Archaeology analogues for geological disposal of spent nuclear fuels (SNFs) – current status and future outlook in Taiwan

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Outline

- Introduction to natural analogue studies
  - Purposes
  - Objectives of this archaeological study
  - Overview of international case studies
- The archaeological analogues of metal artefacts in the present studies in Taiwan
  - Measuring instruments in the analysis of archaeological artefacts
  - Results and discussion (characterization of metallic artefacts and their corrosion rate)
- Comparison of corrosion rates of artefacts with literature
- Preliminary conclusions
- Future works

Introduction to Taiwan

Facts about Taiwan	
Official Name	Republic of China
Continent	Asia
Area	36,193 km^2
Population	23,519,518 (2016 estimate)
Capital	Taipei
Official Languages	Mandarin

Natural Analogue Studies

- Purposes
  - To obtain an understanding of processes expected to occur over geological timescales with the disposal system by studying natural phenomena that are analogous to processes occurring within a repository;
  - To improve the reliability of extrapolation of short-term laboratory data used for long-term safety assessment of disposal system

- The objectives of this study
  - To observe corrosion products of unearthed bronze and ironware relics;
  - To measure the surface corrosion thickness of unearthed bronze and ironware relics in the environmental conditions
  - To analyze the composition of the matrix and corrosion layer of unearthed bronze and ironware relics

Overview of international natural analogues of metallic artefacts (waste container: copper canister and inserted cast iron)

Archaeological object	Site/ Country	Analogue item	Age	Main achievements
Kronan cannon	Baltic Sea	Copper canister	~300 years ago	1. The cannon which was discovered by SKB in 1985 has been embedded for more than 300 years in a clay which largely has the same properties as the clay considered for use in the final storage of Swedish nuclear fuels. 2. The copper corrosion rate is about 0.15 μm/a.
Roman iron nails	Scotland	iron (steel)	~1,900 years ago	1. When the nails were unearthed in the 1950s, the nails on the outside of the mass were badly corroded, forming a solid crust of iron oxides (rust) around the remaining mass of nails 2. Those nails inside the rusty barrier had minimal corrosion. In the same manner, large volumes of iron (steel) in waste canisters can be expected to buffer redox conditions in a deep geological repository.
Bronze artefacts from Zhou and Shang dynasty tombs	China	Copper canister	~3,000 to 3,300 years ago	1. Study on corrosion of unearthed copper relics in different environmental conditions 2. The bronze relics were continuously corroded with time. The corrosion layer of bronze relics consisted of at least two sub-layers, the oxide and carbonate ones.
South Devon native copper	United Kingdom	Copper canister	~176 millions years	1. Found in the 1970s and studied by BGS of SKB during 1999 to 2002 2. The native copper (>99.4% Cu) can remain stable in a saturated and compacted clay (bentonite) environment for geological timescales well in excess of the timescales considered for performance assessment.
Delhi iron pillar	Delhi, India	Cast iron material	~1,600 years ago	Passivating corrosion layer of crystalline iron hydrogen phosphate hydrate, amorphous iron oxyhydroxides and magnetite.
British steel helmet	York, UK	Cast iron material	Helmets made in A.D. 750-775	Study on corrosion of unearthed helmet and effects of buried clay on helmets corrosion

The archaeological analogues of metal artefacts in the present studies in Taiwan

Archaeological metal artefacts: ironware &bronze

Archaeological relics：Hanben site

Year： 1100 ~ 1800 years ago

Unearthed depth: 3-4 m






Environmental conditions at Hanben site

- Climate: sub-tropical & humid
  - Annual average temperature:22.3°C
  - Evaporation 400 mm
  - Accumulated rainfall: 2827.7 mm
- Soil analysis:
  - Moisture：24.8%
  - pH：7.12
  - Conductivity: 335 μs/cm
  - $[Cl^-]$: 3.23 ppm
  - $[SO_4^{2-}]$:11.23 ppm
  - $[CO_3^{2-}]$：5.52 ppm
  - Chemical compositions:

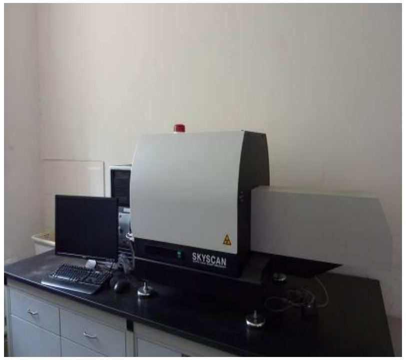
Archaeological relics buried under the ground about 3-4 meters of the excavation site

Oxide	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	Total
Weight (%)	54.78	1.04	14.22	9.39	0.17	3.16	4.40	1.63	1.96	2.40	8.58	101.73

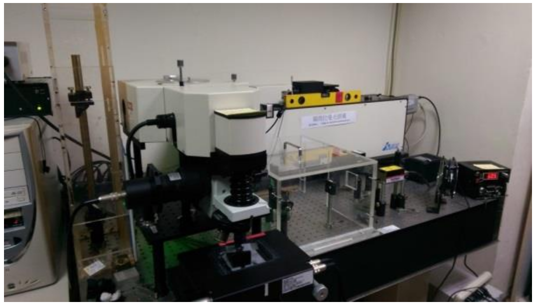
Measuring instruments used in the analysis of archaeological artefacts

- **Archaeological analogue (Bronze & Ironware)**
  - **Non-destructive test (bulk sample)**
    - Micro-CT — Image/ Corrosion depth
    - Portable /desktop XRF — Overall Chemical compositions
    - SEM/EDS — chemical compositions (bronze adornment)
    - Raman spectrometer — Types of corrosion products
  - **Destructive test (debris from natural peeling)**
    - SEM/EDS — Localized chemical compositions
    - (1) ICP-AES; (2) ICP-MS — (1)Conc. of Cu, Pb & Sn (2) Isotopes conc. of Pb
    - XRD — Crystal pattern and mineral contents of corrosion products

Analytical instruments used for archaeological studies



Belgium SkyScan 1076 *in-vivo* micro-CT



Raman spectrometer, Horiba, Jobin Yvon

X-ray Analytical Microscope (EDXRF, Horiba, XGT-5000)

XRF spectrometer (Bruker, S1 TITAN)

X-Ray Diffractometer (XRD, Bruker, Advance D8)

ICP-MS (Thermo, XSeries II)

ICP-AES (Horiba)

