

A Marvel of Medieval Indian Metallurgy: Thanjavur's Forge-Welded Iron Cannon

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Figure 1. The historical forge-welded iron cannon at Thanjavur.

In this article, metallurgical aspects of a 17th century forge-welded iron cannon at Thanjavur are addressed, including an analysis of manufacturing methodology based on careful observation of its constructional details. Microstructural examination of iron from the cannon reveals that the iron was extracted from ore by the direct process. Thus, the cannon was fabricated by forge welding and not by casting. Electrochemical polarization studies indicate that the corrosion rate of the cannon iron can be compared to that of 0.05% carbon mild steel under complete immersion conditions. However, the atmospheric corrosion resistance of the cannon is far superior to that of modern steel and can be attributed to the formation of an adherent protective passive film. It is concluded that this cannon constitutes a marvel of medieval Indian metallurgical skill.

INTRODUCTION

The high status of iron and steel technology in ancient and medieval India is reflected in the manufacture

and use of numerous large iron objects, including forge-welded cannons.¹⁻⁴ Such cannon, found at Nurwar, Mushirabad, Dacca (in Bangladesh), Bishnupur, Bijapur, Gulbarga, and Thanjavur, exemplify the medieval Indian blacksmith's skill in the design, engineering, and construction of large forge-welded iron objects. The wrought-iron cannons found in different parts of India were manufactured from individual iron rings that were forge-welded together. Medieval blacksmiths continued to use this technique in the fabrication of small and large iron objects, such as the Delhi and Dhar iron pillars.^{5,6} The forge-welded cannons have not been properly catalogued in the literature, unlike their European counterparts.⁷⁻⁹ The massive cannon at Thanjavur in Tamil Nadu will be discussed in this article.

Based on its weight and size, the cannon (Figure 1) at Thanjavur, earlier known as Thanjai or Tanjore, must be regarded as one of the largest forge-welded iron cannons in the world. According to a recent authoritative history of the ancient city of Thanjavur,¹⁰ the

cannon was manufactured in Thanjavur during the regime of Raghunatha Nayak (1600–1645 A.D.). Thanjavur was by this time a very important center of Hindu architecture (as exemplified by the Brihadiswara Siva Temple), literature (with thousands of palm leaf manuscripts preserved at the library of the Saraswati Mahal Museum at Thanjavur), and metallurgical skill (as shown by the numerous bronze sculptures executed by the lost-wax process). The Thanjavur cannon was forged as a component of a defense barricade that protected the city, then already a few centuries old. The cannon, located at the eastern entrance of the ancient city, is referred to as *Rajagopala*, according to local traditions.

There is no specific recorded history of the cannon. However, a Thanjavur palace novel that describes Nayak's rule mentions the presence in the Thanjavur fort of an object referred to as a "fire-breathing barrel shaped weapon." The cannon is believed to have been constructed in the Manojipatti area of Thanjavur, famous for iron working.¹⁰

Over the last 40 years, there has been a discernible increase in the number of scholars who have focused their research on early industrial organizations, a field of study that has come to be known as Archaeotechnology. Archaeologists have conducted fieldwork geared to the study of ancient technologies in a cultural context and have drawn on the laboratory analyses developed by materials scientists as one portion of their interpretive program. Papers for this department are solicited and/or reviewed by Michael Notis, a professor and director of the Archaeometallurgy Laboratory (www.Lehigh.edu/~inarcmet) at Lehigh University.

(See sidebar for design details.) The gun is still standing at the same location in Thanjavur, facing east. Its location within Thanjavur is now known as beerangi-maedu in Tamil, literally meaning the cannon-mound. The cannon is a protected monument of the Archaeological Survey of India.

