Copper analogues – status and future outlook

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NAWG-15

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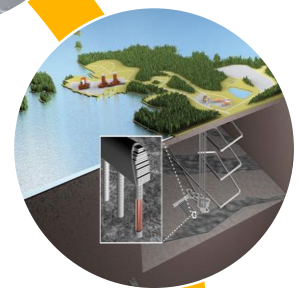
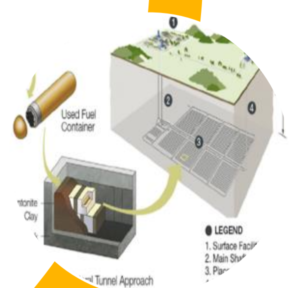
Copper in repository designs

Valid in many designs

SKB (5 cm)

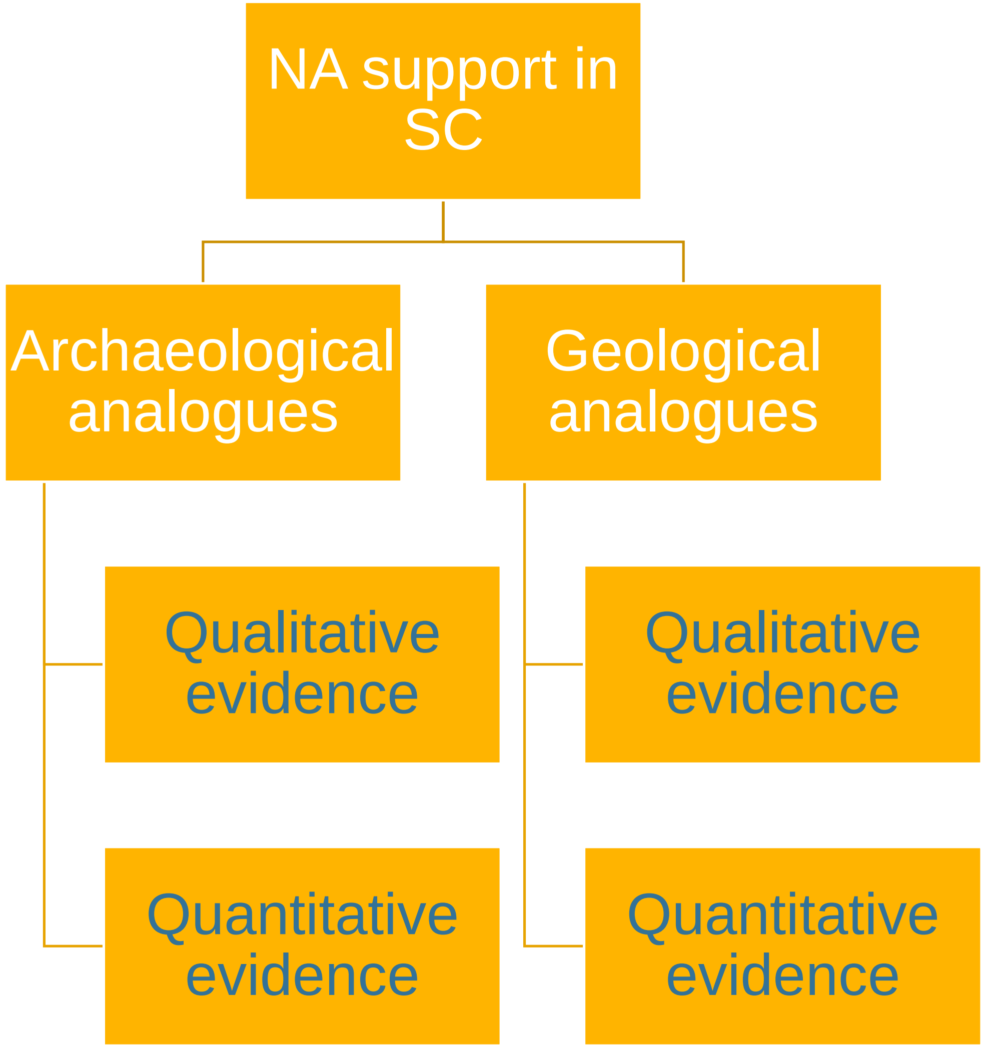


Posiva (5 cm)



NWMO (3-10 mm)

Others?



