

ULUCAK (SMYRNA, TURKEY): CHEMICAL ANALYSIS WITH CLUSTERING OF CERAMICS AND SOILS AND OBSIDIAN HYDRATION DATING

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ABSTRACT

This is a first report on the chemical analysis and clustering of ceramic sherds and some soils derived from the stratigraphy from Ulucak Höyük Neolithic settlement. The habitation in this site extends from Early Neolithic / Late Neolithic to Chalcolithic and Early Bronze Age period. Two obsidian hydration dates are also reported applying the SIMS-SS technique.

More than one clay sources were exploited either within the LN period or in other periods and some persisted been used throughout the entire occupational time.

KEYWORDS: Ulucak Höyük, Neolithic, ceramics, obsidian, dating, analysis, dendrogram, clustering

INTRODUCTION

The excavations at Ulucak Höyük have provided reliable evidence for a long lasting Neolithic culture in the Aegean coast, and a cultural connection with the Lake District of Anatolia in the east and with Trace in the north west. Despite the occurrence of later periods these layers were heavily destroyed by modern agricultural activities. The Early Bronze Ages and the Chalcolithic periods were represented by pottery rather then well documented architectural remains. Despite the destruction occurred at the later layers, the Neolithic period is the most well preserved cultural era from the point of architecture and small finds. Levels IV and V represent the Neolithic culture at

Ulucak. Level IV has 11 sub-levels starting from IVa (ca.5600 B.C.) and going down to IVk(ca.6050 B.C.). Level IV was fallowed by Level V, excavated in recent years, dating to ca.6200 B.C. with the help of C14 dates. It is possible that Level V has more sub-levels going down to the earlier periods of the Neolithic culture. Future excavations will definitely give us further information about the earlier characteristics of Neolithic period of Ulucak (Cilingiroglu et al., 2004; see, also Cilingiroglu and Abay, this volume).

Here, elemental analysis of several ceramics from the excavation site, as well, as some soils from these strata were analysed by XRF and subsequently were subjected to statistical clustering. Also, two obsidian blades were dated by the SIMS-SS obsidian hydration method while several others with the old OHD technique. Last, comparison between pottery from Ulucak and some Aegean sites is made.

Provenance

Provenance studies of the raw materials used during prehistoric lithic industry are of key importance in researches on ancient man. During Palaeolithic, this provides basically information on the extension of the territory exploited by small groups of hunter-gatherers. In the Neolithic and Bronze Age provenance studies contribute to the knowledge of longdistance circulation and exchanges of raw materials and goods, hence on the chaines operatoires of lithic artifacts. Indeed, reconstructing mobility strategies is a major goal of researchers interested in prehistoric hunter-gatherers and the use of geochemical source characterization of obsidian found at sites in a region offers a way to reconstruct the precurement range, or distance traveled to obtain resources of prehistoric groups.

Pottery, due to its remarkable storage properties was a vital item used in every day life food activities. Not only but aesthetic qualities was frequently used by ancient man. Ceramics is also one of the preferred materials in provenance studies. This is because of its mode of formation from characteristic clay sources the physical-chemical properties are most often different at a major, minor but mainly trace element level.

Early ceramic provenance studies were based on bulk physical properties, such as, typology, technology, etc, as well as on petrography. Although useful for sample description, these observations generally do not provide valuable criteria for provenance studies.

The impact on characterization studies was made during sixties when spectroscopic methods allowed the determination of elemental compositions from small-sized samples. Since then till today nearly all provenance studies are based on elementary composition. Among the destructive methods of analysis are electron microprobe (for about 10 major elements), neutron activation analysis (up to ~27 major to trace elements), ICP-MS/AES, with up to more than 50 elements determined, Optical Emission Spectroscopy, Atomic Absorption Spectroscopy, PIXE, and XRF, depending of instrumentation availability and allowance to sample in a destructive manner.

However non-destructive analysis is progressively used employing X-ray fluorescence

Regarding statistical techniques various discriminant approaches have been used, such as, multivariate analysis (Clustering with dendrograms), bivariate plots using discriminant functions (linear combination of elements, ratios of elements), and PCA analysis.

Of the most popular Multivariate statistical technique used in archaeometry is Cluster analysis.

