BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 581—589 (1970)

A Chemical Study on Some Archaeological Samples from Iran and Afghanistan[1)]

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(Received September 28, 1968)

From archaeological interest, chemical analyses were performed on samples which had been collected from Iran and Afghanistan by the Kyoto University Scientific Mission to the Iranian Plateau and Hindukush. As samples were used more than one hundred pieces of glass and glazed material, and two slag-like objects. By analyzing the glass and glazes for major components, it was found that all were made of soda-lime glass except for a fragment of a glaze of tri-colored pottery collected at Kerman, Iran. It is noteworthy that this fragment of tri-colored pottery had a lead content similar to that of Chinese glazes, while Western glasses are rarely found to contain so much lead. Among the minor components detected, detailed consideration was given to the color origins. Although iron and copper were commonly found in blue-colored samples, the origin of the color of the tile from a mosque at Tabriz was confirmed to be cobalt. Investigations of slag-like objects collected from Tepe Sialk have revealed the possibility that these objects are slags from copper smelting. Studies of the silvery effect or of the weathering observed on the surface of glass and glazes of archaeological importance were carried out by semi-quantitative spectrochemical analysis.

Introduction

Until recently, most studies which have been made by historians and archaeologists upon archaeological samples have concentrated on the objects themselves and not on their chemical compositions. It has been and should be recognized, however, that detailed examinations of archaeological materials by physical and chemical methods can bring quite fruitful results in the field of archaeology. Indeed, in discussing age and in estimating the degree of technological accomplishment, furthermore, as part of understanding cultural exchange between the East and the West, archaeology must not neglect the data from the probes of natural science.

In a previous paper,[2)] some results of studies on Chinese and Japanese samples were reported. The author's intention in these works is to contribute to the histories of science and technology through chemical analyses of archaeological samples. The present paper will deal with the results of the chemical analyses of more than one hundred samples of glass, glazes, and slag-like objects, all of which were brought from Iran, Afghanistan, and Pakistan by the Kyoto University Scientific Mission to the Iranian Plateau and Hindukush.

Western Asia is located in a historically-important position through which the interchange of two cultures, the Eastern and the Western, has taken place since most ancient times. Nevertheless, few scientific investigations have been undertaken in that area. Therefore, the project of the Mission was to make a composite study of Western Asia which could serve as one preliminary step to a really thorough plunge into the archaeology of that area. As usual, the collection of these kinds of samples can be neither as systematic nor as complete as one would wish, because the chances of getting samples by excavation can not be foreseen. Moreover, a sample itself is sometimes too valuable for even a part of it to be destroyed; it just has to be kept untouched.

Although the present work was made under these restrictions, care has been taken in choosing samples so that characteristic features of samples from era to era and from area to area may be obtained. The samples chosen here were more than one hundred pieces of glass and glazes and two slag-like objects. For most of the glass and glazes, the major and minor components were qualitatively identified spectrochemically, though for several samples they were determined quantitatively. The main interest in the major components was in finding out whether they were soda-lime glass or lead glass; most Western glass belongs to the former group, while the latter has been manufactured in

1) Presented at The 5th International Congress of Iranian Art and Archaeology (April, 1968, Tehran, Shiraz, Isfahan, Iran).

2) T. Muroga, *Bull. Japanese Studies in The History of Sicence*, **7**, 83 (1968).

