

# Archaeometry of medieval Islamic glazed ceramics from North Yemen

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Received October 17, 1986<sup>2</sup>

JESSICA R. HALLETT, MICHAEL THOMPSON, EDWARD J. KEALL, and ROBERT B. MASON. *Can. J. Chem.* **66**, 266 (1988).

Microscopic examination and electron microprobe analysis were employed to determine the materials and techniques used to decorate ten glazed types of medieval Islamic ceramics from North Yemen. Eight types were underglaze-painted, one was slip-painted, and one was monochrome glazed. The glazes were of two compositions, soda-silica and lead oxide-silica with annealing temperatures of approximately 835 and 640°C, respectively. The colourants used in the glazes and paints were cobalt (blue), iron (green), copper (green and blue), and antimony (yellow). Where clay slips or slip-paints were present, alumina enrichment of the glaze had occurred during application or firing, and pigment-paints on top of slip grounds masked enrichment. The Mellor ratio for the lead glazes ranges from 0.68 to 0.74 and is well above the acceptable safety limit of 0.5.

JESSICA R. HALLETT, MICHAEL THOMPSON, EDWARD J. KEALL et ROBERT B. MASON. *Can. J. Chem.* **66**, 266 (1988).

On a utilisé des examens microscopiques et des analyses à l'aide d'une micro-sonde électronique pour déterminer la nature des matériaux et des techniques qui ont été utilisés pour décorer dix types de céramiques islamiques médiévales émaillées provenant du Yémen du Nord. Huit types avaient été peints sous la glaçure, un avait été engobé et un portait une glaçure monochrome. Les glaçures sont de deux compositions, soude/silice et oxyde de plomb/silice, et les températures de recuisson étaient respectivement de 835 et de 640°C. Les colorants utilisés dans les glaçures et les peintures sont le cobalt (bleu), le fer (vert), le cuivre (vert et bleu) et l'antimoine (jaune). Dans les cas où des engobes d'argile ou des peintures par engobage sont présents, un enrichissement de l'aluminium de la glaçure s'est produit soit durant l'application ou durant la cuisson et les pigments de peinture présents sur les masses d'engobage masquent l'enrichissement. Dans les glaçures de plomb, le rapport de Mellor varie de 0,68 à 0,74 et se trouve bien au-dessus de la limite de 0,5 qui est considérée comme sécuritaire.

[Traduit par la revue]

## Introduction

The Yemen Archaeological Project is concerned with the history and culture of a medieval Islamic university town, Zabid, and its interaction with neighboring settlements and the outside world, from A.D. 700 to 1750 (1). Zabid is 25 km inland, half-way between the Red Sea and the Yemeni highlands, on the Tihamah coastal plain. In the absence of any previous systematic archaeological work in the region, the initial surface reconnaissance involved collection of pot sherds from abandoned sites in order to establish a ceramic typology, as a way of determining the nature, location, and period of settlements in the region. Sherds (2400) were collected and classified from a total of 73 sites within the 100 by 70 km study area. Almost all of the pottery is considered to be of local manufacture, and can be divided into separate *types* according to the colour of the fired clay, shape, and surface decoration treatment. The pottery can be tentatively dated by association with import pieces from other countries, such as 15th century "Ming" blue-and-white porcelain or 13th century Yuan celadons.

Neutron activation analysis of the clay bodies of 20 ceramic types supported the hypothesis that the ceramics were manufactured in the Tihamah coastal plain of Yemen (2). Petrographic analysis has indicated the presence of at least two production centres for the material, Hays and Zabid (3). Similar types appear to have been manufactured at both places in the heyday of the region between 12th–15th centuries, with Hays emerging as the dominant pottery producer once Zabid ceased to be a major administrative centre of the ruling dynasties.

Stylistically, there are no precise parallels for the Yemeni ceramics in the previously documented collections of Islamic

pottery. In order to improve the initial visual classification of the material, it was considered essential to determine the physical components of decoration (glaze, slip, paint, etc.), their composition and order of application, and the firing temperature and kiln atmosphere used. Hence, consistency of composition among different types could indicate contemporaneity, and whether the glazing traditions remained constant throughout this 600 year period.

In the present paper, the application of electron microprobe analysis (EMPA) to selected Yemeni glaze samples is described. The advantages of this technique include the ability to obtain quantitative cross-sectional information, avoiding possible problems associated with glaze surface alteration caused by weathering, or by volatilization of components during manufacturing (4).

## Experimental

### (a) Microscopic analysis

Whole sherds were examined under a binocular microscope to observe the surface structure of the glaze, the state of preservation, degree of crazing<sup>3</sup> or peeling,<sup>4</sup> colour of the glazed areas, and presence of inclusions and of gases trapped in the glaze. Polished thin sections of two sherds per type were examined in reflected and transmitted light under a polarizing microscope to determine the components of decoration, size of slip and pigment particles, degree of vitrification<sup>5</sup> and of bonding between the glaze, slip, and body.

