



# **Input of iron corrosion studies to the Japanese safety case**

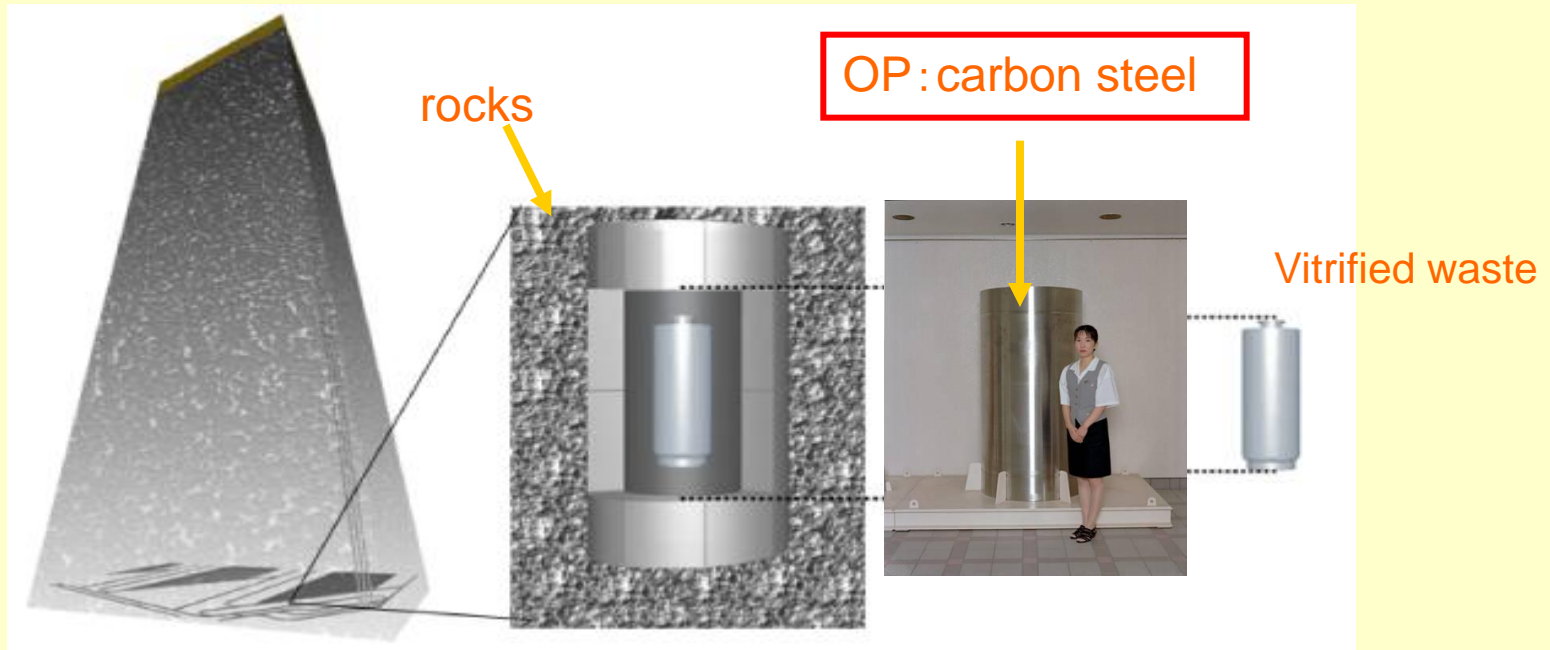
**— Corroborative evidence by using iron-based  
archaeological artifacts to long term stability of  
the overpack —**

**Hideki.YOSHIKAWA**

**Japan Atomic Energy Agency (JAEA)**

**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.**

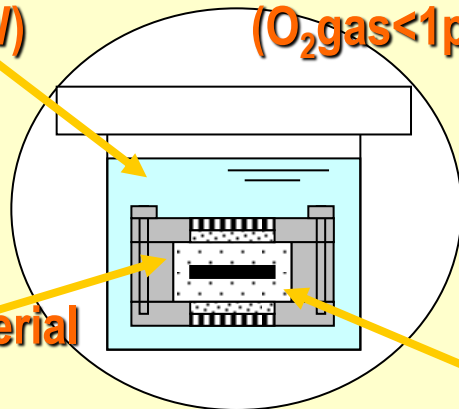
# Corrosion experiment in lab.

to estimate Long-term Corrosion Rate of carbon steel overpack

Test solution  
(SSW, SGW)

N<sub>2</sub> atmosphere grove box  
(O<sub>2</sub>gas<1ppm)

Buffer material  
(bentonite)



Constant  
temperature oven  
80 °C

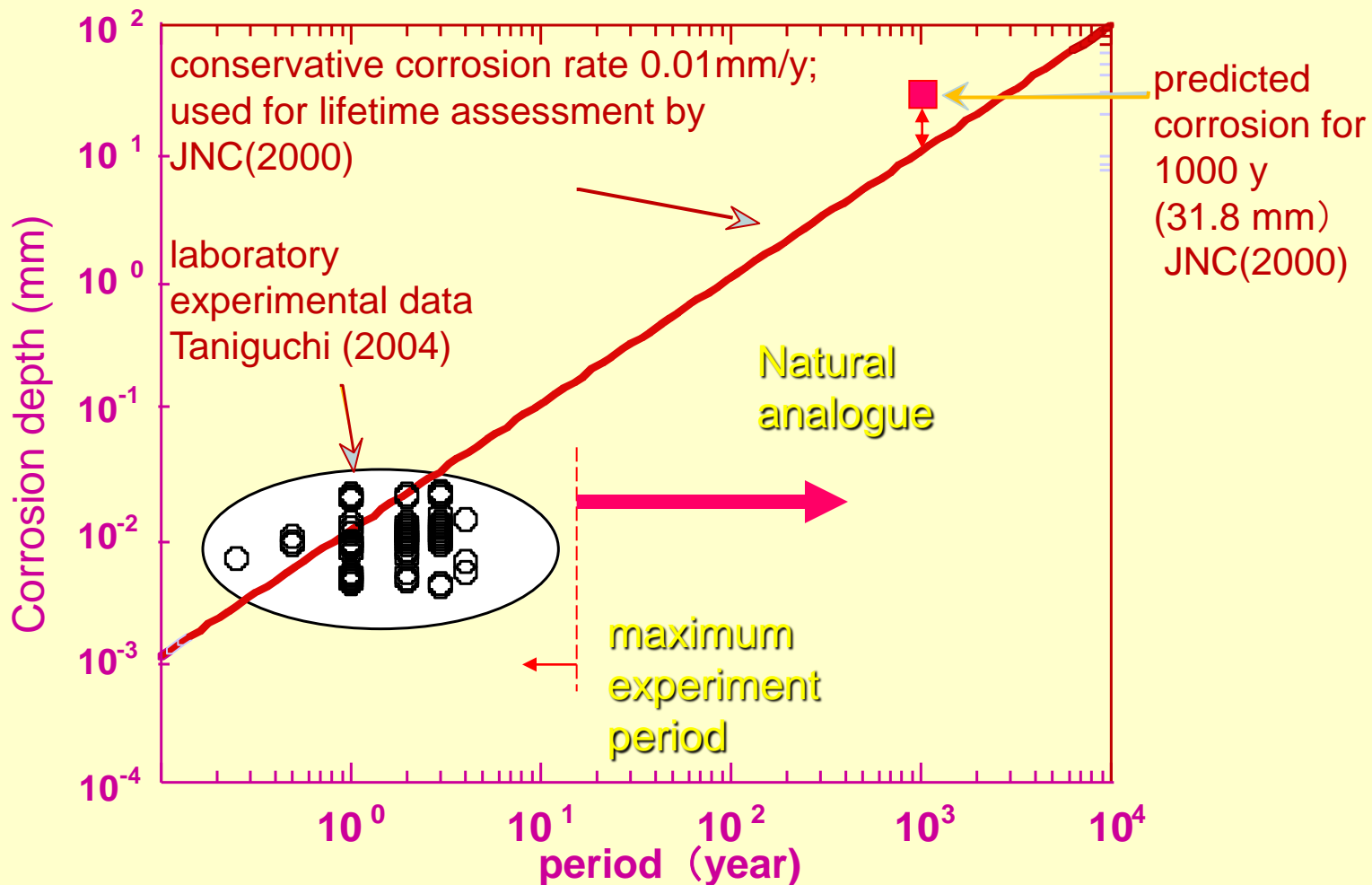
Carbon steel specimen  
(SM400B, SFVC1)



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 2<sup>nd</sup> International Workshop, Nice, September 2004, p24-34

