NEOLITHIC METALLURGY IN ANATOLIA

STAGES OF EARLY COPPER METALLURGY IN ANATOLA

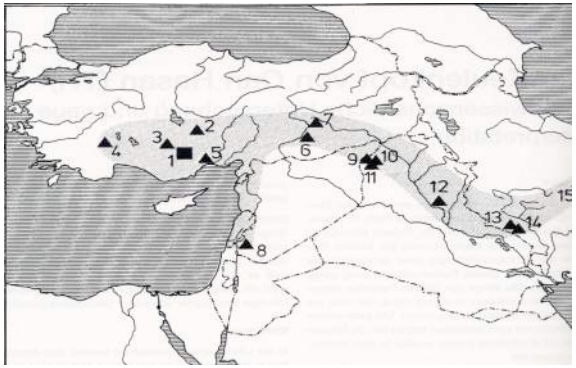
- Non-metallic period (prior to 8200 BC)
- Single metal period (after 8200 BC). Mainly native copper is shaped for simple tools and beads.
- Beginning of extractive metallurgy (after 5000 BC). Reduction of copper ores.
- Advanced metallurgy (after 4000 BC). Reduction of polymetallic ores, first alloys of copper.
- Industrial Period (after 2800 BC). Production of bronze followed by iron during the 1st millennium BC.

MALACHITE BEADS FROM AŞAĞI PINAR, KIRKLARELİ

EARLIEST NATIVE COPPER OBJECTS IN ANATOLIA

- Çayönü: Over 100 simple native copper implements, (8200-7500) BC.
- Aşıklı Höyük: Many copper beads, (7800-7600) BC.
- Nevali Çori: Copper bead, (7500) BC.
- Hacılar: Copper bead, (~6000 BC)
- Mersin: 2 needles, (~6000 BC)
- Can Hasan: Macehead, (~6000) BC.

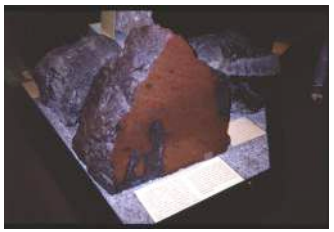
SITES OF EARLY NATIVE METALS



1:Can Hasan, 2:Aşıklı Höyük, 3: Çatal Höyük, 4. Hacılar, 5: Yümük Tepe, 6: Nevali Çori, 7: Çayönü, 8: Ramad,

COPPER BELT OF NEAREAST

Native Copper Examples



ÇAYÖNÜ

Fig. 4. Pottery Neolithic Settlement with stone foundation

ÇAYÖNÜ METAL OBJECTS

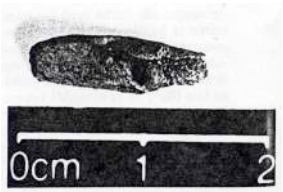
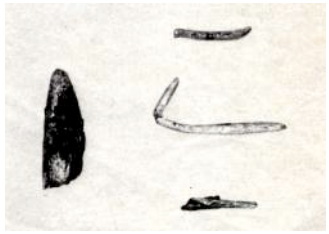


Fig. 3. Çayönü, worked sheet rolled to form a head (ÇT 72.I.13).



MICROSTRUCTURE OF ÇAYÖNÜ METAL OBJECTS

7. Structure of hook with no intermediate anneal.

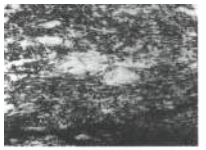


Figure 1.3 Awl from Çayönü Tepesi (ÇT B1.1.6) showing customary cracking resulting from extensive cold-working. PIXE analysis gave 99.6% Cu, 0.03% Ni, 0.028% As, 0.031% Zn, 0.033% Ag, and 0.014% Pb.