CONSTRUCTION

A high level of engineering skill was involved in the construction of this cannon. Some insights on its possible method of manufacture can be obtained from a detailed study of its structural condition, described in the sidebar. Ultrasonic measurements conducted by Roessler³ on the wall of the cannon indicated three layers of rings, each of them about 5 cm thick, which were fitted around each other. The iron rings appear to have been joined by hooping and later by forge welding. Only three ring layers were used to construct the length of the cannon barrel, as evident from the measured diameter of the cannon at the front face and along the gun barrel. The front face, where the three inner iron rings can be discerned, shows the presence of an additional outer ring (see also Figure A) that provided further strengthening. Additional outer rings are also seen at the clamping locations (Figure B). The front view of the cannon further indicates an additional layer of 1.5 cm thick iron strips tightly placed in the inner pipe along the innermost ring. These strips, which progress across the length of the cannon, were bent on the front side of the gun and tightly placed to hold the whole structure together.

Although medieval Indian blacksmiths successfully used casting in the manufacture of intricate bronze objects, available evidence indicates that few practiced iron-casting techniques.¹¹ The blacksmiths' lack of interest in casting was likely due not only to the high temperatures required for casting, but also to their mastery over the forge-welding technique to produce large iron objects. It is certain that the iron cannon was not cast, implying that the cannon is made of wrought iron. The cannon was fabricated by forge welding (i.e., forging together rings of forge-welded iron). Forge welding was also used to join the layers of secondary and

DESIGN

The Thanjavur iron cannon rests on three concrete supports, about 60 cm thick, 120 cm high, and 2.25 m apart from each other. The cannon is a muzzle-loading type, wherein the gunpowder and the projectile object are loaded from the muzzle (i.e., front end). The cannon is 751.5 cm in length from end to mouth, including the 31.5 cm projection at the end of the barrel. The outer and inner diameters of the gun barrel are 93 cm and 63 cm, respectively. All the dimensions in this article are in centimeters. However, the cannon's dimensions are closely related to the inch system of measurement, which was the unit of measure in ancient India.⁶ In this context, the entire length of the cannon is 25 feet and the rear portion is 1 foot long. The inner and outer diameters of the cannon barrel are 25 inches and 37 inches, respectively, with each ring approximately 2 inches thick.

Assuming the hollow cylinder of the cannon barrel to extend to the complete end of the cylindrical barrel (length of 720 cm), the minimum weight of the cannon estimated from the known thickness of the barrel (i.e., 15 cm) is 20.6 t. The size of the solid portion in the rear of the cannon is not known with certainty and therefore, this estimate is a lower-bound value because the solid will add weight to the cannon. The distance from the fuse hole to the end of the barrel is 36 cm. It is reasonable to assume that the fuse hole represents the rear end of the hollow section of the cylindrical barrel, as is usually the case with medieval wrought-iron cannon designs.⁷ Therefore, the rear solid portion of the cannon will add approximately another ton to the estimated weight. Counting the weight of additional supporting external rings, the minimum weight of the cannon is more than 22 t.

The front end of the cannon indicates that 39 iron strips were folded out from inside the cannon. Each strip is about 1.5 cm thick and 5 cm wide. These iron staves continue longitudinally through the length of the inner bore of the barrel. Their purpose appears to have been to provide a smooth inner surface to the cannon barrel. The front end also reveals that concentric layers of iron rings were used to construct the barrel of the cannon. Four concentric rings are clearly visible in the front plane of the cannon barrel. (The iron strips and iron rings are addressed in the construction methodology section of this article.) The complete barrel is made up of three rings, hooped over the iron staves.

A detailed dimensional analysis found that the width of the individual rings along the length of the cannon was not constant. Generally, rings of smaller widths were also located along the length of the cannon. An example from just behind the cannon front face is shown in Figure A. It has been suggested that the smaller rings might have been placed for filling the gaps or for sealing the cannon barrel.³ This may be true for some of the smaller rings. In this regard, it is also important to note the systematic placing of smaller rings between larger rings at two specific locations, just behind the muzzle of the barrel and in the middle of the cannon. In these locations, the smaller rings seem to have been placed in a very calculated manner. Therefore, the design of the cannon required the use of smaller width rings not only to close the gaps between the larger width rings, but also to ensure greater toughness for the barrel.

