

PROVENANCE STUDIES OF SGRAFFIATO AND LATE GREEN GLAZED
WARES FROM SĪRĀF, IRAN

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The application of the Physical Sciences to Medieval Ceramics is one of many new areas of interdisciplinary research. Techniques and technology have been developed in other fields which can have broad application to many of the humanities, leading eventually to a better understanding of the medieval world and its technology.

The development of neutron activation analysis, the primary tool used in this work, as a powerful analytical tool came about in the last ten years as a spin-off from the semi-conductor electronics industry and the development of nuclear reactors for power sources.

This technique,^{1,2} as applied to ceramics, involves the quantitative analysis of about thirty different chemical elements in the body fabric of the potsherd. A small sample (100 mg) of the interior fabric is powdered, pressed into a uniform sized pellet and irradiated along with appropriate standards in a reactor. The now radioactive samples are then analyzed for the various characteristic gamma rays using a germanium gamma-ray spectrometer at five different times selected to achieve the best data from nuclides with a variety of half lives, from a few minutes to several years long.

Clays formed in a particular geological setting have a minor and trace element chemical composition pattern, or fingerprint, which can distinguish one general clay source from another. The addition of frit, temper or limestone, variations in the firing temperature can modify the basic fingerprint,³ but the effect of these modifications can sometimes be readily identified and give

information about the pottery making process.

Only brief mention of the procedure⁴, for analyzing the chemical fingerprints will be made here. A group of pottery known from stylistic or other criteria to be locally made and which is chemically homogeneous serves as a reference group for a particular location. For each chemical element, the mean value of its concentration and the root-mean-square deviation (σ) from this value is determined for all the pots in the reference group. In our work if the average value of σ for approximately 20 elements is 10% or less, the group is considered to be a 'good' reference group suitable for classification purposes. For a pot of unknown provenance to be a member of this group, and therefore presumably to have the same provenance, the abundance of about 2/3 of its elements should agree with the corresponding value in the reference group within 1σ and usually only 1 or 2 elements should disagree by more than 2σ .

The sherds in this study are from the excavation⁵, at Sirāf, Iran done under the direction of Dr. David Whitehouse and generously supplied by him. We studied sgraffiato ware from two time periods; early being the 9th to 10th Century material found in the sounding (Site A) and the Great Mosque (Site B), and the late sgraffiato dating from c. 1050 to the late 12th Century found in other levels of the same two sites. Figure 1 is a photograph of the Early Sgraffiato pieces studied. As you can see, two of the sherds adjoined and have been placed together as one sample.

The glazes of Sirf-102 and 103 are lead-tin while Sirf-100 and 101 are lead-tin with much smaller amounts of tin.

The late sgraffiato ware is shown in figure 2. These glazes were qualitatively identified by X-ray fluorescence analysis. All pieces were lead glazed, the green portions of Sirf-23, 109, 111, 114, 115, and 117 contained copper. Spectrographic analysis of the brown area on Sirf-27 revealed strong lines of Fe, Al, Pb, Mg and Si. There were moderate lines of Ca and Ti which were probably from the slip. The late sgraffiato wares were from level 6, 10 and 11 of the sounding. Level 10 had sgraffiato wares stylistically characteristic of Sirāf from about 1050 to the late 12th Century.

The chemical composition of the sgraffiato wares can be seen in Table 1. Also shown is the reference group of Samarra ware. The second line is the number of pieces of pottery in each group. The third line is the average standard deviation of the mean for all 23 elements. The average abundance for each element is listed \pm the root-mean-square deviation. The values are expressed

in ppm. except where listed as percent.

