Doubting radiocarbon dating from in-slag charcoal: five thousand years of iron production at Wetzlar-Dalheim?

Pochybné radiokarbonové datování z dřevěného uhlí uvízlého ve strusce: pět tisíc let železářské výroby ve Wetzlar-Dalheim?

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A Roman-Period bloomery smelting site had been excavated in the Lahn valley at Wetzlar-Dalheim in central Germany during 2006–2012. The production unit consisted of a big rectangular workshop pit with 13 slag pit-furnaces, two waste dumps and a small sunken hut. The stratigraphical sequence, along with abundant pottery and small finds, allows the dating of short-lived smelting activity to a time slot around the third quarter of the first century AD. As a first series of radiocarbon measurements from in-slag charcoal samples resulted in a bewildering date range from the Iron Age right back into the Neolithic, a second dating series has been undertaken. This time exclusively charcoal samples taken from the bottom of the furnace pits have been analysed. The resulting dates fit to the archaeologically derived dating. It is clear that the ^{14}C content of the in-slag charcoal samples must have been altered already during the process in antiquity. With none of the analysed dates younger than the archaeologically fixed date of the bloomery production unit, it is obvious that a contamination with fossil carbon must have taken place. The wide and inconsistent date range suggests that fossil carbon has entered the metallurgical system within the furnace in an uncontrollable manner. The observed phenomenon has wide implications for other metallurgical sites with high temperature processes under strongly reducing conditions. Charcoal samples from such sites, especially from inside slags, might be contaminated to an unpredictable degree and produce seemingly older dates. A first review of previously published data series calls for a reconsideration of the reliability of radiocarbon dates from metallurgical slags.

radiocarbon dating – methodology – charcoal samples – slag – fossil carbon

V průběhu let 2006 až 2012 byla v údolí řeky Lahn ve Wetzlar-Dalheimu ve středním Německu odkryta lokalita s doklady výroby železa z doby římské. Výrobní jednotka sestávala z velké dílenské jámy obdélníkového půdorysu se třinácti pecemi se zahloubenou nístějí, dvěma odpadními haldami a malou polozemnicí. Stratigrafická posloupnost spolu s hojně přítomnou keramikou a drobnými nálezy umožňují datovat krátkodobou výrobní činnosti do zhruba 3. čtvrtiny 1. stol. n. l. Jelikož první série radiokarbonových měření provedená na kouscích dřevěného uhlí, které uvízlo ve strusce, vymezila ohromující časový úsek od doby železné až po neolit, byla provedena druhá datovací série. Tentokrát byly analyzovány výlučně vzorky dřevěného uhlí, které byly odebrány z nístějí pecí. Výsledné datování vykazovalo shodu s datováním archeologickým. Vzhledem k tomu, že kontaminaci po exkavaci můžeme vyloučit, je zřejmé, že obsah ^{14}C ve vzorcích dřevěného uhlí musel být změněn už při výrobním procesu v průběhu starověku. Široký a nekonzistentní časový interval naznačuje, že fosilní uhlík vstupuje do metalurgického systému v peci nekontrolovaně. Pozorovaný fenomén má velký dopad na další lokality s doklady metalurgických aktivit, při kterých vysokoteplotní procesy probíhaly za silně redukčních podmínek. Vzorky dřevěného uhlí z takových lokalit, zejména pak uhlíků ze strusek, mohou být kontaminovány nepředvídatelným způsobem a zapříčinit zdánlivě starší datování. První přezkoumání dříve publikovaných datových řad vyzývá k přehodnocení spolehlivosti údajů z radiokarbonového datování metalurgických strusek.

radiokarbonové datování – metodika – vzorky uhlíků – struska – fosilní uhlík

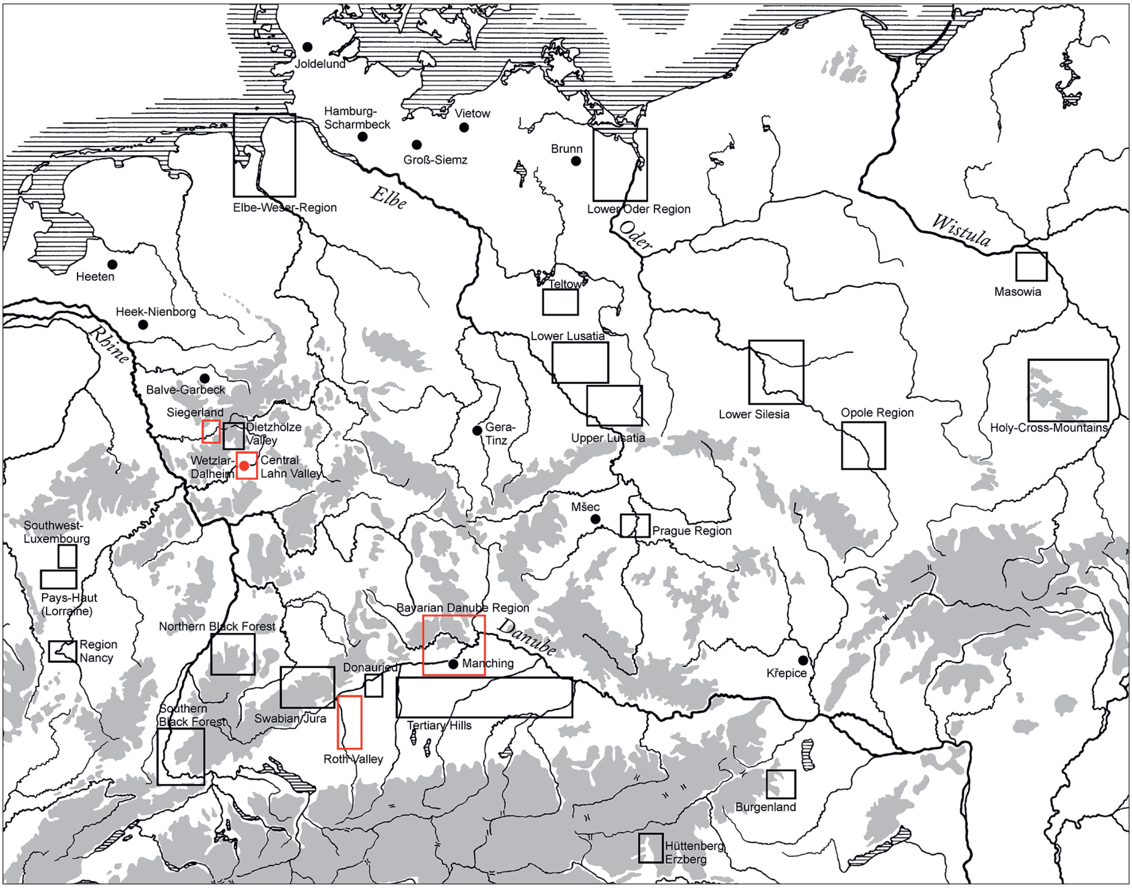

Fig. 1. Important sites and regions of early iron production in Central and Eastern Europe with those mentioned in the text highlighted in red (adapted from *Schäfer 2009*, 218 fig. 128).
Obr. 1. Lokality a oblasti významné pro poznání časného železářství ve střední a východní Evropě; místa zmiňovaná v textu vyznačena červeně (podle *Schäfer 2009*, Abb. 128).

1. The setting

During the years 2006–2012 a bloomery smelting site of the early Roman Period had been excavated in the Lahn valley in Hesse, central Germany (*fig. 1*; *Schäfer 2014*; cf. *Gassmann – Schäfer 2014*, maps B and C with further references). The production unit at Wetzlar-Dalheim, Lahn-Dill-District, site C86 'Unterbodenfeld' had survived well preserved in the infill of a natural gully and could be uncovered completely using single find recording. It consisted of 13 slag-pit furnaces with free-standing shafts typical of the Roman Period (*Pleiner 2000*, 152), two waste dumps and a small sunken hut (*fig. 2*). The iron smelting furnaces were situated alongside the walls in a large rectangular workshop pit, with two ground plans overlapping each other. The furnaces would have been used up to a dozen times each, as dislocated slag blocks and evidence of structural repairs at the furnace bases