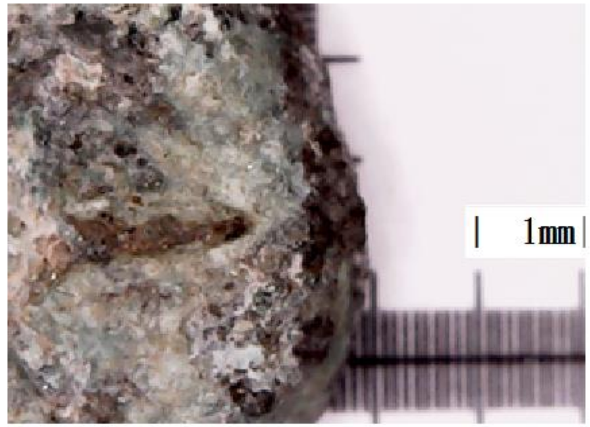
Scanning electron microscopy (SEM/EDS, JEOL)

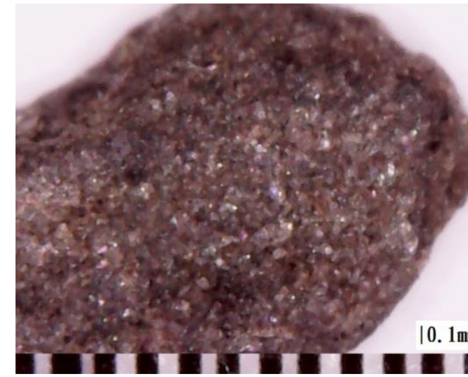
USB optical microscope

Results and discussion

Appearance of bronze adornment and iron hook using (3D) optical microscope

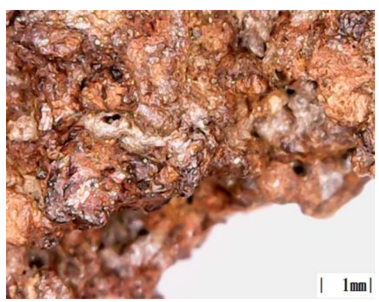
Bronze adornment

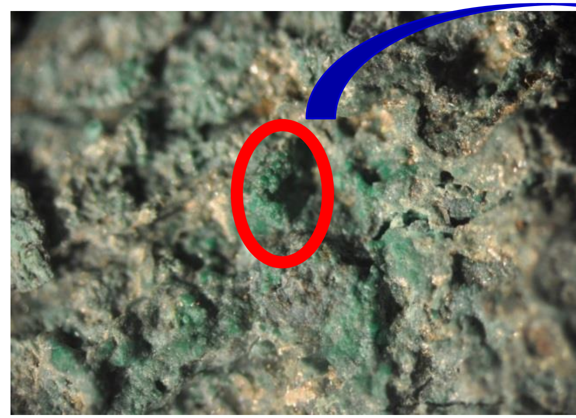




Description: Spherical aggregates of green radiating acicular crystals associated with olivenite and bayldonite

Iron hook

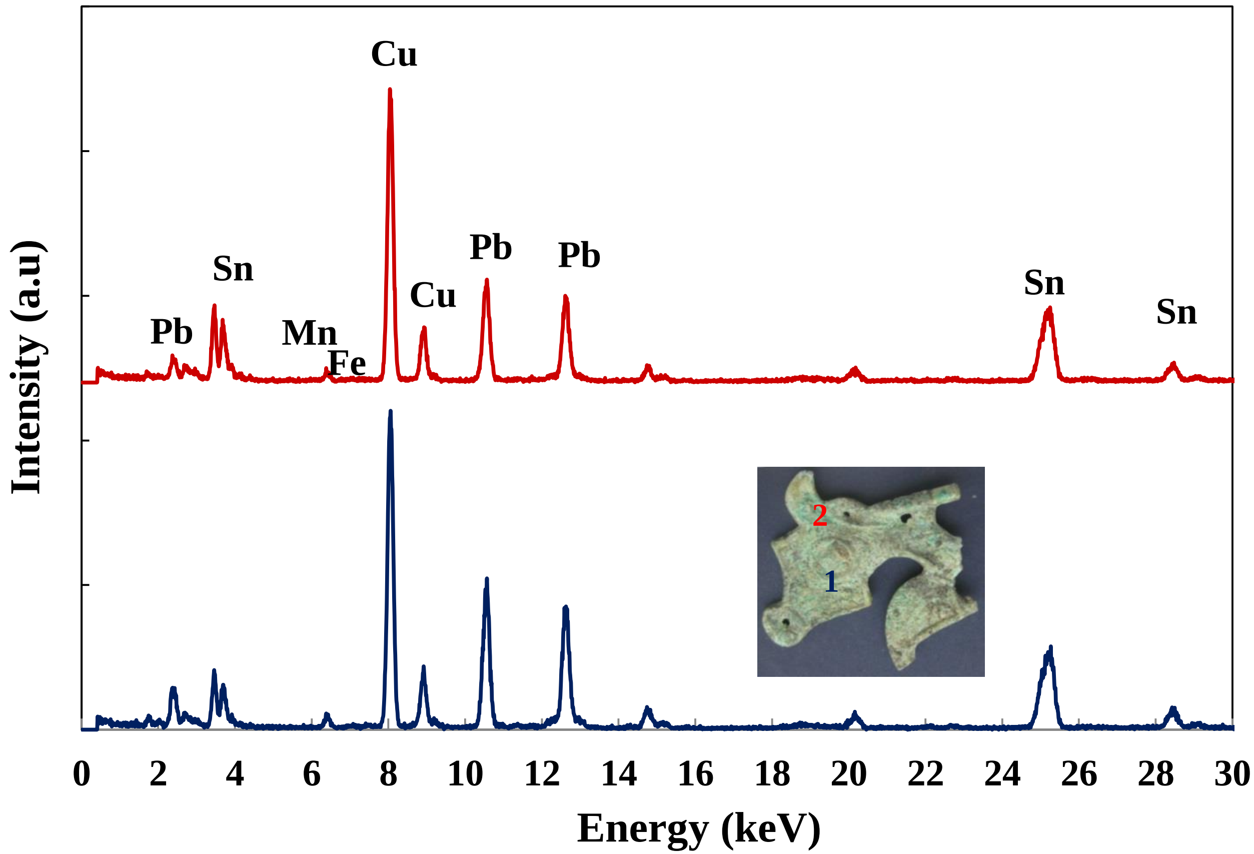




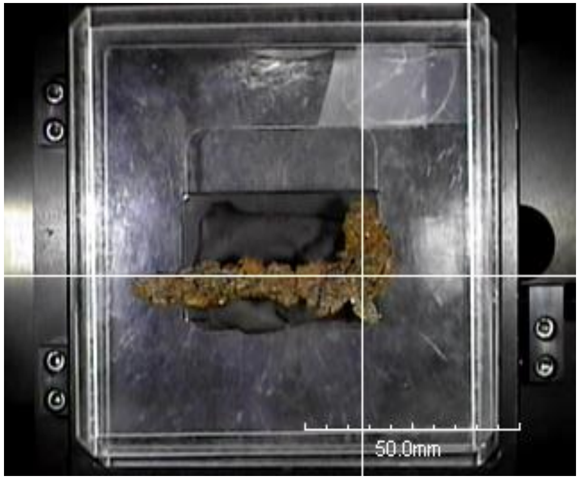
Malachite mineral crystals of bronze shank