Although a powerful approach, a geochemical characterization does not in certain cases allow one to ascertain apparent

similarities as these may derive from distant clay sources which however may resemble. On the other hand, obtained differences may not imply trade or unknown clay source due to a mixing of two known clays and / or different fillers (sand).

Nevertheless, in the present work, classification of Ulucak Neolithic ceramics by a well calibrated portable ED-XRF and Cluster techniques complemented by multivariate mixture of normals with unknown number of components and PCA (Papageorgiou and Liritzis, 2005) is shown here to offer several advantages; a) swift counting time, b) analysis of tools by a destructive but if needed non-destructive measurement too, c) low cost, d) versatile as a portable analyzer performing *in situ*, and e) safeguarding the provenance.

Sample Preparation

In all ceramic sherds the outer surface was discarded to avoid weathering implying leaching/ infiltration of ions, thus altering elemental composition. Solid pieces were powdered (<90 μ m), dried, and measured by a portable ED-X-Ray Flourescence analyzer (ED-XRF).

The Analyser

The system (spectrace 9000 TNT) was calibrated on several standard clay and brick, and the application software Fine particle of soil application was used.

The EDXRF field portable analyzer Spectrace 9000 TN was used with a mercuric iodide (HgI₂) detector, which has a spectral resolution of about 260 eV FWHM at 5.9 keV, and three excitation sources of radioisotopes within the probe unit – Americium Am-241 (26.4 KeV K-line and 59.6 KeV L-lineV) measuring Ag, Cd, Sn, Ba, Sb; Cadmium Cd-109 (22.1 K-line, 87.9 K- & L-line KeV) measuring Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Zr, Mo, Hg, Pb, Rb, Th, U; and Iron Fe-55 (5.9 KeV K-line) measuring K, Ca, Ti, Cr.

CERAMICS

A total number of 47 ceramic sherds were analysed by the ED-XRF portable analyzer (TN Spectrace 9000). Table 1 gives the samples references and Table 2 all results.

Only those chemical elements with low error (less than 20%) were included in the Cluster analysis to identify similar groups. Those were: Ba, K, Fe, Rb, Pb, Hg, Ti, Mn, Sr, Zr, Ca, Zn and As.

The following observation are made:

There appears a variation in the contents of several chemical elements, which imply different clay source.

Fig.1a shows the dendrogram in which distinct groupings are evident.

The groups are the following:

- 1st Group: Samples RHO-38, 102, 93, 73, 69, 75, 77, 70, 98, 78. Sample from EB (38) have same clay source with LC period (69, 77) and even earlier LN/EN period (78).
- 2nd Group: RHO-48, 91, 105, 96, 88, 103, 84, 76, 104, 106, 82. These LN ceramics form a cluser implying exploitation of same clay source.
- 3rd Group: RHO-85, 94. This may well form part of 2rd Group.
- 4th Group: RHO-74, 86, 99. Other LN clay was used too.
- 5th Group: RHO-81, 100.
- 6th Group: RHO-50, 97
- 7th Group: RHO-60, 61 the soil samples from LN layers.

Sample RHO-108 is quite distinct from all others.

- 8th Group: RHO-101 to 107 from LN strata (see figure 1)
- 9th Group: RHO-151 to 154 form a group with ceramic RHO-118 of Late Roman Period and soil RHO-155 with LN ceramic RHO-148.

In general different clay sources were used during LN period, while some of them seem to have been exploited during a long period of time from EN/LN to EB period.

TABLE 1:

Ulucak ceramic sample codes and ages based on some calibrated C-14 dates. LC=Late Chaslcolithic, 3000-4000 BC; LN=Late Neolithic, 5750-5900 BC; EB=Early Bronze Age, 2000-3000 BC, LNsoil stands for two soil samples from respective strata.

