Chemistry reveals the secrets of the Terracotta Army.

As the sun rose over the fields of Xi'an, Shaanxi Province on the morning of 29th March 1974, a group of farmers set off for another day's toil unaware of the astounding discovery they were about to make. There had been reports of fragments of terracotta figures in the past but as the farmers dug a water-well they uncovered one the greatest archaeological sites in the world.

One can only imagine the consternation, intrigue and bemusement that the farmers must have felt after removing about 5m of the loess sediment that had accumulated over the past two millennia. This soil had held its secret for thousands of years but it was now going to be revealed to the world. Peering into the gloom, faces could be seen staring back as a few of the estimated 7000 terracotta warriors emerged from the necropolis.

Fast forward nearly 40 years and the Terracotta Army of Xi'an is world famous with sell out tours attracting more fans than a One Direction concert. The Terracotta Army is, in fact, just one part of a much larger mausoleum built for Qin Shihuangdi, the First Emperor of China (259-210 BC). Ascending to the throne at the age of thirteen, the emperor commissioned its construction and it was largely completed by the time of his death. In less than 40 years, a colossal funerary space was created that covers about 56km^2. It includes a funerary pyramid, various pits with life-sized servants, acrobats and musicians, water channels with delicate bronze birds, bronze carriages fitted with gold and silver implements and lavishly decorated with polychrome pigments. Thousands of workers were involved in the construction of the site. The main burial chamber, for example, involved digging down to a depth of 30-40 m, diverting water courses and arranging a huge number of burial goods before covering all of this with a pyramid of over 80 m in height. The workforce was drawn from all over the empire and it included criminals recruited as forced labour. It is even possible that these were killed after completion of the work since many are buried in a cemetery near the emperor's burial chamber. The famous terracotta warriors are distributed in three pits at the eastern end of the complex and are thought to be there to protect the emperor in his afterlife (see Fig 1.). Excavation of the largest of these pits (Pit 1) has so far recovered over a thousand ceramic warriors in battle formation and eight chariots pulled by horses.

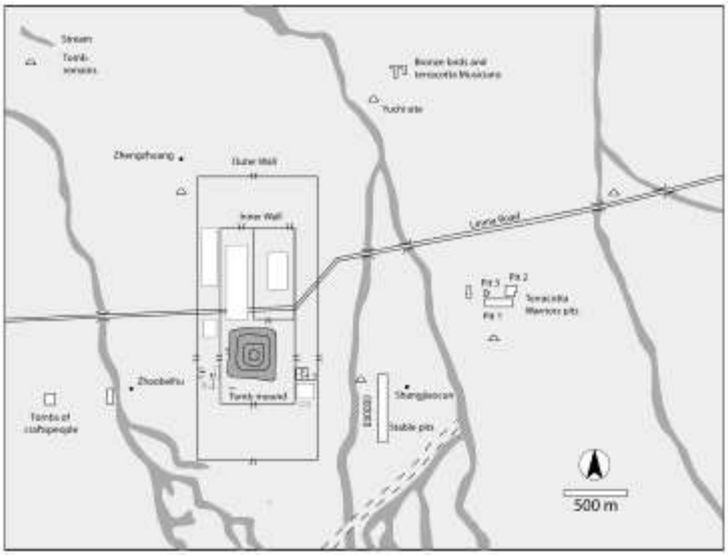

Fig. 1. Site plan of the First Emperor's Mausoleum showing the location of the emperor's tomb towards the centre, the Terracotta Army to the east, and other elements of the complex (original figure from[1] ©Imperial Logistics Project).

The wealth of knowledge that we now have about this site is down to the diligent work of many scholars over the past forty years. Through painstaking recording and investigation much has been determined but in more recent years archaeologists have turned to chemistry to help provide new evidence about the construction of the Terracotta Army.

A joint team from the UCL Institute of Archaeology in London and the Emperor Qin Shihuang's Mausoleum Site Museum has been studying the organisation and construction of this vast enterprise[1,2,3,4]. Led by Dr Marcos Martinón-Torres (UCL), the Imperial Logistics Project brings together specialists from several different fields in order to open up entirely new insights into the warriors and their world by combining close typological study, materials science and spatial analysis.

