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The oldest steel in the world?

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Introduction

- The main perturbations associated with massive steel canisters are:
  - failure through corrosion
  - hydrogen gas production due to anaerobic corrosion
  - redox changes around the canister (bentonite) following canister failure

- Historically (e.g. NWGCT, 1984), the safety case Base Case corrosion rate estimates were from a mix of short-term* lab experiments, natural (rare) and archaeological analogues

*when compared to the assessment periods

Introduction

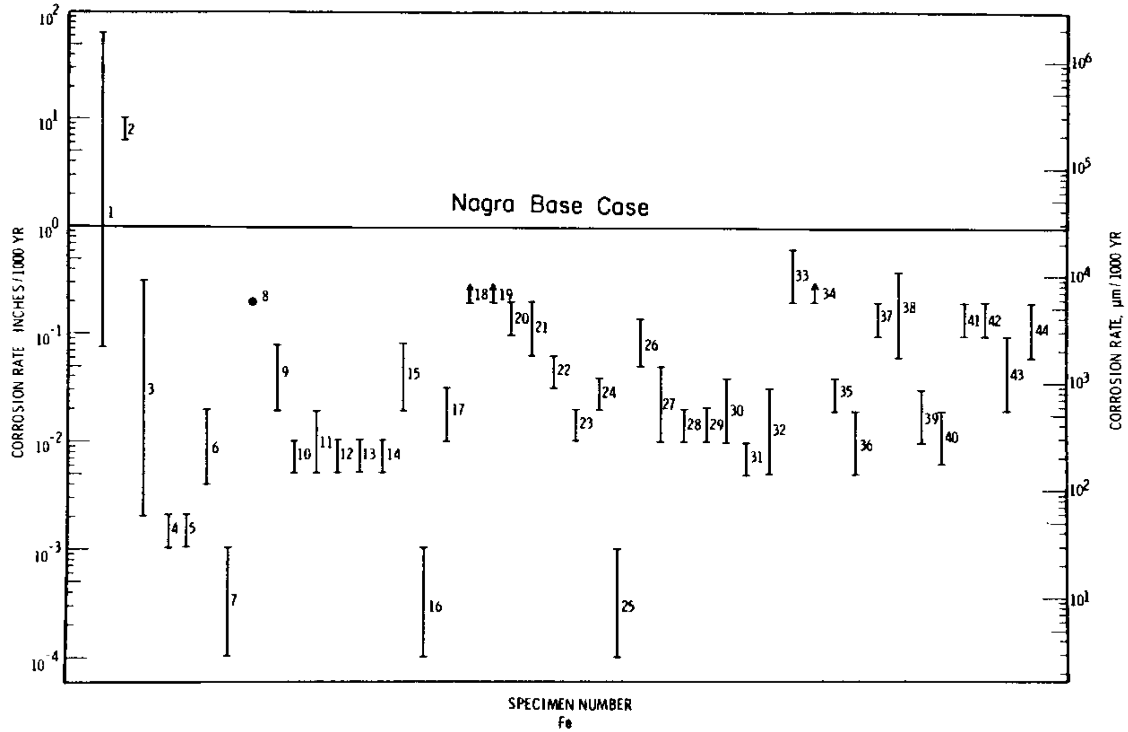
Form of data	Corrosion depth (per 1000 a)	Reference (see abstract)	Comments
Short-term lab	31.8 mm	[2]	**Uniform corrosion of carbon steel. Base Case value**
Short-term lab	29 mm	[4]	**Conservative corrosion rate, including an allowance for pitting. Base Case value**
Natural analogue	0.09×10^{-3} mm	[5, 6]	**Weathering of native iron in basalt (Disko Island)**
Archaeological analogue	10 mm	Range of studies cited in [1]	**Uniform corrosion of iron and steel**
Archaeological analogue	<15 mm	Range of studies cited in [2]	**Uniform corrosion of iron and steel**
Archaeological analogue	0.1 - 10	[7]	**Literature review of corrosion of archaeological samples**
Archaeological analogue	**<10 mm**	**Range of studies cited in [3]**	**Uniform corrosion of iron and steel**