9. Structures of awl (below) and hook (above) showing recrystallization.

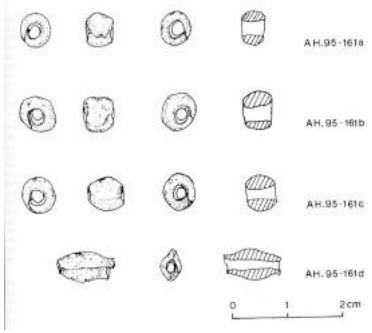
CHEMICAL ANALYSIS OF ÇAYÖNÜ METALS

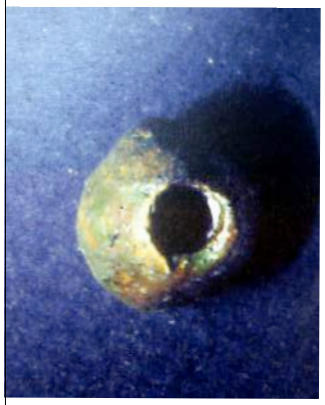
NUMBER	ITEM	Cu	Al	Cl	Ni	As	S	Zn	Ag	Pb	Si	Fe
8119 (A)	malachite	80.63	4.530	0.047	0.112	0.013	0.100	0.011		0.004	6.000	2.490
8116 (B)	awl	99.67	0.019	0.055	0.030	0.082	0.010	0.031	0.035	0.014		
8118 (C)	malachite	85.42	2.360	0.147	0.018	0.007	0.457	0.041		0.013	8.810	0.446
8117 (D)	lump	99.70	0.030	0.038	0.027	0.048		0.034	0.051	0.020		0.018
(E)	Nat Cu	99.89	0.018	0.023	0.020							
6419 (F)	disc	98.97	0.324	0.012	0.005	0.092	0.343			0.006		0.019
7219 (G)	lump	99.86	0.036			0.015	0.010	0.016			0.030	0.013
72114 (H)	hook	99.69		0.163	0.020		0.014	0.040		0.011		0.017
72111 (K)	lump	99.85	0.026	0.021		0.013		0.028		0.010		0.016
72113 (M)	sheet	99.64	0.036	0.075	0.039	0.116	0.012	0.032				0.021
7014 (P)	hook	99.83	0.026	0.012	0.011		0.022	0.028			0.022	0.019
7015 (R)	awl	98.91	0.031	0.065	0.025	0.875		0.019	0.014			0.014
6414	awl	99.80		0.015		0.031	0.039			0.007		0.014
6414*	»	97.03			n.d.	0.067		n.d.	n.d.	0.006		n.d.
8011	awl	99.54		0.033		0.108	0.021	n.d.	0.018	0.004		0.014
78113*	sheet	99.58			n.d.	0.420		n.d.	0.018	0.004		0.024
84119*	hook	95.04			n.d.	0.038		n.d.	0.015	0.006		0.026
84120*	awl	99.09			n.d.	0.056		n.d.	0.003	0.005		0.010
8114	wire	99.80		0.010		0.019	0.009			0.010		0.019

n.d. = not detected ; * = Atomic Absorption ; Others by PIXE

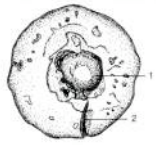
AŞIKLI HÖYÜK

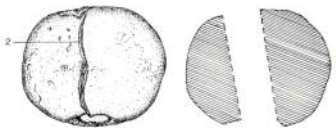
AŞIKLI HÖYÜK METAL BEADS



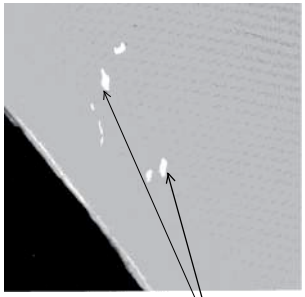


CAN HASAN MACE HEAD





CHEMICAL ANALYSIS



Silver crystals which Means copper is not melted

Cu:	100 %		**Co:**	0,6
Fe:	1920 ppm		**Te:**	<37
Sn:	<50		**Ni:**	<10
Zn:	1160		**Cr:**	94
As:	6,0		**Ag:**	550
Se:	<2,0		**Hg:**	1,5
Sb:	<1,0		**Au:**	<0,03
Ir:	<0,006			

	Can Hasan (Keulenkopf)	Aşıklı Höyük (9 Perlen)	ged.Kupfer (Rapp 1998) Mittelwert	Maximum
Sn	<50	26	58	7400
As	6	43	976	86000
Sb	<1	1	6	890
Co	0,6	6	14	3800
Ni	<30	10	140	32000
Ag	550	340	238	29000
Au	<0,03	<1	<1	14
Fe	1920	313	970	50000
Zn	1160	<10	170	82000
Se	<2	1	9	3100
Ir	<0,006	<1	<1	12
Te	<37	<10	4	1100
Cr	94	20	9	1100
Hg	1,5	32	17	1200

RECOGNIZING OBJECTS MADE FROM NATIVE COPPER

- The grain size is generally very course (0.1 to 1 mm and above)
- Grains have long irregular twins from geological strains causing partial crystallization
- Metal is free of inclusions, especially copper oxides.
- Copper tends to be very pure although arsenic and silver can occur.