Many potential study sites and localities still to be investigated

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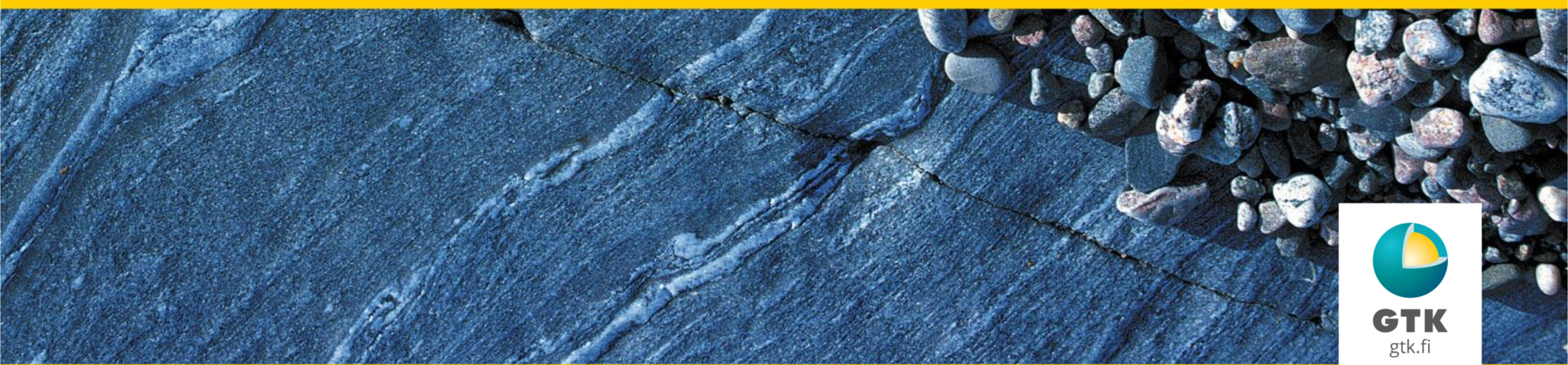
Copper analogues in recent safety cases



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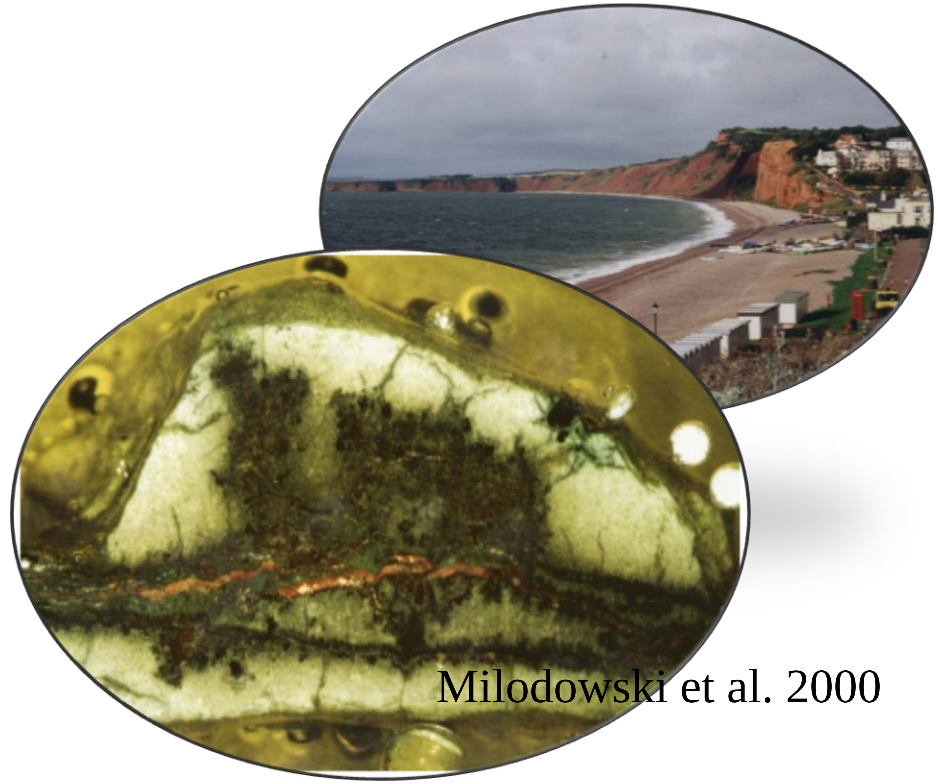
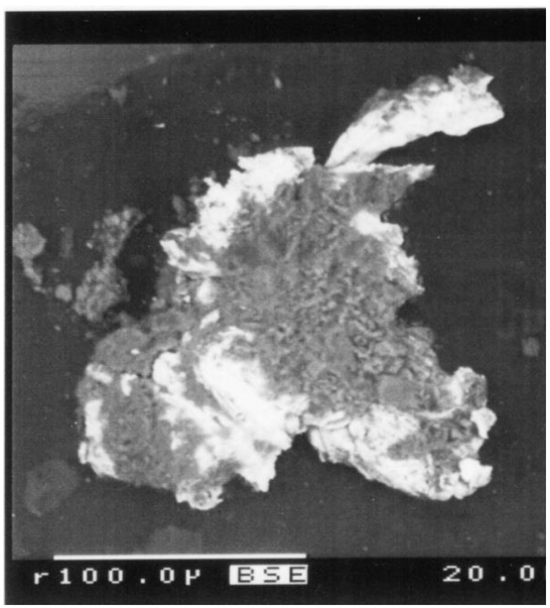
NA support in safety cases

- E.g. Posiva 2012 - Qualitative evidence, (e.g. Hyrkkölä, Finland; Littleham cave, England)
- Elemental (or ‘native’) copper has persisted for millions of years in a range of geological environments such as (Marcos 1989):



Milodowski et al. 2000



Marcos 2002

- **In sedimentary rocks:** Keweenaw Peninsula, Lake Superior region, Michigan, U.S.; Corocoro, Bolivia; South Devon, United Kingdom;
- **In basaltic lavas:** Keweenaw Peninsula; Appalachian States from central Virginia to southern Pennsylvania, U.S.; Coppermine River area, NWT, Canada; Dalane, Norway;
- **In granitic rocks:** Hyrkkölä and Askola, Finland;
- In the oxidised zones of **sulphide deposits** (many places in the world, including Finland, Chile, Japan etc.).