Limitations I

- **Many of the metals (such as stainless steel, metallic titanium, Inconel and Zircaloy) which will be used in repositories have been produced only in recent times they have no direct counterparts in nature or in archaeology**
- **Archaeological analogues are potentially prone to bias if they focus on metal samples from museum collections because museums will (naturally) tend to house the best preserved artefacts**
- **This sample bias problem is likely to be less important if artefacts are collected *in situ*, rather than from a museum, for then it would be possible to see artefacts in all possible corrosion states for that environment**

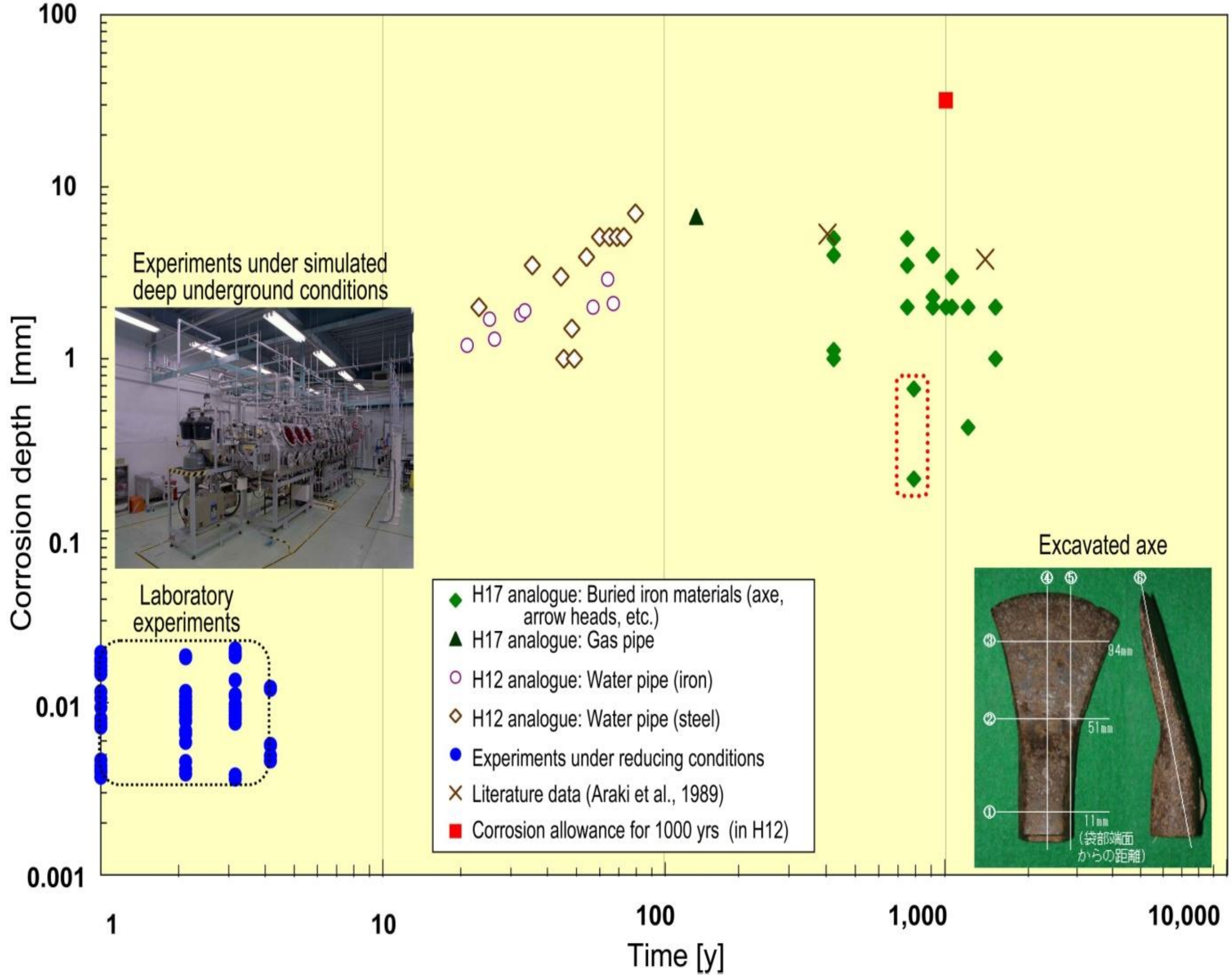
Limitations II

- **Most of the metals examined were iron, not steel**



Limitations III

- When steel has been examined, the materials tend to be rather young (0.1 – 1 ka)
- Arguably OK as Nagra only looks for 1 ka



Is older possible? Iron….

