Input of iron corrosion studies to the Japanese safety case

－Corroborative evidence by using iron-based archaeological artifacts to long term stability of the overpack －

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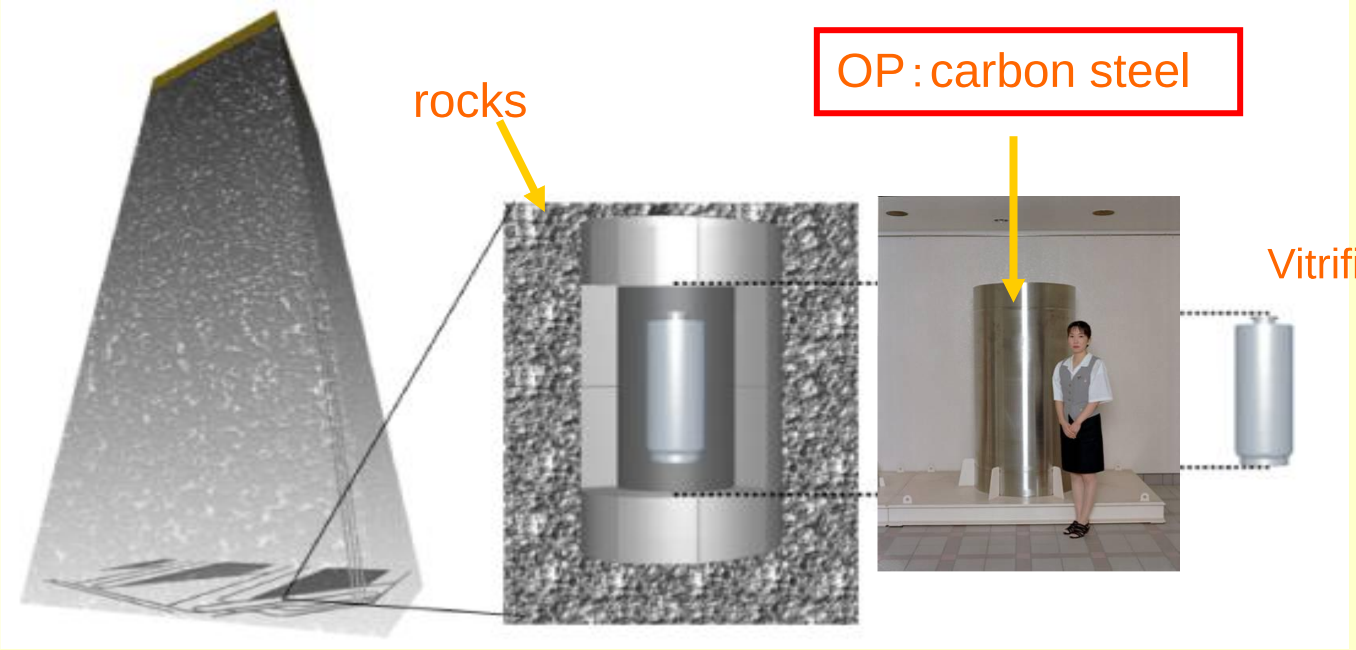
OBJECT： to obtain the data on corrosion rates of archaeological iron-based artifacts buried underground for about several hundred year for natural analogue study to increase confidence in the robustness of using a metal container (overpack) in high level radioactive waste disposal (HLW).

How much thickness of OP is required ?



OP：H12 specific （JNC,2000)

height： 173 cm

diameter： 82 cm（thickness：19 cm）

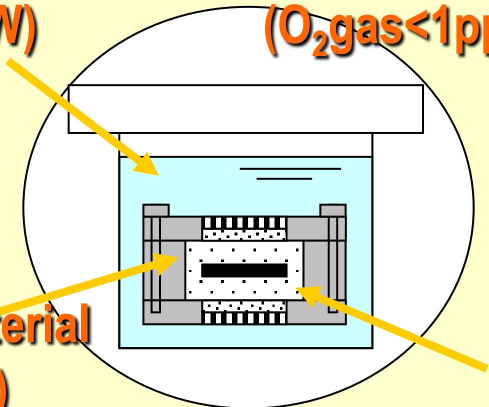
4 cm: corrosion allowance (3.18cm/1000y)

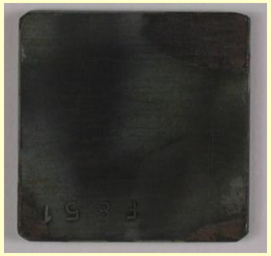
15 cm: radiation proof

It is very important to estimate long corrosion behavior of OP.

Corrosion experiment in lab.

to estimate Long-term Corrosion Rate of carbon steel overpack

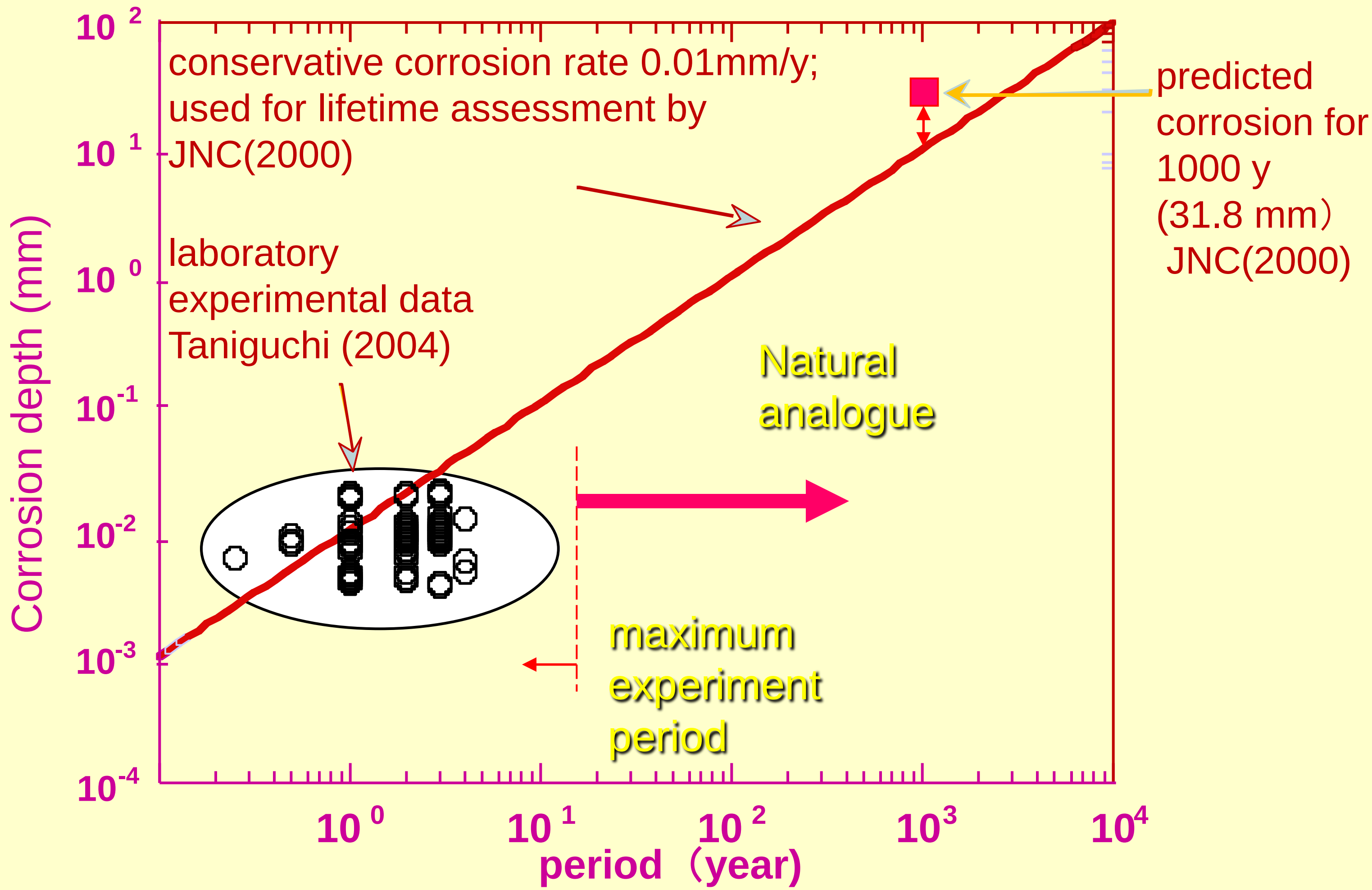




Carbon steel
Sample (10 y)

Immersion test in bentonite

Laboratory experimental data (Carbon steel)



