

CHARACTERIZATION OF ANCIENT MATERIALS USING PIXE SPECTROMETRY

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The first part of this paper describes some of the novel features of the Bartol Research Institute's PIXE facility that have made it such an effective analytical tool for the study of a diversity of ancient materials. The gains of selective filtering of the X-ray spectrum (to enhance detection limits for minor and trace elements), and of a "microbeam" mode of operation of the facility, are illustrated by two practical applications: (i) a new look at the nature of colorants used in late 2nd millennium Egyptian glassmaking, and (ii) a study of Panamanian gold artifacts finished by the "depletion gilding" process.

1. Introduction

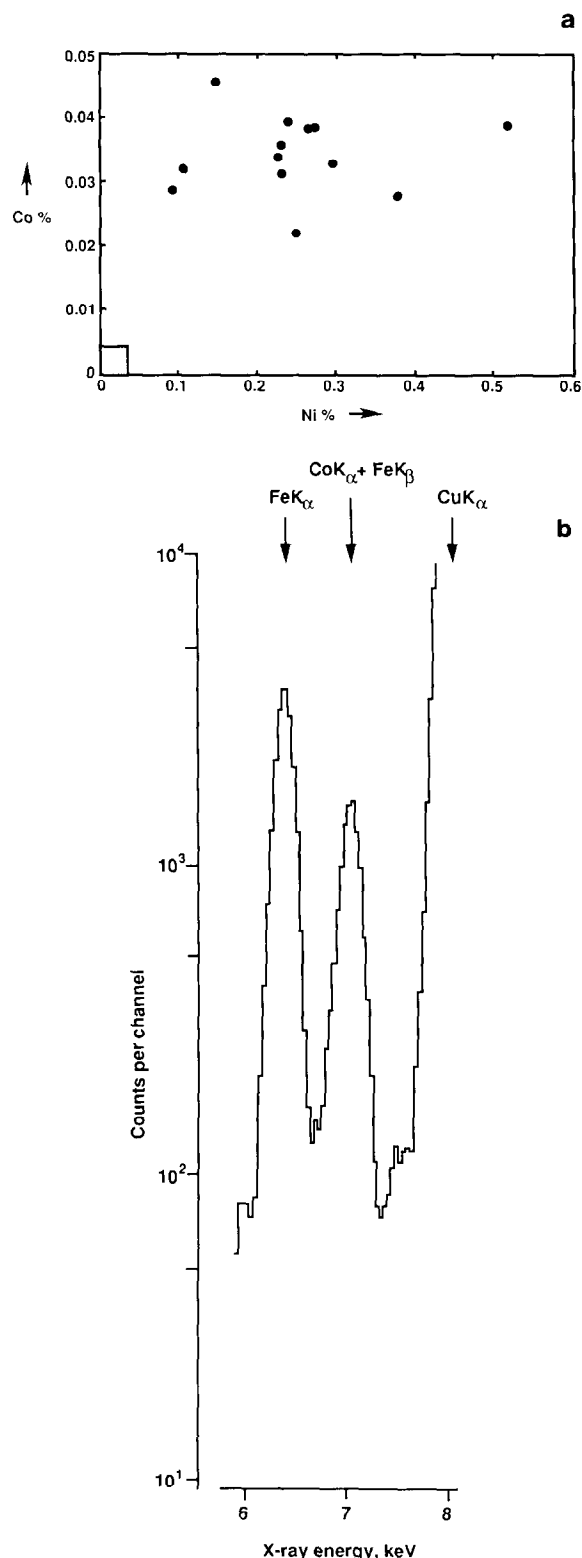
Over the past eight years the Bartol Institute's PIXE facility has been used to study the composition of more than 2500 ancient artifacts of widely varying material types and cultural origins. There has been a steady improvement in the detection limits for minor and trace elements of potential importance in archaeological research – primarily through the use of novel selective filtering in the detection system [1] – to a point where several of those limits are currently an order-of-magnitude lower than they were a decade ago (see fig. 1, by way of illustration of this for the analysis of cobalt and nickel in a bronze matrix).