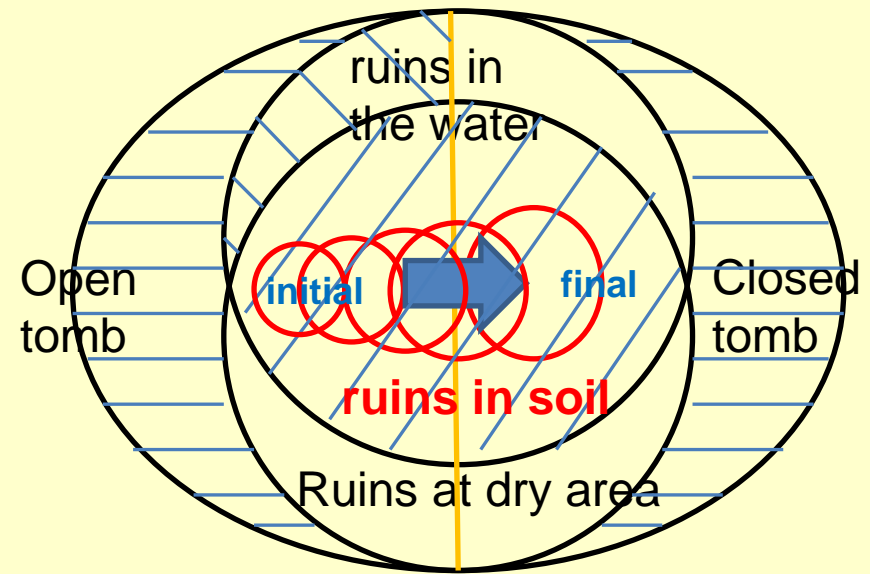
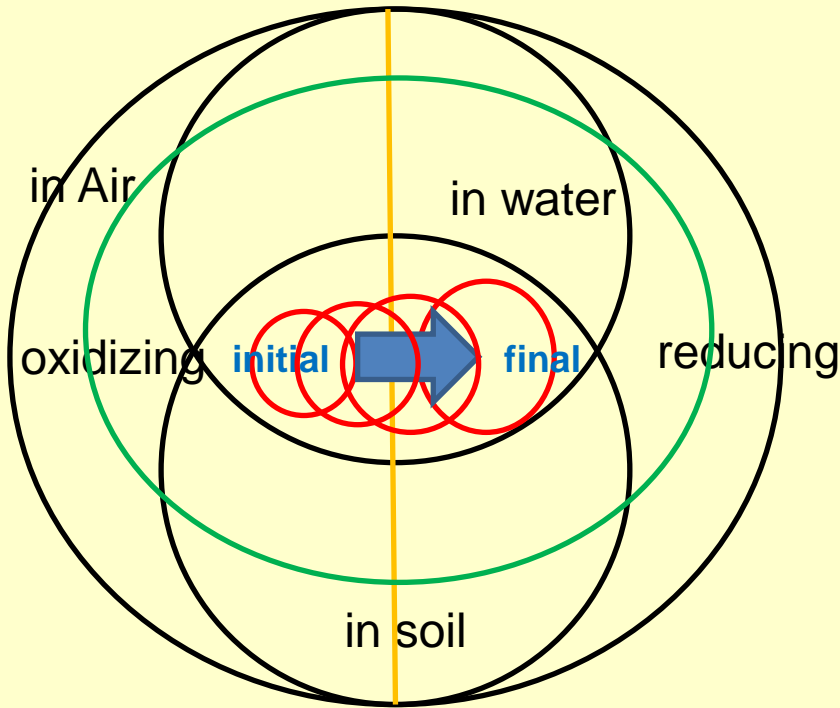
# What is required for useful evidence as natural analogue ?

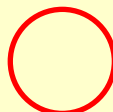
- **Required data**
  - degree of corrosion (corrosion volume, density of rust layer , chemical composition of rust)
  - environment parameter (oxygen concentration, water content, salinity, soil potential, redox potential, biomass, buried period)
- **Sample**
  - iron based artifacts (in soil, in a 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<sub>4</sub><sup>2-</sup>, Fe<sup>2+</sup>/<sup>3+</sup>, Cu<sup>2+</sup>, Cl<sup>-</sup>, soil potential, soil pH) , Microbial analysis (SRB, IRB, IOB) , Dating (AMS)
- **Required information**
  - corrosion rate, corrosion environment (corrosion factor) , corrosion period, material components

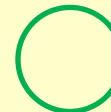
# Useful sample as natural analogue ?

Various environment

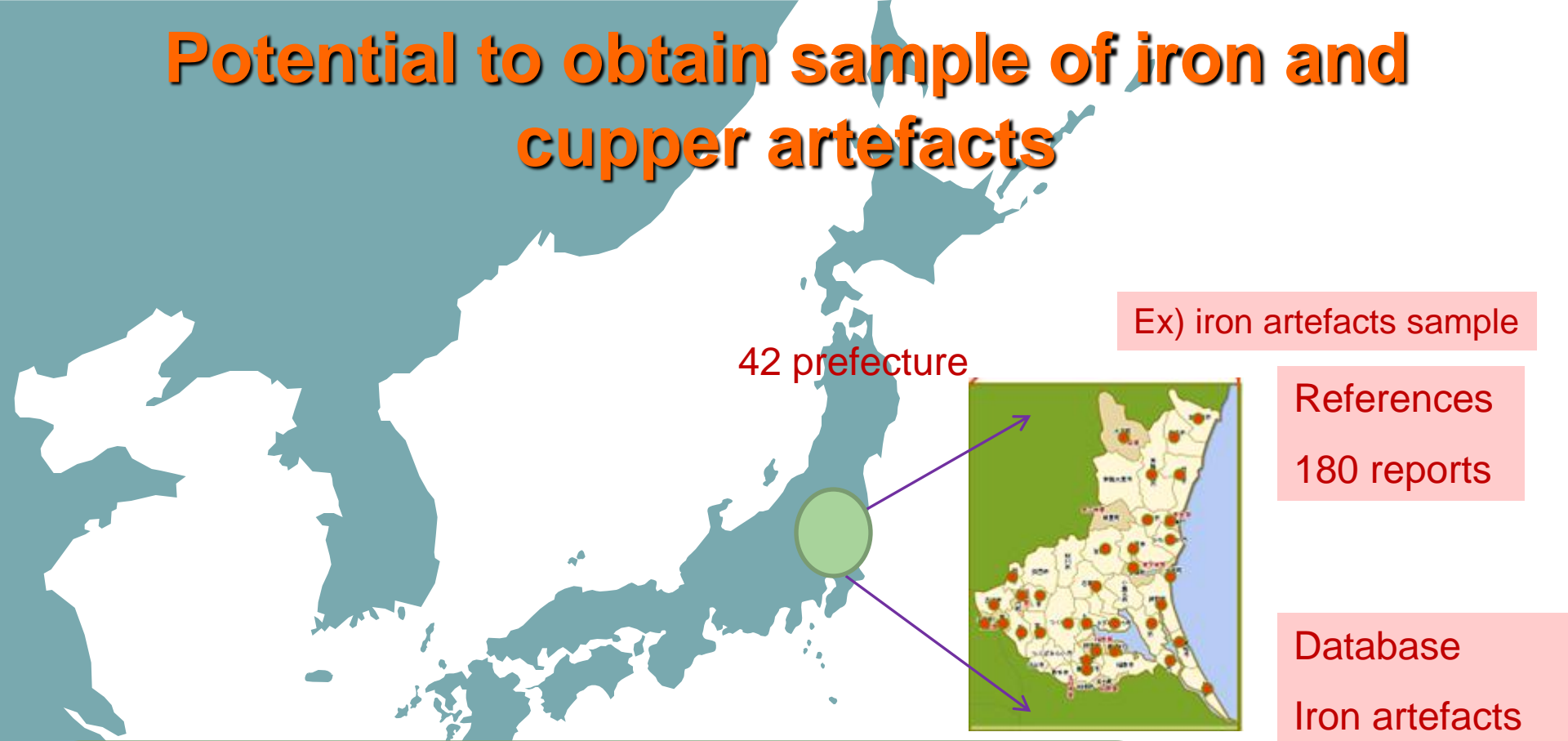
Various artifacts from ...