- **The Inchtuthil iron nails were the oldest (2 ka) assessed in these studies, but the first signs of iron use come from Ancient Egypt and Sumer where, around 6 ka ago, small items, such as the tips of spears and ornaments, were being fashioned from iron recovered from meteorites**

- **Oldest known samples of smelted iron are small lumps found at copper-smelting sites on the Sinai Peninsula, dated to about 5 ka ago**

- **But the analogy arguably remains weak insofar that the archaeological materials are iron and not steel**

Is older possible? Steel….

- **Forms of steel were being made in China around 2.3 ka ago and high quality steels reportedly first appeared in Sri Lanka by 2.2 ka ago**

- **More recently, steel artefacts have been reported from an Iron Age settlement in Scotland which was occupied between 2.2-2.8 ka ago, making these possibly the oldest steel materials found to date**

Broxmouth Hillfort, Scotland

Image courtesy RCAHMS

Broxmouth Hillfort, Scotland

Broxmouth Hillfort excavation was a rescue project, necessary when a new cement works and limestone quarry were built

Images courtesy RCAHMS

Broxmouth Hillfort, Scotland

- **Broxmouth was occupied from the early Iron Age right through to its abandonment during Roman occupation, nearly 1 ka later**
- **Remarkably well-preserved roundhouses, elaborate hill fort entrances and an exceptionally rare Iron Age cemetery are among the discoveries made there**

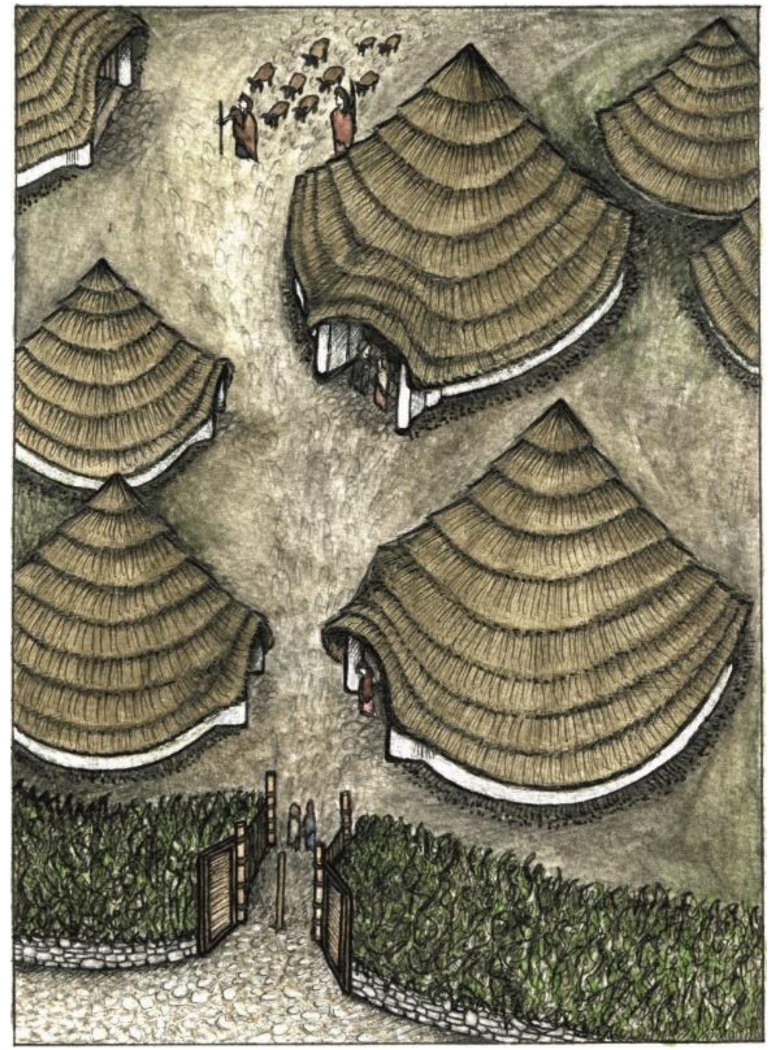


Image courtesy Historic Scotland

Broxmouth Hillfort, Scotland

- Resources available at the time of the excavation in the 1970s were limited so full analysis of the material collected only took place in 2008 and final reporting only occurred in 2013!
- The new analysis of metal artefacts dated them to 2.4 – 2.5 ka ago
- The high-carbon steel is earliest evidence of sophisticated blacksmithing skills in the UK
- Oldest steel in the world?