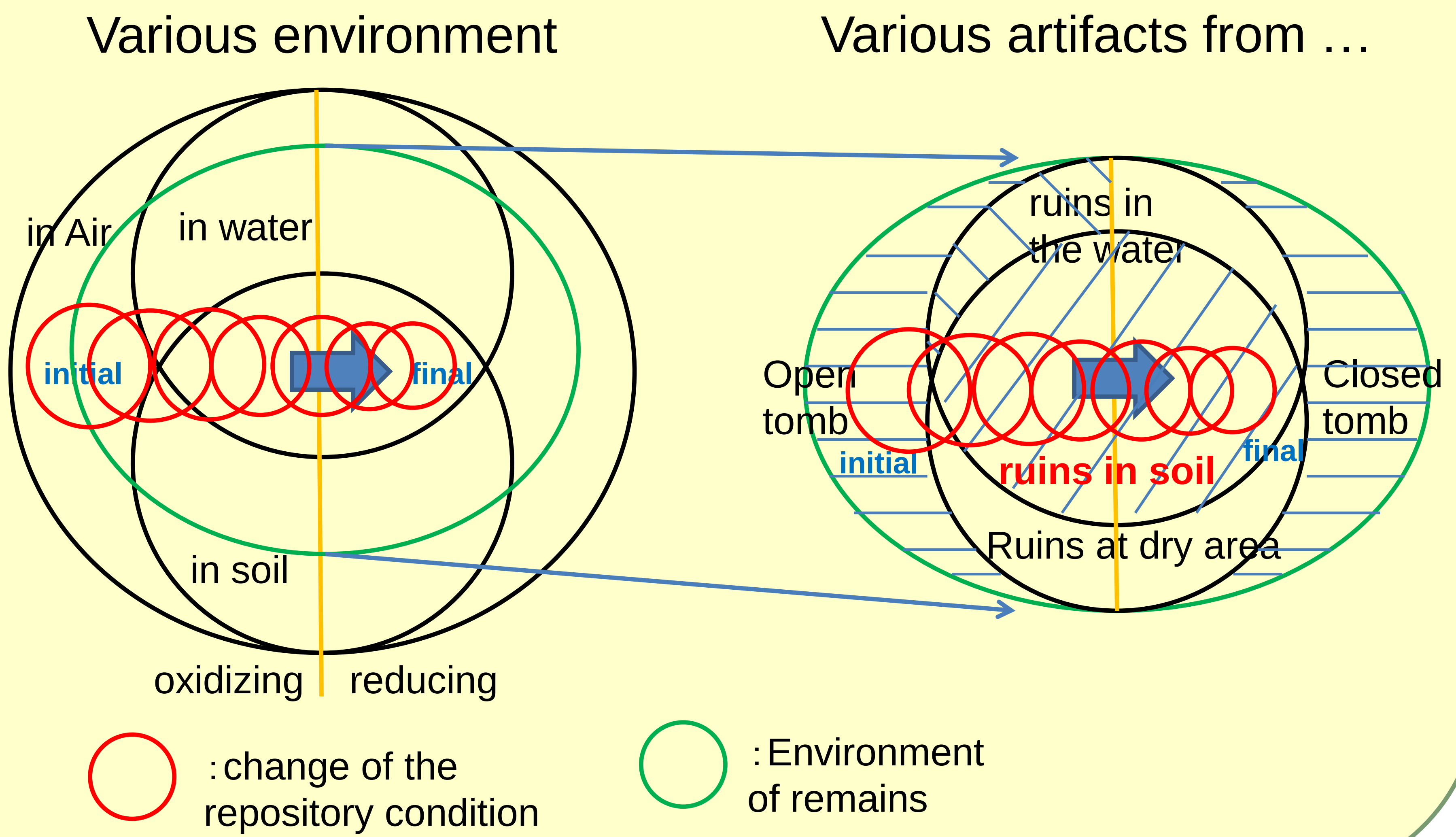
useful evidence for long-term lifetime of a waste container are required

Taniguchi(2004): Proceedings of the 2nd International Workshop, Nice, September 2004, p24-34

What is required for useful evidence as natural analogue ?

- Required data
  - degree of corrosion（corrosion volume、density of rust layer 、chemical composition of rust）
  - environment parameter（oxygen concentration、water content、salinity、soil potential、redox potential、biomass、buried period）
- Sample
  - iron based artifacts（in soil、in a closed space、in the sea）、bronze or copper based artifacts（ in soil、in a closed space、in the sea ）、soil、ground water、dating sample
- Measuring method
  - Instrumental analysis（XRD、X-CT、SEM)、Chemical analysis（SO_4^{2-}、Fe^{2+3+}、Cu^{2+}、Cl^-、soil potential、soil pH）、Microbial analysis（SRB、IRB、IOB）、Dating（AMS）
- Required information
  - corrosion rate、corrosion environment（corrosion factor）、corrosion period、material components

Useful sample as natural analogue ?



