Sn, Sr, Ta, Tb, Th, U, W, Yb, Zn). The findings of this study suggest that the fragments are remnants of blacksmithing slags. The established methods of neutron activation analysis and processing of characteristic gamma spectra of activated samples hold significant interest for archaeologists of Uzbekistan, as they provide valuable new insights into the provenance, production techniques, and technological advancements of the archaeological artifacts, which in turn contribute to a better understanding of the region's historical and cultural development.

Keywords Neutron activation analysis · Nuclear reactor · Gamma-ray spectrometry · Archaeometallurgy · Metallurgical furnace · Slag · Bloom

Introduction

The investigation of metallurgical slags is significant, as they provide valuable insights into the origin and development of ancient metallurgical industries. The analysis of ancient slags requires a thorough examination of their both microconstituents and composition as they are the primary waste byproducts of a range of metallurgical activities, including primary smelting (the reduction of ores to metal), secondary melting (the purification, consolidation, or mixing of metals), and smithing. Therefore, a collaboration between scientists and archaeologists is essential for the study of ancient technological practices [1].

Slag serves as an important indicator for interpreting manufacturing processes, offering clues about the design of metallurgical furnaces, smelting stages, and the ingredients used in the smelting process (e.g., fuel, fluxes). The composition of slag is influenced not only by these ingredients, but also by the walls and lower parts of the furnace, as chemical elements can move into slag through diffusion processes.

Thus, examining the distribution and composition of slags can shed light on ancient metallurgical and industrial practices, including land use, resource management, and trading systems. Understanding the level of ancient technologies also helps assess the development of labor forces, which contributed to the emergence of more advanced forms of human social organization (stone age, copper and bronze age, early iron age, iron age).

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The significance of studying ancient artifacts, such as slag and other archaeometallurgical finds, has been recognized in the literature [2–8]. Numerous studies have highlighted the value of analyzing ancient slags and archaeological artifacts (metal, ceramics, etc.) using modern analytical techniques [9–18]. The global relevance of evaluating archaeological artifacts is exemplified by the IAEA program on radiation technologies [19], which emphasizes the importance of identifying artifact origins to understand prehistoric human contact and migration.

The composition of ancient slag has been investigated using various physical methods. Examples in the literature include activation analysis as employed by Schubiger et al. [20] for determination slags from mainland Greece, spectroscopy as demonstrated by Gratuze and Janssens [21] for characterizing Roman glass slags, X-ray fluorescence (XRF) as shown in the study by Killick and Fenn [22] for identifying the chemical composition of iron slags from African iron production, hydride generation as applied by Baron et al. [23] for investigating lead isotopes in metallurgical slags, gravimetric and volumetric analysis as reported by Olovčić et al. [24] for determining metal concentrations in slags from a Bronze Age site, and photometry as illustrated by Khosravi and Agha-Aligol [25] for examining slags from Lorestan, Western Iran metalworking sites. In Uzbekistan, only some examples are available in the literature on slags, and the efforts of most research groups are concentrated on finished metal products [26–30]. In light of this background, the present work aims to study archaeometallurgical products found in ancient metallurgical furnaces in Uzbekistan by employing the neutron activation analysis (NAA) method.

Materials and methods

Some aspects of ancient furnaces

It is crucial to consider and properly identify the remains of furnaces, ore, slag, crackers, coal, and other relevant materials when describing ancient metallurgical activities. A fundamental understanding of basic concepts in ancient metallurgy can assist archaeologists in accurately identifying various archaeometallurgical objects, such as metal processing and smelting sites, as well as the materials discovered at these locations. Consequently, this paper places considerable emphasis on several ancient iron production technologies.