RHODES	Ref TURKISH Ref. & Age
RH0-38	DAT II B1, II a, EBA ±3000-2000 BC
RH0-39	DAK II a, EBA ±3000-2000 BC
RH0-48	DON IV a, LN
RH0-49	DMK IV d, LN
RH0-50	DON IV a, LN
RH0-60	CHG-NII A IVc, LN soil
RH0-61	DIV-NII,Va, LN/EN soil
RH0-62	DAH IV c, LN
RH0-63	DNU IV h, LN
RH0-64	DAL II b1, EBA ±3000-2000 BC
RH0-65	DAG I, Late Roman Period
RH0-66	DND IV a, LN
RH0-67	DAH IV c, LN
RH0-68	DHZ, IV b1, LN
RH0-69	DHJ, III b, LC
RH0-70	DHJ, III b, LC
RH0-71	DIN, IV g, LN
RH0-72	DHJ, III b, LC
RH0-73	DFO, IV b2, LN (C-14 date: 5990-5730 BC)
RH0-74	DHJ, III b, LC
RH0-75	DIO, IV h, LN
RH0-76	DPM, V a, LN/EN
RH0-77	DIG, III c, LC
RH0-78	DPM, V a, LN/EN
RH0-79	DFO, IV b2, LN (C-14 date: 5990-5730 BC)
RHO-80	DIG, III c, LC
RH0-81	DIN, IV g, LN

RH0-82	DND, IV a, LN
RH0-83	DIG, III c, LC
RH0-84	DIG, III c, LC
RH0-85	DIO, IV h, LN
RH0-86	DAL, II b1, EBA ±3000-2000 BC
RHO-87	DIN, IV g, LN
RHO-88	DND, IV a, LN
RHO-89	DIU, IV e, LN
RHO-90	DIN, IV g, LN
RHO-91	DIA, IV b2, LN (C-14 date: 5990-5730 BC)
RH0-92	DFO, IV b2, LN (C-14 date: 5990-5730 BC)
RH0-93	DIV, IV f, LN
RH0-94	DPM, V a, EN/LN
RHO-95	DIV, IV f, LN
RHO-96	DND, IV a, LN
RHO-97	DIA, IV b2, LN (C-14 date: 5990-5730 BC)
RHO-112	DHZ, IV b1, LN
RH0-113	DNU, IV h, LN
RH0-114	DII, IV a, LN/EN
RH0-115	DII, IV a, LN/EN
RH0-116	DAG, I, Late Roman Period
RH0-117	DIV, IV f, LN
RH0-118	DAG, I, Late Roman Period
RH0-148	DIU, IV e, LN
RH0-151	DBN N11 a-IV g, soil room no 17, Trench N1a
RH0-152	N12 6 no'luMekan (soil room 6 trench N12
RHO-153	N11 4 no'luMekan (soil room 4 trench N11
RH0-154	N12 9 no'luMekan (soil room 9 trench N12
RH0-155	N13 20 no'luMekan (soil room 20 trench N13

TABLE 2: Chemical elements of Ulucak ceramics and soils measured by the portable ED-XRF. Concentration in ppm values.

