X-ray diffraction and fluorescence analysis of archaeological Anatolian artifacts by portable equipments

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Material World is continuous

What is the meaning of an excavated material

Every substance has its own history ⇨ A truth

Premise

In the past, somewhere it was made

Existence of people

excavation

who made it (Factory, Technology)

meaning who sell it (Economy, Trade)

decode

who buy/use it (Culture, Race)

Outline

1）Development of portable X-ray powder diffractometer

2）Development of portable X-ray fluorescence spectrometer

3）Application - On site analysis in Turkey and Egypt

i) The oldest iron dagger with golden haft excavated from Alacahöyük analysis carried out at the Ankara Museum of Anatolian Civilizations

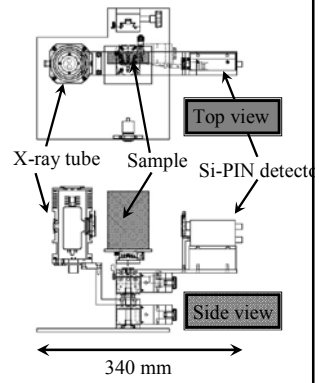
ii)Blue painted pottery from Abusir South hill remain, near Saqqara, Egypt (S. Yoshimura Waseda University,Japan)

iii) On site analysis of archaeological materials excavated from Kaman-Kalehöyük, Anatolia

iv)Amulet from Giza Plateau Map. Proj.(Mark Lehner, USA)

4）Future prospects

Prototype powder diffractometer (2003)



X-ray tube: Cu
Power 30kv,0.3mA
2θ : 20° < 2θ < 70°
Detector: Si-PIN
（Maeo, Taniguchi et al. 2003)

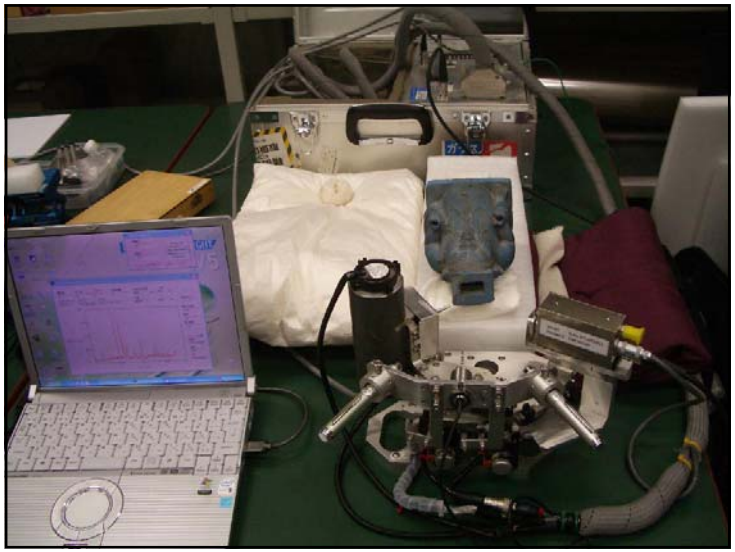
Specification of the developed diffractometer.

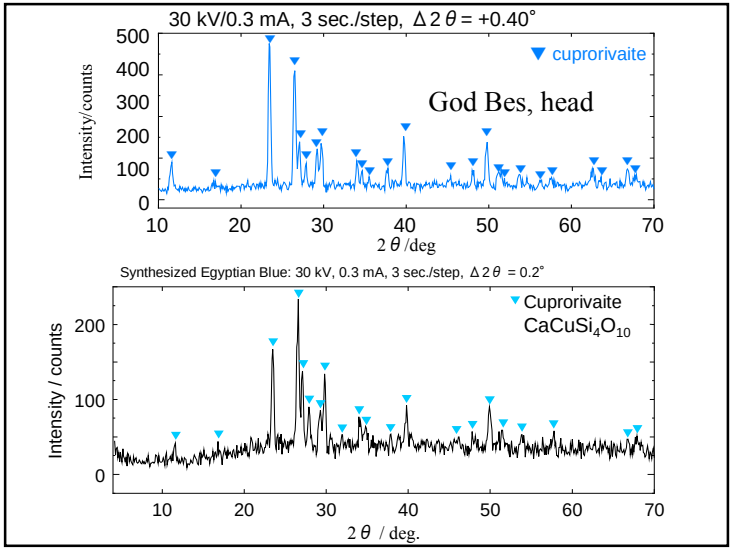
(Nakai et al.2007)