OBTAINING COPPER FROM ITS ORES

EXTRACTIVE METALLURGY

COPPER SOURCES OF TURKEY

COPPER ORES

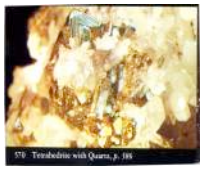
NAME	FORMULA	%Cu
Antherite	$Cu_3SO_4(OH)_4$	53.8
Azurite	$2CuCO_2CU(OH)_2$	55.1
Bornite	Cu_5FeS_4	63.3
Chalcosite	Cu_2S	79.8
Chalcopyrite	$CuFeS_2$	34.5
Covellite	CuS	66.5
Cuprite	Cu_2O	88.8
Enargite	$Cu_3As_5S_4$	48.5
Malachite	$CuCO_3Cu(OH)_2$	57.3
Native copper	Cu	100

SOME COPPER ORES

Azurite

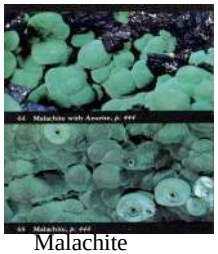
Chalcopyrite

Chalcosite



Tenantite

Cuprite

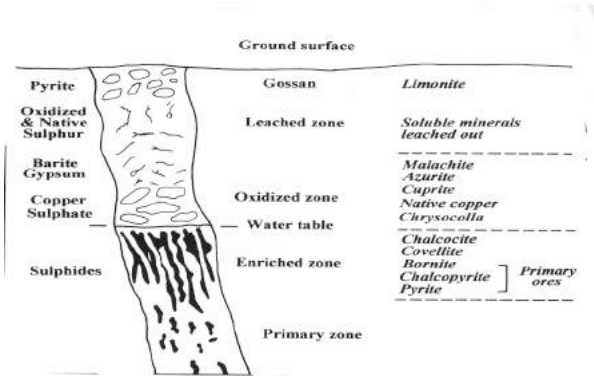


Malachite

SMELTING OF "OXIDE ORES"

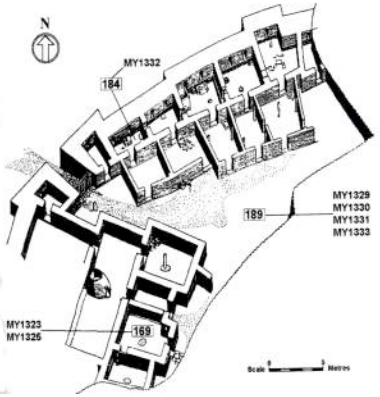
- Rich relatively pure oxidized secondary copper ores are used during the earliest copper smelting in antiquity.
- Reduction can be achieved in a crucible or in a small furnace by heating the ore only with carbon.
- Also known as slagless process since the ores do not contain impurities or gangue minerals.
- Copper produced was very pure with only trace of iron impurity.

