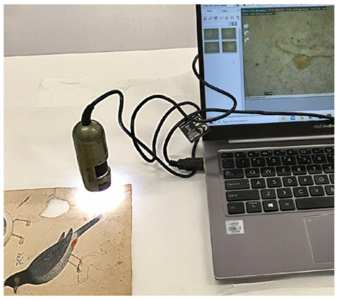
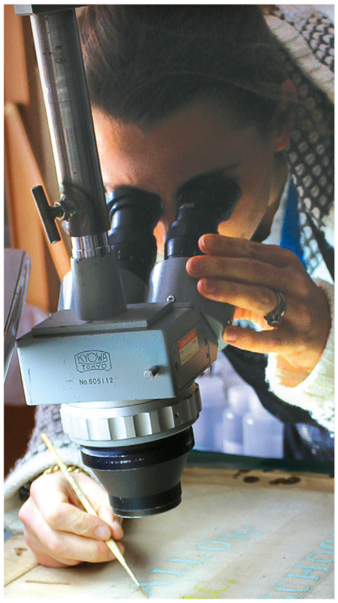
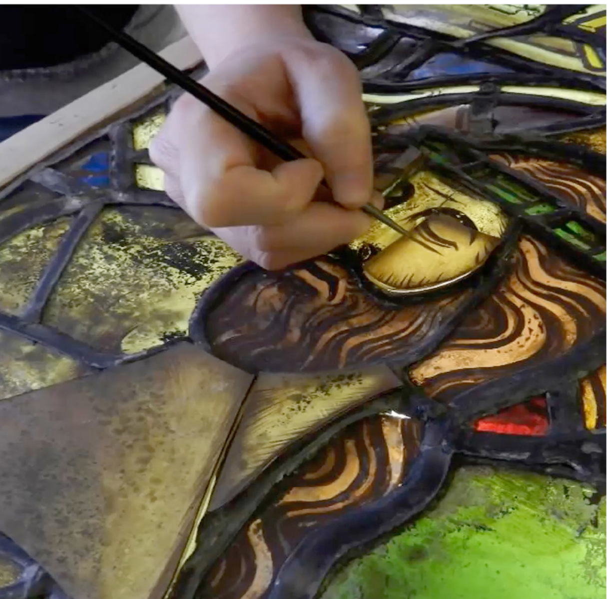
CONSERVATION INSIGHTS 2020

Lectures







INTACH

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Contents

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Indian Metallurgical Heritage and Archaeometallurgical Approaches

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She is a Fellow of the Royal Asiatic Society of Great Britain and World Academy of Art and Science. She is a recipient of Dr. Kalpana Chawla Young Women Scientist Award 2011, Indian Institute of Metals, Certificate of Excellence 2007, Materials Research Society of India Medal 2006, Malti B. Nagar Ethnoarchaeology Award 2005, DST-SERC Nurture Award and Young Scientist Fellowship, Materials Research Society USA Graduate Student Award 1996 and Flinders Petrie Medal 1989 from University of London. She has been co-recipient with Exeter University of awards from British Council (UKEIRI I & II), Royal Society-DST and AHRC schemes. She was Forbes Research Associate at Department of Scientific Research and Conservation, Freer Gallery of Art, Smithsonian Institution, USA in 1999 and Homi Bhabha Fellow at Indian Institute of Science, Bangalore from 1996-8.8.

Introduction

Archaeometallurgy pertains to the technological study of metallic archaeological artefacts and art objects to gain insights into the manufacturing techniques and history of technology and to also the provenance and sources of metal which could help in their classification. Archaeometallurgy is increasing becoming a widely inclusive discipline of archaeology which attempt to trace the history of ancient metal production, distribution and usage in antiquity and the related socio-cultural and economic ramifications (Srinivasan 1996, Srinivasan 2017). Metals have played a crucial role ever since post-Neolithic societies being used progressively through the Copper Ages, Bronze Ages and Iron Ages across different regions. The early metals to be exploited were those which were found in the native state, followed by those which could be smelted or reduced easily from ores, while those which were more difficult to smelt were discovered last. The commonly used metals in antiquity include gold, silver, copper, iron, tin, lead, zinc and mercury (Srinivasan and Ranganathan 1997). Many modern developments in metallurgy draw from in ancient practices that pre-date the Industrial Revolution. The earliest usage of copper seems be around the 8th millennium BCE in Turkey or Anatolia (Rehren and Pernicka 2008). The use of non-ferrous metals is seen in the river valley cultures of Mesopotamia, Egypt; and also the coeval Harappan civilisation of the Indian subcontinent (*c.* 2500 BCE) (Possehl and Rissman 1992, Kenoyer 1998).