### (b) Sample preparation

Resin impregnated polished thin sections of sherds from each of ten

<sup>3</sup>Shrinkage cracks caused when glaze shrinks more than clay body; glaze is in tension and body in compression.

<sup>4</sup>Glaze separates from clay body; glaze is in compression and body in tension.

<sup>5</sup>Point at which raw materials fuse to form a glass.

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<sup>2</sup>Revision received October 9, 1987.

TABLE 1. Geological standards

Soda-silica glaze		Lead oxide – silica glaze	
Standard	Element	Standard	Element
Scapolite	Si, Ca, Na, Cl	Crocoite	Pb
Orthoclase	K	Amphibole	Si, Al, Ti, Fe, Mg, Ca, Na, K
Pyroxene	Al, Mg, Fe, Ti		
Doped troilite	Co, Cu	Chalcopyrite	Cu

ceramic types were prepared as follows. Small slivers of the glaze and body were removed from the sherds using a diamond impregnated steel saw perpendicular to the glaze surface. The samples were impregnated with epoxy resin, and mounted on glass slides. This section was cut and ground to 30  $\mu\text{m}$  using a thin section grinder, followed by treatment with 1000 mesh silicon carbide grains, and finally polished with 1  $\mu\text{m}$  diamond compound on a nylon cloth.

### (c) Electron microprobe analysis

Electron microprobe analyses were performed using an ETEC Autoprobe (ETEC Corp., USA) with an energy dispersive method of X-ray detection. A thin layer of carbon was vacuum deposited on the sample to prevent charging of local areas of the surface and subsequent distortion and deflection of the electron beam. The accelerating voltage was 20 kV; the probe current, approximately 200 picoamperes; take-off angle, 38°; beam size, 2  $\mu\text{m}$ ; and counting time, 100 s. Twelve elements were determined and the data were reduced with full ZAF correction. For Pb, the M  $\alpha$  line was used; for Sn and Sb, the L  $\alpha$  line; and for all other elements, the K  $\alpha$  lines. Areas that appeared to be optically homogeneous glass, free from inclusions and devitrification products, were selected for analysis. The counts were checked throughout the analysis to detect wide variations which could indicate inhomogeneity. In addition to using a low probe current, the sample was slightly moved every 25 s to avoid problems associated with diffusion of the more mobile ions, like Na, under the effect of the beam. At least three analyses were made of the glaze, pigment-paint in solution with the glaze, or pigment particle. Elemental concentrations are reported here as equivalent oxide weight percent concentrations.

Peak overlaps occur with the EDS method which the software at our disposal could not resolve, in particular, the overlap of Pb and S. Hence, these two elements could not be analysed simultaneously. For Type J with a soda-silica glaze coloured with copper, the concentration of S was sought owing to the probability the pigment was CuS. In the case of the lead oxide – silica glaze of Type A, also coloured with a Cu pigment, Pb was determined as it was important to our understanding of the basic glaze composition. However, sulphur is usually present only in small concentrations in glazes owing to vaporization during firing (5).

Finally, the concentrations of the glass-forming oxides and colourants were not consistently similar to any one glass or mineral standard available. The standards used are listed in Table 1.

## Results and discussion

Microscopic examination was used to refine the descriptions of the potting process for the ten types (Table 2). The process consists of the manufacture of a clay body, and the application of a slip, paint, and glaze. A slip is a mixture of clay in water and can be applied all over the surface as a ground for painting. Paint is either a slip-paint, where a slip is brushed on as a design, or a pigment-paint where either common ores, earthy materials, or ground coloured glass, with water as a vehicle, are used. The painted design can be applied beneath a transparent glaze (underglaze-painted) with or without colouring, or can be painted onto the wet glaze. A third method involving applica-

tion of the paint on top of a vitrified glaze which is fixed in a second firing was not observed.

Microscopic examination identified four methods of glazed decoration (Fig. 1). Type A was "monochrome glazed"; types B, C, D, E, F, and I were "underglaze-painted" on a white slip ground over a red body; types G and H were underglaze-painted directly on a white clay body; and type J was underglaze "slip-painted".

For all ceramic types with pigment-painted decoration, the colourant transferred into solution with the glaze during firing, and only in green and brown paints were pigment particles identified. Where a slip ground was observed in types defined as underglaze-painted, the glaze is well fused with the slip. But, the slip poorly adheres to the body and is the weakest interface in the structure. Thus, the only function of an overall slip is to provide a white ground for painting.

