NAWG-18, 9-11th June, 2026
University of Manchester, UK

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

Examples of older corrosion studies

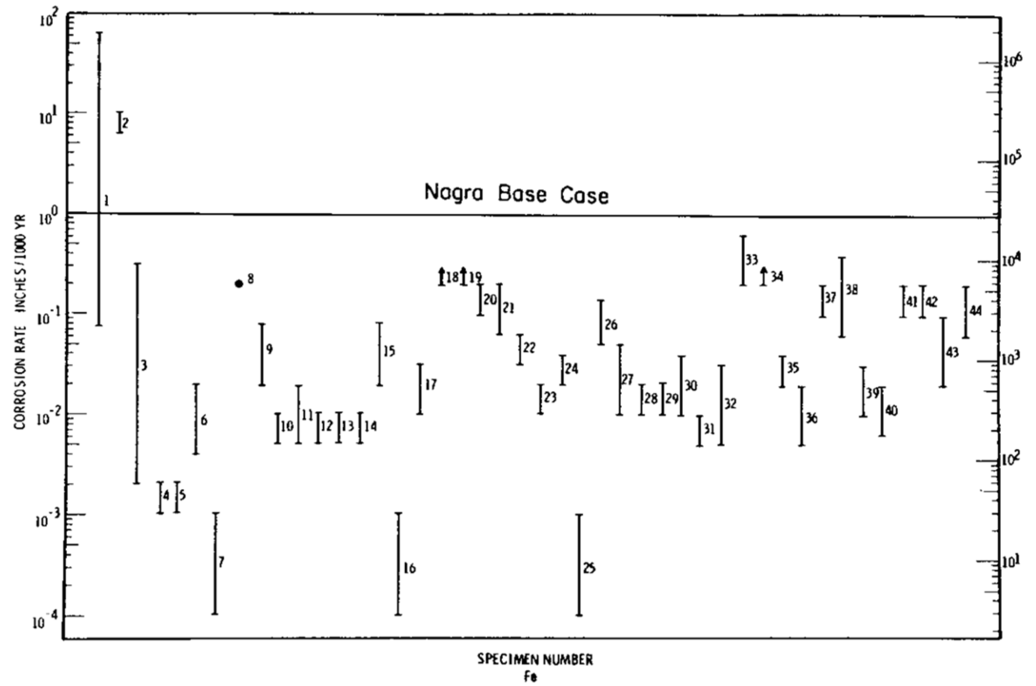
Form of data	Corrosion depth (per 1ka)	Reference	Comments
Short-term lab	31.8 mm	[2]	**Uniform corrosion of carbon steel. Base Case value**
Short-term lab	29 mm	[4]	**Conservative corrosion rate, including pitting. Base Case value**
Natural analogue	0.09×10^{-3} mm	[5, 6]	**Weathering of native iron 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