The most ancient and primitive technology is ore smelting in pits. The first bloomery furnaces with slag pits appeared later. The slag from the smelting process either accumulates at the bottom of the internal pit or is tapped outside the furnace. As bloomery furnaces advanced, another technology emerged, which featured furnaces with molten slag poured through a special offtake at the base of the furnace (tapped slag). Archaeologists can distinguish these slags by their appearance (heterogeneous slag lumps, slag cakes, and vitreous fragments). The furnace charge heating temperature in ancient metallurgical furnaces typically reached 1150–1200 °C, lower than the iron melting temperature of 1540 °C [31, 32]. When the furnace reached 800 °C, iron oxide in the ore was reduced into metallic iron. Partially reduced iron did not melt but remained as a paste-like mass with numerous voids and slag inclusions (the so-called bloom). For non-specialists in metallurgy, distinguishing ancient bloom from ancient slag based on outer appearance can be challenging.

Iron bloom is a semi-finished iron product, requiring blacksmithing technology to transform it into finished products by hot forging. For example, the bloom was typically softened in special furnaces before being forged with a hammer on an anvil. During primary forging, ancient blacksmiths removed the largest part of the slag remaining on and within the bloom. Industrial iron was also heated in such furnaces, and blacksmiths crafted finished iron products through secondary forging. Archaeologists generally use the terms “smelting furnace” and “smithing furnace” to refer to these metallurgical furnaces.

Neutron activation analysis

The method of measuring element concentrations known as neutron activation analysis (NAA) has been widely exploited in many domains of research [10, 12–15, 33]. NAA is employed for determining the elemental composition in numerous materials. It is based on the measurement of gamma rays emitted from a sample that has been irradiated by neutrons. As activation analysis relies on nuclear processes, NAA results are related to isotopic composition and independent on chemical bond types of the element of interest. NAA also offers multi-element properties, allowing for sample to analysis without decomposition, and high sensitivity, enabling the determination of concentrations down to ppm units.

The relative analysis approach is most commonly used in examining multi-element samples through neutron activation. In this technique, the samples under study are irradiated simultaneously with certified reference material (SRM), which contains known concentrations of elements. After irradiation, the samples under study and SRM are measured under the same conditions and with the same detecting device. The quantitative content of the elements to be determined in the sample under study is calculated by comparing the intensity of the analytical gamma lines of the radionuclides contained in the sample with the intensity of the gamma lines of the corresponding radionuclides in the SRM or control samples.

When the relative method of analysis and testing of the samples and SRM is carried out under identical geometric conditions, there is no need to establish the constancy of the neutron flux density or the exact value of the activation cross-section, uncertainties in the detector efficiency are eliminated. Consequently, the NAA equation for each element is reduced to its simplest form [34].

$$\frac{W_s}{W_{st}} = \frac{I_s}{I_{st}}, \tag{1}$$

where W_s and W_{st} are the content of the element to be determined in the sample under study and in SRM, respectively; I_s and I_{st} are the intensity of the total absorption peak of the analytical gamma radiation line of the radionuclide in the sample under study and in the SRM, respectively.

The VVR-SM nuclear reactor at the Institute of Nuclear Physics of the Academy of Sciences of Uzbekistan, Tashkent, was used to irradiate samples in this research. The VVR-SM is a pool-type research reactor that operates at 10 MW, providing neutron fluxes with energies ranging from 0.1 to 9 MeV and flux densities between $1 \cdot 10^{12}$ and 1.4×10^{14} cm^{-2} s^{-1}.

In this study, only thermal neutron fluxes and radiative capture inducing (n, γ) reactions in the target (samples and SRM) were employed. The influence of epithermal neutrons, which account for around 2% of all neutrons in the reactor, was disregarded.

The effect of self-shielding for elements with a high neutron absorption cross-section and the relevant calculations were addressed in work [35], focusing on neutron activation analysis of rocks. The calculation results from that study allowed the authors to conclude that the effect of self-absorption is minor for small sample portions. As a result, the effect of self-absorption was not considered in our work.

Our study concentrated on delayed gamma quanta emitted by the beta decay of a radioactive isotope produced from target nuclei as a result of neutron capture. The registration of gamma quanta and processing of obtained spectra were carried out using a customized CANBERRA semiconductor gamma spectrometer. This spectrometer comprises the following components: coaxial germanium detector GC2018 (with 20% relative efficiency and resolution of 1.8 keV for gamma line of ^{60}Co at 1332 keV); charge sensitive preamplifier; 16 K channel integrated multichannel analyzer DSA 1000 operating through the Genie 2000 spectroscopy software.