Historically, the research emphasis has lain with the study of bronze [4–6], though iron, glass, vitreous materials such as faience glazes and smelting slags (from the processing of both copper and iron ores), and copper- and iron-rich ores, all now also figure strongly in our routine output of PIXE data. (For iron and steel, see refs. [7,8]. For glass and faience, see refs. [9–11]. For slags and ores, see refs. [12,13].) Detection limits for these different materials are summarized in refs. [8,13,14]. We have gained a great deal of information about alloying preferences in metal production, and about base recipes and choice of colorants in glassmaking, while building up a data bank on trace element patterning which may, at some future point, be a key to the definition of trading patterns of raw materials and/or the items produced from them.

Up to early 1986, all the PIXE data were obtained in

what might be described as a "minibeam" mode of operation, i.e., data were gathered using a proton beam $500\ \mu\text{m} \times 500\ \mu\text{m}$ in size, that was usually set to automatically scan an area of about $20\ \text{mm}^2$. Constraints on the area of analysis were set less by the maneuverability of the proton beam, than by practical aspects related to the shape and state of preservation of an artifact. (For example, to avoid the superficial area of a glass artifact where elemental leaching might have occurred during long-term archaeological burial, we would prefer to focus on the pristine matrix exposed by a modern fracture or chipping.) There were, however, certain kinds of artifacts that had to be excluded from our research program. Heavily corroded bronzes are the most obvious example. Over the millennia, the corrosive agents in ground water (particularly carbonic acid, water-soluble chlorides and sulphate salts) react with the copper matrix of an artifact, often to reduce it to no more than an irregular central core of sound metal. The thick bands of corrosion products surrounding that core would retain only a fraction of the minor and trace elements in the original bronze [15,16].

The subsequent development of a "microbeam" mode for the Bartol PIXE facility (i.e., a mode in which the proton beam is pinched down to a $50\ \mu\text{m} \times 50\ \mu\text{m}$ size and routinely used to scan areas of as little as $0.5\ \text{mm}^2$) has resolved such practical problems [17]. Its novel focusing component, an electrostatic quadrupole triplet [18], has proven thoroughly reliable and robust throughout its first three years of operation. During that time we have advanced our areas of material interest to



include gold alloys used in pre-Columbian burial goods (see section 4), pigments used to decorate early Iranian pottery, and partially corroded Iranian silver items.

2. Limits to beam focusing

As designed, the Bartol PIXE facility now has the potential for much tighter beam focusing, certainly down to 10 μm size. There are, however, at least two reasons why this is actually undesirable for the analysis of archaeological material:

(i) The need to be able to adjust easily the orientation of artifacts of all shapes and sizes, from weighty axeheads to delicately decorated jewelry, means that we have to run the Bartol facility in an "external beam" mode. Spatial resolution is then limited by proton scattering processes both in the air (or helium-filled) gap in front of the artifact's surface, and within the artifact's matrix (since, in terms of the range of protons in bronze, glass, etc., the latter is always a thick target).

(ii) On the microscopic scale, there is appreciable inhomogeneity of structure and composition in most archaeological materials. In bronzes, for example, the process of alloying copper with arsenic or tin at additive levels of 1% and above leads to the development of "dendritic" microstructures with a composition significantly different (over a spatial scale of 20 μm or so) from that of the surrounding eutectic. And the primitive nature of early smelting and refining procedures ensures that most bronze matrices are littered with fine inclu-

Fig. 1. (a) Scattergram of Co versus Ni for bronzes from the site of Harappa in the Indus Valley of Pakistan. The low Co detection limit of about 40 ppm was achieved in part through the use of a novel selective filter comprising (15 mg/cm^2 Fe foil + 15 mg/cm^2 muscovite) which efficiently suppresses Ni X-rays (see fig. 1b; also ref. [2]), in part through better data management in the PIXAN peak-fitting program developed at AAEC Lucas Heights [3]. The Ni detection limit of about 230 ppm was achieved using a selective filter array comprising (15.6 mg/cm^2 Co foil + 7.5 mg/cm^2 V foil) which suppresses "pile-up" contributions from the 95%+ Cu-content of the matrix. Up to a decade ago many PIXE facilities used only a simple mass absorption filter which offered detection limits that were some ten times poorer than the present one, i.e., a limit which would have excluded half of the measurements of Co- and Ni-contents in the study from any further statistical analysis. (b) PIXE spectrum for the X-ray energy range of 6 to 8 keV, for a Harappan bronze containing 1260 ppm Fe; 1470 ppm Ni; and 460 ppm Co. These data were gathered with the proton beam set at 2 MeV, and with the selective filter array comprising (15 mg/cm^2 Fe foil + 15 mg/cm^2 muscovite) in front of the detector. Quantitative analysis for nickel and cobalt was based in part upon the U.S. NBS reference copper matrices #1275 (Ni, 9.76%) and #C1123 (Co, 2.3%).