The analyses for the glazes and paints are reported in Table 3. The sets of analyses are referred to by type, name, and number. In ancient times borax was not used in glazes. Boron could not be detected with the facilities available, but the fact that the analytical totals are reasonably close to 100% suggests that boron cannot be present in substantial amounts in these medieval glazes.

The general composition of all glaze samples with silica and soda as their major constituents (types D–J) are approximately 12 parts  $\text{SiO}_2$ , 2 parts  $\text{Na}_2\text{O}$ , and 1 part each of  $\text{Al}_2\text{O}_3$ , FeO, MgO, CaO,  $\text{K}_2\text{O}$ . Potash and soda are useful fluxes for a wide range of temperatures, however the alkaline earths, calcia, and magnesia are active fluxes only at high temperatures (6). The melting point of a soda-silica eutectic mixture ( $\text{Na}_2\text{O}-4.579\text{SiO}_2$ ) with 18.4% soda and 81.6% silica, comparable to this general composition, is 860°C (7). The average of the calculated fusion temperature for these glazes, using West and Gerow's (5) coefficients, was  $835 \pm 24^\circ\text{C}$ . Thus, these glazes should have been fired at a temperature of approximately 813°C for fusion of the glaze.

Silica was probably added to the glaze batch in the form of quartz sand, but no consistent stoichiometric relationships between  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , CaO, or MgO were observed that could conclusively identify plant ash ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} + \text{K}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$ ), dolomite ( $\text{CaCO}_3 \cdot \text{MgCO}_3$ ), or carnallite ( $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ ) as raw materials. The small concentrations of chlorine and sulphur detected suggest that part of the alkalis were added to the frit as chlorides and sulphides.

Calculations were performed to determine the coefficient of linear expansion for each of the glaze samples, using the empirical values established by English and Turner (6). The relationship between the thermal expansion coefficient of glass and composition is expressed by the Winkelmann and Shott equation (16):

$$P = p_1x_1 + p_2x_2 + p_3x_3$$

where  $P$  is the volume coefficient of expansion,  $p_1 \dots$  are the percentages of the constituent oxides of the glass, and  $x_1 \dots$  are values for the volume coefficients of expansion of the oxides (from English and Turner). The linear coefficient of expansion is one-third of  $P$ .

Dayton (6) calculates the linear expansion of a typical ancient alkaline glaze to be  $10.54 \times 10^{-6} \text{ cm } ^\circ\text{C}^{-1}$ . For the soda-silica glazes the linear coefficient of expansion varies from 7.1 to  $9.1 \times 10^{-6} \text{ cm } ^\circ\text{C}^{-1}$ . A typical earthenware body has a value of  $7.8 \times 10^{-6} \text{ cm } ^\circ\text{C}^{-1}$  (6). In cases where the glaze has a smaller factor than the body, the glaze would be compressed and thus

TABLE 2. Descriptions of ten types of Yemeni ceramics from microscopic examination of whole sherds, and of thin sections through glaze, paint, slip, and clay body

Type name	Clay*	Slip	Paint	Glaze
Monochrome glazed				
A. Monochrome Green	Red	No slip	No paint	Lead oxide – silica glaze, opaque green (CuO), abraded and pin-holed, partially devitrified, 0.07–0.12 mm thick
Underglaze-painted on white slip ground				
B. Green-on-White	Red	Continuous white clay slip, 0.04 mm thick	Green paint (CuO), pigment particles 0.02 mm in diameter	Lead oxide – silica glaze, colourless, abraded and pin-holed, partially devitrified, up to 0.07 mm thick
C. Green-on-Yellow	Red	Continuous white clay slip, 0.02 mm thick	Green paint (CuO), pigment particles 0.02 mm in diameter	Lead oxide – silica glaze, yellow (Sb <sub>2</sub> O <sub>3</sub> ), slightly opaque, abraded and pin-holed, partially devitrified, 0.05–0.15 mm thick
D. Bleeding Green	Red	Continuous white clay slip, rich in quartz, 0.4–0.1 mm thick	Green paint (CuO), pigment particles 0.05 mm in diameter	Soda-silica glaze, transparent with yellow tinge, numerous bubbles, crazed and abraded, 0.11–0.20 mm thick
E. Brown-on-White	Red	Continuous white clay slip, rich in quartz, 0.08 mm thick	Brown pigment-paint, quartz grains in opaque ground mass, 0.05 mm thick	Soda-silica glaze, transparent with yellow tinge, numerous bubbles, crazed and abraded, pin-holing only above painted areas, 0.17 mm thick
F. Blue-on-White (red)	Red	Continuous white clay slip, rich in quartz, 0.08 mm thick	Blue paint (CoO), in solution with glaze	Soda-silica glaze, transparent (slight green tinge from FeO), numerous bubbles, crazed and abraded, 0.2 mm thick
I. Black-on-Blue	Red	Continuous white clay slip, quartz and mica inclusions, 0.04–0.08 mm thick	Black paint, opaque grains, non-vitreous, 0.05–0.08 mm thick	Soda-silica glaze, transparent turquoise (CuO) with green tinge from FeO, numerous bubbles, crazed and abraded, pin-holing above black paint only, 0.2 mm thick
Underglaze-painted on white clay body				
G. Blue and Green on White	White	No slip	Blue paint (CoO) and green stain (CuO?), in solution with glaze	Soda-silica glaze, transparent (slight green tinge from FeO), numerous bubbles, crazed and abraded, 0.1–0.16 mm thick
H. Blue-on-White	White	No slip	Blue paint (CoO), in solution with glaze	Soda-silica glaze, transparent (slight green tinge from FeO), numerous bubbles, crazed and abraded, 0.15 mm thick
Underglaze slip-painted				
J. Blue Tihamah	Red	No slip ground	White clay slip-paint, quartz and mica inclusions, 0.1 mm thick	Soda-silica glaze, transparent turquoise (CuO), numerous bubbles, crazed and abraded, 0.1–0.2 mm thick