The trajectory of some of the metals used in antiquity is traced in this paper with some archaeometallurgical insights, field studies and technical investigations by the author, particularly from southern India. Various techniques of scientific examination find increasing use in archaeometallurgical and archaeometric study, including microscopy, spectro-chemical and elemental analysis, x-ray fluorescence and others. Investigations of archaeometallurgical debris such as slags, crucible and furnace remnants can be made using SEM-EDAX, EPMA-WDS and so on. Lead isotope ratio analysis can be a useful technique for identifying the source of lead alloyed in an artefact since the lead isotope ratios remain unchanged through smelting processes (Srinivasan 1999a), which has been attempted by the author on some artefacts as reported here.

The use of native copper, tin bronze and arsenical bronze was known in antiquity. Copper alloys come into vogue in the Bronze Age civilisations in Egypt, Mesopotamia and the Indus Valley as well as in China. The making of statuary figurines in received an impetus in the Indian subcontinent following the Hellenistic incursions in northwest India. Metal icons of bronze and brass, including gilt images, were cast of Buddhist, Jaina and Hindu affiliations especially from about the 5th century CE in different parts of the subcontinent with ramifications in East Asia and Southeast Asia. The making of metal icons for processional worship by the lost wax process still continues in parts of Thanjavur district in southern India, harking back to the great medieval Chola bronzes such as the celebrated Nataraja bronze. Although there are often problems in making stylistic attributions for south Indian bronzes due to longstanding continuing traditions, archaeometric techniques are useful in the classification of metal artefacts apart from gaining insights into history of technology (Srinivasan 1996, 1999a, 2016a-f).

Gold in antiquity

The noble metal of gold is found in nature in the native state. Gold has been used to make jewelry not only due to its golden lustre but also due to its great ductility which facilitated forging it into sheet metal and a range of shapes. The most spectacular gold artefact is the Egyptian artefact of the enigmatic mask of the young Pharaoh Tutenkhamen (*c.* 1300B CE) made by hammering sheet metal. Early gold and silver ornaments from the Indian subcontinent are found from Indus Valley sites such as Mohenjodaro (*c.*3000 BCE). Gold and copper usage is reported from Neolithic Merhgarh in Baluchistan, Pakistan (*c.* 6000 BCE). Diadems and belts of gold are reported from Mohenjodaro. Harappan silver artefacts are reported from Kunal, in north-western India (Agrawal 2000: 6). The lighter colour of some gold artefacts from Mohenjodaro suggests the use of naturally occurring gold with silver impurities. Skilled practices of goldworking are noted in the Harappan period

***Fig. 1:** Micro-beads from Harappan site, National Museum, Delhi (2500 BCE)*

such as the use of gold micro-beads (figure 1).

Gold mining seems to have had a long history in parts of southern India such as in Karnataka. It has been speculated that gold from the Karnataka region collected from the surface by Neolithic cultures of the mid third millennium BC might even have supplied the Indus regions (Allchin and Allchin 1982: 337, More recent studies have also pointed to other probable nearer minerals sourced for the Indus period (Law 2011). The author had made preliminary field surveys in north Karnataka in the Hutti-Maski region in 1991 where she noted extensive old workings for gold. Most outcrops had open cast mines with old mining galleries with large mullacker fragments scattered about indicating ore crushing activity in antiquity (figure 2). Old timber from a 200 metres deep mine shaft was carbon dated the mid 4th century BC (Radhakrishna and Curtis 1991: 23-4), ranking amongt the deepest known old gold mines. The Jalagarus were a traditional community in the Dambal region who undertook alluvial washing and panning for gold (Foote 1874: 140).

***Fig. 2:** Neolithic Ashmound, Wandalli, Karnataka; with mullackers or grinding stones related to gold extraction found near old gold mine workings*

The Nilgiri hills and Wynad bordering, Tamil Nadu, Kerala and Karnataka host some sparse hard rock and alluvial gold deposits. Roman Pliny's account (1st century) of gold from the country of Naris might well refer to the land of the Nairs, ie the region of the alluvial gold tracts of the Nilambur valley below the Wyand hills (Radhakrishna and Curtis 1991: 23). While they are currently uneconomical, it is interesting they have been illegally mined/panned by local Kurumba tribes as observed by the author. In 1990 the author and Digvijay Mallah had identified some old gold workings in Gudalur, and observed children from the local Kurumba community engaged in hard rock mining for gold and panning for gold from the streams for alluvial gold using large wooden pans, whereby the heavier particles of gold would segregate into the pan while the lighter sand grains would wash away (Srinivasan 2018, Srinivasan 2016a). The Kurumba tribe was traditionally believed to have had magical powers apart from knowledge of mining and metallurgy according to Thurston (1909). There are also accounts that Hoysalas used gold from the region.