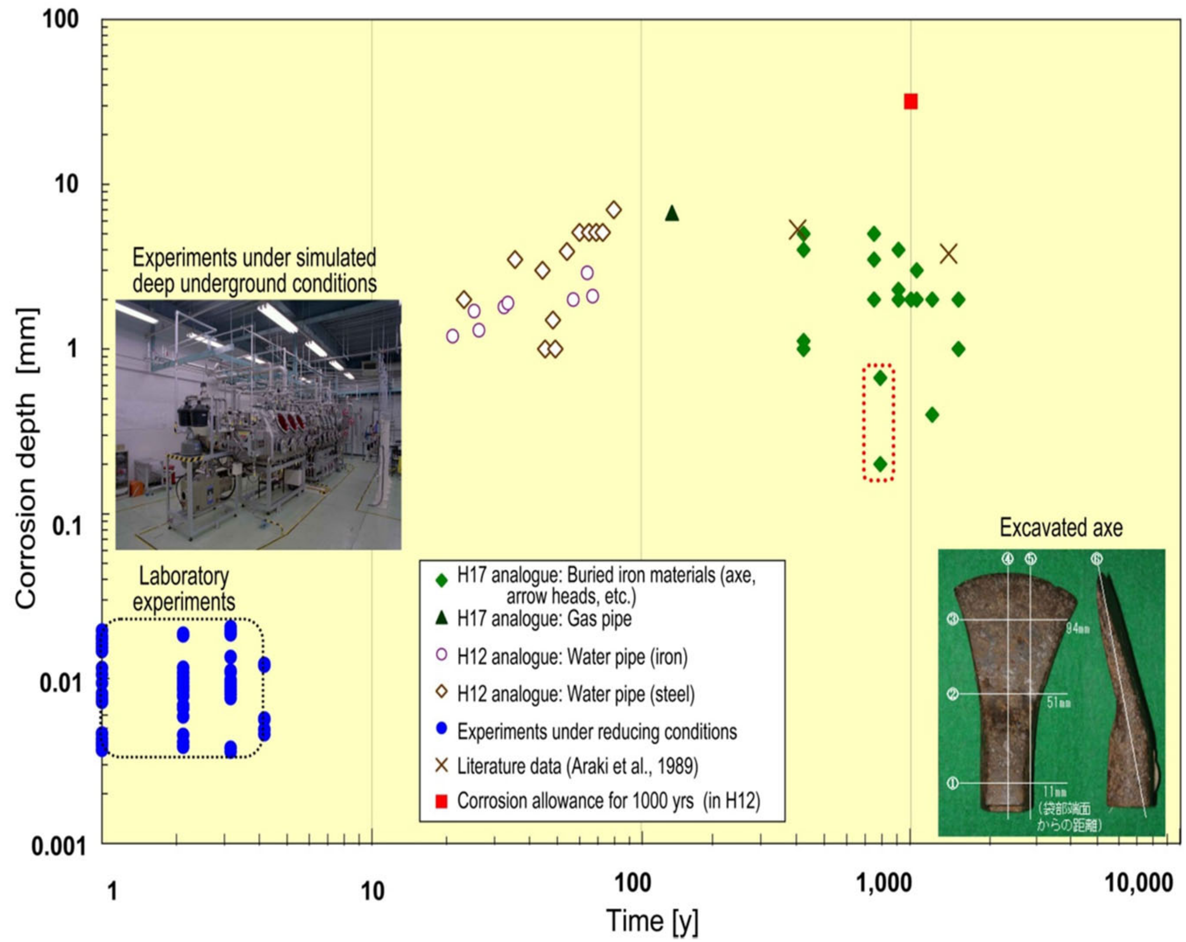
Limitations II

- Most of the metals examined to date were iron, not steel



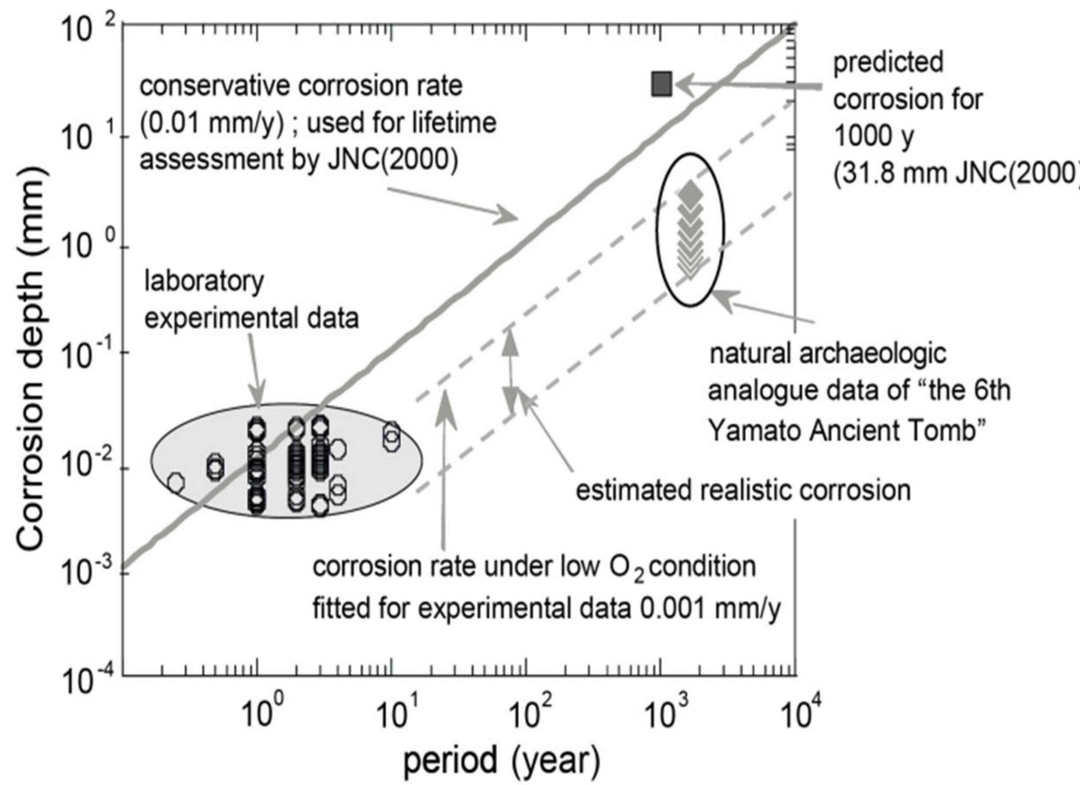
Limitations III

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



Limitations III

- The range of “estimated realistic corrosion” depths proposed by the authors is equivalent to a corrosion rate of 0.3 – 2.0 mmka-1 after 10,000 years [8].
- In comparison, the range of long-term anaerobic corrosion rates for carbon steel estimated from experimental studies in compacted bentonite is 0.026 – 0.7 mmka-1 [9]