\*As designed by INAA (2).

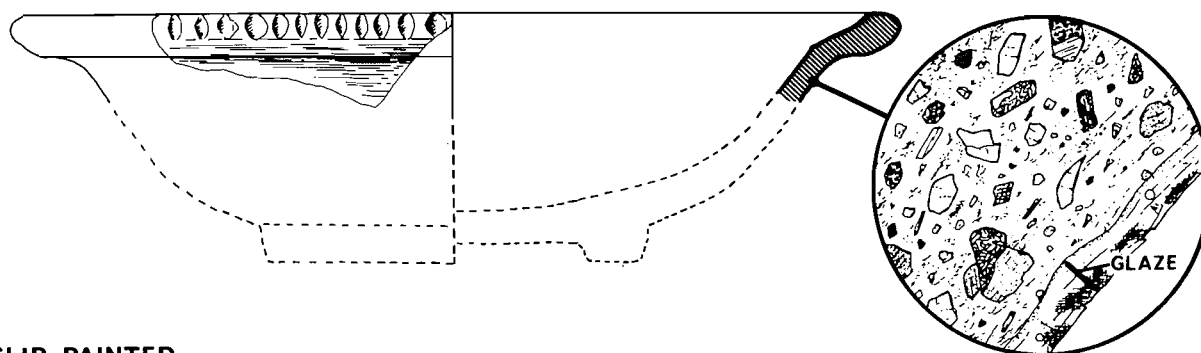
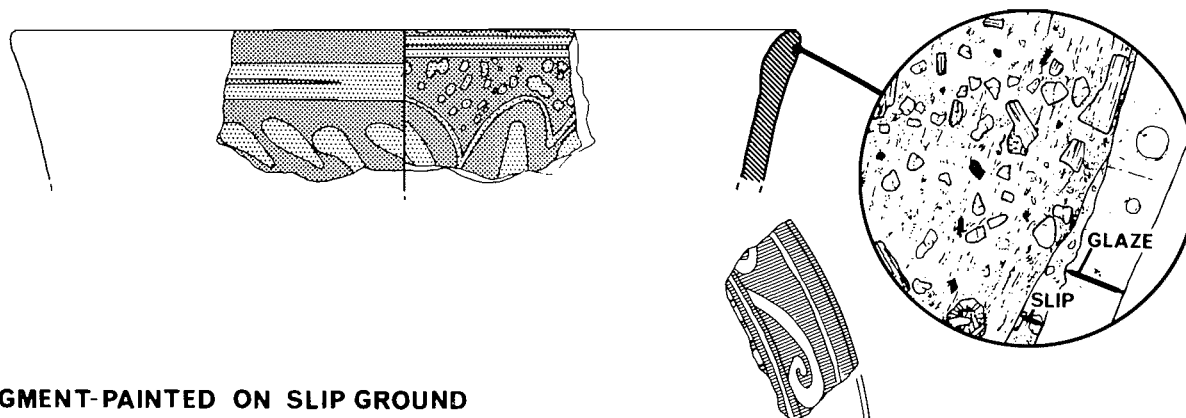
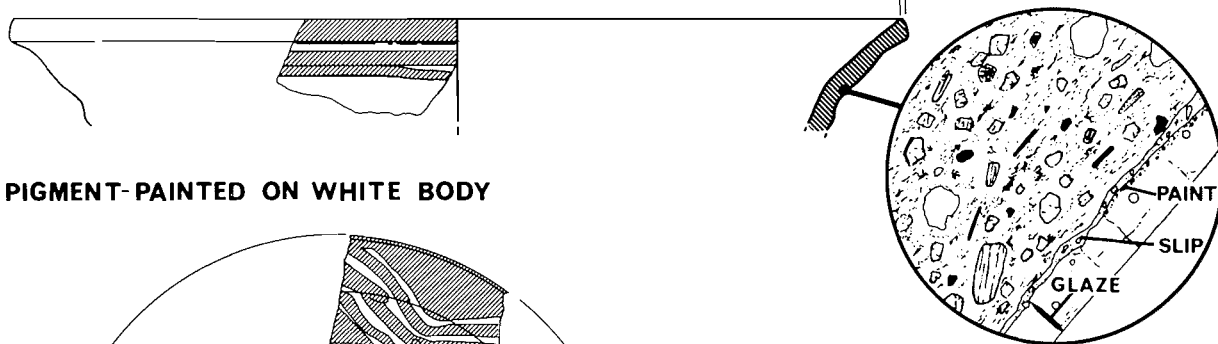
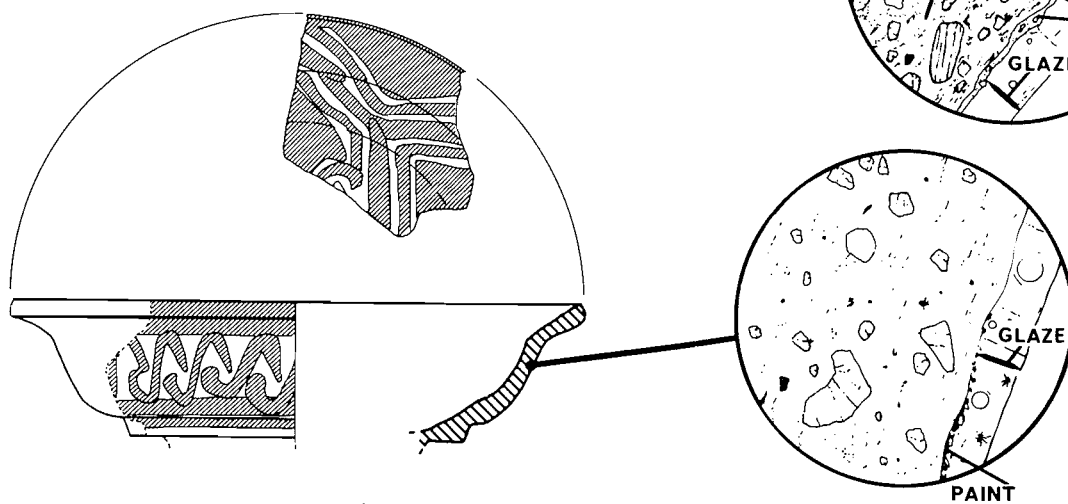
grip the clay body (providing the tensile strength of the glaze is not exceeded). Hence, medieval Yemeni glaze technology is a definite advancement over the ancient composition.

