Proton-Induced X-Ray Emission Spectrometry in Archaeology

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PROTON-INDUCED X-RAY EMISSION SPECTROMETRY IN ARCHAEOLOGY

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Abstract

Proton-induced x-ray emission (PIXE) spectrometry is fast developing a reputation as a powerful analytical tool in the study of a range of ancient materials, including bronze, iron, gold, glass, faience, and smelting slag. PIXE data allows determination of the primary constituents which would indicate their recipe of production and determine their bulk physical properties (e.g., color of a glass, brittleness in a metal), and of a wide range of trace elements which may indicate the source of raw materials from which an artifact was constituted. Over the past seven years, PIXE spectrometry's primary advantage over other recognized methods now being applied in archaeological research (particularly, xrf spectrometry and SEM/EDAX) -- that protons induce very little bremsstrahlung and therefore contribute very little to spectrum background during analysis -- has been much enhanced through the use of various kinds of selective filters in the detection system that heavily suppress the x-ray signal of dominant element(s) in the artifact's matrix (Cu in bronze, Si and Ca in glass, etc.). PIXE detection limits are kept exceptionally low (usually in the 10 ppm to 100 ppm range), because the selective filters almost entirely eliminate secondary background effects arising from response inertia in the detection system's electronics. Archaeological applications of the PIXE method, as reviewed here, now cover both the Old World, the New World, ancient Asia and Polynesia, and a time-span of the 5th millennium B.C. through to the 19th century A.D.

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Introduction

Over the past two decades, particle-induced x-ray emission (PIXE) spectrometry, primarily using protons as the source of excitation, has been developed into a powerful and standard technique of trace element analysis. During that time, several review articles have been published that cover in detail the fundamental physics of the PIXE method and experimental arrangements appropriate for its application (e.g., Bosch et al. 1978; Folkmann 1975; Legge 1984; Richter 1984). The more general literature on the application of the PIXE method has demonstrated its exceptional value in the study of trace levels of impurities in low Z organic materials such as blood cells, body soft tissue, human hair, tree growth-rings and plant roots (Heck and Rokita 1984; Henley et al. 1977; Legge et al. 1984; Lopes et al. 1978; Stelzer 1984; Weber et al. 1984), of particulates derived from environmental pollution and entrapped on low Z filter substrates (Martinsson 1987; Winchester 1984, among others), and of the inks and pigments used for postage stamps and early printed paper (Cahill et al. 1981; Cahill et al. 1984; Johansson et al. 1986; Malmqvist 1986a). The medical application of the PIXE method, in particular, seems to be advancing most rapidly, now that it is becoming clear that anomalous levels of trace elements are a sign of impending or active health disorders (Johansson and Lindh 1984; Malmqvist 1986b; Van Rinsvelt et al. 1984; Sha Yin et al. 1987; Uda et al. 1987; Watt et al. 1984, among others).

By comparison, the development of PIXE spectrometry as an archaeological tool has been relatively slow. In part, this is because the materials of primary interest -- metals precious and mundane, and silicates including glass, faience, obsidian and smelting slags -- are constituted from higher Z elements (i.e., the analysis of their x-ray spectra is complicated by an appreciable background signal), are massive relative to the proton's penetration into their matrices, and tend to have quite complex compositions because of variability in their production recipes (i.e., matrix effects are important and difficult to deal with, either theoretically or through use of reference standards: see Clayton et al. 1981; Reuter and Lurio 1977). Up to early 1982, most of the

published papers which documented a use of the PIXE method in connection with an archaeological problem described the study of either a single artifact (Epstein 1981; Moorey and Fleming 1979; Skupinska-Lovset and Fleming 1979; Mommsen et al. 1980) or just a small group of them (Ahlberg et al 1976; Ferreira and Gil 1981; Fleming 1982; Fleming and Crowfoot-Payne 1982; Fleming and Nicklin 1982; Weinstein 1980), and often with the PIXE data used as only supplementary information in the application of another analytical tool (Fleming 1981a,b). The major exception to these generalizations was a study of more than three hundred Melanesian obsidian artifacts (Ambrose et al. 1981: see also Glass and glassy matrices below).

Limited in scale as those earlier studies were, they did serve to demonstrate the range of artifact types (gold coins, silver statuary, bronzes from Cyprus, Egypt, West Africa and medieval France, etc.) to which the PIXE method was applicable, and underscored one of its primary advantages -- that, in its "external beam" mode, it could be used to study artifacts of varying size and shape (Fig. 1). As clearly, however, those studies indicated the need for research into ways in which some features of PIXE systems could be customized, in part so that the detection efficiency of several trace elements could be maximized for different matrices, in part so that multi-component artifacts could be studied in appropriate detail. The summary of PIXE applications that follows, in its coverage
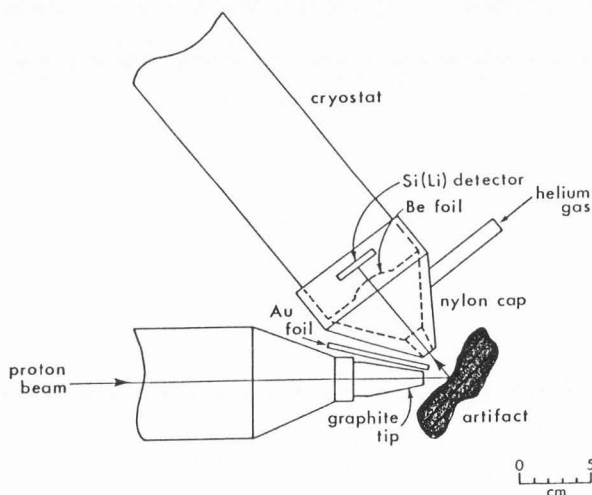