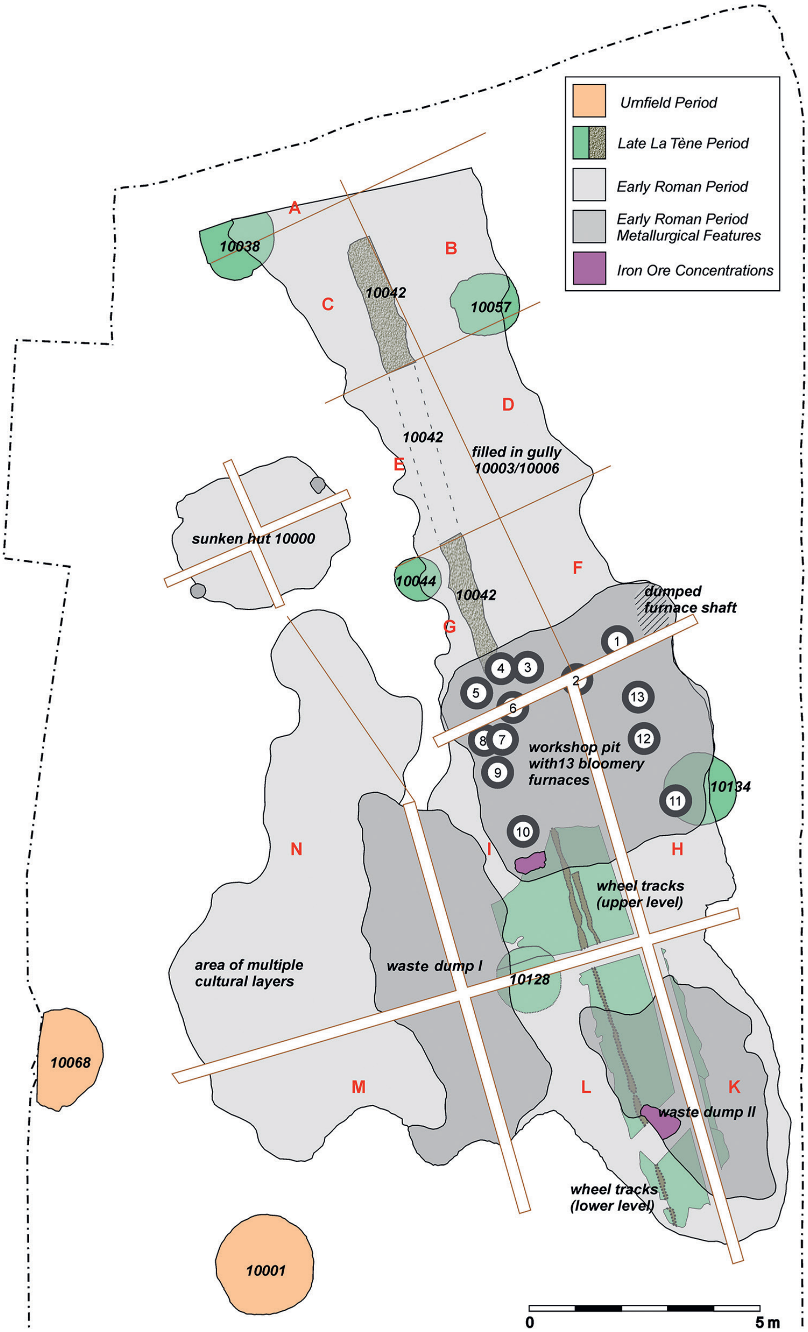

Fig. 2. Wetzlar-Dalheim, Lahn-Dill-District, Germany, Site C86 'Unterbodenfeld'. Schematic site plan with chronological phases (graphics A. Schäfer and B. Schroth).
Obr. 2. Wetzlar-Dalheim, zemský okres Lahn-Dill, Německo, lokalita C86 „Unterbodenfeld". Schematický plán lokality s chronologickými fázemi.

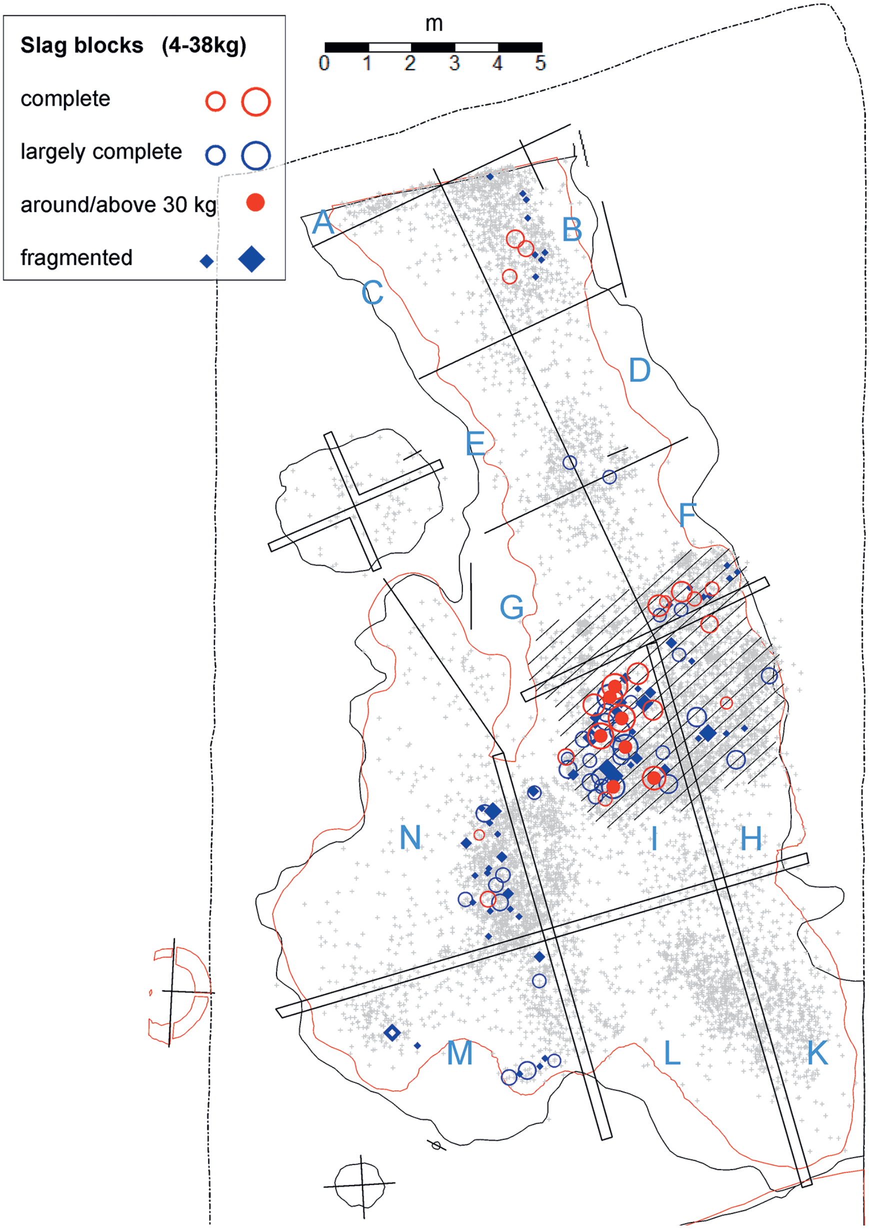

Fig. 3. Wetzlar-Dalheim C86, Lahn-Dill-District, Germany. Spatial distribution of slag blocks and their fragments (> 1 kg). The mass of small slag fragments (n = 8900) is plotted underneath. Most of the slag blocks had been left inside the workshop pit (hatched). Only smaller pieces and fragments were deposited on the dump or in the gully (no details available yet for sections K and L). Graphics in figs. 3, 6–8 and 11 A. Schäfer.
Obr. 3. Wetzlar-Dalheim C86, zemský okres Lahn-Dill, Německo. Prostorová distribuce struskových bloků a jejich fragmentů (> 1 kg). Množství malých fragmentů strusky (n = 8900) je vyneseno ve spodnější vrstvě. Většina struskových bloků zůstala uvnitř dílenské jámy (vyšrafováno). Pouze menší kusy a fragmenty byly odkládány na haldu nebo do strouhy (detaily pro úseky K a L zatím nejsou k dispozici).