Although soda in glazes acts as a strong flux, it has a very high coefficient of thermal expansion. In the case of the Yemeni glazes the coefficient is directly related to the concentration of soda. Glazes high in soda tend to craze, and are often soft and easily abraded (8). Re-examination of the glazes on the sherds themselves revealed that the degree of crazing discernable to the unaided eye reflects the extremes calculated (as noted by Lawrence (7)). The brilliance of the coloured soda-silica glazes and pigment-painted decoration can also be attributed to the high concentration of soda (9).

The blue pigment used in the blue painted designs is cobalt. The turquoise-green glaze of type I (Black-on-Blue) and the turquoise-blue glaze of type J (Blue Tihamah) are coloured with copper. The concentration of sulphur detected is too small

to establish, on the basis of stoichiometry, that it is Copper Blue (CuS). However, one cannot rule out the possibility considering that sulphur could easily have vaporized during firing (5). Although both of these glazes are coloured with copper, they have slightly different colours. The iron oxide concentration in the type I glaze is higher (2.3%) than observed for type J (1.6%). This increased concentration of iron in the presence of an alkali glaze (9) is the reason for the green tinge in type I. The colourless glazes of types F, H (Blue-on-White) have a marked green tinge, unlike the glazes on types D, E (Bleeding Green; Brown-on-White), and have a higher FeO concentration than the latter. The green paint used in type D is also copper.

Rye and Evans (10) state that in order to characterize the compositional changes occurring in a glaze during firing, it would be necessary to have complete analytical data for glaze, slip, pigment, and body materials before firing. However, the nature of the decoration of the Yemeni ceramics provides a

**MONOCHROME GLAZED****SLIP-PAINTED****PIGMENT-PAINTED ON SLIP GROUND****PIGMENT-PAINTED ON WHITE BODY**

0 10 20 cm

FIG. 1. Drawings of four methods of decorating Yemeni ceramics showing whole pottery sherd, vessel profile and reconstruction, and microscopic observation of decoration.