FORMATION OF SECONDARY ORES

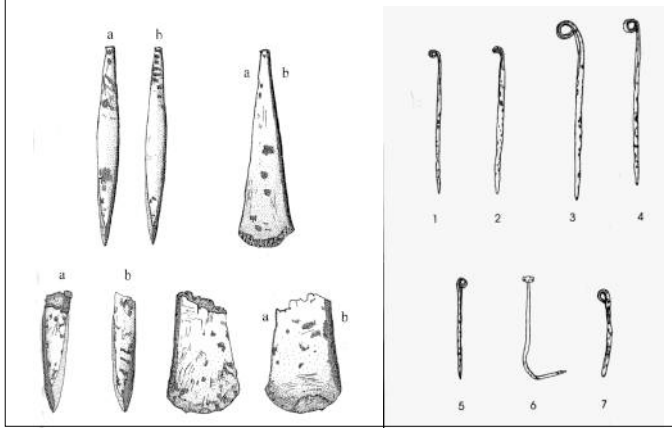


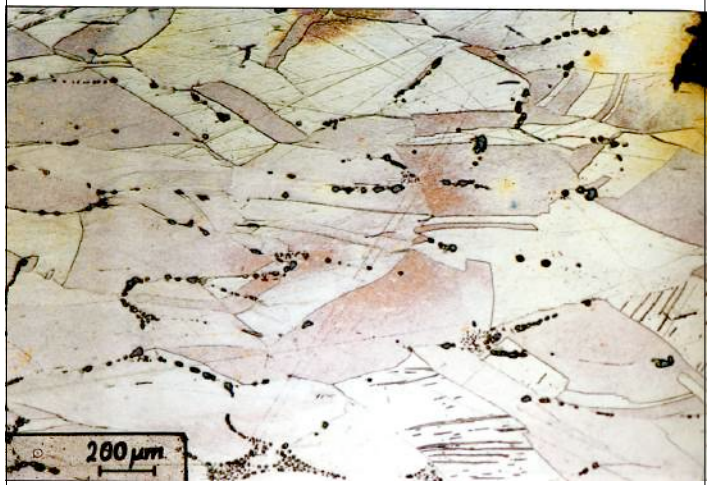
MERSİN YÜMÜKTEPE

GARSTANG EXCAVATION 1940's



Tools from Mersin made out of smelted copper (5000-4900 BC)





REDUCTION OF SULPHIDE ORES

- The earliest evidence is observed by the 4th millennium BC.
- Since sulphur interfered with the reduction process, complex technology was needed.
- The ores were partially roasted to remove some or all of the sulphur as SO_2.
- Since ores were of lower grade, siliceous impurities were to be removed by using iron fluxing agent.
- Copper produced contain higher levels of iron impurity.

ROASTING OF SULPHIDIC COPPER ORES

$CuFeS_2 + 4O_2 \longrightarrow CuSO_4 + FeSO_4$

$2CuS + 7/2O_2 \longrightarrow CuO.CUSO_4 + SO_2$

$2CuFeS_2 + 13/2O_2 \longrightarrow 2CuO + 4SO_2$

COMPOSITION OF MATTE AND BLISTER COPPER

	MATTE (%)	BLISTER Cu (%)
Cu	35-65	98.5-99.5
Fe	10-40	0.1
S	20-25	0.02-01
O	2-3	0.5-0.8
As	0-0.5	0-0.3
Sb	0.1	0.03
Pb	0.5	0-0.1
Zn	0.5	0.0005
Au	$0\text{-}15\times10^{-4}$	$0\text{-}100\times10^{-4}$
Ag	0-0.01	0-0.1

TRACE ELEMENTS IN COPPER RESULTING FROM ORES AND SMELTING

- Iron is the major element. Since iron is added as a fluxing agent, copper obtained from low grade ores may have 2-10 % Fe.
- Most copper ores contain certain amount of metals such as As, Sb, Bi, Pb, Ag, Au, Ni, Co and Zn. These elements will partition between the metal and the slag depending on the smelting conditions.

PARTITION OF TRACE ELEMENTS OF COPPER ORES DURING SMELTING

SLAG	METAL	BOTH
Fe	Co	Zn
Mn	Ni	As*
	Pb	Sb*
	Ag	
	Au	

* Volatile elements.

Fe CONTENT OF BRONZES FROM VARIOUS CULTURES

Culture	Sample size	Average Fe Content (%)	% of artifacts Below 0.05% Fe
Egypt (Predynastic)	14	0.03	82
Egypt (New Kingdom)	250	0.33	6
Cycladic (EBII)	16	0.04	55
Roman (Etruscan)	3062	0.23	26
British (BA)	773	0.05	79
British (IA)	56	0.18	29
British (Roman)	129	0.27	4
Spain (Chalcolithic)	195	0.05	79
Spain (LBA)	49	0.04	95
Spain (Phoenician)	104	0.27	14

CHALCOLITHIC CULTURES

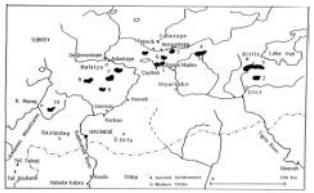
This is the period that yielded the earliest copper smelting evidence in Anatolia. The period is divided into three periods, roughly corresponding to cultural interactions with Mesopotamia:

- Early Chalcolithic (6th millennium BC) is also known as the Halaf Period.
- Middle Chalcolithic (5th millennium BC) is also known as the Obeid Period.
- Late Chalcolithic (4th millennium BC) is also known as the Uruk Period.

