Meteoritic iron artefacts redux

Opět o artefaktech z meteoritického železa

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The earliest iron artefacts are often presented as products made of meteoritic iron, which is characterised by its high iron content. However, recent studies have shown that high nickel and iron content cannot be taken as a firm criterion for establishing its meteoritic origin. The most effective tool for helping to specify the elemental composition in such cases is a metallographic analysis. It turns out that the material of many artefacts regarded as having been forged from meteoritic iron could in fact be bloomery iron. An analysis of ample yet scattered evidence suggests that the production of items from meteoritic iron could in fact be irregular and sporadic.

meteoritic iron – nickel – bloomery iron – archaeometallurgy – prehistory – Early Middle Ages

Nejstarší železné artefakty jsou namnoze prezentovány jako výrobky z meteoritického železa, jehož typickým rysem je vysoký obsah niklu. Nedávné studie však ukázaly, že vysoké obsahy niklu v železe nelze brát jako pevné kritérium pro stanovení jeho meteoritického původu. Nejúčinnějším nástrojem, který v takových případech pomáhá zpřesnit interpretaci prvkového složení, je metalografická analýza. Ukazuje se, že materiál mnoha předmětů, které jsou považovány za výkovky z meteoritického železa, může být ve skutečnosti železem svářkovým. Analýza četné, byť porůznu rozptýlené evidence nasvědčuje tomu, že výroba předmětů z meteoritického železa mohla být ve skutečnosti prostorově nerovnoměrná a sporadická.

meteoritické železo – nikl – svářkové železo – archeometalurgie – pravěk – raný středověk

1. Introduction

The issue of meteoritic iron occupies a special place in the history of the development of ferrous metallurgy due to the fact that the use of meteoritic iron in the earliest times remains rather controversial. Some aspects of the debate on this issue, such as a selection of criteria for identifying artefacts made from meteoritic iron and the role of this sort of iron in the advent and development of iron metallurgy, appear to be fundamental and as such worthy of comments and remarks. An article was recently published by the authors to shed more light on this issue (*Zavyalov – Terekhova 2016*), but new investigations and the ambiguity of interpretation of both new and old results indicate that the problem is yet far from a positive solution.

For a long time, early finds made from ferrous metal (3000–2000 BC) were considered to have been made from meteoritic iron simply because of their age. With the advent of chemical element analyses on archaeological objects, a body of objective data emerged to address this issue. It is widely accepted that a high level of nickel in iron is the signature of meteoritic iron. Most scholars tend to believe that the level of nickel in meteoritic iron exceeds 5 % (*Buchwald 1977*; *Photos 1989*). For example, this is clearly demonstrated in the nickel distribution histogram by *V. Buchwald* (*2005*, 23, fig. 11). *Ü. Yalçin* (*1999*) believes that iron with a nickel concentration less than 5 % cannot be considered of meteoritic origin without additional (metallographic) analyses. Some specialists also take the view that a level of nickel of 3–5 % cannot be used as evidence of unquestionable meteoritic origin, because it may simply suggest the use of rare types of nickel-rich ores (*Blomgren 1980*; *Bronson 1987*).[1] Besides nickel, other elements such as cobalt, copper, phosphorus or carbon also appear in iron meteorites. These do not exceed 2 % in total and cobalt mostly falls into the 0.3–0.6 % range (*Photos 1989*).

In recent years, *A. Jambon* has summarized published data on the chemical composition of several iron items dated from the Late Bronze Age and Early Iron Age, and also a number of artefacts he examined himself. *Jambon* (*2017a*; *2017b*) rightly notes the importance of metallography for the unambiguous distinction between items made from terrestrial and extraterrestrial (meteoritic) iron. However, since the earliest iron artefacts are both very scarce (and hence valuable) and preserved in poor condition, their metallographic examination is, in most cases, simply impossible. Being aware of the importance of Ni and Co for tracing the origin of iron (meteoritic vs terrestrial), Jambon proposes basing conclusions on the correlation between Ni/Fe and Ni/Co ratios. He has conducted comparative analyses of the Ni/Fe and Ni/Co ratios obtained for both artefacts and real meteorite specimens. When obtained results are plotted on a chart, Jambon believes that mutual overlaps may serve as good evidence that studied artefacts are made of meteoritic iron. The proposed methodology leads the author to the conclusion that "(most or) all irons from the Bronze Age are derived from meteoritic iron, until some transition period, which occurred supposedly close to about 1200 BC" (*Jambon 2017a*, 52).

Although the proposed approach appears to be very promising, its reliability should not be overstated. We can provide a few examples showing that it can also produce dubious results. The weakness of Jambon's approach is the omission of metallurgical principles that can play a significant role when assessing concentrations of elements such as Ni and Co. There is abundant evidence that nickel and cobalt can appear in highly elevated levels in welding seams (see, e.g., *Hošek 2003*, 207–214; *2005*; *Gurin 1987*). Welding seams are enriched by elements such as Ni, Co, As and Cu due to oxidation enrichment, which takes place in the subscale layer of iron pieces (to be subsequently welded to each other) when heated in a hearth (for more details see, e.g., *Tylecote 1990*; *Melford 1962*). Naturally, for the subscale oxidation enrichment, these elements must be present in the metal base as residual elements. It is important to know that subscale enrichment strongly depends on scaling conditions and that the resulting chemical element composition of welds is also affected by consequent heating cycles in the course of forging (*Košta – Hošek 2014*, 285; *Hošek – Merta – Malý 2004*). The highest enrichment is observed in affected surface layers and subsequently in 'fresh' welds (e.g. *Hošek 2000*, 94). The gradual decreases of such local enrichments are the result of diffusion processes occurring during repeated heating and forging (*Hošek – Merta – Malý 2004*).