TABLE 3. Electron microprobe analysis of glazes and paints of eight types of Yemeni ceramics\*  
(a) Set 1

Mineral composition	Sample type and sherd number			
	A. Monochrome green green glaze 33		C. Green-on-yellow yellow glaze 23	
			D. Bleeding green Clear glaze 30      Green paint 25	
SiO <sub>2</sub>	27.6±1.5		63±2	67.0±0.3
Al <sub>2</sub> O <sub>3</sub>	1.6±0.1		5.4±1.4	2.5±0.3
FeO	0.7±0.1		1.76±0.04	1.6±0.2
MgO	1.1±0.3		3.0±0.4	3.1±0.4
CaO	1.2±0.1		3.7±0.6	4.4±0.6
Na <sub>2</sub> O	3.0±0.4		13.2±0.4	10.1±0.3
K <sub>2</sub> O			3.6±0.2	3.23±0.03
TiO <sub>2</sub>			0.30±0.08	0.34±0.01
Cl			0.72±0.06	0.5±0.1
CoO				
SnO <sub>2</sub>	1.5±0.5	1.1±0.5		
CuO	1.2±0.2			2.3±0.2
PbO	61.0±1.1	62.2±1.8		
Sb <sub>2</sub> O <sub>5</sub>		0.8±0.3		
Total	98.9	97.0	94.7	95.0
coefficient of expansion (×10 <sup>-6</sup> cm °C <sup>-1</sup> )	7.8	7.7	8.3	7.5
Fusion temperature (°C)	640	630	786	810

(b) Set 2

Mineral composition	Sample type and sherd number					
	F. Blue-on-White (red body)					
	E. Brown-on-White		Clear glaze		Blue paint	
	83	84	06	04	06	04
SiO <sub>2</sub>	69.2±1.3	66.4±0.3	64±3	65.7±0.7	63.5±0.4	63±2
Al <sub>2</sub> O <sub>3</sub>	5.2±0.5	7.2±2.6	4.8±0.1	5.4±1.4	3.7±0.5	4.4±0.4
FeO	2.4±0.4	1.7±0.4	3.5±0.7	2.6±0.1	3.8±0.5	2.7±0.1
MgO	3.1±0.2	3.5±0.7	5.2±0.2	4.2±0.3	4.3±0.7	4.8±0.2
CaO	3.0±0.4	4.1±1.3	4.5±1.3	6.0±0.3	5.32±0.03	5.5±0.1
Na <sub>2</sub> O	10.5±0.8	12.0±1.0	10.3±0.8	9.5±0.3	9.9±0.1	10.2±0.2
K <sub>2</sub> O	3.29±0.03	3.4±0.3	3.5±0.3	3.6±0.2	3.38±0.09	3.0±0.10
TiO <sub>2</sub>	0.3±0.1	0.36±0.08	1.3±0.6	0.6±0.08	0.52±0.06	0.7±0.1
Cl	0.41±0.03	0.6±0.2			0.17±0.07	0.19±0.07
CoO					0.42±0.05	0.5±0.2
SnO <sub>2</sub>						
CuO						
PbO						
Sb <sub>2</sub> O <sub>5</sub>						
Total	97.4	99.3	97.6	97.7	95.0	95.5
Coefficient of expansion (×10 <sup>6</sup> cm °C <sup>-1</sup> )	7.1	7.1	7.4	7.3	7.4	7.4
Fusion temperature (°C)	844	860	857	877	827	843

TABLE 3 (concluded)  
(c) Set 3

Mineral composition	Sample type and sherd number				
	H. Blue-on-White clear glaze 111	I. Black-on-Blue turquoise-green glaze		J. Blue Tihamah turquoise-green glaze	
		105	104	No slip 07	Slip 07
SiO <sub>2</sub>	66±2	66.4±0.3	64±3	65.7±0.7	63.5±0.4
Al <sub>2</sub> O <sub>3</sub>	5.6±0.9	5.5±0.3	6.9±0.6	3.2±0.5	3.9±0.2
FeO	2.4±0.4	2.34±0.06	2.3±0.1	1.51±0.08	1.7±0.1
MgO	3.9±0.1	4.2±0.6	3.6±0.2	4.6±0.1	4.8±0.4
CaO	3.9±0.3	4.5±0.2	4.1±0.3	3.4±0.1	3.5±0.1
Na <sub>2</sub> O	15.0±0.8	13.5±0.3	12.73±0.06	16.4±0.6	16.2±0.7
K <sub>2</sub> O	2.8±0.1	2.91±0.03	3.8±0.2	2.3±0.1	2.5±0.3
TiO <sub>2</sub>	0.5±0.1	0.34±0.05	0.39±0.08	0.43±0.03	0.30±0.09
Cl	0.4±0.2	0.71±0.04	0.66±0.09	0.9±0.3	0.7±0.1
CoO					
SnO <sub>2</sub>					
CuO		0.71±0.04	0.66±0.09	1.6±0.7	1.5±0.6
PbO					
Sb <sub>2</sub> O <sub>5</sub>					
Total	100.8	98.5	99.5	97.9	99.6
Coefficient of expansion (×10 <sup>-6</sup> cm °C <sup>-1</sup> )	9.0	8.5	8.5	9.1	9.1
Fusion temperature (°C)	840	829	834	816	816