Study area and sample collection

Based on the proposal of archaeologists from the Samarkand Institute of Archaeology (SIA), we studied artifacts from the archaeological monument “Eski Khovos,” located in the present-day Khavast (Uzbek Xovos) district of the Syrdarya region. The monument dates back to the Early Middle Ages (V-VIII centuries AD) and holds historical significance. This is because the current Syrdarya region was traversed by the famous Great Silk Road trade routes, which connected the East with the West in ancient times and the Middle Ages. Various services were provided to trade caravans in villages along this route, including commercial cargo transport, and the exchange of goods, food, and shelter. This led to intensive trade and handcraft production development in these locations [36].

During excavations at the “Eski Khovos” monument, archaeologists discovered traces of ancient metallurgical production. Metallurgical furnace remains were found in one of the premises in excavations № 3 and № 11 and on the territory of the monument in excavation № 15-8. Amorphous porous pieces, outwardly resembling slag, were found and collected among the remains of furnaces from excavations № 11 and № 15-8. These samples, Khov-2/11 from excavation № 11 and Khov-1/15-8 from excavation № 15-8, have been preliminary classified as slag. In excavation № 3, two samples were collected from fragments of clay walls of the furnace—Khov-3/3 and from the furnace wall and furnace bottom of Khov-4/3. In excavation № 11, the furnace walls were crumbling, and samples were collected only from the bottom of the furnace—sample Khov 5/11. Melted clay fragments of furnace walls, common in high-temperature melting furnaces, were not observed.

In excavation № 3, small drops of metallic copper were found next to the remains of the furnace. No ore fragments were observed in the vicinity of the furnaces.

Sample measurements

Before analysis, samples of archaeometallurgical finds collected by archaeologists from the Samarkand Institute of Archaeology underwent proper sample preparation stages. The sample preparation and clean-up procedures consisted of the following steps:

1. The samples were dried in a drying chamber at a temperature of 40 °C.
2. The adhered dirt and various debris were removed using a rigid plastic brush.
3. Dust particles from the pores and cracks of amorphous samples were eliminated by the air blown through a construction dryer.
4. Large pieces were crushed in a steel mortar, and then small pieces were crushed in an agate mortar to a fine powder.
5. The resulting powder was poured onto a polyethylene sheet and thoroughly mixed to obtain a homogeneous representative sample. Each stage of sample grinding

was done in thoroughly cleaned, washed, and dried mortars. After mixing, an aliquot of 70–110 mg was taken from these samples.

After mixing, an aliquot of 70–110 mg was taken from these samples. The samples under study and reference material (SRM) were weighed and placed in bags of 0.2–0.5 mm thick polyethylene film, which were then sealed and wrapped in pure aluminum foil. The prepared samples and SRM were placed in a special aluminum-sealed container for irradiation in the reactor. When determining the manganese content, aliquots weighing 50 mg were taken from the samples under study and placed in plastic bags, sealed, and placed in paper bags.

Concerning the packing materials (polyethylene and aluminum), it should be mentioned that the polyethylene film has almost no impurities that can influence the analysis, and it has a greater radiation resistance, withstanding neutron fluxes of the order of 10^{13} cm^{-2} s^{-1} for 6–7 h [35]. It is worth noting that radiation destruction of the polyethylene film was not observed in our studies. The use of pure aluminum foil as a wrapper may be explained by the fact that pure aluminum consists of the isotope ^{27}Al; when irradiated with thermal neutrons, the beta-active isotope ^{28}Al is generated with a half-life of 2.31 min. This radionuclide almost completely decays within 20–30 min after expose to radiation; therefore, it will not produce interfering gamma lines in the energy spectrum being analyzed. However, even in a pure foil, there may still be other elements that will be activated by thermal neutrons. Therefore, the irradiated samples must be repackaged before measuring (removed from the foil in which they were irradiated).