Some pieces of the Late Sgraffiato ware were analyzed for volatile material⁵, and the average volatile components for these 10 pieces was $4.1\% \pm 2.9$. The Early Sgraffiato ware had $11.3 \pm 2\%$ volatile material and the reference group of Samarra ware had $3.8 \pm 1.4\%$ volatiles. Therefore in order to compare the basic clay the abundances were normalized to account for the different amounts of CO_2 and water in each of the groups. The Late Sgraffiato ware does not match any type of pottery from Siráf that we have analyzed or any other reference groups we have in our library of fingerprints. It is known that kilns were in use at nearby Site D during this time period, however no kiln wasters of this material have been found. Siráf is known to have been very prosperous at this time and was a great trading port. It is therefore not surprising to find pottery imported from more than one locality.

The four pieces of Early Sgraffiato are chemically similar to the Samarra ware which is characteristic of the general Mesopotamian clay. One unfortunate characteristic of the Mesopotamian clays is the relatively large standard deviation (30%) of all of the alkali metals thus making these individual elements of little value for fingerprinting.

Fourteen elements in the Early Sgraffiato ware have abundances which match within 1σ the corresponding elements in the Samarra group. The abundances of two elements differ by 1σ . The alkali metals, Na and K differ by 3σ . This could be explained by an exchange in the clay of Na and K. Until we have established fingerprints of Mesopotamian clays characteristic of more specific areas we can only say that the Early Sgraffiato ware was made from clay from this general geographic area, not from clay local to Siráf.

Figures 3 & 4 show the other type of pottery, the Late Green Glazed ware from the time period of 1050 to the late 12th Century, studied from this excavation. We analyzed 19 pieces of Late Green Glazed ware falling into two chemically distinct groups. In the first group of four pots, (see Fig. 3) designated Late Green B, Sirf-9 and 11 have Pb and Cu uniformly distributed in the glaze in addition to Fe. Sirf-12 has Pb and Cu only in the green band with Fe in all portions of the glaze. Sirf-8 has no Pb or Cu in the glaze and Sirf-13 has Fe but no Pb or Cu in the glaze. Figure 4 shows the five pieces used to form the late Green A group: Sirf-69, 71, 72, 74 and 98. The glaze of one of the pieces shown (Sirf-66) was analyzed by Al Hebert and Harry Bowman using XRF. It was an alkali silicate glaze with approximately 12% Na_2O , 5% CaO , and 7% Fe_2O_3 .

Table 2 shows the abundances of 23 elements for the Late Green A and B groups and once again the Samarra ware as a reference group. The standard deviation for 23 elements in both groups is about 6% and σ for the 29 pots in the Samarra ware group is 8.4% for 20 elements. These abundances have been normalized to take account of the volatile components. The groups A and B are somewhat similar but you will notice that the abundances of all elements except K, Cs, Cr, Hf in group A are all lower than the corresponding abundances in group B. The Ca also is different, but we know that its abundance can vary because of addition of limestone to the clay before firing. Being a major constituent, this variation affects all trace element abundances. However, if we normalize the two groups to 0% Ca (as CaO) we can see in Table 3 that the two groups of Late Green Glazed ware have the same basic clay composition or fingerprint but were probably treated differently in the pottery making process. That is, the A group had more limestone added or group B was depleted in limestone. Now, if we compare this clay with the reference group also normalized to 0% Ca as CaO we again see the general fingerprint of Mesopotamian clay but note several differences. The U, Hf and Cr abundances in the Sīrāf wares are higher, and the Co, Sc and Ta are slightly lower, than the Samarra ware reference group.

In summarizing the provenance of the Late Green Glazed ware found at Sīrāf, what we call the Late Green B ware found at Site C in Dr. Whitehouse's excavation has the same basic clay composition as the Late Green A found at Site A and the 15th Century house at Site E. These do not match the fingerprints of kiln furniture found at Sīrāf discussed in the previous paper⁶, but have the general fingerprint of the Mesopotamian area and are measurably different from the Samarra and Early Turquoise ware mentioned in the previous talk. The Early Sgraffiato ware from the Sounding (Site A) fits the Samarra ware fingerprint very well. The Late Sgraffiato ware from the Sounding (Site A) is chemically a very tight group and unique in our library of fingerprints.