The rich finds of gold jewellery from the Nilgiri cairns, now housed in the British Museum, London may date from the early or mid 1st millennium BC to AD by some commentators (Knox 1985). The gold granulation technique seen in some of the ear-rings, whereby tiny spheres of gold were formed, may relate to Hellenistic influences, although the use of gold micro-beads was also noted at Harappan sites such as Lothal. Other early Tamil examples of gold jewellery include an ear-ring from Souttoukeny of the 2nd century BCE from Tamil Nadu depicting a prickly fruit, now in the Musee Guimet in Paris (Postel 1989: 130). These bring to mind the rich poetry of the classical Tamil Sangam era (*c.* 3rd century BCE to CE) which evoke local fruits and flowers such as *kurinji*.

Silver

Silver was extracted in the Old World using the method of cupellation, by the smelting and refining of silver rich lead ores. The old mines and working in Dariba and Agucha in the region of Rajasthan indicate production of silver from argentiferous lead in antiquity. These mines were found to be comparable in extent to the mines of Rio Tinto in Spain used in the Classical and Hellenistic World (Craddock *et al.* 2017). Silver anklets were also found from the Harappan site of Mandi. Use of silver is seen in punch-marked Mauryan coins from the 4th century BCE onwards. From the Satavahana period, (1st-2nd century CE), lead isotope finger-printing suggested the Agnigundala mine in Andhra Pradesh as one source of silver for coins, while Sardinia seemed likely to be another source, indicative of maritime trade (Srinivasan 1999b, 2016b). The largest cast silver urns are seen in the Jaipur palace and museum which would made of alloyed metal since pure silver is too soft for such large castings.

Cast copper-bronze icons and icons

The use of copper-bronze tools is seen from Harappan times, ranging from utilitarian artefacts such as chisels, nails, hooks and axes to cast miniature figurines. Several examples of low tin bronze with less than about 10% tin are found, whereby tin would have been added to harden the softer copper metal and to improve its castability. The fine miniature bronze of the Mohenjodaro dancing girl, *c* 2500 BCE is about 10 cm in height (figure 3). Cast in the round, it was very likely made of the lost wax/resin casting process where a model would have been made of wax/resin, invested with clay to make the mould and the wax melted out and metal poured into the hollow. Mortimer Wheeler in a TV programme of 1973 described the image as, 'a girl, perfectly confident, there is nothing like her in the world' (Possehl 2002). There are aspects of the figurine that connect to folk or indigenous practices such as the sideways hair bun still worn by Gond women of Central India and Kota women of the Nilgiris in southern India. In figure 4, a wax model for the casting of a metal figurine by the Gond community of Bastar (akin to Dhokra work) is seen with a tripartite headgear which brings to mind the

Fig. 3: *Dancing girl, Mohenjodaro, 2500 BCE (courtesy John Marr)*

Fig. 4: *Wax model for image being made by Gond community of Bastar*

kinds of headgears worn by figures depicted in Indus seals.

The casting of copper alloy icons came widely in vogue from the early historic period onwards. Spectacular bronzes were also cast under the Cholas in southern India. The celebrated Nataraja bronze of the Chola period (figure 6), was hailed as 'poetry but nonetheless science' by Ananda Coomaraswamy in 1912. The connections to surviving South Indian dance practices of Bharata Natyam derived from Sadir, the temple dance tradition of Thanjavur area are still to be seen (figure 5). Excellent examples of Gupta statuary are known such as the life-size Sultangunj Buddha now in the Birmingham Museum, which was found to be of predominantly of copper and standing at 2.28m (figure 7). Bronzes continue to the cast by the lost wax process even in the present day at Swamimalai, in Tanjavur district. In this process an image was made of wax and invested

Fig. 5: *Bharata Natyam dance pose of Nataraja by Sharada Srinivasan*

Fig. 6: *Nataraja, Kankoduvanithavam, Government Museum, Chennai*

Fig. 7: Sultanganj Buddha, 6th century, Birmingham Museum

Fig. 8: Metal icon casting at Swamimalai, Thanjavur district, Tamil Nadu

with clay to form the mould. The mould was then heated to melt and get rid of the wax and then metal poured in which solidified to give the final metal icon. At Swamimalai the images are first minutely carved in wax and then covered in layers of clay to form the mould, using the fine alluvial clay of the Kaveri, the vandal munn, and then the wax expelled by heating the mould and then metal poured in to form the castings (figure 8). The hollow casting process used a clay core and was used more in the north of India for casting. In this the final icon was made of a thin layer of metal with the clay core retained inside. Hollow cast icons can appear damaged due to the thinner layer of metal being prone to damage.

Harle (1992: 302) memorably commented that the early Chola bronzes represent the finest representations of godhood, unsurpassed in any place or age. These bronzes were made by the lost wax process or investment casting process. The image was cast by first making a model in wax, and then invested with moulding material to form a mould and thereafter the mould is heated to expel the wax and the molten metal is poured into the hollow to generate the metal icon. The Sanskrit phrase *'madhuchchehistavidhanam'* refers to the lost wax process and is described in the artistic treatise of the Manasara of about the 4th-5th century (Reeves 1962: 29-31, Srinivasan 2016 *c*). That the lost wax process is also invoked in a poem by the Tamil women poet-saint Andal (*c.* 800) who compares dark rain clouds to the mould holding liquid wax, entreating them to rain on the Lord Visnu (Srinivasan 2016 *c*).