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NA support in safety cases

- Quantitative evidence, archaeological analogues only (Posiva 2012)

Form of data	Corrosion depth (per 1000a)	Reference	Comments
Short-term lab	**13 mm**	JNC (2000a)	Uniform corrosion of copper
Archaeological analogue	**<3 mm**	Range of studies cited in JNC (2000a)	Uniform corrosion of copper and bronze
Archaeological analogue	**0.26−39 mm**	Bresle et al. (1983)	Pitting corrosion of copper
Archaeological analogue	**0.025−1.27 mm**	Tylecote (1979), Johnson & Francis (1980)	Uniform corrosion of mixed artefacts
Archaeological analogue	**0.15 mm**	Hallberg et al. (1987)	Kronan cannon
Archaeological analogue	**0.13−1.13 mm**	Appendix A in IAEA (2005)	Bronze artefacts from a river
Archaeological analogue	**<0.27 mm**	Appendix B in IAEA (2005)	Bronze artefacts in soils
Archaeological analogue	**0.4−1.2 mm**	Appendix D in IAEA (2005)	Copper artefacts in flood plain soil
Archaeological analogue	**0.01−1.91 mm**	Appendix D in IAEA (2005)	Bronze artefacts in flood plain soil

SKB

- In SR-site 1.5 pages of listing most well know native/archaeological copper occurrences, not connected to safety case results that much.
- SKB lists Keweenaw, Hyrkkölä, Littleham Cove, Kronan cannon…
- But the main emphasis is given experimental results and modeling in the safety case.