Potential to obtain sample of iron and cupper artefacts

42 prefecture

Ex) iron artefacts sample

References

180 reports

Database

Iron artefacts excavated at 580 sites

Japanese archaeological history

2000	1000	B.C.	1000	2010

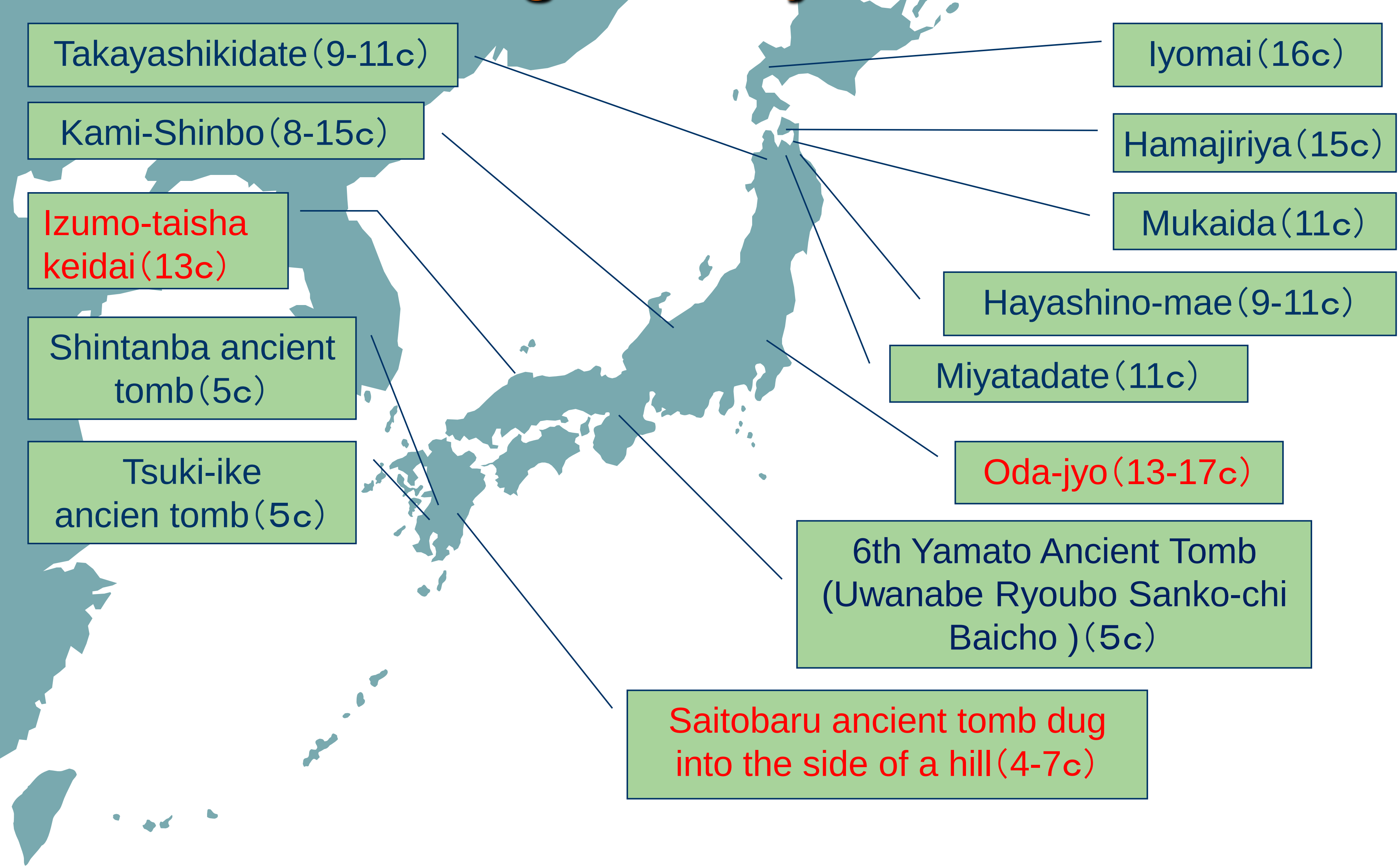
Stone Age

Bronze Age

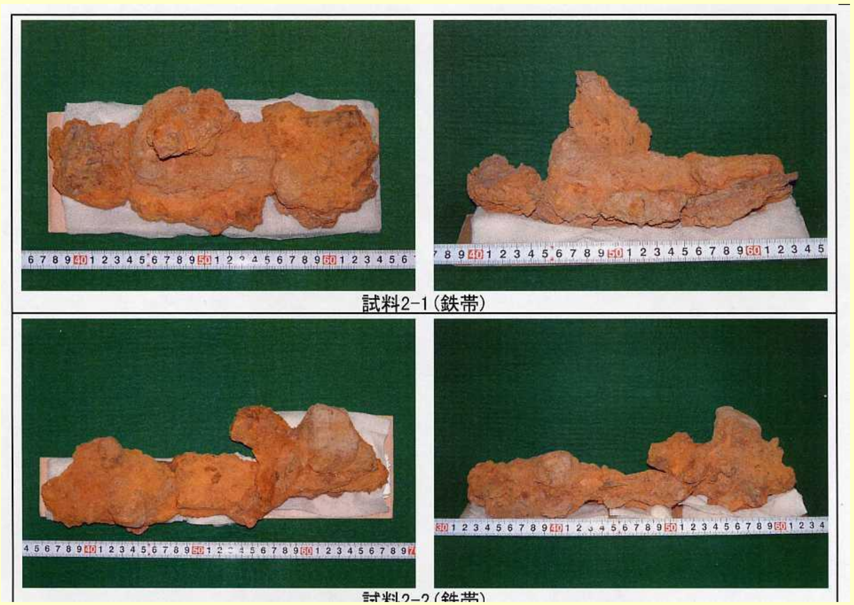
Iron Age

Copper

Some investigate locations for this natural analogue study of iron artefacts



Corrosion Environment



Iron-based artifacts corroded in strongly oxidizing condition

Iron-based artifacts corroded in slightly oxidizing condition

Site investigation for environment of soil

Measurement of redox potential

Site investigation for environment of soil

Polarization resistance method
(portable corrosion rate measurement, Rohrback Cosasco Systems, Corrater® Aquamate):
corrosion rate of original metal without rust layer using a carbon steel（P/N 850-K03005）

Measurement of soil potential

in soil : 0.169～0.173mm/y
in groundwater : 0.047～0.050mm/y
from iron-based artifacts : 0.0006～0.002mm/y (X-CT data)

Soil sampling for microbe

A sampling for microbe analysis

contacted with upper side surface of the sample

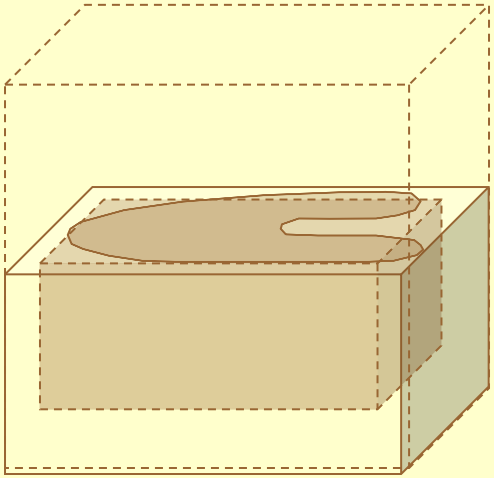
03: soil include some carbide under the sample

04: conglomerate layer under the sample

Soil sample

at site
- No.01
- No.02

in Lab.
- No.03
- No.04



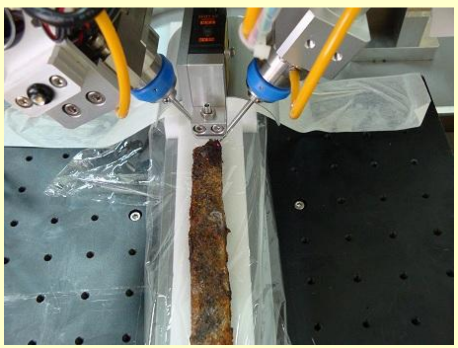
Results of microbe analysis

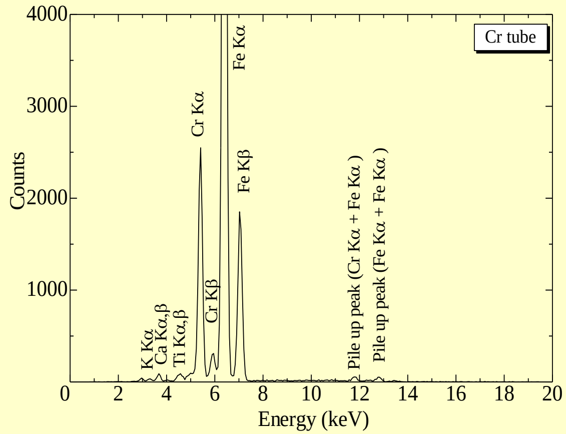
No.	Most Probable Number (MPN method) (cell/g)			
	aerobe	Iron oxidizing bacteria	iron reducing bacteria	sulfate reducing bacteria
01	7.0×10^{8}	N.D.	1.2×10^{4}	3.4×10^{3}
02	2.2×10^{9}	N.D.	2.3×10^{4}	1.5×10^{3}
03	4.9×10^{8}	N.D.	9.0×10^{2}	6.0×10
04	7.9×10^{8}	N.D.	2.2×10^{4}	7.3×10^{3}

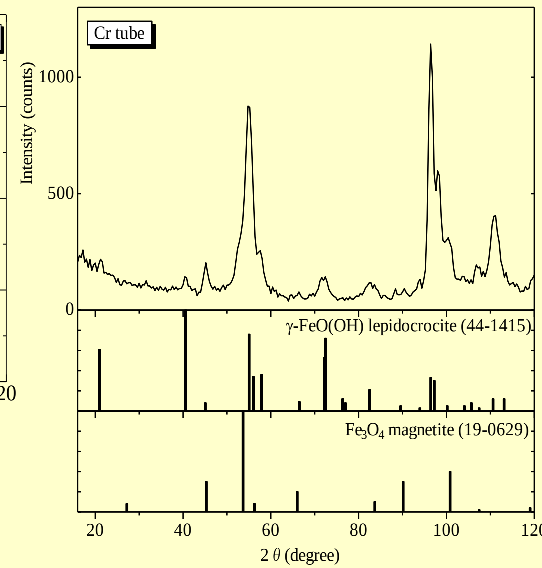
01,02:contacted with upper side surface of the sample