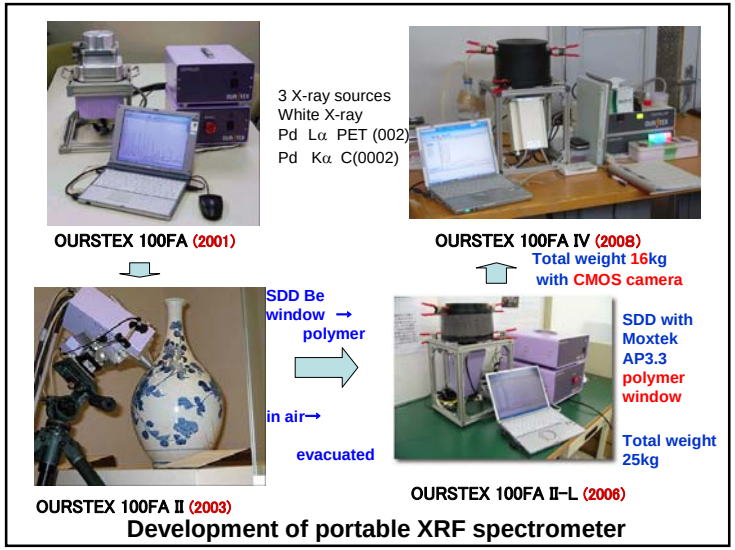
Manufactured by X-tec Co. under direction of Drs. K..Taniguchi & S. Maeo

X-ray Tube	Oxford **Cu** Target Focus : 0.1 mmϕ	50 kV - 0.3 mA Air-cooled X-ray window : Be 150 μm
Goniometer	θ - 2θ scan	$6^\circ \leqq 2\theta \leqq 80^\circ$
X-ray detector	**Si-PIN** Be window 25 μm	AMPTEK XR100CR Energy resolution 180 eV at 5.9eV
X-ray generator	Tube voltage : 10, 15, 20, 25, **30 kV** Tube current : 0, 0.05, 0.1, 0.15, 0.2, 0.25, **0.3 mA**	
Digital Signal Processor (DSP)	Channel : 1024, 2048, 4096, 8193 Channel size : 10, 20, 40 eV Peaking time : 0.75, 1.125, 1.5 2.25, 3.0 μsec. at 8 MHz or 0.375, 0.563, 0.75, 1.125, 1.5 msec. at 16 MHz	
Storage box	Aluminum trunk Size : 439(W)×340(D)×210(H) mm Total weight including all instruments : **15 kg**	

XRF function was introduced (Abe et al.2008).



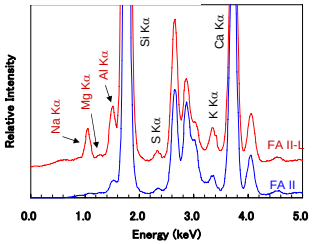




OURSTEX 100FA Ⅱ (2003)

OURSTEX 100FA Ⅱ–L (2006)

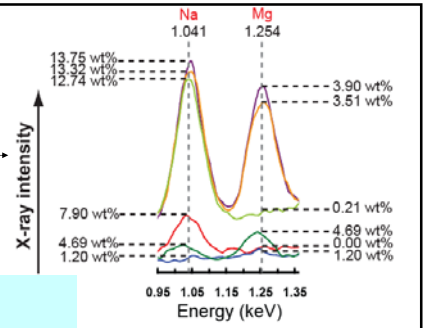
Roman glass
form Zadar
Na_2O 14.6 wt%
MgO 0.5 wt%



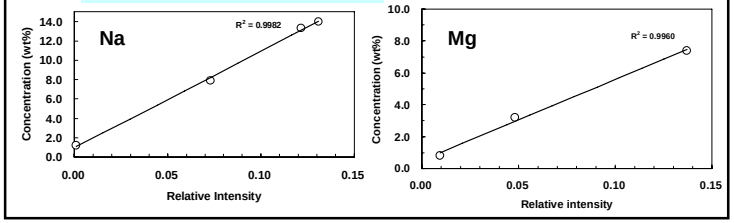
Analysis of Na and Mg in glass

Analysis of Na and Mg

XRF spectrum (300sec) of standard Points with known Na and Mg contents.

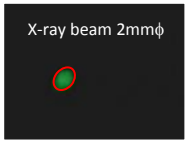


Calibration curves for Quantitative analysis.