Lab. No.	Find No.	Material	Conventional ^{14}C age (yr BP) (± 1σ)	Delta C13 (‰)	Calibrated calendar age (cal AD/BC) (2σ)
ETH-35454	490	organics, charcoal?	*no carbon for dating*		
ETH-35455	2205	organics, charcoal?	*no carbon for dating*		
ETH-35456	2211	organics, charcoal?	2825 ± 50	-34.1 ± 1.3	1130BC (95.4%) 840BC
ETH-35457	89	organics, charcoal?	2010 ± 45	-21.0 ± 1.3	170BC (4.0%) 130BC 120BC (91.4%) 80AD
ETH-35458	3831	organics, charcoal?	2015 ± 45	-21.8 ± 1.3	170BC (95.4%) 80AD
ETH-35459	4241	organics, charcoal?	2045 ± 45	-21.7 ± 1.3	180BC (95.4%) 60AD
ETH-35460	4421	organics, charcoal?	1990 ± 45	-26.3 ± 1.1	110BC (95.4%) 130AD
ETH-35461	3681	organics, charcoal?	3055 ± 45	-20.8 ± 1.2	1430BC (95.4%) 1190BC
ETH-35462	4215	organics, charcoal?	3065 ± 45	-21.5 ± 1.2	1440BC (95.4%) 1210BC
ETH-35463	6588	organics, charcoal?	2175 ± 45	-17.8 ± 1.2	380BC (95.4%) 100BC
ETH-35464	6616	organics, charcoal?	2040 ± 45	-24.9 ± 1.1	180BC (95.4%) 60AD
ETH-35465	A0982	organics, charcoal?	4695 ± 70	-34.3 ± 1.5	3640BC (95.4%) 3350BC
ETH-35466	7865	organics, charcoal?	*no carbon for dating*		
ETH-35467	6469	organics, charcoal?	3110 ± 50	-28.7 ± 1.1	1500BC (95.4%) 1260BC
ETH-35468	6472	organics, charcoal?	2410 ± 45	-22.1 ± 1.2	760BC (16.7%) 680BC 670BC (6.5%) 610BC 600BC (72.2%) 390BC
ETH-35469	6949	organics, charcoal?	2275 ± 45	-29.3 ± 1.1	410BC (40.3%) 340BC 330BC (55.1%) 200BC
ETH-35470	7093	organics, charcoal?	*no carbon for dating*		
ETH-35471	7118	organics, charcoal?	*no carbon for dating*		
ETH-35472	7119	organics, charcoal?	2120 ± 45	-24.8 ± 1.1	360BC (13.2%) 280BC 240BC (82.1%) 20BC
ETH-35473	7163	organics, charcoal?	*no carbon for dating*		
ETH-35474	A0582	organics, charcoal?	2320 ± 45	-26.8 ± 1.1	520BC (73.3%) 340BC 310BC (22.1%) 200BC
ETH-35475	A0592	organics, charcoal?	2715 ± 55	-31.5 ± 1.5	1000BC (95.4%) 790BC

Tab. 1. Wetzlar-Dalheim C86, Lahn-Dill-District, Germany. First set of radiocarbon measurements, taken in 2008, mostly from in-slag charcoal samples (cf. *fig. 6*). Calibration with Oxcal Version 3.10 (data provided by ETH Zurich [I. Hajdas, G. Bonani]).
Tab. 1. Wetzlar-Dalheim C86, zemský okres Lahn-Dill, Německo. První série radiokarbonových měření, která byla provedena v roce 2008 povětšinou na vzorcích dřevěného uhlí uvízlého ve strusce (srov. *obr. 6*). Kalibrováno programem OxCal Verze 3.10 (Data poskytl ETH Zurich [I. Hajdas, G. Bonani]).

indicate. The metallurgical debris from the site amounts to about 2.8 tons of bloomery slag together with vitrified furnace wall, tuyère fragments and iron ores. Most of the about 120–150 slag blocks of 8–38 kg in weight had been left in the workshop right next to the furnaces. Only a comparatively small number had made their way to the adjacent dumps or the infill of the gully (*fig. 3*).

Judging from the small number of furnaces and the comparatively modest amount of metallurgical waste, the smelting activities could hardly have been going on for more than a few seasons, if not just one or two. Abundant pottery and small finds, including a fair number of Roman imports, date the production unit at Wetzlar-Dalheim quite precisely to a short time slot in the second half of the first century AD (*Schäfer 2010*, 77–81). Thus,

Fig. 4. Wetzlar-Dalheim C86, Lahn-Dill-District, Germany. Furnace 6 (features 10052/53) cutting through pebble reinforcement (feature 10042) of Iron Age trackway. Photograph B. Schroth.
Obr. 4. Wetzlar-Dalheim C86, zemský okres Lahn--Dill, Německo. Pec 6 (objekty 10052/53) protínající oblázky zpevněnou stezku (objekt 10042) z doby železné.

from the archaeological point of view the metallurgical complex at site C86 at Wetzlar-Dalheim with its workshop pit and the two waste dumps clearly marks one contemporaneous assemblage. Taphonomic analysis is indicative of a systematic abandonment of the site. After shutting down the last furnaces in the northwest corner of the workshop, the remaining structure was refilled with cultural debris of the nearby settlement.

The workshop was found in superposition to a preceding late Iron Age trackway that had made use of the natural gully. The small road or path, linking the nearby Lahn River to a settlement further up the hill, was flanked by large storage pits on either side. Tracks of cart wheels and some reinforcement with gravel and pebbles could be identified over a distance of more than 20 metres in the loess subsoil. In a clear stratigraphical sequence, the Roman Period slag pits cut into the Iron Age trackway underneath (*fig. 4*).

2. The radiocarbon dates

A first series of radiocarbon dates was analysed in 2008 with the excavation still in an early stage (*tabs. 1* and *2*). The charcoal samples were directly extracted from the inside of broken up or cut up slag blocks to make sure to date the production process itself. Apart from these in-slag samples some 'normal' charcoal samples were also analysed from the adjacent sunken hut and a Bronze Age storage pit.

Figures 5–6 show some of the analysed slag blocks and display the very astonishing results of this first series of AMS-radiocarbon measurements.[1] Taking only the six dates from slag blocks that derive directly from inside the early Roman workshop pit, the date range of the analyses reaches from the later Neolithic (A0982), through the Bronze Age

[1] Thanks are due to I. Hajdas and G. Bonani (ETH Zurich) for the radiocarbon measurements (cf. *Hajdas et al. 2004*) and for some helpful comments on an earlier draft. Some of the in-slag charcoal samples from this data set seem to have been quite low in carbon content (I. Hajdas, ETH Zurich, pers. comm.), other samples handed in did not contain any carbon for dating (cf. *tab. 1*). Due to sample size the tree species could not be established.

