KNIFE WITH A GROOVE ON BOTH SIDES DEV 995 814 PR – FE ALLOY – EARLY MEDIEVAL TIMES – SWITZERLAND

Artefact name	Knife with a groove on both sides DEV 995 814 PR
Authors	Marianne. Senn (EMPA, Dübendorf, Zurich, Switzerland) & Christian. Degrigny (HE-Arc CR, Neuchâtel, Neuchâtel, Switzerland)
Url	/artefacts/326/

The object



Credit HE-Arc CR.

Fig. 1: Iron and steel knife (after Eschenlohr et al., 2007, 266 & 302),

Description and visual observation

Description of the artefact	Knife, with a groove on both sides of the blade spine (Fig. 1). Dimensions: L = 20.1cm; WT = 30g.
Type of artefact	Household implement
Origin	Settlement Develier, Courtételle, Jura, Switzerland
Recovering date	Excavated in 1995, farm 1
Chronology category	Early medieval times
chronology tpq	550 A.D.
chronology taq	750 A.D.
Chronology comment	550 _ 750 AD
Burial conditions / environment	Soil
Artefact location	Office de la Culture, Porrentruy, Jura
Owner	Office de la Culture, Porrentruy, Jura
Inv. number	DEV 995/814 PR
Recorded conservation data	Conserved between 1995 and 2000: desiccation below 80°C, mechanical cleaning, passivation with tannic acid and protection with Paraloid B72® (Eschenlohr et al. 2007, 75).

Complementary information

Nothing to report.

This work is licensed under CC BY-NC-ND 4.0

Study area(s)



Credit HE-Arc CR.

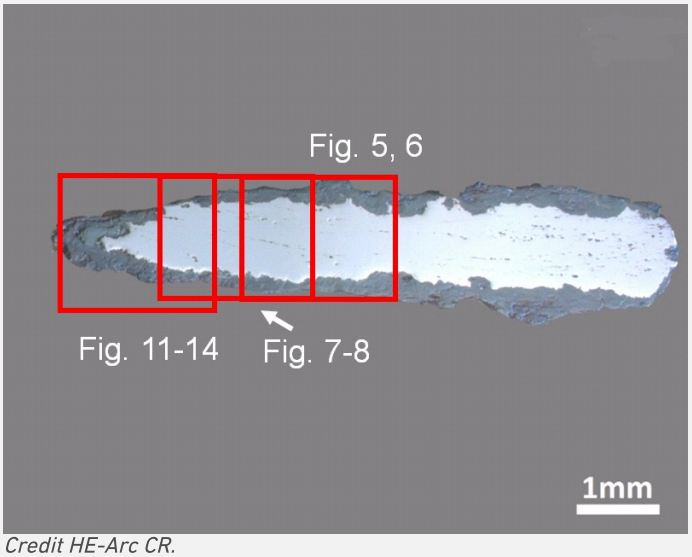
Fig. 2: Location of sampling area,

Binocular observation and representation of the corrosion structure

Stratigraphic representation: none.

MiCorr stratigraphy(ies) – Bi

Sample(s)



Credit HE-Arc CR.

Fig. 3: Micrograph of the cross-section showing the location of Figs. 5 to 8 and 11 to 14,

Description of sample	The cross-section shows a cut through the tip of the knife (Fig. 2). The metal is surrounded by thick corrosion products (Fig. 3). Dimensions: L = 8mm; Wmax. = 2mm.
Alloy	Fe Alloy
Technology	Hot worked, composite of two wrought iron bars, tip cemented, quench-hardened and tempered
Lab number of sample	DEV 814
Sample location	Empa (Marianne Senn)
Responsible institution	Office de la Culture, Porrentruy, Jura
Date and aim of sampling	2000, metallography and chemical composition of the metal

This work is licensed under CC BY-NC-ND 4.0

Complementary information

Nothing to report.

Analyses and results

Analyses performed:
Metallography (nital etched after etching with Oberhoffer's reagent), Vickers hardness testing, LA-ICP-MS, SEM/EDS.