03:soil include some carbide   04:conglomerate layer

Portable X-ray Diffraction and X-ray Fluorescence analysis

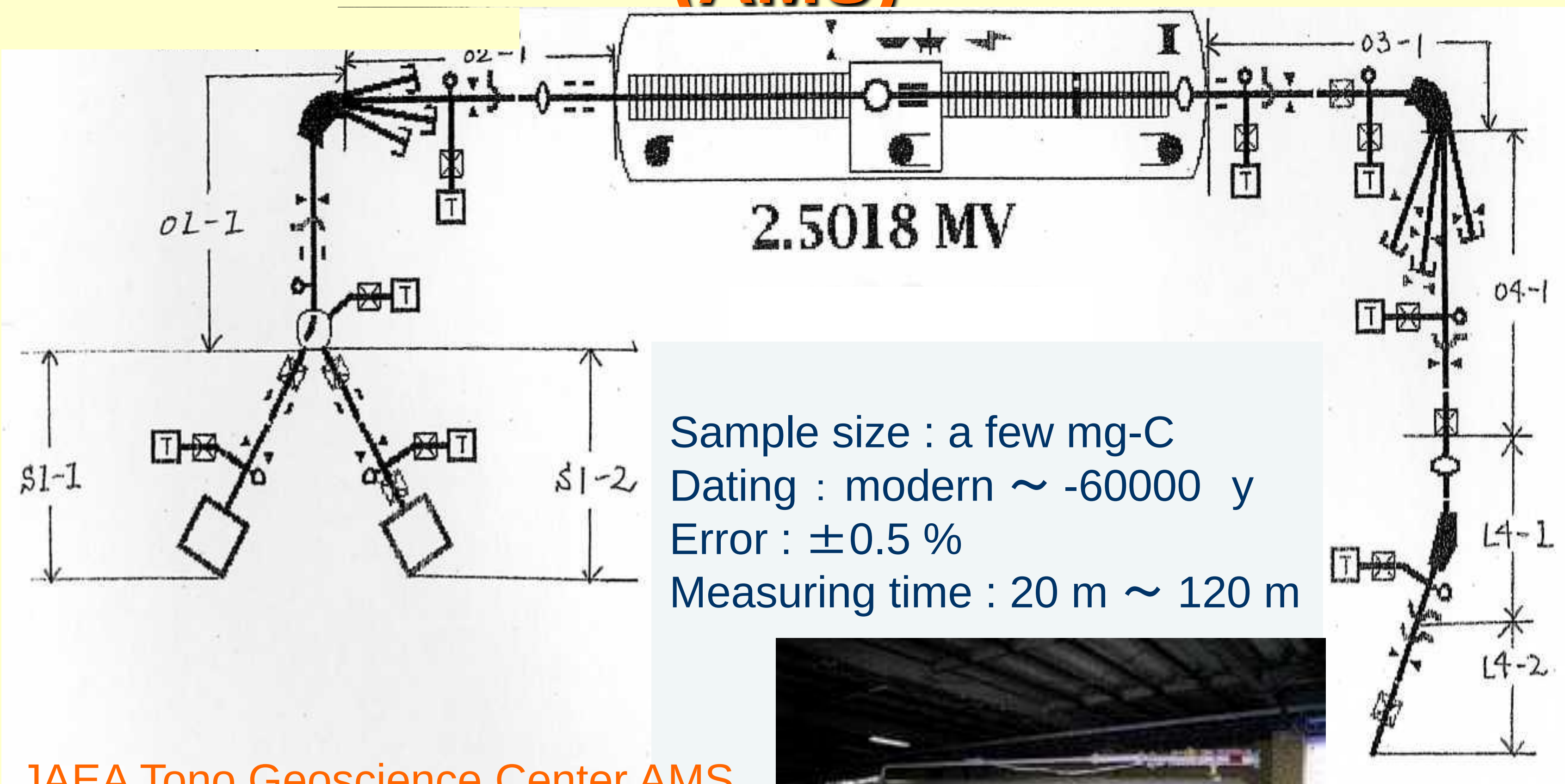






Result of X-RD shows that the rust was mainly amorphous materials. Chemical composition of a crystal part of the rust were goethite (alpha-FeOOH), magnetite ($Fe3O4$), lepidocrocite (gamma-FeOOH), and akaganeite (beta-FeOOH).

Dating : Accelerator Mass Spectrometry (AMS)

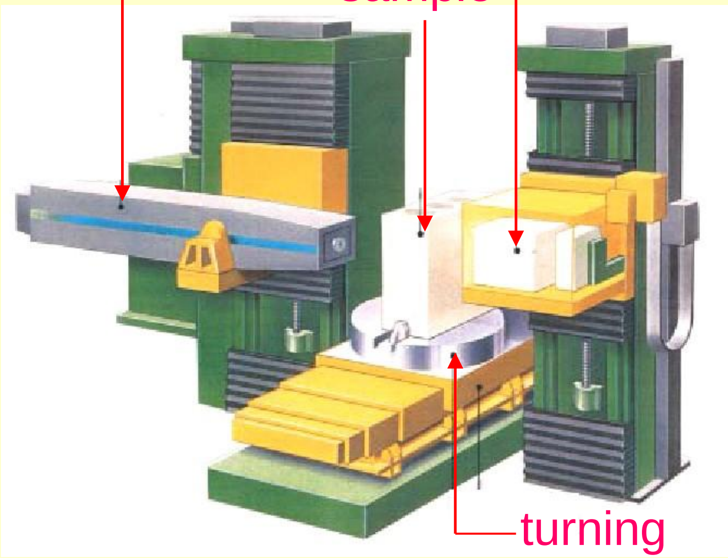


Sample size : a few mg-C
Dating ： modern ～ -60000　y
Error : ±0.5 %
Measuring time : 20 m ～ 120 m

JAEA Tono Geoscience Center AMS

Analytical Method：X-ray computer tomography (X-CT)

X-ray energy	max. 6MeV (280mm as iron)
thickness range of measurement	0.4mm
size of pixel image	0.2 - 0.34 mm
number of pixel data	900x900 or 2760x2760

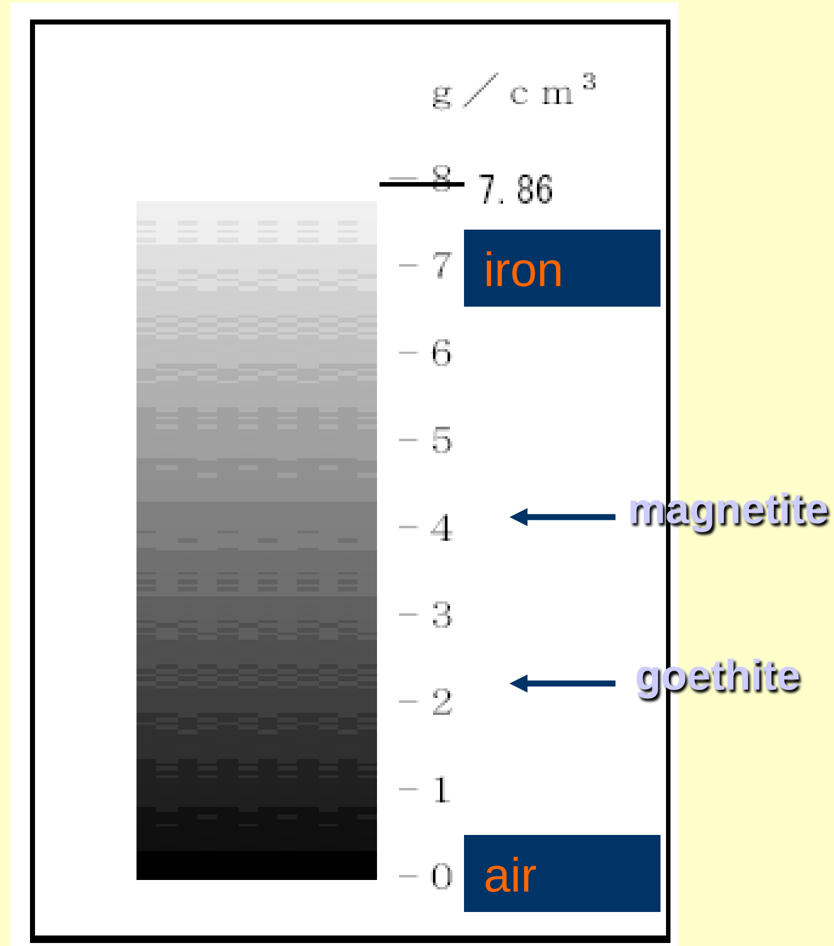


X-ray CT (HiXCT-6M)

Case of iron artifacts

sample: belts and nails

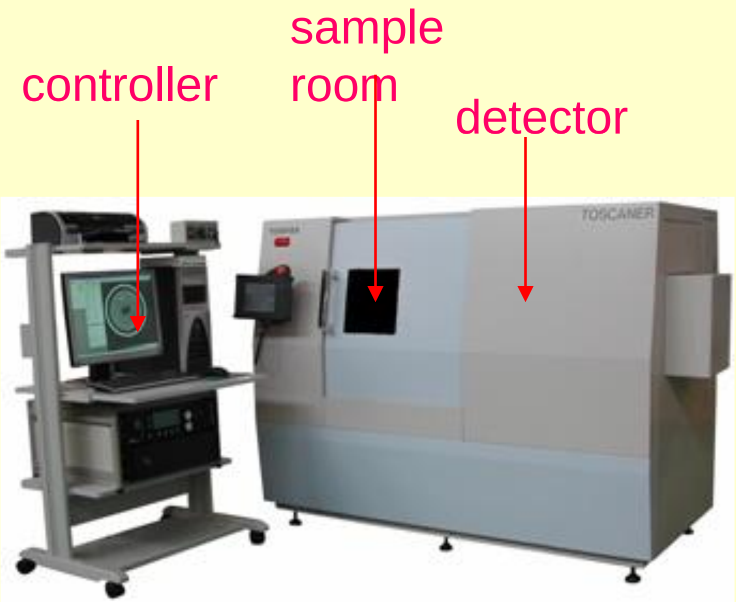
surface : cinnamon color
(high oxygen concentration)
material : iron is a little remained or not
rust : low density rust,
total corrosion depth : 0.7 – 5.7 mm
analytical method: X-ray computed tomography



