CORRODED METAL SHEET FN 655.13.01 – FE ALLOY – MODERN TIMES – SWITZERLAND

Artefact name	Corroded metal sheet FN 655.13.01
Authors	Marianne. Senn (EMPA, Dübendorf, Zurich, Switzerland) & Christian. Degrigny (HE-Arc CR, Neuchâtel, Neuchâtel, Switzerland)
Url	/artefacts/696/

The object

Credit HE-Arc CR.

Fig. 1: Metal sheet (after Senn Bischofberger 2005, 137),

Description and visual observation

Description of the artefact	Metal (iron-based) sheet with middle rib. The shape is no longer discernible (Fig. 1). The metal is covered by a thick corrosion crust. Dimensions: L = 4.5cm; WT = 35g.
Type of artefact	Iron (and steel) sheet
Origin	Steinmöri, Neftenbach / Dorf Neftenbach, Zurich, Switzerland
Recovering date	Excavation of the Roman villa, 1986-1990, phase S2, StbII.2 (2nd/3rd century AD)
Chronology category	Modern Times
chronology tpq	1900 A.D.
chronology taq	2000 A.D.
Chronology comment	Product of the 20th century AD introduced accidentally into a Roman layer
Burial conditions / environment	Soil
Artefact location	Kantonsarchäologie, Dübendorf, Zurich
Owner	Kantonsarchäologie, Dübendorf, Zurich

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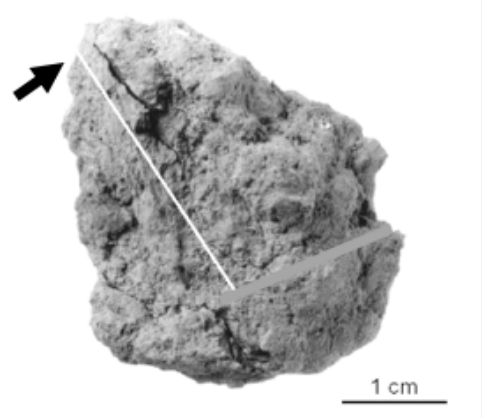
Inv. number	FN 655.13.01
Recorded conservation data	Not conserved

Complementary information

Nothing to report.

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)

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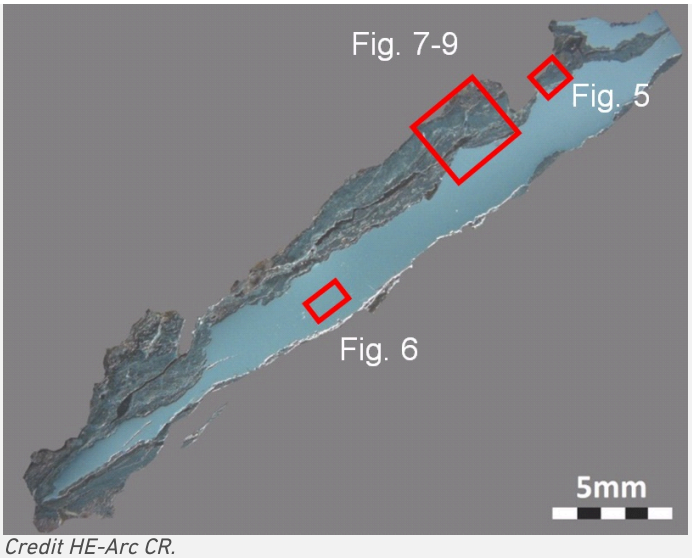

Credit HE-Arc CR.

Fig. 3: Micrograph of the cross-section of the iron-based sheet showing the location of Figs. 5 to 9,

Description of sample	A longitudinal cut has been made through the sheet (Fig. 2). Large parts of the corrosion crust fell off during sampling (Fig. 3).
Alloy	Fe Alloy
Technology	Forged with final cold work
Lab number of sample	NEF 655
Sample location	Empa (Marianne Senn)
Responsible institution	Kantonsarchäologie, Dübendorf, Zurich
Date and aim of sampling	2000, metallography

Complementary information

Nothing to report.

Analyses and results

Analyses performed:
Metallography (nital etched), Vickers hardness testing, LA-ICP-MS, SEM/EDS.