METALLURGY DURING THE LATE CHALCOLTHIC PERIOD (4th Millennium BC)

EARLY MESOPOTAMIAN SITES

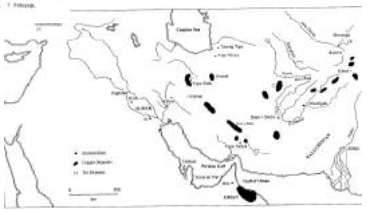
POSSIBLE METAL RESOURCES FOR EARLY MESOPOTAMIAN SITES



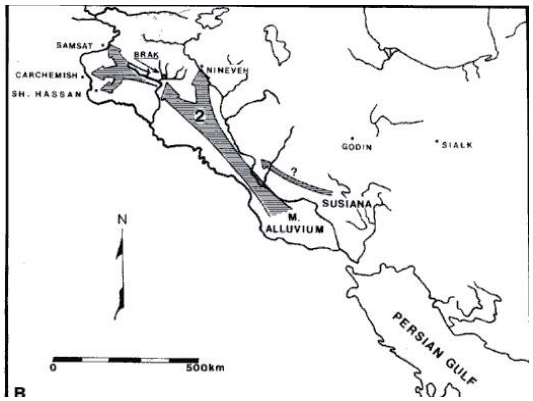
1) Southeastern Anatolian sources reached via Euphrates and Tigris rivers.

2) Copper sources in the Zagros mountains

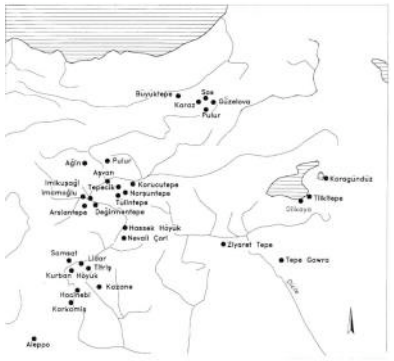
3) Sources of Oman reached via the gulf by sea trade.



URUK TRADE NETWORK



EAST AND SOUTHEASTERN ANATOLIAN SITES

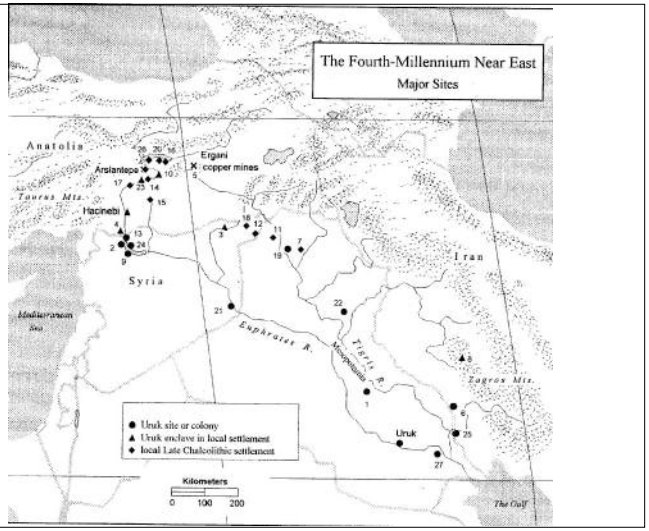


METALLURGICAL ACHIEVEMENTS DURING LATE CHALCOLITHIC

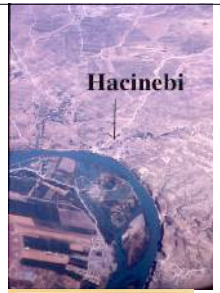
- Sulfide ores of copper were smelted at the Degirmentepe.
- Arslantepe metallurgists were utilizing polymetallic ores and were producing some of the earliest examples of Cu-As alloys.
- Silver was produced by cupellation at Fatmalı Kalecik
- Copper was produced in workshops of proto-urban sites such as Tulintepe, Norsuntepe, Hacinebi, Degirmentepe, Arslantepe etc. by exploiting the rich local sources.