In the event of simultaneous multi-element NAA, activating a sample of a complex composition would be necessary. The sample under study simultaneously generates numerous different isotopes with various half-lives (from several hours to several or more years). Because of this, the optimal measurement conditions (neutron flux, duration of irradiation, cooling) for one element may not be adequate for other elements of the sample. Thus, when measuring both short-lived and long-lived isotopes in a single sample, 2–3 analytical samples were used, conditionally distributing them into groups of elements with relatively similar half-lives. In this case, the measurement conditions were selected individually for each group.

In this research, samples are divided by half-life into three conditional groups:

1. Short-lived: Mn, K, Na, W, As, Br with half-lives $T_{1/2}$ ~ 2–40 h.
2. Medium-lived: La, Sm, U, Au, Sb, Mo, Re, Yb, Ca, Lu, Nd, Ba with $T_{1/2}$ ~ 40–276 h.
3. Long-lived radionuclides: Rb, Th, Cr, Yb, Ce, Hf, Fe, Sb, Sr, Tb, Sc, Ta, Se, Zn, Ag, Cs, Co, Eu with $T_{1/2}$ ~ more than 400 h.

Samples from these groups simultaneously and together with reference materials (SRM IAEA-SL-1 [37], IAEA SL-3 [38]) were gradually irradiated under the same conditions in the reactor channels.

To reduce the induced activity of radionuclides, irradiated samples were kept in a hot chamber of the reactor (the sample cooling). The stages and the test conditions in the reactor (duration of irradiation and cooling, neutron flux density) are shown in Table 1.

After cooling, the sample container was transported to the institute's radiochemical laboratory, where it was opened. The samples under study and SRM were repackaged in paper bags and sent to the measurement station for gamma spectrometry.

The measuring geometry was selected based on the induced activity of the irradiated samples and the SRM.

In this study, the distance between the sample under study and the detector was chosen to ensure normal loading of the detector (dead time was below 5%). This distance ranged from 1.5 to 10 cm and was the same when measuring irradiated samples and SRM. The measuring time was chosen based on the intensity of the analytical line of the radionuclide under study and ranged from 300 to 900 s. The measuring time of the sample and the SRM were chosen to be the same, ensuring consistency and accuracy in the comparison of results. This careful selection of measurement parameters is crucial

Table 1 Stages and test conditions in the reactor

First stage of testing Short-lived isotopes	Determination of Mn content Irradiation of samples and SRM in the dry channel of the reactor. Neutron flux density $F = 3 \cdot 10^{13}$ cm^{-2} s^{-1}. Irradiation time—30 s. Cooling time—6 h
	Irradiation of samples and SRM in the vertical reactor channel. Neutron flux density $F = 5 \cdot 10^{13}$ cm^{-2} s^{-1}. Irradiation time- 2 h. Cooling time—3 days
Second stage of testing "Medium-lived" isotopes	Irradiation of samples and SRM in the vertical reactor channel. Neutron flux density $F = 7 \cdot 10^{13}$ $cm^{-2} \cdot sec^{-1}$. Irradiation time—2 h. Cooling time—6 days
Third stage of testing Long-lived isotopes	Irradiation of samples and SRM in the vertical reactor channel. Neutron flux density $F = 7 \cdot 10^{13}$ cm^{-2} sec^{-1}. Irradiation time—2 h. Cooling time—20 days

for obtaining reliable data and reducing uncertainties in the analysis.

When processing the gamma radiation spectra of the samples under study and SRM, it is important to consider that the samples and SRM are measured on a gamma spectrometer at different times in practice. This necessitates a temporary modification to formula (1), which takes the following form.

$$W_{s} = W_{st}\frac{I_{s}}{I_{st}} \cdot 2^{(t_{s}-t_{st})/T_{1/2}}, \tag{2}$$

where $T_{1/2}$ is the half-life of the radionuclide under study in the sample and in SRM, t_s and t_{st} are the end of irradiation time and beginning of detector counting time, respectively.