Conclusion

Not much detailed information available

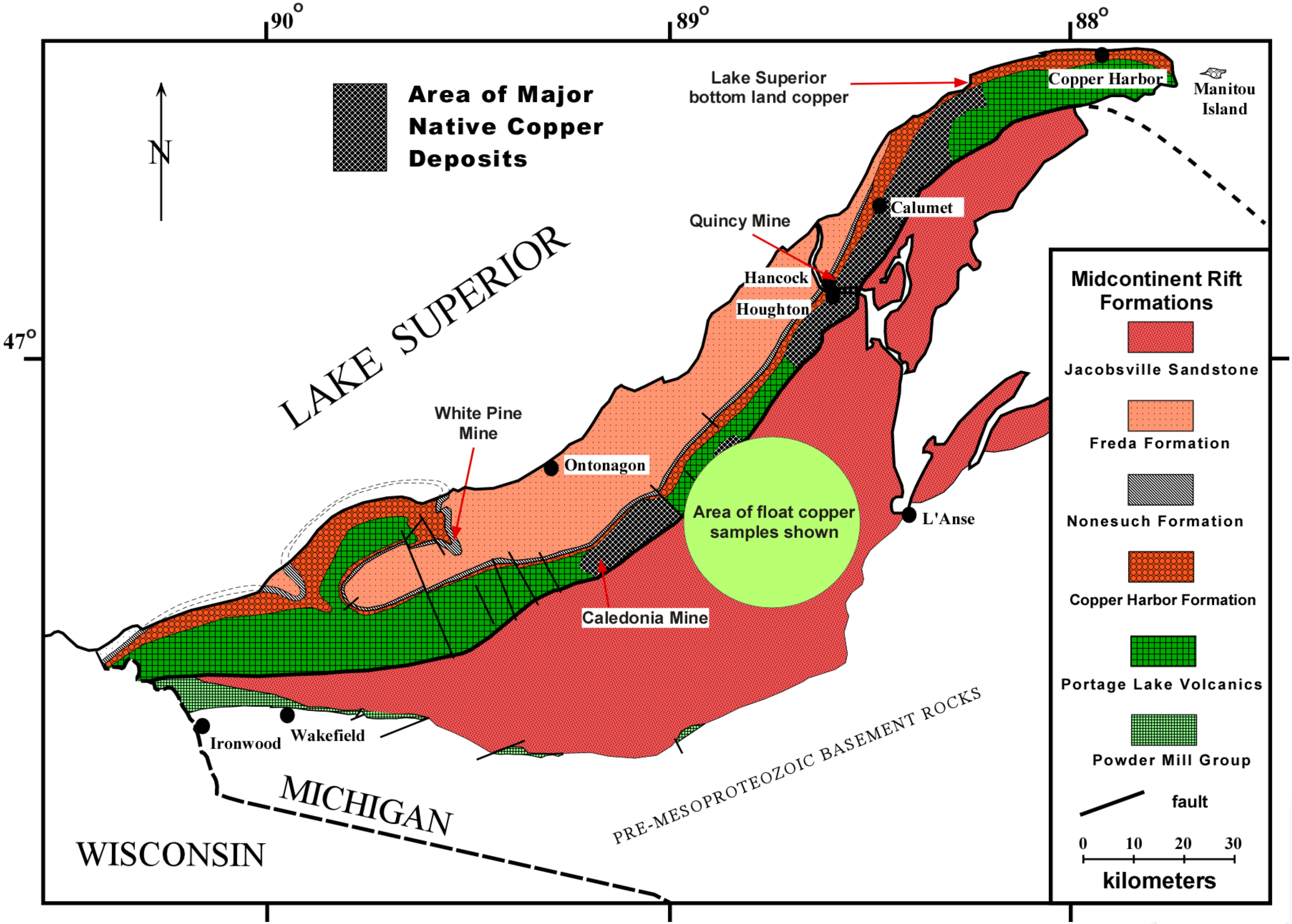
Current status

- Qualitative discussion
- Some quantitative data on archaeological analogues
- Geological record under studied compared to available localities
- Why?
  - Thick copper includes safety margins
- Why study more?
  - To optimize and use thinner copper?
  - To reduce conservativeness in assumptions through conceptual understanding?

Future outlook - Anything new to be done?

Keweenaw – potential for natural analogue studies – RECCE by GTK results

- Field investigation trip made to site
- Assessment of potential localities for future investigations
- Local connections made



90°
89°
88°
47°
N
Area of Major Native Copper Deposits
Lake Superior bottom land copper
Copper Harbor
Manitou Island
Calumet
Quincy Mine
Hancock
Houghton
LAKE SUPERIOR
White Pine Mine
Ontonagon
Area of float copper samples shown
L'Anse
Caledonia Mine
Ironwood
Wakefield
PRE-MESOPROTEOZOIC BASEMENT ROCKS
MICHIGAN
WISCONSIN
Midcontinent Rift Formations
Jacobsville Sandstone
Freda Formation
Nonesuch Formation
Copper Harbor Formation
Portage Lake Volcanics
Powder Mill Group
fault
0 10 20 30
kilometers