Investigations by the author as previously reported in Srinivasan (1996, 2016 b) indicate that a majority of the South Indian medieval bronzes were of leaded tin bronze. About 80% of 130 south Indian images from the early historic to late medieval period were leaded bronzes with tin contents not exceeding 15% and keeping within the limit of solid solubility of tin in copper. Beyond this limit as-cast bronzes become increasingly brittle due to the increasing presence of delta phase. The Chola bronzes (10th-12th century) in general had an average composition of about 6% tin and 6% lead (Srinivasan 2015). The 11th century Chola Nataraja from Kankoduvanithavam in figure 5 analysed by the author by ICP-OES analysis had 8% tin and 8% lead as leaded bronze (Srinivasan 1998a). Of the total number of images only 15% were leaded brass images with more brass being used in the post-Chola period. Figure 9 shows the micro-structure of a cast predominantly copper image of the late Chola period studied by the author. Although south Indian icons are often described as ‘pancha-loha’ or five-metalled icons, the analyses by the author indicated rather they are largely leaded bronzes or leaded brasses. Such nomenclatures of pancha-loha and ashtadhatu (eight elements) more symbolic since it is not practically possible to make alloys with a significant content of so many metals. Archaeometallurgical investigations by the author on slag specimens recovered near the Ingaldhal copper mines in Karnataka confirmed that they were from copper smelting, likely of the Satavahana period from associated finds of early historic russet coated pottery (Srinivasan 2016d).

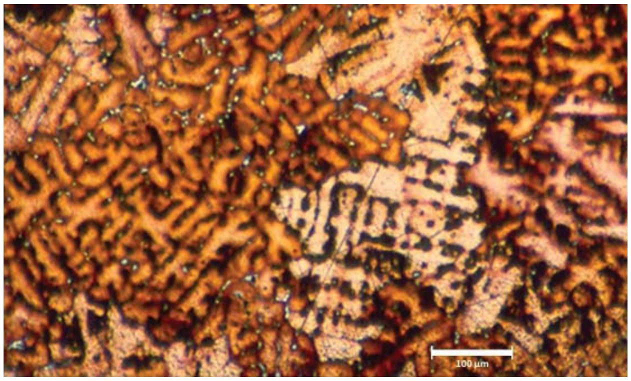

***Fig. 9:** Micro-structure of cast predominantly copper alloy of late Chola era (200X)*

***Fig. 10:** Making of mould for bell casting at Nacharkoil, Tamil Nadu (Bell maker late Govindrajan with Sharada Srinivasan)*

The lost wax casting of bronze bells has been practiced in the Thanjavur region of Tamil Nadu, which is another declining tradition Nacharkoil, a small village located four kilometres from Kumbakonam, has traditionally been renowned for the making of temple bells and temple lamps. In the past it had a sizeable community of Kammalar or bronze and bell metal workers. The *Kammalar* community have also been involved in making lost wax castings of large and medium sized temple bells by the lost wax process. Here the mould and wax model were build up using hand lathes in ingenious ways (figure 10), although the traditional lost wax casting of bells is declining and giving way to other industrial processes.

Binary high-tin bronze vessels and mirrors

As-cast binary copper-tin alloys with over 15% were not widely used in the ancient world as they are embrittled due to the presence of the delta phase component. Previously, the Indian subcontinent had not been regarded as a significant region in the exploitation of tin and bronze. However, metallurgical investigations by the author on artefacts from megalithic contexts and early historic contexts, continuing into medieval to modern south India demonstrated longstanding familiarity with the exploitation of the intermetallic properties of binary high-tin bronzes, as seen in the manufacture of vessels, coins and musical instruments of wrought and quenched beta bronze with 22-5% tin, and the manufacture of mirrors of delta bronze with about 33% tin (Srinivasan 1994, Srinivasan and Glover 1995, Srinivasan 2016e), which are also the last surviving crafts of their kind in the world.