Welding seams enriched in nickel are metallographically recognized as white or pale lines (due to their nickel content, they are more resistant to etching). Because such white or pale lines are observed in virtually (or nearly) all iron artefacts made by welding, the subscale oxidation enrichment is indeed a common phenomenon. Maximum nickel content

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[1] Based on the data provided in H. H. Coghlan's paper, there are meteorites with a level of nickel in the range of 2.5–4.5 % (*Coghlan 1956*, 36–37). It should be noted that the data provided by Coghlan refer to the analyses conducted in the early 20th century; therefore, it is difficult to judge to what extent the methods used were accurate and to what extent the drawn conclusions were consistent.

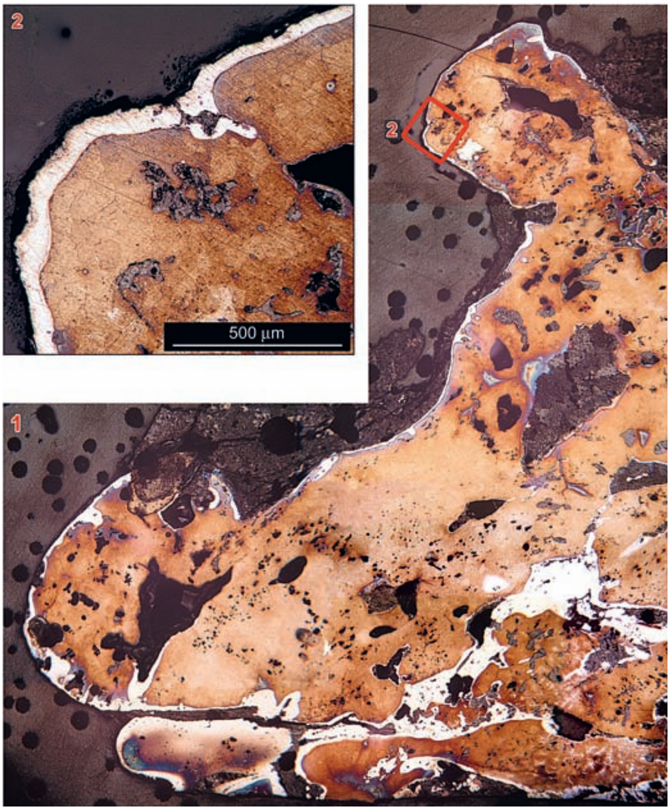

Fig. 1. An example of surface subscale enrichment; part of a bloom from experimental smelting with an arsenic-rich surface layer (white); etched with Oberhoffer's reagent. Photo J. Hošek.
Obr. 1. Příklad obohacení povrchu kovu pod vrstvičkou okují; část železné houby z experimentální tavby s povrchovou vrstvou bohatou na arsen (bílá); leptáno Oberhofferovým činidlem.

in welds does not exceed the level of 3 % in the vast majority of iron objects. However, enrichment in the range of 4–10 % is not exceptional and a maximum nickel content reaching tens of percentage points is occasionally encountered as well (see, e.g., *Hošek 2005*).

This demonstrates that the determination of the chemical composition *per se* cannot be used as unambiguous evidence in support of the meteoritic origin of artefacts. In this respect, the most efficient approach is a combination of chemical element analysis and metallographic examination (when the item studied is preserved in good condition). Hence, the question is whether the origin of all iron artefacts with an elevated nickel content, which are said to be made of meteoritic iron, can be positively determined and whether all such items can be used as support for claiming that the handling of meteoritic iron by early metalworkers led to the discovery of iron metallurgy.

2. Iron artefacts with an elevated nickel content

Fe/Ni and Ni/Co ratios seem to be a significant clue for determining the meteoritic origin of iron objects. Therefore, it is necessary to investigate how the ratios featuring fresh meteorites differ, if at all, from those featuring enriched surface layers and welding lines. A few examples of an elevated nickel and cobalt content encountered in welds are listed in *table 1*.