The relevant information on isotope half-lives and analytical gamma line energies was obtained from [39] and [40].

Results and discussion

The results obtained from our analysis of the samples are presented in Table 2, which shows the elemental composition of slag-like samples and fragments of the walls of metallurgical furnaces from the ancient settlement of Khovos.

Table 2 Elemental composition of the archaeological samples under study (n.d. – not defined)

Element	Khov-1/15-8	Khov-2/11	Khov-3/3	Khov-4/3	Khov-5/11
	$W \pm \Delta W$	$W \pm \Delta W$	$W \pm \Delta W$	$W \pm \Delta W$	$W \pm \Delta W$
As	21.5 ± 2.5	11.3 ± 1.4	12.3 ± 1.7	11.6 ± 1.6	9.5 ± 1.4
Au	0.043 ± 0.004	n.d	n.d	0.008 ± 0.002	n.d
Ba	242 ± 29	270 ± 36	863 ± 104	719 ± 72	723 ± 74
Br	1.9 ± 0.7	2.7 ± 0.4	14.8 ± 3.7	12.4 ± 3.1	20.2 ± 4.4
Ca	45,300 ± 5500	56,600 ± 5130	48,200 ± 6800	69,400 ± 7860	63,600 ± 5940
Ce	14.0 ± 1.3	44.0 ± 3.4	61.1 ± 5.6	57.4 ± 5.4	53.1 ± 5.1
Co	15.7 ± 1.8	19.6 ± 1.9	14.9 ± 1.8	11.9 ± 2.5	12.2 ± 1.4
Cr	36.4 ± 3.7	52.0 ± 4.4	63.0 ± 6.2	58.2 ± 6.2	62.0 ± 7.2
Cs	n.d	3.0 ± 0.3	5.0 ± 0.5	5.7 ± 0.5	6.1 ± 0.6
Eu	0.11 ± 0.02	0.59 ± 0.15	0.75 ± 0.19	0.47 ± 0.15	0.86 ± 0.24
Fe	347,000 ± 21,500	123,000 ± 7950	28,900 ± 2380	28,600 ± 2540	27,400 ± 2410
Ga	84.9 ± 6.8	32.1 ± 3.1	10.2 ± 1.0	8.2 ± 0.9	11.6 ± 1.2
Hf	0.60 ± 0.07	3.75 ± 0.48	3.85 ± 0.46	4.55 ± 0.58	3.65 ± 0.47
K	12.2 ± 1.3	25.7 ± 2.4	n.d	39.7 ± 3.5	12.2 ± 1.3
La	8.0 ± 0.7	21.9 ± 2.0	28.0 ± 2.0	27.1 ± 2.0	26.5 ± 1.9
Lu	0.09 ± 0.01	0.33 ± 0.03	0.50 ± 0.05	0.46 ± 0.05	0.47 ± 0.05
Mn	0.44 ± 0.02	0.60 ± 0.03	n.d	0.75 ± 0.04	0.74 ± 0.04
Mo	52.2 ± 4.9	22.4 ± 2.7	20.6 ± 2.6	4.3 ± 0.7	21.5 ± 2.6
Na	5300 ± 302	7890 ± 456	12,400 ± 709	6980 ± 398	8400 ± 479
Nd	n.d	n.d	26.6 ± 4.0	31.0 ± 4.4	n.d
Rb	n.d	58.8 ± 8.8	75.6 ± 9.4	76.5 ± 9.6	76.2 ± 10.4
Re	n.d	0.15 ± 0.02	0.18 ± 0.02	0.16 ± 0.02	0.20 ± 0.02
Sb	1.2 ± 0.1	1.8 ± 0.2	2.0 ± 0.2	1.9 ± 0.2	1.9 ± 0.2
Sc	2.5 ± 0.2	9.2 ± 0.5	10.6 ± 0.6	9.8 ± 0.5	9.6 ± 0.3
Sm	1.3 ± 0.1	3.5 ± 0.2	4.7 ± 0.2	4.3 ± 0.2	4.1 ± 0.2
Sn	695 ± 58	1280 ± 101	1610 ± 111	1630 ± 112	1700 ± 123
Sr	3670 ± 585	3740 ± 531	2090 ± 360	4790 ± 546	4410 ± 533
Ta	n.d	0.28 ± 0.04	0.48 ± 0.10	0.44 ± 0.08	0.40 ± 0.12
Tb	n.d	0.40 ± 0.08	0.40 ± 0.08	0.41 ± 0.07	0.41 ± 0.07
Th	1.7 ± 0.2	4.7 ± 0.4	8.8 ± 0.8	7.5 ± 0.6	7.7 ± 0.7
U	1.4 ± 0.3	2.0 ± 0.4	2.3 ± 0.4	2.3 ± 0.4	1.8 ± 0.4
W	6.2 ± 0.8	40.5 ± 2.6	n.d	n.d	n.d
Yb	0.58 ± 0.16	1.67 ± 0.29	1.93 ± 0.38	1.82 ± 0.31	1.86 ± 0.28
Zn	n.d	n.d	68.0 ± 4.8	101.0 ± 17.6	59.0 ± 4.4