Accessible mine sites

Quincy Mine

Caledonia Mine

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Copper in rock: 1000 Ma


CENTIMETER

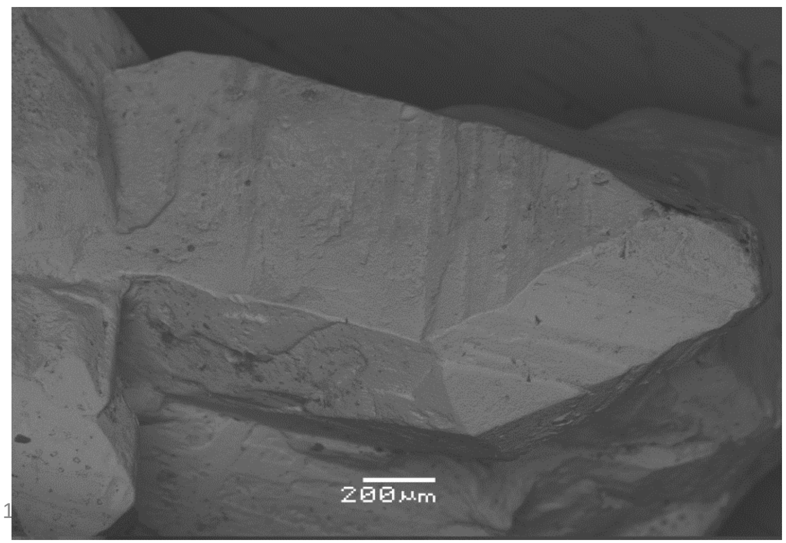
White Pine mine

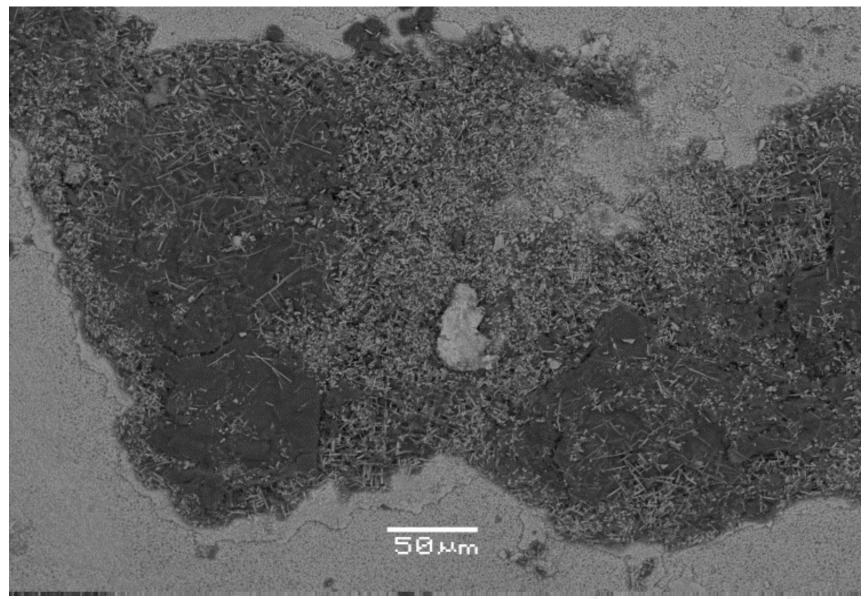
Quincy mine

Copper as inclusions in other minerals

Lake Superior bottom exposure: ~10 000 a

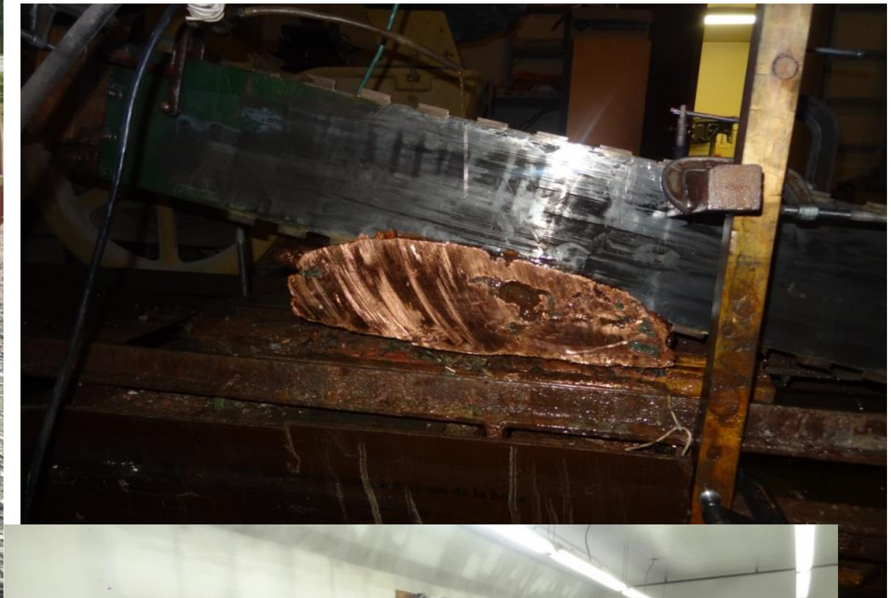
Lake Superior bottom exposured copper: ~10 000 a