 : change of the repository condition

 : environment of remains

# Potential to obtain sample of iron and copper artefacts

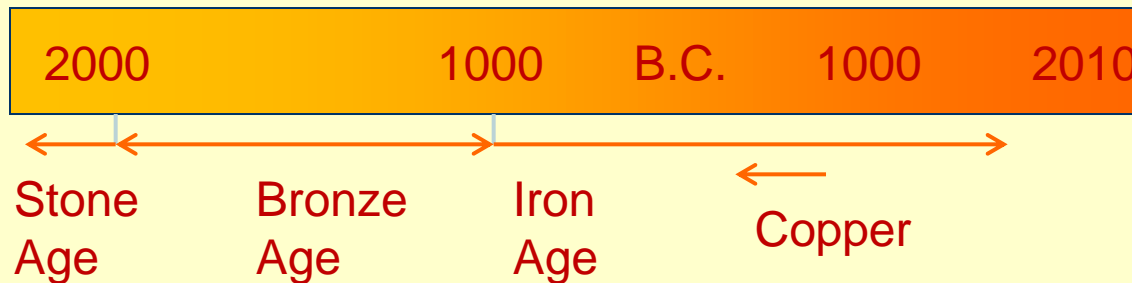


Ex) iron artefacts sample

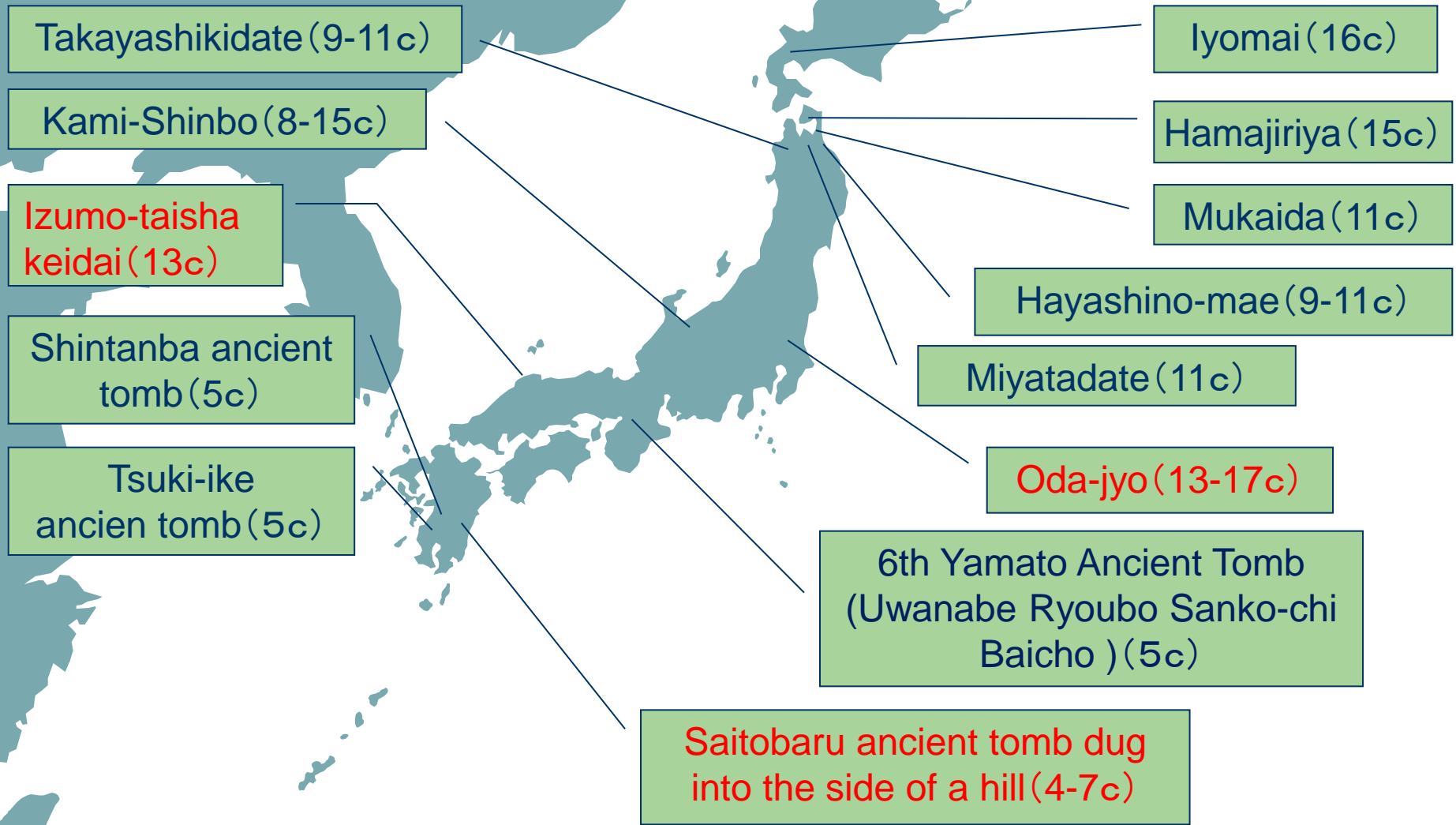
References  
180 reports

Database  
Iron artefacts  
excavated at  
580 sites

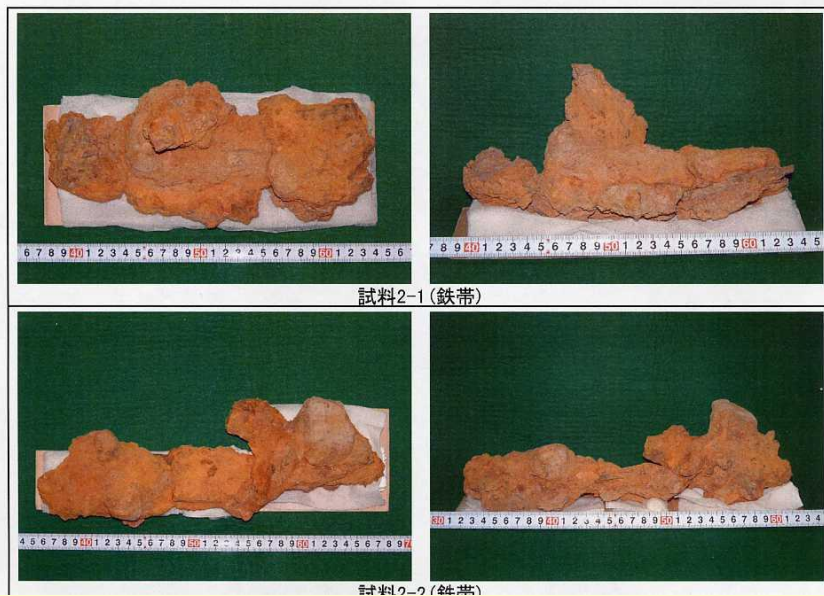
## Japanese archaeological history



# 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, Corratel®  
Aquamate):  
corrosion rate of original metal without rust  
layer using a carbon steel (P/N 850-K03005)



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)

Measurement of soil potential

# 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

at site

in Lab.

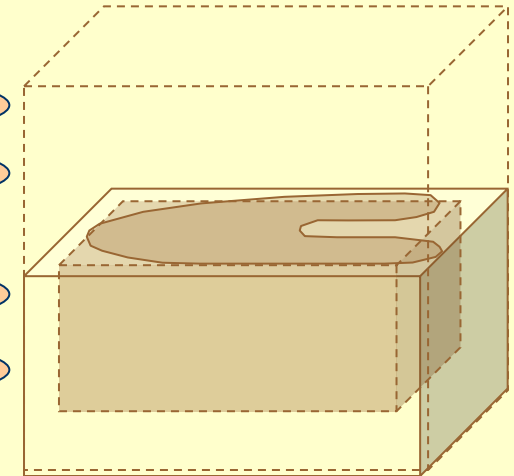
Soil sample

No.01

No.02

No.03

No.04



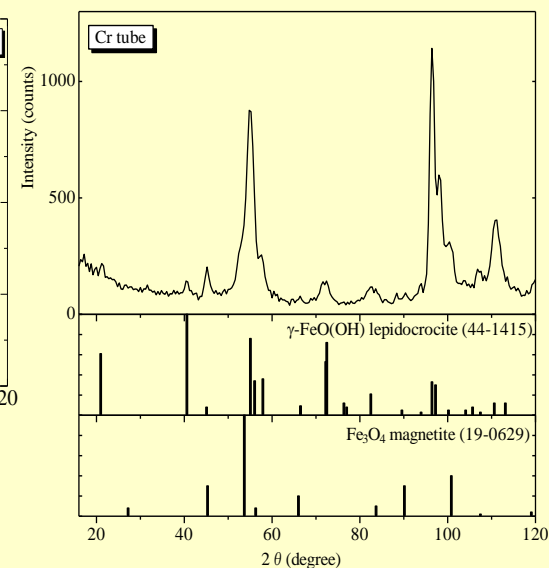
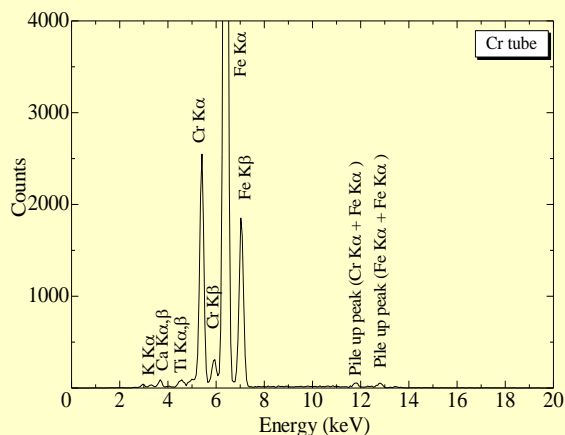
# Results of microbe analysis