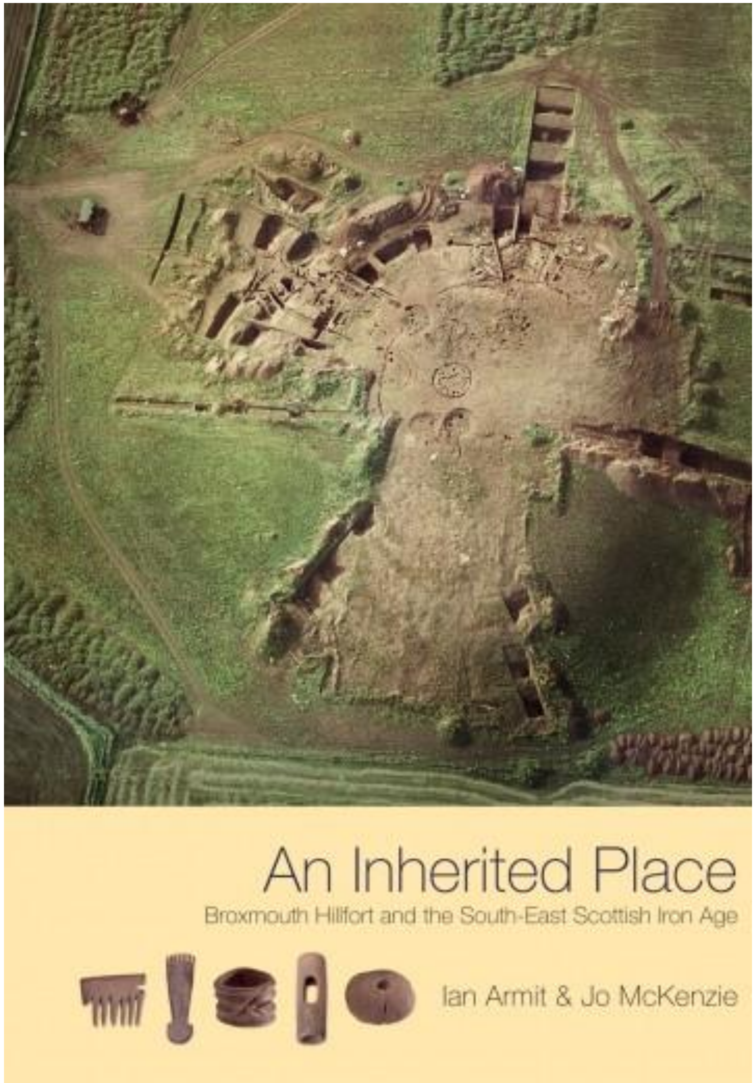


Image courtesy Society of Antiquaries of Scotland

Steel artefacts analysed

A range of steel artefacts have been analysed, including:

- **jewellery (e.g. rings, brooches, cloak pins)**
- **metal bars and wires (to be reworked elsewhere)**
- **tools (e.g. tangs, punches, handles)**
- **weapons (e.g. spear ends)**
- **fittings (e.g. nails, tacks, staples)**