\*Values are reported as percent equivalent oxide concentrations (where no value is given component was not detected above two standard deviations). Also shown are linear coefficients of expansion and temperature of fusion values.

means of establishing certain changes without prior knowledge of the original materials. For example, type J (Blue Tihamah) has a slip-painted decoration and samples of this type provide a direct means of determining how glaze and slip react, since the slip is discontinuous in this case. Alumina concentration is higher in the glaze area with slip (3.9%) than where the glaze was in contact with the body (3.2%).

All of the underglaze-painted ceramics with red bodies have an overall white slip to mask the clay colour, and enhance the pigment-painted decoration. The glazes of these types are consistently higher in alumina than types with white bodies which do not require an overall slip. The alumina concentration is higher in glaze directly above a slip than in areas where pigment-paint had been applied on top of the slip prior to the glaze. For example, in type D (Bleeding Green) the alumina concentration for the colourless glaze is 5.4% and for the green paint, 2.5%. Similarly, for type F (Blue-on-White) the alumina concentration for the clear glaze is 4.8% and for the blue paint, 3.7%. Thus, the level of alumina enrichment appears to be highest where an overall slip is present, masked by a pigment-paint on top of a slip, and lowest where no clay slip is present. It is not possible to extrapolate from this observation whether alumina migration occurred during application of the aqueous glaze mixture, or during firing.

Alumina enrichment is also observed for glazes applied over white firing pottery (types G, H). Neutron activation analysis determined the Al content in white pottery to be as high as 30%, in contrast to 8% for red pottery (2). Unfortunately, it is too difficult to cleanly separate slip from glaze in sufficient quantity to determine its trace element concentration for comparison with the data available for white pottery.

In general all glaze samples with lead oxide and silica as their major constituents (types A, C) have from approximately 1 part silica to 2 parts lead oxide. The calculated average temperature of fusion for these glazes is 640°C; this is 200°C lower than for the soda-silica glazes. The linear coefficient of thermal expansion is approximately  $7.8 \times 10^{-6} \text{ cm } ^\circ\text{C}^{-1}$  for these glazes. Here too, the coefficient is directly related to the concentration of soda.

The lead oxide - silica glazes are mostly devitrified. This suggests that the glazes were cooled too slowly, or not fired at a sufficiently high temperature for annealing (just below the liquidus temperature the rate of crystal growth in glasses reaches a maximum). Since these ceramics were probably made at the same workshop as those with soda-silica glazes, it seems likely that a higher kiln temperature than necessary was used, along with too long a cooling period. Owing to devitrification, the glazes are more heterogeneous and the three analyses of each sample are not as consistent as observed for the soda-silica glazes.

The green colourant in the paints of types B, C (Green-on-Yellow; Green-on-White), and in the glaze of type A (Monochrome Green) is copper. The source of the yellow colouring of the glaze in Type C is antimony (lead antimonate). Tin was detected in these glazes but not in the soda-silica glazes. The intense colouring of the glazes and pigment-paints indicates that an oxidizing kiln atmosphere was used since lead glazes, if reduced, will turn grey or black (11).

The lead content in these glazes is sufficiently high that consistent use of these vessels for food storage and consumption could result in lead poisoning. Calculation of the Mellor ratio for the Yemeni glazes gives values from 0.68 to 0.74, above the

acceptable limit of 0.5 (8).<sup>6</sup> The solubility of lead into food or beverages stored in pottery is dependent on the type of lead compound used, its particle size, and the nature, pH and temperature of the chemical compounds present in the food or beverage. An increase in surface area and a decrease in lead compound particle size will increase lead solubility (12). The crazing due to the high soda content, and pitting due to escaping gases in the Yemeni glazes, would enhance the possibility of lead dissolving into the vessel contents. The presence of copper oxide in the paints and glazes of all of these types is also cause for concern, as a 2% addition of CuO to a low temperature lead glaze results in PbO release ten times that of the base glaze (8).