Artefact no.	Artefact (ID)	Site	Dating	Ni	Co	Cu	As	Reference
1	spearhead (44/96)	Turnov district	medieval	4.1 – 9.0	–	–	–	*Hošek 2003a*, 213, tab. 26: 1; *Hošek 2001*
2	iron fitting	castle of Trosky	medieval or post medieval	10.3	–	–	–	*Hošek 2003a*, 213, tab. 26: 2
				7.6	1.1	–	–	
				28.5	2.9	2.5	5.6	
3	iron fragment	Příšovice	14th–15th c.	7.7	1.6	1.8	–	*Hošek 2003a*, 213, tab. 26: 3
				3.1	1.6	–	–	
4	knife (vz.749)	Stará Boleslav	9th/10th–11th c.	1.2 – 10.7	0.8 – 2.3	–	–	*Hošek 2003b*
				1.2 – 10.5	0 – 2.6	–	–	
5	fragment of a bridle	Praha	15th–16th c.	19.5	–	–	–	*Bouzková – Vojtěch – Starec 2001*
6	auger (166.826)	Břeclav–Pohansko	9th–10th c.	19.2	1.2	–	–	*Hošek 2003a*, 213, tab. 26: 9
				4.8	1.2	–	–	
				2.9	0.7	–	–	
7	axe (159.578)	Břeclav–Pohansko	9th–10th c.	11.3	*	–	–	*Hošek 2003a*, 213, tab. 26: 10
				3.7	*	–	–	
8	auger (vz.149)	Nejdek	9th–10th c.	0.5 – 4.3	*	–	–	*Hošek 2003a*, 213, tab. 26: 11
				0.4 – 2.3	*	–	–	
9	axe (vz.140)	Ivanovice na Hané	9th–10th c.	6.1 – 14.2	*	–	–	*Hošek 2003a*, 213, tab. 26: 12
				5.1 – 9.2	*	–	–	
10	sword (H1–55091)	Kolín	9th c.	4.2	*	–	–	*Košta – Hošek 2008*
				2.6	*	–	–	

Tab. 1. Chemical element composition (by SEM-EDX) of nickel-rich welding seams (max. Ni content at least 4 wt%), observed in some of medieval iron artefacts from the Czech Republic. * Cobalt content was under detection limit of the SEM-EDX and/or the result was considered unreliable.

Tab. 1. Prvkové složení (stanovené pomocí SEM-EDX) svarů bohatých niklem (max. obsah niklu alespoň 4 hm. %), které byly pozorovány v některých středověkých železných artefaktech z ČR. * Obsah kobaltu byl pod detekčním limitem SEM-EDX nebo byl výsledek považován za nespolehlivý.

Weld	Element	Analysed spot												
		1	2	3	4	5	6	7	8	9	10	11	12	13
A	**Ni**	0	0	0	0	2.7	6.9	10.3	10.7	9.4	3.7	1.2	0	0
	Co	0	0.8	0	0.9	0.8	1.6	2.4	2.3	1.6	1.2	0.8	0	0
B	**Ni**	0	0	2.1	5.9	7.3	10.5	7.9	7.1	4.4	1.8	3.5	1.7	1.2
	Co	0	0	1.1	1.7	2.1	2	2.6	2.2	0	1.2	1.4	0	0

Tab. 2. Nickel and cobalt content measured across welding seams A and B in the knife (sample) 749 from Stará Boleslav, Czech Republic (according to *Hošek 2003b*).

Tab. 2. Obsah niklu a kobaltu měřený napříč svary A a B v noži vz. 749 z raně středověké Staré Boleslavi (podle *Hošek 2003b*).

It is important to remark that neither nickel nor cobalt content is uniform across the width of common (i.e. relatively narrow) welding lines. The highest contents are seen in their middle; towards their borders, the contents decrease (see *table 2*, for example). Moreover, the Co/Ni ratios are not entirely consistent over the entire width of welding lines and they also fluctuate over their length (*fig. 2b*). Therefore, more measurements should always be taken to obtain representative results. On the other hand, long-term exposure to certain scaling conditions can result in wider surface-enriched layers with a more or less uniform