Density distribution obtained by X-ray CT

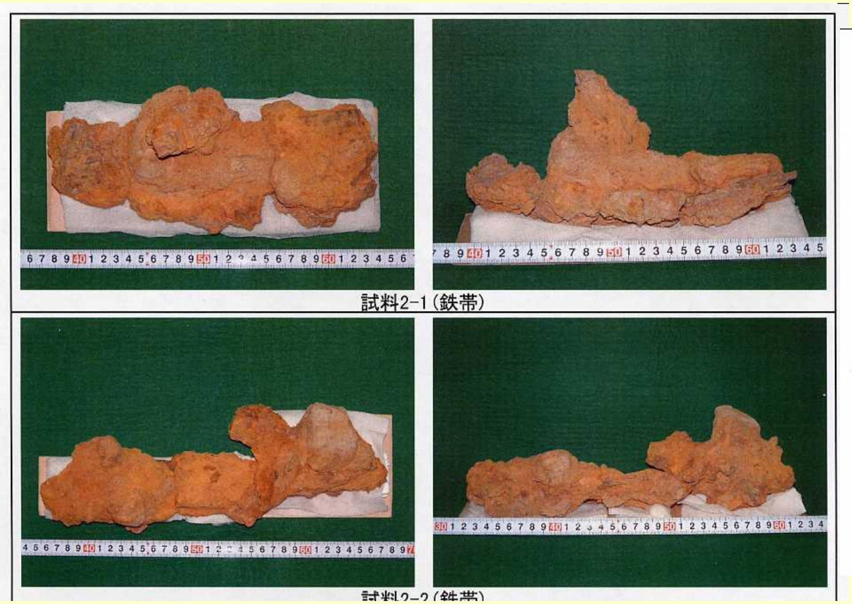
Analytical Method：X-ray computer tomography (X-CT)

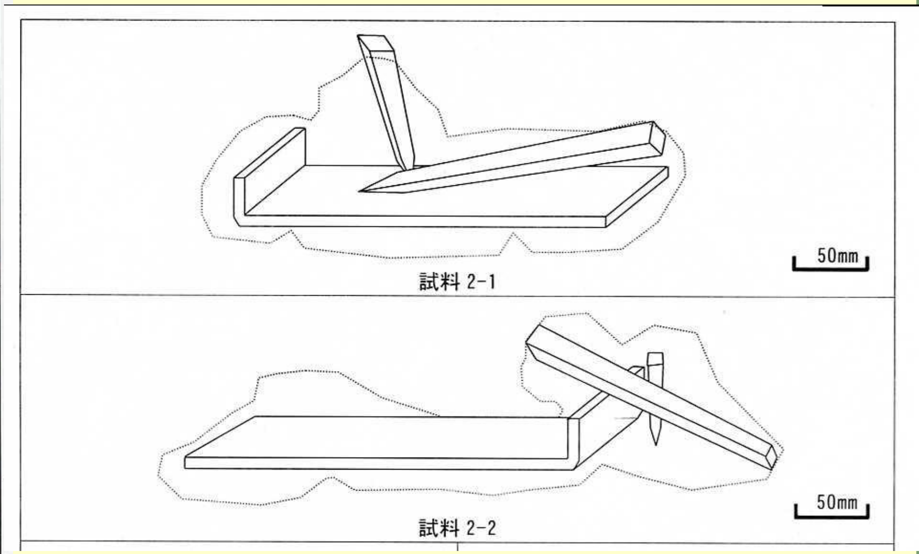
X-ray energy	max. 230kV（ca50mm as iron）
thickness range of measurement	0.1mm
Max scan size of sample	200 - 300 mm



X-ray CT (TOSCANER-3000μ)

A) Complete corrosion sample





Iron-based artifacts corroded in strongly oxidizing condition

Simulation their original form based on the data of X-ray CT

B) Two layer corrosion sample

Case of iron artifacts (Hoe)

"Odajyo" ruin, (13c～17c)

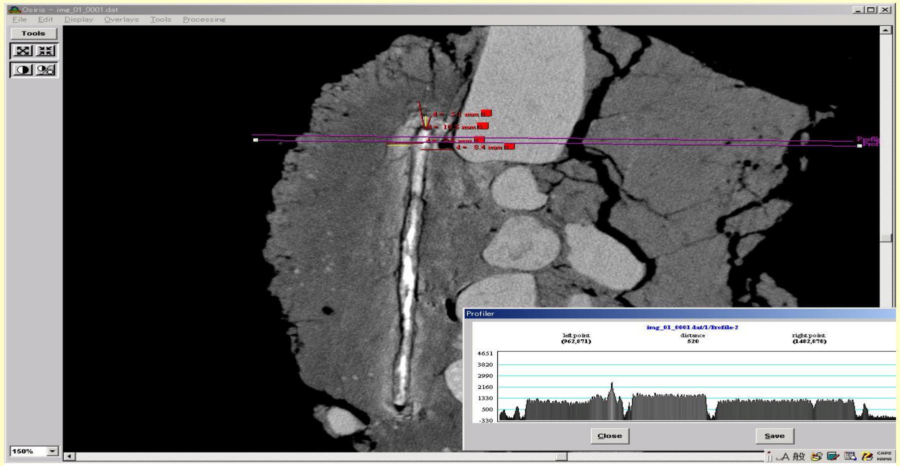
Excavated sample :
The hoe was picked up with surrounded soil using polyurethane resin

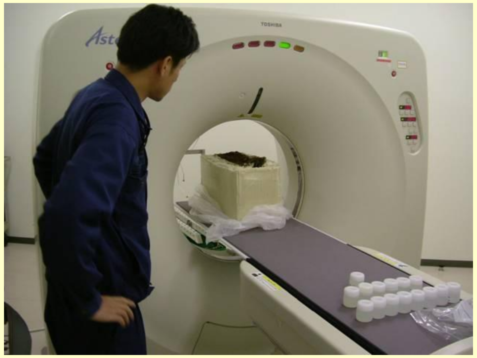
Tsukuba-city

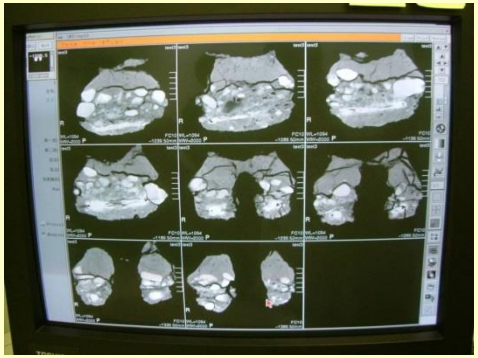
Length : about 300 mm,
Width : about 100 mm

An iron-based hoe had been buried in a soil under rice field. (2006)

The result of X-ray CT measurement







X-ray CT (Toshiba co.) for medical use

C) One layer corrosion sample

Case of iron artifacts

"Izumo Taisha Keidai" ruin, (13th C)

Excavated iron hand axe buried in clay soil

long : approx. 120mm,
width : approx. 75 mm

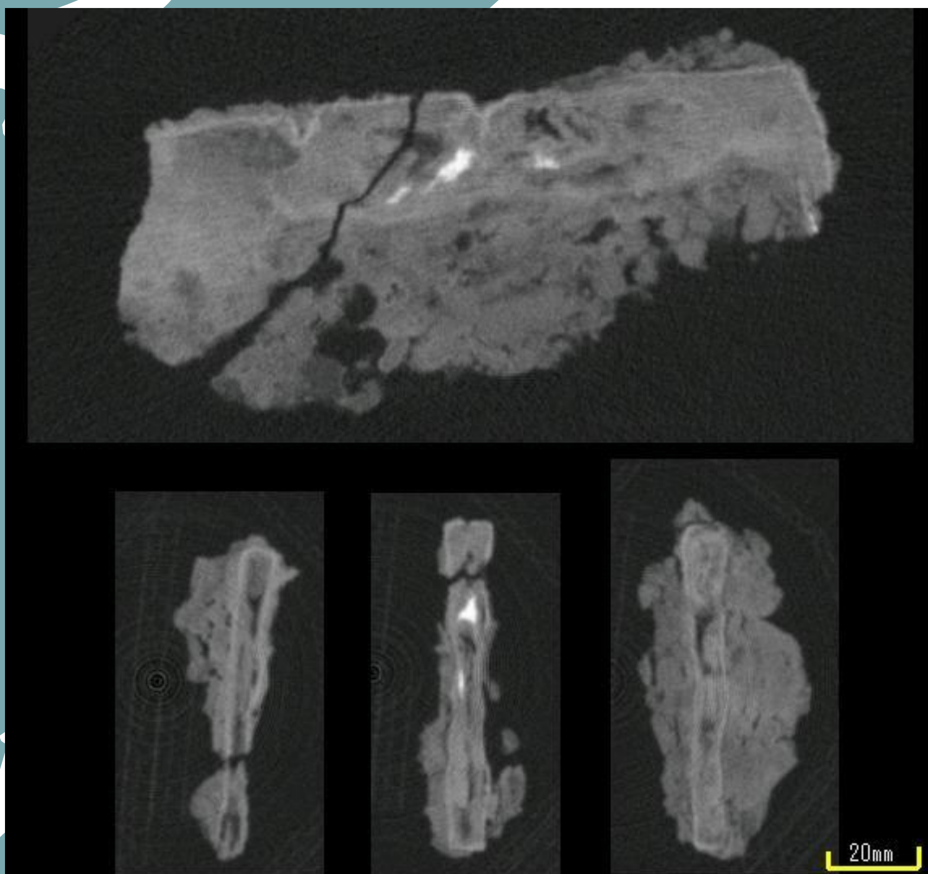
- **in Shimane-prefecture, west of Japan**
- **buried period : c.a.750 years (AMS dating 1228) excavated at Dec.2000**
- **Investigated sample : some excavated iron artifacts**