Their latest results focus on investigating the logistics of technology and labour organisation behind the construction of the Terracotta Army and its bronze weaponry. Each of the individually crafted warriors was fully equipped with state of the art bronze weapons. Over 40,000 arrowheads (most bundled in groups of 100 and placed into quivers) have been excavated as well as hundreds of crossbow triggers, swords, lances, spears and honour weapons. Detailed measurement and scrutiny of the crossbow triggers identified very subtly different subgroups in the collection, which suggested the existence of different casting moulds and workshops. With the arrowheads, however, the degree of standardisation was too high to provide a similar indication so the research team turned to chemical analysis to investigate the elemental composition of the artefacts. The use of a portable X-ray fluorescence spectrometer (pXRF) allowed the researchers to perform chemical analyses on a large number of artefacts quickly, inexpensively and without removing them from the museum. All the major elements present in pre-modern copper alloys have relatively high atomic numbers and can, in principle, be accurately quantified by pXRF even if the analyses are not carried out in vacuum.

X-ray fluorescence spectrometry works by bombarding the material of interest with short wavelength X-rays resulting in ionisation of the component atoms. The X-rays are sufficiently energetic to expel electrons from the inner orbitals of an atom and the electronic structure becomes unstable. Electrons "fall" into the lower energy levels and energy is released as X-ray fluorescence. The energy of this X-ray is equal to the difference between the orbitals involved and is therefore characteristic of the atoms present (see Fig. 2), while its intensity is relative to the abundance of that particular element in the sample.

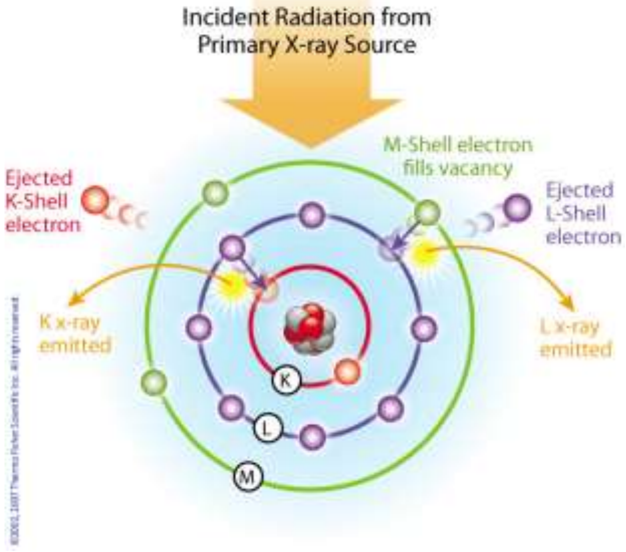

Fig. 2. Diagrammatic representation of X-ray fluorescence spectroscopy.

It was uncertain, however, whether the material would produce meaningful results given that mild corrosion and contamination by soil deposits on the surface of the arrowheads has occurred since they were manufactured. This sampling uncertainty means that the results could not be considered as fully representative of the overall composition. There was, however, no alternative as it would be unacceptable to damage the artefacts in any way to reveal the original metal underneath.

Despite this limitation, when the results were analysed some interesting observations were made. When the lead and tin contents of the arrowheads were plotted as a scatterplot, each bundle was found to form a relatively tight cluster that is marginally different to the others (see Fig. 3). The same pattern was observed for the tangs (the part behind the arrow that extends into the shaft), and the presence or absence of metal impurities such as antimony and arsenic was generally consistent within bundles. Furthermore, the team analysed 20 arrows from a single bundle, differentiating between better preserved arrows and those that were more corroded. The best preserved examples showed a much closer chemical clustering, whereas the more corroded ones scattered more widely and showed higher lead and tin levels. This suggested that the degree of chemical similarity between arrows in a bundle was even higher than that detected by pXRF.