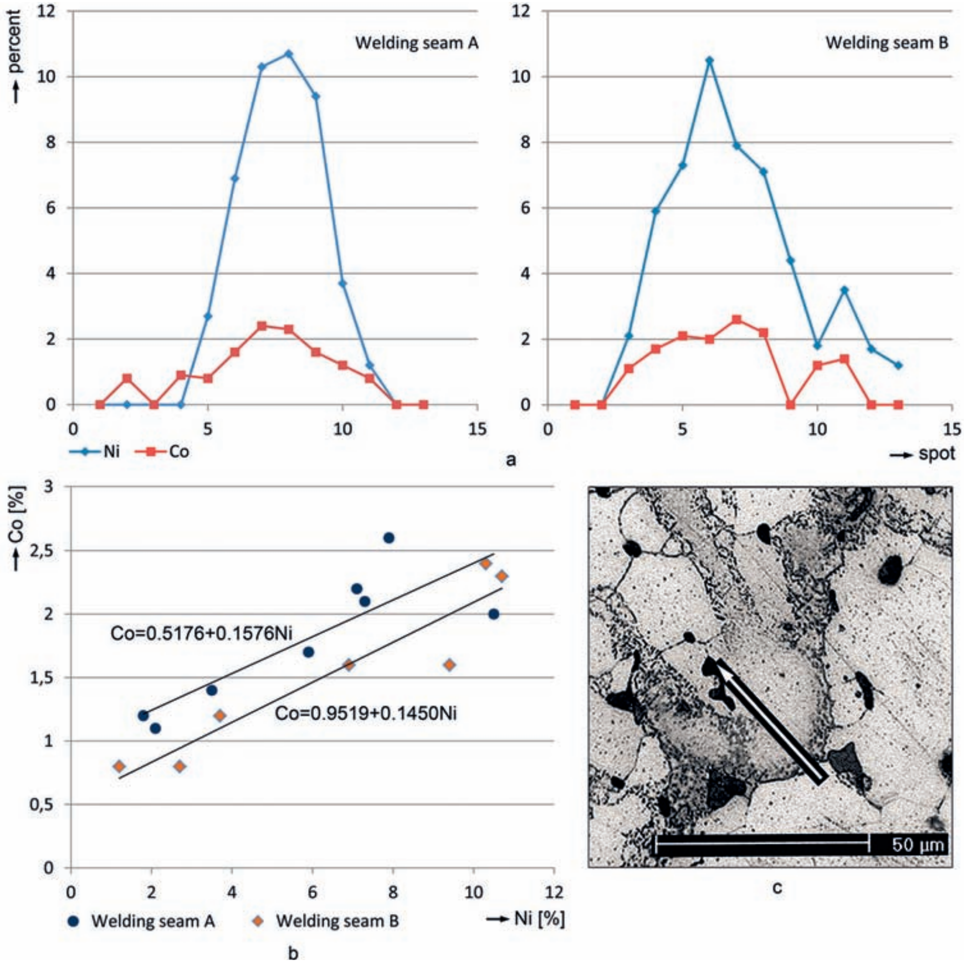

Fig. 2. The element composition of welds (A and B) of early medieval knife no. 749 from Stará Boleslav, Czech Republic (see *table 2* for data); a – distribution of Ni and Co across the welds; b – Co vs Ni with added linear trend lines; c – microphotograph of the welding seam B.
Obr. 2. Prvkové složení svarů (A a B) v noži vz. 749 ze Staré Boleslavi (data převzata z *tab. 2*); a – distribuce Ni a Co napříč analyzovanými svary; b – Co vs. Ni s přidanými lineárními spojnicemi trendu; c – mikrofotografie svarového švu B.

composition; after forge-welding, such layers can form larger nickel-rich areas inside artefacts (*Dostál 2010*, 28–32).

In any case, data from *table 1* plotted on the Ni/Fe-vs-Ni/Co chart show that the majority of welding lines (in which a cobalt content was determined) contain a relatively high amount of cobalt, and therefore they fall out of the area typical for iron meteorites (see *fig. 3a*). There are also several welds whose cobalt content was either zero or under the limit of (reliable) detection (by SEM-EDX; see *table 1*, artefact nos. 7–9). These welding lines can hypothetically contain up to roughly 1 % of cobalt. In such case, they can overlap the values typical for meteoritic iron (*fig. 3b*). A well-determined composition of

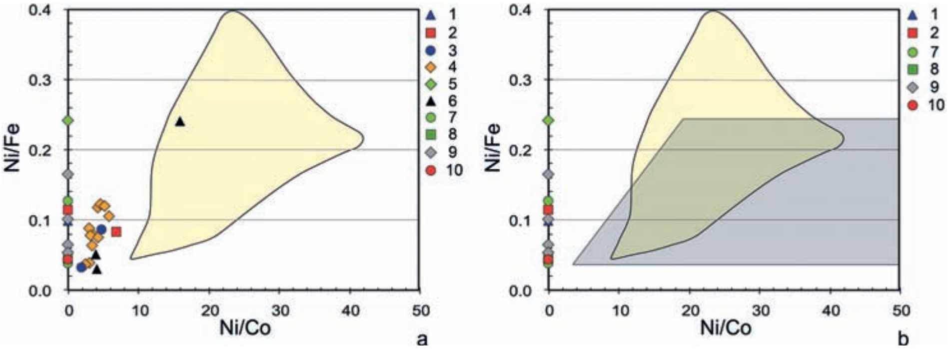

Fig. 3. Ni/Fe vs Ni/Co in welding seams; data were taken from *table 1*. The yellowish area was delimitated by A. Jambon by plotting Ni/Fe and Ni/Co ratios of fresh iron meteorites (for details see *Jambon 2017a*): a – compositions of virtually all welds are displaced to lower Ni/Co ratios; b – the grey area corresponds to possible plotting if the undetermined cobalt content would be within the range of 0 to 1 %.
Obr. 3. Ni/Fe vs. Ni/Co ve svarových švech; data byla převzata z *tabulky 1*. Nažloutlá oblast byla vymezena A. Jambonem vynesením poměrů Ni/Fe a Ni/Co neopracovaných meteoritů železa (pro podrobnosti viz *Jambon 2017a*): a – složení prakticky všech svarů je posunuto směrem k nižším poměrům Ni/Co; b – šedá plocha odpovídá možnému zanesení do grafu, pokud by obsah neurčeného kobaltu ležel v mezích 0 až 1 %.