Fig. 1. A schematic close-up of the sample irradiation stage of the Bartol PIXE system, in the configuration appropriate to measurement of low Z elements. For the measurement of high Z elements, the nylon cap with the He gas inflow line is replaced by one which is slotted to take various configurations of selective filters. A 7 μm thick kapton foil is wrapped over the graphite tip, to protect the vacuum in the preceding beam line. The 250 μm thick Au foil which lies along the side of the graphite tip shields the detector from stray X-rays scattered off the various apertures which define the path of the proton beam.

of both our own research efforts and that of others, indicates the route which that customizing took; specifically, the introduction of some novel selective filter arrangements in the PIXE system's detection unit, to improve the overall sensitivity of detection of trace elements.

Copper-based alloys

Though the origins of copper metallurgy in antiquity are obscure, the archaeological record indicates that, in many areas of the world, its technological development progressed through three overlapping steps.

That development is best documented in the Near East. There a simple perforated pendant excavated at Shanidar (a large cave site in the Zagros mountains of northeastern Iraq, dating circa 9500 B.C.) provided our earliest instance of the use of native copper (i.e., of naturally-occurring copper metal). For the subsequent five millennia, that form of copper was the only one that man knew. It was extensively traded throughout the Near East more for it potential in the making of ornamental items than as a raw material for functional items such as agricultural tools. Sometime around 4000 B.C., however, perhaps as a by-product of potters experimenting with copper oxide ores as a means of adding a blue glaze to their wares, the notion of extraction of copper through the smelting of its various ores -- cuprite, malachite, melanconite, etc. -- took root and was soon itself the subject of some important empirical experimentation. In particular, the new metal smiths recognized that certain ores provided metal which could be cast more reliably and tended to be less brittle when worked and shaped. Those ores we now know will have been rich in arsenic (e.g., domeykite and algodonite, which are both plentiful throughout the Near East); and the alloys which they yielded typically contained arsenic levels in the range of 0.5% to 8%.

By 2500 B.C., a new alloy -- copper and tin, to make bronze -- was gaining popularity among the economically powerful city states of southern Mesopotamia. There are no naturally-occurring tin-rich copper ores, so the tin had to be introduced into the bronze as a deliberate additive. Initially that may have meant the co-smelting of copper and tin ores (with the latter almost certainly being cassiterite), but Mesopotamian cuneiform texts would suggest that such an approach very soon gave way to independent smelting operations, followed by co-melting of refined copper and tin metal. Tin additive levels typically range 2% to 18%, dependent upon the working properties sought for the alloy. Though bronze and arsenical copper share similar metallurgical merits relative to near pure copper -- structural hardness, and ease of reworking or sharpening -- for reasons that are ill-understood (Stech and Pigott 1986), bronze steadily gained in popularity over the subsequent two millennia, and the use of arsenical copper became quite unusual.

In two areas of the New World, the evolution of copper metallurgy was somewhat different. Around the Great Lakes, and in the Arctic regions of North America, several Indian cultures heavily

exploited the locally rich resources of native copper from the beginning of the early third millennium onwards, without ever adopting a smelting technology. And in pre-Conquest Peru, it was the arsenical copper-to-bronze transition that was never made (Shimada et al. 1982).

Over the past six years we have tended to specialize in the PIXE study of copper-based materials, and have contributed to a better practical and cultural understanding of all three of the traditions of copper metallurgy outlined above. We have confirmed the high purity of the Lake Superior native copper sources that were exploited as early as the third millennium B.C. (see Vernon 1985). We have characterized the nature of several components of the copper smelting process used in the La Leche Valley of northern coastal Peru over the period of the mid-9th to mid-16th centuries A.D., including the primary furnace product, prills later recovered from the smelting slag, and ingots derived from fusing those prills together during a re-melting step (Epstein 1982; Shimada et al. 1983). And, as part of a major assessment of Mesopotamian metallurgy currently in progress at the University Museum of the University of Pennsylvania, we have determined (though not yet published) the general alloy composition and trace element patterning for more than three hundred artifacts ranging in date, circa 3100 B.C. to circa 1550 B.C.

As far as the PIXE method is concerned, the primary practical problem posed in all these studies has been how to minimize the contribution to the x-ray spectrum's background that comes from "pile-up" in the detector while it is trying to process the x-ray input from copper (as the artifact's primary constituent). The Cu $K_{\alpha 1}$ x-rays at 8.026 keV contribute a "pile-up" spectrum which has maximum extent at twice the $K_{\alpha 1}$ energy (i.e., at 16.052 keV, and an intense continuum which extends beneath the main x-ray peaks of Bi, Pb and As (at 10.837 keV, 10.550 keV and 10.542 keV, respectively).