At periodic intervals along the length of the cannon, additional external rings are on the external surface of the cannon. These raised locations can be noticed in Figure 1. Seven



Figure A. A close-up view of one of the forge-welded joint regions on the outer surface showing that a smaller ring has been used to join the gaps between larger rings. The provision of a handling hole on the smaller ring should also be noted.



Figure B. The rear portion of the barrel showing the additional outer rings provided as three-ring assemblies. These additional ring assemblies would have provided further strengthening to the cannon.

such locations can be identified along the length of the barrel. These additional rings usually are present as three-ring assemblies (see Figure B). At four locations along the length of the cannon (i.e., the first, third, fourth, and sixth three-ring assemblies assuming the first one to be closest to the muzzle), the outer forged central ring, of larger diameter, ends in a 2.5 cm thick plate (Figure C). Each of these four plates is provided with arrangements for holding two handling rings. All but two of the original rings are missing. The rings are 40 cm in diameter and the diameter of the cross section of the ring is 4 cm. These rings were provided to manipulate the cannon's direction and also, possibly, to aid its movement and transportation. Similar iron rings can be noted on the large forge-welded cannons at Mushirabad and Gulbarga.¹ Long iron rods or wooden beams, inserted through these clamp rings, would have aided in positioning of the cannon during its use. The method by which the gun was moved using these clamping rings is not known, but it must have involved lifting by means of either a chain-and-pulley arrangement or manual methods. The former method appears likely given the enormous weight of the cannon. Trunnions (i.e., supporting cylindrical projections on the sides of the cannon) like those usually found on smaller cannons are not provided. Trunnions were used to house the cannon on wheels, thereby aiding its easy transportation. The absence of such a device on the Thanjavur cannon indicates that it was not meant for mobile use.

The rear end (Figure D) is not flat but consists of successively smaller diameter circular iron rings, presumably to provide impact resistance to the rear section of the cannon. A fuse hole of 10 cm diameter, located on top of the cannon near the rear end, was used for ignition of gunpowder. Based on the location of this fuse hole and the measured dimensions of the cannon (i.e., cross-sectional area of 630 mm² and length of 500 mm), Roessler estimated that at least 155 L of gunpowder must have been utilized to fire the cannon.³ However, this estimate is not reliable because Roessler assumed the rear portion of the cannon barrel to be hollow, whereas it is known that the rear end of the cannon up to the location of the fuse hole is solid. The amount of gunpowder that was packed to create the explosion must have depended on the type, number, size, and nature of the projectile material. Therefore, it would not be possible to speculate on the gunpowder volume used to fire this cannon. It is obvious, however, that this must have been quite a significant amount based on the dimensions of the cannon. It is interesting to note that an additional three-ring assembly just behind the fuse hole location (see Figure B) was provided for strengthening and additional impact resistance.

The actual size of the cannon ball fired from this cannon is not known with certainty. Assuming the diameter of the spherical cannon ball to be slightly smaller than the inner diameter of the cannon barrel, the weight of the ball can be estimated as 1,000 kg if made of iron or 300 kg if made of stone.³ The type of balls used, however, is not known. Cannon balls were usually made of iron and not of stone, as recent discoveries of cannon balls in Thanjavur testify. The amount of gunpowder that must have been required to force a 1 t iron cannonball must have been enormous and moreover, the impact from the explosion of such a large amount of gunpowder must have been very severe. Therefore, the cannon ball must have been much smaller than the actual inner diameter of the cannon barrel.



Figure D. The rear of the cannon.