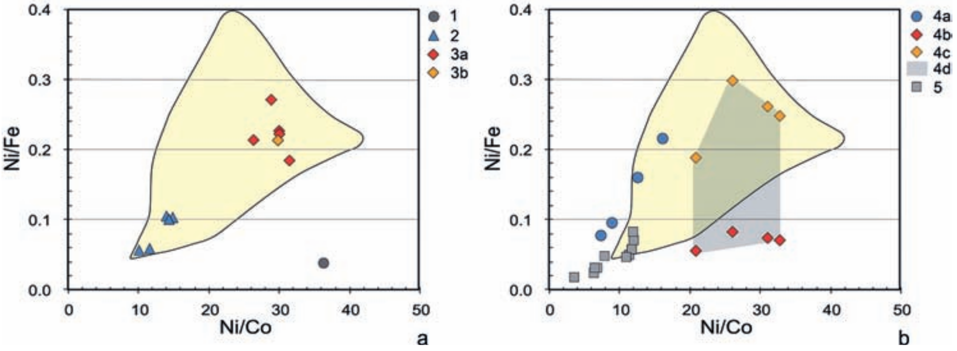

Fig. 4. Ni/Fe vs Ni/Co for the iron objects discussed: 1 – Bichkin-Buluk (data from *Shramko – Fomin – Solncev 1965*); 2 – Boldyrevo I (data from *tab. 3*); 3 – Częstochowa-Raków (a – data from *Jambon 2017b*; b – data from *Piaskowski 1982*); 4 – Wietrzno-Bóbrka (a – data for the nickel-rich layers from *Piaskowski – Bryniarska 1978*; b – data from *Jambon 2017b*, c – re-calculated Jambon's data for the nickel-rich layers – when expected that the nickel-rich metal covers max. 30 % of the sample; d – area in which data for the nickel-rich layers can be expected); 5 – Ugarit (data from *Jambon 2017b*).
Obr. 4. Ni/Fe vs. Ni/Co u sledovaných železných předmětů: 1 – Bičkin-Buluk (data viz *Shramko – Fomin – Solncev 1965*); 2 – Boldyrevo I (data viz *tab. 3*); 3 – Częstochowa-Raków (a – data viz *Jambon 2017b*, b – data viz *Piaskowski 1982*); 4 – Wietrzno-Bóbrka (a – data pro vrstvy bohaté na nikl viz *Piaskowski – Bryniarska 1978*, b – data viz *Jambon* (*2017b*), c – přepočítaná Jambonova data pro vrstvy bohaté na nikl (za předpokladu, že kov bohatý na nikl pokrývá max. 30 % vzorku), d – oblast, ve které lze očekávat vynesení dat pro vrstvy bohaté niklem); 5 – Ugarit (data viz *Jambon 2017b*).

nickel-rich welding seams can therefore be used to identify smelted iron, though probably not in all cases. The Ni/Co ratio can also (hypothetically) fall into the range featuring iron meteorites. In addition, nickel and cobalt surface enrichment also takes place in meteoritic iron when heated (e.g. *Socha – Suliga – Krawczyk 2014*), therefore, the mere presence of nickel-rich welding lines should not be regarded as evidence of terrestrial origin.

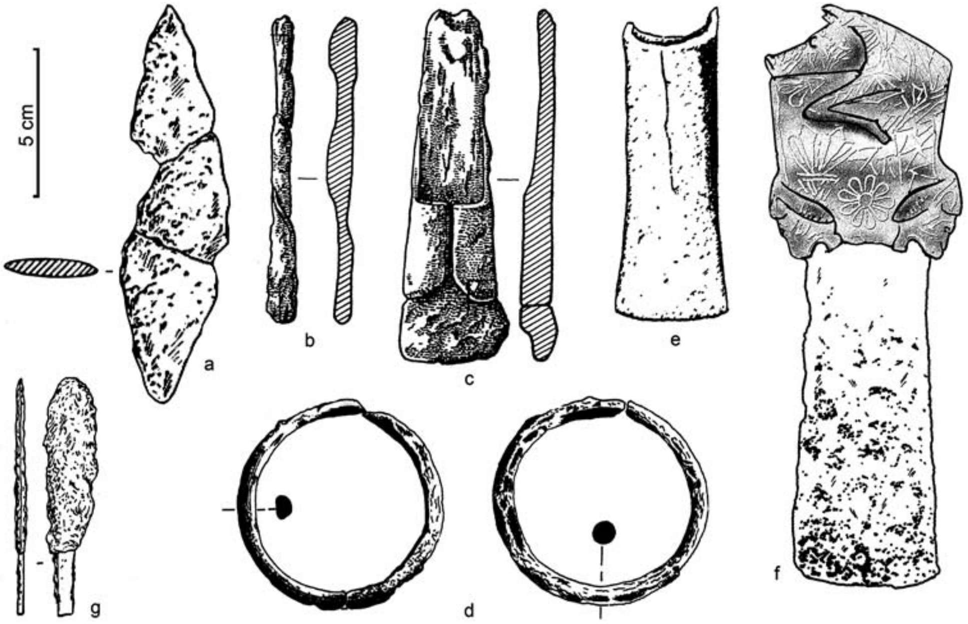

Fig. 5. Iron artefacts discussed in this paper: a – spearhead from Bichkin-Buluk (after *Pleiner 2000*, 26); b – adze-shaped tool from Boldyrevo I; c – chisel-type tool from Boldyrevo I; d – bracelets from Częstochowa-Raków (after *Kotowiecki 2004*); e – axe from Wietrzno-Bóbrka (after *Kotowiecki 2004*); f – axe from Ugarit; g – knife from Gerasimovka (after *Shramko – Mashkarov 1992*).
Obr. 5. Železné artefakty diskutované v tomto článku: a – hrot oštěpu z Bičkin-Buluk (podle *Pleiner 2000*, 26); b – teslicovitě tvarovaný nástroj z Boldyreva I; c – dlátovitý nástroj z Boldyreva I; d – náramky z Częstochowa-Raków (podle *Kotowiecki 2004*); e – sekerka z Wietrzno-Bóbrka (podle *Kotowiecki 2004*); f – sekera z Ugaritu; g – nůž z Gerasimovky (podle *Shramko – Mashkarov 1992*).