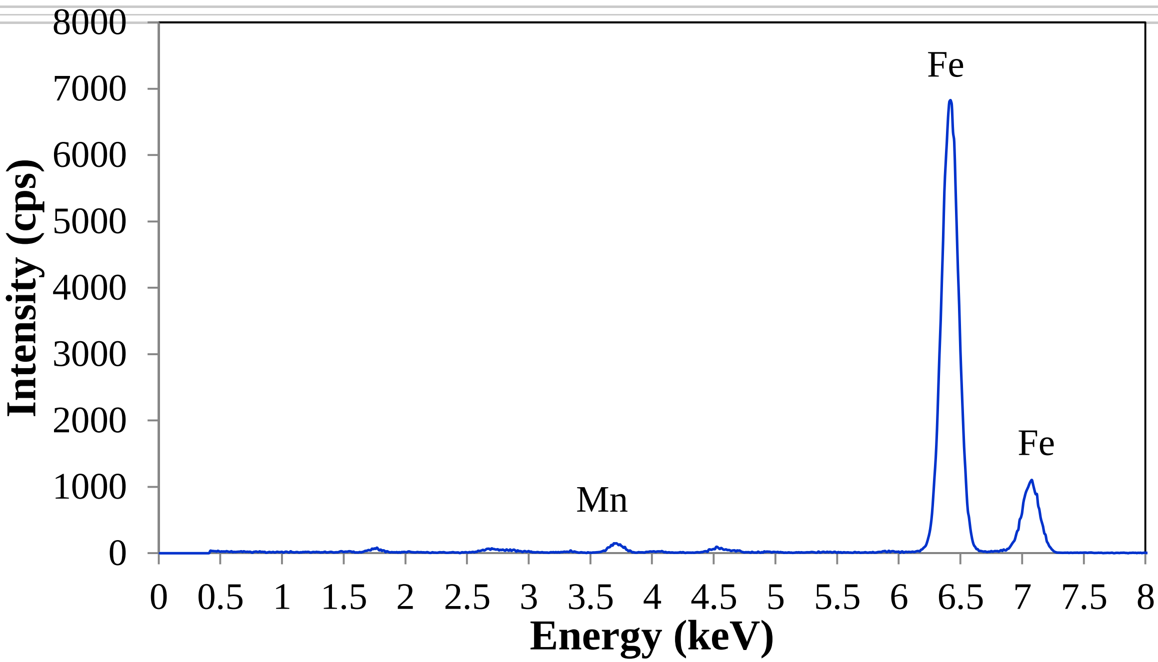
XRF elemental analysis results for bronze adornment

Element	Mass (%) Location 1	Mass (%) Location 2
Cr		0.11
Mn	0.00	0.00
Fe	0.82	0.72
Cu	18.95	20.58
Sn	48.78	53.48
Sb	0.56	
Pb	30.89	25.10