Figure C. Details of one of the handling clamps.

tertiary rings that further strengthened the entire structure. The manufacturing technology of the Thanjavur cannon can therefore be classified under forge welding of pre-forged iron rings, hooped over longitudinally placed iron staves, with correct positioning and alignment. Available evidence and examples from medieval European wrought-iron cannons⁷ indicate that they were divided into two distinct parts—the chamber and the barrel. The function of these parts and, hence, the material and design requirements, are also different. For example, the barrel's main function was to contain the lateral exhaust of the gas (from the explosion of the gunpowder) and, in this process, the projectile was pushed out. The barrel needed to be tough and not deformable. It also needed to possess a smooth inner surface. On the other hand, the chamber was exposed to much higher gas pressures than the barrel due to the exploding gunpowder at the point of ignition. The rear side had to be tightly closed to withstand the gunpowder explosion. Therefore, this part had to be impact resistant.

External observations of the cannon surface indicate that the same type of material (i.e., wrought iron) and manufacturing methodology (i.e., forge welding) was used for the chamber and the barrel. Interestingly, while the wrought-iron cannons were manufactured by separately fabricating the chamber and the barrel and later joining them together, the cast guns were fabricated as one piece. The manufacturing methodology of the barrel can be deduced from the appearance of the barrel. However, the manufacturing method for the chamber is not known with certainty and the proposals presented here are based only on the features clearly evident on the cannon surface.

The solid part of the cannon, from the extreme rear end to the fuse hole, could have been built using forged iron plates or rings over a cylindrical central solid iron shaft. Some details of the methodology can be gleaned from the appearance of the rear portion of the cannon (Figure D). It appears that iron rings were forge welded over a solid cylindrical shaft that made the rear portion. The solid cylinder's outline can

be seen in the extreme rear section of the cannon. The depth of the hollow slot of the cannon could not be determined for want of a sufficiently long pole. However, based on the design of the forge-welded-iron cannon at Bishnupur¹² and also based on the design of cannons in general, the solid portion of the rear of the cannon should extend up to the fuse hole location. This portion appears to have been constructed of rings that were successively forged over each other. It appears that the medieval engineers were familiar with the idea of structural design for improved fracture toughness because the solid structure created with successively larger diameter rings would have possessed a better impact resistance compared to a single solid piece of wrought iron. The solid rear portion of the cannon was constructed by forge welding iron rings of different diameters over a central solid cylindrical shaft.

The barrel must have been fabricated separately from the chamber. Initially, the long iron strips were placed on a mandrel in order to provide it support and to aid manufacturing operations that followed. Pre-fabricated iron rings were expanded and then shrunk fit over the long iron strips. The rings of the first layer were brought from the front end. After the first layer was forge welded, the other two layers were subsequently built up. Roessler suggested that after the rings of the first layer were forged welded, the rings in the second layer were positioned in such a manner that the middle of each ring closed the gap between the rings of the first layer.

Similarly, the rings of the outermost layer were proposed to close the gaps in the second layer. This hypothesis has to be verified by careful non-destructive studies. Once the barrel had been fabricated, the protruding iron strips on the front face were folded up. The protruding iron strips at the rear end must have been connected at appropriate locations to the solid cannon rear section, and the complete cannon realized. The chamber and the barrel must have been joined using the protruding longitudinal staves of the barrel and by strengthening this joint area externally with additional rings.

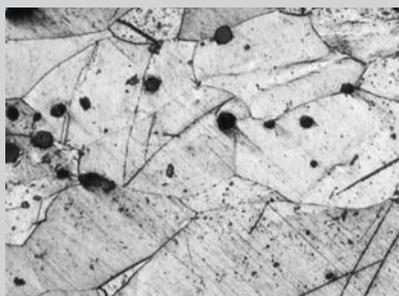
The total number of rings counted on the cylinder barrel surface is 95, with six rings visible in the rear end. Three rings are found across the thickness of the barrel, while the number in the solid rear portion is not known. Therefore, there is a minimum number of 291 iron rings used in the construction of the cannon. It is important to realize that the iron rings had to be engineered to exact dimensions to allow for expansion and shrinkage on heating and cooling while the rings were laid on each other to form the final three-layer structure over the strips.