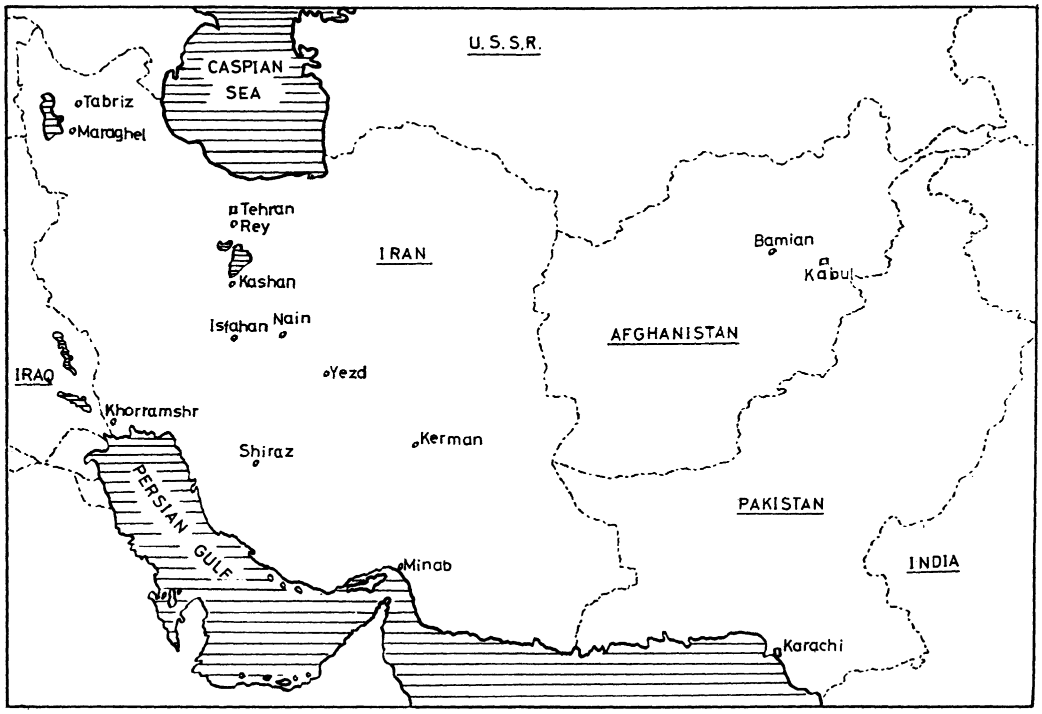

Fig. 1. A map of sampling stations.

China since the ancient period.[3] For the minor components, attention was paid to color origins, which may offer clues to the origin and to the exchange of the techniques of glassmaking. The two slag-like samples, which were picked up at the ruins of a smelting furnace, were subjected to the quantitative determination of their major components. If they were indeed slags of copper smelting, the quality of the techniques of extracting copper from the ore could be estimated from them. The last subject was the silvery effect or weathering which is frequently observed on the surface of glass or glazes of archaeological importance. Semi-quantitative analysis showed a continuous change in composition from the surface to the inner part of the sample.

Experimental

Semi-quantitative spectrochemical analyses were performed on the archaeological samples by using the internal standard (Ge, Pt) method.

The quantitative analytical methods used especially for the glass and glazes were described in the previous report.[4] In brief, the glass and glazes were brought into solution by carbonate fusion and then treated with hydrochloric acid. The analytical methods used subsequently are given in Table 1. In some cases, X-ray micro-probe analysis was performed in order to examine the distribution of elements in a non-destructive way.

TABLE 1. ANALYTICAL METHODS USED

Element	Methods of determination
Si	Gravimetrically as SiO_2
Ca	Chelatometrically
Mg	*ibid.*
Cu	Polarographically
Zn	*ibid.*
Ni	*ibid.*
Pb	*ibid.*
Al	Colorimetrically
Fe	*ibid.*
Co	*ibid.*
Mn	*ibid.*
Ti	*ibid.*
P	*ibid.*
Na	Gravimetrically as $Na(C_2H_3O_2)\cdot Mg(C_2H_3O_2)_2\cdot 3UO_2(C_2H_3O_2)\cdot 6\frac{1}{2}H_2O$
K	Gravimetry as $K_2NaCo(NO_2)_6H_2O$ or $K(ph)_4B$

3) M. Yoshida, "Sekai Toji Zenshu" (The Complete Works of Pottery in the World), Vol. 8, Heibonsha, Tokyo (1955), p. 282.

4) T. Muroga and M. Yoshida, *Kagakushi Kenkyu*, **46**, 17 (1958).

Results and Discussion

Glasses and Glazes. *Major Components.* All of the samples were soda-lime glass. Representative results are given in Tables 2 and 3. Contrary to