W and ΔW are given in ppm

As mentioned earlier, samples Khov-2/11 from excavation № 11 and Khov-1/15-8 from excavation № 15-8, were preliminary classified as slag. In excavation № 3, samples were collected from fragments of clay walls of the furnace—Khov-3/3 and from the furnace wall and furnace bottom of Khov-4/3. The sample Khov-5/11 consists of fragments of clay walls of the furnace crumbled to the bottom of the furnace from excavation № 3.

Our analysis of these samples revealed the presence of up to 34 different the following chemical elements—As, Au, Ba, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Ga, Hf, K, La, Lu, Mn, Mo, Na, Nd, Rb, Re, Sb, Sc, Sm, Sn, Sr, Ta, Tb, Th, U, W, Yb, Zn. This comprehensive elemental profile provides valuable insights into the materials used and the metallurgical processes that took place in the ancient settlement of Khovos.

The analysis of the slag-like samples Khov-1/15-8 and Khov-2/11 revealed that iron (Fe) had the highest concentration, with 347,000 and 123,000 ppm, respectively. Furthermore, the relative iron concentrations among the other analyzed elements were 86% for (Khov-1/15-8) and 64% Khov-2/11, as shown in Table 3. In addition, our analysis identified high calcium concentrations, ranging from 48,200 to 69,400 ppm, in the samples Khov-3/3 and Khov-4/3 which were collected from the furnace walls and furnace bottom.

There is a noticeable difference in the relative calcium concentrations between the clay samples and slag-like samples. As can be seen in Table 3, the relative calcium concentration in samples of clay (furnace walls) is significantly higher at 51–62%, compared to the slag-like samples which have concentrations of 11% and 29%. This difference in calcium concentrations could provide important information about the materials and processes used in the ancient settlement of Khovos, as well as the role of calcium in the metallurgical operations that took place during that time.

Throughout this study, we frequently use the term “slag-like sample” due to our initial uncertainty about whether the archaeometallurgy samples we received from archaeologists were indeed slag-rich bloom fragments or remnants of smelting or smithing furnaces that had been buried for centuries. At the beginning of our research, only fragments of furnace clay walls were identified. It is important to emphasize that the iron concentrations in both Khov-1/15-8 and Khov-2/11 samples are relatively high (34.7% and 12.3%, respectively). The presence of high iron concentrations in these samples raised a questions about whether such iron concentrations in slags are possible or if they could indicate iron blooms.