ppni values.													
Sample	Hg	Ba	Fe	Rb	K	Pb	Ti	Mn	Sr	Zr	Ca	Zn	As
RH0-38	30	1068	43775	103	22830	21	4180	1065	359	278	25740	59	105
RH0-39	30	676	38710	79	18230	48	3210	580	120	98	127590	91	86
RH0-48	83	539	30210	140	19310	15	3210	400	221	197	68190	107	120
RH0-49	63	1198	44430	108	19605	15	5000	1000	390	268	21590	84	222
RH0-50	28	617	29565	126	17415	15	3120	360	216	140	111850	99	170
RH0-60	36	772	3720	44	3840	132	457	540	308	29	276575	86	31
RH0-61	57	312	1765	13	1775	21	200	423	291	20	291498	42	28
RH0-102	37	1256	44880	105	21805	41	4725	760	419	258	20780	77	65
RH0-103	61	686	27145	115	19035	20	3360	420	210	206	81910	62	77
RH0-104	73	644	35370	134	22500	40	3525	585	204	179	19105	124	57
RH0-105	37	1177	31258	124	20768	15	3452	503	207	186	50508	97	67
RH0-106	106	483	25870	104	17495	19	2740	265	218	146	81800	74	53
RH0-107	77	825	35625	103	15440	73	2085	570	261	130	144095	88	335
RH0-69	30	1083	42235	106	19985	36	4120	620	342	213	24235	62	109
RH0-70	59	1068	42285	77	24420	29	4090	590	496	237	17715	129	41
RH0-71	56	601	37735	160	26065	24	3645	455	217	3	30665	142	152
RH0-72	49	994	28175	99	22145	24	3075	700	373	154	19165	137	86
RH0-73	40	1246	42510	86	27830	37	4595	615	475	258	22955	96	68
RH0-74	66	1015	35080	104	17685	18	2975	495	232	183	89830	88	137
RH0-75	63	718	23315	102	21190	16	2560	405	230	141	93810	126	74
RH0-76	92	574	28565	132	21875	22	3740	340	166	239	61420	117	59
RH0-77	59	867	33600	107	16650	52	3980	435	335	225	20445	86	90
RH0-78	85	1032	36195	108	26130	28	4310	575	391	237	18480	95	53
RH0-79	137	1488	47035	171	35890	189	4930	950	446	3	29795	110	28
RH0-80	30	734	25160	81	16050	109	2500	600	225	145	110535	73	104
RH0-81	38	501	21755	71	13245	15	1985	495	254	109	130970	76	157
RH0-82	77	611	25370	110	17435	31	2780	350	284	168	128450	92	61
RH0-83	31	707	33815	119	19115	21	3690	825	159	234	32470	143	127
RH0-84	71	615	30240	125	18405	66	3195	755	166	175	54835	96	87
RH0-85	71	607	27815	107	15660	22	2945	940	258	180	75370	140	46
RH0-86	63	612	39633	155	23327	34	4370	793	115	209	25770	165	58
RH0-87	70	788	37680	129	21975	38	4235	1070	176	239	11430	72	210
RH0-88	71	415	28100	127	21225	15	3025	300	220	178	75275	95	36
RH0-89	93	1007	24155	82	15600	30	2510	1475	279	153	129050	133	136
RH0-90	50	641	42895	198	31670	20	4465	665	183	248	16720	131	81
RH0-91	72	598	29360	115	20415	15	3460	380	226	186	72650	119	106
RH0-92	30	752	18980	78	16800	15	1880	480	256	102	103390	153	64
RH0-93	56	1075	46895	92	22800	21	4950	910	463	281	19340	64	61
RH0-94	68	531	26325	115	18850	29	3280	370	189	199	62835	166	36
RH0-95	87	573	31645	131	25735	37	3115	660	612	145	50695	128	18
RH0-96	59	611	31715	104	21180	27	2805	600	183	164	68835	90	61
RH0-97	30	664	27975	119	22635	16	3260	635	230	164	96345	93	114
RH0-98	75	873	36435	86	23690	20	3780	245	383	236	15335	69	120
RH0-99	105	1183	27070	117	19305	31	3310	555	271	209	83865	115	108
RH0-100	58	549	20115	103	12005	15	2265	220	221	143	99990	64	115
RH0-101	116	671	40665	132	24620	22	4525	485	216	278	29535	146	25
RH0-108	30	1044	38410	117	25880	22	4045	610	438	243	17290	85	194

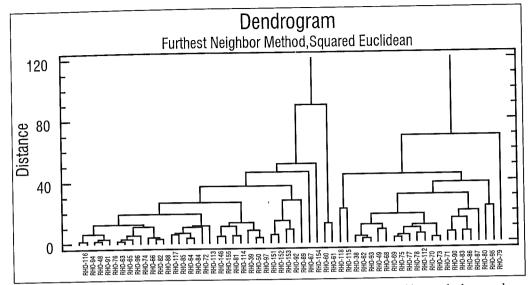


Fig. 1a Dendrogram. Cluster analysis of Ulucak ceramics based on the furthest neighbor method, squared Euclidean. Sample codes are given with Rhodes reference. Analysis is based on elements:

K, Ca, Ti, Fe, As, Sr, Zr, Hg, Pb, Rb, Ba, Mn, Zn.

Further soil analyses have shown distinct groupings between them. Fig.1b shows a relevant dendrogram with soil sources deriving from respective strata of the excavated settlement. Soils 153, 154 and 155 group together with closest soil 151; the 152 is different, following different from all 60 and 61.

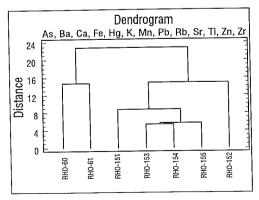


Fig.1b Dendrogram of seven soil samples from Ulucak.