Non invasive analysis

Metal

The remaining metal consists of two forged wrought iron bars, one of which includes a carburized tip (M1, Table 1). They are separated by a welding seam (M2, Figs. 9 and 10). The ferritic part (M3) is Cu-rich, whereas the carburized tip has a low and medium content of trace elements (Table 1). The metal contains elongated slag inclusions (Fig. 5) showing a structure of wüstite (FeO) in a glassy matrix (Fig. 6 and Table 2). Most of the slag inclusions are arranged in rows, marking the welding seam (Figs. 5 and 9) and following the forging direction. Their chemical composition differs in the Mn content (Table 2): the latter is higher in the slag inclusions of the carburized tip. The high P content of the slag in the ferritic part must be noted since the metal in general has a medium P content (Tables 1 and 2). Etching with Oberhoffer's reagent solution makes the P distribution visible (Fig. 10). Dark areas are depleted of P whereas P-rich zones, such as those found in the welding seam, appear in white. After nital etching, the very fine steel microstructure of the tip shows the transition from hypoeutectoid to eutectoid steel (ferrite component in white and pearlite component in black, partly bainite, Figs. 7, 8 and 9). The body of the knife is made of wrought iron with an annealed, irregular ferritic structure (Figs. 7 and 8). The average hardness of the wrought iron (HV1 130) is a little higher than expected, whereas the hardness of steel in the hypoeutectoid-eutectoid tip (HV1 360) is an indication of quench-hardening followed by tempering.

Elements	V	Cr	Mn	P	Co	Ni	Cu	As	Ag	Ni/Co	C* mass%
Body M3 (median of 2 similar analyses) mg/kg	<	<	7	400	60	20	1300	300	<	0.3	0/0.2
Tip - M1 (median of 7 similar analyses) mg/kg	<	4	100	500	40	70	400	70	<	1.8	0.8
Detection limit mg/kg	0.7	2	0.4	68	0.4	3	2	0.8	0.4		
RSD1 %	-	26	95	92	9	3	79	24			
RSD2 %	-	-	112	42	13	26	20	47			

*visually estimated

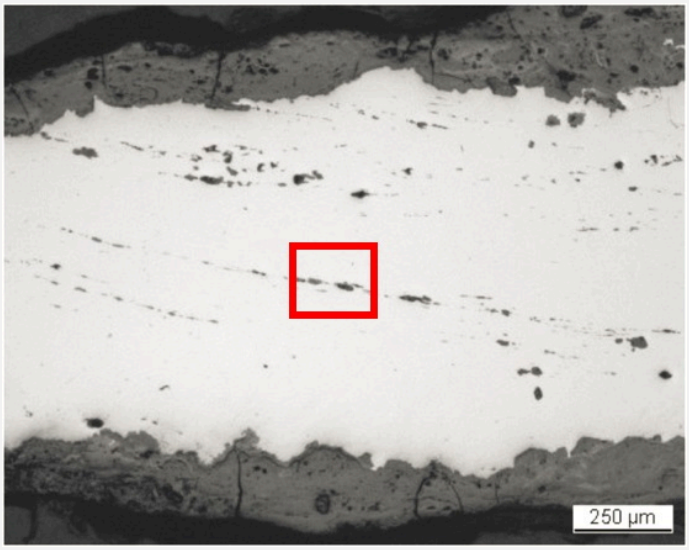
Table 1: Chemical composition of the metal. Method of analysis: LA-ICP-MS, Laboratory of Analytical Chemistry, Empa (for details see Devos et al. 2000).

Location	Environment	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	FeO	Total	SiO_2/Al_2O_3
Glass	Pearlite, tip	0.7	<	9.8	72	<	6.2	3.3	0.9	1.7	8.9	104	7.3
n. d.	Pearlite, tip	<	<	3.5	34	<	1.5	1.1	<	1.0	65	107	9.8
n. d.	Ferrite (average of 4 similar analyses), body	<	0.9	3.8	30	1.2	1.5	1.6	<	<	64	104	7.8
n. d.	Ferrite, body	<	<	1.5	14	<	0.7	0.6	<	<	88	105	9.3