Like many other PIXE laboratories, the Bartol PIXE system includes a "rejector" unit which electronically removes the bulk of the "pile-up" continuum (Woldseth 1973). That rejector unit will not, however, remove the so-called "sum peak" which represents the true coincidence of two Cu $K_{\alpha 1}$ x-rays within the time resolution of the detection and processing components of the system, i.e., the discrete peak which occurs at the higher energy limit of the "pile-up" continuum, at 16.052 keV. The elimination of this sum peak is achieved by the expedient of including an x-ray absorbing filter in front of the detector system. Our choice for this comprises two foils, one of 15.6 mg/cm^2 of Co, the other of 7.5 mg/cm^2 of V. The cobalt (Z = 27) heavily suppresses the main copper K_{α} and K_{β} x-ray contributions; the vanadium (Z = 23) cuts out the fluorescence that the intense copper x-rays excite in the Co filter. With such a filter array in place, the proton beam's intensity can be greatly increased so that the spectral peaks of minor and trace elements of atomic number greater than copper are boosted about eighty-fold, while the copper K_{α} peak is still easily measured at about 10% of its unfiltered value. A much weaker copper x-ray signal means a "pile-up"

contribution that is only about 1% of its level when filters are not used. The limit to the extent to which the proton beam can be increased is finally set by a need to avoid burn-out of the kapton foil which is used as the vacuum-to-air interface (Fig. 1: Swann and Fleming 1986).

The proton beam's energy is set at about 2.0 MeV when the selective filters are in position for the PIXE analysis of higher Z elements. This energy is lowered to about 1.3 MeV when the selective filters are removed and the PIXE analysis focuses on the lower Z elements such as chlorine and sulfur (Z = 17 and 16, respectively). The reasoning here is that the x-ray yield will be increasingly attenuated the deeper the excitation occurs within the artifact. That yield will also be a function of Z, since the x-ray's energies of lower Z elements are less than those of higher Z ones. Thus, the use of a lower energy proton beam effectively enhances the observation of lower energy x-rays. All elements down to silicon (Z = 14) are detected with high sensitivity in this mode, since their x-rays are energetic enough to penetrate the air space between the artifact's surface and the detection system's input point (a fine nylon collimator in front of the thin beryllium window of the silicon detector). To be able to measure magnesium (Z = 12) in a copper matrix that space has to be bathed by a helium gas stream during PIXE measurement.

The detection limits achieved on a routine basis with the Bartol PIXE system for various trace elements in a relatively pure copper matrix are given in Table 1.

Table 1. PIXE detection limits for various trace elements in a copper matrix.

Element	Detection limit (ppm)*
Mg	72
Si	17
S	22
Cl	28
Ti	26
Cr	115
Mn	36
Fe	120
Ni	92
Zn	780
As	160
Ag	63
Sn	98
Sb	118
Pb	119
Bi	53

* Calibration of the system is based largely on a series of standards provided by BNF Metals Technology Centre, Wantage (England), including a leaded bronze (C50x20) and a gunmetal (C71x08). The poor detection limit for Zn derives from the fact that its main x-ray line (K_{α}, at 8.637 keV), is flanked by the two main x-ray lines of Cu (K_{α} and K_{β}).

Several of the detection limits quoted here are subject to upward revision in situations where alloy constituents, such as As and Sn, contribute strongly to the x-ray spectrum. For example, the Mg detection limit will be nearer 160 ppm in a bronze with an As-content of about 1%, because of overlap between the Mg Ka peak and the As L_α peak (at energies of 1.253 keV and 1.282 keV, respectively). Similarly, for equal run times, the Sb detection limit will be nearer 220 ppm in a bronze with an Sn-content of about 10%, because of the overlap between the Sb K_α peak and the high energy tail of the Sn K_α peak (at energies of 26.35 keV and 25.27 keV, respectively).

The practical strength of the PIXE method in the study of archaeological bronzes is provided by data recently obtained for a group of thirty artifacts of diverse form (tanged weapons, knives, toggle pins, razors, etc.) from the Bronze Age (2300-1600 B.C.) cemetery at Lapithos, in Cyprus. A plot of Sn-content versus S-content (Fig. 2) yielded a scatter of data which indicates: (i) that the local copper ores invariably contain less than 0.13% Sn as an impurity; (ii) that the metal in the sulfur-free bronzes may have originated from a foreign oxide ore source, since the most readily accessible copper ore sources in Cyprus are all sulfur-rich chalcopyrites (Balthazar 1986); and (iii) that, with the decision of whether or not to use tin as an alloying component not seemingly related to the functionality of the end-product, artifacts with intermediate tin contents (circa 0.5% to 2.5%) probably contain at least a portion of re-melted bronze scrap.

Iron

Though iron did not go through any chemically complex steps of alloying in antiquity, its method of production has changed appreciably from the time when it was first produced on an industrial scale in western Europe in Roman times (most notably in the Alpine province of Noricum, in the late 1st century B.C.) to when it became the symbol of the Industrial Revolution from the early 18th century onwards. Each new innovation in iron-making, particularly those that altered the thermodynamics of ore smelting (e.g., Henry Cort's introduction of the puddling process in 1785, and the movement from cold-blast to hot-blast furnaces late in the 18th century), were likely to cause matching shifts in minor and trace element patterning in the final iron product. (In fact, some were deliberately intended to do so, removing elements that might produce undesirable properties such as embrittlement.) And some innovations allowed the exploitation of new ores which had previously proven difficult to smelt efficiently, thus introducing a quite different mineralogy (and its related trace element pattern) into iron's history.