Astonishingly, highly sophisticated and thin-rimmed bronze vessels have been uncovered from the megalithic cairns and burials of the Nilgiris (figure 11) and Adichanallur, Tamil Nadu (*c.* 1000-500 BC), while metallurgical investigations on some of these by the author confirmed that they were of hot forged and quenched binary unleaded high-tin beta (23% tin) bronze (Srinivasan 1994, Srinivasan and Glover 1995, Srinivasan 2010). Such an alloy of copper and tin with around 23% tin can be forged greatly at high temperatures due to the presence of a high temperature plastic beta phase which when quenched gives additionally properties of strength and lustre to the alloy. These extraordinarily thin-rimmed vessels were fabricated by extensively hammering out such an alloy between 586-798^0 C when a plastic beta intermetallic compound (Cu_5Sn) of equilibrium composition of 22.9% tin forms. This was followed by quenching which resulted in the retention of needle-like beta phase, as seen in the microstructure of a vessel from Adichanallur in figure 12, and which prevents the formation of brittle delta phase and also gives a golden polish. Low-tin bronzes have limited workability in comparison. Indian influences were also discerned in examples of high-tin bronze vessels found in Thailand in southeast Asia (Bennett and Glover 1992).

Fig. 11: *Vessel from Nilgiri Cairns, Tamil Nadu, Government Museum, Chennai (early to mid 1st mill BCE)*

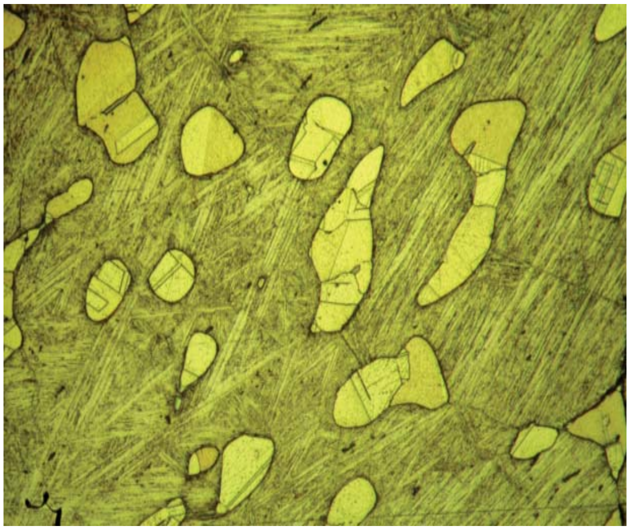

Fig. 12: *Micro-structure of vessel from Adichanallur, Government Museum, Chennai, hot forged/wrought and quenched high-tin beta bronze structure of 23.9 % tin bronze, 400 X*

Such high-tin bronze vessels have continued to be used among the local communities of the Nilgiris such as the Todas. Such high-tin beta bronze vessels also show high corrosion resistance due to the retention of the beta intermetallic compound phase as also seen in the Nilgiri vessel in figure 11. The making of such high-tin bronze vessels by similar processes survived in many places till recently, such as in Kerala and in Nacharkoil in Tamil

Nadu. The author observed large vessels being made in parts of Kerala especially in Palghat district in the 1990s of 23% beta bronze, 25 cm in diameter and 1mm rim thickness, being wrought and hot forged from ingots of 15cm diameter and 1.5 cm thick followed by quenching. However this tradition has virtually died out today.

Although tin is scarce in India compared to other regions such as southeast Asia, it is possible that some minor local tin deposits were accessible in antiquity. Eastern India has tin deposits in the Hazaribagh region (Chakrabarti 1979, 1985-6), where Mallet observed the pre-industrial smelting of tin by local tribals in furnaces resembling shaft furnaces for iron smelting. Investigations by the author on slags from the ancient mining region of Kalyadi within Hassan district of Karnataka indicate that these are bronze smelting slags with up to 7% tin from co-smelting copper and tin ores due to the presence of metallic iron, rather than casting slags from alloying copper and tin (Srinivasan 1997), which might suggest the exploitation of minor local sources of tin.

The making of reflective mirrors of a composition of high-tin delta bronze is a rare artisanal tradition which survives in Aranmula in Kerala (figure 13). Studies by the author have documented the making of unique highly reflective specular metal mirrors of a composition of around 32% delta tin bronze, optimising the presence of a hard, silvery and reflective alloy which can be highly polished to get the best mirror effect. Her studies showed that the specular intermetallic delta phase which formed in 33% high-tin bronze was skilfully optimised and exploited to make traditional mirrors in Aranmula as indicated in the micro-structure in figure 14. Using low-cost methods and organic materials, an innovative closed-crucible-cum mould casting process was used to cast the blank which was then skilfully polished to get the reflective mirror (figure 13). Its reflective properties can be compared very favourably with those of the glass mirrors that are manufactured in modern day factories with mercury coating. This ancient tradition with its technological and ritualistic significance is, however, greatly in decline. The traditional weddings of the Nairs included the ashtamangalyam comprising of eight auspicious articles that were to be part of the wedding trousseau the brides. These included the Aranmula mirror (valkannadi in Tamil and Malayalam) as reported even from the early 20th century by Thurston (1909).