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CONCORDANCE

Early Sgraffiato: SIRF-100-103.

Late Sgraffiato: SIRF-23, 26-29, 104-115, 117, 120.

Late Green A: SIRF-69, 71, 72, 74, 98.

Late Green B: SIRF-9-12.

Samarra Ware: SIRF-146, 150-158, 161, 168-73, 177, 180-191.

TABLE I
Normalized for volatile

Type of ware	Late Sgraffiato	Early Sgraffiato	Samarra ware
# of pieces	19	4	29
σ	6.1%	6.6%	8.4%
Al(%)	8.84±.42	6.32±.22	6.53±.26
Ca(%)	4.5±1.1	13.2±3.2	13.51±.09
Dy	4.57±.22	4.05±.18	3.75±.23
Mn	650±72	971±36	916±49
Na(%)	1.167±.077	.794±.109	1.75±.03
K (%)	3.11±.21	1.832±.025	.23±.338
U	2.757±.100	2.453±.258	2.14±.16
Sm	4.90±.12	3.911±.274	4.08±.16
La	30.2±1.3	22.8±1.6	22.8±1.0
Ti(%)	.431±.026	.414±.014	.426±.048
Lu	.385±.022	.307±.019	.307±.028
Co	24.0±1.5	25.06±1.2	27.2±1.4
Sc	20.21±.62	18.59±.75	19.04±.65
Fe(%)	5.15±.16	4.95±.19	5.02±.16
Cs	11.53±.52	3.23±.52	2.9±1.0
Cr	204±7	250±5.7	254±10
Ni	157±20	262±17	251±14
Eu	1.154±.027	1.011±.031	1.010±.030
Ce	62.76±1.87	46.39±.84	46.94±1.64
Hf	4.65±.20	3.17±.15	3.26±.14
Ta	.815±.021	.808±.049	.817±.026
Th	12.13±.31	7.16±.23	7.19±.27
Yb	2.711±.073	2.112±.076	2.08±.10
Ave. vol.	4.1±2.9%	11.3±2.%	3.8±1.4%
	(10 pieces)	(4 pieces)	

TABLE II
Normalized for volatile

Type of ware	Late Green A	Late Green B	Samarra ware
# of pieces	5	4	29
σ	5.9%	6.3%	8.4%
Al (%)	6.03±.34	6.38±.17	6.53±.26
Ca (%)	17.2±2.0	12.3±1.7	13.51±.09
Dy	3.66±.06	3.96±.21	3.75±.23
Mn	807±35	846±19	916±49
Na (%)	1.37±.09	1.65±.28	1.75±.23
K (%)	2.38±.41	2.33±.31	.83±.338
U	2.47±.22	2.72±.20	2.14±.16
Sm	3.82±.13	4.095±.056	4.08±.16
La	20.8±1.0	22.5±.7	22.8±1.0
Ti (%)	.368±.018	.399±.03	.426±.048
Lu	.297±.015	.322±.010	.307±.028
Co	21.93±.88	24.08±.87	27.2±1.4
Sc	16.27±.43	17.90±.24	19.04±.65
Fe (%)	4.153±.089	4.650±.053	5.02±.16
Cs	3.44±.81	2.58±.72	2.9±1.0
Cr	349±30	340±30	254±10
Ni	180±14	223±25	251±14
Eu	.935±.031	1.022±.019	1.010±.030
Ce	43.±1.0	47.09±.88	46.94±1.64
Hf	3.50±.17	3.48±.17	3.26±.14
Ta	.648±.033	.706±.019	.817±.026
Th	6.61±.13	7.14±.07	7.19±.27
Yb	2.045±.045	2.26±.05	2.08±.10
Ave. vol.	15.9±2.3%	12.5±.9%	3.8±1.4%