Despite the appreciable potential the PIXE method must have as an aid to unravelling technological aspects of the dynamic history of early iron, we seem to have been the only researchers to become involved in such work.
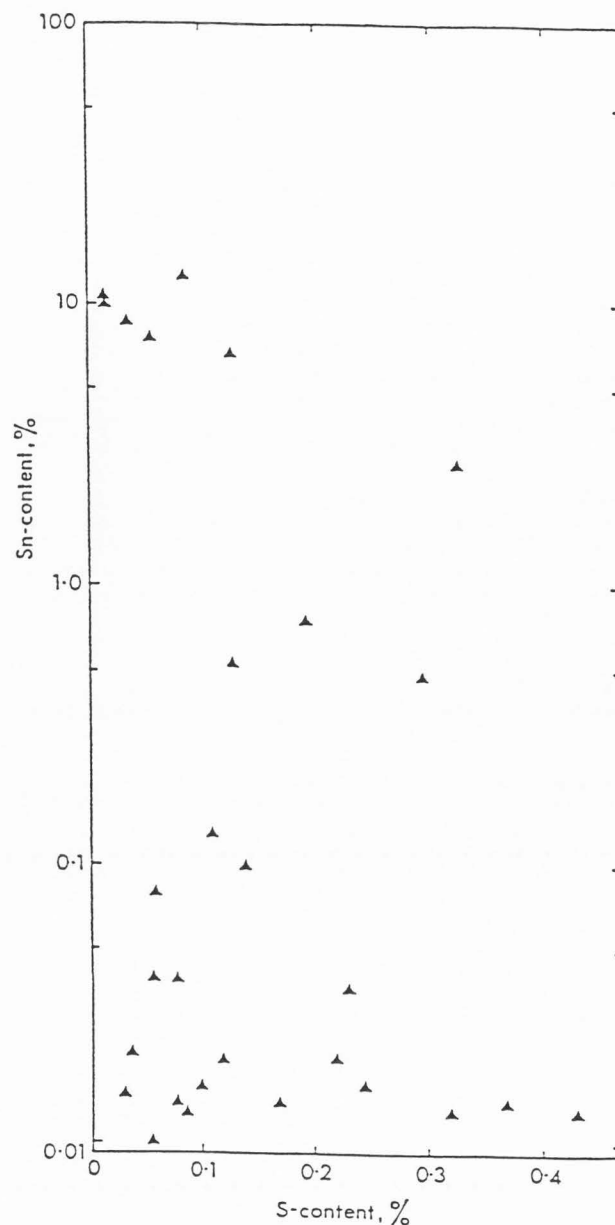

Fig. 2. Variation in the concentrations of S and Sn (plotted on a log. scale) in bronze artifacts from the Bronze Age cemetery at Lapithos, in Cyprus. (Data derived from Balthazar 1986: Table 2.)

Applications have been as diverse as the study of the earliest steel from Transjordan, dating circa 1200 B.C. (Pigott et al. 1982); and the study of historic American iron making processes at the mid-19th century site of Catoctin, in Maryland (Schenck 1982, 1983), and at the Revolutionary era site of Valley Forge, in Pennsylvania (Schenck and Knox 1985; see below for an expanded discussion).

For such analysis we have developed a selective filter array which comprises 15 mg/cm^2 of V foil + 15 mg/cm2 of mica sheet. The vanadium

(Z = 23) heavily suppresses the main iron K_α and K_β x-ray contributions (at 6.403 keV and 7.057 keV, respectively); the potassium in the mica (Z = 19) cuts out the fluorescence that the intense iron x-rays excite in the V filter. The detection limits achieved on a routine basis with the Bartol PIXE system for various trace elements in a relatively pure iron matrix are given in Table 2.

Table 2. PIXE detection limits for various trace elements in an iron matrix.

Element	Detection limit (ppm)*
Mg	57
Si	20
P	15
S	12
Cl	10
K	13
Ca	17
Ti	19
Cr	49
Mn	81
Ni	52
Cu	33
Zn	18
As	8
Sr	16
Sb	100

* Calibration of the system is based largely on a series of NBS standards, including SRM 1136, SRM 362, and SRM 467. Though the detection limit for Ca is very low, it should be noted that the actual Ca-content of irons seems to be prone to appreciable spatial variability. Some consideration of the typical degree of data scatter that occurs in routine of the application of the PIXE method to the measurement of trace elements in iron matrices is given in an Appendix by the authors, in Schenck and Knox (1985).

The kind of information that PIXE analysis of iron can provide is illustrated by data recently obtained for a group of five artifacts from the site of Valley Forge, in Pennsylvania (Schenck and Knox 1985). Though best known as the location of the encampment set up by George Washington and the Continental army during the bitter winter of 1777, the name Valley Forge does correctly reflect the area's prior role in the local iron industry. The artifacts themselves -- two cast iron pig fragments, one of which was marked Andover; and three pieces of wrought iron -- were recovered sixty years ago from a building which has subsequently been labeled the Upper Forge, to distinguish it from the nearby Mount Joy Forge which was erected in 1742. Both may well have served as magazines of Continental stores early in 1777, only to be destroyed by the British forces as they moved towards their winter quarters in Philadelphia a few months later.