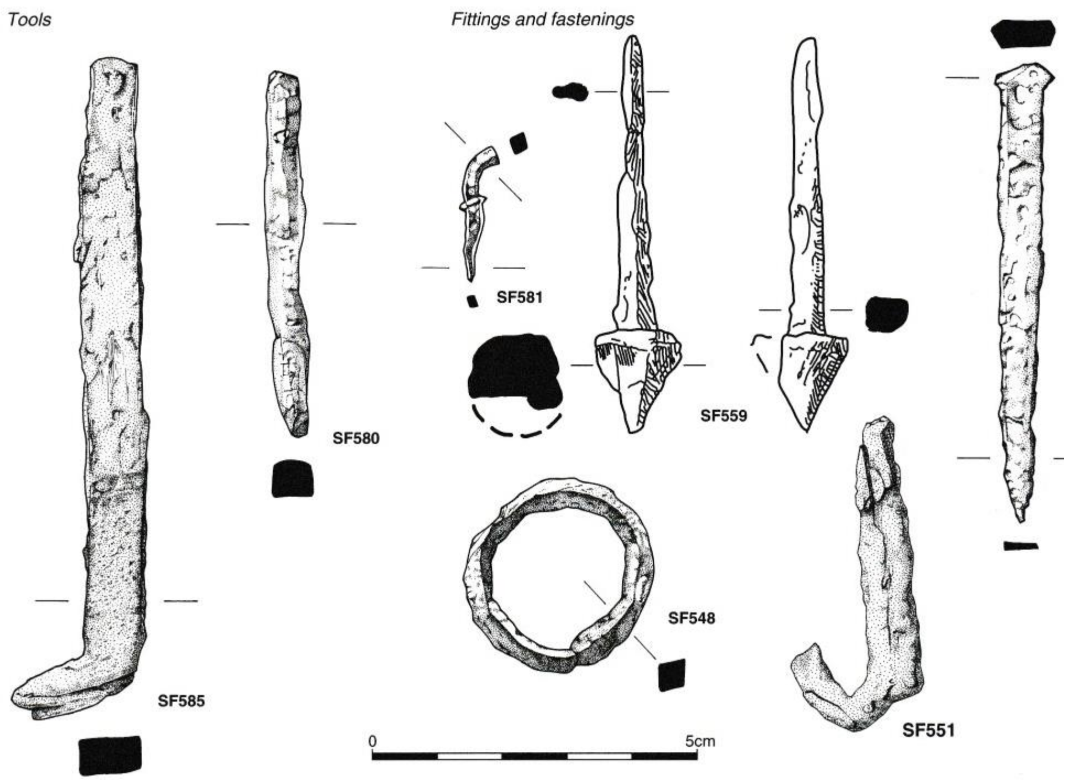


Image courtesy Society of Antiquaries of Scotland

Steel artefacts analysed

They were collected from a range of sources, including:

- **house post holes**
- **defensive ditches**
- **middens**
- **fort entrance gates**
- **roadways**

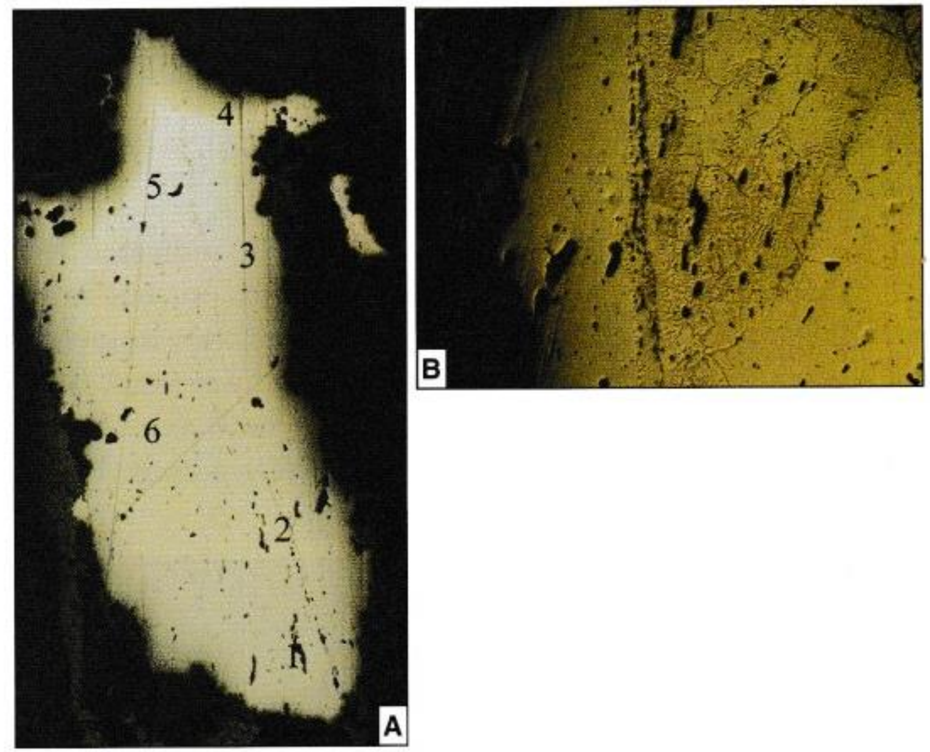
and from a range of ages across the period of occupation of the site