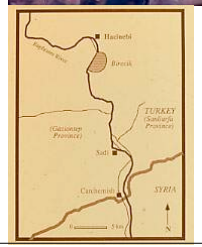
URUK TRADE NETWORK

- Uruk trade period took place between 3700-3100 BC.
- Trader from Uruk came to Anatolia along Tigris and Euphrates valleys.
- They established small enclaves in local Anatolian settlements.
- There were also settlements that were completely Mesopotamian in nature such as Hassek Höyük and Habuba Kabire.
- Anatolian miners and smelters produced the copper desired by the urbanized Mesopotamian cultures.
- The copper was via the rivers.
- By 3100 BC, the Uruk trade network collapsed suddenly.
- Metallurgy in the eastern and southeastern Anatolia declined consistently afterwards.

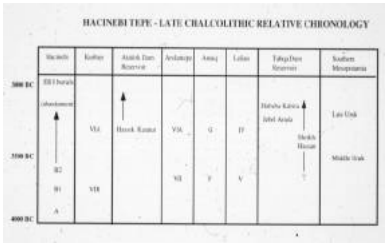


HACINEBI TEPE





HACINEBI CHRONOLOGY



URUK EVIDENCE IN HACINEBI

An Uruk house

Tokens in stamped container

Beveled Rim Bowls (BRB)

Wall cones (Uruk decoration)

EXAMPLES OF URUK POTTERY

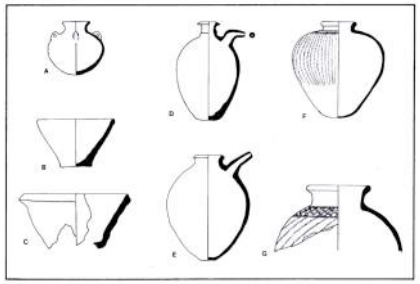
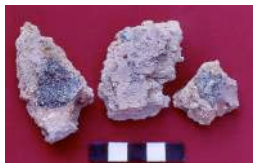
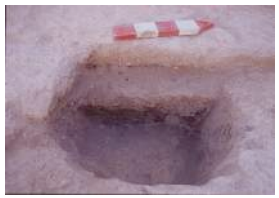


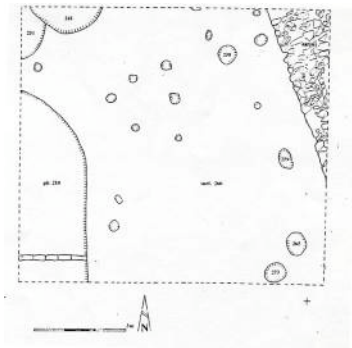
Fig. 33. Selected ceramics of Uruk origin or Uruk type from Period VIA levels at Arslan Tepe (not to scale).