TABLE III
Normalized for a as Ca O

	Late Green A	Late Green B	Samarra ware
# of pieces	5	4	29
σ	5.9%	6.5%	8.4%
Al(%)	7.94 \pm .45	7.70 \pm .20	7.98 \pm .32
Ca(%)	-- (17.2)	-- (12.3)	-- (13.5)
Dy	4.82 \pm .08	4.78 \pm .25	4.58 \pm .28
Mn	1063 \pm 46	1021 \pm 23	1120 \pm 60
Na(%)	1.80 \pm .12	1.99 \pm .34	2.14 \pm .28
K (%)	3.13 \pm .54	2.81 \pm .37	1.01 \pm .41
U	3.25 \pm .29	3.28 \pm 1.21	2.62 \pm .20
Sm	5.03 \pm .17	4.943 \pm .067	4.99 \pm .20
La	27.4 \pm 1.3	27.16 \pm .84	27.9 \pm 1.2
Ti(%)	.485 \pm .024	.482 \pm .036	.521 \pm .059
Lu	.391 \pm .020	.389 \pm .019	.375 \pm .034
Co	28.89 \pm 1.6	29.06 \pm 1.1	33.3 \pm 1.7
Sc	21.43 \pm .57	21.61 \pm .29	23.28 \pm .79
Fe(%)	5.47 \pm .12	5.613 \pm .064	6.14 \pm .20
Cs	4.53 \pm 1.07	3.11 \pm .87	3.54 \pm 1.2
Cr	460 \pm 40	410 \pm 36	311 \pm 12.
Ni	237 \pm 18	269 \pm 30	307 \pm 17.
Eu	1.232 \pm .041	1.234 \pm .023	1.235 \pm .037
Ce	56.77 \pm 1.32	56.84 \pm 1.06	57.38 \pm 2.0
Hf	4.61 \pm .22	4.20 \pm .21	3.98 \pm .17
Ta	.854 \pm .043	.852 \pm .023	.800 \pm .032
Th	8.71 \pm .17	8.62 \pm .084	8.79 \pm .33
Yb	2.69 \pm .059	2.73 \pm .060	2.54 \pm .12

FIGURE CAPTIONS

Figure 1. Early Sgraffiato Ware excavated at Sīrāf, Iran.

Figure 2. Late Sgraffiato Ware excavated at Sīrāf, Iran.

Figure 3. Late Green B Ware excavated at Sīrāf, Iran.

Figure 4. Late Green A Ware excavated at Sīrāf, Iran

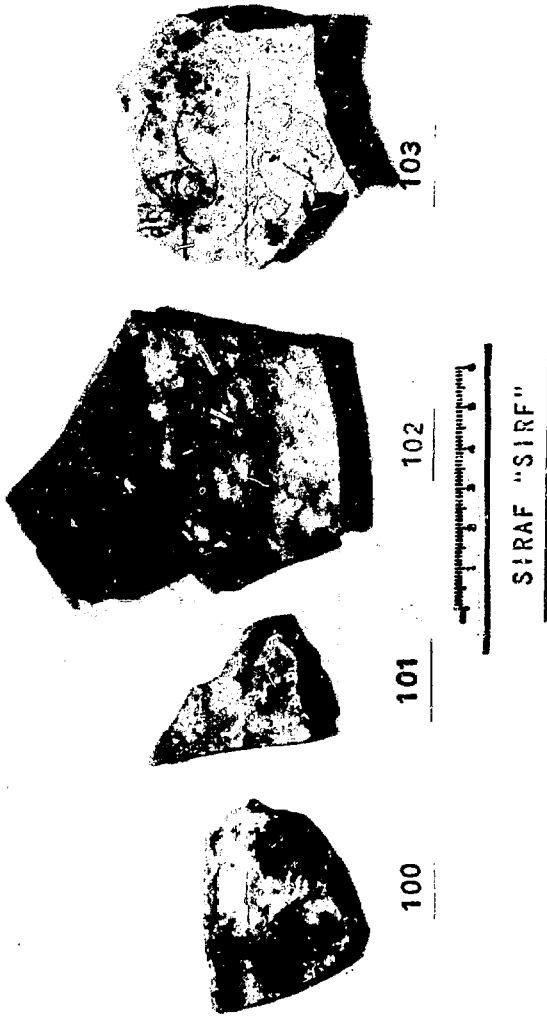
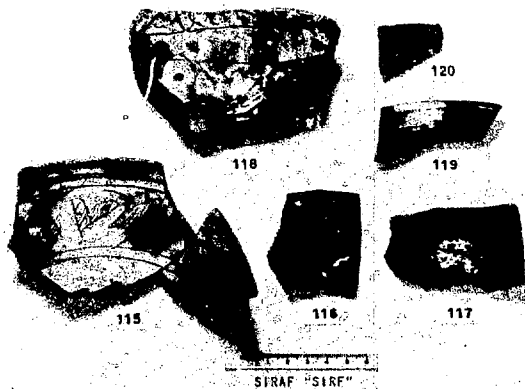