The method by which the entire cannon was handled during its manufacture is not known, but the method must have been ingenious because of the additional complications due to the high temperatures involved in the forge-welding operation. The cannon must have been handled with an arrangement similar to that utilizing the iron handling rings. A careful non-destructive study

will offer further insights into the manufacturing methodology, especially in the rear solid portion of the cannon. Interestingly, iron cannons were also manufactured by forging together round, solid pancakes of iron and later punching out holes in the center using chisels.¹¹ There is mention of iron cannons fabricated in this manner in North India during the reign of Akbar (1556–1605 A.D.).¹¹

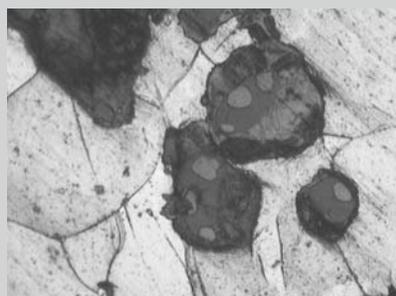
MATERIAL CHARACTERIZATION

An extremely small iron sample was extracted from the plate, at the first clamping location, for analysis. It was used for all the scientific studies reported here. The chemical composition of the iron, determined by a Jobin Yvon JY-38S inductively coupled plasma atomic emission spectrometer, is 93.4 wt.% Fe, 0.01 Cr, 0.003 Al, 0.026 Ni, 0.003 Mo, 0.042 P, and 0.411 C. A separate analysis found the carbon content to be 0.419%, while a separate analysis for sulfur content revealed that it was less than 500 ppm. The low amount of phosphorous at this location is not typical of ancient and medieval irons,^{5,6} because limestone was not added in the charge of bloomery furnaces and therefore, a higher amount of phosphorous was retained in the metal at the time.¹³ The unusually low phosphorous content could be due to a lower amount of phosphorous in the particular sample that was analyzed. Metallographic investigations revealed that the iron sample extracted contained a relatively high slag volume fraction and this could



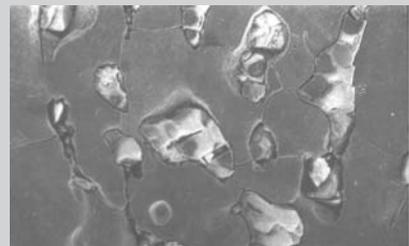
a

200 μ m



b

200 μ m



c

10 μ m

Figure 2. (a) and (b) Optical micrographs showing slag inclusions in ferrite matrix, and (c) a SEM micrograph showing the same features.

Table I. Parameters Measured from Tafel Extrapolation Studies

Material	pH	β_a (V/dec)	β_c (V/dec)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	$\mu\text{m}/\text{y}$
Thanjavur iron	7.62	0.110	0.146	0.129	1.499
Thanjavur iron DDW*	7.00	0.223	0.210	0.244	2.827
0.05% C steel	7.62	0.237	0.075	0.346	4.010

* DDW indicates double-distilled water.

be one reason for the lower amount of phosphorous. The microsegregation of phosphorous in archaeological iron is quite different from macrosegregation that is observed in modern iron- and steel-making practices. The microsegregation is strongly influenced by the presence of entrapped slag inclusions and also by high-temperature metallurgical phase transformations.¹⁴ Another reason for the low phosphorous (and the relatively high carbon) could be the deliberate heat treatment (by carburization) of the iron used in the location from where the sample was obtained. Metallographic investigations, to be discussed in the following, did not reveal any deliberate carburized structure. Therefore, some of the carbon in this analysis may have arisen from entrapped cinder in the iron sample.