Comparison of the time-dependence of the depth of corrosion from laboratory experiments and from iron objects from a 1.5 ka analogue site in Japan [8]

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 [10]
- Oldest known samples of smelted iron are small lumps found at copper-smelting sites on the Sinai Peninsula, dated to about 5 ka ago
- In their latest safety case [cf. 9], Nagra uses evidence from analogue studies to support canister lifetimes predictions and is a partner in a study of artefacts from the Aventicum Roman site near Avenches, Switzerland. Iron-based artefacts, such as nails, are being studied as part of the Corint (Elucidating Corrosion of Iron by New Quantitative Multimodal In Situ Tomography [11]) project with the aims of developing new methodologies for characterisation of artefacts in an undisturbed state, understanding the long-term corrosion mechanisms and developing improved conservation methods for archaeological artefacts.
- But the analogy arguably remains weak insofar that the archaeological materials are iron and not steel

Is older possible? Steel….

- The oldest known steel (ca. 3.8 ka) is from a site in Turkey (Kaman-Kalehoyuk, ca. 100 km SE of Ankara) and was produced incidentally during iron smelting [12] and indirect evidence exists for 2.9 ka steel in Spain [13].
- 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 [14]

- More recently, steel artefacts have been reported from an Iron Age settlement in Scotland [15] which was occupied between 2.2-2.8 ka ago, making these possibly the oldest steel materials found to date

Broxmouth Hillfort, Scotland [15]

Image courtesy RCAHMS

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Broxmouth Hillfort, Scotland

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

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?

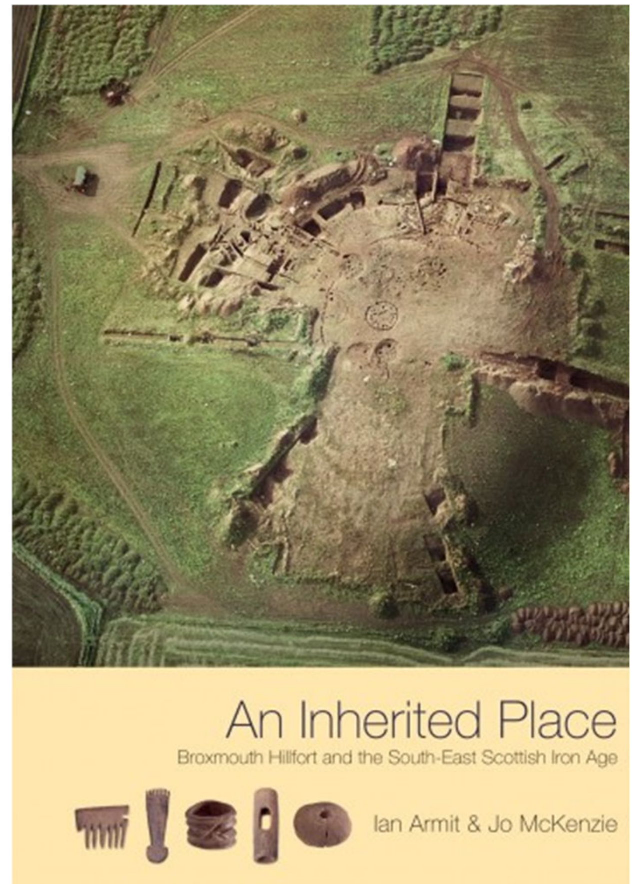


Image courtesy Society of Antiquaries of Scotland

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)