OURSTEX 100FA-IV(2008)

◆Introduction of CMOS Camera



Fluorescence screen

Heart amulet
(B.C. 14-11C.)
H.2.0cm, W. 2.3cm

CMOS View: Yellow part

Osiris (A.D. 2C.) H.7.2cm, W. 3.5cm

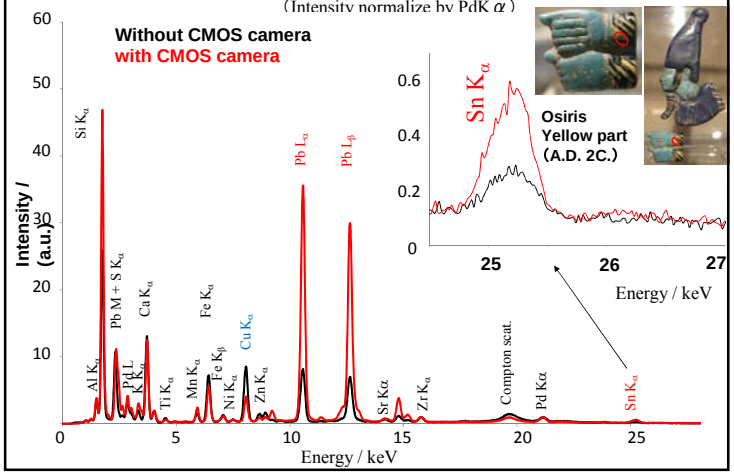
Osiris
H. 1.3cm, W. 1.6cm

CMOS View: Yellow Part

(Kikukawa et al. 2009)

A comparison of the XRF spectra of yellow part of Osiris measured with and without COMS camera.

(Intensity normalize by PdK α)



XRF analysis of iron dagger with golden heft excavated from Alacahöyük , grave K, which is the oldest iron goods in the world

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S. Omura[2] • S. Elucult[3]
[1]Tokyo Univ. of Science, [2]Middle Eastern Culture Center,Japan
[3]Ankara University

The beginning of iron metallurgy

- The Iron Age in the Ancient Near East is believed to have begun with the discovery of iron smelting and smithing techniques in Anatolia in the 2nd millenium (ca. 1300 B.C.)
- The use of iron weapons was initiated by the Hittites, which was believed to have been a major factor in the rapid rise of the Hittite Empire.
- The earliest iron finds of the third millennium BC, like gold-handled dagger from Alacahöyük, show that iron was used in Anatolia before the Hittites.

Question ! Where does iron come from ?

- Early iron metallurgy

Iron ore ⇒ iron oxide
⇒ smelting at high temperature (**iron manufacturing**)

Origin of iron before the smelting technique has invented

Meteorite origin

○ Use of iron meteorite

Terestial origin

○ Slug which is a by product during the smelting of copper or tin

- What is iron meteorite?

◆Alloy of iron and Nickel

◆3 phases exist depending on the formation process and composition

Ni: rich → poor

Ataxites (Ni : 14 %～)

Octahedrites (Ni : 6～14 %)

Hexahedrites (Ni : 4～6 %)

75 % of iron metorite

Widmanstätten pattern

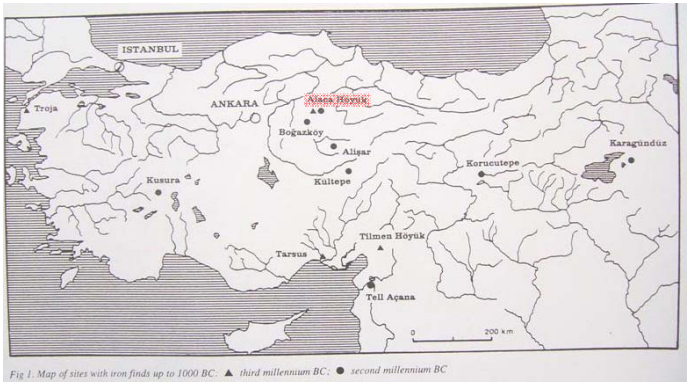


Fig 1. Map of sites with iron finds up to 1000 BC. ▲ third millennium BC; ● second millennium BC

Alacahöyük

1935～ Excavation : H.Z.Kosay、R.O.Arik

IVth level Late Chalcolithic

IIIrd level Early bronze age (～2300 B.C.)
13 Tomb
gold-handled dagger from grave K

IInd level Middle bronze age (～1800B.C.)
Hittite empire

- Previous analytical study of the iron dagger*

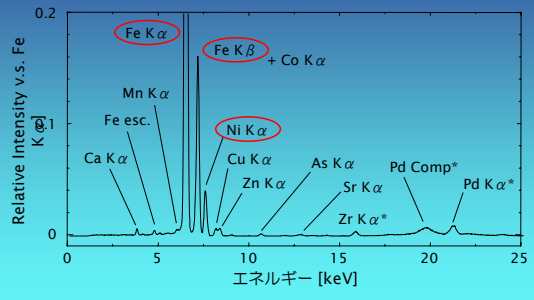
Analysis of excavated objects from Alaca Hoyuk

objects	comments	Reference
Gold-handed dagger	Low Ni	Kosay 1951,Wertime1973
Two gold-headed pins	2.7 % Ni	Kosay1938
Necklace terminal	No analysis	Kosay 1938
Semi-lunate disc	2.4 % Ni	Kosay 1938,1944
Knife fragment	No analysis	Arik 1937

Method Unknown → Accurate Analysis

* Ünsal Yaıç1n: "Early iron metallurgy in Anatolia", *Anatolian Studies*, **49**, 177-187, (1999).
** Wertime, T. A.: "The biginings of metallurgy: a new look", *Science*, **182**, 875-886 (1976).