### Conclusions

The results of this exploratory investigation have significantly extended understanding of glaze technology in medieval Yemen. What is apparent from the analysis of the pottery from this and other studies is that there was a viable ceramic industry, with a relatively wide variety of different decorative types being produced using four basic production techniques. Questions that are raised by the study involve comparison of the results with known data on ceramics from the high cultural centres of the Islamic world, notably from Egypt, Syria, Iraq, and Iran. Comparative data on Iranian ceramics is particularly significant. The "Monochrome Green", "Green-on-Yellow" and "Green-on-White" lead glazed ceramics are associated with Rasulid occupation of the region from the 13th–15th centuries. Contemporaneous Iranian lead glazes (13) contain much higher concentrations of tin oxide (13–20%) and lower concentrations of lead oxide (13–21%) than the Yemeni ceramics (less than 1% SnO<sub>2</sub>, 52–62% PbO). However, Iranian glazes from the 9th–10th centuries (14) are similar to the Yemeni composition (less than 1% SnO<sub>2</sub>, 28–36% PbO). Thus, the 13th–15th century Yemeni tradition of lead glazing may be perceived as similar to that of 9th–10th century Persia.

Lane (15) mentions that in the ninth century A.D., the potters of Samarkand (north of modern day Afghanistan) made the important discovery that "painted decoration, normally apt to 'run' if the fluid lead glaze were applied over it, would stay if the metallic colouring agents were mixed with a paste of fine clay slip." The painted decoration in "Green-on-Yellow" and "Green-on-White" does not bleed in the lead glaze, and microscopic examination of thin sections of these types did not reveal the presence of clay in the paint. It has also been assumed that the tin present in Iranian glazes came into the region from the north, presumably by way of the Caucasus, as well as from

the west (from Europe) and the east (from China) (11). Tin was detected in three Yemeni types. It is clear that, in the future, the composition of the glass-forming constituents and pigments identified must be compared with geological surveys of the area to determine whether these raw materials were locally available or imported. This investigation of the geology of the region, together with analysis of historic texts, may enhance our understanding of cultural diffusion, and how innovations in glaze technology migrated through the Middle East.

### Acknowledgements

We are indebted to the Natural Sciences and Engineering Research Council of Canada for support (M.T.). The archaeological fieldwork was sponsored by the Royal Ontario Museum, and operated under license from the Office of Qadi Isma'il al-Akwa', General Organization for Libraries and Antiquities, Yemen Arab Republic. We are very grateful to C. Cermignani of the Department of Geology, University of Toronto, for valuable assistance with the analyses by the electron microprobe.

1. E. J. KEALL. *World Archaeology*, **14**, 378 (1983).
2. J. R. HALLETT, E. J. KEALL, V. VITALI, and R. G. V. HANCOCK. *J. Radio-Nucl. An. Chem. Articles*, **110**, No. 1, 293 (1987).
3. R. B. MASON, J. R. HALLETT, and E. J. KEALL. *Proceedings of the International Symposium on Archaeometry*, Athens. 1986.
4. I. C. FREESTONE. *Archaeometry*, **24**, 99 (1982).
5. R. WEST and J. V. GEROW. *Trans. J. Brit. Ceram. Soc.* **70**, 265 (1971).
6. J. DAYTON. *Minerals, metals, glazing and man*. Geo. G. Harrap and Co. Ltd., London. 1968. Chapt. 4. pp. 40–45.
7. W. G. LAWRENCE and R. R. WEST. *Ceramic science for the potter*. Chilton Book Co., Radnor, PA. 1982.
8. R. A. EPPLER. *Glass: science and technology*. In *Glass forming systems*. Vol. 1. Edited by D. R. Uhlmann and N. J. Kreidl. Academic Press, Toronto. 1983. Chapt. 4. pp. 301–310.
9. W. D. KINGERY and P. VANDIVER. *Ceramic masterpieces*. Free Press, New York. 1986. Chapt. 14. pp. 269–277.
10. O. S. RYE and C. EVANS. *Smithsonian Contributions to Anthropology*. **21**, 147 (1976).
11. J. W. ALLAN. *Iran*, **11**, 111 (1973).
12. D. DJURIC. *Proceedings of the International Conference on Ceramic Foodware Society*. World Health Organization, Geneva. 1974. pp. 40–45.
13. J. W. ALLAN, L. R. LLEWELLYN, and F. SCHWEIZER. *Archaeometry*, **15**, 165 (1973).
14. R. E. M. HEDGES and P. R. S. MOOREY. *Archaeometry*, **17**, 25 (1975).
15. A. LANE. *Early Islamic pottery*. Faber and Faber, London. 1947. Chapt. 4. p. 17.

<sup>6</sup>Mellor ratio:  $(RO + Al_2O_3)/RO_2 = 0.5$  maximum.