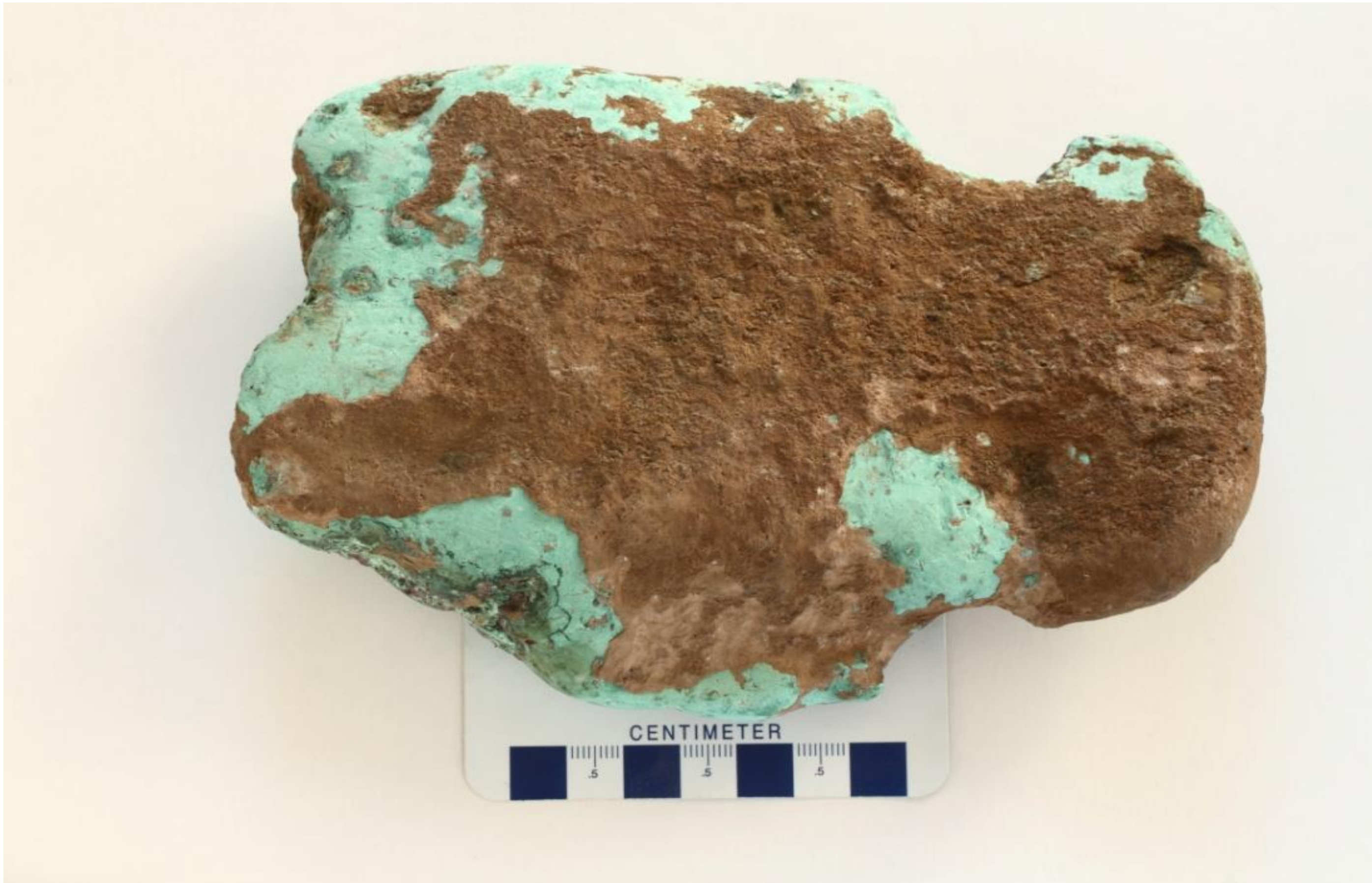


Copper from bottom of Lake Superior.
17 ton weight

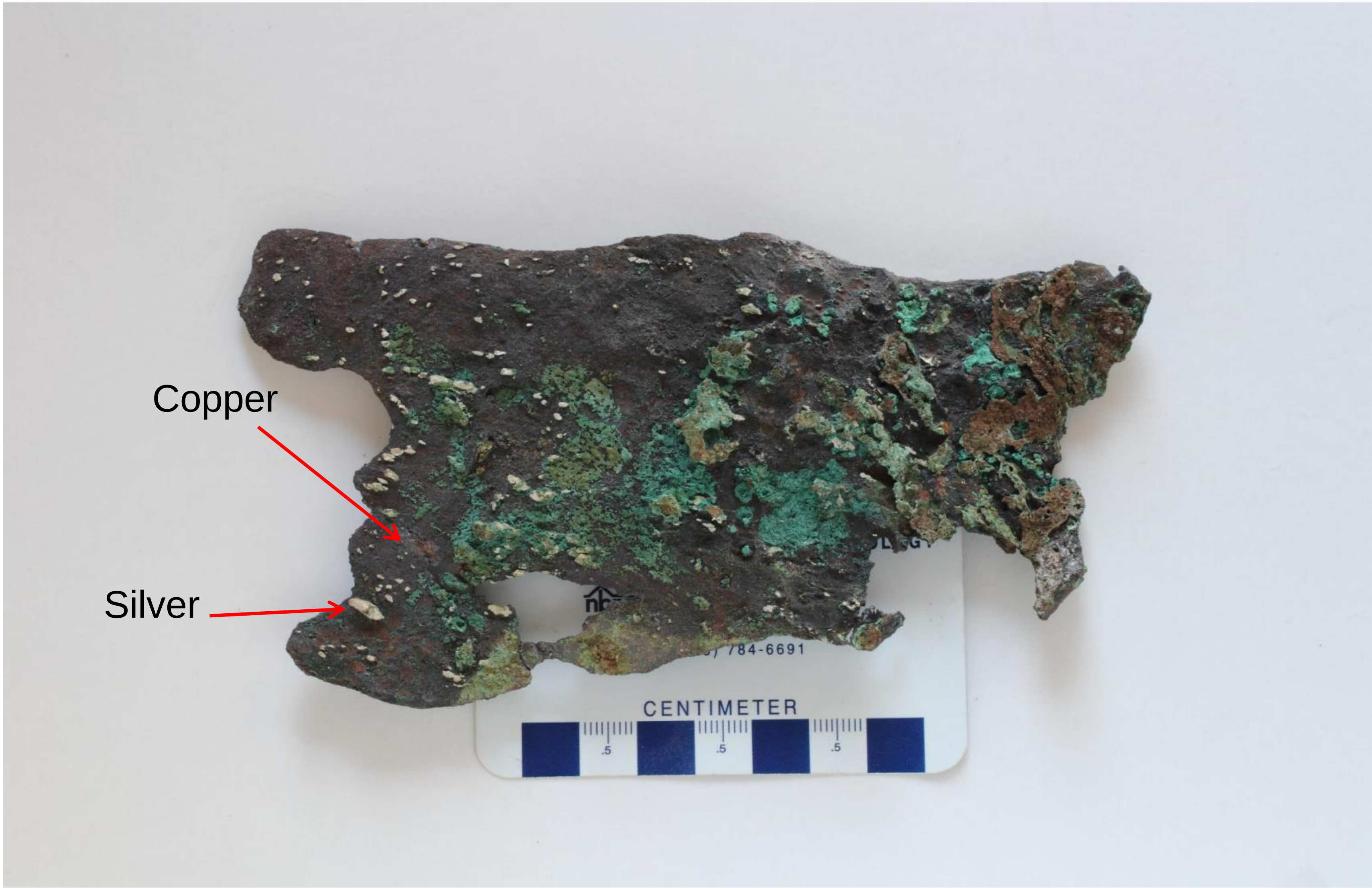
Glacial float copper: copper pebbles/boulders in till and gravel, 10 000 + a