Non invasive analysis

Metal

The remaining metal is an iron containing elevated (more than 1g/kg) concentrations of Co and Ni (Table 1), small round slag inclusions and cracks resulting from corrosion and deformation (Fig. 5). The composition of the round, elongated slag inclusions is similar to wüstite-FeO (Table 2). Iron reduced in the direct smelting process never contains such pure compounds and only FeO inclusions. In modern steels FeO occurs in low carbon alloys and Armco-iron (Schumann 1991, 474). After etching, the cross-section shows a heavily deformed ferritic microstructure from cold working (Fig. 6). The cracks have the same orientation as the deformation. The average hardness of the metal is HV1 195.

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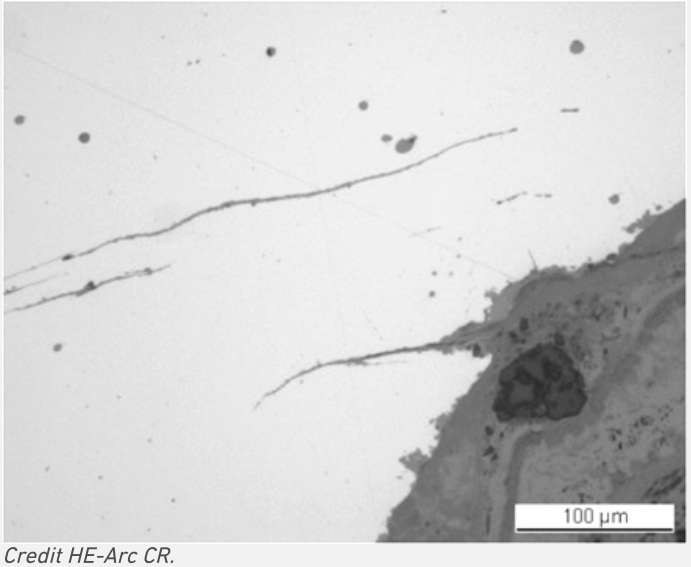
Elements	Al	Ti	V	Cr	Mn	P	Co	Ni	Cu	As	Mo	Ag	Sn	Sb	W	Ni/Co
Median, mg/kg	<	<	<	<	20	300	1100	1200	800	200	<	<	60	10	<	1.1
RSD %	-	-	-	-	3	17	6	5	35	15	13	-	35	45	-	4
Detection limit mg/kg	6	9	19	17	2	77	1	4	2	3	3	1	1	1	3	-

Table 1: Chemical composition of the iron. Method of analysis: LA-ICP-MS, Lab of Inorganic Chemistry, ETH.

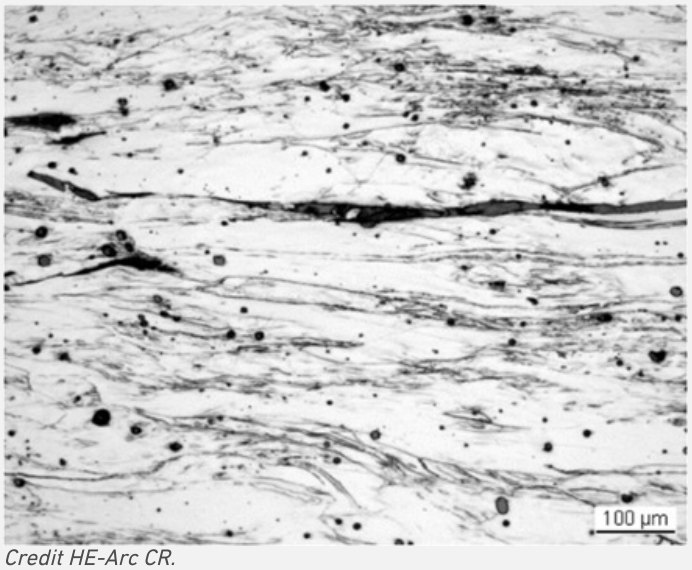
Elements	O	Fe	Total
Round inclusion 1	21	75	96
Round inclusion 2	20	74	95
Round inclusion 3	20	75	96
Round inclusion 4	20	73	93

Table 2: Chemical composition (mass %) of some of the round inclusions of Fig. 5. Method of analysis: SEM/EDS, Laboratory of Analytical Chemistry, Empa.



Credit HE-Arc CR.

Fig. 5: Micrograph of metal sample from Fig. 3 (inverted picture, detail), unetched, bright field. In white the metal with round slag inclusions as well as cracks filled with corrosion products,



Credit HE-Arc CR.

Fig. 6: Micrograph of metal sample from Fig. 3 (detail), etched, bright field. The heavily cold worked metal shows elongated grains with nearly invisible grain boundaries and cracks parallel to the grains,

Microstructure Heavily deformed ferritic microstructure

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First metal element	Fe
Other metal elements	Co, Ni

Complementary information

Nothing to report.