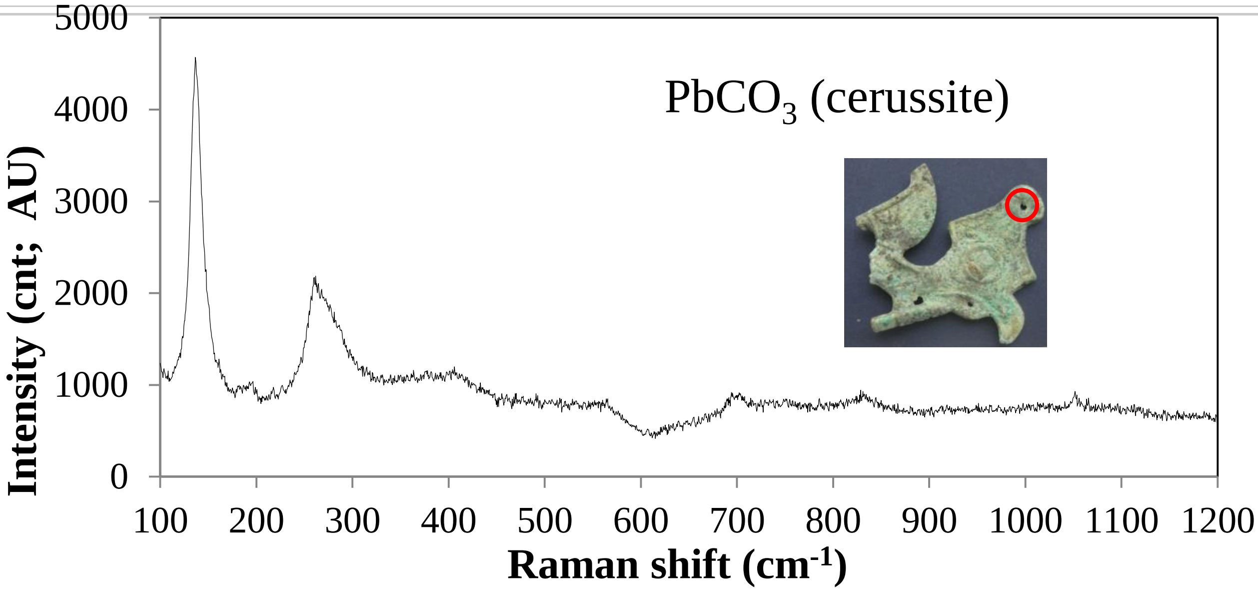
XRF elemental analysis for iron hook

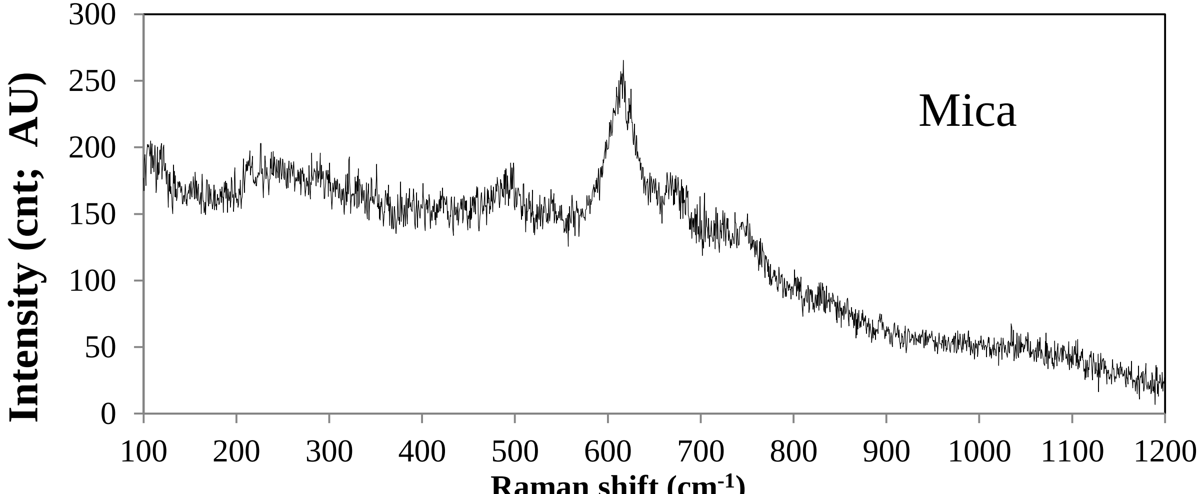




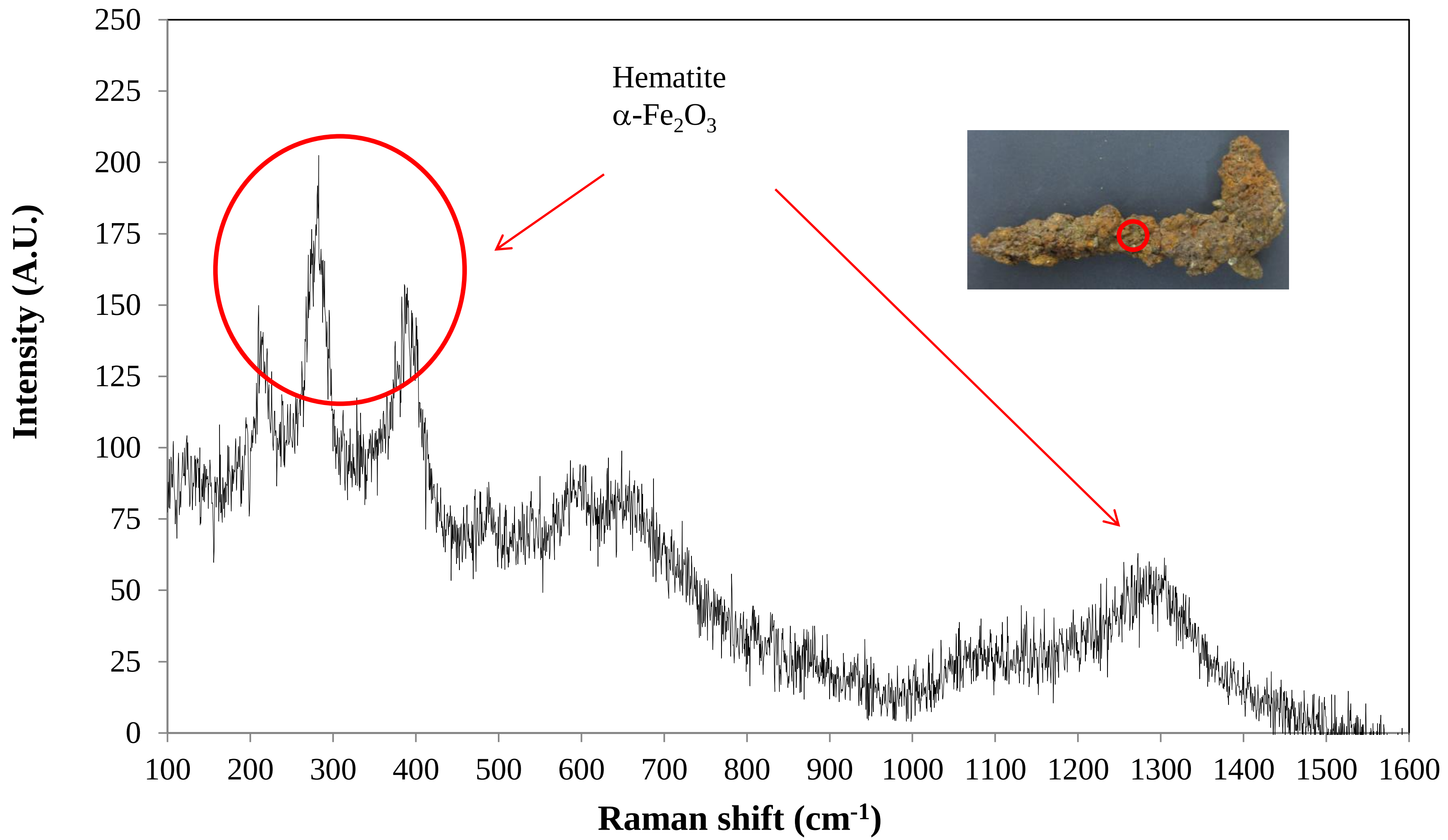
Element	Mass (%)
Si	**3.04**
S	**1.5**
Ca	**2.4**
Cr	**0.03**
Mn	**0.00**
Fe	**93.03**