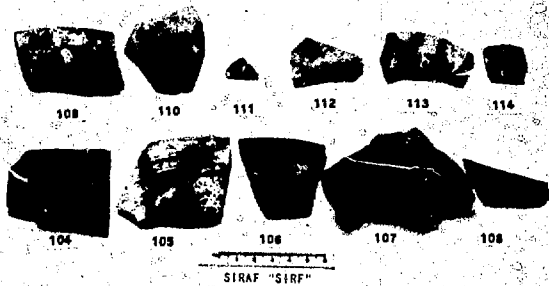
Fig. 1



SIRAF "SIRF"



SIRAF "SIRF"



SIRAF "SIRF"

XBB 756-4359

Fig. 2

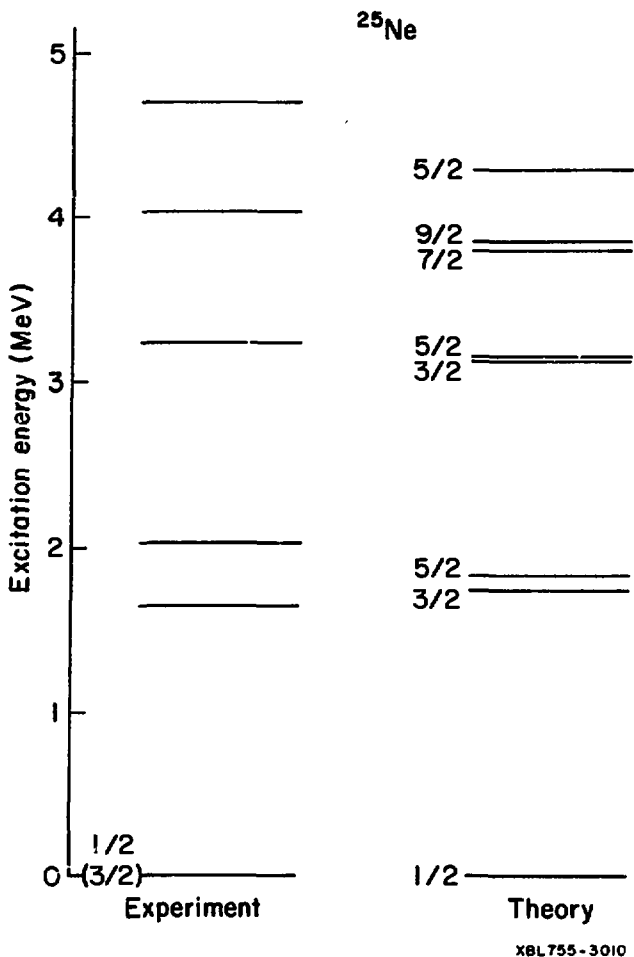


Figure 25. Experimental level scheme of ^{25}Ne compared to the calculation of Cole et al.¹

SIRAF "SIRF"