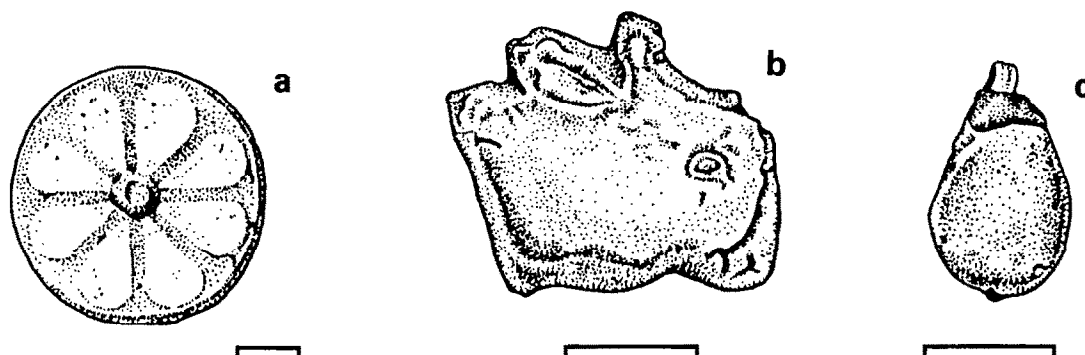


Fig. 2. Examples of glazed faience artifacts from New Kingdom Egypt: (a) A brownish blue, transparent white, and yellow "rosette" tile, from Tell el-Yahudiyeh (●BR/BL1 in fig. 3); MnO 0.16%, CuO 0.03%, CoO 0.084%. (b) A greyish blue miniature cattle head, from Thebes (▲GY/BL1 in fig. 3); MnO 0.10%, CuO 6.7%, CoO \leq 0.011%. (c) A violet and red pendant in the form of a poppy petal, from el-Amarna; MnO 0.17%, CuO 2.6%, CoO 0.16%. The scale marker represents 1 cm. (Artwork by Jennifer Hook, MASCA.)

sions (typically 10 μm in size) of copper and iron sulfides, oxides and complex silicates.

In ancient glass and faience glazes, some of the ingredients may have been poorly fused and have retained some of their particulate nature or have formed discrete crystalline structures, at the 5 μm level (see fig. 3 in ref. [9]). Glassy slags, though often themselves thoroughly homogenized in a well-operated furnace or forge, will retain remnants of metal (impure copper or iron particulates in the 10 μm size range) that were unable to escape the slag's viscosity. Truly fine PIXE probing of any of these materials (e.g., with a proton beam size of 10 μm , or less) would obviously be highly susceptible to strong element bias, poor data reproducibility, and dubious subsequent archaeological interpretation.

Below we summarize two studies where the availability of a PIXE probe facility has proven invaluable in gaining archaeologically significant data. In each instance, the discussion is prefaced by details of the selective filters used in the detection system to suppress the "pile-up" contributions from the dominant matrix element [19]. In each application, lower Z elements (sodium through iron) were determined without any such selective filters in position, but with the space between the artifact's surface and the detector's beryllium window bathed by a helium atmosphere.

3. Glaze colorants for Egyptian faience

Ancient sites: Thebes (about 500 km south of modern Cairo), a political and religious capital of Egypt during the New Kingdom (circa 1550–1070 B.C.); and Tell el-Yahudiyeh (about 20 km north of Cairo, in the Nile Delta), the site of an elaborately decorated palace built by Ramesses III (circa 1180–1150 B.C.).

Material: Low alkali silicate glaze (Σ alkali oxides, circa 3%; though perhaps reduced somewhat by leaching effects during burial)

Filter arrays: (i) 3.8 mg/cm² Al foil (to suppress complex "pile-up" contributions from Si and Ca).

(ii) 3.8 mg/cm² Al foil + 7.5 mg/cm² V foil + 15 mg/cm² muscovite (to suppress the Fe X-ray contribution, where necessary).