AMS ^{14}C Lab Code	HEKAL Sample Nr.	Sample name (sample material dated)	furnace / charcoal layer pl. = planum	Carbon yield (%)	Conventional ^{14}C age (yr BP) (± 1σ)	Calibrated calendar age (cal AD/BC) (2σ)
DeA-10950	I/1446/8L	C86-A1726 (Charcoal-Fagus)		22.35	1910 ± 22	*control measurement*
DeA-10966	I/1446/8H	C86-A1726 (Charcoal-Fagus)	furnace 01, pl. 06	27.48	1968 ± 23	cal BC 37 – cal AD 77
DeA-10951	I/1446/9L	C86-B2571 (Charcoal-Quercus)		24.88	2008 ± 23	*control measurement*
DeA-10952	I/1446/9H	C86-B2571 (Charcoal-Quercus)	furnace 03, pl. 10-11	31.24	2026 ± 23	cal BC 94 – cal AD 49
DeA-10953	I/1446/10L	C86-B2572 (Charcoal-Quercus)		25.80	1983 ± 23	*control measurement*
DeA-10954	I/1446/10H	C86-B2572 (Charcoal-Quercus)	furnace 03, pl. 10-11	29.66	1974 ± 24	cal BC 39 – cal AD 73
DeA-10955	I/1446/11L	C86-B2570 (Charcoal-Fagus)		25.81	1946 ± 23	*control measurement*
DeA-10956	I/1446/11H	C86-B2570 (Charcoal-Fagus)	furnace 04, pl. 10-11	30.55	1967 ± 23	cal BC 37 – cal AD 78
DeA-10957	I/1446/12L	C86-B2621 (Charcoal-Fagus)		23.09	1921 ± 23	*control measurement*
DeA-10958	I/1446/12H	C86-B2621 (Charcoal-Fagus)	furnace 04, pl. 11-12	30.97	1910 ± 23	cal AD 28 – cal AD 133
DeA-10959	I/1446/13L	C86-B2939 (Charcoal-Quercus)			1966 ± 23	*control measurement*
DeA-10960	I/1446/13H	C86-B2939 (Charcoal-Quercus)	furnace 05, pl. 11-12	27.50	2031 ± 23	cal BC 105 – cal AD 47
DeA-10961	I/1446/14L	C86-B2968 (Charcoal-Quercus)		25.39	2013 ± 23	*control measurement*
DeA-10962	I/1446/14H	C86-B2968 (Charcoal-Quercus)	furnace 05, pl. 11-12	31.72	1981 ± 23	cal BC 39 – cal AD 66
DeA-10963	I/1446/15L	C86-B3845 (Charcoal-Quercus)		24.96	2049 ± 23	*control measurement*
DeA-10964	I/1446/15H	C86-B3845 (Charcoal-Quercus)	furnace 07, pl. 09-10	30.00	1989 ± 23	cal BC 42 – cal AD 60
DeA-10978	I/1446/16L	C86-B3716 (Charcoal-Quercus)		27.43	1971 ± 25	*control measurement*
DeA-10979	I/1446/16H	C86-B3716 (Charcoal-Quercus)	furnace 09, pl. 08-09	27.05	1974 ± 25	cal BC 39 – cal AD 73
DeA-10980	I/1446/17L	C86-B3749 (Charcoal-Tilia)		22.66	1926 ± 26	*control measurement*
DeA-10981	I/1446/17H	C86-B3749 (Charcoal-Tilia)	furnace 09, pl. 09-10	29.87	1954 ± 24	cal BC 32 – cal AD 122
DeA-10968	I/1446/18L	C86-B3731 (Charcoal-Quercus)		20.83	2024 ± 24	*control measurement*
DeA-10969	I/1446/18H	C86-B3731 (Charcoal-Quercus)	furnace 10, pl. 07-08	30.26	2019 ± 24	cal BC 90 – cal AD 52
DeA-10970	I/1446/19L	C86-B6516 (Charcoal-Quercus)		28.99	1991 ± 24	*control measurement*
DeA-10971	I/1446/19H	C86-B6516 (Charcoal-Quercus)	furnace 12, pl. 08-09	28.97	1990 ± 24	cal BC 43 – cal AD 61
DeA-10972	I/1446/20L	C86-B6565 (Charcoal-Carpinus)		27.76	2004 ± 25	*control measurement*
DeA-10973	I/1446/20H	C86-B6565 (Charcoal-Carpinus)	furnace 12, pl. 08-09	30.06	2029 ± 24	cal BC 104 – cal AD 49
DeA-10974	I/1446/21L	C86-B4033 (Charcoal-Quercus)		23.51	1962 ± 24	*control measurement*
DeA-10975	I/1446/21H	C86-B4033 (Charcoal-Quercus)	layer 10096, pl. 07-08	30.25	1992 ± 24	cal BC 43 – cal AD 60
DeA-10983	I/1446/22L	C86-A4797 (Charcoal-Quercus)		23.21	1986 ± 28	*control measurement*
DeA-10984	I/1446/22H	C86-A4797 (Charcoal-Quercus)	layer 10021, pl. 04-05	28.69	1982 ± 27	cal BC 42 – cal AD 70
DeA-10985	I/1446/23L	C86-B3970 (Charcoal-Quercus)		25.76	2044 ± 26	*control measurement*
DeA-10986	I/1446/23H	C86-B3970 (Charcoal-Quercus)	layer 10021, pl. 07-08	23.38	2019 ± 26	cal BC 92 – cal AD 54

Tab. 2. Wetzlar-Dalheim C86, Lahn-Dill-District, Germany. Second series of radiocarbon measurements directly related to the production process, taken in 2017. Calibration data set: intcal13.14c (data provided by Isotoptech Zrt., Debrecen [I. Futó, M. Molnár, V. Mihály]).

Tab. 2. Wetzlar-Dalheim C86, zemský okres Lahn-Dill, Německo. Druhá série radiokarbonových měření přímo souvisejících s výrobním procesem, pořízená v roce 2017. Kalibrační datová sada: intcal13.14c (Data poskytl Isotoptech Zrt., Debrecín [I. Futó, M. Molnár, V. Mihály]).

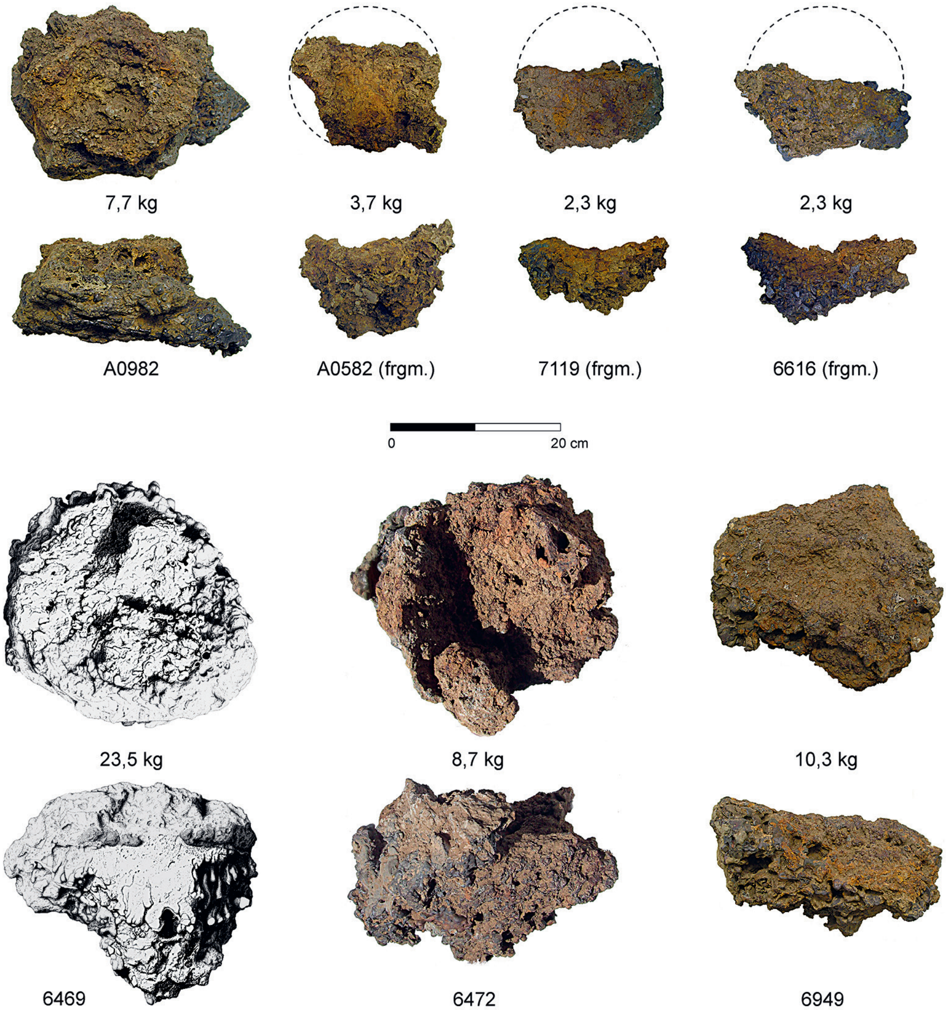

Fig. 5. Wetzlar-Dalheim C86, Lahn-Dill-District, Germany. Range of slag blocks from the Roman-Period smelting site dated by radiocarbon analysis. The charcoals extracted from inside the slags yielded dates from the later Neolithic (A0982), the Bronze Age (6469), the Hallstatt to early La Tène Periods (6472, A0582, 6949), the later La Tène Period (7119) and the late Iron Age/Early Roman Period (6616). Drawing P. Thomas; photographs A. Schäfer.
Obr. 5. Wetzlar-Dalheim C86, zemský okres Lahn-Dill, Německo. Škála struskových bloků z lokalit s doklady železářské výroby datovaných radiokarbonovou metodou do římského období. Kousky dřevěného uhlí vyjmutého ze strusek byly datovány do mladšího neolitu (A0982), do doby bronzové (6469), halštatské až rané doby laténské (6472, A0582, 6949), mladší doby laténské (7119) a pozdní doby železné/doby římské (6616).