n. d. = structure not determined

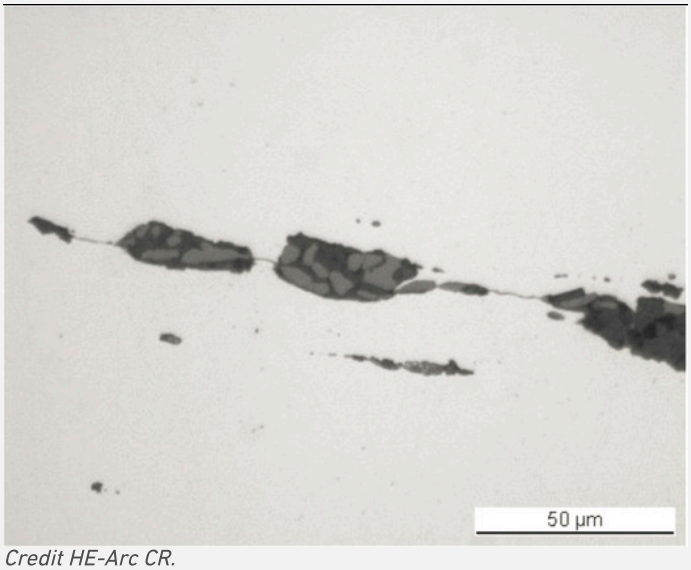
Table 2: Chemical composition of the slag inclusions (mass%) at the tip (pearlite) and the body (ferrite) of the knife. Method of analysis: SEM/EDS, Laboratory of Analytical Chemistry, Empa.

This work is licensed under CC BY-NC-ND 4.0



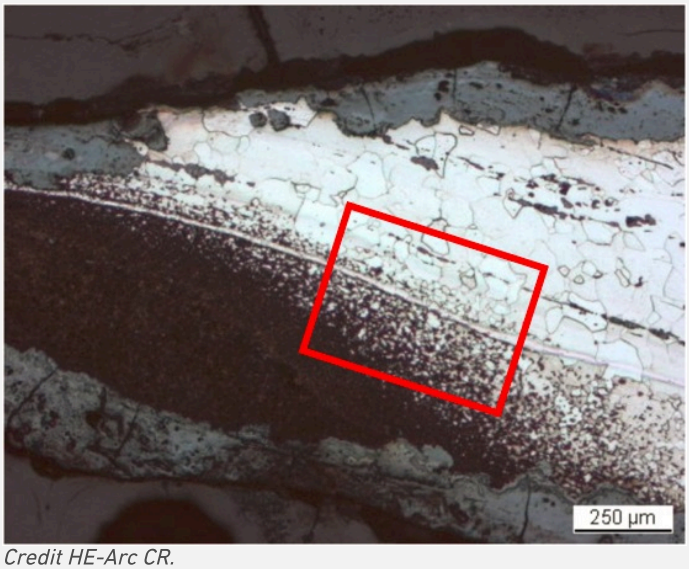
Credit HE-Arc CR.

Fig. 5: Micrograph of the metal sample from Fig. 3 (detail), unetched, bright field. In white the metal, in light-grey the slag inclusions and the corrosion layer. The micrograph of Fig. 6 is marked by a rectangle,



Credit HE-Arc CR.

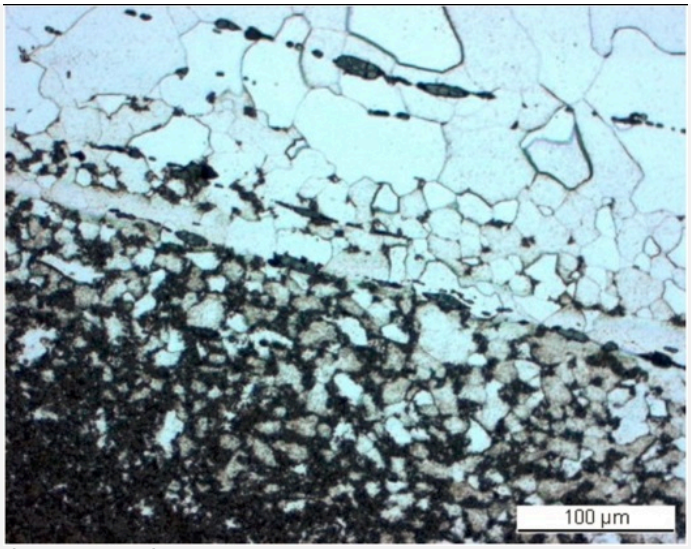
Fig. 6: Micrograph (detail of Fig. 5), unetched, bright field. The slag inclusions have a structure of wüstite dendrites (light-grey) in a glassy matrix (dark-grey),



Credit HE-Arc CR.