- A representative XRF spectrum



An XRF spectrum of iron part (monochlomatic excitation)

- Summary and conclusion

○Despite the compositional variation due to the rust, all parts of the iron blade from grave K containshigh level of nickel(4.4 -9.0 wt% as Ni ; 3.1 – 7.6wt% as NiO) .

○Semi-lunate disc excavate from grave M.C. also contains the same level of nickel(3.6-4.8 wt% as Ni, 2.8,3.9wt% as NiO)

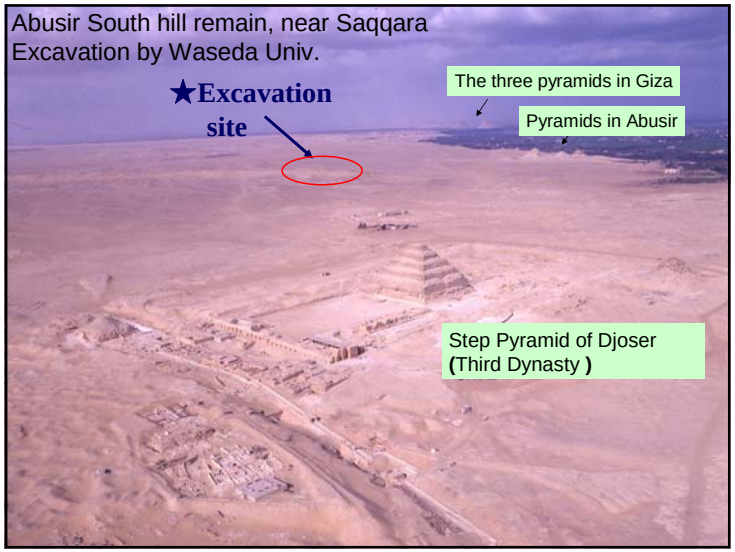
○Strong compositional similarity between iron dagger and iron meteorite were observed

○Iron goods from Hittite period contained Ni less than 0.1%*

○The silver content of the gold heft contains 15～20%

It is reasonable to assume that the source of iron for the iron dagger is iron meteorite

* Akanuma, H.: "Production of Iron Artifacts in the Hittite and Phrygian Period: An Inference from Metallurgical Analysis of the Relics of Kaman-Kalehöyük", *AAS*, **VI**, 241-257 (1997). etc.



An oldest transparent glass excavated in Egypt
“ Second Intermediate (1650-1550BC) to early 18th dynasty”

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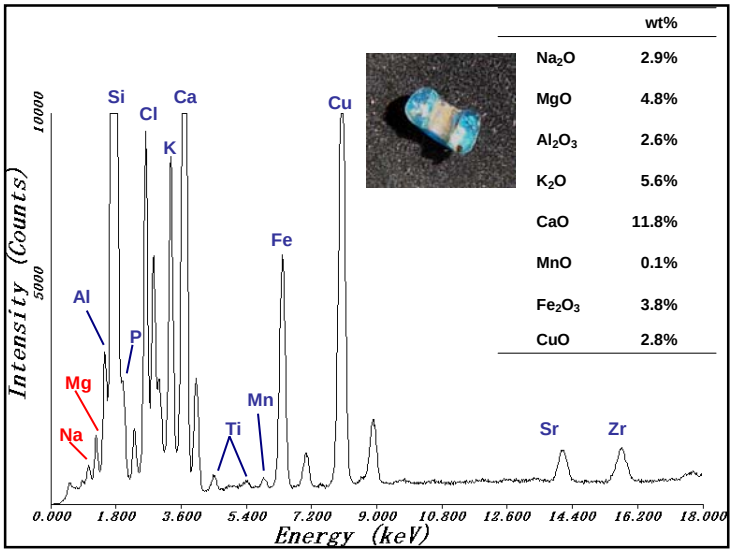


	wt%
Na_2O	2.9%
MgO	4.8%
Al_2O_3	2.6%
K_2O	5.6%
CaO	11.8%
MnO	0.1%
Fe_2O_3	3.8%
CuO	2.8%

Blue Pigment (Abusir, 2007)