From the information provided above, it follows that (1) the chemical element composition determined from a limited volume of an artefact can be affected by the presence of nickel-and-cobalt-rich welding lines, and that (2) the surface of iron object, when heated, can hypothetically be enriched in nickel and cobalt in such a way and extent that the reliable distinction from meteoritic iron might have been difficult. Moreover, the subscale oxidation enrichment can obviously have a negative effect on the proper assessment of hot-forged artefacts made of real meteoritic iron.

3. Is high-nickel iron necessarily meteoritic?

There are several early iron artefacts in which a high nickel content was documented. While some of them are undoubtedly made of meteoritic iron, the origin of metal used for some others is rather unclear (though also in general considered to be meteoritic). The problem is that sometimes we rely on outdated analytical results, and even new examinations or re-examinations are sometimes not carried out in sufficient detail.

Let’s have a look at three items from Eastern Europe considered to be made of meteoritic iron that *A. Jambon* (*2017a*) did not include in his study.

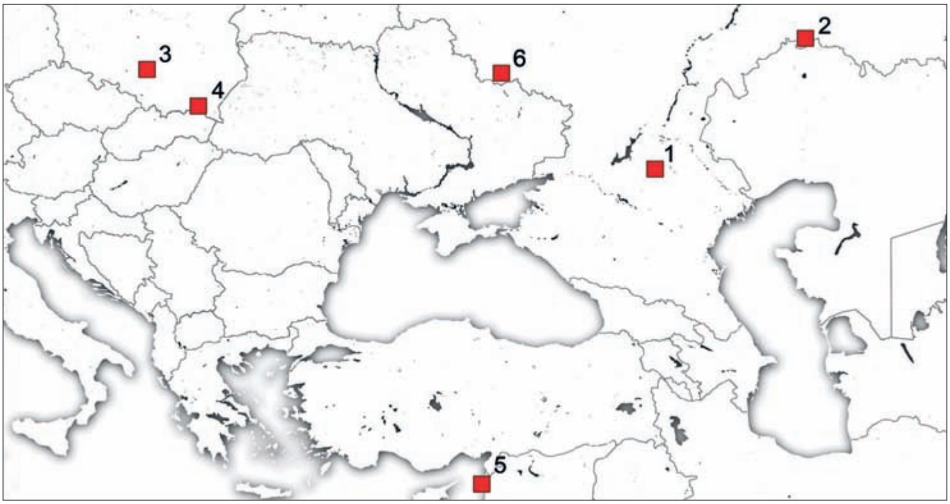

Fig. 6. Locations of the sites: 1 – Bichkin-Buluk (Russia); 2 – Boldyrevo I (Russia); 3 – Częstochowa-Raków (Poland); 4 – Wietrzno-Bóbrka (Poland); 5 – Ugarit (Syria); 6 – Gerasimovka (Russia).
Obr. 6. Polohy lokalit: 1 – Bičkin-Buluk (Rusko); 2 – Boldyrevo I (Rusko); 3 – Częstochowa-Raków (Polsko); 4 – Wietrzno-Bóbrka (Polsko); 5 – Ugarit (Sýrie); 6 – Gerasimovka (Rusko).

The first find interpreted as an artefact made from meteoritic iron was discovered in Eastern Europe more than 80 years ago. The object comes from the Bichkin-Buluk area (*fig. 6: 1*) near the city of Elista (Kalmykia) and was found in barrow no. 6. It is a leaf-shaped spearhead (*fig. 5a*) dated from the end of the 2nd to the beginning of the 1st millennium BC (*Sinitsyn 1948*). Due to its poor state of preservation, a metallographic examination could not be conducted. The conclusion on the meteoritic origin was made on the basis of chemical element analyses showing the presence of nickel (3.65 %) and cobalt (0.1 %) as well as small concentrations of elements such as silicon, manganese, vanadium, magnesium, calcium, germanium, and copper (*Shramko – Fomin – Solncev 1965*). However, the published values for nickel and cobalt cannot be taken as firm evidence for the extra-terrestrial origin of the metal. In addition, the Ni/Fe and Ni/Co values are clearly inconsistent with Jambon's data obtained for pieces of meteoritic iron affected by 'weathering' (*Jambon 2017a*).