OBSIDIAN TOOLS

Table 3 shows the sample codes for them and the corresponding code for Rhodes. The Rhodes codes are RHO-4 to RHO-20.

Only two obsidian blades were submitted to hydration dating following the new method of SIMS-SS developed by the Greek side in Rhodes.

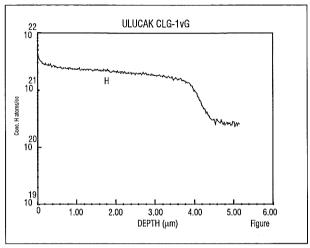
The samples were a) RHO-4 (CLG IVg) and b) RHO-8 (BE IVa).

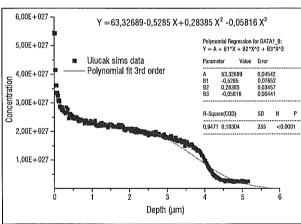
Fig.2 shows the secondary ion mass spectrometry (SIMS) profiles for the two samples.

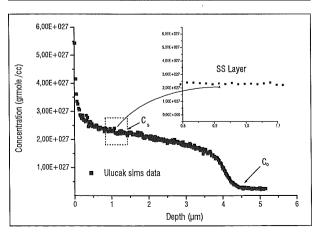
Fig.3 shows the Infrared Photoacoustic Spectroscopy (IR-PAS) calibration for hydrated rims versus IR absorbance. Employing IR-PAS the hydration rim is measured and this is a measure of their age.

Fig. 4 shows IR-PAS spectra for two dated (see below) samples.

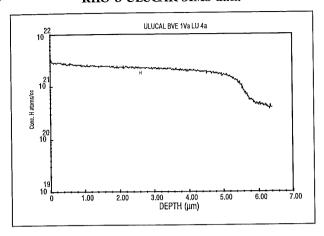
RHO-4 ULUCAK SIMS data







RHO-8 ULUCAK SIMS data



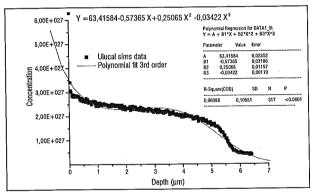


Fig.2: SIMS data for the RHO-4 and RHO-8 for C in atoms / cc (upper) and SIMS profiles with the fitting by a 3rd order polynomial (lower). For RHO-4 the SS layer is also indicated. This spectrum analysis is a prerequisite step to the age calculation by SIMS-SS.

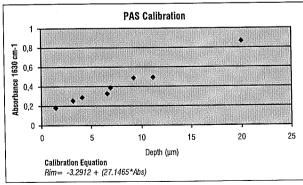


Fig.3: Calibration plot of IR-PAS absorbance versus hydration depth (Chris Stevenson, pers. comm.).

Rhodes sample ref.	Ulucak samp	Ulucak sample code				
RH04	CLG lvg, Late (5750-5900					
RH05	CRN Ivd,	»	»			
RH06	CGS IVb1,	»	»			
RH07	CHA IV b1,	»	»			
RH08	BVE Iva,	»	»			
RH09	CLM IVb2,	»	»			
RH010	CHE IV c,	>>	»			
RH011	CRT IV e,	»	»			
RH012	CKT IV e,	»	»			
RH013	CER IV c,	»	»			
RH014	CIR Ivc,	>>	»			
RH015	CPR IV d,	»	»			
RH016	CIA IV c,	>>	»			
RH017	CLZ IV b2,	»	»			
RH018	CPO IV d,	>>	>>			
RH019	BVJ IV a,	>>	>>			
RH020	CKT IV b2,	>>	>>			

Table 3: Obsidian reference samples.

For the rest of the obsidians the hydration depth has been deduced from this calibrated plot (see, Table 4).

Applying the old Obsidian Hydration Dating (OHD) method the hydration depth is related to the age ($x^2 = K.t$, where k = diffusion rate, X = hydration depth, t = age). However, this is an empirical equation with many assumptions and gives uncertain results.