Fig. 13: *Polished metal mirror blank at Aranmula (with reflection of Sharada Srinivasan)*

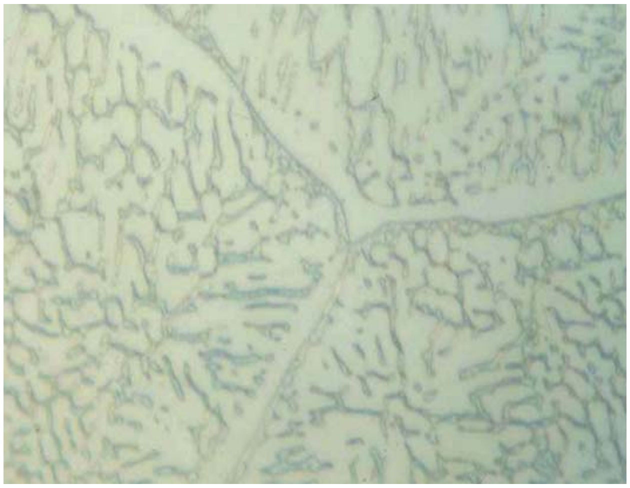

Fig. 14: *Micro-structure of Aranmula mirror of high-tin delta bronze (400X)*

Iron, steel and wootz steel

The Indian subcontinent has a vibrant iron and steel in antiquity. The celebrated Iron Pillar (figure 14) is renowned as the 'rustless wonder' for its relative corrosion resistance. It is about 7.375 m high and 41.6 m in diameter and is the earliest surviving massive iron forging. The Sanskrit inscription on the pillar of the late 4th century to early 5th century CE is attributed to the Gupta king Chandragupta II, alluding to the erection of a *dhwaja* or pillar by Chandra, as a devotee of the Hindu deity Vishnu, on the hill of Vishnupadagiri. A sample studied by Sir Robert Hadfield was found to be iron of high purity with about 0.1% phosphorus and 0.04% carbon (Hadfield 1912). The formation of a protective passive film on the surface and an amorphous oxyhydroxide layer next to the metal-rust surface of the phosphoric iron may have aided the corrosion resistance (Balasubramiam 2008). Ultrasound investigations suggested that the pillar was built up by forge-welding cakes of wrought iron in a perpendicular and radial fashion (IGCAR).

Fig. 15: *Delhi Iron Pillar, Gupta, 400 CE, upper portion*

India has also been famed for the legendary Indian wootz steel, or *ukku* in south Indian languages, a high-grade high-carbon steel, especially produced in southern India according to several European travelers' accounts from the about 16th to 17th centuries (Srinivasan 2016f). As indicated in accounts of 17th century traveler Tavernier, tens of thousands of shipments of wootz steel from sent from the kingdom of Golconda (in modern Telangana) to Persia and West Asia to make the fabled Damascus blades. The Damascus steel blade, believed to have been forged of Indian wootz steel of a high carbon content of 1.5-2%, was reputed for its cutting edge (Smith 1982, Srinivasan 1994, Srinivasan and Ranganathan 2014). The attempts to characterize wootz by scientists of the caliber of Michael Faraday spurred many developments in 19th century metallurgy and contributing to the Industrial Revolution. Vast amounts of archaeometallurgical debris related to the production of wootz steel are still found in the region of northern Telangana. Wootz steel production sites with crucible debris were also uncovered in the region of Mel-siruvalur (figure 16) and Tiruvannamalai in Tamil Nadu by the author (Srinivasan 2016f, Srinivasan 2007).

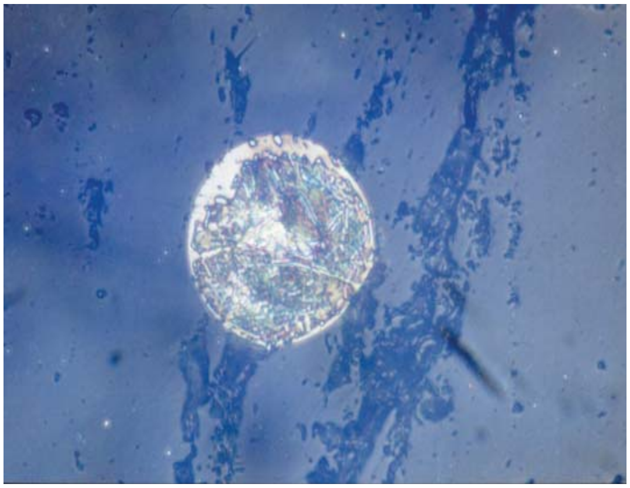

Fig. 16: *Micro-structure of wootz steel making crucible debris from Mel-siruvalur showing remnants of ultra-high carbon steel (400X)*

As far as the archaeological evidence is concerned, three specimens of ferrous blades had high carbon contents of 1.2-1.7% C of the composition of wootz steel from the Bhir mound of Taxila (*c.* 3rd century BCE (Marshall 1951: 534). Greek alchemist Zosimos in the 3rd *c*, AD mentioned that the Indians made steel for sword by melting soft iron in crucibles recalling to the wootz process Srinivasan (2016f). Kadebakele is an Iron Age site near the World Heritage site of Hampi in Karnataka. A small iron ring (acc. no. 900, 22E-28 N, Level 7) radiocarbon dated to 800-440 BCE yielded a through pearlitic structure of at least 08% carbon steel, suggesting it could have been cast steel produced from crucible processes (Srinivasan *et al.* 2009).