Table 3 Relative concentration of chemical elements in the samples under study

Element	Khov-1/15–8	Khov-2/11	Khov-3/3	Khov-4/3	Khov-5/11
Ba	0.1%	0.1%	0.9%	0.6%	0.7%
Ca	11%	29%	51%	62%	60%
Fe	86%	64%	31%	25%	26%
Sn	0.2%	0.7%	1.7%	1.4%	1.6%
Sr	0.9%	1.9%	2.2%	4.3%	4.1%

To address these concerns, we referred to the iron concentrations of various slags previously examined by others [41]. In this work, a large number of different metallurgical slags have been studied using polarization energy dispersive X-ray spectrometry (P)EDXRF and scanning electron microscopy EDS-SEM. The results of the analysis performed in [41] demonstrated that the concentration of chemical elements in ancient metallurgical slags can vary widely–Al (1.16–6.67%), Ba (up to 2.21%), Ca (0.14–5.86%), Cr (0.0052–0.0361%), Cu (0.00004–1.6%), Fe (3.26–49.51%), K (up to 0.75%), Mg (up to 1.57%), Mn (0.0775–30.67%), Na (0.1484–1.9289%), S (0.1–3.3%), Si (7.1–15.84%), Sr (0.0007–0.3816%), Ti (0.06–0.4197%), V (0.0145–0.116%), and Zn (0.0055–1.981%).

Table 4 compares the concentration of chemical elements found in the samples we studied from Eski Khovos and in some slags from Cyprus [41].

A comparison of the quantitative iron concentration in our samples and the identified slag samples from [41] shows that our results for iron concentration are comparable to those of [41]. Additionally, the data from [41] demonstrate that the iron concentration in slags might even be higher, reaching 50%. This allows us to claim that at the settlement Eski Khovos slag fragments were found, which can be identified as blacksmithing slag that generates during the bloom's forging process.

During sampling, the AMT06 sample [41] was initially found to be furnace slag.

However, subsequent analysis revealed that AMT06 is actually a weathered iron mineral with quartz and a minor quantity of copper (Fe—32.96%, Cu—1.6%). Archaeologists should take into account the possibility of such errors when analyzing the elemental composition of archaeometallurgical findings before drawing conclusions about their nature.

Iron and copper deposits, as well as ore fragments, were not discovered in the vicinity of the furnaces or the reachable area around the settlement Eski Khovos. Because transporting ore to settlements is complicated and inefficient, the ore is typically melted near ore deposits. Bloom, a finished product, is received by ancient metallurgists at ore smelting sites if blacksmithing workshops were not organized in those locations. Therefore, the furnaces found at the settlement Eski Khovos should be classified as smithing furnaces, where metal ingots and various metal products made of iron, bronze, and copper were processed and prepared for sale.

It should be emphasized that while crushing the samples, we found no discernible fractions of metallic iron in the slag,

Table 4 Comparison of the average content of some chemical elements in slag samples from "Eski Khovos" and from Cyprus [41]

Element	Khov 1/15–8	Khov 2/11	AMT04 [41] TS	AMT05 [41] TS	AMT09 [41] FS	AMT10 [41] FS	AMT06 [41] FC
Ba	242	270	506	22,086	3720	5532	
Ca	45,300	56,600	30,017	43,597	15,723	32,162	1429
Cr	36.4	52.0	129	310	291	250	63
Cu			6000	6000	7000	5000	16,000
Fe	347,000	123,000	327,243	92,499	92,499	94,831	329,575
K	12.2	25.7	2490	2490	2490	2490	830
Mn	0.44	0.60	30,206	253,262	306,702	257,909	4647
Na	5300	7890	5935	5193	3710	5193	1484
Sr	3670	3740	165	3816	624	572	

TS tap slag, *FS* furnace slag, *FC* Fe + Cu mineral

The content of elements is given in ppm

which should have been expected in the bloom. We also tested the reaction of samples to a powerful magnet. Since they include fractions of reduced iron, the bloom must react to the magnet to some extent. However, there was almost no reaction.