Corrosion products of bronze adornment using Raman spectrometer

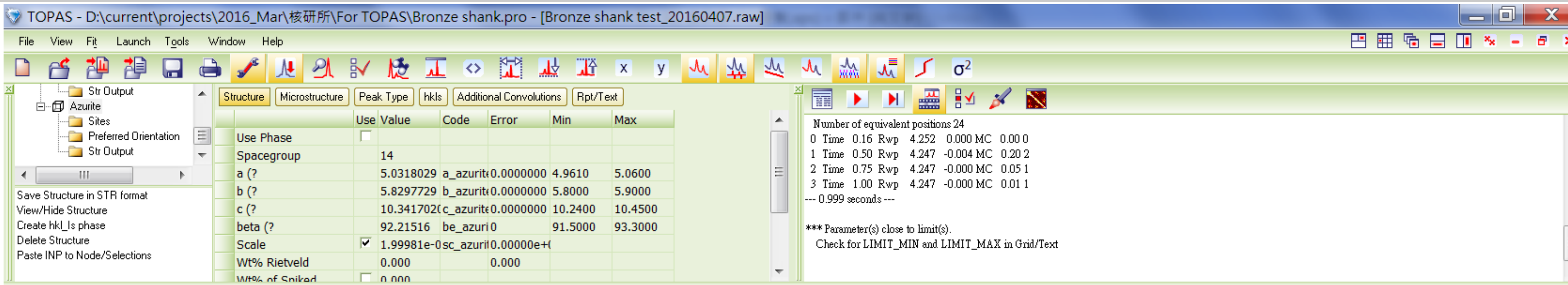


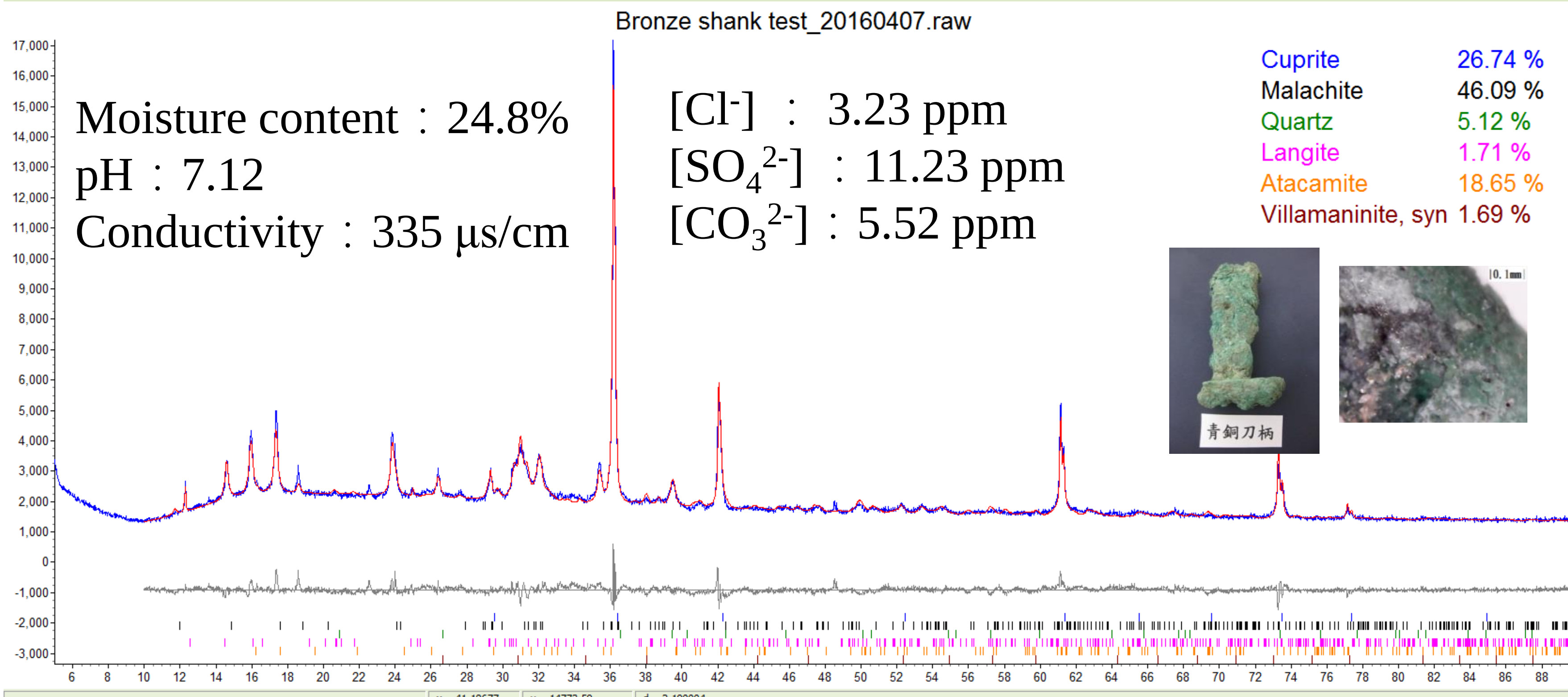


Corrosion products of iron hook using Raman spectrometer



XRD quantitative analysis of corrosion products of bronze shank using TOPAS software





Moisture content ： 24.8%

pH ： 7.12

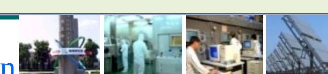
Conductivity ： 335 μs/cm

[Cl^-] ： 3.23 ppm

[SO_4^{2-}] ： 11.23 ppm

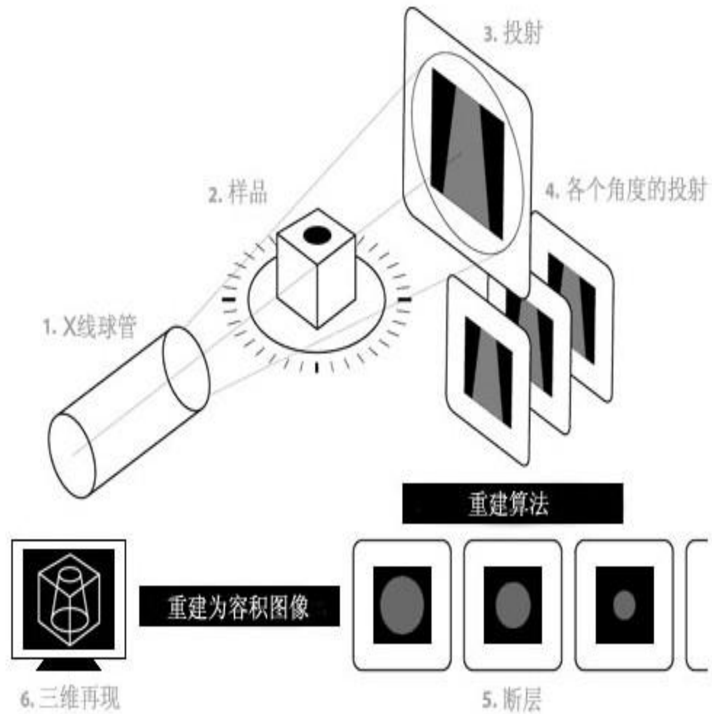
[CO_3^{2-}] ： 5.52 ppm

Cuprite	26.74 %
Malachite	46.09 %
Quartz	5.12 %
Langite	1.71 %
Atacamite	18.65 %
Villamaninite, syn	1.69 %