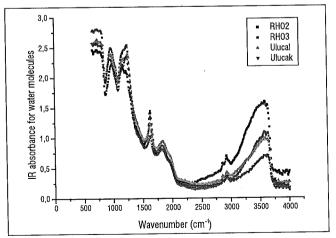


Fig.4 IR-PAS spectra for two obsidians (RHO-4 and RHO-8) in comparison with two Japanese obsidians. The X axis gives the wavenumber in cm⁻¹ and Y axis the IR absorbance for water molecules at 1630 cm⁻¹ (sharp peak).

Lab No.	Abs 1630cm-1	Rim (um)	Density	EHT	%rH/100	%0H-	A	E	RATE	Date BP	AD/-BC	S.D.
Rho-4	0,2618	3,82	2,380568	20	1,0000	0,10	1,10	85460	4,81	3.028	-1078	161
Rho-5	0,3863	7,20	2,368196	20	1,0000	0,11	1,19	85166	5,42	9.550	-7600	267
Rho-6-1	0,2324	3,02	2,373477	20	1,0000	0,11	1,15	85289	5,16	1.765	185	119
Rho-7	0,2718	4,09	2,3572	20	1,0000	0,12	1,27	84923	5,97	2.796	-846	139
Rho-9-1	0,276	4,20	2,361022	20	1,0000	0,12	1,24	85006	5,78	3.053	-1103	147
Rho-10-1	0,2501	3,50	2,373788	20	1,0000	0,11	1,15	85296	5,14	2.379	-429	138
Rho-12	0,276	4,20	2,3639	20	1,0000	0,11	1,22	85069	5,64	3.131	-1181	151
Rho-14	0,2646	3,89	2,362131	20	1,0000	0,12	1,24	85030	5,73	2.645	-695	138
Rho-15	0,2919	4,63	2,348154	20	1,0000	0,12	1,34	84733	6,43	3.336	-1386	146
Rho-16-1	0,2658	3,92	2,370507	20	1,0000	0,11	1,17	85219	5,31	2.902	-952	150
Rho-17	0,3799	7,02	2,362796	20	1,0000	0,11	1,23	85045	5,69	8.662	-6712	248
Rho-18-1	0,2473	3,42	2,370623	20	1,0000	0,11	1,17	85222	5,30	2.209	-259	131
Rho-19-1	0,3368	5,85	2,362055	20	1,0000	0,12	1,24	85028	5,73	5.977	-4027	206
Rho-20-1	0,334	5,78	2,359792	20	1,0000	0,12	1,25	84979	5,84 5	.709	-3759	199
Rho-20-2	0,3116	5,17	2,361972	20	1,0000	0,12	1,24	85027	5,73	4.658	-2708	182

TABLE 4: Hydrated depths (rims) calculated from Fig.3 for all Ulucak obsidians. The absorbance is based on the 1635 cm⁻¹ peak of IR-PAS spectrum. Also shown the density per sample and intrinsic (structural) water as %OH-, activation energy E and prexponential A from Arrhenius equation, as well as the calculated diffusion rate (Chris Stevenson, pers. comm.).

As expected, this traditional OHD along with data deduced from density versus OH content does provide erroneous (large uncertainty) results. Even negative the result it is worth presenting the case to appreciate the order or error, as well as, some (by chance) close to expected ages.

Introducing SIMS-SS method

Diffusion of environmental water into the surface of obsidian tools of archaeological origin is monitored by secondary ion mass spectrometry (SIMS), which provides a H+concentration (C) versus hydration depth profile. The modelling of this diffusion process, as one-dimensional phenomena, is based on the idea that a saturated surface (SS) layer is encountered near the surface. A novel

software program has been developed, using MATLAB, incorporating all numerical parameters for the dating of hydrated obsidians using the SIMS profile. This approach has been applied to several archaeological obsidians from the Aegean, Hungary, and Asia Minor and compared with samples from radiocarbon dated cultural phases where the agreement is excellent. The infrared absorption peak for the molecular water within the hydration layer at 1630 cm⁻¹ linearly correlates with the SIMS-SS data and provides a secondary calibration for the estimation of age (Liritzis et al., 2005).