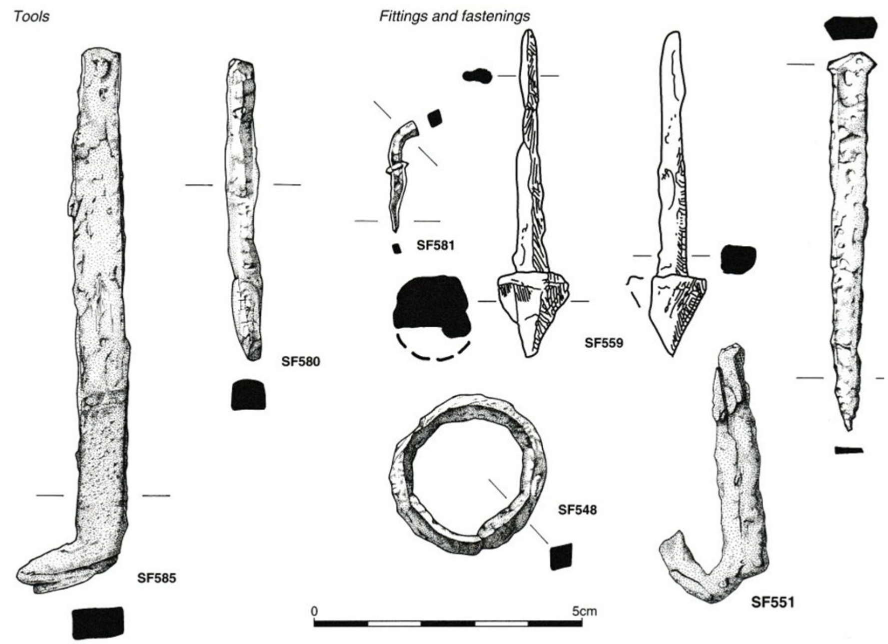


Image courtesy Society of Antiquaries of Scotland

Steel artefacts analysed

- They were collected from a range of sources, including:
  - house post holes
  - defensive ditches
  - middens
  - fort entrance gates
  - roadways
- Note, it is stated in the report that "The selected artefacts (*for analysis*) were among the best-preserved objects in the assemblage..."
- Note also that the finds were from a range of ages across the period of occupation of the site (suggesting they were not thought particularly valuable)

Example steel artefacts I

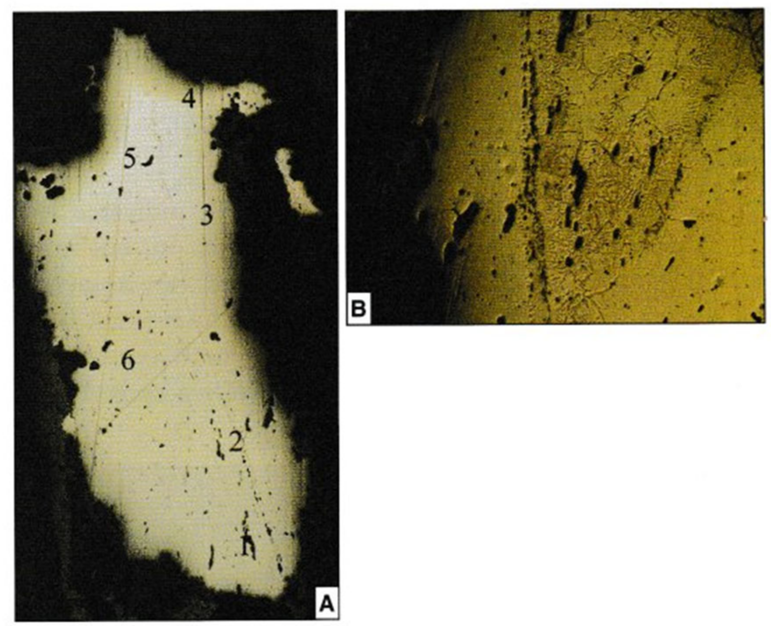
- Steel tang (chisel)

➢ 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 iron, but not as hard as heat-treated medium-high carbon steel

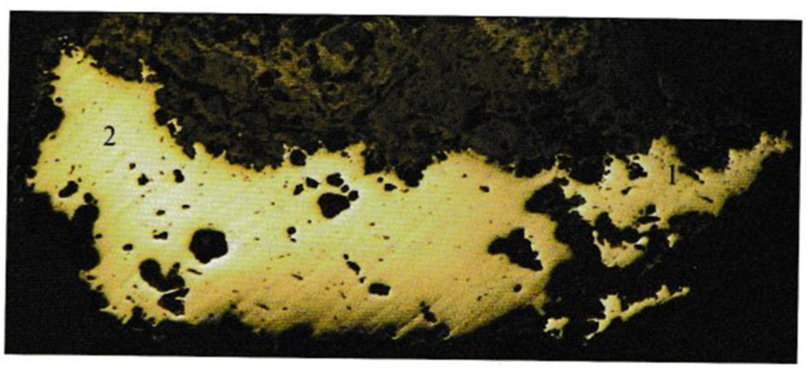


Illustration 10.60
SF566: unetched cross-section.