But note, it is stated in the report that "The selected artefacts (*for analysis*) were among the best-preserved objects in the assemblage…"

Example steel artefacts I

Steel tang (chisel)

- heavily corroded, but pristine core remains
- slag inclusions have corroded preferentially
- ‘weld’ lines obvious
- shown to be (cold) manufactured from phosphoric iron (0.7-0.9% P)



A unetched B etched

Image courtesy Society of Antiquaries of Scotland

Example steel artefacts II

Unidentified fragment

- unetched is clean metal with little slag
- where present, slag inclusions have corroded significantly
- artefact made from high carbon steel which has been heat-treated and quenched

A unetched B etched

Image courtesy Society of Antiquaries of Scotland

Example steel artefacts III

Tool

- **unetched is corroded, mainly following the slag inclusions**
- **artefact made from phosphoric iron, so is harder than ferritic iriôn, but not as hard as heat-treated medium-high carbon steel**

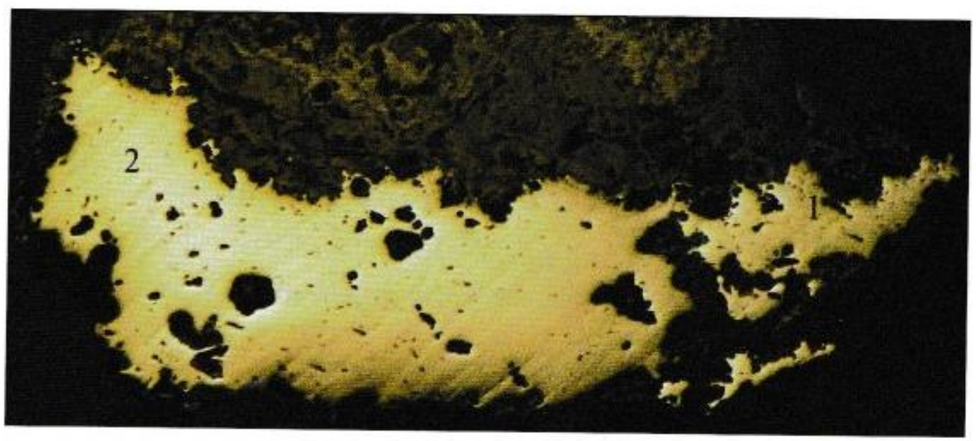


Illustration 10.60
SF566: unetched cross-section.

Image courtesy Society of Antiquaries of Scotland

Conclusions

- possibly the world's oldest steel artefacts identified in a site in the UK: ca. 2.4-2.5 ka old
- collected from a range of burial environments across the site, some aerobic, some anaerobic
- artefacts had a range of uses from jewellery to tools to stock metal bar, produced by reworking of different types of iron
- enough background data for quantitative use?
- enough background data for qualitative use/communication?

Further reading

- [1] Nagra (1994). Kristallin-1. Safety assessment report. Nagra Technical Report Series NTB 93-22, Nagra, Wettingen, Switzerland.
- [2] JNC (2000). H12: Second progress report on R&D for the geological disposal of HLW in Japan. JNC TN1410 2000-001, JAEA, Tokai, Japan.
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- [5] Hellmuth, K-H. (1991). The existence of native iron - implications for nuclear waste management, Part I: evidence from existing knowledge. Finnish Centre for Radiation and Nuclear Safety, STUK-B-VALO 67, Helsinki, Finland.
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- [7] David, D. (2001). Analogues archéologiques et corrosion. Andra Report, Chatenay-Malabry, France (*in French*).
- [8] Tylecote, R.F. (1992). A History of Metallurgy. Institute of Materials, London, UK. ISBN 0901462888
- [9] Juleff, G. (1996). An ancient wind-powered iron smelting technology in Sri Lanka, Nature, 379, 60-63.
- [10] Armit, I. & McKenzie, J. (2013). An inherited place: Broxmaouth Hillfort and the south-east Scottish Iron Age. Society of Antiquaries of Scotland, Edinburgh, UK.