- Powder diffraction data compared with cuprorivaite

Blue Pigment		Cuprorivaite (PDF: 12-0512)		
d / Å	Int.	*d* / Å	Int.	*hkl*
7.62	26	7.630	40	002
		5.220	15	102
3.83	100	3.780	90	004
		3.660	25	200
3.36	39	3.360	80	104
3.29	48	3.290	100	202
3.20	17	3.190	50	211
		3.050	40	114
3.01	17	3.000	90	212
2.63	52	2.629	40	204
2.58	30	2.585	40	220
2.36	35	2.386	20	106
		2.321	30	302
2.27	83	2.270	50	116
		2.136	10	224
2.05	35	2.007	20	321
1.96	57	1.970	20	314
		1.890	15	008
1.82	91	1.831	60	108
1.78	57	1.784	40	324
1.76	39	1.758	20	411
1.70	87	1.704	40	316
		1.636	20	218
1.60	78	1.603	40	414
		1.528	10	415
1.49	52	1.483	10	1$\underline{1}$10
1.45	48	1.456	5	431
1.40	48	1.398	20	20$\underline{1}$0
1.38	65	1.380	20	328

$\Delta 2\theta$ = -0.1°

Synthesis of **Egyptian blue**
(cuprorivaite: $CaCuSi_4O_{10}$)

after W. T. Chase(1971)

CuO 3.6 g + $CaCO_3$ 2.8 g + SiO_2 12 g
+ Na_2CO_3 1.6 g →

850℃ 4hr →
pulverize →
850℃ 4hr →
850℃ 5hr →
950℃ 2hr→
pulverize →
HCl →

synthetic Egyptian blue

Powder diffraction data of Synthesized Egyptian Blue

Synthesized Pigment		Cuprorivaite (PDF: 12-0512)		
d / Å	Int.	*d* / Å	Int.	*hkl*
7.62	10	7.630	40	002
5.27	11	5.220	15	102
3.78	69	3.780	90	004
		3.660	25	200
3.35	100	3.360	80	104
3.29	55	3.290	100	202
3.20	33	3.190	50	211
3.05	31	3.050	40	114
3.00	53	3.000	90	212
2.63	27	2.629	40	204
2.58	21	2.585	40	220
2.37	16	2.386	20	106
2.32	15	2.321	30	302
2.26	34	2.270	50	116
		2.136	10	224
		2.007	20	321
1.97	14	1.970	20	314
1.89	14	1.890	15	008
1.83	33	1.831	60	108
1.78	18	1.784	40	324
		1.758	20	411
1.70	15	1.704	40	316
		1.636	20	218
1.59	18	1.603	40	414
		1.528	10	415
		1.483	10	1110
		1.456	5	431
1.40	13	1.398	20	2010
1.38	14	1.380	20	328

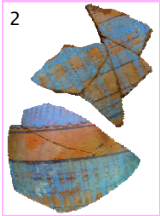
$\Delta 2\theta$ = 0.2°

Tetragonal a = 7.279(8), c = 15.12(1)

(PDF: 12-512) a = 7.300, c = 15.120 Å

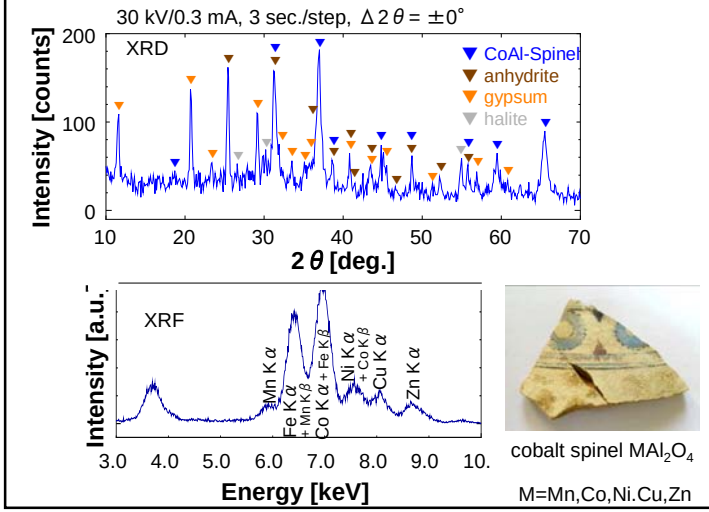
18 Dynasty (middle)
(1427-1390 B.C.)

18 Dynasty(late)
(1390-1352 B.C.)



19 Dynasty
(1279-1213 B.C.)

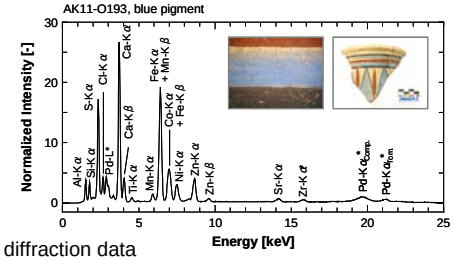
XRD and XRF data are obtained from the same analytical point measured by p-XRD