Corrosion layers

The corrosion is massive and large parts of the outer corrosion layers have been lost during the sample preparation. The heavily cracked corrosion crust represents about one third of the thickness of the sample (Fig. 3) and is located on one side of the metal (the rest having been lost during the cutting process). It does not show well defined layers. Despite this, three areas can be distinguished (Figs. 7 and 8). Adhering to the metal (area 1), we find an orange-red-brown layer enriched in Cl (CP3 in Fig. 4, Fig. 9 and Table 3). The dark or violet middle area 2 is richer in Fe (CP2 in Fig. 4). The outer area 3 is red-brown (CP1 in Fig. 4) and strongly contaminated by soil material (rock fragment inclusion and elements like Si, Al, P etc.). This layer is enriched in O (Fig. 9).

Elements	Location	O	Na	Al	Si	P	Cl	Fe	Cu	Mo	Total
Area 1 (CP3)	Dark-brown	31	<	<	<	<	<	67	<	<	99
	Dark-brown	35	<	<	<	<	0.7	64	<	<	100
	Red-brown	38	<	<	<	<	2.2	64	<	0.6	104
	Red-brown	36	<	<	<	<	3.3	67	<	<	106
	Red-brown	39	<	<	<	<	1.3	63	<	<	104
	Orange-brown	35	1.3	<	<	<	<	61	<	<	98
Area 2 (CP2)	Orange-brown	31	<	<	<	<	0.7	63	<	<	95
	Violet-brown	30	<	<	<	<	<	75	0.8	1.0	108
	Brown	30	<	<	<	<	<	77	<	0.6	108
	Violet-brown	35	<	<	<	<	<	68	<	<	103
	Yellow	33	<	<	<	<	<	67	<	<	100
	Violet-brown	32	<	<	<	<	<	74	<	<	106
Area 3 (CP1)	Quartz inclusion	54	<	<	52	<	<	<	<	<	106
	Mixture brown	42	<	<	1.6	0.7	<	58	<	<	102
	Mixture brown	39	<	1.9	4.3	<	<	56	<	<	102
	Mixture brown	35	<	<	0.9	<	<	59	<	<	95

Table 3: Chemical composition (mass %) of the corrosion products from near the metal (area 1, CP3) to the outer surface (area 3, CP1). Method of analysis: SEM/EDS, Laboratory of Analytical Chemistry, Empa.

Corrosion form	Uniform - transgranular
Corrosion type	?

Complementary information

Nothing to report.

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MiCorr stratigraphy(ies) – CS

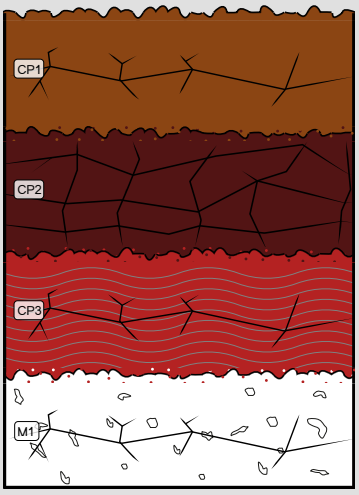

Fig. 4: Stratigraphic representation of the iron-based sheet in cross-section (dark field) using the MiCorr application. The characteristics of the strata are only accessible by clicking on the drawing that redirects you to the search tool by stratigraphy representation. This representation can be compared to Figs. 7 and 8, Credit HE-Arc CR.

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

Corrected stratigraphic representation: none.