Excavations at an iron age megalithic site at Kodumanal, Tamil Nadu (3rd *c.* BCE), near Karur, the Chera capital of the Sangam era (3rd *c.* BCE-3rd *c.* AD) revealed furnaces with vitrified crucibles (figure 17) and iron slag (Rajan 1990). A vitrified crucible fragment from Kodumanal showed ferrous metal processing remains (Srinivasan and Griffiths 1997, Srinivasan 2007). Figure 18 is an elemental distribution map of a crucible fragment from Kodumanal, examined using EPMA-WDS by the author which shows the presence of ferrous remnants. The bardic poems of the Sangam Tamil poetess (3rd *c.* BCE-3rd *c.* AD evoke warring chieftains and their spears (*ekku*). *Ukku* may derive from the Sangam Tamil word *uruku*, meaning boiling over. The Sanskrit Arthasasthra (3rd *c.* BCE) refers to *vaikruntaka* which might possible allude to steel. Pliny’s ‘Natural History’ mentions the import into the Roman world of iron from the ‘Seres’, which might be identified with the ancient Southern Indian kingdom of the Cheras. Roman accounts of the ‘Periplus of the Erythrean Sea’ refer to the flourishing port of Muziris or Muciri on the Malabar coast. Interestingly, an iron nail from Pattanam, identified with the Muziris revealed a microstructure typically associated with ultra-high carbon wootz steel containing about 1.5% C (Srinivasan 2007).

Fig. 17: *Crucible and tuyere fragments, Kodumanal, 3rd century BCE*

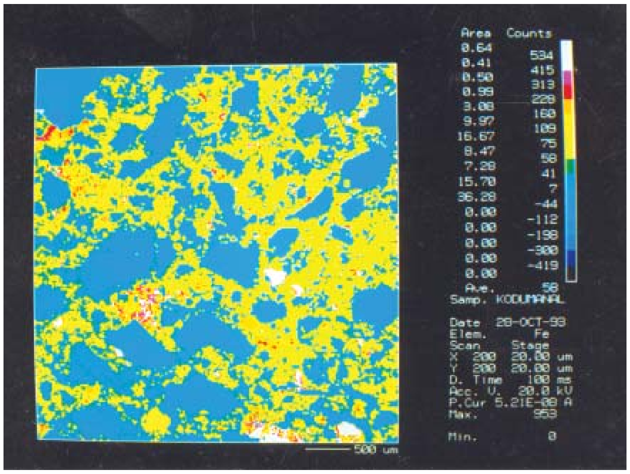

Fig. 18: *Elemental distribution map by EPMA-WDS on cross-section of crucible from Kodumanal, 3rd century BCE, Tamil Nadu*

Early production of metallic zinc

The earliest firm evidence for pre-industrial extraction of metallic zinc seems to comes from India. Zinc is one of the most difficult of metals to isolate since zinc metal oxidizes and volatalises readily around the same temperature of about 1000°C as is needed to smelt zinc ore. Hence it forms as a vapour in the furnace which would immediately get re-oxidised. Therefore finds of metallic zinc are not very common from early antiquity.

There is remarkable evidence for the semi-industrial extraction of metallic zinc by the 12th century CE from the Zawar area of Rajasthan (Craddock et. al. 1998). Zinc was smelted by downward distillation of the zinc vapour formed after the reduction of zinc ore. The *Rasaratnakara,* a Sanskrit text ascribed to the great Indian scientist Nagarjuna, of the early Christian era describes the process of downward distillation or *tiryakpatana* (ibid.) Using retorts with condensers and specially designed perforated furnaces, the zinc vapour could be drastically cooled down to about 500^0 to collect at the bottom of the furnace to get a melt that could solidify into zinc metal. Remnants of perforated furnaces with zinc smelting retorts have been found from Zawar, whereby more than 30 retorts seen to have been packed in each furnace (Craddock *et al.* 1998, Craddock *et al.* 2017). The remains suggest that production of Zawar was almost on semi-industrial scale in an era preceding the Industrial Revolution and continued on a large scale during the Moghul era until the 17th century. A sample with 34% zinc was excavated from the Buddhist site of Taxila (ca 4th *c.* BC) or Takshashila, now in Pakistan (Marshall 1951) which may have been made by alloying metallic zinc.