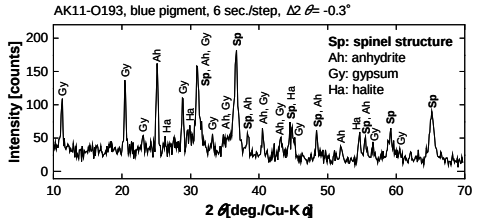
cobalt spinel MAl_2O_4

M=Mn,Co,Ni.Cu,Zn

High resolution XRF data of blue pigments on blue painted pottery



Powder diffraction data



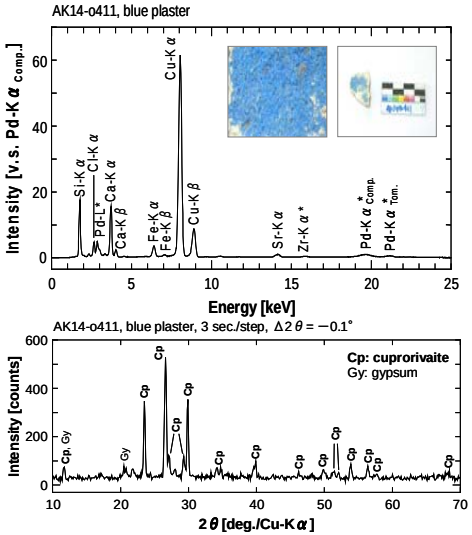
Blue Painted Pottery (Abusir)

- Powder diffraction data

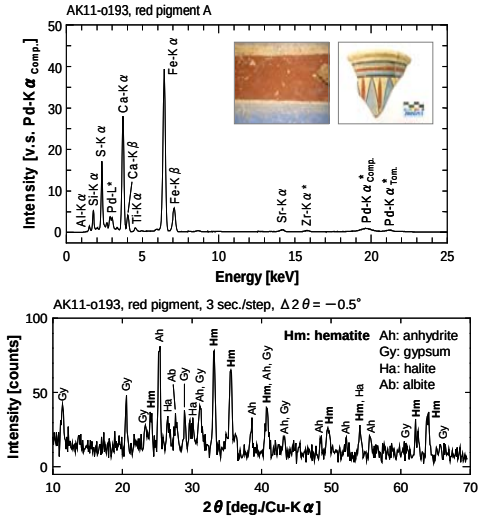
Blue Pigment A		Cobalt Spinel (PDF: 44-0160)			Gypsum (PDF: 33-0311)			Halite (PDF: 05-0628)		
d / Å	Int.	*d* / Å	Int.	*hkl*	*d* / Å	Int.	*hkl*	*d* / Å	Int.	*hkl*
8.04	47				7.630	100	020			
4.35	61	4.679	8	111	4.283	100	021			
3.74	31				3.799	17	130, 040			
3.23	31							3.260	13	111
3.03	51				3.065	75	041			
2.89	77	2.865	65	220	2.873	45	-221	2.821	100	200
					2.789	10	-112			
2.68	47				2.685	35	150, 220			
2.43	100	2.444	100	311	2.496	11	-202			
2.31	31	2.339	2	222						
					2.219	15	151			
2.08	31				2.086	25	-242			
2.03	36	2.026	14	400	2.074	15	-152, -311	1.994	55	220
1.90	19				1.900	16	080, 260			
1.87	17	1.860	4	331	1.880	12	241			
1.82	19				1.812	13	062			
					1.779	12	-262			
1.67	12	1.654	13	422						
1.62	19							1.628	15	222
1.56	36	1.560	27	511						
1.43	48	1.433	33	440						