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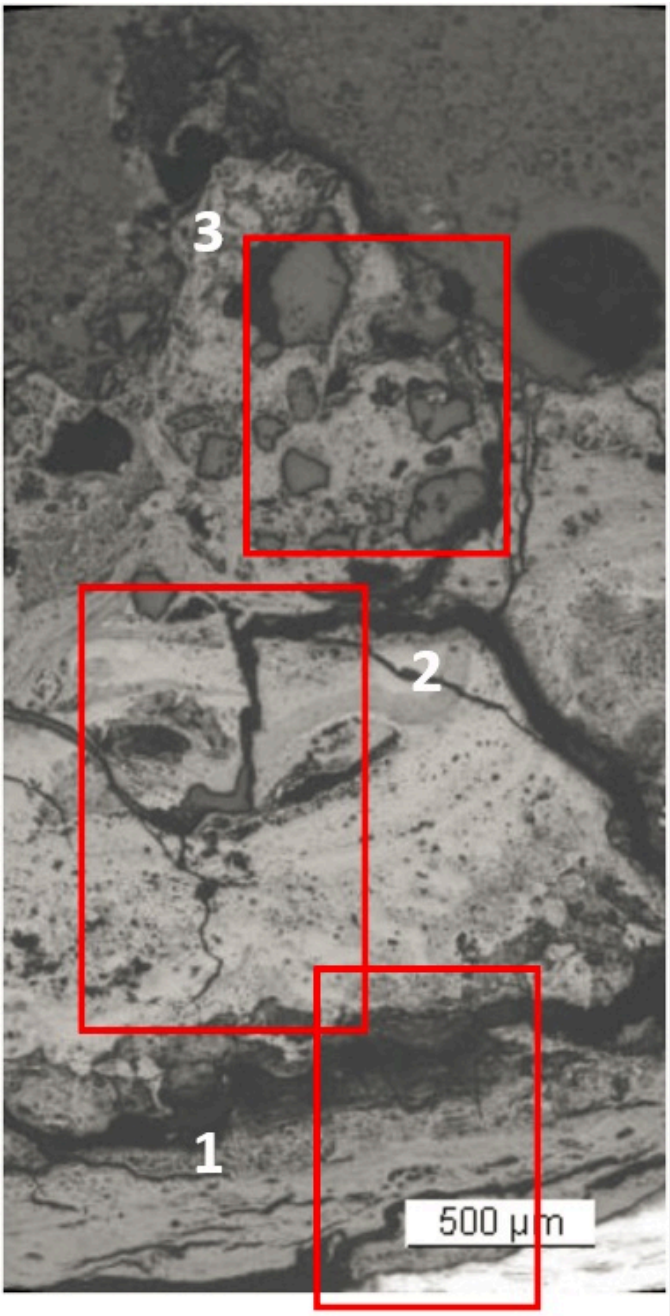

Credit HE-Arc CR.

Fig. 7: Micrograph of the corrosion layer from Fig. 3 showing the metal - corrosion crust interface (detail, rotated by 45°) and corresponding to the stratigraphy of Fig. 4, unetched, bright field. The areas 1 (for CP3), 2 (for CP2) and 3 (for CP3) selected for elemental chemical distribution (Fig. 9) are marked by red rectangles,

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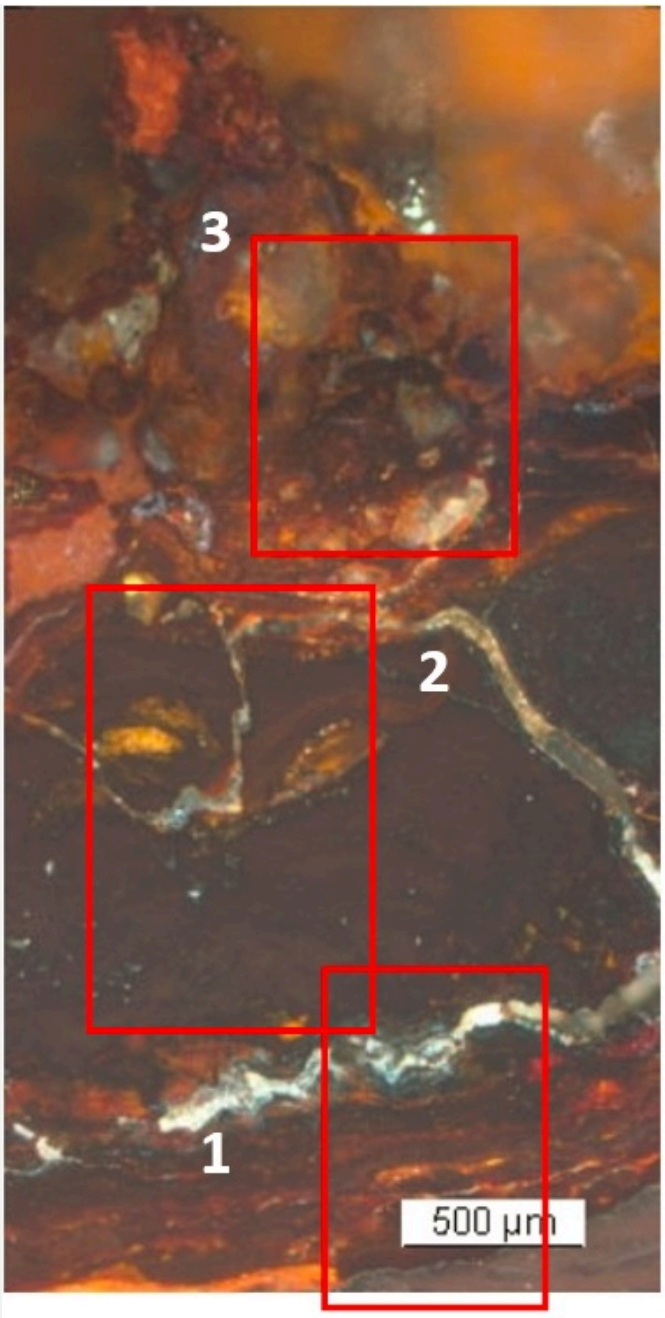