PIXE-determined low levels of Si and S in the cast irons from the Upper Forge (Fig. 3) are consistent with the assumption that those irons were produced in cold-blast charcoal furnaces,

since the switch to the use of sulfur-rich anthracite and coke as fuel, and of a hot-blast in the smelting process, was generally delayed until the 1840s in the United States (Paskoff 1983). Sulfur and phosphorus, at high levels (circa 0.3%), tend to make the refinement of cast iron to wrought iron somewhat difficult, and thereafter make the conversion of the wrought iron to bar stock a time-consuming process, so the low level of those impurities in both the cast and the wrought irons studied here also indicates that the products of the Forge were of quite good quality. And high Cu-contents in one
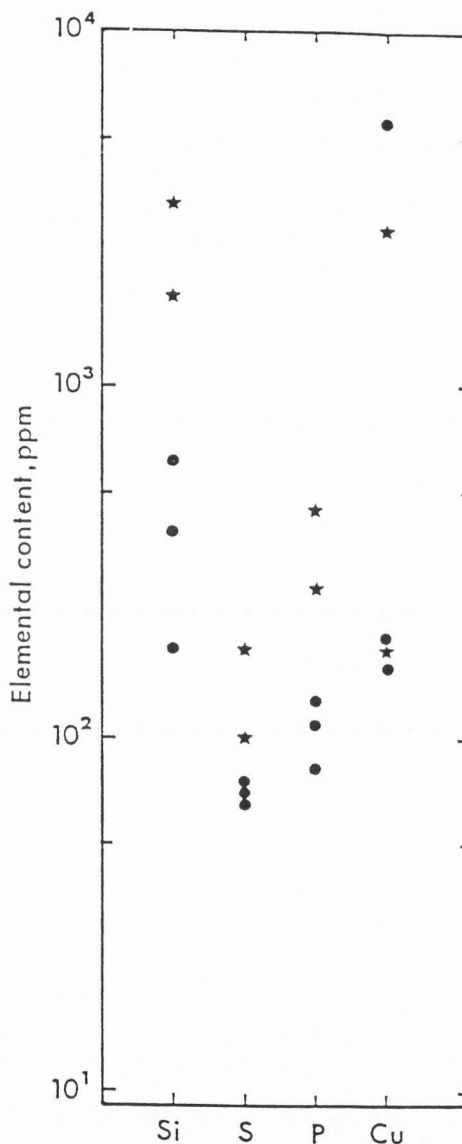

Fig. 3. Concentrations of Si, S, P, and Cu (all plotted on a log. scale) in cast iron (solid stars) and wrought iron (solid circles) artifacts from the Revolutionary Era Upper Forge, at Valley Forge in Pennsylvania. (Data derived from Schenck and Knox 1985: Table 1.)

cast iron pig and one wrought iron (circa 2770 ppm and 5630 ppm, respectively) that were not matched by a similar impurity level in the Andover pig (Cu, circa 180 ppm), suggests that the Upper Forge received some of its stock from another furnace, perhaps the nearby Warwick Furnace which is known to have supplied the Mount Joy Forge both before and after the Revolutionary War. These data, together with detailed metallurgical examination of the wrought irons, have led to the conjecture that the Upper Forge may have been trying to produce steel (Schenck and Knox 1985), something that would give Valley Forge primacy in such technology in the United States by more than three decades.

Gold

Many archaeologists believe that gold, because of the way it catches the eye, was the first metal exploited by man. One can imagine a hunting party many thousands of years ago being attracted to tiny nuggets of gold glistening in the sand of shallow stream beds, or shimmering among the rocks of a rain-washed hillside. A resourceful ancient artisan would soon have realized that gold was nearly indestructible and yet could be cut with a flint blade. When cold it could be hammered into new shapes and to a remarkable thinness without fracture: when heated in a fire, it was even more malleable and could be worked into intricate designs. Thereafter, gold's usage followed two main paths of development, one that established gold as the standard for trading transactions (most obviously with coinage, but assuredly in nugget or bar form for some barter transactions), one that was purely artistic (with delicate repousse manipulation of foil, and a granulated decoration of jewelry surfaces).

Recent PIXE studies of gold coinage include Brazilian reis (Ferreira and Gil 1981) and early Byzantine tremissi and solidi (Demortier et al. 1986); and of decorated gold artifacts include an Iranian pendant, Hellenistic and Roman earrings, a Roman necklace and an early Byzantine phial (Demortier and Hackens 1982; Demortier 1983,1984,1986).

Demortier's research has demonstrated the value of the use of a zinc foil (of thickness, circa 5 mg/cm2) as a selective filter in the study of gold matrices, either for the determination of the general alloy components or in the detection of impurities in solder joints underlying decorative elements. The zinc absorption edge at 9.659 keV is most effective in the suppression of the $L_{\alpha 2}$ and $L_{\alpha 1}$ Au x-rays at 9.626 keV and 9.712 keV, respectively, but also serves to significantly reduce L_β Au x-rays at 11.440 keV and above.

In terms of archaeological application of the PIXE method, we would highlight the detection of as much as 0.1% cadmium impurity in joints used to affix gold granulation in Roman and Byzantine times (Demortier 1984), a situation that suggests the deliberate use of the naturally- occurring cadmium sulfide (greenockite) in the applied solder. For our part, we have studied only the means by which such granulation motifs were applied to Etruscan jewelry (circa 6th century B.C.), and failed to detect either any trace of cadmium or copper (as a survey of Classical texts would have predicted: see Carroll 1981). Subsequently, Follett (1985) has shown that the natural tree-resin, amber, was used as a flux-cum- adhesive for such purposes, rather than an inorganic additive.