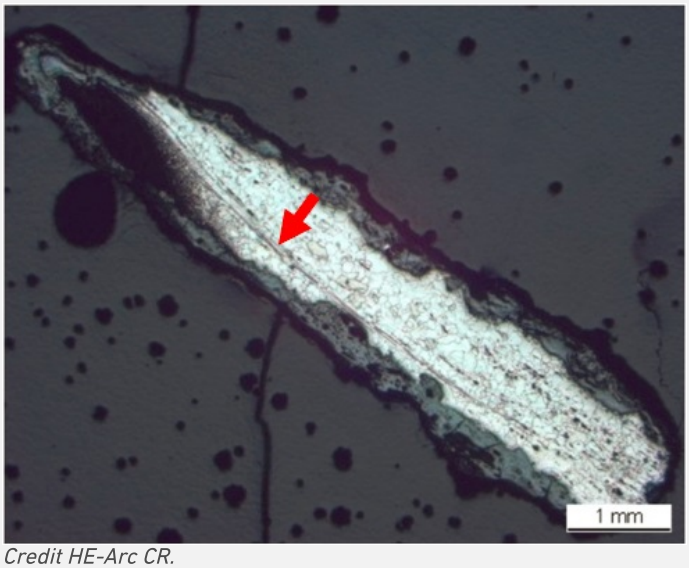
Fig. 7: Micrograph of the metal sample from Fig. 3 (detail), nital etched, bright field. In white we observe the ferrite, in black or dark-grey the pearlite and bainite. The micrograph of Fig. 8 is marked by a rectangle,

This work is licensed under CC BY-NC-ND 4.0



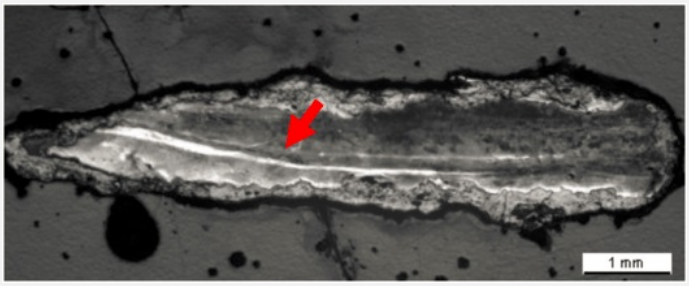
Credit HE-Arc CR.

Fig. 8: Micrograph (detail of Fig. 7), nital etched, bright field,



Credit HE-Arc CR.

Fig. 9: Micrograph of the metal sample from Fig. 3 (rotated by 45°), nital etched, bright field. In white we observe the ferrite, in black or dark-grey the pearlite. The red arrow shows the welding seam,



Credit HE-Arc CR.

Fig. 10. Micrograph of the metal sample from Fig. 3, etched with Oberhoffer's reagent. The welding seam appears in white (red arrow),

Microstructure	Recrystallized grain structure
First metal element	Fe
Other metal elements	C, P, Cu

Complementary information

Nothing to report.