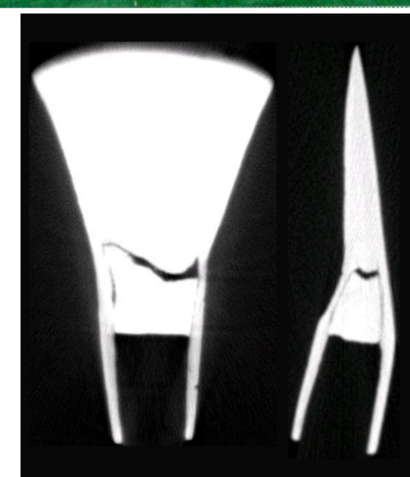
  2 pieces of "chouna" (iron hand axe),
  3 pieces of belts, 5 pieces of nails

- **buried condition : reducing condition (2 axes)**
  surrounded clay soil material

Case of iron artifacts

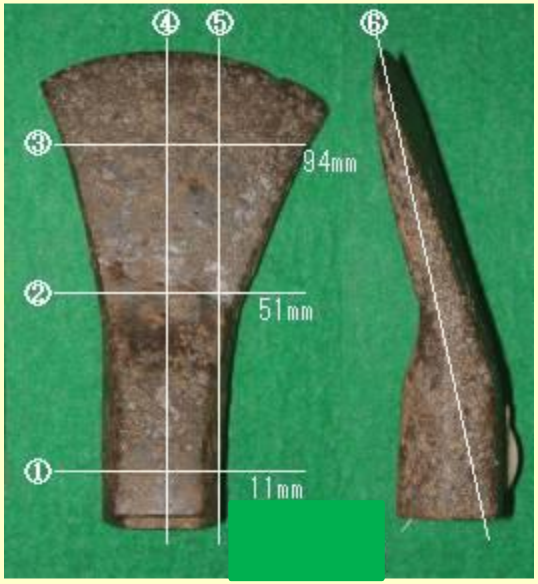
“Izumo Taisha Keidai” ruin, (13th C)

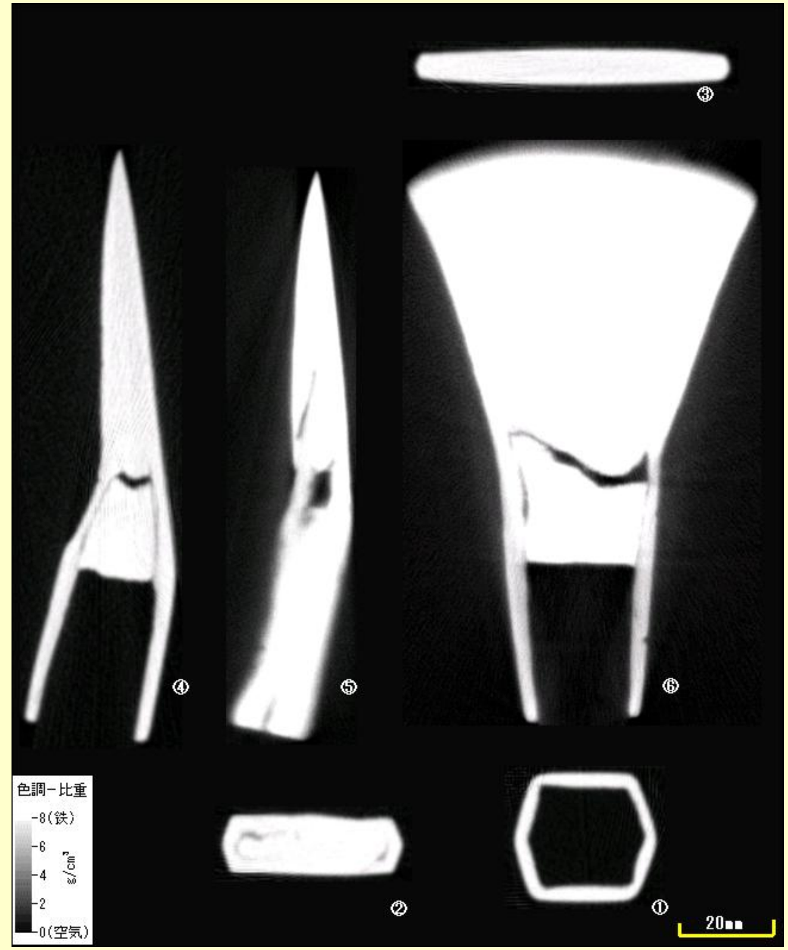




Case of iron artifacts

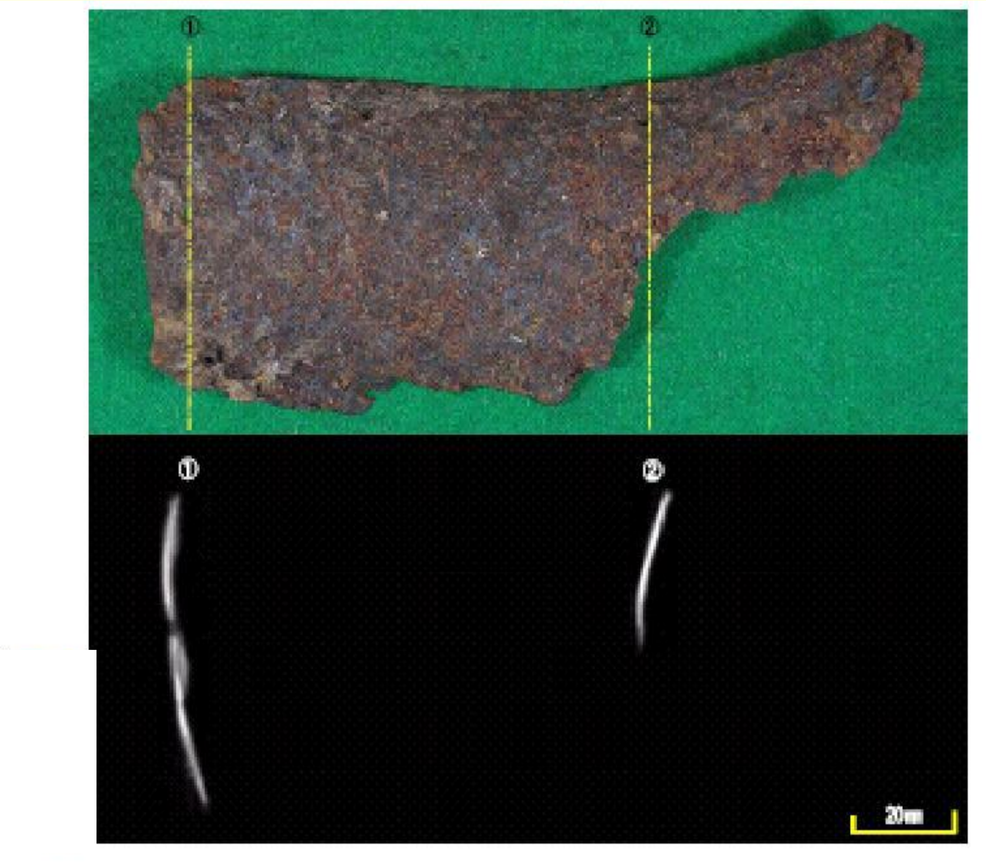
sample: chouna" (iron hand axe)