Image courtesy Society of Antiquaries of Scotland

Conclusions - overview

- 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?

Conclusions – is this the oldest steel in the world?

- No, it is clearly not....

- The fact that the steel artefacts (of wide-ranging utility, from weapons to tools to jewellery) were found carelessly discarded across the site implies they were not thought of as particularly valuable by the site inhabitants

- This suggests that such steel artefacts should be present at other similar (neighbouring?) sites of a similar age: is it worth getting in on the ground floor with a soon-to-be initiated archaeologocal study of nearby and/or similarly aged sites to produce SC relevant data on steel longevity?

References

- [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.
- [3] JNC (2005). H17: Development and management of the technical knowledge base for the geological disposal of HLW - Knowledge Management Report JNC TN1400 2005-022, JAEA, Tokai, Japan.
- [4] NWGCT (Nagra Working Group on Container Technology) (1984). An assessment of the corrosion resistance of the high-level waste containers proposed by Nagra. Nagra Technical Report Series NTB 84-32, Nagra, Wettingen, Switzerland.
- [5] Hellmuth, K-H. (1991a). 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.
- [6] Hellmuth, K-H. (1991b). The existence of native iron - implications for nuclear waste management, Part II: evidence from investigation of samples of native iron. Finnish Centre for Radiation and Nuclear Safety, STUK-B-VALO 68, Helsinki, Finland.
- [7] David, D. (2001). Analogues archéologiques et corrosion. Andra Report, Chatenay-Malabry, France (*in French*).
- [8] Yoshikawa, H., Gunji, E. & Tokuda, M. (2008): Long term stability of iron for more than 1500 years indicated by archaeological samples from the Yamato 6th tumulus. Journal of Nuclear Materials 379/1-3, 112-117. DOI: 10.1016/j.jnucmat.2008.06.009.
- [9] Diomidis, N., Janin, Y.J. et al. (2024). Design and Performance Assessment of HLW Disposal Canisters. Nagra Technical Report Series NTB 24-20, Nagra, Wettingen, Switzerland.
- [10] Tylecote, R.F. (1992). A History of Metallurgy. Institute of Materials, London, UK. ISBN 0901462888
- [11] CORINT: Elucidating corrosion of iron by new quantitative multimodal in-situ tomography https://corrosion-corint.ch/
- [12] Daily Yomiuri Online , 14 May 2005. Yomiuri Shimbun Holdings, Tokyo, Japan.
- [13] Gonzalez, R.A., Asmus, B. et al. (2023). Stone-working and the earliest steel in Iberia: scientific analyses and experimental replications of final bronze age stelae and tools. J. Archaeol. Sci. 152, 105742.
- [14] Juleff, G. (1996). An ancient wind-powered iron smelting technology in Sri Lanka, Nature, 379, 60-63.
- [15] Armit, I. & McKenzie, J. (2013). An inherited place: Broxmouth Hillfort and the south-east Scottish Iron Age. Society of Antiquaries of Scotland, Edinburgh, Scotland, UK.

Further reading

- Alexander, W.R. & Reijonen, H.M. (2023). Natural Analogues – a catalogue. GTK Research Report for NWS Ltd, UK (archive no. GTK/175/03.02/2020). GTK, Espoo, Finland.
- Alexander, W.R., Reijonen, H.M. & Norris, S. (2024). Assessing the performance of a radioactive waste repository over geological timescales: past experience and the way forward. Geoenergy v2 https://doi.org/10.1144/geoenergy2023-046
- Chapman, N.A., Dansie, A. & McCombie, C. (2007). Archaeology has a lot to tell us about the potential behavior of materials and structures during a high-level waste repository's first 10 000 years. Radwaste Solutions 14, 22-31.
- Crossland, I. (2006). Corrosion of iron-based alloys – evidence from nature and archaeology. Crossland Consulting Ltd Report CCL/2006/2 for UK Nirex Ltd, NWS, Harwell, UK.
- Drake, S.M. et al. 2018. Discovery of a meteoritic ejecta layer containing unmelted impactor fragments at the base of Palaeocene lavas, Isle of Skye, Scotland. Geology 46, 171–174.
- Neff, D., Saheb, M. et al. (2010). A review of the archaeological analogue approaches to predict the long-term corrosion behaviour of carbon steel overpack and reinforced concrete structures in the French disposal systems. Journal of Nuclear Materials 402, 196-205. DOI: 10.1016/j.jnucmat.2010.05.003