A classic model of comprehensive research into the earliest iron finds (metallography and the determination of chemical element composition) can be introduced on iron finds from Boldyrevo. The artefacts were found in a barrow dated by radiocarbon dating to 2872–2476 BC and located near the village of Boldyrevo I in the Orenburg Region (*fig. 6: 2*), which is the largest excavated burial site of that time in the Urals region (*Morgunova 2014*). The excavations revealed a rich burial with a complex construction above it. The grave goods included, among others, several iron items such as an adze-shaped tool, a bimetallic chisel-like tool (with an iron blade and a copper socket), and a disc-shaped artefact (*fig 6: b, c*). It should be emphasized that the Boldyrevo finds are considered today as the earliest artefacts made from ferrous metal in North Eurasia. The objects were subjected to analysis at the laboratory of the Institute of Archaeology, Russian Academy of Sciences, Moscow (see *Terekhova et al. 1997*). Observed metallographic characteristics

Sample	Ni	Co	Ga	Au	As	Ir	Cu	Sb	Mo	Ru	Re	Os
	%		ppm									
OR-1	9.30	0.62	3.2	0.7	6.5	52.7	270	0.5	4.0	30.0	8.9	60.0
OR-1	9.10	0.63	3.4	0.7	7.4	51.7	260	–	–	–	7.1	46.1
OR-1	9.45	0.67	–	–	–	–	250	–	–	–	–	–
OR-2	5.50	0.47	54.0	1.0	13.0	–	2012	0.5	2.4	2.0	1.0	0.1
OR-2	5.30	0.52	–	–	–	–	680	–	–	–	–	–

Tab. 3. The chemical element composition of the objects from Boldyrevo. Iron is the basis.
Tab. 3. Prvkové složení předmětů z Boldyreva. Základ tvoří železo.

led to a preliminary conclusion that meteoritic metal was used in the manufacture of these items. The chemical element analysis (*table 3*) also indicated a meteoritic origin; the nickel content varied from 5.3 to 9.45 %, the cobalt content from 0.47 to 0.67 %. At the same time, meteorite specialists clarified that both artefacts had been forged from iron of meteorites classified as pallasites. The same hot forging techniques and temperature settings as those used in working with copper were employed; for instance, the working parts of the objects were strengthened by work hardening (they were plastically deformed in a cold state). Using Jambon's method, we plotted values of Ni/Fe and Ni/Co on a chart in order to compare them with values determined for real meteoritic iron. As *fig. 4a* shows, our results are consistent with those featuring the meteorites.

Also, few examples can be given where the determination of iron as meteoritic iron is accompanied by certain doubts, even though recently re-analysed by *Jambon* (*2017a*; *2017b*). This is, for instance, the case with two bracelets (*fig. 5d*) dated to the Hallstatt period (Lusatian culture) from Częstochowa-Raków, Poland (*fig. 6: 3*). The first scholar examining these items, *J. Zimny* (*1965*), reported the high level of Ni (18.25 % and 12.47 %) and Co (0.56 %), and came to the conclusion that both objects were made of meteoritic iron. The same conclusion was pronounced by *Jambon* (*2017a*), who examined the finds by pXRF and plotted his data on the Ni/Fe-Ni/Co chart. However, on the basis of metallographic and chemical element analyses, J. Piaskowski claimed that the bracelets are bloomery iron. The main support for this claim was the presence of silica inclusions, which are an inevitable companion of the iron obtained by the bloomery process. The microprobe revealed a maximum of Si in the inclusions reaching about 17.7 % Si, and because this value corresponds well to the common silica content in bloomery slag, *Piaskowski* (*1982*) considered the inclusions the result of smelting. Some iron meteorites also contain similar silica inclusions, but these are very rare (see *Ruzicka 2014*).

Another interesting artefact mentioned by *Jambon* (*2017a*) is the axe from Wietrzno-Bóbrka, Poland (*fig. 5f*; *6: 4*). *Jambon* (*2017a*; *2017b*), relying on his own measurements (by pXRF), follows *A. Kotowiecki* (*2004*) and considers this object to be made of both meteoritic and bloomery iron. The axe was studied in detail by Piaskowski, who conducted metallographic and chemical analyses, and described the manufacturing technology as follows: "The blade of the axe was composed of five welded layers, the outer layers on both sides and the middle layer consisting of low-phosphorus bloomery iron of a mono-uniform carburization … the intermediate layers had a structure of high-nickel iron" (*Piaskowski 1982*, 238; *Piaskowski – Bryniarska 1978*). From this description, A. Jambon draws the conclusion: "This unexpected result suggests that the similarity between meteoritic iron and smelted iron was recognized and that the use of meteoritic iron was still a viable practice.” (*Jambon 2017a*, 50). In contrast, Piaskowski came to the conclusion that the structure of the nickel-rich iron was undoubtedly different from those we encounter in meteorites (*Piaskowski 1988*, 43), and hence the high-nickel iron is also a product of the iron-smelting process. Piaskowski himself then turned his attention to so-called Chalybean steel, which could be a deliberately produced high-nickel steel in Antiquity, but the phenomenon of extremely strong subscale oxidation enrichment also seems to be very likely. In either case, data of both, *Jambon* (*2017b*) and Piaskowski (*Piaskowski – Bryniarska 1978*), can fit the ‘meteoritic area’ in the Ni/Fe-Ni/Co diagram (*fig. 4b*).