In a previous paper [11] we outlined some of the distinctive production features of the earliest well-attested glassmaking factory in Egypt, at mid-14th century B.C. el-Amarna, the short-lived capital of the heretic pharaoh Akhenaten [20]. The Amarna glassmakers gained their reputation from their sophisticated use of the core-forming technique in the production of delicate multi-colored vessels. But the traditional faience industry, by then already some two thousand years old in Egypt, also advanced swiftly at this time. To the ever-popular blue/green glazing (achieved by manipulating copper and soda contents [21,22]) was added a wide range of novel glaze colorants. The origins of these new colorants can be traced back to a phase of experimentation in the smelting of metal ores in upper Mesopotamia early in the 2nd millennium B.C. [23]. The new "palette" included calcium antimonate white, lead antimonate yellow, and cobalt blue, as well as some uniquely Egyptian combinations of colorants such as lead antimonate yellow with cupric blue to give a green glaze.

The technological and stylistic transformation of the Egyptian silicate industry continued for only about another two centuries. Thereafter, as Egyptian political and economic fortunes declined, there was a wholesale return to the blue/green glazes and rigid, formalized styles. In the interim, however, "local idioms" of faience production sprang up at sites where local silicate industries are also attested archaeologically [24,27]. Our

Table 1
Alkali components of Egyptian glazed faience

Site	Mean oxide contents ^{a)} [wt. %]			
	Na ₂ O	MgO	Al ₂ O ₃	K ₂ O
Thebes (n = 13)	2.91 (±0.34)	1.02 (±0.41)	0.43 (±0.07)	0.17 (±0.03)
Tell el-Yahudiyeh (n = 13)	1.10 (±0.14)	0.41 (±0.05)	0.39 (±0.04)	0.19 (±0.03)
el-Amarna (n = 4)	3.39 (±0.66)	1.60 (±0.19)	2.13 (±0.26)	0.65 (±0.14)

^{a)} Standard errors are quoted in parentheses.

PIXE program has defined the nature of some of these idioms by focusing on two groups of faience glazes (fig. 2): (i) jewelry included in the foundation deposits of the mortuary temples of three pharaohs (Ramesses II, Siptah, and Tewosret) at Thebes [25,26]; and (ii) tiles in the form of multi-colored rosettes from the palace of Ramesses III at Tell el-Yahudiyeh [27].

Among the primary glaze-making ingredients, we found that alkali contents for both the study groups were quite similar to one another, but that their alumina, magnesia, and potash contents were significantly lower than those characterizing the earlier Amarna faience industry (table 1). (These differences most likely reflect the availability of more or less pure raw materials at each site.) Different mixtures of transitional metal ion colorants do, however, serve to differentiate the Rames-

side groups from one another (fig. 3: dendrogram). For example, a manganese/copper greyish blue glaze (GY/BL) was prevalent in the Theban group, whereas a manganese/cobalt brownish blue glaze (BR/BL) was only found in the Tell el-Yahudiyeh group. By varying the relative amounts of either element in a mixture, a far bluer glaze (with more copper) was produced at Thebes (BLU5); and a distinctive purplish brown glaze (PU/BR1) was produced at Tell el-Yahudiyeh by further addition of manganese. Manganese ores are scattered throughout Egypt; copper ores were exploited by the Egyptians both in the Sinai and at Timna in the Wadi Arabah [21,28]. The alum deposits of the Western Desert oases are the most likely source of cobalt [29]. Although these alums contain manganese, the relatively high MnO-to-CoO ratio of about 2.2 that we found in the faience glazes (versus that ratio for cobalt blue glass, of about 1.2) strongly suggests that manganese was deliberately added (see also ref. [30]).

Such admixtures of copper, cobalt, and manganese are a predictable outcome of the prior use of colorants involving these three elements not only at el-Amarna but also in even earlier times at sites in the neighboring Near East [10,20]. The site-specific nature of these admixtures (and, to a lesser extent, of transparent white glazes: see fig. 3) supports a view that the faiences were locally produced according to specific recipes. Nuances of color were possible, actively sought, and enabled these early glassmakers to recreate images of the natural and human worlds about them as never before.