TABLE 2. SPECTROCHEMICAL ANALYSES OF GLASSES

No.	Place of collection	Color*	Major						Minor												Trace							
			Si	Na	Al	Ca	Mg	K	Al	Ti	Fe	Mn	Cu	Zn	Pb	Sn	P	Ni	Co	Cr	Ag	Ba	V	B	Sr	Sb	Bi	
1	Tehran	L.B.	○	○		○	○	○	○		○	○	○		○			○	○	○				○				Jug
2	Rey	B.	○	○	○	○	○	○		○	○	○	○							○		○						Bowl
3	Nishapul	G.B.	○	○	○	○	○	○			○	○										○						Bottle
4	Nishapul	L.B.	○	○	○	○	○	○			○	○	○									○						Bottle
5	Nishapul	D.G.	○	○	○	○	○	○			○	○	○							○		○						Bottle
6	Nishapul	L.G.	○	○	○	○	○	○			○	○	○							○								Vessel
7	Nishapul	L.G.	○	○	○	○	○	○			○		○											○				Bottle
8	Nishapul	L.B.	○	○	○	○	○	○			○		○									○						
9	Hirzabad	L.B.	○	○	○	○	○	○		○	○									○		○						
10	Hirzabad	G.	○	○	○	○	○	●			○	○	○							○		○						
11	Hirzabad	B.	○	○	○	○	○	●			○	○	○							○		○						Lump
12	Hirzabad	G.B.	○	○	○	○	○	○			○																	Vessel
13	Hirzabad	Co.	○	○	○	○	○	○			○		○						○	○		○						Lump
14	Atteshekhada	G.Y.	○	○	○	○	○	○			○									○								Vessel
15	Salvistan	L.B.	○	○	○	○	○	○			○									○								Jug
16	Amrash	L.G.	○	○	○	○	○	●		○	○		○										○	○				Bead
17	Amrash	N.B.	○	○	○	○	○	●		○	○		○										○	○				Bead
18	Amrash	Y.	○	○	○	●	●			○	○		○		○								○	○				
19	Amrash	P.	○	○	○	○	○	●		○	○	○								○		○	○		○			Bead
20	Amrash	L.P.	○	○	○	○	○	○		○	○	○								○			○		○			
21	Armash	L.G.	○	○		○	○		○	○	○												○		○			
22	Amrash	Br.	○	○	○	○	○	●		○	○												○	○	○			
23	Amrash	W.	○	○	○	○	○	●		○	○	○											○		○			
24	Tehran	L.G.	○	○		●	●	○	○	○	○	○	○							○			○					
25	Tehran	D.G.	○	○	○	○	○	○		○	○	○	○						○	○		○	○		○			
26	Tehran	G.B.	○	○	○	○	○	○		○	○	○	○						○	○		○	○		○			

No.	Place of collection	Color*	Major						Minor												Trace							
			Si	Na	Al	Ca	Mg	K	Al	Ti	Fe	Mn	Cu	Zn	Pb	Sn	P	Ni	Co	Cr	Ag	Ba	V	B	Sr	Sb	Bi	
27	Tehran	W.	○	○	○	○	○	○			○											○	○		○			
28	Tehran	L.G.	○	○		○	●		○	○	○	○											○	○				
29	Tehran	L.Y.	○	○	○	○	○	●		○	○	○											○					
30	Tehran	D.B.	○	○	○	○	○	●		○	○	○	○						○			○	○		○			
31	Minab	R.	○	○	○	○	●				○		○	○	○					○				○				
32	Minab	Co.	○	○		○	○	○	○		○	○	○	○	○			○	○	○				○				
33	Minab	Co.	○	○		○	○	○	○		○	○	○					○	○	○				○				
34	Minab	D.Br.	○	○	○	○	○	●		○	○	○	○			○				○		○			○			Bracelet
35	Minab	G.B.	○	○	○	○	○	○		○	○	○	○		○	○		○		○	○	○	○	○	○			Bracelet
36	Minab	L.B.	○	○		○	○	○	○		○		○							○				○				Bracelet
37	Minab	L.G.	○	○		○	○	○	○		○	○	○		○	○				○				○				Bracelet
		Y.	○	○		●	○	○	○		○	○	○		○	○				○	○			○				Bracelet
		W.	○	○		●	○	●			○	○	○		○	○				○	○		○	○				Bracelet
38	Minab	M.	○	○		○	○	○	○		○	○	○							○			○	○				Bead
39	Minab	L.G.	○	○		○	○	○	○		○		○							○				○				
40	Minab	G.Y.	○	○	○	○	○	○		○	○	○	○							○		○	○	○	○			
41	Minab	Br.	○	○		○	○	○	○		○		○							○				○				
42	Minab	G.B.	○	○		○	○	○	○		○		○					○		○				○				Jug
43	Minab	L.Br.	○	○	○	○	○	○			○	○	○							○				○				Jug
44	Share-Bonn	D.Br.	○	○		○	○	○	○		○	○	○		○						○							Bracelet
45	Share-Bonn	Bl.	○	○	○	○	○	○			○	○	○											○				Bracelet
46	Share-Bonn	L.B.	○	○	○	○	○	○			○	○	○							○		○		○	○			
47	Share-Bonn	L.G.	○	○	○	○	○	○			○									○			○	○				Jug
48	Share-Bonn	L.Co.	○	○	○	○	○	○			○	○	○					○	○	○				○				
49	Share-Bonn	L.B.	○	○	○	○	○	○			○		○		○	○				○	○			○				Bottle
50	Share-Bonn	G.B.	○	○	○	○	○	○			○	○	○							○				○		○		Jug
51	Share-Bonn	Y.	○	○	○	○	○				○	○	○		○	○		○	○	○	○	○			○		○	Bracelet
		D.G.	○	○		●	○	○	○		○	○	○	○	○	○		○		○	○			○		○	○	Bracelet