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

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

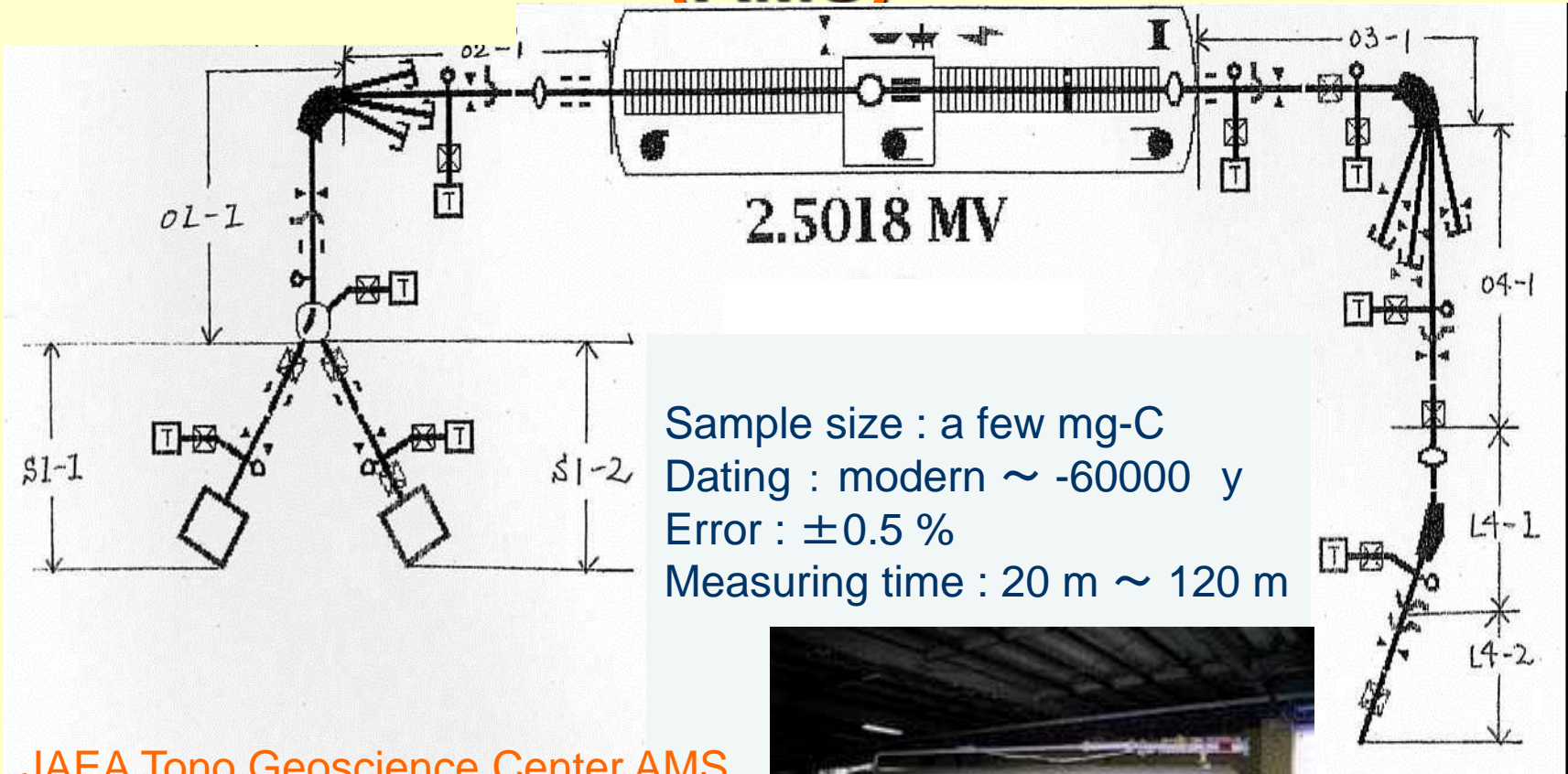
03:soil include some carbide    04:conglomerate layer

# Portable X-ray Diffraction and X-ray Fluorescence analysis



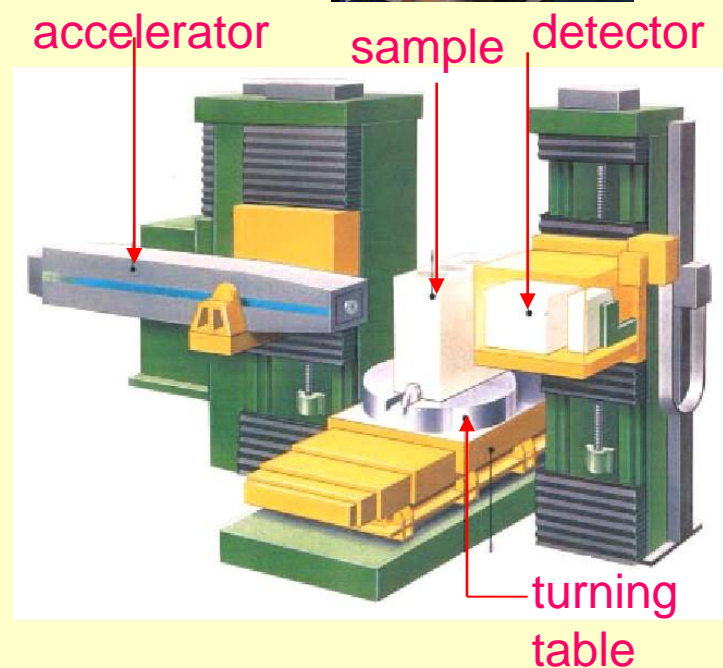
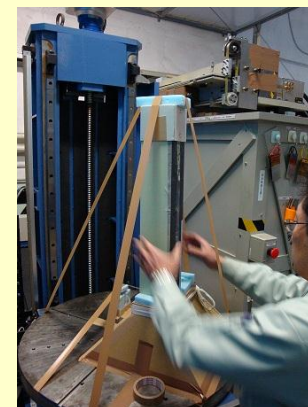
Result of X-RD shows that the rust was mainly amorphous materials. Chemical composition of a crystal part of the rust were goethite (alpha- $FeOOH$ ), magnetite ( $Fe_3O_4$ ), lepidocrocite (gamma- $FeOOH$ ), and akaganeite (beta- $FeOOH$ ).

# Dating : Accelerator Mass Spectrometry (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



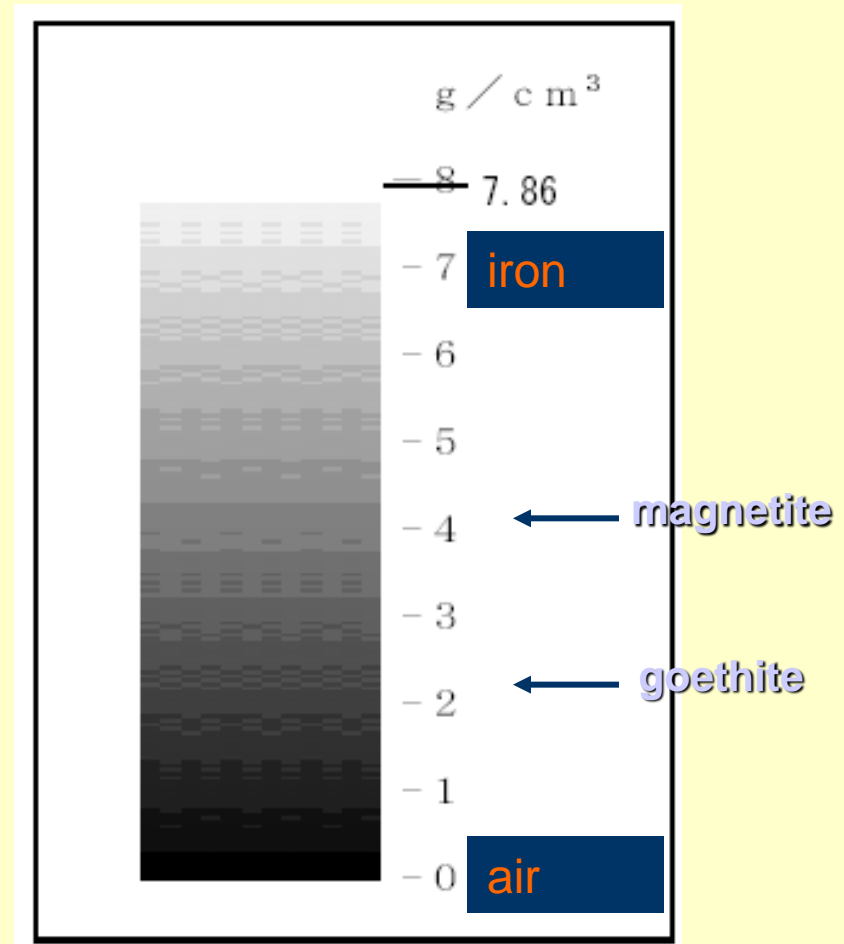
X-ray CT (HiXCT-6M)