(6469; A0597) to the Early Iron Age (6472; A0582) and the Later Iron Age (7119). Four of these slag blocks were dumped in a layer of debris stratigraphically superseding the slag pit of furnace 1 after its abandonment and destruction. Three more samples in slag blocks from the infill of the gully (6588; 6949) and from the western dump (2211) produced dates

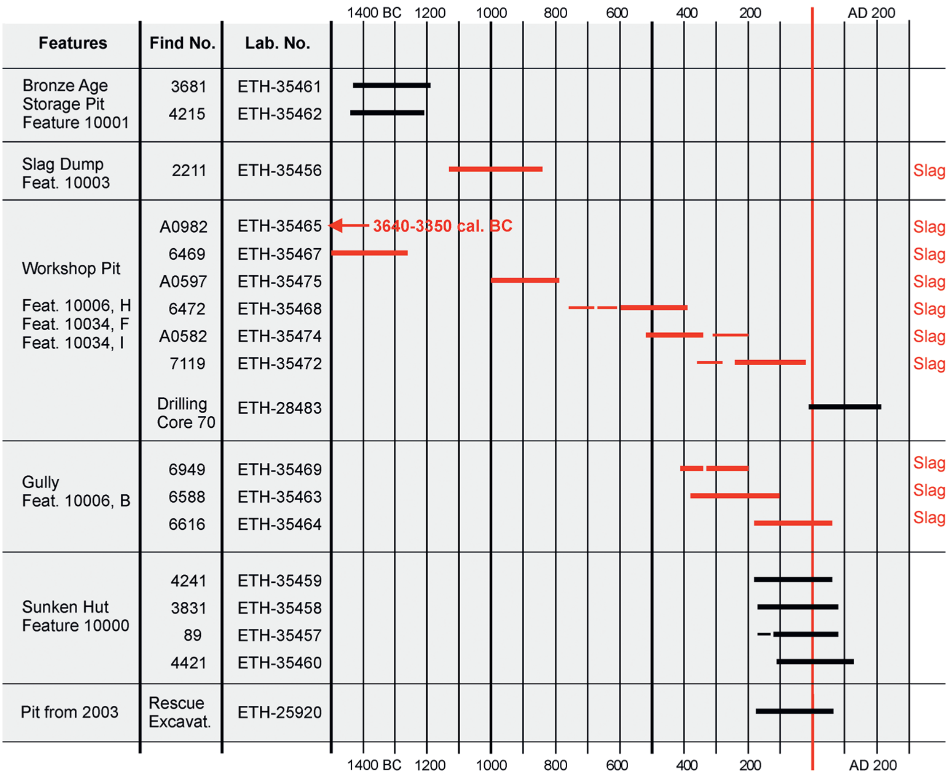

Fig. 6. Wetzlar-Dalheim C86, Lahn-Dill-District, Germany. Results of the first series of radiocarbon measurements, taken in 2008, mostly from in-slag charcoal samples (in red). 2σ standard deviation (data provided by ETH Zurich [I. Hajdas, G. Bonani]).
Obr. 6. Wetzlar-Dalheim C86, zemský okres Lahn-Dill, Německo. Výsledky první série radiokarbonových měření, pořízených v roce 2008, povětšinou provedených na vzorcích dřevěného uhlí uvízlého ve strusce (červeně). Směrodatná odchylka 2σ (data poskytl ETH Zurich [I. Hajdas, G. Bonani]).

of the Bronze Age and the Later Iron Age respectively. Only one of the ten samples (6616), located furthest north in the gully, produced a late Iron Age/early Roman Period date in accordance with the archaeological evidence. While the in-slag samples yielded these astonishing results, the ‘normal’ charcoal samples taken from the sunken hut and the Bronze Age storage pit matched the archaeologically derived dating. Two more samples, processed a few years previously, also produced Roman Period dates and did not derive from slags. One was taken from a drilling core from inside the working pit close to one of the furnaces (core 70). The other derives from the infill of an archaeological feature immediately north of our excavation trench. There, tuyère fragments, slags and charcoal may belong to another production unit further up the hill and were collected there in 2003 during rescue work in a freshly cut cable trench along the road.

The broad date range of this first dating series with some clearly unacceptable results brought us to hand in another series of samples for radiocarbon dating also directly related to the smelting activities. This time we restricted our samples to charcoal fragments from

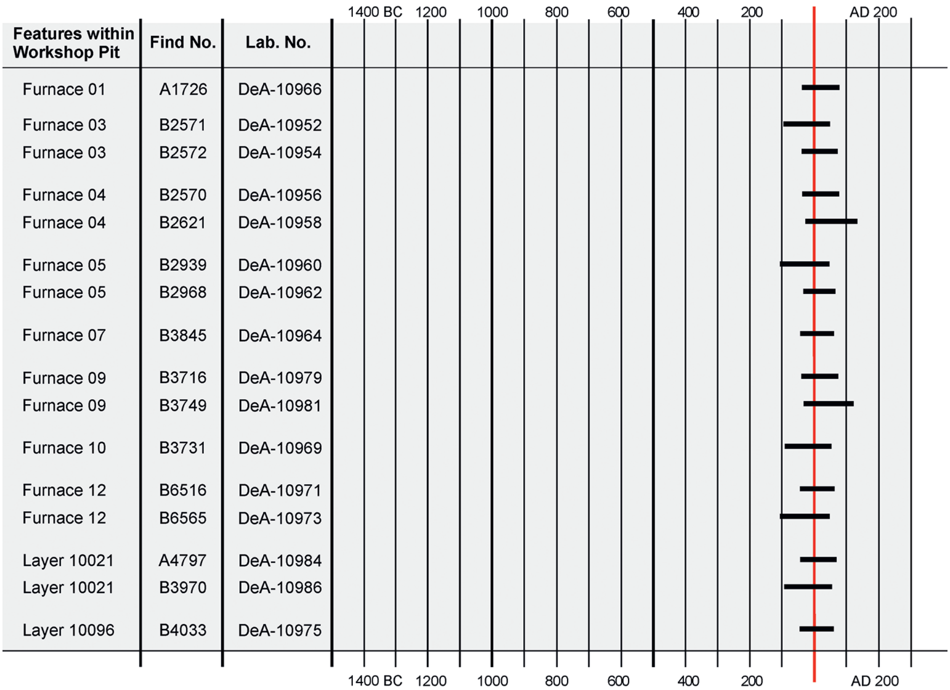

Fig. 7. Wetzlar-Dalheim C86, Lahn-Dill-District, Germany. Results of the second series of radiocarbon measurements in 2017. The charcoal samples were exclusively taken from the bottom layers within the slag pits of the bloomery furnaces and from two additional charcoal-bearing layers inside the workshop pit. 2σ standard deviation (data provided by Isotoptech Zrt., Debrecen [I. Futó, M. Molnár, V. Mihály]).
Obr. 7. Wetzlar-Dalheim C86, zemský okres Lahn-Dill, Německo. Výsledky druhé série radiokarbonových měření z roku 2017. Vzorky dřevěného uhlí byly výlučně odebírány ze spodních vrstev zahloubených nístějí železářských pecí a ze dvou dalších vrstev obsahujících dřevěné uhlí uvnitř dílenské jámy. Směrodatná odchylka 2σ (data poskytl Isotoptech Zrt., Debrecín [I. Futó, M. Molnár, V. Mihály]).

the bottom of the slag pits of as many furnaces as possible.[2] The resulting radiocarbon dates consistently back up the archaeological dating of the production unit, all staying within the two centuries around the turn of the Christian era (*fig. 7*).[3] The location of all samples on site addressed in this paper can be seen in *fig. 8*.

3. Discussion

The two dating series feed the suspicion that we had uncovered a severe methodological problem in radiocarbon dating of in-slag charcoal samples. The clear discrepancy of the two data sets rules out any effect of the old-wood theory, 'the perpetual bug bear of archaeolo-

[2] Four tree species were represented in the 16 samples: *Quercus* (11), *Fagus* (3), *Tilia* (1), *Carpinus* (1).

[3] Thanks are due to I. Futó, M. Molnár, V. Mihály (Isotoptech Zrt., Debrecen) for the radiocarbon measurements. (cf. *Molnár et al. 2013a*; *2013b*).