Powerful tool for corrosion rate measurement using Micro-CT

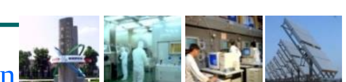
Belgium SkyScan 1076
***in-vivo* micro-CT**



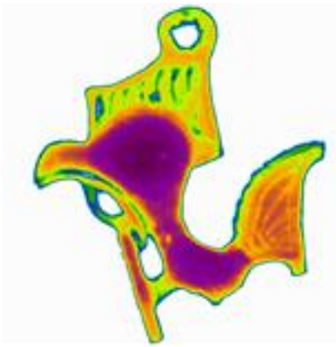
MicroCT成像原理

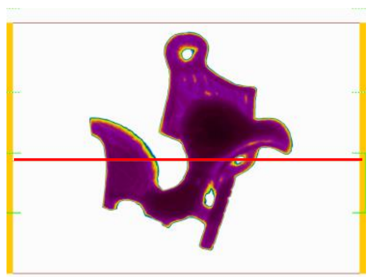
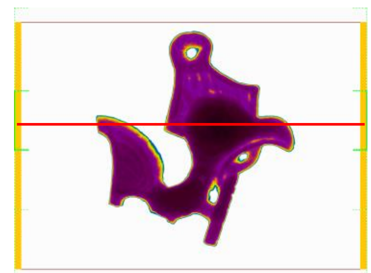
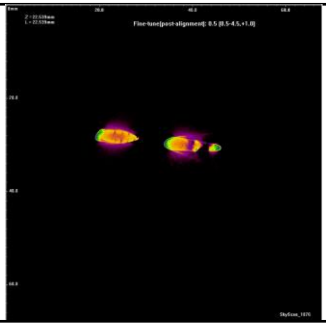
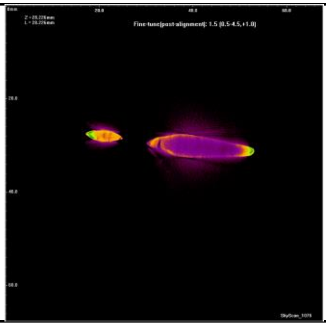
Features and advantages:

- Maintenance-free 100kV X-ray source
- Fully distortion corrected 11Mp X-ray camera
- Up to 8000x8000 pixels in every slice
- Down to 9µm in-vivo 3D spatial resolution
- Integrated physiological monitoring and gating
- Software for 2D/3D image analysis, bone morphometry and realistic visualization

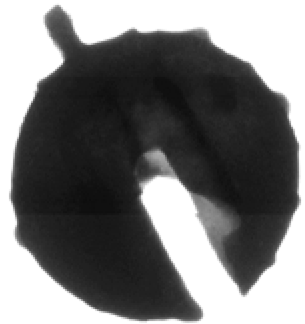
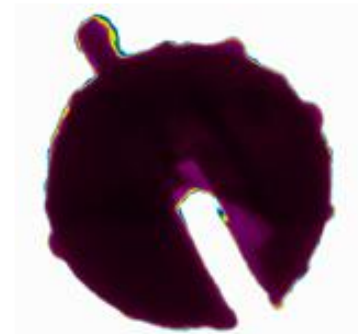


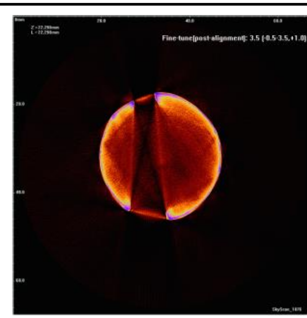
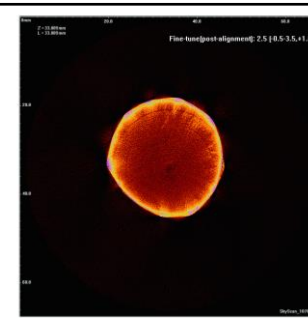
Micro-CT detection results of bronze adornment

		
Original sample	Micro-CT image (greyscale)	Micro-CT image (colored)

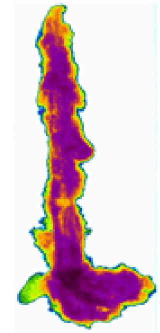
Sample image		
Sample cross section image		

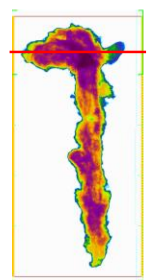
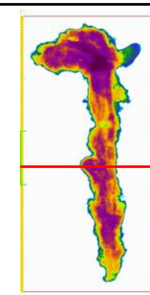
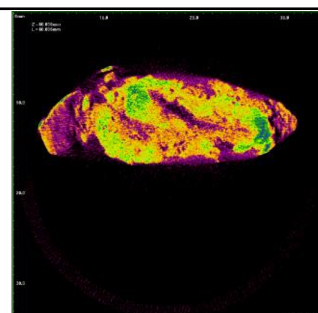
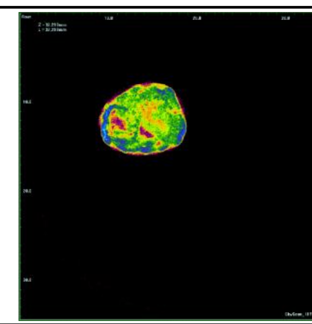
Micro-CT detection results of bronze bell

		
Original sample	Micro-CT image (greyscale)	Micro-CT image (colored)

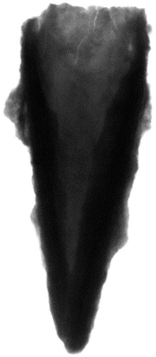
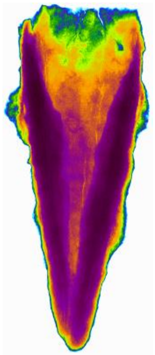
Sample image		
Sample cross section image		

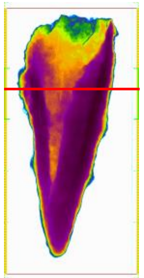
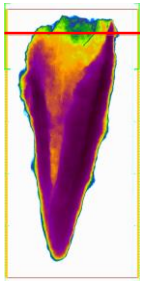
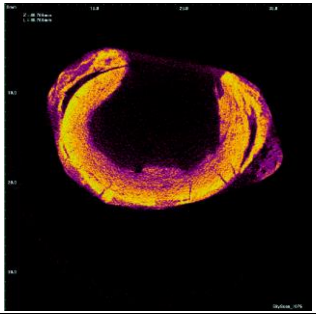
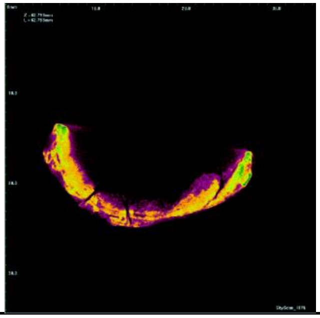
Micro-CT detection results for iron hook