METAL FINDS AT HACINEBI

METALLURGY AT HACINEBI







Tablo 1 HACINEBİ METALLURJİK MALZEMESİNİN KİMYASAL ANALİZİ

ÖRNEK	TANIM	Ag	Sn	Pb	As	Sb	Ni	Zn	Co	Fe	Cu	Bi
HN-6561.1	Bakır Keski	0.02	nd	0.03	0.06	0.08	0.17	0.14	0	0.6	98.1	0.07
HN-6561.2	Bakır Keski	0.03	nd	0.05	0.14	0.28	1.24	0.09	0	0.56	90.5	0.18
HN-13211	Bakır İğne	0.06		0.15	nd	nd	0.12	nd		0.16	93.9	nd
HN-15415	Bakır parça	0.03	nd	nd	0.47	nd	nd	0.01	nd	0.11	79.6	nd
HN-17153.1	İğne parçası	0.06	nd	nd	0.34	0.04	0.49	nd	nd	0.03	98	nd
HN-15882.1	İğne parçası	0.36	nd	nd	1.37	0.26	1.32	nd	nd	0.04	94.5	nd
HN-14762	Bakır parça	0.02	nd	nd	0.36	nd	1.46	nd	nd	0.01	83.5	0.01
HN-14145	İğne parçası	0.04	nd	nd	0.61	nd	0.39	nd	nd	0.27	52	nd
HN-15533	Bakır parça	0.04	nd	nd	1.01	0.13	0.46	0.01	nd	0.06	81.4	nd
HN-12939	Çok metalli cevher	nd		43.1	nd	nd	0.02	4.27		2.3	30.2	nd
HN-12285	Malahit cevheri	nd		0.04	0.29	nd	2.98	0.01		2.98	22.1	nd
HN-8051	Pota	nd		nd	0.04	nd	0.14	0.06	0.02	6.2	2.86	nd
HN-8061	Pota	nd		0.06	0.33	nd	0.2	0.01		4.71	8.29	nd
HN-12264	Pota	nd		0.08	0.37	nd	0.09	0.02		3.62	14.1	nd
HN-16012	Pota parcası	nd	nd	nd	0.01	nd	0.01	0.01	nd	4.94	0.11	nd
HN-16017.1	Pota parcası	0.01	nd	nd	0.14	nd	0.21	0.02	nd	4.53	18.6	nd
HN-16017.2	Pota parcası	0.01	nd	nd	0.13	nd	0.2	0.01	nd	6.19	19.1	nd
HN-16002	Pota parcası	nd	nd	nd	0	nd	0.01	0.01	nd	4.24	0.03	nd
HN-16912.1	Pota parcası	nd	nd	nd	0.07	nd	0.46	0.01	0.02	3.73	29.5	nd
HN-16013.1	Pota parcası	nd	nd	nd	0	nd	0.01	0.01	nd	2.75	0.1	nd
HN-16013.2	Pota parcası	nd	nd	nd	0	nd	nd	0.01	nd	2.94	0.05	nd
HN-16013.3	Pota parcası	nd	nd	nd	0	nd	nd	0.01	nd	0.7	0.03	nd
HN-12097	Cüruf	nd	nd	0.06	0.32	nd	0.18	0.02		9.51	0.05	nd
HN-16911	Cüruf	0.01	nd	nd	0.19	nd	0.27	0.02	nd	2.99	12.6	nd
HN-16010	Cüruf	nd	nd	nd	0.07	0.08	0.25	0.01	nd	0.23	20.2	nd
HN-15533	Cüruf	0.01	nd	nd	0.14	0.05	0.15	0.01	nd	1.07	21.2	nd
HN-15534	Cüruf	0.01	nd	nd	0.59	0.14	0.5	0.02	nd	5.47	12.3	nd
HN-16010.1	Cüruftan Cu parça	0.03	nd	nd	0.75	2.89	0.59	nd	nd	0.99	88.4	nd
HN-16010.2	Cüruftan Cu parça		nd	nd	0.05	nd	0.16	nd		0.12	90.8	
HN-16010.3	Cüruftan Cu parça		nd	nd	0.62	0.24	0.76	nd		0.23	84.6	
HN-15533	Cüruftan Cu parça	0.12	nd	nd	1.88	0.12	0.69	0.09	nd	0.37	91.5	nd
HN-16017	Potadan Cu parça	0.11	nd	nd	0.25	nd	nd	nd	nd	0.83	86.1	nd
HN-16911.1	Cüruftan Cu parça		nd	nd	0.1	nd	0.12	0.12		0.37	90.9	
HN-16911.2	Cüruftan Cu parça		nd	nd	0.94	nd	0.23	0.06		0.12	94.6	
HN-16911.3	Cüruftan Cu parça	0.05		nd	0.42	0.09	0.09	0.04	nd	0.1	91.2	nd
HN-6549	Kalıp parçası	nd		nd	0.16	nd	0.09	0.01		4.49	0.03	nd

Chemical analysis of Hacinebi metallurgical finds

Mold for casting copper ingots

SEM OF A CRUCIBLE FRAGMENT

HN8061 - crucible accretion

	analysis number	
inclusions	**12**	**13**
S		29.14
Ca	0.38	0.06
Fe	0.08	0.07
Cu	98.78	70.41
As	0.76	0.31
matrix	**14**	
Mg	10.63	
Al	3.75	
Si	23.94	
S	0.18	
K	0.92	
Ca	11.24	
Ti	0.37	
Fe	4.39	
Cu	0.4	

h8061-1.bmp
BSE
Magnification : 120