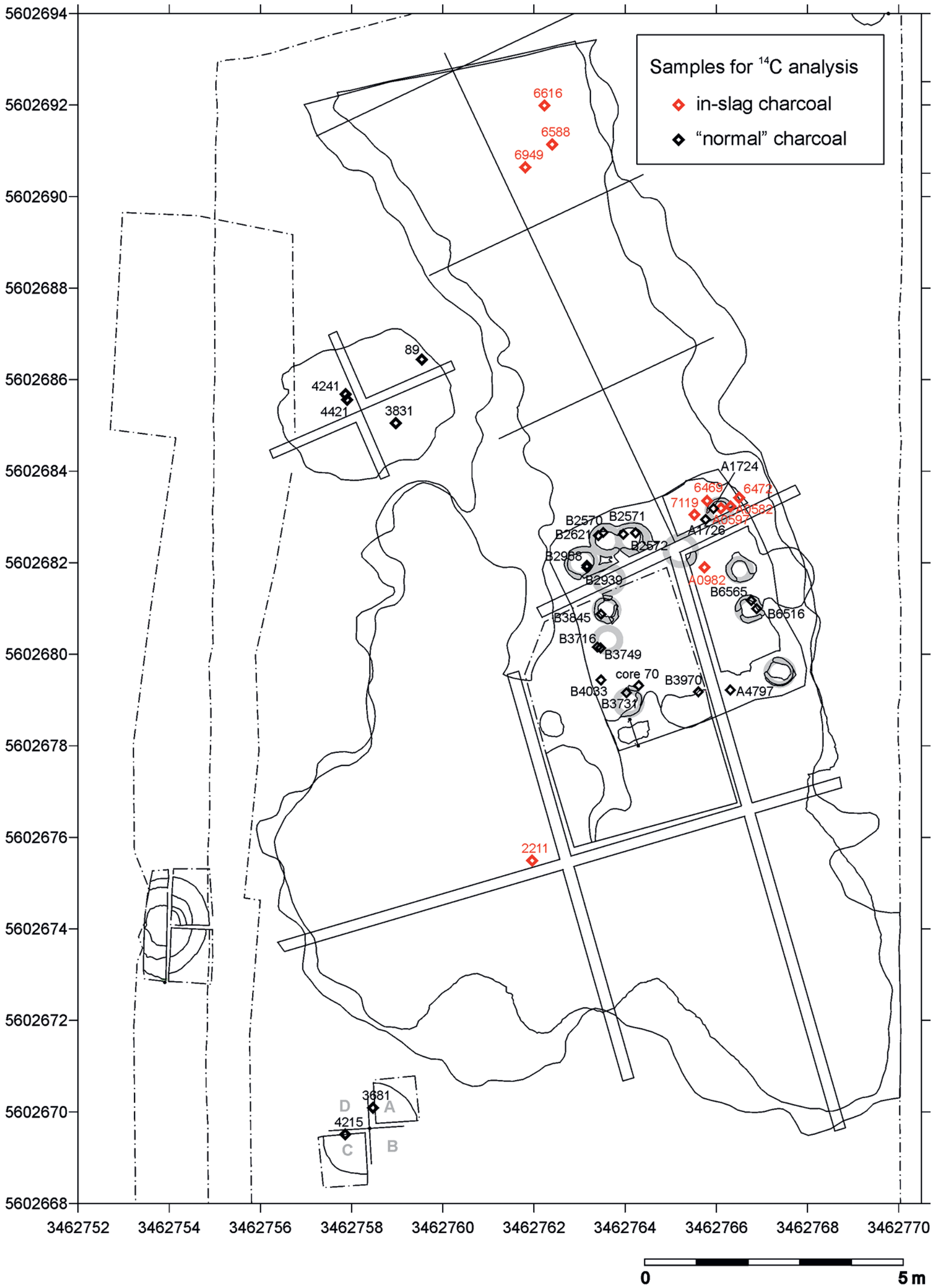

Fig. 8. Wetzlar-Dalheim C86, Lahn-Dill-District, Germany. Location of charcoal samples referred to in the text.
Obr. 8. Wetzlar-Dalheim C86, zemský okres Lahn-Dill, Německo. Nálezová poloha vzorků dřevěného uhlí, na které je v textu odkazováno.

gists' (*Hendrickson – Hua – Pryce 2013*, 45), as the most common remedy for radiocarbon results that are too old to match the archaeological record. While we do not want to rule out the odd old oak tree ending up in a charcoal burning fire, it is to be rendered wholly impossible that it was only their charcoals being trapped in the slags inside the furnace while contemporary charcoals gathered at the bottom of the slag pits. What is more, the use of branches and smaller trees in charcoal production for metallurgical purposes is regularly to be found in archaeological contexts[4], while the valuable timbers of large trees were carefully selected for building and construction.

The enormous range of dates in our first radiocarbon sequence for the very short-lived smelting activities at Wetzlar-Dalheim C86 points to a contamination of the samples within the slag blocks. To a varying degree the dates obtained tend to be (much) older than the dates expected from the archaeological record. There is not one measurement younger than the expected date of deposition in the earlier Roman Period. As all other samples from our site that were not extracted from a slag block do not show any significant deviations from the expected time range, we can rule out a contamination of the specimens after deposition as well as during or after sampling.

So we are clearly left with a problem inherent in the carbon of the charcoal samples from inside the slags themselves. The temperatures within a bloomery furnace reach up to 1250 °C. Fayalitic bloomery slag has a liquifying point between 1150–1200 °C. The charcoals trapped in such slags would have been subjected to very high temperatures for several hours in a closed system under highly reducing conditions.

It is at this point in the process that the contamination must have occurred. The only explanation for a radiocarbon date getting older than the true date of the original sample is the addition of fossil carbon. So we have to conclude that our in-slag charcoal samples from Wetzlar-Dalheim have been contaminated with fossil carbon to a varying and unpredictable degree.

4. Implications

If this is true for our site, there could be similar problems at other sites where high temperature metallurgical processes have been dated by radiocarbon analysis from charcoals within slags. As this short note cannot present a systematic survey of radiocarbon datings from metallurgical contexts, we will only pick out a few sites and regions to show the range of possible implications (see *fig. 1*). It is not our intention to offend any of our colleagues but to raise awareness of a methodological problem in radiocarbon dating that has been there right from the beginning, but has not been addressed to date and has always been explained away with the help of 'the old wood story'.[5] One could even argue that the 'old

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[4] *Thiébault 2002*; *Tegtmeier 2009* (Iron Age, Middle Ages); *Stöllner et al. 2014*, 55–57 (Iron Age); *Overbeck 2011*, 287–293 (13th–14th cent. AD); *Nelle 2003* (post medieval; more likely related to glass making).

[5] It may be noted, that one of the largest laboratories for radiocarbon analysis in the world already for an number of years explicitly does not recommend in-slag charcoal samples for radiocarbon dating: […] 'many times the charred material found in slag originates from very large "old" trees that were used in the fires for smelting operations. As such, the wood can be several hundreds of years old when it is burned and this old wood (charcoal) ends up in the slag yielding a much older age than the actual time of manufacture. We have

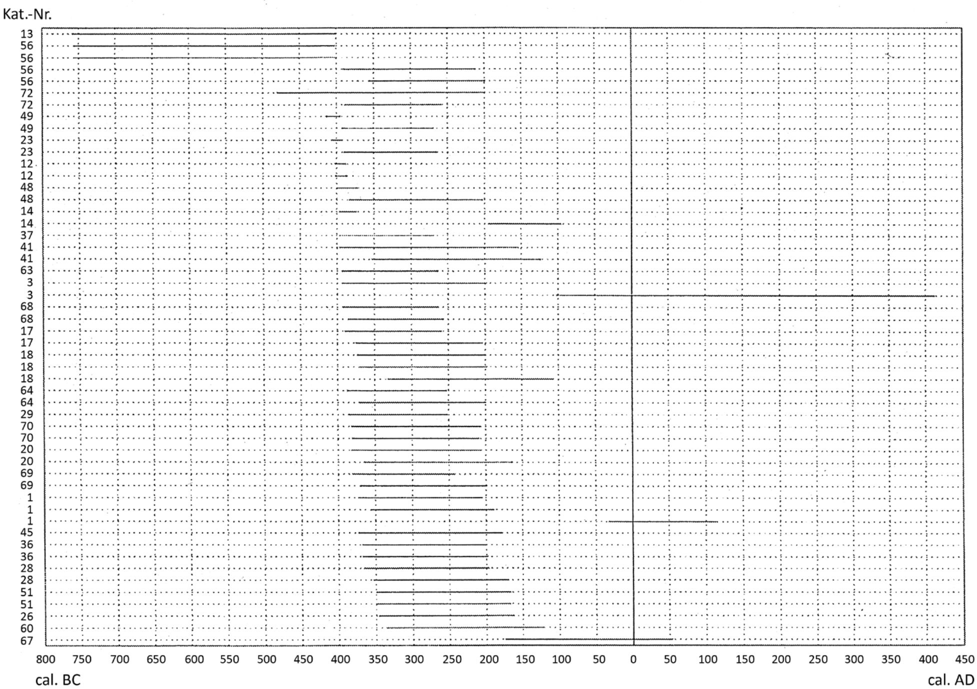

Fig. 9. Roth Valley, Bavarian Suebia, Germany. 52 AMS-radiocarbon measurements (1σ standard deviation) from 28 bloomery production sites of the region (after *Ambs – Gassmann – Wischenbart 2001*, 25, fig. 13).
Obr. 9. Povodí řeky Roth, Bavorské Švábsko, Německo. 52 AMS-radiokarbonová měření (směrodatná odchylka 1σ) z 28 lokalit s doklady železářské výroby v daném regionu (podle *Ambs – Gassmann – Wischenbart 2001*, 25, fig. 13).

wood effect' has up to now severely inhibited any serious scientific discussion on interpreting (too) old dates, especially from charcoals taken from inside metallurgical slags.