Glass and glassy matrices

Man-made glass seems to have evolved from the manufacture of faience, a low-fired mixture comprising primarily crushed quartz coated with a colored alkaline glaze. The production of faience began as early as the 4th millennium B.C., and the same ingredients in slightly different proportions form a true glass if subjected to high enough temperatures. Before the discovery that glass could be blown on the end of a long hollow pipe, various forming techniques were used, including casting and pressing into molds, and carving from solid glass blocks. In the mid-2nd millennium B.C., the Egyptians developed the idea of core-molding, to make small vessels for precious ointments and liquids (Grose 1984). The use of this technique continued to be popular throughout the Old World well after the invention of glass-blowing in Syria during the 1st century B.C. Thereafter, glassmakers found ways to manipulate glass in ever-increasingly sophisticated ways (Forbes 1960), creating exquisite filigree patterns in and around vessels (for which Venetian glass was particularly famed), and optically-remarkable effects such as the dichroism of the late Roman Lycurgus Cup (Harden 1963) and the Bohemian lamination techniques of the 18th century known as Zwischengoldglas (Edwards 1977). The very use of glass as a craft medium also diversified far beyond vessel-making, to include cameo inlays, mosaics, and liturgical stained glass.

Recent applications of the PIXE method to glass include a study of South African 19th century Woodstock wares and their European imitations (Gihwala et al 1984); of pendants and beads from Late Bronze Age burial caves in the Baq'ah Valley of Jordan (McGovern 1986a); of multi- colored vessels from the early Greek settlement of Cyrene in modern Libya (Fleming and Swann 1987a); of cosmetic items and decorative wares from the Islamic cities of Istakhr and Raay (Fleming and Swann 1987b); and of the various colorants used in pendants, beads and vessels from the early Palestinian settlement of Beth Shan (McGovern 1986b; also see below).

For such analysis we have developed three different selective filter arrays. One array comprises no selective filter at all, but the area between the sample's surface and the detector's face is bathed with a stream of helium gas, so that the lower Z elements which are usually the main ingredients of any recipe for glassmaking (e.g., Na, Al, Si, K and Ca) can be precisely determined. The second array comprises 3.8 mg/cm^2 of Al foil, and is used to suppress complex "pile-up" contributions from Si and Ca in the glass matrix, and thereby allow a high sensitivity measurement of Ti, Cr, Mn, and Fe (Fig. 4). A third array comprises a combination of 3.8 mg/cm^2 of Al foil + 15 mg/cm^2 of mica sheet + 7.5 mg/cm^2 of V foil, to generally suppress the Fe x-ray contribution (see Iron
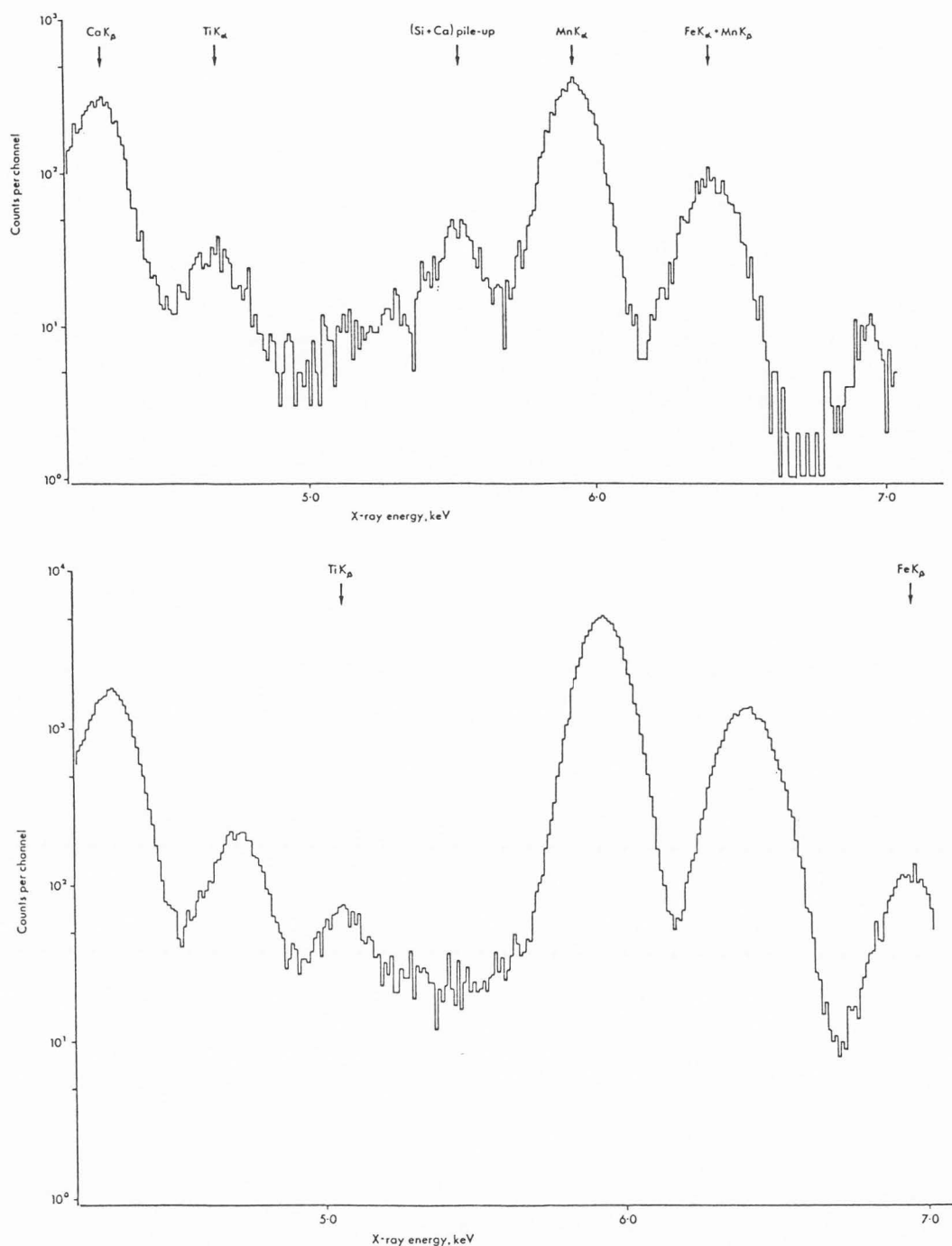
Fig. 4. <u>Upper</u>: The X-ray spectrum obtained during the PIXE analysis of a small brown glass cup from the Islamic site of Rayy, with a proton beam energy of 1.3 MeV and a He gas atmosphere in the gap between the glass's surface and the nylon cap of the detection unit (see Fig. 1).