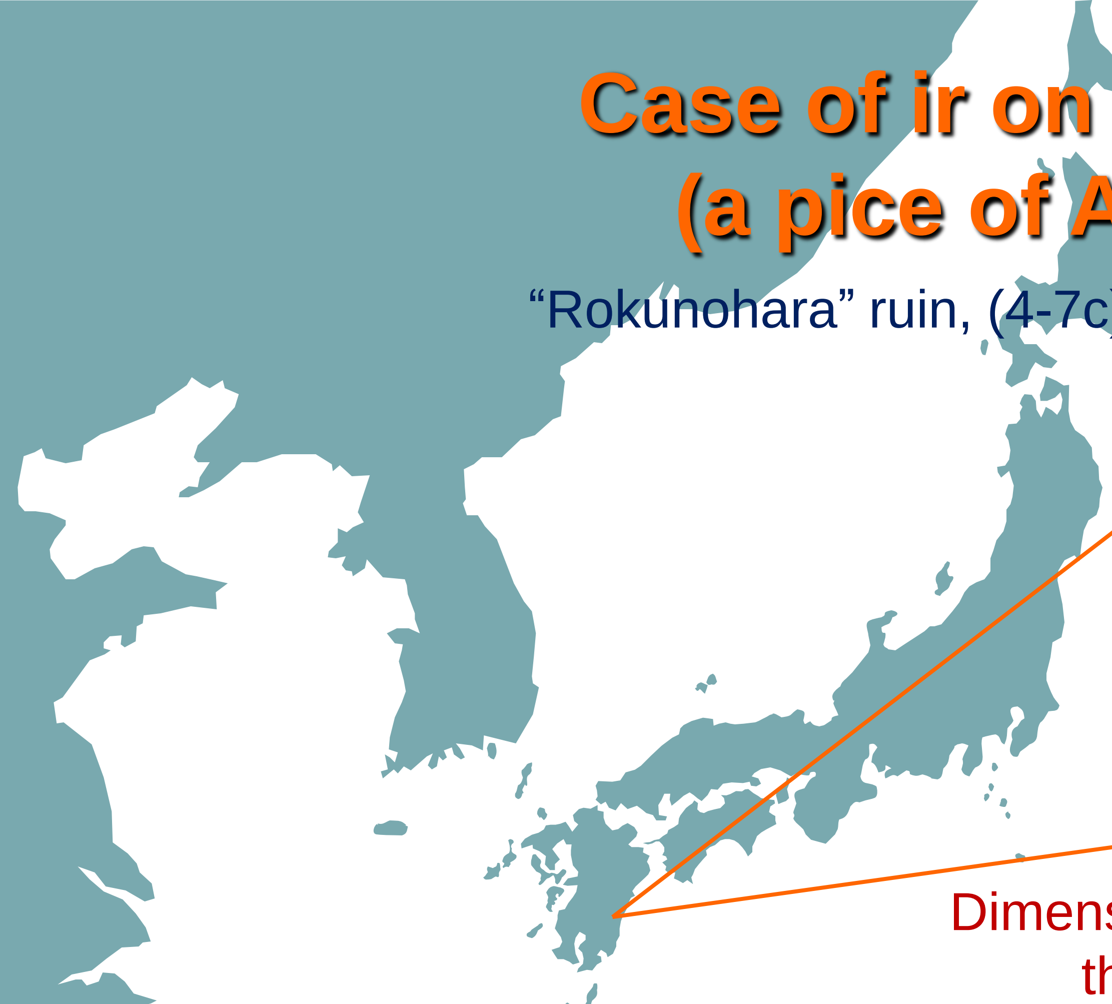
surface : black umber
(low oxygen concentration)
material : iron is almost remained
rust : high density rust,
total corrosion depth : 0.2 – 0.67 mm
corrosion rate : (0.26 – 0.89) x10^{-3} mm/y
analytical method: X-ray computed tomography

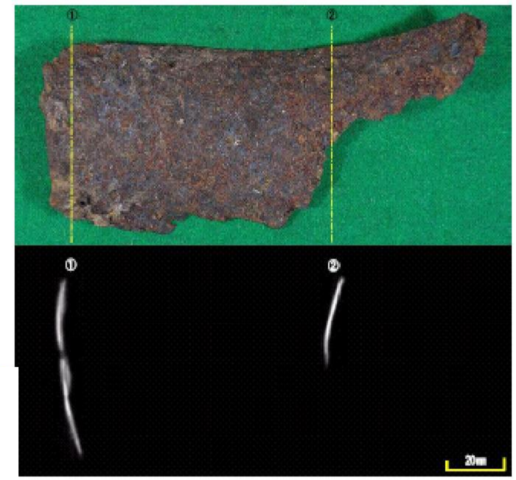
D) One layer and pitting corrosion sample

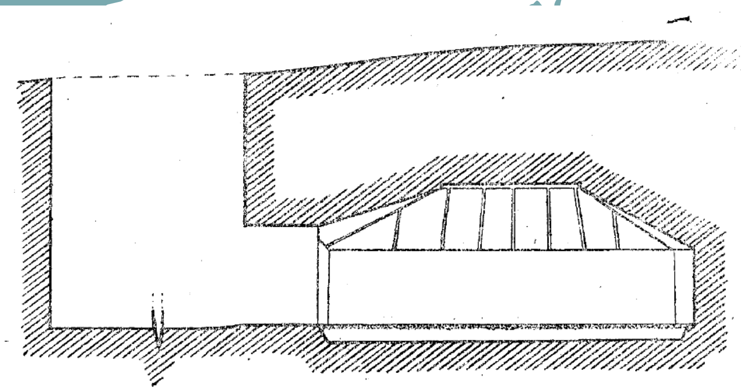


Case of ir on artifacts (a pice of Armor)

"Rokunohara" ruin, (4-7c) Ancient tombs







Dimension : :width about130㎜
thickness about 2 ㎜
Color: black surface
（slightly oxidizing condition）
XRD : magnetite
pitting and general corrosion
（general corrosion＜about 0.2mm）
(pitting corrosion = about 2.0 mm)

Classification for corroded iron artifacts （4 types）

A）complete corrosion : achieve a state of perfection under oxidation, corrosion rate is estimated as minimum A

B）two layer corrosion : remain a little material, two layer(e.g. magnetite and goethite,…), under corrosion condition B

Difference for corrosion state for corroded iron artefacts

No. (Izumo)	sample	thickness and corrosion depth (mm)		total corrosion depth (mm)	corrosion rate (mm/y)	corrosion state
		Inner layer	Outer layer			
2-1	belt	2:0.67	50:5.7	6.3	$>8.6\times10^{-3}$	**complete** A
2-3	belt	4:1.3	20:2.2	3.5	4.7×10^{-3}	**remaining iron** B
2-4	nails	10:3.3	15:1.7	5.0	6.8×10^{-3}	**remaining iron** B
2-5	nails	2:0.67	20:2.2	2.8	$>3.8\times10^{-3}$	**complete** A
2-7	nails	2:0.67	30:3.4	4.0	$>5.4\times10^{-3}$	**complete** A