The first example we would like to draw attention to is from an Iron Age smelting region in southern Germany, south of the Danube in the Roth-valley in Bavarian Suebia. Here a large series of 53 AMS-radiocarbon dates were published in 2001 (*Ambs – Gassmann – Wischenbart 2001*, 23ff., tab. 3, 25, fig. 13). The samples all derive from charcoals extracted from bloomery slags from 28 smelting sites of the region. Apart from three dates reaching back to the Hallstatt-Period calibration plateau, the samples very consistently show a date range between the 4^{th} to 2^{nd} centuries BC (*fig. 9*). So in this case there does not seem to be a problem. Another example where no alterations were discernible may be quoted from the region around the La Tène-Period oppidum of Manching in Bavaria (*Gassmann – Schäfer 2013*, 355, Tab. 2).

A very important early iron production district in Germany is the Siegerland region only about 50 km north of the Lahn valley. From early in the twentieth century onwards

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seen this several times when working with this type of sample, and it is why we typically don't recommend this type of material for radiocarbon dating.' (http://www.radiocarbon.eu/carbon-dating-blog/1067/charred--material-dating/ [last call 28.10.2017, 18:40]).

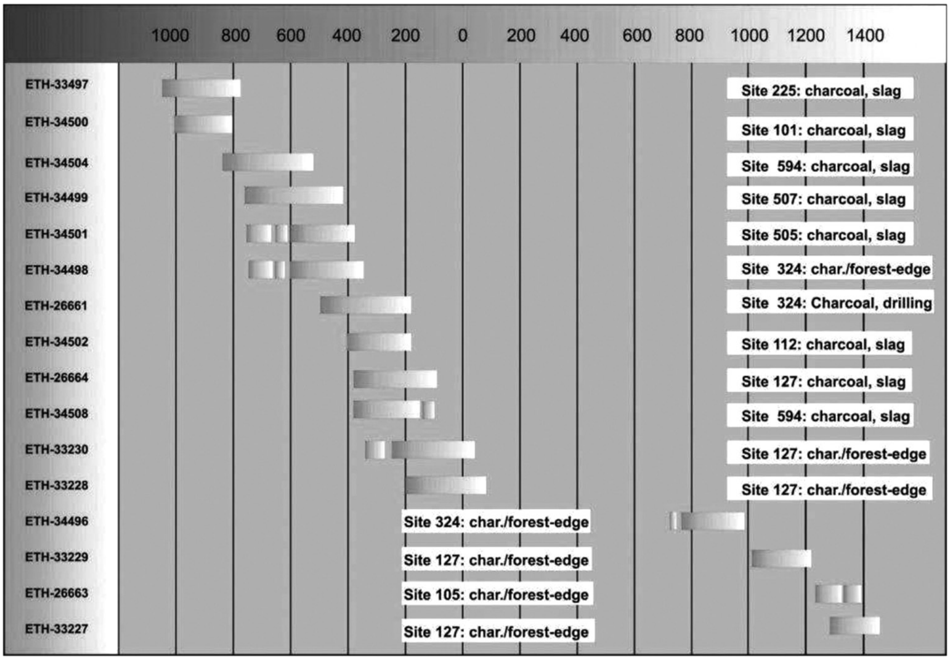

Fig. 10. ^{14}C-dates (2σ standard deviation) from sites investigated between 2002 and 2007 in the north--western part of the Siegerland, Central Germany (after *Stöllner et al. 2014*, 54, fig. 11).
Obr. 10. ^{14}C data (směrodatná odchylka 2σ) z lokalit zkoumaných v letech 2002 až 2007 v severozápadní části Siegerlandu ve středním Německu (podle *Stöllner et al. 2014*, 54, Abb. 11).

it had been famous for its late Iron Age bloomery production and also features a second production phase in the Middle Ages. New research has been undertaken there in recent years (*Stöllner et al. 2009*; *Zeiler 2013*) and a series of radiocarbon dates from several smelting sites has been published (*fig. 10*; *Stöllner et al. 2014*, 54, fig. 11). A closer look reveals a similarly wide range of dates as in Wetzlar-Dalheim. For the Siegerland, however, the published sequence 'only' goes back to the late Bronze Age, also without a distinct concentration of dates in the archaeologically known main production periods. The first five dates from the beginning of the sequence were all derived from charcoals in slags. Yet some of the dates indeed fall into the production periods expected by archaeology. Thus the differences between the radiocarbon dates and the archaeological evidence are not as marked and obvious as at Wetzlar-Dalheim. This may probably be true for a great many other sites, where similar date ranges occurred without being as clearly unacceptable as at Wetzlar-Dalheim.

The argument may be pushed further yet. We can suspect that there would be quite a number of unreported cases, where the dates obtained by radiocarbon analysis were too old to be plausibly connected to iron production. Who would want to publish a 'sensational' Neolithic or early Bronze Age iron smelting activity in Central Europe? At the beginning of our research in the Lahn valley in 1999 we ourselves put aside a first and seemingly isolated far too early date from charcoal within a slag from a later Iron Age smithy site

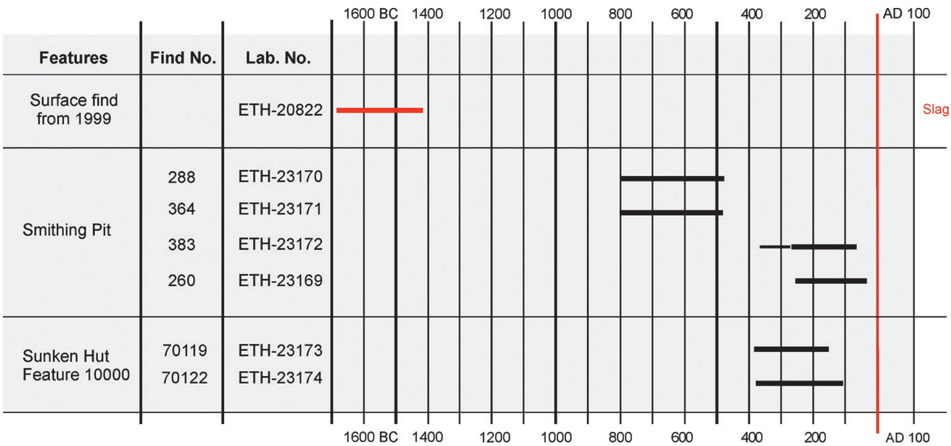

Fig. 11. Lahnau-Atzbach, Lahn-Dill-District, Germany (excavation 2000). Radiocarbon dates from a later Iron Age smithy with 2σ standard deviation (data from ETH Zurich [I. Hajdas, G. Bonani]).
Obr. 11. Lahnau-Atzbach, zemský okres Lahn-Dill, Německo (arch. výzkum 2000). Radiokarbonové datování (směrodatná odchylka 2σ) materiálu kovárny z mladší doby železné (data poskytl ETH Zurich [I. Hajdas, G. Bonani]).

at Lahnau-Atzbach, Lahn-Dill-District (*fig. 11*; cf. *Schäfer – Stöllner 2002*, 104, fig. 15). While we used the old-wood theory to explain two dates on the Hallstatt-Period calibration plateau (*Schäfer – Stöllner 2002*, 99 with note 42), we left aside the middle Bronze Age date from a small surface slag as somehow severely altered or contaminated. This example additionally raises the issue that the dating problem might also affect materials from iron working (smithing) contexts.

More than twenty years ago, a series of very old iron production sites in Sweden were published that astonished scholars at the time (*Hjärthner-Holdar 1993*). While we do not want to question the results in Sweden in general, it could be worth having a new and fresh approach to them, in the light of the new evidence presented here.