# Case of iron artifacts

sample: belts and nails



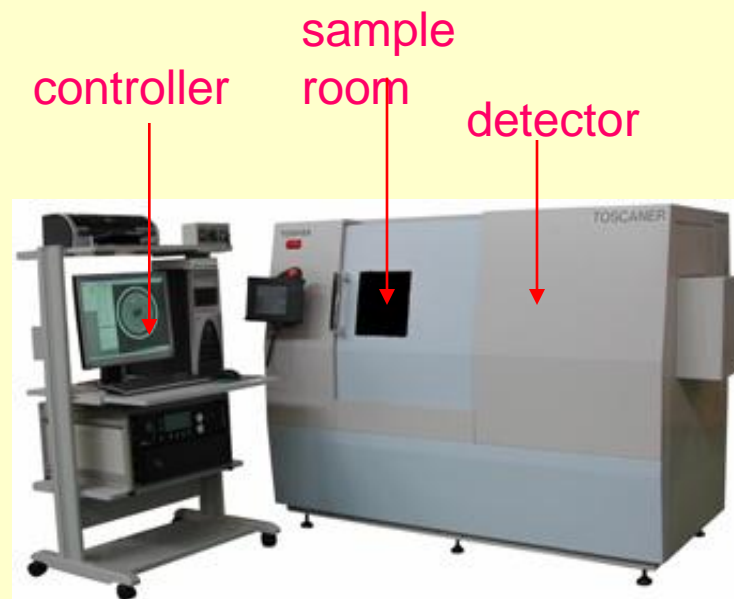
surface : cinnamon color  
(high oxygen concentration)  
material : iron is a little remained or not  
rust : low density rust,  
total corrosion depth : 0.7 – 5.7 mm  
analytical method: X-ray computed tomography



Density distribution obtained by X-ray CT

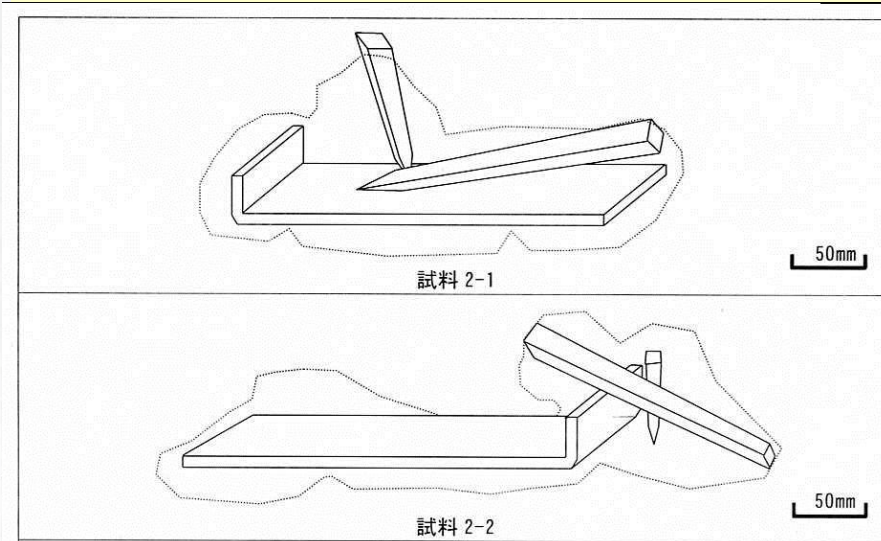
# Analytical Method: X-ray computer tomography (X-CT)

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-3000 $\mu$ )

# 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

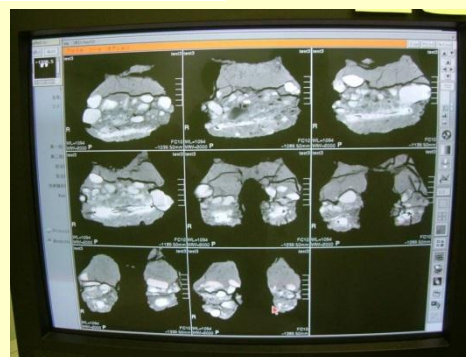
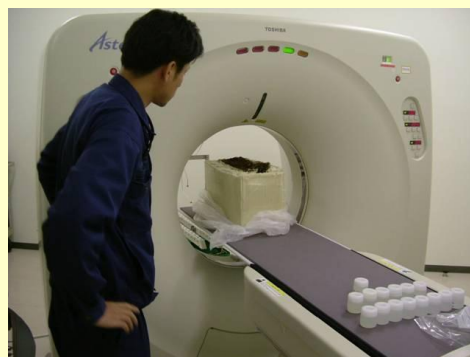
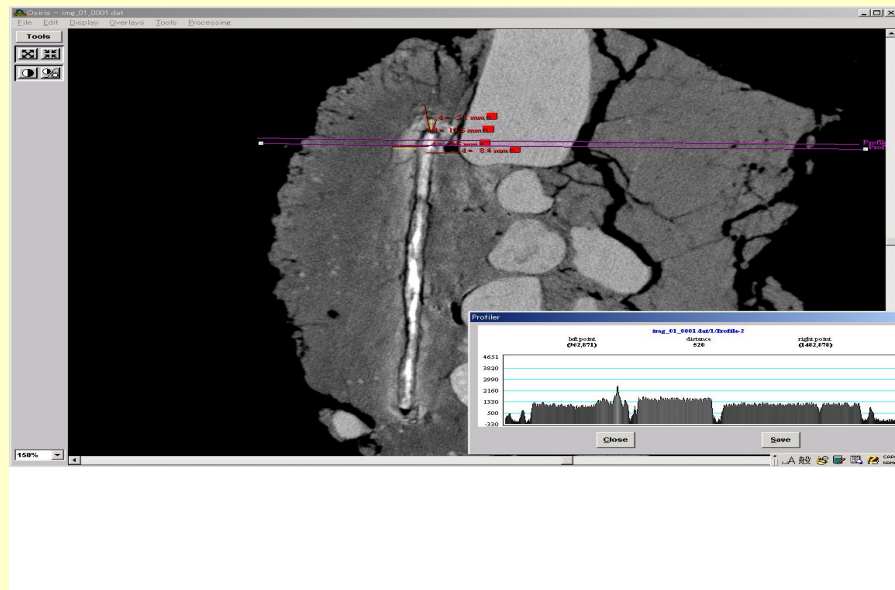


Length : about 300 mm,  
Width : about 100 mm



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, (13<sup>th</sup> C)



Excavated iron hand axe buried in clay soil  
long : approx. 120mm,  
width : approx. 75 mm