The elemental composition of clay fragments of furnace walls collected from the bottom of the furnaces (Khov-4/3 and Khov-5/11) and extracted from the walls (Khov-3/3) slightly differs. The only noticeable differences are a high concentration of calcium (69,400 ppm and 63,600 ppm vs. 48,200 ppm) and strontium (4790 ppm and 4410 ppm vs. 2090 ppm) in the samples obtained from the bottom of the furnaces, a lower concentration of sodium (6980 ppm and 8400 ppm vs. 12,400 ppm). All three furnaces were located within the same settlement and were used by blacksmiths to produce metal and products. Assuming that the blacksmiths utilized the same metal processing methods and conditions, the variation can be attributed to a variable level of influence of natural factors on the bottom of the furnaces and their walls, as the remnants of the furnaces have been exposed to the environmental conditions for centuries (precipitation, etc.).

Our research results indicate that neutron activation analysis using thermal neutrons can be employed to assess the quantitative elemental composition of archaeometallurgy products and clarify their identification. This is the strongest point of the NAA, underlining the significance and applicability of the NNA in archaeological research.

On the other hand, it is also essential to point out its shortcomings. Because placing detecting equipment in reactor channels to record instantaneous gamma quanta is difficult (special equipment, radiation protection, etc.), NAA at nuclear reactors is often conducted through delayed gamma quanta outside the reactor. This necessitates the exposure of activated samples to minimize induced radioactivity. The exposure time can range from 20 to 30 days, meaning a long process that may not always be suitable for archaeologists performing many analyses on various samples. In addition, the detection of aluminum in samples, which is frequently found in many archaeometallurgical products and is almost entirely composed of the stable isotope ^{27}Al, is another issue when using delayed gamma quanta. Thermal neutrons are used to irradiate aluminum, producing the beta-active isotope ^{28}Al, which has a half-life of 2.31 min. This radionuclide almost completely decays 20–30 min after the termination of irradiation, making it impossible to detect its characteristic gamma lines after a brief exposure.

The composition of metallurgical slags highly depends not only on the ore used but also on the ingredients used in metal smelting. These include the coals and fluxes that are utilized, the elements of which inevitably fall into the slag. The composition of the slag can be affected by diffusion processes that occur when the melting charge and slag make contact with the furnace walls and bottom. Ancient metallurgy products that have remained in the ground for hundreds of years have been affected by precipitation, oxidation processes, diffusion of chemical elements from and into the soil, etc. Therefore, fragments of the same product remaining in the ground at different periods, in other places, and under various environmental conditions may differ in chemical composition. To clarify the identification of unknown samples, a comparison with the results of similar works should be performed. The results of our study revealed that a comparison with the results of previous research [41] allowed us to validate archaeologists' opinions on the discovery of blacksmithing slag at the Eski Khovos settlement.

Conclusion

Studies of ancient metallurgy and archaeological slags have attracted considerable attention in the literature due to their relevance in understanding the technical methods used by ancient metalworkers. Our research demonstrated that neutron activation analysis can be effectively utilized to study archaeometallurgical artifacts. Moreover, our results also indicated that blacksmithing slags were discovered at the Eski Khovos settlement. This supported the archaeologists' opinion about the blacksmithing nature of metallurgical production in this settlement.

The limitations of neutron activation analysis at a nuclear reactor employing thermal neutrons to activate the samples under study and delayed gamma quanta of the characteristic spectrum of activated samples for quantitative elemental analysis, were discussed. However, these drawbacks do not pose significant obstacles to the quantitative analysis of archaeological materials.

The interest shown by the archaeologists of the Samarkand Institute of Archaeology and Samarkand State University in our research underscores the potential for future collaboration. Our partnership with the Institute of Nuclear Physics of the Academy of Sciences of Uzbekistan aims to obtain new and valuable information about the archaeological artifacts of Uzbekistan. Specifically, we plan to expand our investigations to include additional metallurgical sites throughout the region, analyze a broader range of artifacts, and integrate advanced analytical techniques, such as isotopic analysis, to better understand the provenance and production methods employed in ancient Uzbek metallurgy. This comprehensive approach will contribute to a more detailed understanding of the region's archaeological and metallurgical history.

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Declarations

Conflict of interest The authors declare that there are no conflicts of interest to disclose.

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