- Geochemical halos around copper boulders in till

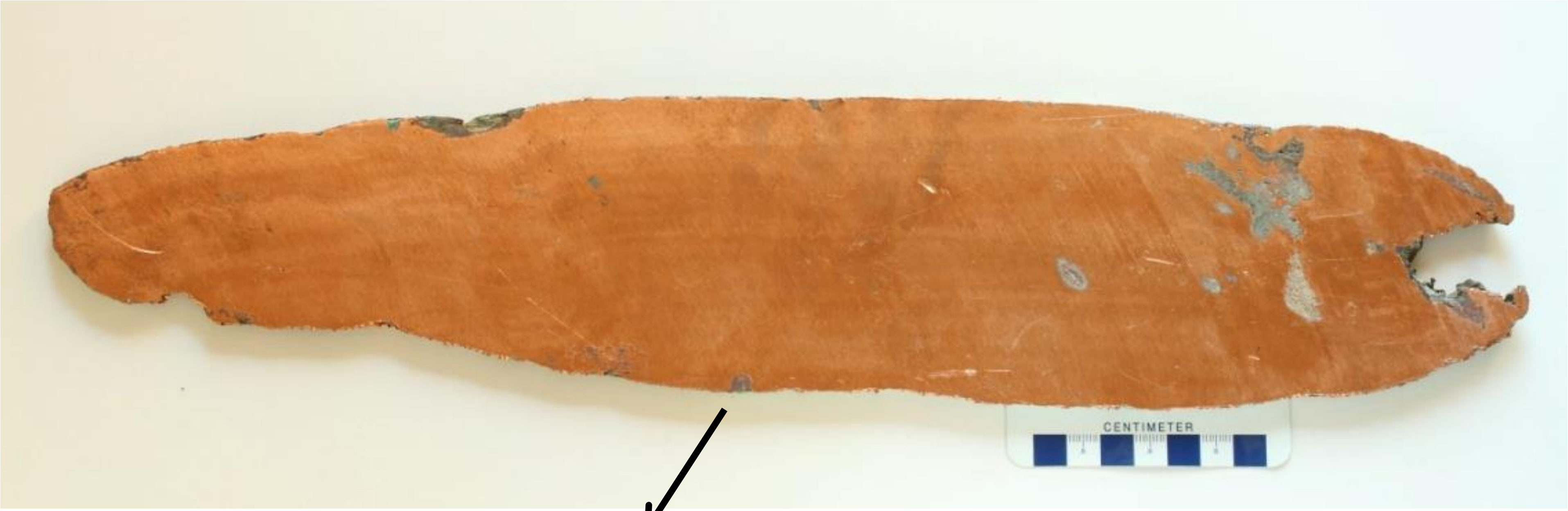


All sizes of float copper. Largest so far found float was 24 ton in weight



Float copper showing rate of corrosion

Float copper alteration



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Copper pebbles and boulders in glacial gravels, surface eroded to pure copper and then altered since ~10 000 a

Waste rock piles: subject to oxic conditions since 1840's

Chisel chips: carved by miners

~150 years of oxic alteration

- Well documented collections from the mines

- Drill core archives

Summary – potential study sites

- In situ native copper (1000 Ma)
  - Mine sites, outcrops
  - Different mode of occurrence: massive veins, aggregates/crystals in cavities, fracture in fillings
  - Different settings: anoxic brines to oxic conditions
- Transported copper (10 000 + a)
  - Copper in Quaternary deposits (’float copper’)
    - Unsaturated/saturated, oxic/anoxic (?)
- Excavated copper (50-150 a)
  - Waste rock piles
  - Chisel chips
  - (Archeological artefacts)

Salinity variation - Chemical composition, redox conditions and temperature of fluids

Ore-forming (1 billion year old) brines (all analogues)
Compilation of existing data on fluid inclusions in minerals / Destructive chemical analysis of fluid inclusions in calcite enclosing native copper
Deep brines (> 700 m) (all analogues)
Compilation of existing data
Shallow brines (< 700 m) (all analogues)
Compilation of existing data / Sampling of waters from artesian brine wells, if possible / New drill hole (age of brines), if possible and appropriate
Deep groundwater
Compilation of existing data / Sampling from existing groundwater wells, if necessary / New drill hole, if possible and appropriate
Shallow groundwater
Compilation of existing data / Sampling from existing groundwater wells, if necessary / Sampling within accessible mine openings
Lake Superior water and precursor glacial lake
Compilation of existing data / Sampling of Lake Superior water at sampling site, if necessary
Rainwater
Compilation of existing data

Metallic copper canister scenarios and corresponding generalized natural analogues

A. Long term exposure of metallic copper canister to anoxic brine

- #1 – ***"Bedrock copper":*** Native copper in bedrock exposed to an anoxic brine water for the past one billion years. Study of existing documented samples and drill core; fluid characterization.