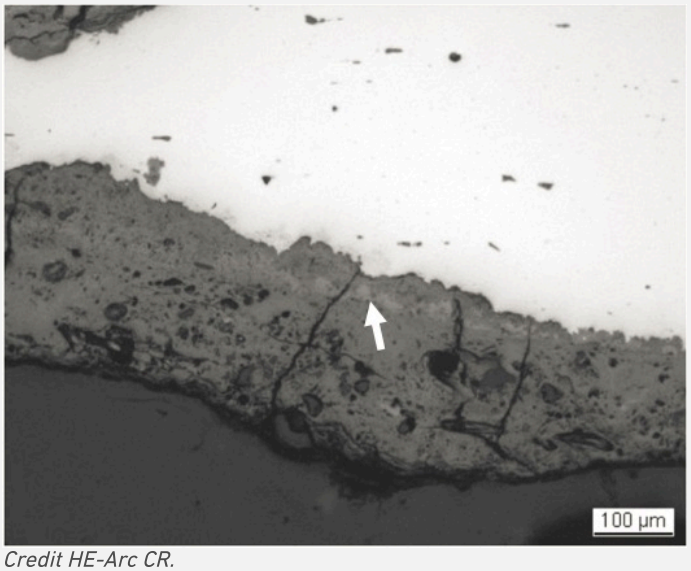
Corrosion layers

This work is licensed under CC BY-NC-ND 4.0

The metal - corrosion products interface is irregular (Figs. 3, 5 and 11) and the average thickness of the corrosion crust is 200µm. In bright field, the corrosion appears grey, rather heterogeneous and heavily cracked. A thin light-grey layer (indicated by an arrow in Fig. 11) can be detected. Under polarised light the corrosion is more clearly stratified, the thin layer mentioned before is black (CP3) and surrounded by dark-brown (CP2) and orange-red (CP1) corrosion layers (Figs. 12 and 13). It contains less O (magnetite or hematite?) than the orange-brown corrosion products (iron hydroxides?) (Table 3 and Fig. 14). The outer corrosion layer (covering the aforementioned thin black layer) contains external markers such as quartz grains and other rock fragments (Ca, Fig. 14). The shape of the blade is preserved in the corrosion crust (Fig. 14, arrows on the SEM image). The absence of P, an external marker, highlights where the limit of the original surface was located (interface CP1 / CP2).

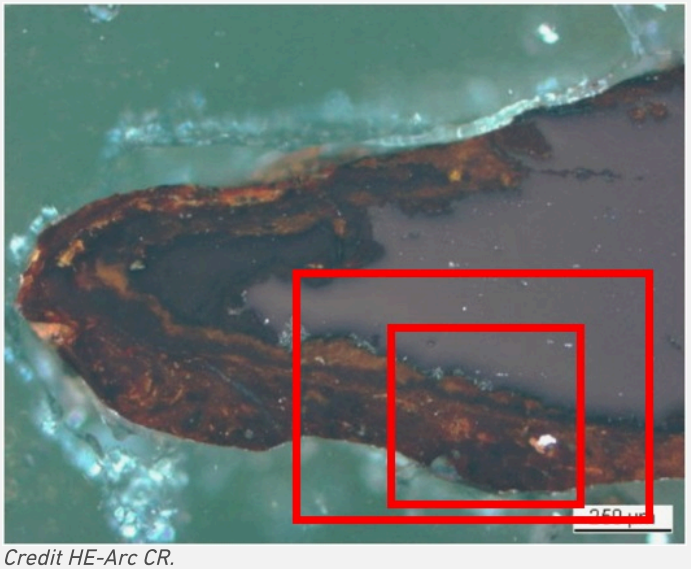
Elements	O	Si	P	Ca	Fe	Total
Black layer (CP3)	26	<	<	<	69	95
Dark-brown corrosion products (average of 3 similar analyses) (CP2)	29	<	<	<	63	92
Red / orange corrosion products (CP1)	32	1.4	1.1	0.7	56	92

Table 3: Chemical composition (mass %) of the corrosion layer (from Fig. 13). Method of analysis: SEM/EDS, Laboratory of Analytical Chemistry, Empa.



Credit HE-Arc CR.

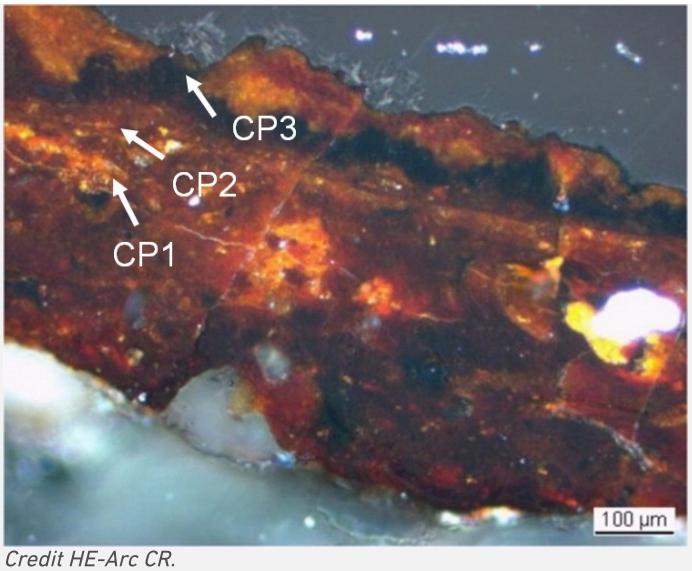
Fig. 11: Micrograph showing the metal - corrosion crust interface from Fig. 3 (detail of Fig. 12), unetched, bright field. The heterogeneous and heavily cracked corrosion layer appears grey enclosing a light-grey layer (indicated by an arrow),



Credit HE-Arc CR.