○>●

* L.B.: Light-blue, B.: Blue, G.B.: Greenish-blue, D.B.: Dark-blue, L.G.: Light-green, G.: Green, Co.: Cobalt-blue, G.Y.: Greenish-yellow, N.B.: Navy-blue, Y.: Yellow, P.: Purple, L.P.: Light-purple, Br.: Brown, W.: White, L.Y.: Light-yellow, D.G.: Dark-green, R.: Red, D.Br.: Dark-brown, M.: Milky, L.Br.: Light-brown, Bl.: Black, L.C.: Light-cobalt blue, Cr.: Crimson

Table 3. Analyses of glasses

Color / Component	No. 52 Light-blue (%)	No. 53 Light-green (%)	No. 54 Deep-green (%)	No. 55 Green (%)	No. 56 Light-blue (%)	No. 57 Green (%)	No. 58 Green (%)
SiO_2	61.24	61.48	65.60	63.40	78.98	69.81	55.46
TiO_2	2.82	1.72	0.37	0.08	0.02	0.14	0.95
Fe_2O_3	0.15	0.35	1.54	0.32	0.06	0.82	1.90
MnO	0.12	0.03	1.05	5.10	tr	4.25	0.16
Al_2O_3	5.89	8.95	4.15	1.16	1.16	0.38	4.57
MgO	2.37	1.19	3.06	1.13	0.97	2.68	3.16
CaO	3.43	6.26	16.34	3.16	1.83	5.84	7.62
CuO	0.15	tr	0.06	0.27	2.13	0.09	0.25
ZnO	0.32	tr	0.01		0.73	0.71	
Na_2O	17.79	15.12	2.04	14.00	1.57	8.06	16.79
K_2O	4.19	3.63	6.45	4.27	9.92	4.49	9.16
H_2O	1.07	0.87	0.53	0.93	1.53	0.77	
P_2O_5			1.13	0.03	0.02	0.07	0.58
SnO_2				1.07	0.83		
Place collected	Kerman	Kerman	Neyriz	Nain	Malagha	Kerman	Kerman

expectation, specimens containing tin were quite rare in these samples. Only four samples contained tin; the results on these sample, all glass bracelets from Minab and Share-Bonn, were shown in Table 2. It should be emphasized here that the other glass samples from the same area, Minab, were found to be soda-lime glass. This fact is in clear contrast with the case in China, where most of the glass manufactured in ancient periods was lead glass. As Minab was a famous port in old Hormus, a trading center between East and West, much Chinese porcelain was imported there.[5,6] Hormus is said to have prospered between the thirteenth and the fifteenth centuries, and to have declined with the collapse of the Kerman Kingdom; now it is only ruins. It can be thought that the porcelain in Minab was produced under the influence of China. From the results of the chemical analyses of glass samples of many colors and sorts, it can be said that all soda-lime glass; none of these samples was of the lead-glass type. This fact suggests that the glassmaking in Minab was, unlike the porcelain-making, not influenced by Chinese glassmaking. It is very interesting that the glassmaking technique is thus in striking contrast to that of porcelain.

The only sample which contained a large amount of lead was a fragment of tri-colored pottery found at Kare-dokhtal, Kerman. The tri-colored glaze was found to be very similar to that in China, not only in the external appearance but also in the lead content.