The last case study that we want to put forward adds a global perspective and sums up the inherent problems very well. It is concerned with medieval iron production of the Angkorian Khmer Period (9th–15th centuries AD) in Cambodia (*Hendrickson – Hua – Pryce 2013*). Here, analysis of in-slag charcoal was deliberately adopted to reconstruct the 'spatial history' of over a dozen iron smelting sites with substantial slag deposits within the 22 km² large temple complex Preah Khan in Preah Vihear province, Cambodia. The decision for the sampling strategy was identical to our own intentions at Wetzlar-Dalheim, trying to make sure to date the production process itself. At Preah Khan slag blocks or cakes were collected from the surface or upper edge of the slag heaps to date the end of the production sequence. Fifteen AMS ^{14}C results were obtained from twelve slag cakes, representing seven separate slag concentrations from four different sites (*fig. 12*). While the archaeological evidence presents itself rather uniformly (site topography and layout, typology of tuyères, slag cakes), the radiocarbon measurements cover a period of more than 600 years. Typically again, no concentration of any main production period may be seen, but rather a continuous flow, spanning the times from the early 11th to the mid-17th centuries AD (*Hendrickson –*

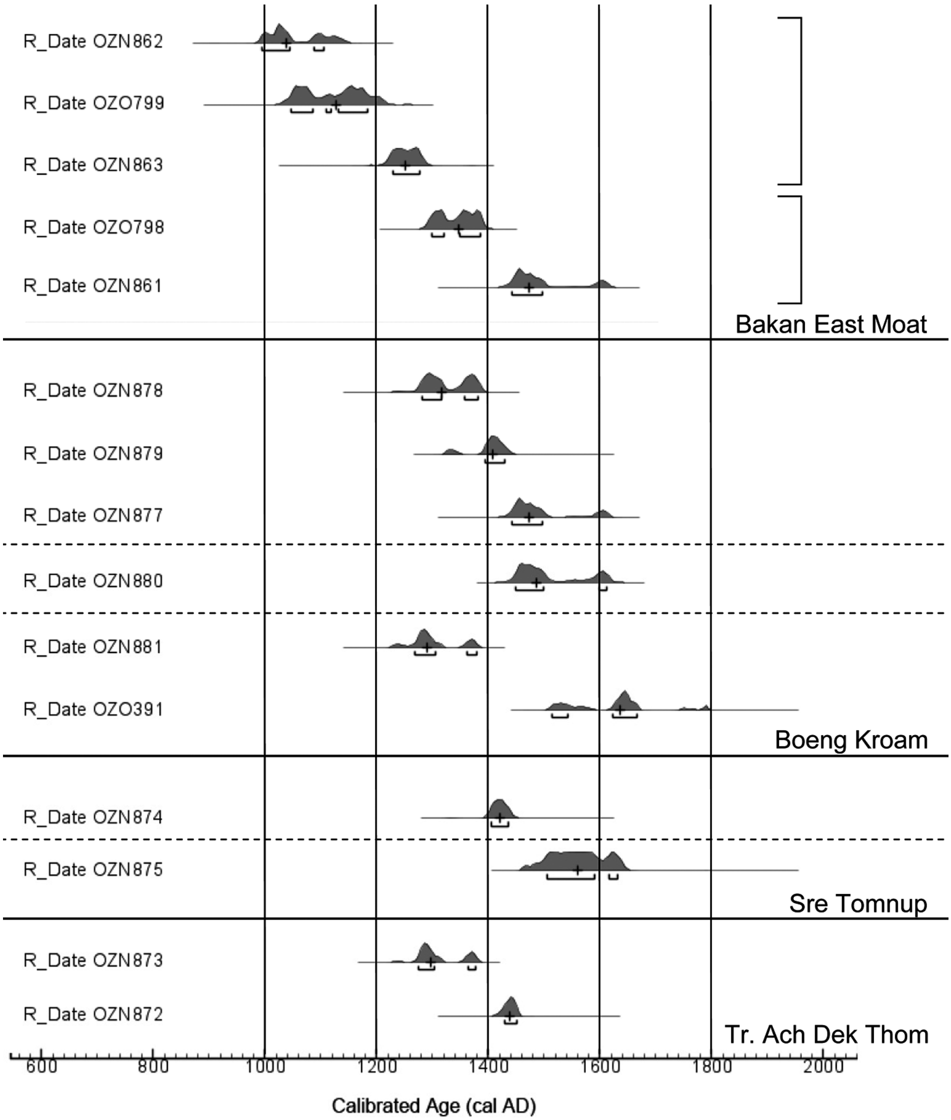

Fig. 12. Calibrated radiocarbon ages (2σ standard deviation) of in-slag charcoal samples from slag cakes of four bloomery production sites of the Angkorian Khmer Period at Preah Khan in Preah Vihear province, Cambodia (rearranged and altered after *Hendrickson – Hua – Pryce 2013*, 42, fig. 7).
Obr. 12. Kalibrované radiokarbonové stáří (směr. odchylka 2σ) vzorků dřevěného uhlí zataveného v koláčích strusky ze čtyř lokalit s doklady železářské výroby v období „Angkorian Khmer“ v provincii Preah Vihear v Kambodži (upravené a pozměněné podle *Hendrickson – Hua – Pryce 2013*, 42, fig. 7).

Hua – Pryce 2013, 42, fig. 7). In two cases more than one sample was taken from an individual slag cake and the resulting dates all differed markedly from each other. The three most ancient dates of the published sequence even derive from within one single slag.

This last example can stand for a great many more that do show signs of 'something not being quite right' but are not as disastrous not to be explainable any more. What is more, the ageing effect for samples from the Middle Ages or the Post Medieval Period, when more ^{14}C is still available in the sample, might not be as marked as at older sites, so that a small amount of fossil carbon will not alter the sample too dramatically and render the result wholly impossible.

What are the possible sources of fossil carbon to cause the contamination? The examples listed above have shown that in some cases the radiocarbon datings match with the archaeologically derived dates and in some cases there are more or less severe differences. In our first example in the Roth valley (Bavarian Suebia), where we had matching results, it is evident that the local geology does not contain any calcium carbonate in the soils. The Central Lahn valley at Wetzlar-Dalheim, however, features a geology rich in limestone and loess. Both contain fossil carbon in high amounts. Under strongly reducing conditions and at temperatures above 900 °C calcium carbonate ($CaCO_3$) disintegrates completely into CaO and 2CO. The CaO will react with the slag and is not important for our dating problem.[6] With the carbon monoxide, however, we have a possible source of gaseous fossil carbon entering the slag smelting system. We do not know exactly what happens during the several hours within the semi-liquid slag block, but it seems to be enough time and the right conditions to cause a contamination with fossil carbon. The most likely source of calcium carbonate entering the furnace would be via the furnace wall/lining or coming in with the charge in regions with natural calcium carbonate resources. Incidentally in some regions the iron ore itself contains fossil carbon in the form of limestone, dolomite ($CaCO_3 \cdot MgCO_3$) or siderite ($FeCO_3$).

5. Conclusions

In recent years an ever growing number of seemingly old radiocarbon dates from bloomery sites have become known. The dating series from Wetzlar-Dalheim and the others discussed above have shown the inherent problems when dating charcoal samples from inside metallurgical slags. The problem is aggravated as datable archaeological material like pottery or small finds is often conspicuously absent at metallurgical sites especially from survey programmes and charcoal from slags may often be the only possibility to obtain a date.[7]

Our results suggest that radiocarbon analysis of in-slag charcoal samples should not be the first – let alone the only – choice, when dating bloomery sites.[8] It became apparent, that especially in regions with high fossil carbonates like in loess or limestone areas, severe problems with contamination during the ancient reduction process could have occurred.

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6 Yet, a considerable CaO content in the slag may reflect a contribution of calcium carbonate to the smelting process: cf. *Oinonen et al. 2009*, 878 f.

7 Cf. the survey find of a 13.6 kg slag block from Clemency 'Hansenbernsheck', Luxembourg, that morphologically belongs to a Roman Period slag pit furnace but yielded an Iron Age date (*Gassmann – Schäfer 2017*, 40 ff.; 46 fig. 37). In-slag charcoal samples of two slag tongues from the surface of a medieval slag heap in the vicinity at Clemency 'Lamerbierg' yielded disparate dates from cal 570–780 and cal AD 800–1020 respectively (*ibid.*, 46, fig. 37).

8 Contrary to *Park – Rehren 2011* and *Hendrickson – Hua – Pryce 2013*, 37.

Thus, such datings should be judged with great caution, all the more so when only isolated analyses of that kind are available for a site. As our second dating series from Wetzlar-Dalheim indicates charcoal samples from the bottom layer of a furnace base may be a better choice. The same probably applies for charcoal layers within slag heaps. For future investigations we suggest that more emphasis should be given to typological and technological studies to get further hints on the chronological differentiation. The value of a slag typology is still not widely recognised, but will in many cases be able to provide a technological and chronological framework for metallurgical complexes in a given region.

The methodological problem in radiocarbon dating from in-slag charcoal samples was discussed above with reference to the iron technology. But of course the same problems will occur with other metallurgical technologies, where slags were produced at high temperatures under strongly reducing conditions, like in copper, lead and silver smelting.

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