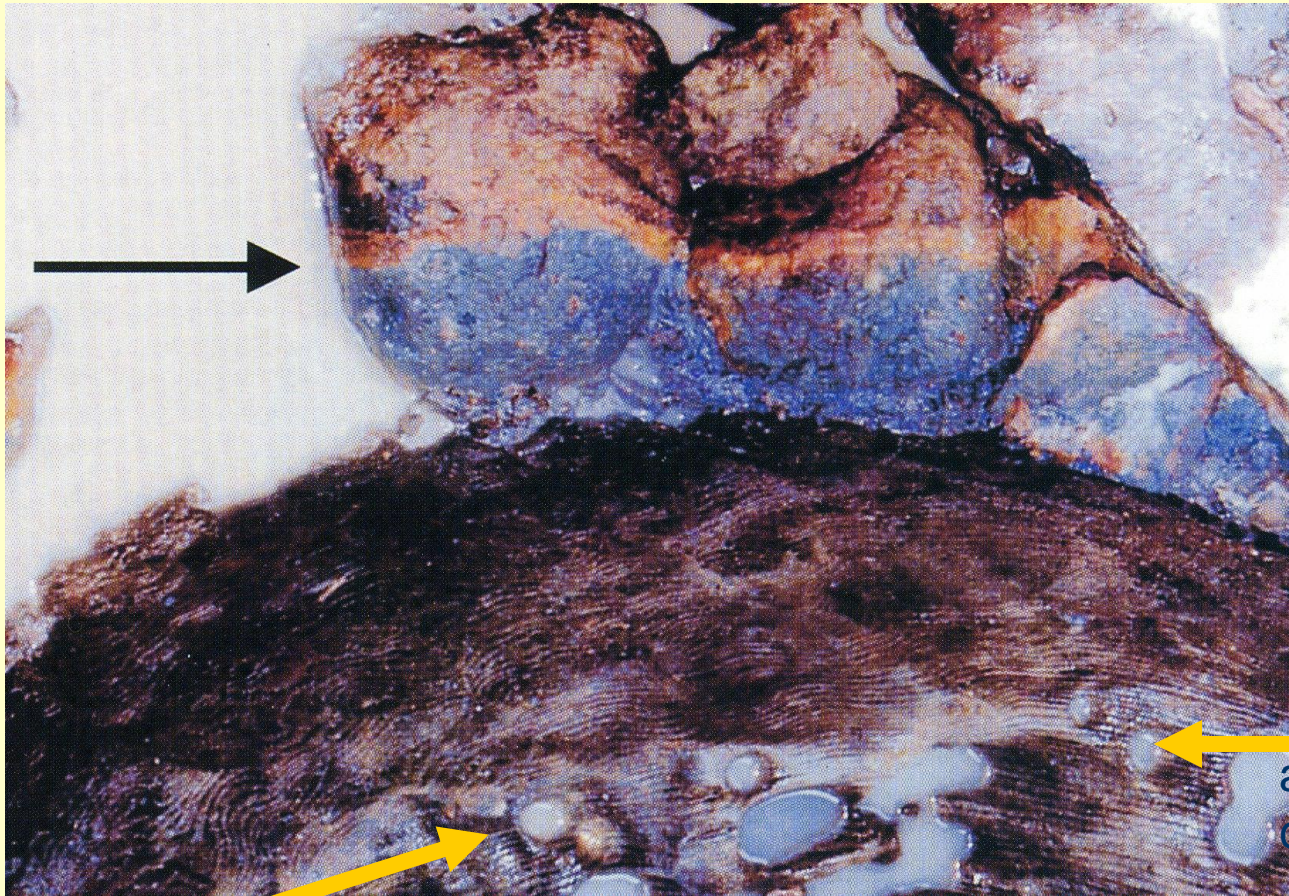
- in Shimane-prefecture, west of Japan
- buried period : c.a.750 years (AMS dating 1228) excavated at Dec.2000
- Investigated sample : some excavated iron artifacts
  - 2 pieces of “chouna” (iron hand axe),
  - 3 pieces of belts, 5 pieces of nails
- buried condition : reducing condition (2 axes)  
surrounded clay soil material

# “Izumo Taisha Keidai” ruin, (13th C)

Shrine



# Redox boundary at the site



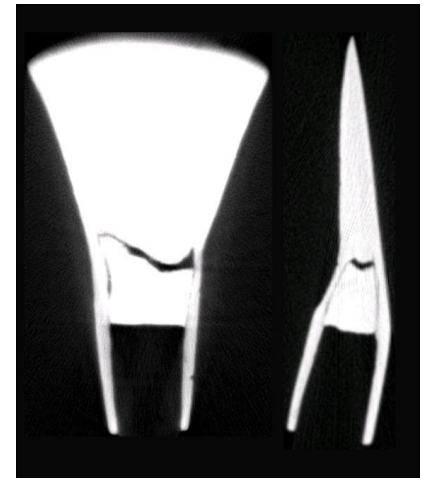
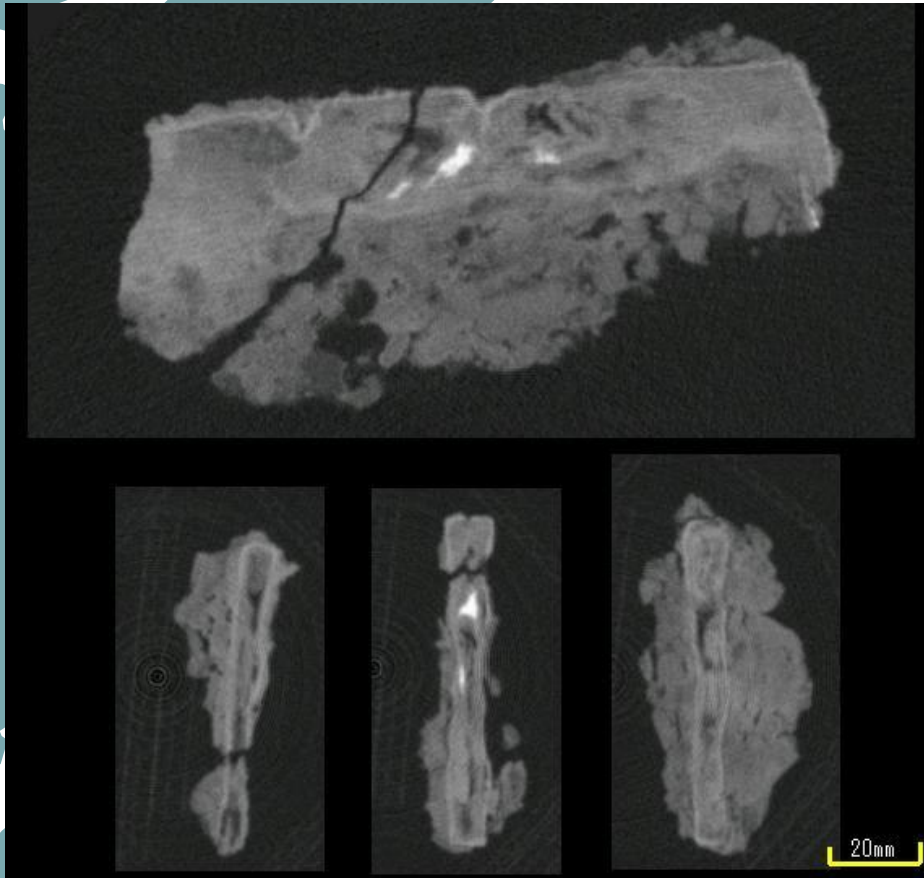
**An iron hand axe was sampled under this column**

a big wooden  
column

(1m in  
diameter / 1  
column x 3)

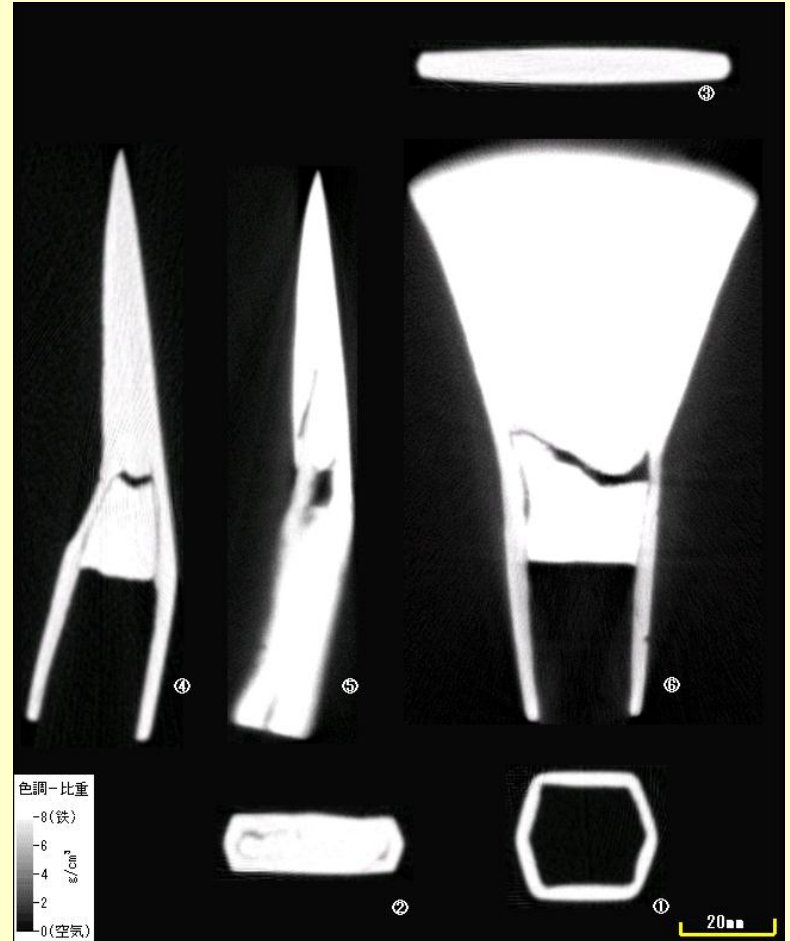
# Case of iron artifacts

“Izumo Taisha Keidai” ruin, (13<sup>th</sup> C)