The other samples which were found to contain small amounts of lead were beads. Beads which were made in China before the fourth century B.C.[7] have also been found in Iran, but, like the glass from China, the Chinese beads show greater

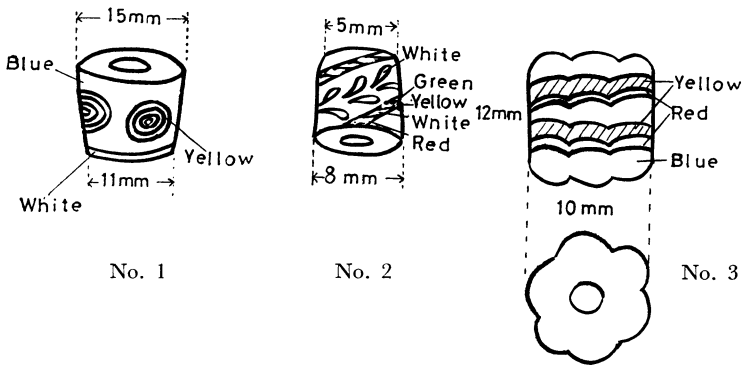

Fig. 2. Schematic diagrams of Beads Nos. 1—3.

5) M. Yoshida and K. Koyama, "Nishi-Ajia no Gijutu" (Western Asia at Work), Kyoto University Scientific Mission to Iranian Plateau and Hindukush, Kyoto (1960).

6) T. Wan, "To-i Shi-ryaku," China, Yuan Dynasty.

7) K. Yamazaki, "Kokogaku Taikei" (The Outline of the Archaeology), Vol. 16, Heibonsha, Tokyo (1962), p. 132.

TABLE 4. SPECTROCHEMICAL ANALYSES OF BEADS

Place of collection	Color*	Major						Minor												Trace							
		Si	Na	Al	Ca	Mg	K	Al	Ti	Fe	Mn	Cu	Zn	Pb	Sn	P	Ni	Co	Cr	Ag	Ba	V	B	Sr	Sb	Bi	As
Tehran B-1	W.	○	○		●	○				○	○	○		○			○	○		○			○		○		
	B.	○	○		○	○	○	○	○	○	○	○		○			○	○	○			○	○				
	Y.	○	○		●	●				○	○	○		○			○	○		○			○		○	○	
B-2	P.	○	○	○	○	○			○	○	○	○		○			○	○	○	○	○	○	○	○		○	
	Y.	○	○			●						○	○	○	○					○					○	○	○
	R.	○	○									○		○						○					○	○	○
	W.	○	○			●				○	○	○		○						○			○			○	○
	B.	○	○									○		○	○					○			○		○	○	○
B-3	B.	○	○	○	○	○	○		○	○	○	○		○	○		○	○	○	○	○		○	○			
	Y.	○	○	○	○	○			○	○		○		○	○		○		○	○	○	○			○		
B-4	W.	○	○	○	○	○	○		○	○	○	○		○	○				○	○	○	○	○	○			
	Y.	○	○	○	○	○	○		○	○	○	○		○	○		○		○	○	○	○	○	○			
	Cr.	○	○		●	○	○	○		○	○	○		○	○		○	○	○	○		○	○				
	B.	○	○	○	○	○			○	○	○	○		○	○				○	○	○		○				
	Y.p.	○	○	○	○	○	○		○	○	○	○		○	○		○		○	○			○	○			
	B.	○	○	○	○	○	○		○	○	○	○		○	○		○		○	○		○	○				

p: projection

TABLE 5. ANALYSIS OF THE BEAD No. 1*

Component \ Color	Blue (%)	White (%)	Yellow (%)
SiO_2	77.8	74	64
Al_2O_3	2.2	2.2	2
CaO	23.3	20.1	13.1
TiO_2	0.02	0.03	0.03
PbO			19.6
Fe_2O_3	0.5	0.3	1.26
MnO	0.7	0.3	tr

amounts of lead. The beads of Western Asia are usually larger in size, more colorful, and more complicated in design than those from China, Figure 2 presents an example with the eye pattern and also a bead with cord-design. They were obtained in Tehran and are estimated to have been manufactured in about the fifteenth century A.D. The No. 4 bead has a very complicated structure. The results of the analyses are shown in Tables 4, 5, and 6. The details, shown in Fig. 3, reveal a black cylindrical body upon which white lines have been placed, with a yellow knob at the corners and with larger varicolored knobs imbedded within the square formed by the white line. Lead is detected in all parts of all the beads examined. However, lead might have been put in the glass not for the purpose of making lead glass, as was done in China, but for the purpose of lowering the melting point of glass in order to make it more