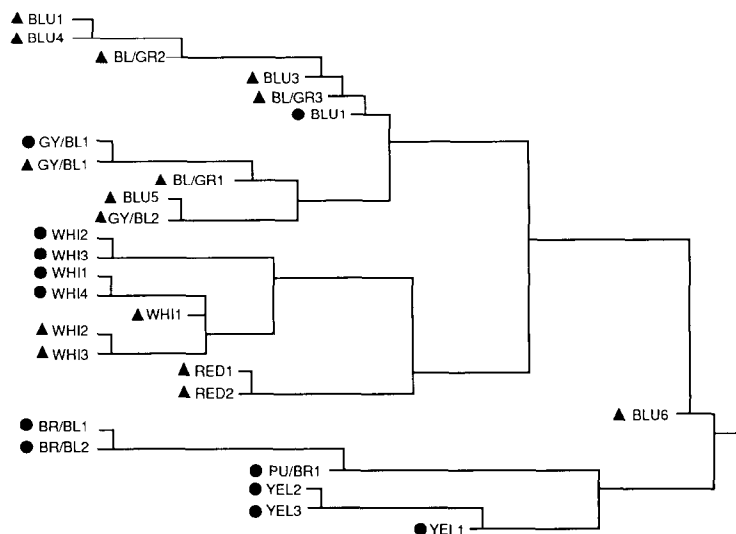


Fig. 3. Dendrogram for the PIXE data obtained for glazed faience from Thebes (▲) and Tell el-Yahudiyeh (●). The chart was generated using a hierarchical aggregative clustering algorithm (AGCLUS) that in this instance calculated the mean Euclidean distances for 13 oxides of minor and trace elements. The outlier here, BLU6, owes its coloration to the addition of the synthetic calcium copper tetrasilicate known as Egyptian Blue [31]. The Theban glazes RED1 and RED2 owe their red coloration to the presence of hematite and copper in the Cu⁺ state. The Tell el-Yahudiyeh glazes YEL 1-3 are colored yellow by lead antimonate crystals.

4. Gold compositions at Sitio Conte

Ancient site: The cemetery of Sitio Conte (about 100 km southwest of modern Panama City), with unplundered pre-Columbian burials dating circa 400 to 900 A.D.

Matrix: Gold and gold/copper alloys (Cu ranging from 0.1% to 35%).

Filter array: 21 mg/cm² brass foil (to suppress “pile-up” contributions from Au).

Metalworking techniques in the New World first appear in the Andean region, sometime during the first millennium B.C. They spread gradually north into Ecuador and Colombia, reaching the Panamanian Isthmus by the first few centuries A.D. Over the next few hundred years, a number of regional goldworking styles developed there, all of which are represented in the finds at Sitio Conte [32,33].

PIXE data for a wide range of artifacts from one of Sitio Conte’s richest burials indicate that gold was used in two ways: (i) in a near-pure form as it occurred in placer deposits or shallow mines, the metal containing a minor amount of silver and a trace of copper; and (ii) as an intentionally produced gold–copper alloy in a variable proportions known today as tumbaga. Whether an artifact was shaped of gold or tumbaga correlates with the method of manufacture: the choice was apparently technological and had to do with the metal’s working and thermal properties. Unalloyed gold is soft and malleable: it can be hammered into thin foil directly from gold nuggets. (At Sitio Conte these foils, which were used as decorative sheathing over bone, ivory and

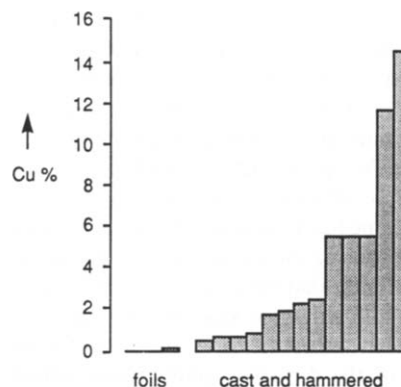


Fig. 4. Histogram of the individual Cu-contents for tumbaga items used as body ornaments in Burial 11 at the early Panamanian site of Sitio Conte.

resin carvings, were about 0.1 to 0.5 mm thick.) Tumbaga, because of its lower melting point – 910 °C for a 80Au/20Cu eutectic, versus 1064 °C for pure gold – was more easily cast, and because of its hardness, more wear-resistant. Among Sitio Conte burial items, it was used for various body ornaments and breast plates of hammered repoussé sheet work.