The total elemental composition added up to 93.895 wt.%, thereby indicating that the remainder of the material used for the chemical analysis must have been the entrapped slag inclusions. The presence of those inclusions was verified by volume fraction analysis using an optical microscope (Figure 2a and b). These inclusions were not uniformly distributed. At some locations, there was a much larger fraction of these inclusions compared to other locations (Figure 2c). In addition to their distribution inside the ferrite grains, slag inclusions were also observed to coat some of the grain boundaries. The grain size of the sample was not uniform. These observations coincide with the general characteristics of ancient Indian irons.^{5,6} The volume fraction of the entrapped inclusions was determined by the grid intercept method, based on a large number of fields of view. The volume fraction of entrapped slag was found to be 6.07%, slightly greater than the 2–4 vol.% slag inclusions generally observed in ancient Indian

irons. Microstructural analysis revealed that the material of construction was not a cast structure, thereby firmly verifying that the cannon was manufactured by forge welding of wrought iron and not by casting.

ELECTROCHEMICAL CHARACTERIZATION

In order to conduct electrochemical studies, the iron sample from the Thanjavur cannon was mounted, with an electrical connection on the backside. The surface area exposed for electrochemical studies was precisely maintained by a protective layer coating at the edges. Microstructural analysis of the area exposed for electrochemical studies indicated that the volume fraction of slag inclusions at this location was low. The same sample was used for all electrochemical experiments, with the surface prepared to 4/0 emery paper finish before every experiment. The sample surface was also thoroughly cleaned and degreased before each electrochemical experiment. Electrochemical polarization studies were conducted in double-distilled water containing 0.005 M Na_2SO_4 (to aid

solution conductivity) of pH 7.00 and a borate-buffered solution (0.01 M KNO_3 , 0.5 M H_3BO_3 , and 0.05 M $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$) of pH 7.62. For comparison purposes, a 0.05% C mild steel (the composition determined by wet chemical analysis was found to be 0.062 wt.% C, 0.005 Si, 0.006 P, 0.02 Ni, 0.004 Co, 0.185 Mn, 0.042 Cr, 0.005 Mo, 0.024 Cu, 0.0007 Ti, 0.032 Al, and 0.012 S) was also investigated. The electrochemical studies were conducted on a Model 263A EG&G Princeton Applied Research potentiostat. A round-bottom electrochemical cell was used for the studies, with a saturated calomel electrode (+0.242 volts versus standard hydrogen electrode) as the reference electrode and graphite as the auxiliary electrode. All the polarization experiments were performed after stabilization of free corrosion potential.

The potentiodynamic polarization behavior of the Thanjavur cannon iron has been compared with that of mild steel in Figure 3. Both the irons exhibited active behavior in pH 7.00 solution and stable passive behavior in the pH 7.62 solution. The polarization behavior of the irons was comparable. The breakdown potential for both the samples in the borate-buffered solution was similar, thereby indicating that the slag inclusions did not affect passive film breakdown. The corrosion rates were determined by the Tafel extrapolation method as per ASTM standards. The results are tabulated in Table I. The corrosion rates of the ancient and modern irons were comparable and of the same order of magnitude.

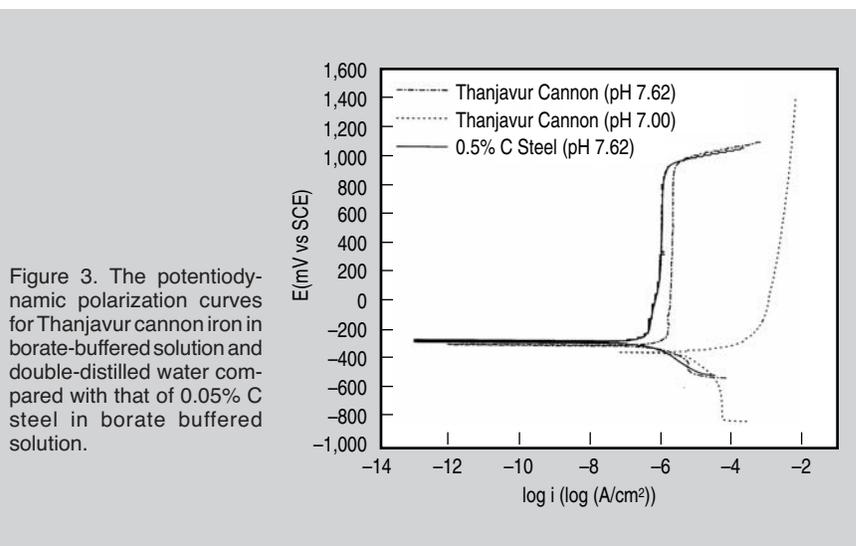


Figure 3. The potentiodynamic polarization curves for Thanjavur cannon iron in borate-buffered solution and double-distilled water compared with that of 0.05% C steel in borate buffered solution.