Diffusion of water into amorphous silicates (glass) has been investigated on a theoretical and experimental basis (Crank, 1975). Amorphous rhyolitic glass (obsidian), has

been studied for dating purposes based upon the rate of water diffusion into the surface. The traditional age equation (X² = kt, where X=hydration depth, k=diffusion rate, t = diffusion age) is not highly reliable, since k depends on short-term temperature measurements (Friedman and Smith, 1960). Other problematic areas include hydration depth measurement by optical microscopy that has an unacceptable error of +/-0.25 um.

Surface analytical techniques have been used to study ancient materials since the 1970s and secondary ion mass spectrometry (SIMS) is now well established as a surface technique, which provides elemental data and allows depth profiling, mapping or imaging (Liritzis et al., 2004). The depth and shape of the hydrogen diffusion profile on ancient obsidian tools has been determined by SIMS (Liritzis & Diakostamatiou, 2002, 2005; Liritzis et al., 2004). The obsidian hydration dating (OHD) method is based upon modeling the rate of water diffusion into the natural glass surface. A variety of strategies have been developed over the years to calibrate the movement of ambient water into glass. Many of these approaches have developed procedures for controlling the chemical composition of the glass and modeling the environmental history of the artifact context (e.g. temperature, humidity). However, the development of calibrations to compensate the variation in external variables has proven to be difficult. This has been the major impediment to making OHD a fully chronometric dating method comparable to radiocarbon dating.

In the past few years we have developed alternative solutions to the OHD age equation based upon the concentration-dependent diffusion water profile by modeling the concentration-to-depth sigmoid shape of the diffused water as determined by SIMS. In this procedure, the hydrogen profile incorporates all unknown environmental parameters, especially temperature. Thus, by modeling

the H⁺ versus hydration depth (X) profile, an age equation can be obtained. This is based on the observation that in the course of water diffusion into obsidian a surface saturation layer forms where water concentration remains constant. The location of this plateau layer is achieved conducting successive regressions starting from the beginning of the shape to the point where the slope significantly changes (Brodkey and Liritzis, 2004). Statistically, this region is determined in the change of slopes from near zero to negative values. The exclusion of some initial points to achieve the best fit with the first half of S-curve is justified because of the near surface disturbances due to sputtering conditions and/or variable environmental effects.

The new SIMS-SS dating method is based upon the profile of water versus humidity penetration depth, X. Thus, the concentration of water molecules (C) versus depth (X) is used following Fick's diffusion law and an age equation is produced.

The SIMS-SS method gives the following ages a) RHO-4, $t = 5,295 \pm 100$ BC, and b) RHO-8, $t = 7,450 \pm 150$ BC (Table 5).

DISCUSSION

The clustering of the ceramics has been further investigated in comparison with other Aegean Neolithic ceramics – Sarakinos cave, Boeotia, central Greece, Yali and Pergussa islands near Nissyros at Dodecanesse (across the Smyrna coasts in Turkey) (Papageorgiou and Liritzis, 2005).

Comparison with Sarakinos cave group (SARA) exhibits a greater spread around an apparent central nucleus, and several SARA (6, 46, 50, 23, 55) fall within the Ulucak, Asia Minor group. The latter possibility is enhanced from the fact they are of the same period i.e. Late Chalcolithic / Early Bronze Age (4000-2500 BC). Others, from SARA,

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Sample Ref.	Dating SIMS-SS (years BP)	Dating <i>C-14</i> (years BP)	C _s (grmol/cc)	C _{int} (grmol/cc)	X _s (cm)	ek	Ds (cm²/y)
ULUCAK1 (L) RHO-8	7,450±150	6,500 - 7,200	0.001896 ±3E-5	0.0003614 ±2.15E-5	0.0002735 ±7E-6	11.7	1.378E-12
ULUCAK2 RHO-4	5,295±100	6,500- 7,200	0.001822 ±1.9E-5	0.0002148 ±1.17E-5	0.0001612 ±4.5E-6	9	4.661E-13

TABLE 5: SIMS-SS data and deduced ages by SIMS-SS and C-14 (Liritzis et al., 2005)

however resemble to Late Neolithic Ulucak.

Two soil samples from local floor of Ulucak settlement (RHO60, 61) though form an expected group, was not used as a clay source and pottery production. In all techniques they both are quite distant from main Ulucak cluster (s).