Unlike pure gold, tumbaga is reddish in color. To give them an outwardly golden appearance, tumbaga pieces were often “depletion gilded,” i.e., treated by an oxidizing and pickling technique, so that copper was drawn out preferentially from the artifact’s surface [34]. But the depleted surface, which is typically about 15 μm thick, always retains at least a tenth (and sometimes

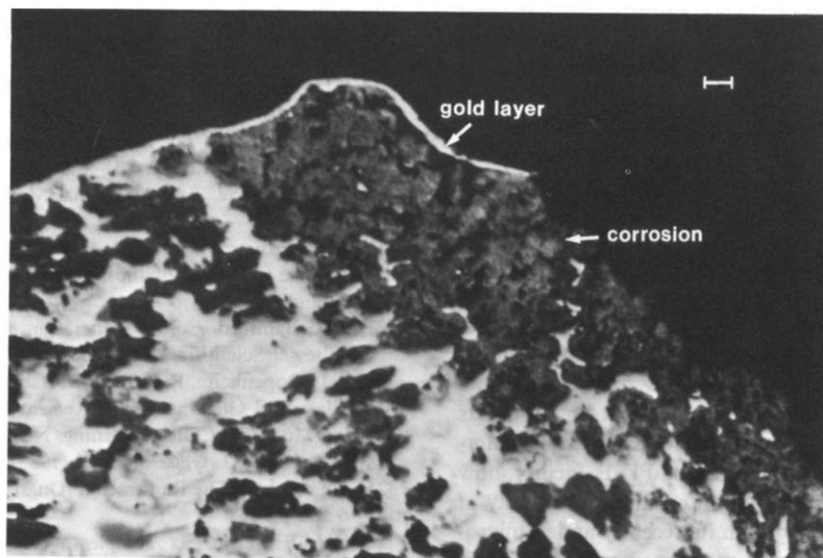


Fig. 5. Photomicrograph of the cross-section of a small tumbaga chisel from Sitio Conte. Note how the swollen corrosion products are forcing off the thin depletion gilded layer away from the underlying tumbaga. The white scale bar (upper right) is equivalent to 10 μm. (Courtesy: V.C. Pigott, MASCA.)

more than a half) of its original copper content [34,35]. Thus, PIXE study of just the surfaces of depletion gilded gold artifacts will provide evidence for the alloyed nature of the underlying material (fig. 4).

Unlike pure gold, tumbaga is prone to corrosion. If the tumbaga's copper content is high ($\geq 25\%$, by weight), the corrosion process is capable of eroding away the tumbaga immediately beneath the depletion gilded layer, sometimes causing the surface to peel off like a thin foil [36,37]. Artifacts that have suffered in this way (or those that have suffered some kind of physical damage) can provide what amounts to a sliver of tumbaga with remnants of the depletion gilding layer adhering to it (fig. 5). In such situations, the Bartol PIXE facility, in its "microbeam" mode, provides access to the artifact's bulk composition.

Thus far we have studied only two artifacts in this way. One was a plaque decorated with complex mythical creatures, which was slightly fragmented at its edge: Depleted surface Au 92.7% Ag 1.6% Cu 5.7%, Tumbaga matrix Au 46.1% Ag 2.7% Cu 51.3%. The other was a small undecorated chisel, which was fragmented at its tip:

Depleted surface Au 83.7% Ag 1.6% Cu 14.7%,
Tumbaga matrix Au 49.7% Ag 2.7% Cu 47.6%.

The fact that the original tumbaga recipes of these two very different items were quite similar, while their surface compositions were not, raises the intriguing possibility that the most prestigious burial goods – in this case, the plaque – were the most conscientiously worked, to ensure that their surfaces had the highest possible golden luster. Because of its techno-cultural implications, we will be studying this notion in far more depth over the coming year. As it is, these data highlight the Sitio Conte goldsmith's achievements in the use of the depletion gilding process, turning items that were as much copper as gold into ornaments of such high luster that they were thought fit for burial with a chief.

5. Conclusions

Archaeology is a broad discipline, with a diverse material expression, a time-frame of some 15 millennia, and a spatial influence that is worldwide. Reconstruction of the tempo of practical change and advancement in antiquity is a slow process, calling for the gathering of as much information as possible about how artifacts were made and how resources were exploited at different points in time. As the Bartol PIXE facility now stands, with its detection system optimized for study of a range of materials, and with its recently added microbeam capacity allowing for specialized spatial analysis, we foresee that output could rise to around six hundred artifacts per year. Over the next decade we can expect therefore that the statistical footing for the interpreta-

tion of PIXE data will become much firmer, and that PIXE spectrometry will become increasingly the analytical tool of choice in resolution of archaeological problems.

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