Δ2θ = 0.8°

- **Blue plaster**



- Brown pigment

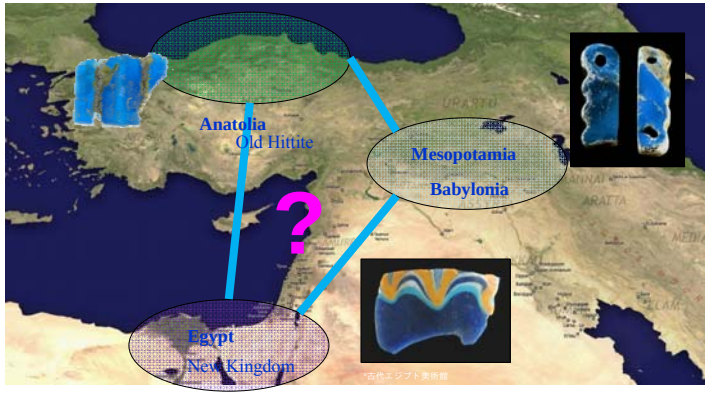


A summary of the identified pigments and their lattice parameters

Anhydrite ($CaSO_4$) : orthorhombic (PDF: 37-1496) Experimental: *a* = 6.975(5) Å, *b* = 6.993(3) Å, *c* = 6.236(6) Å Literature: *a* = 6.9933 Å, *b* = 7.0017 Å, *c* = 6.2411 Å	Slip on pottery
CoAl-spinel ($CoAl_2O_4$) : cubic (PDF: 44-0160) Experimental: *a* = 8.105(9) Å Literature: *a* = 8.104 Å	Blue pigment on painted pottery
Cuprorivaite ($CaCuSi_4O_{10}$) : tetragonal (PDF: 12-0512) Experimental: *a* = 7.300(8) Å, *c* = 15.122(9) Å Literature: *a* = 7.3000 Å, *c* = 15.1200 Å	Blue pigment on plaster
Hematite (Fe_2O_3) : hexagonal (PDF: 33-0664) Experimental: *a* = 5.037(2) Å, *c* = 13.733(13) Å Literature: *a* = 5.0356 Å, *c* = 13.7489 Å	Red pigment on plaster& pottery
Hematite (Fe_2O_3) : hexagonal (PDF: 33-0664) Experimental: *a* = 5.038(3) Å, *c* = 13.710(21) Å Literature: *a* = 5.0356 Å, *c* = 13.7489 Å	Black pigment A on pottery
Mn_3O_4 : cubic (PDF: 33-0664) Experimental: *a* = 8.435(2) Å Literature: *a* = 8.42 Å	Black pigment B on pottery

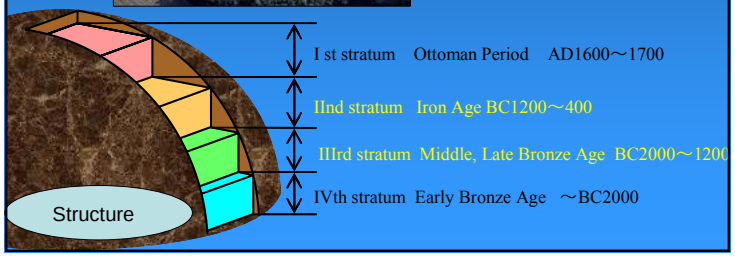
Bronze age (B.C. 16-14)

Near East

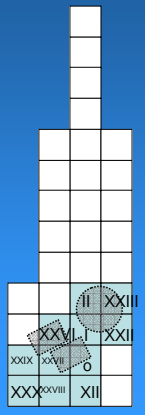


Kaman-Kalehöyük

Director: Sachihiro Omura (Middle Eastern Culture Center, Japan)



North section



North

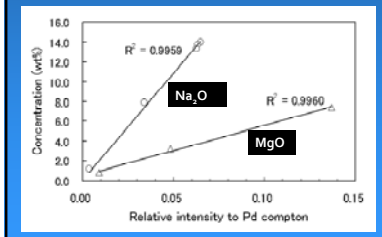
Analyzed samples

Round structure Middle Bronze Age & Iron age

Period	Sample
Middle Bronze Age（B.C. 16～14）	37
Iron Age （B.C.12～4）	128
計	165

Quantitative analysis by XRF

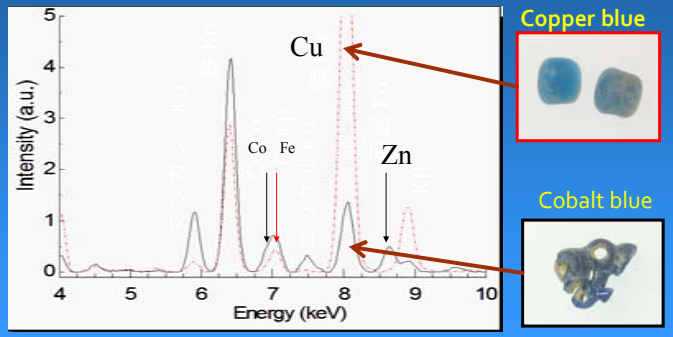
NIST SRM1831 glass



Calibration curve for Na_2O and MgO

	Certified (wt%)	Measured (wt%)	Deviation (%)
Na_2O	13.32	13.33 ±1.04	0.04
MgO	3.51	4.06 ±0.08	15.75
Al_2O_3	1.21	0.54 ±0.04	55.54
SiO_2	73.08	72.42 ±2.57	0.90
SO_3	0.25	0.25 ±0.01	0.53
K_2O	0.33	0.32 ±0.02	1.92
CaO	8.20	8.86 ±0.28	8.06
TiO_2	0.019	0.019 ±0.005	1.32
Fe_2O_3	0.087	0.092 ±0.007	5.75
SUM	100.01	99.89 ±2.35	