Table II. Identification of Major and Minor Phases from μ XRD Analysis at the Locations Analyzed

Distance from Environment Interface (μm)	Pattern Reference No.	Major Phases	Minor Phases
		140	TG05
120	TG06	Goethite, magnetite	Lepidocrocite, akaganeite
100	TG13	Goethite, magnetite	Lepidocrocite, akaganeite
50	TG12	Goethite, magnetite, lepidocrocite	Akaganeite

Rust thickness can be predicted from atmospheric corrosion rates of iron in several environments:¹⁵ 4–45 $\mu\text{m}/\text{y}$ in rural environments, 26–104 $\mu\text{m}/\text{y}$ marine, 23–71 $\mu\text{m}/\text{y}$ urban, and 26–175 $\mu\text{m}/\text{y}$ industrial. Assuming the Thanjavur weather to be rural, the estimated corrosion product layer over 350 y should be between 2,800 μm and 31,500 μm . Utilizing the corrosion rate measured in the polarization testing of immersed sample, the total approximate corrosion suffered by the Thanjavur cannon iron must be 350 y \times 2 $\mu\text{m}/\text{y}$ = 700 μm . When converted to rust, it should have resulted in a rust thickness of 1,400 μm . This has certainly not been the case because the Thanjavur cannon does not show any evidence of significant rusting (Figure 1). Measurement of the rust thickness at one location by cross-sectional microscopy indicated a maximum thickness of about 140 μm . As the surface was not significantly corroded, the surface apparently was protected against atmospheric corrosion by a protective passive film. Further ideas about the atmospheric rust nature were, therefore, obtained by rust characterization studies.

RUST CHARACTERIZATION

Samples of atmospheric rust were scraped out from the atmosphere side of the Thanjavur cannon. This rust was used to identify the constituents of the atmospheric rust by x-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). Fourier transform infrared spectroscopy is a powerful technique to identify the iron oxides and oxyhydroxides, even if they are present in the amorphous form. Therefore, analysis of any rust in general by XRD would provide information about the crystalline phases, while the FTIR spectroscopy, in addition to confirming

the results of the XRD analysis, would also provide information about the amorphous phases. The presence of lepidocrocite ($\gamma\text{-FeOOH}$), goethite ($\alpha\text{-FeOOH}$), magnetite ($\text{Fe}_{3-x}\text{O}_4$), and $\delta\text{-FeOOH}$ is confirmed by peaks in the FTIR spectrum at 1,104.10 cm^{-1} and 797.38 cm^{-1} ($\gamma\text{-FeOOH}$), 887.72 cm^{-1} ($\alpha\text{-FeOOH}$), 559.05 cm^{-1} (magnetite), and 455.01 cm^{-1} ($\delta\text{-FeOOH}$).¹⁶ The spectrum shows a shoulder broadening at 1,000–1,200 cm^{-1} , which may be attributable to the presence of ionic phosphates.^{16,17}

The XRD pattern obtained from the rust on Thanjavur cannon iron was compared with the JCPDF database using the *Diffra+* program. Sharp diffraction peaks were not observed from iron oxyhydroxide and oxide phases, presumably due to the low thickness of the surface oxide. Some phases identified were lepidocrocite,

iron phosphate, and magnetite.