TABLE 6. ANALYSIS OF THE BEAD No. 4*

Component \ Color	Varicolored knob: Crimson (%)	Blue (%)	Black (%)	White line (%)	White spot (%)	Black (%)	White (%)	Yellow (projection) (%)
SiO_2	67	68.5	67	72	70	69.5	70.2	69.5
Al_2O_3	3	3.2	3	1.9	3.2	3	2	1.2
MgO	2	1.5	1.5	1.5	1.5	1.5	3.5	3.5
CaO	13.6	12.6	13.6	17.1	16.4	12.6	19.2	16.5
SnO_2	1.4	1.9	tr	1.7	3.4	0.3	tr	2.8
TiO_2	0.2	0.2	0.2	0.2		0.2	0.03	0.07
PbO	2.1	2.3	tr	2.3	3.7		2.88	0.81
Fe_2O_3	3.4	1.3	0.7	0.7		1.1	0.4	0.5
MnO	0.71	0.7	2.4	1.3	2.1	2.3	0.4	0.5
CuO						0.2		

* Determined by X-ray micro-probe analyzer

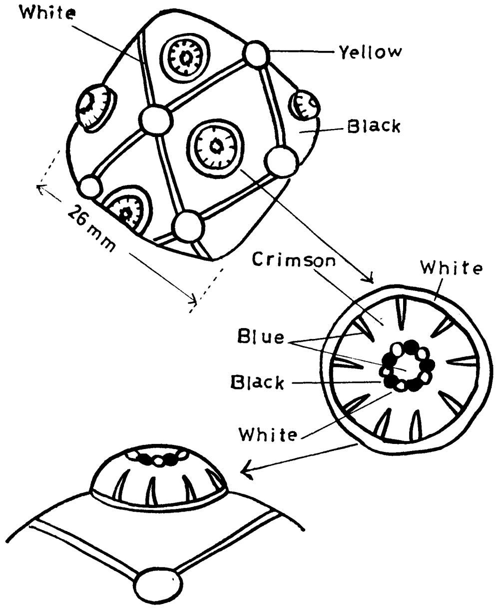

Fig. 3. Schematic diagram of Bead No. 4.

malleable. At any rate, as their specific gravities were less than 3.3 and contained much silicon and sodium, those pieces of glass, on the whole, are of the soda-lime-glass type.

Coloring Materials. As for the color origins of the bead No. 1, the blue color comes from iron, and the yellow, from lead and iron. In the bead No. 2 the purple color is due to the combination of manganese and nickel, and the blue color is due to copper. In No. 3 the blue color may be due to nickel, and the crimson, and the blue, to copper. In the yellow parts of the beads No. 3 and No. 4, more lead was detected than in the other colored parts. A similar fact has been also described by another researcher.[8] Since these beads are unknown provenance, no definitive conclusion can be reached here.

In Iran and Afghanistan there are many mosques decorated with tiles of a blue called "cobalt blue." One fragment of a blue tile was collected from the blue Mosque at Tabriz in Iran, and the other, from Balkh in Northern Afghanistan. The results of chemical analyses, presented in Tables 7 and 8, demonstrate that cobalt was the origin of the color in both cases.

The coloring materials used on the pottery (*ca.* 3000 B.C.) from Tepe Sialk were also investigated. Although a similar pottery in pattern has been found in prehistoric China,[9] the coloring materials have not as yet been closely investigated. A fragment of pottery about 5×5 cm, which appeared to be a part of the base and side of a vessel, was examined. The body was light gray, and upon one surface there