- #2 – ***"Initial copper":*** Natural conditions resulting in the precipitation of native copper from brines as indicative of conditions in the repository that will lead to dissolution. Existing data and study of native copper included in calcite; fluid characterization.

continued

- **B. Long term exposure of metallic copper canister to anoxic brine followed by incursion of anoxic to oxic groundwater to the repository level during future glaciation**
- #3 – ***"Shallow mine"****:* Native copper in bedrock originally in an anoxic brine water environment exposed to shallow groundwater (not brine) for a minimum of 10,000 yrs. Study of accessible mine openings and existing documented samples; fluid characterization.
- #4 – ***"Lake copper":*** Native copper originally in an anoxic brine water environment on the surface today exposure to glacial water and fresh lake water for past 10,000 yrs. Study of samples recovered by divers from the bottom of Lake Superior; fluid characterization.
- #5 – ***"Gravel copper":*** Native copper originally in an anoxic brine water environment plucked by glaciers from the bedrock and now as pebbles and boulders in glacially deposited gravels. Most if not all of the pre-existing alteration products on the native copper was likely removed as the native copper pebbles and boulders were tumbled in glacial rivers. Thus, current native copper alteration is the result of exposure to shallow groundwater (not brine) for the past 10,000 years. Study of samples collected from gravel and sand mine; fluid characterization.
- #6 – ***"Float copper":*** Native copper originally in an anoxic brine water environment plucked by glaciers from the bedrock and now as pebbles and boulders in shallow glacial sediments/soil. The erosive processes within the glacier have variably removed pre-existing alteration products on the native copper. New native copper alteration products have resulted from exposure to surface and shallow groundwater for the past 10,000 years. Study of samples collected from surface occurrences; fluid characterization.

Continued

C. Oxidation of the metallic copper canister prior to anoxic brine incursion

- #7 – ***"Chisel chips":*** Native copper chiseled from large underground masses of native copper yields chips with fresh copper at the surface. These chisel chips are now in waste rock piles exposured to continuous downward percolating precipitation for the past 150 years. Study of samples collected from rock piles; fluid characterization.
- #4 – ***"Lake copper"***

D. Long term exposure of metallic copper canister to anoxic brine followed by incursion of anoxic to oxic groundwater to the repository level during future glaciation followed by a return to anoxic brines

- #8 – ***"Precambrian weathering":*** Native copper in bedrock originally in an anoxic brine water environment was exposed to groundwater during the Precambrian and subsequently exposed to brine during the Paleozoic. Study of existing documented samples; fluid characterization.
- #3 - ***"Shallow mine"***

E. Overall stability of metallic copper exposed to variable geologic history

- Natural analogues #1, #2, #3, #4, #5, #6, #7, and #8

Information needed for communication / safety case : An example

Very good for communication, but what about using this information in safety case?

Information needed for communication / safety case : An example

- *“The* ***abstrasion during transport in the glacier left the surface of the float copper pieces as "shiny" copper****.*
- *How do you prove that the surface was abraded?*
    - *Detailed description of the sedimentary location, comparison with other boulders…*
    - *Dating alteration?*
    - *Some uncertainty remains, but a good case can be made*

Information needed for communication / safety case : An example

- *Since the glaciers retreated about 10,000 years ago, these surfaces have been* ***in contact with oxygen in the atmosphere and with oxygenated water*** *(rain and groundwater connected with the atmosphere).*
- *Backed up with quaternary science*
- *Good case can be made based on existing literature*

Information needed for communication / safety case : An example

- *The "shiny" native copper on the surface underwent chemical reactions during this time that* ***altered the copper*** *on the surface of the float copper mass from pure native copper to other forms of copper including cuprite (copper oxide), tenorite (copper oxide), malachite (hydrated copper carbonate) and rarely azurite (hydrated copper carbonate).* ***These copper oxide and carbonate minerals are stable at surface conditions****. During the past 10,000 years the typical thickness of surface alteration is* ***only a few mm because the coating of the surface of the native copper mass by stable copper minerals generally protects the interior of the float copper mass from further alteration****.*
- Supporting natural analogue with laboratory data
- Good case can be made
- Supporting geological analogue with industrial analogue?

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Information needed for communication / safety case : An example

- ***Highly porous and fractured float copper pieces can be more altered*** *as they allow continuing access of water to alter the native copper.*
- More details, quantification would be needed to support this statement in the safety case
- Information like this could directly support for example scenarios where manufacturing errors are assessed as initial defects

Conclusions

- Further geological investigations with tailored analytical part would greatly benefit the safety case use of copper corrosion related NAs
  - Corrosion in different environments (salinity variation, oxic, anoxic)
  - Protective properties of corrosion products
  - Effects of material flaws
- As examples for communication, the current descriptions are enough, but
- As a general question:
  - Should there be more back up for the qualitative analogues by getting some more hard data?