Classification for corroded iron artifacts （4 types）

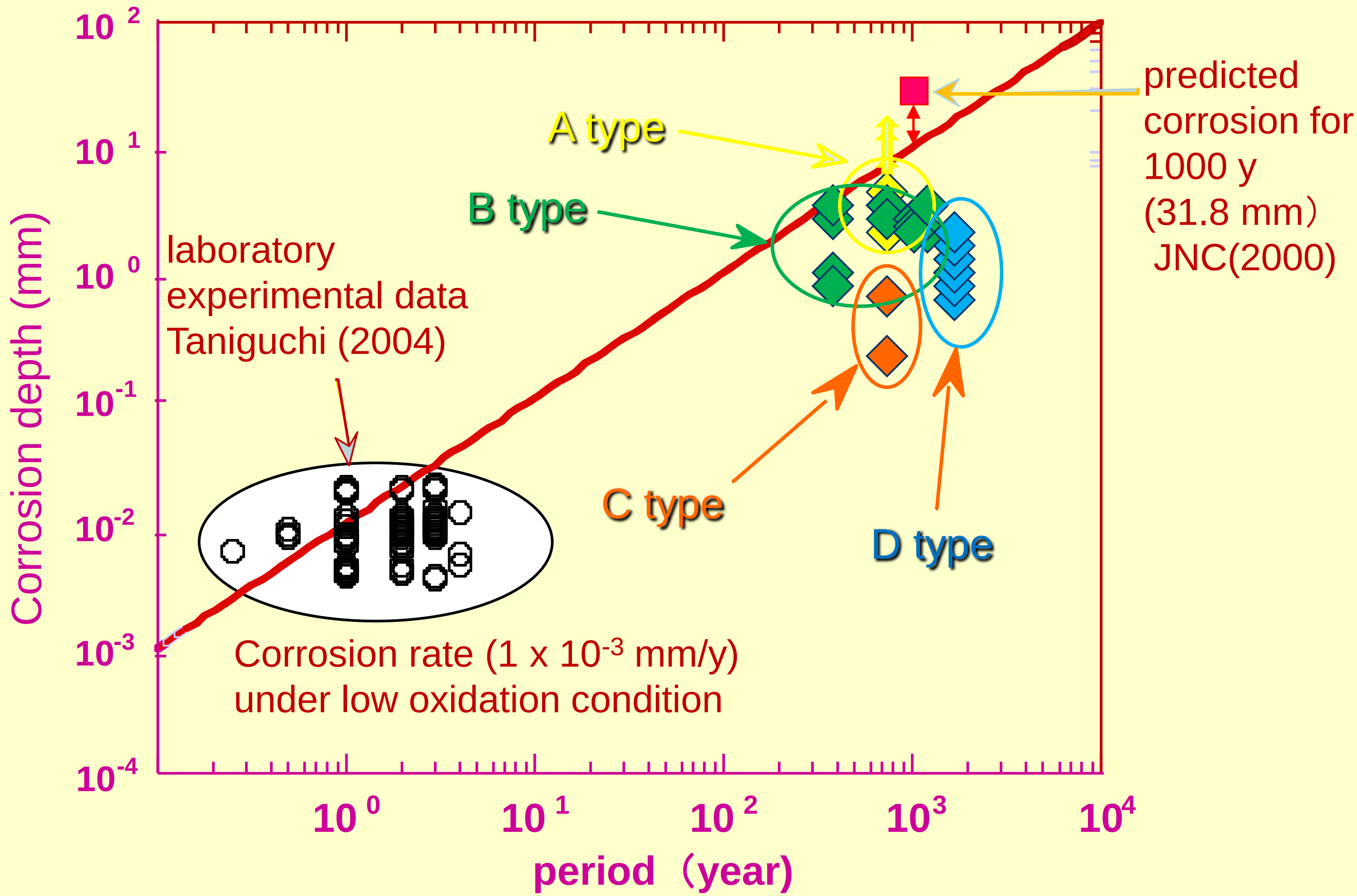
C）one layer corrosion : remain almost iron material, one layer(e.g. magnetite, siderite…) under low oxidyzing condition, general corrosion

D）one layer and pitting corrosion : remain iron material, pitting corrosion under initially high oxidation condition and then uniform corrosion (e.g. magnetite, siderite…) under low oxidation condition

Difference for corrosion state for corroded iron artifacts

No.	sample	thickness and corrosion depth (mm)		total corrosion depth (mm)	corrosion rate (mm/y)	corrosion state
		Inner layer	Outer layer			
Izumo-1	hand axe	0.3～0.6 : 0.1～0.2	ND	0.2	$0.3x10^{-3}$	**general** C
Izumo-2	hand axe	2 : 0.67	ND	0.67	$0.9x10^{-3}$	**general** C
Rokunohara	body armor	0.5 : 0.2	ND	2.2	$1.5x10^{-3}$	**pitting and general** D

Data comparison between laboratory experiments and artifacts (iron)



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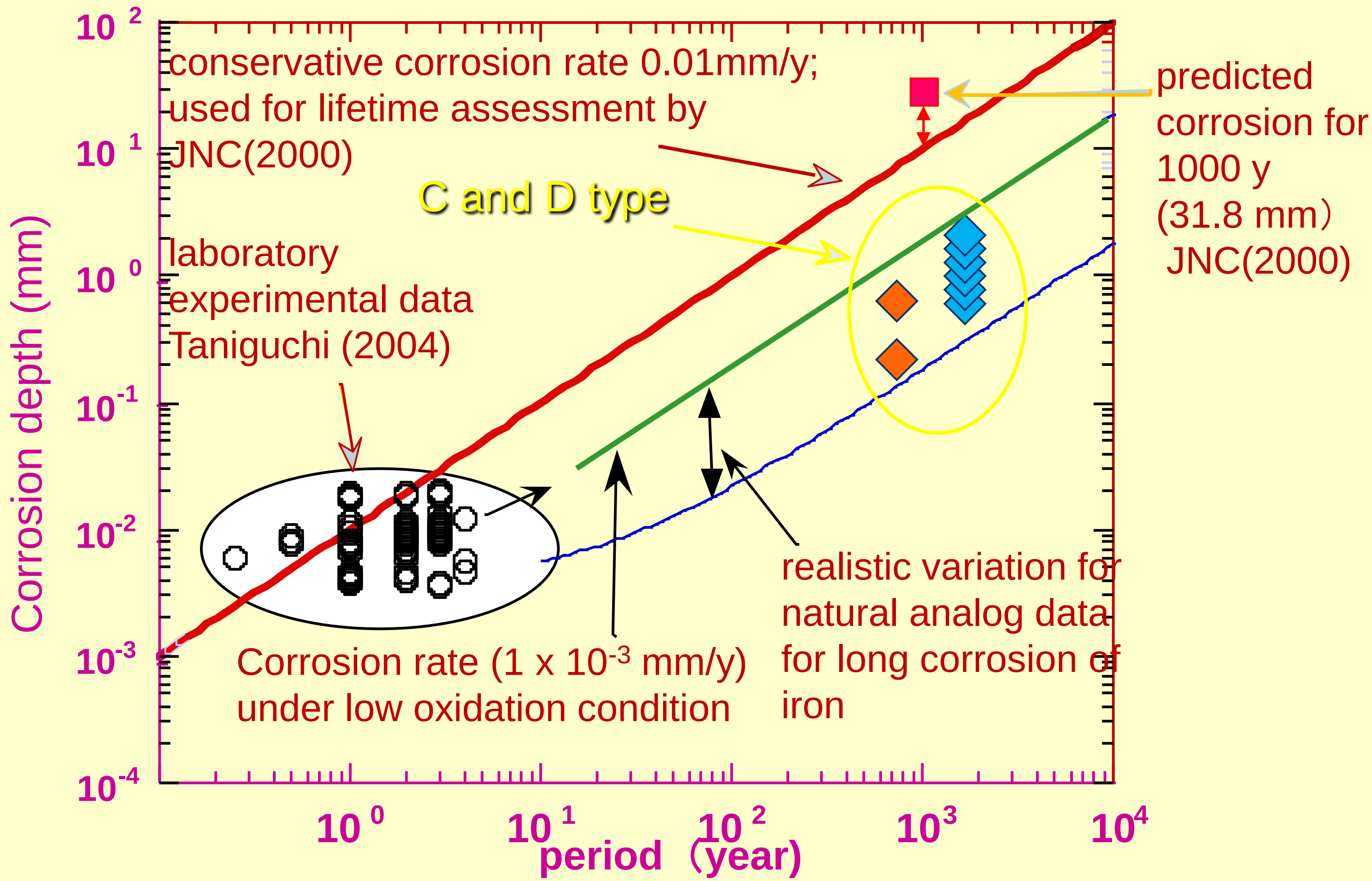
Data comparison between laboratory experiments and artifacts (iron)



useful evidence for long-term lifetime of a waste container are obtained

Taniguchi(2004): Proceedings of the 2nd International Workshop, Nice, September 2004, p24-34

Conclusions 1

- Iron artifacts : about 40 samples which were excavated at 13 ruin sites, were analyzed their corrosion depth and arranged classification in 4 groups.
- Type A : The sample was corroded completely because the environment was oxidizing condition or their thickness was thin. Data shows minimum corrosion depth at the environment.
- Type B : Two main rust were obtained, e.g. siderite-goethite, magnetite-lepidcrocite. The condition could be considered to be under slightly oxidizing conditions.
- Type C : The sample were general corroded and mainly formed siderite or magnetite rust layer.
- Type D : The sample were localized and general corroded because of change their surrounding environment.
- Type C and D could be considered to be under slightly oxidizing or reducing conditions and were corroded 0.1 – 1.0 mm for 1000 years. They are useful for natural analogue of overpack.

Conclusions 2

- The measured corrosion rates of the iron artifacts are one order of magnitude less than the design allowance of 31.8 mm / ka, which supports the argument that the designed corrosion allowance is conservative.
- The archaeological study can provide useful evidence for long-term lifetime of a waste container, which is an important element for making a robust safety case.

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Thank you for your kind attention.