Iron Age blue glass beads

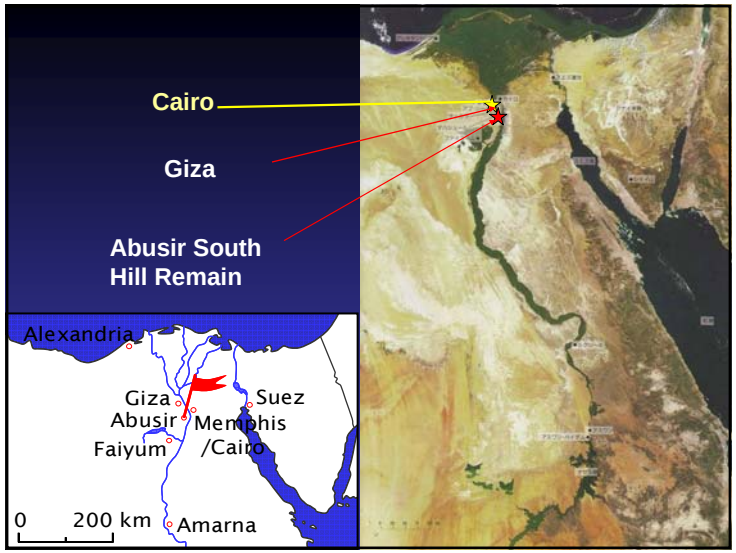


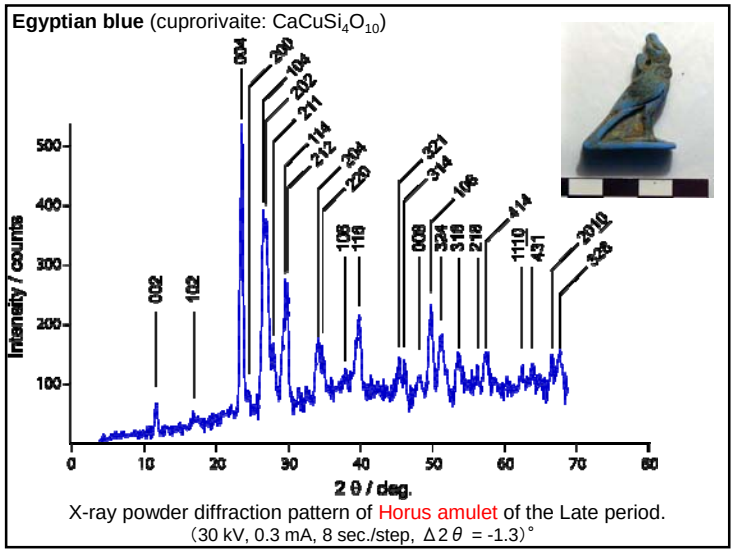
Copper blue

Cobalt blue

Summary

- **Glass artifacts are made of plant ash soda lime glass**
- **Evidence of glass trade between Mesopotamia in Middle Bronze Age**
- **Origin of cobalt blue would be not from Egypt but from Mediterranean region.**





X-ray powder diffraction pattern of Horus amulet of the Late period.
（30 kV, 0.3 mA, 8 sec./step, Δ2θ = -1.3）°

- Powder diffraction data of Horus amulet

Sample		Cuprorivaite (PDF:12-512)		
d /Å	Int	*d* / Å	Int	*hkl*
7.69	11	7.63	40	002
5.27	7	5.22	15	102
3.78	100	3.78	90	004
3.64	12	3.66	25	200
3.35	71	3.36	80	104
3.31	68	3.29	100	202
3.20	27	3.19	50	211
3.02	48	3.05	40	114
2.99	47	3.00	90	212
2.62	28	2.629	40	204
2.58	25	2.585	40	220
2.38	16	2.386	20	106
		2.321	30	302
2.26	34	2.270	50	116
		2.136	10	224
2.01	16	2.007	20	321
1.97	18	1.970	20	314
1.89	13	1.890	15	008
1.83	36	1.831	60	108
1.78	24	1.784	40	324
		1.758	20	411
1.71	17	1.704	40	316
1.65	15	1.636	20	218
1.60	18	1.603	40b	414
		1.528	10	415
1.48	13	1.483	10	1110
1.46	13	1.456	5	431
1.40	16	1.398	20	2010
1.38	17	1.380	20	328
		1.336	25	522
		1.315	10	435

Δ2θ = -1.3 deg.

Egyptian blue (cuprorivaite: $CaCuSi_4O_{10}$)

Tetragonal a=7.289(18),c=15.25(3) Å　　PDF: a=7.30, c=15.12 Å

Conclusions

・A combined use of XRF and XRD is essential.

Advantages of on site analysis by portable instruments

- An unlimited number of samples can be analyzed under a restriction of the time.
- Analysis can be made in collaboration with curators and archaeologists.

Future prospect

・Further downsizing of power source and controller.
・Introduction of polycapillary and mapping function.
・To prove sea silk road between middle east and Japan based on the chemical analysis of excavated objects.