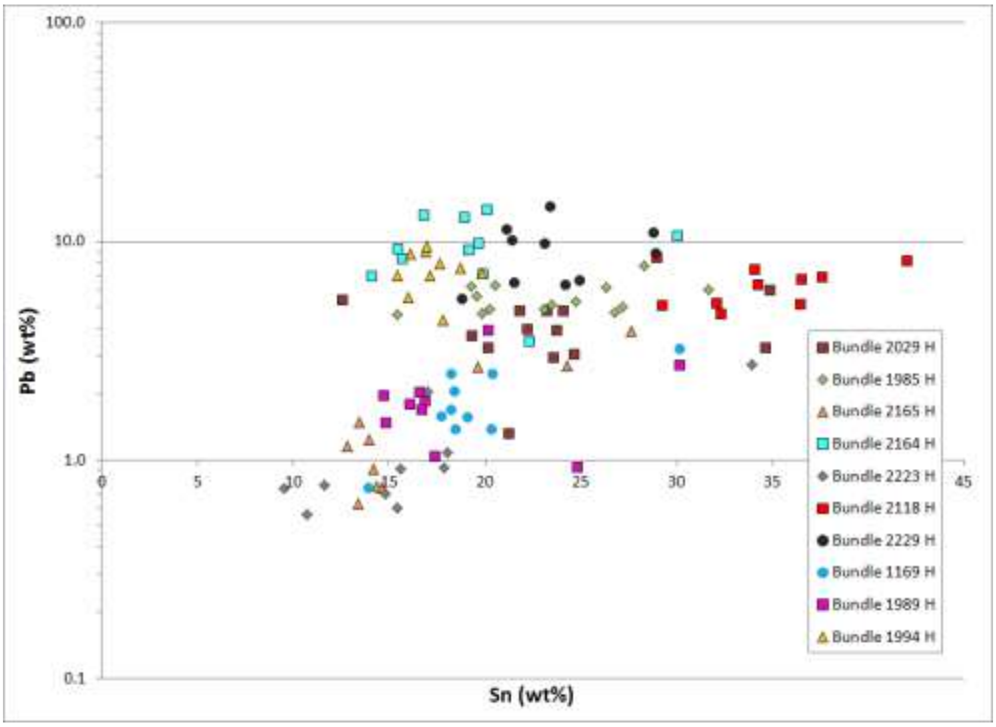

Fig. 3. Scatterplot of the lead and tin values of a sample of arrowheads, discriminated by bundle (results from [1] ©Imperial Logistics Project). Note how different bundles tend to aggregate in different areas of the graph.

Based on these results the research team suggest that each bundle represented an individual metal batch, probably cast from a single crucible, and each set of tangs would constitute another batch. Therefore, bundles would leave the workshop as a finished item and were not mixed with any others. It suggests that relatively small, specialised groups of workers would have cast 100 arrowhead and tangs and immediately proceeded to finish and assemble them with the wooden shaft and feathers, and possibly place them in a quiver, before casting the next two batches.

Furthermore, comparison of the arrowheads and the tangs revealed that, with very few exceptions, the heads have a higher tin content than the tangs (see Fig. 4). High tin bronzes are very hard and can be polished to a sharp finish, increasing the penetration power of the arrow but at the expense of higher brittleness. The tangs, on the other hand, were made of a lower tin bronze and are tougher and less likely to fracture when inserted into the bamboo shaft. This may also allow for a certain degree of flexibility for its oscillation during the arrow's flight. The implication is, therefore, that the weapon makers consciously optimised the composition of the alloys for the different functions of the various arrow parts. It is likely that the copper, tin (and probably lead) entered the workshops as relatively pure metals to be mixed in the preferred proportions by the weapon makers. Adding more tin to the melting crucibles when they were going to cast arrowheads, for example.