# Case of iron artifacts

## sample: chouna” (iron hand axe)



surface : black amber

(low oxygen concentration)

material : iron is almost remained

rust : high density rust,

total corrosion depth : 0.2 – 0.67 mm

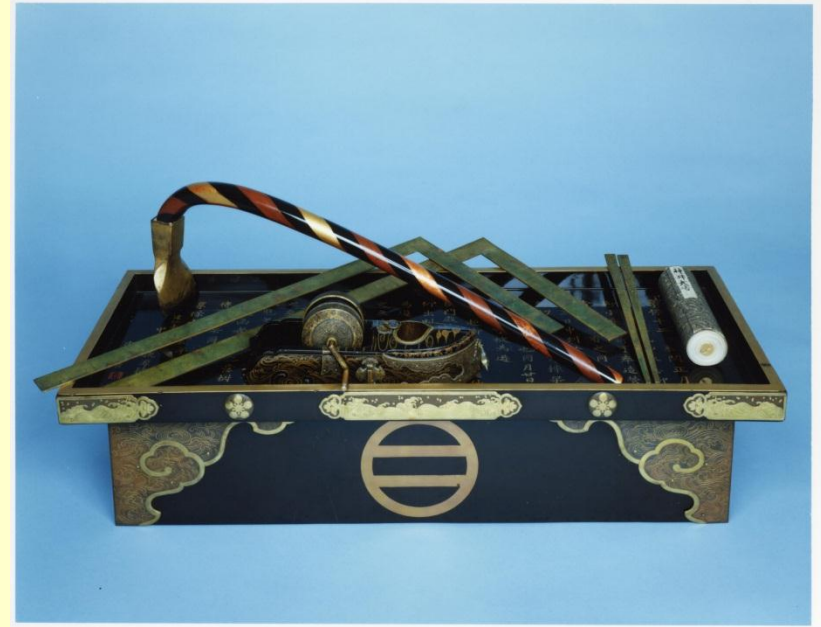
corrosion rate :  $(0.26 - 0.89) \times 10^{-3}$  mm/y

analytical method: X-ray computed tomography

# A hand axe used in the special ceremony

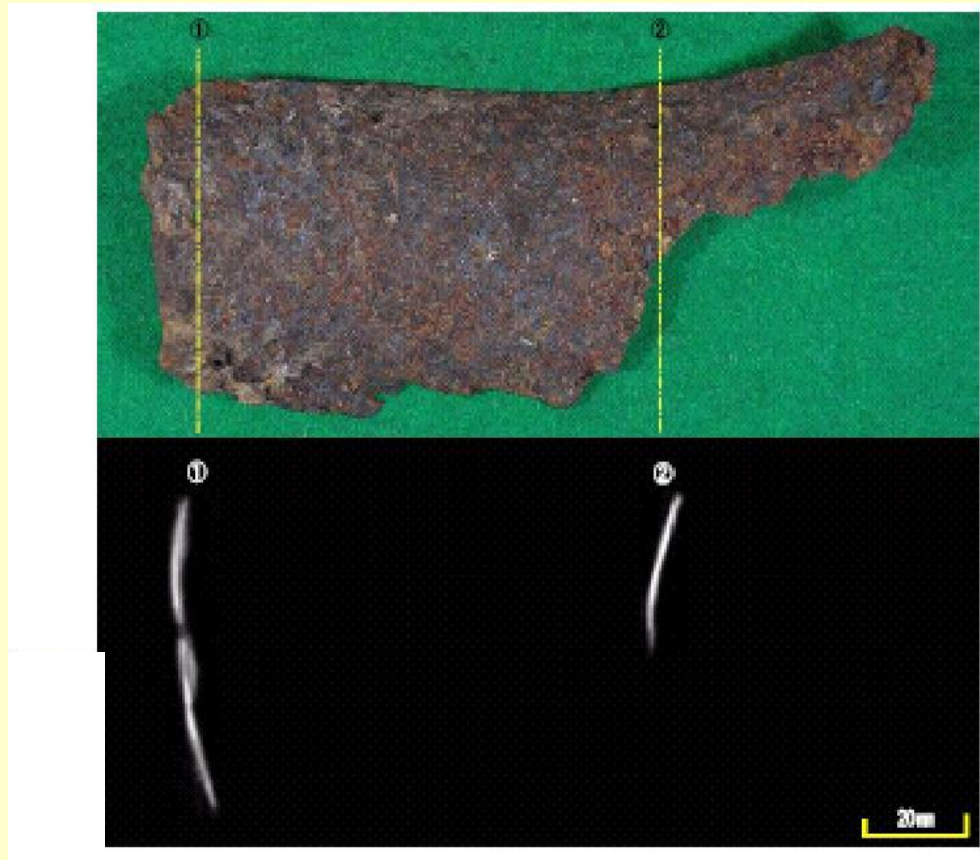


Start construction ceremony of a famous temple in Nara



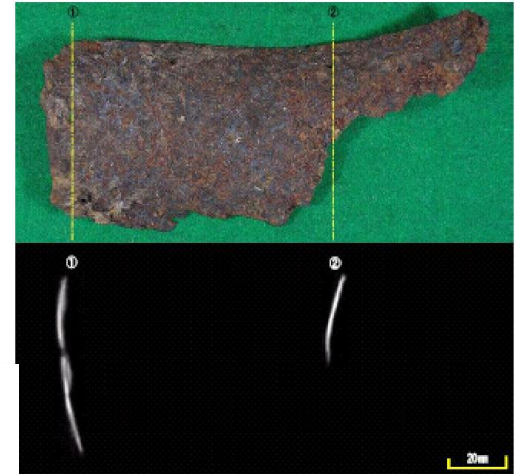
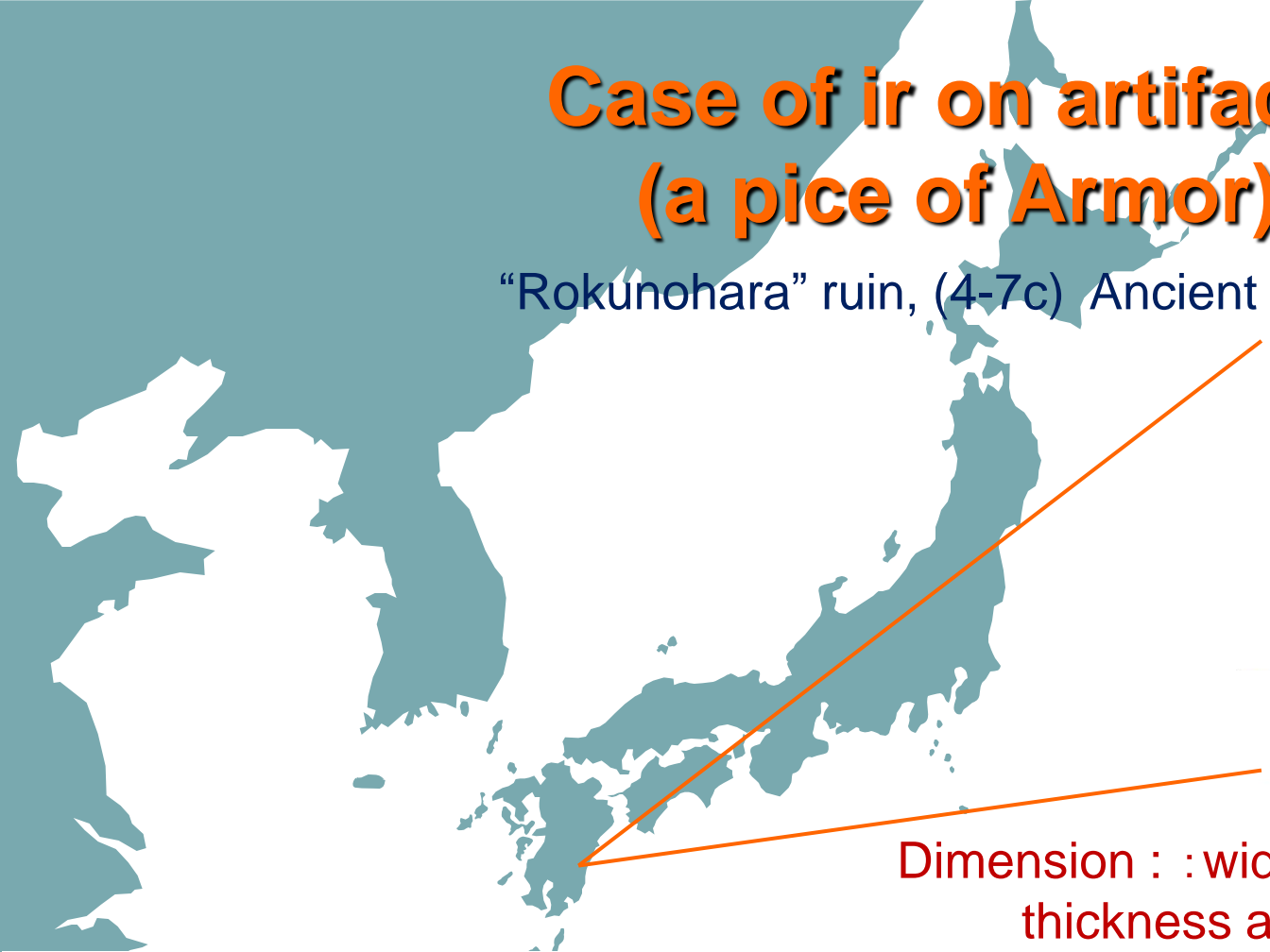
Ceremony tools of construction company