Table 7. Spectrochemical analyses of glazes

No.	Place of collection	Color*	Major						Minor												Trace							
			Si	Na	Al	Ca	Mg	K	Al	Ti	Fe	Mn	Cu	Zn	Pb	Sn	P	Ni	Co	Cr	Ag	Ba	V	B	Sr	Sb	Bi	
59	Bara-hissar	L.B.	○	○	○	○	○	○			○	○	○		○	○		○	○	○	○		○	○		○	○	Mosaic-Tile
60	Bara-hissar	B.	○	○	○	○	○	○			○	○	○		○	○		○	○	○	○		○	○	○		○	
61	Bamiyan	B.	○	○	○	○	○	○		○	○	○	○		○	○		○	○	○	○		○	○				Shard
		W.	○	○	○	○	○	○		○	○	○	○		○			○	○	○	○		○	○	○			Shard
62	Bamiyan	B.	○	○	○	○	○	○			○	○	○		○	○		○		○	○			○		○	○	Dish
63	Bamiyan	W.	○	○	○	○	○	○		○	○	○	○		○	○		○		○	○	○	○	○	○	○	○	Bowl

8) S. Oda, "Dairaman," Vol. I, The University of Tokyo, Tokyo, (1965), p. 45.
9) Kanshuku Saito, (Andersson's Pottery).

TABLE 8. ANALYSIS OF GLAZES

Component \ Color	No. 64 Light-green (%)	No. 65 Dark-green (%)	No. 66 Blue (%)	No. 67 Red (%)
SiO_2	67.80	66.52	64.15	61.90
TiO_2	1.08	1.14	0.93	0.92
Fe_2O_3	0.68	0.78	2.42	1.20
MnO	tr	tr	tr	tr
Al_2O_3	12.56	3.87	4.74	2.95
MgO	1.16	0.55	1.24	4.04
CaO	2.75	7.63	3.46	6.59
CuO	0.25	7.43	0.74	0.18
ZnO		0.02		
Na_2O	8.79	8.44	16.38	16.71
K_2O	4.25	2.32	6.34	5.10
H_2O	0.98	0.40		
P_2O_5		0.18	0.53	0.43
SnO_2		1.37		
CoO			0.20	
Place collected	Kerman	Neyriz	Blue-Mosque	Yezde

TABLE 9. ANALYSIS OF THE SEPIA-COLORED MATERIAL OF A SHARD FROM TEPE SIALK

	Fe (%)	Mn (%)	Fe/Mn
Body	3.6	0.2	18.00
Paint	22.7	1.26	18.01
Paint/Body	6.3	6.3	

was a curved painted line. On this line there appeared a node of paint. A part of the body and a part of the node were removed and subjected to chemical analysis. As can be seen in Table 9, approximately 6.3 times as much iron and manganese were found in the sepia-colored part as in the body itself. It is thus obvious that iron was used as the coloring agent. However, it is difficult to state definitely whether manganese was also purposely used as an additive. The ratio of iron to manganese is about the same for both the paint used for the design and the body itself. If the manganese was purposely added to produce this sepia color, it seems to be a highly-advanced technique. The possibility exists, however, that the color was produced by an accidental discovery. Further studies will be necessary to clarify this problem.

Bronze (Slag-like Objects). In 1956 Mitsukuni Yoshida, a member of the Kyoto University Scientific Mission to the Iranian Plateau and Hindukush, discovered rock-like objects in a site at Tepe Sialk, in Iran, which is considered to be the ruins of a refinery (*ca.* 2000 B.C.). From the archaeological point of view, these pieces were obviously pieces of the slag of smelting. Although

TABLE 10. ANALYSIS OF SLAG-LIKE OBJECTS

Component \ Sample	Green (%)	Black (%)	Black/Green	Black (Calculated)*
SiO_2	30.83	44.67	1.45	42.19
P_2O_5	0.46	0.21	0.46	
Fe_2O_3	14.30	20.38	1.43	19.57
TiO_2	1.22	1.07	0.88	
CuO	15.52	0.13	0.009	
Al_2O_3	10.52	8.51	0.81	
CaO	9.73	13.75	1.41	13.31
MgO	3.87	3.19	0.82	
MnO	0.06	0.11	1.83	0.83

* See text

they were collected from the same site and layer, however, they were of different colors, one being greenish and the other black. It was believed that this was an important find because it sheds more light upon the actual processes used in the smelting of copper.

Both lumps of slags were about 1.5×1.5 cm in size. Qualitative examinations showed that the chemical compositions of the two were approximately the same. The results of the quantitative determination of the major components are given in Table 10, together with the ratios of the contents of each component in the two samples. As is obvious in the table, the greatest difference between the two samples is in their copper contents. The contents of the other components change to a lesser extent. If, however, one takes the ratios of the contents of the major components, silica, ferric oxide, and calcium oxide, in the two samples, one obtains strikingly constant values, which are shown in the third column of the table.