Microdiffraction (μXRD), which is XRD analysis performed on small samples or small areas of large samples, is the technique of choice when samples are too small for optics in conventional diffraction instruments. A microbeam is used as an x-ray probe so that diffraction characteristics can be mapped as a function of sample position. With the ability to accurately and precisely position the x-ray beam on a sample surface, the information can be plotted as a diffraction function map. Diffraction data can contain information about compound identification, crystallite orientation (texture), stress, crystallinity, and crystallite size. In this regard, the unique features of synchrotron radiation renders possible the investigation of materials in a way not feasible with conventional instrumentation. In particular, wavelength tunability gives control over penetration depth as well as for spectroscopy measurements. Microdiffraction experiments were performed at several different locations in one area of the Thanjavur cannon rust. The μXRD experiments were conducted on the D15 beamline at Laboratoire pour l'Utilisation du Rayonnement Electromagnetique at Orsay, France. The entire experimental procedure is outlined elsewhere.¹⁸ Photons centered around 14 keV ($\lambda = 0.8857 \text{ \AA}$) were

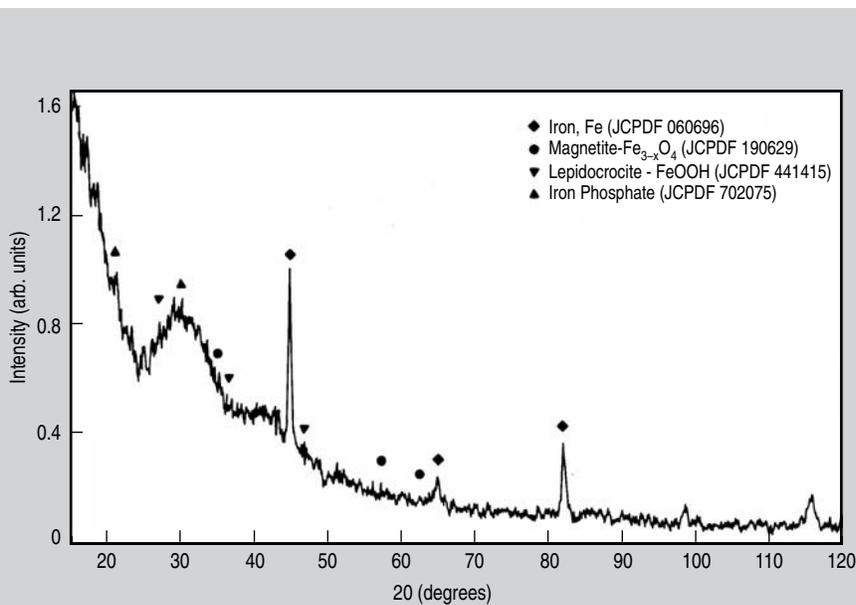


Figure 4. An x-ray diffraction pattern from rust, confirming the presence of lepidocrocite, goethite, and magnetite.

focused down to a $10\mu\text{m}^2 \times 10\mu\text{m}^2$ beam. The diffraction patterns were collected with an image plate downstream from the sample. One-dimensional diffraction patterns were obtained by circularly integrating diffraction rings using the *FIT2D* software developed at the European Synchrotron Radiation Facility. The spectra were compared with the JCPDF database using the *Diffra+* program.

The rust was approximately $150\mu\text{m}$ thick at the location investigated. The μXRD patterns were analyzed and the results of the analysis are provided in Table II. The major phases identified in this pattern have been indexed. Notice that the inner region of the rust is primarily composed of magnetite and goethite while lepidocrocite appears as a major phase only toward the rust-environment interface. The identification of akagaenite ($\beta\text{-FeOOH}$), which forms in the presence of chloride ions, indicates some chloride has been present in the environment, either from local sources or from the ocean (which is situated about 50 km east of Thanjavur). Phosphates were not identified in the rust location studied by μXRD and this must be related to the low phosphorous content in the iron matrix underneath, as revealed by the compositional analysis. However, the color of the surface of the cannon is quite indicative of the enrichment of phosphorous in the atmospheric rust of the cannon. The

phosphorous content in rusts on ancient Indian iron generally follows the mesoscopic variation of phosphorous contents in the iron matrix.¹⁹

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