# D) One layer and pitting corrosion sample



# Case of ir on artifacts (a pice of Armor)

“Rokunohara” ruin, (4-7c) Ancient tombs



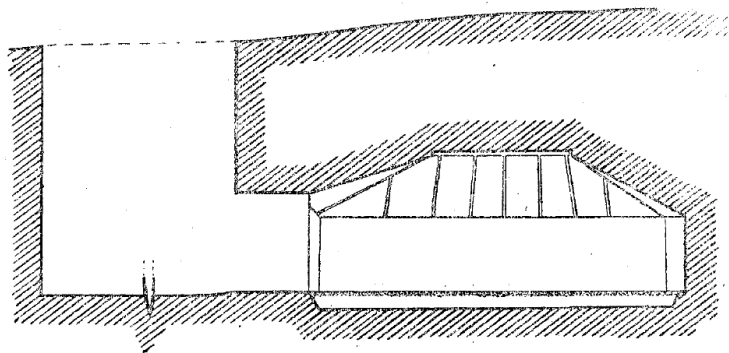
Dimension : : width about 130mm  
thickness about 2 mm

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	$>8.6 \times 10^{-3}$	complete <b>A</b>
2-3	belt	4:1.3	20:2.2	3.5	$4.7 \times 10^{-3}$	remaining iron <b>B</b>
2-4	nails	10:3.3	15:1.7	5.0	$6.8 \times 10^{-3}$	remaining iron <b>B</b>
2-5	nails	2:0.67	20:2.2	2.8	$>3.8 \times 10^{-3}$	complete <b>A</b>
2-7	nails	2:0.67	30:3.4	4.0	$>5.4 \times 10^{-3}$	complete <b>A</b>

# Classification for corroded iron artifacts (4 types)

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

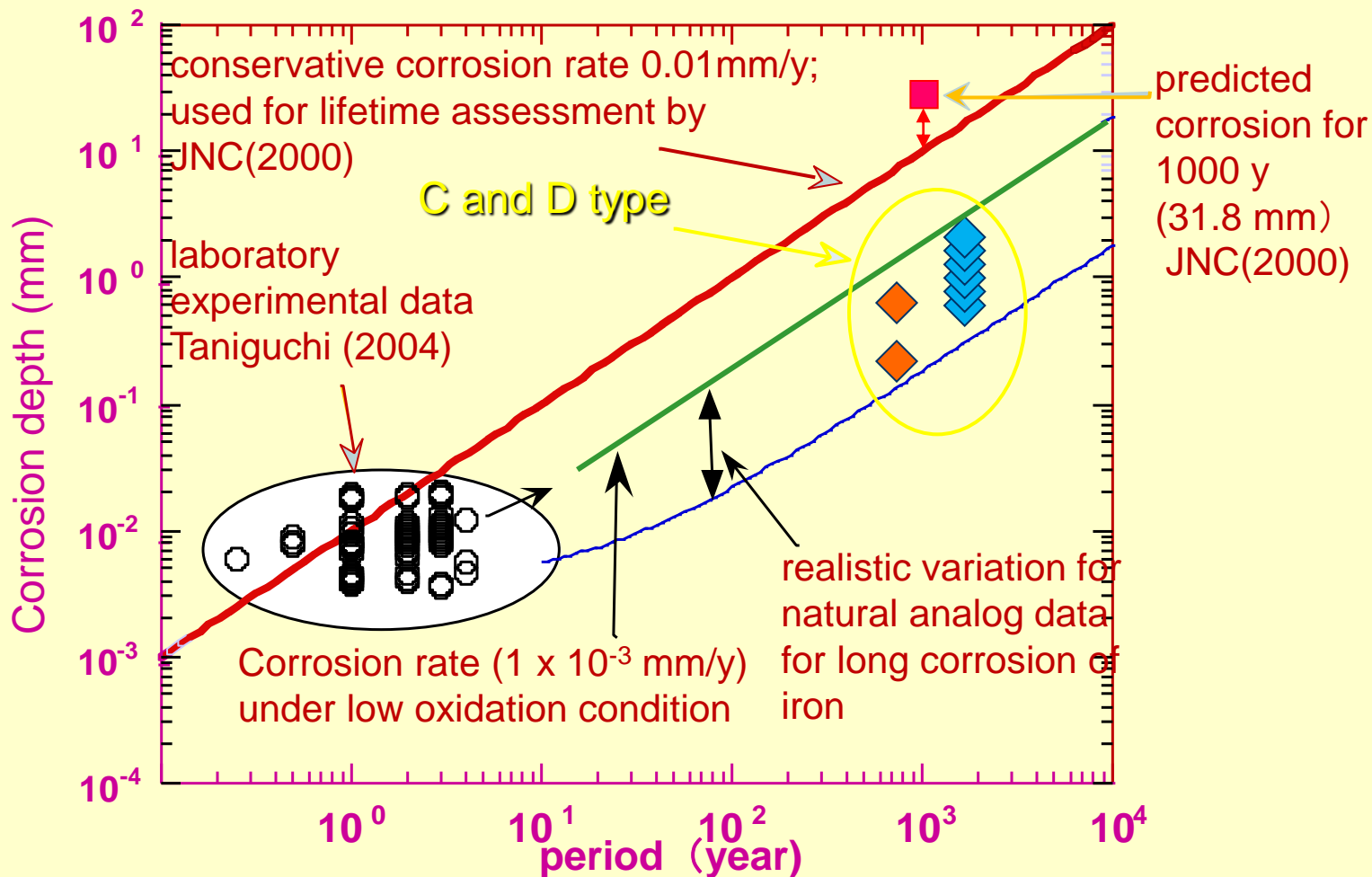
**D) one layer and pitting corrosion** : remain iron material, pitting corrosion under initially high oxidation condition and then uniform corrosion ( e.g. magnetite, siderite...) under low oxidation condition 

## 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	$0.3 \times 10^{-3}$	general 
Izumo-2	hand axe	2:0.67	ND	0.67	$0.9 \times 10^{-3}$	general 
Rokunohara	body armor	0.5:0.2	ND	2.2	$1.5 \times 10^{-3}$	pitting and general 



# 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 2<sup>nd</sup> 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-lepidocrocite. 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.

## 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.**

A teal-colored map of Japan is positioned in the background of the slide. The map shows the four main islands: Hokkaido, Honshu, Shikoku, and Kyushu, along with the surrounding sea.

**Hideki.YOSHIKAWA**

**Japan Atomic Energy Agency (JAEA)**

**Thank you for your kind attention.**



The 13<sup>th</sup> Natural Analogue Working Group Workshop, 13<sup>th</sup>-16<sup>th</sup> May, 2013, Nagoya, Japan

# 下田遺跡の銅鐸



大きさ: 総高21.7cm, 最大幅13.5cm, 重量560.9g  
埋蔵期間(推定): 1800±100 年

# 本試料の特徴と分かったこと

- 場所：茨城県つくば市小田城遺跡（13世紀～17世紀）
- 調査出土物：池跡から鉄製鍬が出土
- 埋蔵推定年数：700-300 年間
- 発掘日：2006年12月
- 埋蔵環境：酸化性環境（推定）
- 分析項目：非破壊分析・・・X線CT測定  
その他分析・・・土壌分析（化学成分、微生物）
- 1000年間あたりの鉄の錆びた量： 1.5 mm

## 【調査方法】

- ・鉄遺物の腐食診断、鉄還元細菌数(MPN法、Most Probable Number)、土壌の含水率、腐食生成物の同定(X線回折分析)、腐食生成物の強度比率

### MPN法(Most Probable Number, 希釈法)

: 遺跡土壌の連続希釈液を液体培地に接種培養して『陽性』となった

試験管数の出現率から、元の土壌中の鉄還元細菌数を算出する

### 鉄還元の判定(ジピリジル法)

: 培地に 0.2%  $\alpha\alpha'$ -ジピリジルを分注し、培地が赤く変色したものを鉄還元陽性と判断する。