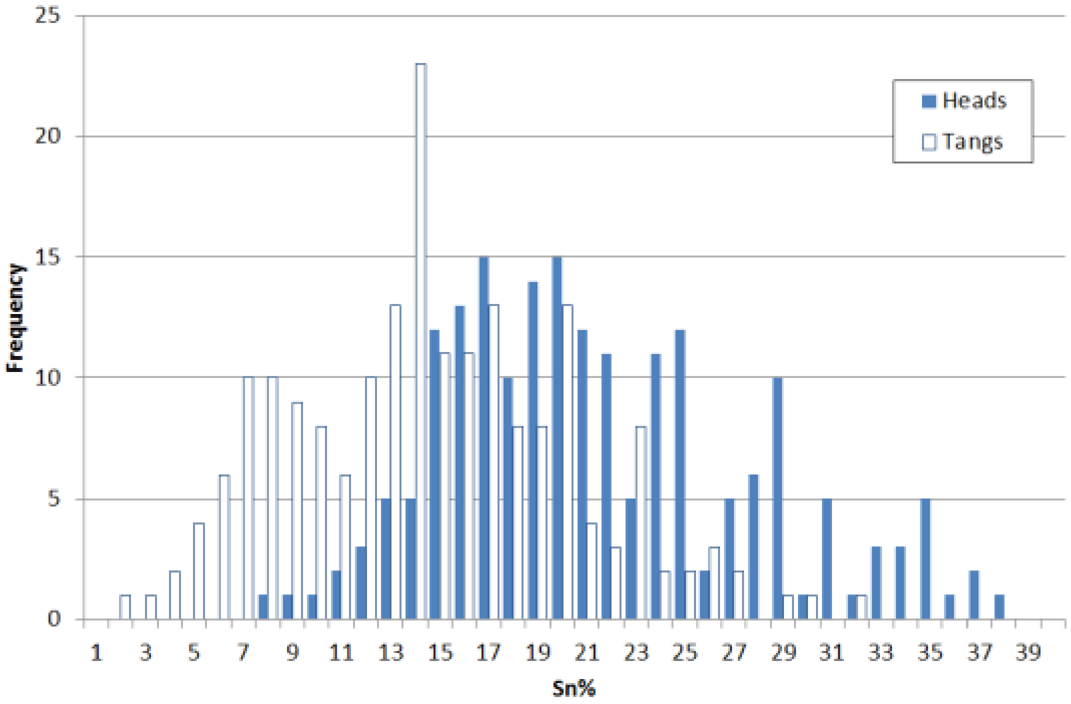

Fig. 4. Frequency distribution histogram comparing the tin levels in tangs and heads of all the arrows analysed (results from [1] ©Imperial Logistics Project)

Once the arrowhead had been cast it then it had to be polished and finished. The researchers used vinyl polysiloxane material (as used by dentists for denture impressions) to obtain precise moulds of the weapons' surface. Under the scanning electron microscope (SEM), these rubber impressions displayed densely packed, extremely fine and perfectly parallel, grinding and polishing marks (Fig. 5). Such features are diagnostic of the use of rotary mechanical devices for the painstaking polishing that ensured the sheen and sharpness of the weapons – the earliest evidence of the use of lathe for polishing on an industrial scale.

Fig. 5. A bronze lance from the Terracotta Army, with (inset) SEM image of a silicon rubber impression taken on a lance blade, showing the fine polishing marks (original image from [2] ©Imperial Logistics Project).

In terms of the production methods used, the researchers state that this evidence suggests a cellular production system rather than a continuous production and assembly line. If the arrows had been constructed via an assembly line structured around highly specialised units, each producing one part, then it would have been much more likely that different metal batches would be mixed up among various bundles. Instead, in a cellular production model, smaller but more versatile production units function in parallel and semi-autonomously, each with all the skills and resources they need to produce complete, multi-component items such as arrow bundles. Most likely, these versatile cells could produce different finished weapons as and when needed, adapting their output to the progress of the construction of the Terracotta Army.

The modern parallel to this form of production can be seen in the car industry. The moving assembly line was made famous by Henry Ford and it was utilised to ensure low production costs, high productivity and consistent standards. On the other hand, Toyota has utilised cellular production since the 1970s. Cars are manufactured by smaller production units when demand is in place reducing storage costs and overstocking (a production strategy known as “just in time”). In terms of its basic principle and potential advantages, the organisation of labour for the production of the Terracotta army is thought to be closer to Toyotism than Fordism.

The fascinating aspect to these latest results of chemical analysis is that the production of this vast army was undertaken with the highest levels of production standards and weaponry was manufactured that was not simply a funerary offering but was fully capable of lethal use. Martinón-Torres said: “We always talk about chemistry as something helping us shape the future. Here we show that the use of chemistry to understand the past can be very rewarding too. A combination of chemistry, geography and computing, together with more traditional archaeological methods, is allowing fascinating insight into the logistical organisation of the first Chinese empire. Hopefully our work will appeal to students of both humanities and sciences, and it will persuade them that speaking of ‘interdisciplinary research’ is not redundant today, as there is simply no other way of doing research.” It remains to be seen how chemical techniques can be used in the years to come to reveal yet more about the Terracotta Army and the thousands of workers that constructed it over 2000 years ago.

References

[1] Martinón-Torres, M., Li, X. J., Bevan, A., Xia, Y., Zhao, K., & Rehren, T. (in press). Forty thousand arms for a single emperor: from chemical data to the labor organization behind the bronze arrows of the Terracotta Army. Journal of Archaeological Method and Theory, early view available online.

[2] Martinón-Torres, M., Li, X. J., Bevan, A., Xia, Y., Kun, Z., & Rehren, T. (2011). Making weapons for the Terracotta Army. Archaeology International, 13, 65-75.

[3] Li, X. J., Martinón-Torres, M., Meeks, N. D., Xia, Y., & Zhao, K. (2011). Inscriptions, filing, grinding and polishing marks on the bronze weapons from the Qin Terracotta Army in China. Journal of Archaeological Science 38, 492-501.

[4] Li, X. J., Bevan, A., Martinón-Torres, M., Rehren, Th., Cao, W., Xia, Y., & Zhao, K. (in press). Crossbows and imperial craft organisation: the bronze triggers of China’s Terracotta Army. Antiquity.

By Simon Rees October 2013