Also rather disputable is the origin of the ferrous metal used for the blade of the famous Ugarit axe (Syria) dating from 1450–1350 BC (*fig. 5g*; *6: 5*). Based on chemical and micrographic analyses, L. Brun concluded that the axe had been made from smelted iron (*Schaeffer 1939*) obtained from pyrrhotine, which is an iron ore with a high level of nickel (though initially the scholar thought that iron had been derived from a meteorite because it contained a high level of nickel – 3.25 %). However, later *W. Witter* (*1942*) suggested that considering the level of technology in the Bronze Age, it was not possible to produce iron from pyrrhotine and, hence, iron with a level of nickel that is relatively high for bloomery iron had been derived from a meteorite. At the same time, in the view of the researcher, a meteorite of the ataxite type, the microstructure of which is difficult to distinguish from terrestrial iron was used. However, in accordance with the meteorite classification (the Meteorites of Russia website), ataxites is a rare class; another distinctive feature of ataxites is that they are the most nickel-rich meteorites known (over 16 %), which is not consistent with the level of nickel in the Ugarit axe (3.25 %). The presence of nickel (1.72–7.59 %), which is low for ataxites, has been demonstrated by studies carried out by A. Jambon as well. It should be said that the content of some other elements (0.41 % of carbon, 10.8 % of iron oxides) testifies, according to *Schaeffer* (*1939*), in favour of the terrestrial origin of the iron. Therefore, based on existing controversial data, it should be admitted that the question on the meteoritic origin of the Ugarit-axe blade remains open.

4. Discussion

The examples above clearly show that determination of the metal origin (meteoritic *vs.* terrestrial) always requires a complex analysis, because taking into account only partial results can lead to unreliable conclusions. This concerns, in particular, Early Iron Age finds, the production of which from smelted iron being affected by strong oxidation enrichment in subscale layers (resulting in locally elevated nickel and cobalt contents) is at least as likely as the use of meteoritic iron.

This brings us to the question of what role the use of meteoritic iron played in the discovery of the bloomery process, i.e. obtaining ferrous metal from ores. Many researchers tend to believe that the role of meteoritic iron was significant. But, in our view, these processes are not connected, as working with meteoritic iron simply means a transformation of the shape, whereas the metallurgical process is a substance conversion process, i.e. extracting a metal from ore. The latter experience was most likely gained through non-ferrous metallurgy (see *Pleiner 2000*, 11–12 for more details). Besides, the use of material such as meteoritic iron was accidental (*Coghlan 1956*); therefore, it could not lead to the emergence and development of metallurgical production. One can even express such a paradoxical thought that iron smelting and the development of metalworking techniques might have brought improved methods of meteoritic iron working (from the miniature Gerzeh beads, which are the simplest, to the production of daggers of sophisticated forms dating to the Late Bronze Age). This assumption has been confirmed in recent experimental work on the forging of iron meteorites (*Socha – Suliga – Krawczyk 2014*, 112). The example from the history of the development of iron in Egypt is also characteristic. While items made from meteoritic iron came to be known in Egypt quite early (late 4000 BC), knowledge of iron smelting did not appear there until Egypt was conquered by the Persians (8th–7th century BC, *Pleiner 2000*; *Snodgrass 1980*). As noted above, the first items from meteoritic iron appeared in Eastern Europe in mid-3000 BC, whereas artefacts made from smelted iron were found at sites dated from the end of the 2nd – beginning of the 1st millennia BC. Their presence at the sites is a consequence of the spread of metallurgical knowledge from areas where this knowledge was born (Anatolia; *Zavyalov – Terekhova 2018*).

It should be noted that *Jambon*'s (*2017a*) conclusion about a rather late emergence of iron smelting (not earlier than 1200 BC) is not consistent with the relevant data. The researcher substantiates his conclusion with the use of artefacts from Tell Hammeh (10th century BC), considering them to be the earliest. Meanwhile, earlier sites (14th–13th century BC) have been discovered in Serbia (*Stojić 2006*), Palestine (Tel Yin'am; *Liebowitz – Folk 1984*) and Georgia (*Khakhutayshvili 1987*). Moreover, in the Bronze Age, objects made of bloomery iron can also be found at considerable distances from the initial centre of the iron industry (Anatolia). It is well documented by the 18th-century BC bimetallic knife from the burial mounds of Gerasimovka in the Belgorod region of Russia (*Shramko – Mashkarov 1992*). Quantitative spectral analysis of the iron part of this knife revealed a negligible nickel content (0.005 %) proving the terrestrial origin.

5. Conclusion

The method of identifying the meteoritic origin of the earliest artefacts proposed by *A. Jambon* (*2017a*) is unique and promising. However, as attested by metallographic studies of a few examples (the bracelets from Częstochowa-Raków or the axe from Wietrzno-Bóbrka), it does not always lead to firm conclusions. Despite the recent conclusions reached by *A. Jambon* (*2017a*), there is no reason to question that iron smelting was discovered independently of the treatment of meteoritic iron (see, e.g., *Pleiner 2000*, 11–12; *Zavyalov – Terekhova 2016*). These processes are linked neither chronologically nor technologically. Relying on available data, it can be argued that the development of iron smelting techniques can be dated at the latest to the period from the end of the 3rd to the beginning of the 2nd millennia BC (see *Akanuma 2006*). In the middle of the 2nd millennium BC, metallurgical centres emerged outside the area where ferrous metallurgy had originated. By the end of the 2nd millennium BC, carburization and heat treatment (*Fritz et al. 1991*; *Muhly et al. 1985*; *Tavadze et al. 1977*), which were high-tech methods of ironworking in the Iron Age, were already known and practised in the Middle East.

The authors would like to thank Jiří Hošek for helpful comments on this paper.

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