<u>Lower</u>: As above, but with an Al foil filter (thickness, 3.8 mg/cm^2) slotted into the nylon cap, and with the proton beam intensity raised about a factor of five. Note how this filter arrangement not only eliminates the "pile-up" and "sum peaks" from the intense x-rays of the silicon and calcium constituents of the glass, but also enhances the detection efficiency for the X-ray peaks of several minor and trace elements in this region of the spectrum.

above) and thereby allow a high sensitivity measurement of elements with $Z \geq 26$.

An optional fourth array comprises a combination of 3.8 mg/cm^2 of Al foil + 15 mg/cm^2 of mica sheet + 21 mg/cm^2 of brass foil, to suppress the "pile-up" effects from the Pb x-ray contribution, when the lead content of the artifact is appreciable (i.e., in excess of 4%). The copper and zinc of the brass foil have x-ray absorption edges at 8.979 keV and 9.659 keV, respectively, that are quite effective in the general suppression of the lead L x-rays (including $L_{\alpha 1}$, $L_{\beta 1}$ and $L_{\gamma 1}$, at 10.550 keV, 12.612 keV and 14.762 keV, respectively); and will also eliminate the "sum peak" at 25.224 keV (double Pb $L_{\beta 1}$) that will otherwise obscure the main x-ray peak of tin ($K_{\alpha 1}$, at 25.267 keV).

The detection limits achieved on a routine basis with the Bartol PIXE system for various trace elements in a relatively pure glass matrix (for which only the first two of the filter arrays described above would be deployed) are given in Table 3 (Fleming and Swann 1987a).

Table 3. PIXE detection limits for various trace elements in a relatively pure glass matrix.

Oxide (ppm)*	Detection limit
SO_3	150
TiO_2	44
Cr_2O_3	16
MnO	20
Fe_2O_3	41
CoO	48
NiO	8.0
CuO	7.5
ZnO	8.5
As_2O_3	5.8
Br_2O	3.6
SrO	18
MoO_2	17
Ag_2O	33
SnO	98
Sb_2O_5	122
PbO	7.3
Bi_2O_3	5.2

* Calibration of the system is based in part on a series of glass standards (labelled A through D) circulated some years ago by the Corning Museum of Glass. The glass matrix's composition is assumed to be akin to SiO_2, circa 96%, plus about 1% of the oxide of each usual alkali constituent (Al, Na, Ca and K).

In terms of the archaeological application of the PIXE method, we would highlight our recent study of the silicate industry at the ancient settlement of Beth Shan, located at the juncture of the Jezreel and Jordan Valleys of Palestine. That industry, though it began as an offshoot of Syro-Palestinian glass/frit traditions, was considerably influenced by Egyptian technology, as one might expect, once Beth Shan became an Egyptian garrison in the 13th century B.C.

(McGovern 1986b). For example, Egyptian-type faience, sometimes with overlays of Syro-Palestinian glazes, became much more common there.

Especially significant has been the distinction achieved between colorants used for small items (beads and pendants) and those used for larger vessels. The minor elements associated with the latter's colorants (a combination of lead and tin in calcium antimonate white, cupric blue-green, and manganese-iron brown) also frequently occur in vessel glazes and glasses definitely made in New Kingdom Egypt, implying that the Beth Shan vessels were made there and exported to Palestine. The colorants of the small objects were different and, judging by the amount of manufacturing debris found during excavation (including misshapen and overfired refuse glass and faience, an Egyptian Blue frit cake, and several casting molds), they were probably made at Beth Shan itself.

The necessary raw ingredients for the Beth Shan silicate industry, and many of the metallic ores used in coloration, were readily available in Palestine. However, some colorants were imported, notably a cobalt blue from the oases of the Western Desert of Egypt. The diagnostic trace elements in the small objects at Beth Shan, in this instance, were Ni, Zn and Mn, with their oxides occurring at levels of about 0.7%, 1.2% and 1.2%, respectively, for every percent of cobalt blue additive.

The PIXE method has also proven effective in the study of obsidian. This natural volcanic glass was commonly used and traded by many prehistoric cultures around the world, because it could be quite easily fractured to provide material for a variety of sharply edged tools. As a material, obsidian is a complex alumino-silicate glass comprising principally Na, Al, K, Ca and Fe, minor amounts of Ti and Mn ($\leq 0.2\%$), and a relatively abundant suite of trace elements. Duerden et al (1979) have described the advantages of a novel selective filter for the analysis of such a composition -- specifically, a 2 mm thick graphite absorber with a central 70 μm pinhole in it -- and detection limits of 20 ppm and better have been reported in Bird et al. (1983), for determination of all elements between Ni and Mo (i.e., $28 \leq Z \leq 42$).