		
Original sample	Micro-CT image (greyscale)	Micro-CT image (colored)

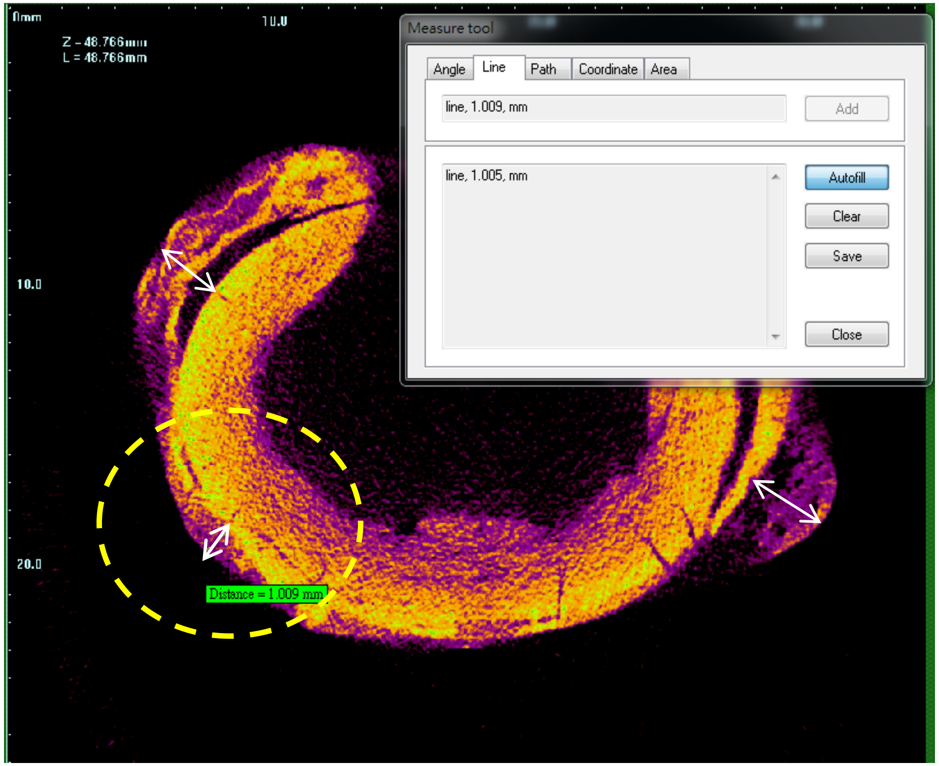
Sample image		
Sample cross section image		

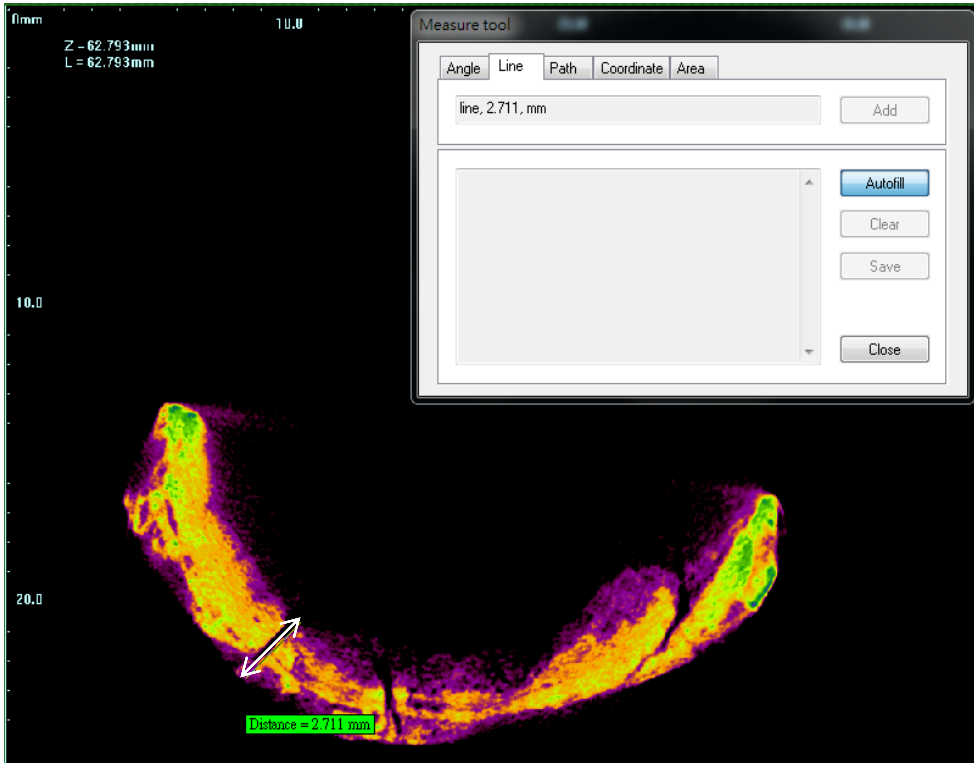
Micro-CT detection results for ironware

		
Original sample	Micro-CT image (greyscale)	Micro-CT image (colored)