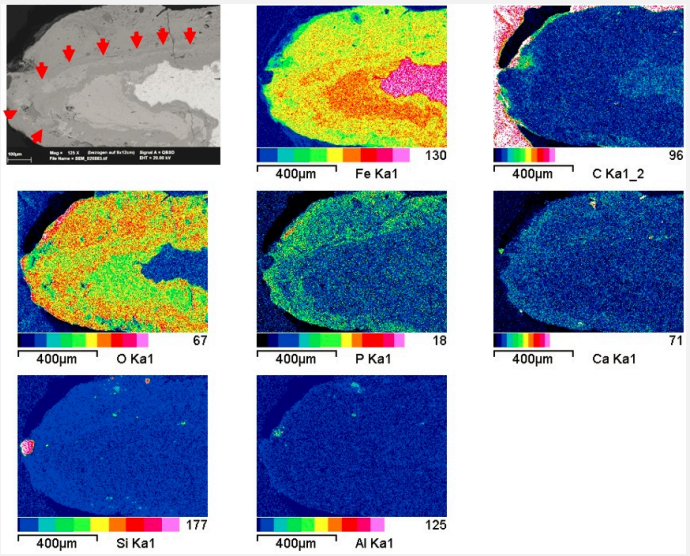
Fig. 12: Micrograph showing the metal - corrosion crust interface from Fig. 3 (detail) unetched, polarised light. The micrographs of Fig. 11 and Fig. 13 are marked by the large and small rectangles respectively. The light-grey layer of Fig. 11 (arrow) appears black whereas the rest of the corrosion layer is brown, red and orange,

This work is licensed under CC BY-NC-ND 4.0



Credit HE-Arc CR.

Fig. 13: Micrograph (detail from Fig. 12) corresponding to the stratigraphy of Fig. 4, unetched, polarised light. The black corrosion layer next to the metal surface corresponds to the light-grey layer indicated with an arrow on Fig. 11,



Credit Empa.

Fig. 14: SEM image, BSE-mode, and elemental chemical distribution of the selected area from Fig. 12 (inversed picture, detail). Method of examination: SEM/EDS, Laboratory of Analytical Chemistry, Empa,

Corrosion form	Uniform - transgranular
Corrosion type	?

Complementary information

Nothing to report.

MiCorr stratigraphy(ies) – CS

This work is licensed under CC BY-NC-ND 4.0

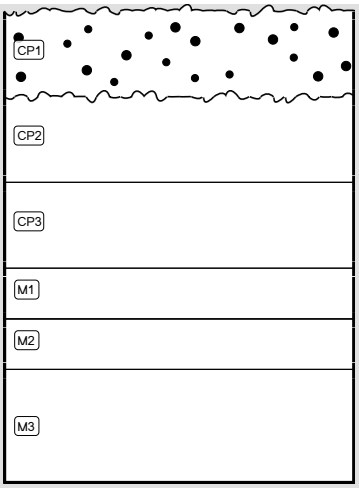


Fig. 4: Stratigraphic representation of the object in cross-section using the MiCorr application. This representation can be compared to Fig. 13.

Synthesis of the binocular / cross-section examination of the corrosion structure

Corrected stratigraphic representation: none.

Conclusion

The knife is forged from two wrought iron bars which have been welded together. The tip is carburized. The recrystallized structure of the ferrite is probably the consequence of tempering the tip. The metal compositions of both alloys differ from the one worked in the forges of Develier-Courtételle (Eschenlohr et al. 2007, 71). For this reason this well worked knife is identified as an importation to the early medieval village Develier-Courtételle. The limit of the original surface (limitos) is still preserved within the remaining corrosion layers. Chemically it can be located at the interface of the P-rich outer corrosion layer and the P-poor inner corrosion products. Visually it can be located by the presence of sediments in the outer corrosion layers and most likely by the hardness and coloration of the inner corrosion products (magnetite?). It is an example of a terrestrial corrosion crust.

References

References on object and sample

References object

1. Eschenlohr, L., Friedli, V., Robert-Charrue Linder, C., Senn, M. (2007) Develier-Courtételle. Un habitat mérovingien. Métallurgie du fer et mobilier métallique. Cahier d'archéologie jurassienne 14 (Porrentruy), 302.

References sample

2. Eschenlohr, L., Friedli, V., Robert-Charrue Linder, C., Senn, M. (2007) Develier-Courtételle. Un habitat mérovingien. Métallurgie du fer et mobilier métallique. Cahier d'archéologie jurassienne 14 (Porrentruy), 266.

References on analytic methods and interpretation

This work is licensed under CC BY-NC-ND 4.0