There appears an interesting overlapping between Late Neolithic Yali, in Nissyros and Ulucak (RHO-69, 70, 72, 74, 77, 80, 83, 84) during Late Chalcolithic (for Ulucak) = Late Neolithic (Greek Neolithic at Yali) [RHO-70= PERG2 (Pergussa island) Early Bronze; RHO-72 Late Chalcolithic=Yali, Late Neolithic]. The two sites are close to the Asia Minor coastline, Ulucak being c.15 km from Smyrna. Also, interaction appears in earlier times, during Late/ Early Neolithic times between Ulucak RHO-82, 106, 75, 101, 106, and Yali/ Pergoussa. The latter is not possible because Ulucak's beginning of Late Neolithic is earlier than in Yali. However, it may imply same clay source.

In Ulucak, a quite interesting observation is the apparent use of a particular clay source throughout the long period of successive cultural phases (Early Bronze, Late Chalcolithic, Late Neolithic, late Early

Neolithic).

The obtained results indicated several useful information regarding long distance trade exchange, usage of same clay source by successive cultural phases, interaction of settlements via sea routes. Some 'outliers' imply very different clay sources.

The extremely interesting Ulucak- Yali-Pergoussa and Sarakinos-Ulucak interaction needs further verification.

Obsidian dating gave one concordant to C-14 result and another later than expected, probably from intrusion from higher levels(?).

CONCLUSION

Ulucak, Höyük Neolithic settlement in Smyrna provided a sequence of well excavated ceramic typology and obsidian tools. Chemical analysis by ED-XRF with subsequent clustering provided interesting groupings implying use of more than one clay sources. A preliminary comparison with Neolithic and EB ceramics from three Aegean sites indicated a possible interaction through trade or use of same clay source. Obsidian dating applying the new OHD method SIMS-SS provided two ages close to anticipated archaeological chronology.

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REFERENCES

- Brodkey. R. S and Liritzis. I (2004) The dating of obsidian: A possible application for transport phenomena (a tutorial). *Mediterranean Archaeology & Archaeometry*, vol.4, No.2, 67-82.
- Cilingiroglu. A, Derin. Z, Abay. E, Saglamtimur. H and Kayan. I (eds.) *Ulucak Höyük. Excavations conducted between 1995 and 2002.* Ancient Near Eastern Studies, Peeters, Supplement 15, pp.161, Louvain.
- Crank. J (1975) The Mathematics of Diffusion, Oxford Science Publication, OUP, Oxford.
- Friedman. I and Smith. R (1960) A new dating method using obsidian: Part 1, the development of the method. *American Antiquity*, 25, 476-522
- Liritzis. I and Diakostamatiou. M (2002) Towards a new method of obsidian hydration dating with secondary ion mass spectrometry via a surface saturation layer approach. *Mediterranean Archaeology & Archaeometry*, 2 (1), 3-20.
- Liritzis. I, Drakonaki. S, Vafiadou. A, Sampson. A and Boutsika. T (2002) Destructive and non-destructive analysis of ceramics, artifacts and sediments of Neolithic ftelia (Mykonos) by portable EDXRF spectrometer: first results. In Sampson.A (ed.) (2002) *The Neolithic settlement at Ftelia, Mykonos*. Dept. of Mediterranean Studies, Univ. of the Aegean, Rhodes, Greece, Chapter 11, 251-271.
- Liritzis. I, Diakostamatiou. M, Stevenson. C. M, Novak. S. W and Abdelrehim. I (2004) Dating of hydrated obsidian surfaces by SIMS-SS. *J. Radioanal. Nucl. Chem.*, 261, 1, 51-60.
- Liritzis. I, Ganetsos. Th, Stevenson. C. M, Novak. S. W and Laskaris. N (2005) Water diffusion dating of ancient obsidian tools by SIMS-SS (in preparation)
- Liritzis. I, and Diakostamatiou. M (2005) SIMS-SS a new obsidian hydration dating method; analysis and theoretical principles. *Archaeometry* (accepted).
- Papageorgiou. I and Liritzis. I (2005) Multivariate mixture of normals with unknown number of components:

 An application to cluster Neolithic ceramics from Aegean and Asia Minor (submitted to Archaeometry).
- Pollard. M and Heron. C (1996) Archaeological Chemistry. The Royal Society of Chemistry, London.