Another way of comparing the two samples is as follows. The contents of the major components in the green sample are recomputed on the assumption that the black sample is a slag of the green one from which the copper has been almost completely extracted out. In this calculation, the copper content of the green sample was excluded and the contents of the rest of the components were assumed to amount to one hundred percent. The values in the last column of Table 10 were thus obtained; they are in good agreement with the experimental results for the black sample. According to the literature, the ore used in that era (2000 B.C.) was mainly malachite consisting approximately seventy percent of copper,[10] and it was quite precious. Although we could not determine the original ore in the present investigation, the following conclusion may be drawn. It is very probable that there were successive smelting processes; that the green sample is the slag from the first smelting processes of the

10) L. Aitchison, "A History of Metals," Vol. I, MacDonald and Evans Ltd., London (1960), p. 38.

Table 11. Composition of efflorescences

Sample layer	Major						Minor									Trace												
	Si	Na	Al	Ca	Mg	K	Fe	Mn	Mg	Ti	Ca	Cu	Na	K	Al	B	Pb	Sn	Cu	Ag	Na	Cr	Ba	Ni	V	Co	Ti	Fe
Blue-galss bowl																												
Silver	○		○				○	○	○	○	○						○	○	○	○	○	○	○					
Silver-white	○		○	○			○	○	○	○		○					○	○		○	○	○	○	○	○	○		
Purple	○		○	○			○	○	○	○			○				○	○	○			○	○			○		
Body	○	○	○	○	○	○	○	○		○		○				○	○	○		○		○	○	○	○	○		
Greenish-blue glass																												
Surface	○		○				○	○	○		○		○						○			○	○				○	
Body	○	○	○	○	○	○	○	○								○			○	○		○	○		○		○	
Light-green glass																												
Surface	○							○	○		○				○		○		○		○	○	○			○	○	○
Body	○	○	○	○	○	○	○	○				○				○	○			○		○	○	○	○	○	○	
White-glass bead																												
Surface	○			○	○		○	○		○					○	○			○	○		○	○			○		
Body	○	○	○	○	○		○	○		○				○		○			○	○		○	○	○	○			

ore, thus retaining 15.52% copper oxides, and that the black sample is the slag from the second process, in which the residue of the first processes was treated, with only 0.13% copper (II) oxide remaining. Thus, it is obvious that these ancient people had achieved a high level of technique in the process of extracting copper, the major component of bronze.

Weathering. Efflorescence caused by weathering is frequently observed on the surface of glass or glaze samples. A typical example is a fragment of a glass bowl, about 4×4 cm, collected at the ruins of Rey. A schematic picture of the sample is

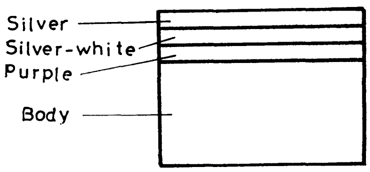

Fig. 4. Schematic diagram of weathering glass.

presented in Fig. 4. The surface of the glass shows the effects of considerable weathering. However, a silvery powder still remained on the surface. Under the weathered surface, there were silvery-white and purple layers beneath which the glass body itself could be seen.

Spectrochemical analysis was performed on each layer of the sample as well as on the sample itself. According to the results, which are shown in Table 11, the contents of such elements as magnesium, sodium, and calcium were found to decrease in proportion to the distance from the inside of the glass to the surface. Potassium was found in substantial amounts only in the glass body; in all the other layers only traces of it were found. The results of other glasses and glazes are also shown in Table 11.

It is very probable, from the chemical point of view, that the ions have partly moved out from the surface to the soil; that is, an ion exchange between the sample and the surrounding materials has taken place, thus forming the outer layers of the sample.

It should be pointed out that the excavation of not only glass objects but also any object should be done carefully, and with the extraction of as much of the surrounding soil as possible, if chemical analyses are desired. It is possible that such ion exchange as occurred with glass objects may occur with other objects. The chemical analyses of surrounding or imbedded soils may yield important clues about this.

The author wishes to express her deep gratitude to Professor Taitiro Fujinaga of the Faculty of Science, Professor Mitsukuni Yoshida of the Research Institute for Humanistic Studies, and Mr. Takenori Sonoda of the Faculty of Engineering of Kyoto University, for their kind guidance and encouragement in the course of this work.