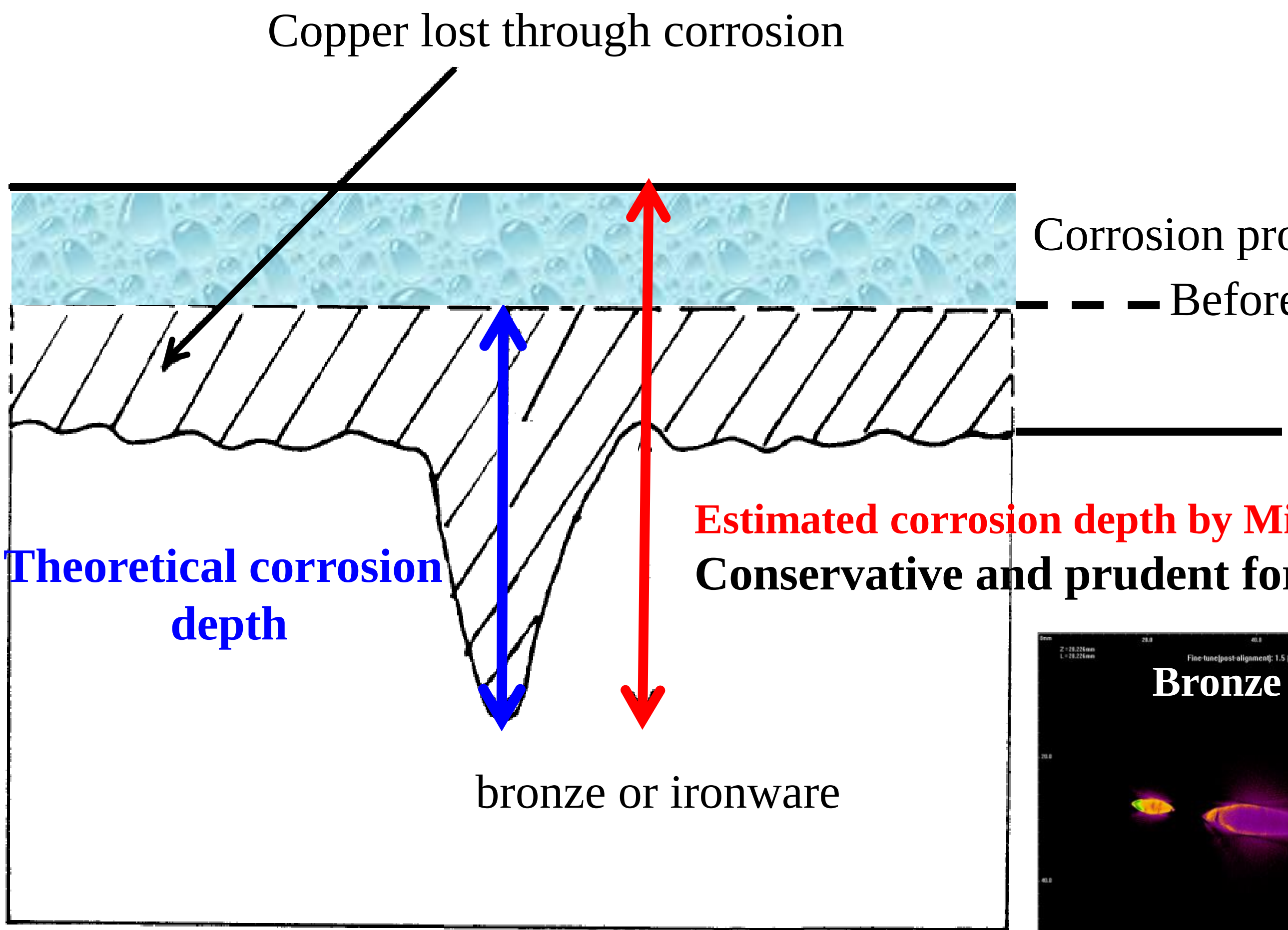
Sample image		
Sample cross section image		

Estimated corrosion depth of ironware by micro-CT image



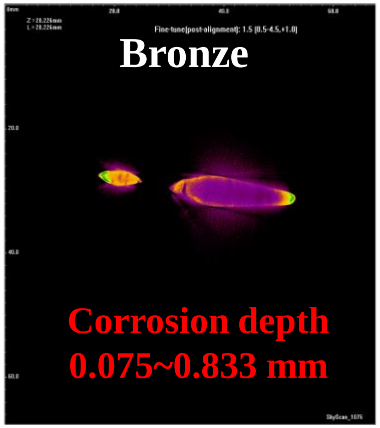


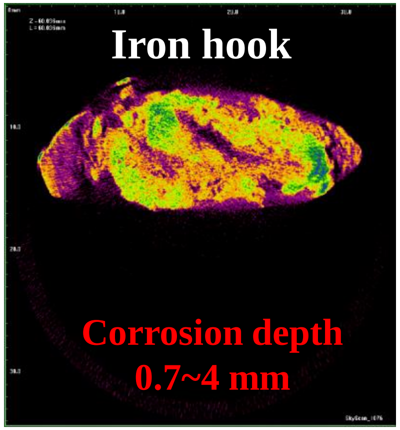
Estimation of conservative corrosion depth of archaeological bronze and ironware



Estimated corrosion depth by Micro-CT measurement

Conservative and prudent for safety assessment





Comparison of copper corrosion depths cited in the safety assessment H12 (JNC 2000) with existing and new archaeological analogue data

Form of data		Corrosion depth (per 1000a)	Reference	Buried environment
Archaeological analogue (Taiwan)	Ironware	1.0~2.7mm	SNFD-05-IPR-002-02 Natural Analogue Research in Taiwan for Final Disposal	Iron artefacts in soils
	Iron hook	0.7~4.0 mm		
	Bronze adornment	0.075~0.833 mm		Bronze artefacts in soils
	Bronze bell	0.198~0.671 mm		
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 D in IAEA (2005)	Bronze artefacts from a river
Archaeological analogue		<0.27 mm	Appendix D 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

Reference: Comparison of copper corrosion depths cited in H12 with existing and new archaeological analogue data for copper/bronze artefacts (POSIVA 2012-11, Safety Case for the Disposal of Spent Nuclear Fuel at Olkiluoto -Complementary Considerations 2012)

Preliminary conclusions

- The sub-tropical climate in Hanben heritage site exhibited more aggressive or dynamic than those that would be encountered in a deep repository.
- The estimated and conservative values of corrosion rates, 0.7-4.0 μm/a and 0.075-0.833 μm/a for respective ironware and bronze artefacts, using 3D image reconstruction software of micro-CT technique were successfully established, indicating that the analytical results were consistent with those of literature.
- Although the geochemical environment of the archaeological site was different to those of potential host rock sites (candidate sites for final disposal in the future), in particular, more oxidizing than anticipated in geological repositories in Taiwan, it can
  - be used for predicted performance of the waste package in geological repositories,
  - give considerable confidence in the value of an engineered barrier system,
  - provide useful qualitative indicators to explain safety assessment of disposal concepts to the public.

Future works

- Measurement of the thickness of corrosion layers of unearthed bronze and ironware relics;
  - FIB or EPMA analysis to examine the cross section (depth profile) and further study the structure of corrosion layer and mechanism
- Interpretation of the relationship between the corrosion process and environmental conditions
  - Soil and water sampling during excavation to further understand the relationship between the corrosion process and buried/ preservation environment
- Establishment of a geochemical model of the corrosion process of unearthed bronze relics

Thanks for your attention

Děkujeme za pozornost

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Questions? Comments?