Ambrose et al. (1981) and Duerden et al (1984) have made a detailed inventory of the obsidian resources that have been available in the past throughout the southwest Pacific region, and have found evidence for appreciable movement of obsidian as much as 11600 years ago. And at the Balof Cave site on the Melanesian island of New Ireland, it appears that about three thousand years ago, the local people began to make use of obsidian from sources on the Admiralty Islands, some 175 km away to the west. (For the previous four millennia they had exploited only the Talasea source on the nearby island of New Britain.) Such cross-ocean trading implies a significant advance in maritime technology, with the development of sailing vessels that were roomy enough to carry supplies and people, and heavy enough to withstand rough seas. It also implies new navigational skills, since the voyagers will have been out of sight of land for considerable periods of time. Soon thereafter,

these same traders stretched their range to include colonizing excursions to Fiji, Tonga and Samoa, more than four thousand kilometers to the east.

We are currently extending our own PIXE research in glassy materials to cover (i) slags from various metallurgical processes such as the smelting of copper (for which iron oxide ores were often used as a fluxing agent), and the smelting and refining of iron; and (ii) vitreous iron oxide paints and slips used to decorate early Old World pottery. We anticipate that the selective filtering described above for the routine PIXE analysis of iron metal will be effective for these studies as well. Publication of PIXE data in these areas of study have so far been limited to Schenck (1982) for the slag remains from a refining forge at the 19th century site of Catoctin (Maryland), and Gaisser and Swann (1984) for the white slip on pottery from mid-2nd millennium contexts at the Cretan site of Gournia. We are, however, well advanced in similar programs for slags from ancient metal production contexts in the Yemen Republic, Thailand and Peru; for slags and other production debris derived from modern simulations of ancient smelting processes in Peru, and at the colonial American site of Williamsburg (Virginia); and for decorative paints and slips used at neolithic settlement sites in the Solduz Valley of northwestern Iran. We anticipate that all these PIXE data will be published within the next two years.

Other researchers have explored the application of PIXE spectrometry to the provenancing of the clay fabrics of pottery (Gihwala et al. 1984; Ryan et al. 1985; Williams et al.1987). In our opinion this is a problematic area of PIXE research, in part because of the inhomogeneity in pottery fabrics that is inherent in the addition of ware-strengthening temper (which can range from impurity-free quartz sand to chemically-complex volcanic rock fragments), in part because PIXE detection limits for some of the recognised trace elements that "fingerprint" the geochemistry of clays (Ti, Mn, V, etc) are generally poorer than can be achieved by neutron activation analysis (Hancock 1978). There is, however a potential role for the PIXE method in the microbeam mode, for the study of individual inclusions which may be as diagnostic as the main clay fabric, when it comes to defining traditions of manufacture among ancient potters.

Concluding remarks

Archaeology is a very broad discipline, with a time-frame of some 40,000 years, a spatial influence that is literally worldwide, and a material expression that is truly diverse. The reconstruction of the tempo of archaeological change and advance is therefore a slow process, calling for painstaking recording of provenance and the gathering of as much information as possible about how artifacts were made and how resources were exploited at different points in time in the past. In almost all the archaeological applications we have reported here, the primary interest has been to identify optimum conditions for the operation of PIXE equipment, rather than to produce large data bases. As the Bartol PIXE facility now stands, however, with its recently added microbeam capacity (Swann and Fleming 1987), and a microcomputer data-handling system due to be on-line before the end of the year, we foresee that output may well rise to around six hundred artifacts per year. Over the next decade, therefore, we can expect that the statistical footing for the interpretation of PIXE data will become ever firmer, and that the PIXE method will become increasingly the analytical tool of choice in the resolution of archaeological problems.

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Discussion with Reviewers

K. Malmqvist: Which major laboratories carry out ion beam analysis on archaeological artifacts either on a commercial basis, or in scientific cooperation?

Authors: Table VII in Bird et al. (1983, text ref.) provides a listing of such laboratories (together with the materials in which they have specialized) that seems to be reasonably current, with the exception that AERE Harwell is no longer active in this area of application.

K. Malmqvist: Are these techniques applied in museum laboratories?

Authors: No. Those museums which do have scientific research capacity have generally committed themselves to conventional x-ray fluorescence (xrf) spectrometry, largely on grounds of cost, but in part because it requires far less operational space and maintenance expertise than a PIXE system. We regard this as somewhat unfortunate, because the relatively poor detection limits of xrf spectrometry (Hall et al. 1973) generally prevents the acquisition of trace element profiles in anything like the detail described in this paper. The Louvre Museum's plans to install a dedicated PIXE facility in Paris in the near future is an exciting prospect that we wholeheartedly endorse (Lahanier, et al. 1986).

J. L. Campbell: Would you please comment on the homogeneity of the specimen types discussed here, indicate the degree of variability incurred in PIXE data due to inhomogeneity, and indicate any precautionary measures such as multiple analyses that you deem necessary?

Authors: In general terms, when the trace element's concentration in the artifact's matrix is more than three times that element's PIXE detection limit (as defined by several years of practical experience, in certain measurement configurations: see Fleming and Swann 1986), we reckon on a reproducibility of close to $\pm 10\%$ (1σ), for scanned areas of 1 mm^2 or more.

With bronze analysis, we have turned a lack of reproducibility in tin and chlorine to some advantage, as an indicator of the degree of corrosion that the artifact has studied.

The most difficult matrix to deal with is leaded bronze, because lead in a concentration of about 3% or more is immiscible in a copper matrix and tends to form sizeable, randomly scattered globules. Additionally, we would expect some problems with copper ores such as malachite, since they often contain complex microcrystalline mineral suites.

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