Credit HE-Arc CR.

Fig. 8: Micrograph (same as Fig.7) and corresponding to the stratigraphy of Fig. 4, polarised light. The inner layer (CP3) is red-brown, area 2 is brown-violet (CP2) and the outer pale brown area contains rock fragment inclusions (CP1),

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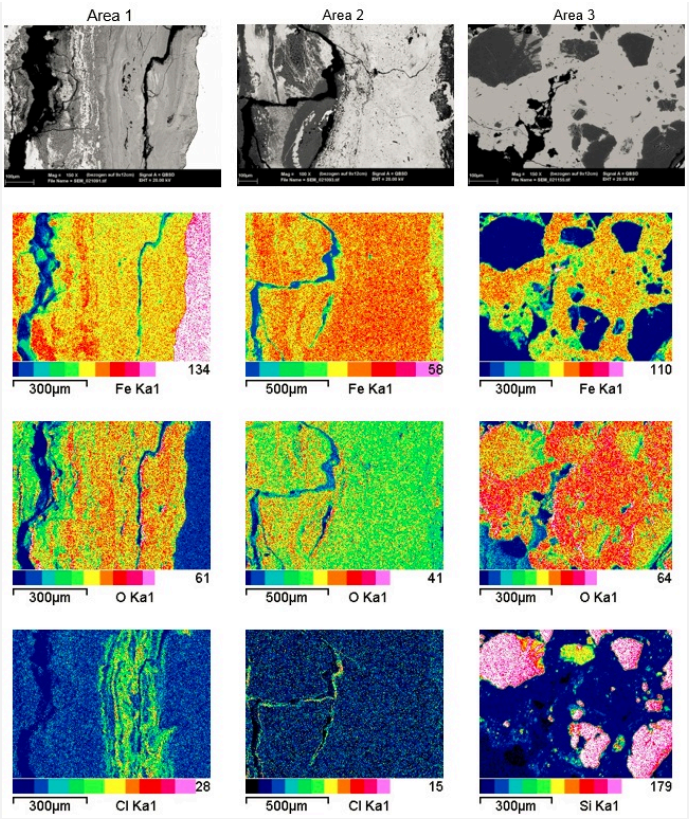

Credit Empa.

Fig. 9: SEM images, BSE-mode, and elemental chemical distribution of the selected areas from Figs. 7 and 8 (reversed picture rotated by 270°, details). First column: mapping on area 1 (CP3) where an inner layer enriched in Cl appears near the metal surface. 2nd column: area 2 (CP2) where iron oxides prevail. 3rd column: area 3 (CP1) where the outer O-rich layer includes rock fragments rich in Si. Method of examination: SEM/EDS, Lab. Anal. Chem. Empa,

Conclusion

This iron-based sheet is entirely cold worked and hard compared to an annealed metal. The corrosion is massive and masks the shape of the object. The presence of Cl adjacent to the metal surface indicates that the corrosion front is potentially active. The very thick top corrosion layers may have slowed down the corrosion. The object was mentioned as being Roman in Senn Bischofberger 2005, however the chemical composition of the slag inclusions shows that it is a product of the 20th century AD which has been accidentally introduced into a Roman layer.

References

References on object and sample

References object

1. Rychener, J. (1999) Der römische Gutshof in Neftenbach. Katalog, Tafeln und Tabellen. Monographien der Kantonsarchäologie Zürich 31/2 (Zürich und Egg), 138.

References sample

2. Senn Bischofberger, M. (2005) Das Schmiedehandwerk im nordalpinen Raum von der Eisenzeit bis ins frühe Mittelalter. Internationale Archäologie, Naturwissenschaft und Technologie Bd. 5, (Rahden/Westf.), 137-138.

References on analytic methods and interpretation

3. Schumann, H. (1991) Metallographie. Leipzig.

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