The remarkable artistic innovation of Bidri ware (figure 17), inspired by Persian inlaying traditions, developed under the late medieval Muslim Sultanate rulers of the Bidar region of Karnakata. The use of metallic zinc was made to make highly elegant metalware, of a patinated high-zinc alloy with 2-10% copper inlayed in silver (La Niece 2015), which was used to make hukka bases, ewers and other artefacts. The Bidri ware sample in figure 19 investigated by surface XRF analysis by the author had 90% zinc and 6% copper.

Fig 19: *Bidriware vessel of zinc alloy of Persian influence*

Fig 20: *Agnigundala, Andhra Pradesh, old copper mine workings (Sharada Srinivasan visit of 1991)*

A metallic zinc ingot with a reported Deccan Brahmi inscription was studied by the author using lead isotope ratio finger-printing and was found to fit a 5th *c.* AD attribution from the Andhra region (Srinivasan 1998, 2016a). The shape of the ingot/coin was also interesting akin to a solidified globular droplet with a flat bottom as it could have been collected at the bottom of the furnace by downward distillation. One of the important polymetallic deposits in southern India is in Agnigundala, Andhra Pradesh which lead isotope ratio studies by the author indicated was exploited at least by the early historic Satavahana period (Srinivasan 1996, 1999b, 2016b). Figure 20 is a view of one of the old copper mine workings.

In Europe, commercial zinc smelting operations were established by William Champion in Bristol in Britain in the 1740's using downward distillation suggesting its inspiration from the Zawar process (Craddock et. al. 1989). Thus Indian metallurgists can justifiably be regarded as inventors of the process of zinc smelting.

Archaeometallurgy and Conservation Science: Challenges and Scope

In the Indian context there are several challenges in developing the fledgeling area of archaeometallurgy. Sadly, many of the surviving crafts traditions linked to ageold practices are rapidly declining with livelihoods increasingly marginalised. Several of the archaeometallurgical production sites and old mining areas are also disrupted by infrastructure development, agriculture and so on, so that the records of these activities are rapidly being effaced. Concerted action is needed to retrieve what is left of the remnants of a rich pre-industrial legacy. The area of conservation research is also one that needs more impetus in terms of scientific research. Even though the Delhi Iron Pillar, has been hailed as the rustless wonder, a closer look (figure 15) suggests that in recent times rust has perhaps indeed been forming perhaps exacerbated by industrial pollution and other factors. Thus there is a need for working concertedly for the scientific documentation and preservation of artefacts and materials heritage.

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In all instances the tarnish was mixed and silver sulfide was only a small part of the surface tarnish layer. The relatively low concentration of silver sulfide in the tarnish is totally at odds with the accepted model for silver tarnishing. Significant concentrations of sulfate, chloride, oxide and a range of carbon containing organic species were also detected in the tarnish. Sulfide and sulfate are the only two sulfur containing species detected. Other sulfur species would generate peaks at different binding energies, which were not observed (Hercules 1980). The aliphatic carbon binding energies indicate three species; a saturated hydrocarbon, an oxygenated organic species and a carbonyl species. The carbonyl species could be interpreted as an inorganic carbonate, but several authors have concluded that silver carbonate does not form under ambient conditions and hence, an organic carbonyl is the most probable identification for this species. All of the coupons also have silica, sodium and zinc on their surfaces. The sodium and silica are common contaminants, possibly from dust deposition, whilst the zinc is a contaminant from a zinc oxide absorbent incorporated in the container used to transport and store the coupons from the showcase to the XPS instrument at Johnson Matthew Special Metals. Significantly higher concentrations of sulfide, sulfate, chloride, oxide and possibly the carbonyl species were observed on the externally exposed coupons compared to those exposed indoors. The silver concentration was also lower on the outdoor coupons and the silver Auger MNN peak was shifting to lower binding energy, indicating ionisation of the silver to Ag(I). The coupons exposed in the gallery ambient conditions showed slightly higher levels of sulfide, sulfate, chloride, oxide and slightly lower silver than those exposed inside showcases. No consistent differences could be identified between those sets of coupons exposed inside showcases.

The results from the SIMS analyses for the second exposure campaign are discussed below. Difficulties in sample preparation, handling, storage and analysis led to unreliable results from the first set of trials and these are not included. Handling the coupons with tweezers was found to be difficult especially mounting them onto aluminium stubs for the SIMS analysis. The slight curvature engendered in the coupons when cut with scissors, was found to lead to bad electrical contact and charging during analysis. This reduced the quality of the analysis. A much better methodology was adopted for the second set of analyses with the silver coupons mounted onto the SIMS stubs with self adhesive carbon pads for exposure. The surface SIMS results confirmed the XPS observations of a mixed tarnish layer, containing sulfide (S^- negative ions at m/z 32 and 33), sulfate (negative ions at m/z 85{SO_4^-} and 80{SO_3^-}), chloride (Cl^- at m/z 35 and 37), organic carbonyl species (M/Z 58{$C_3H_6O^-$}, 59{$C_2H_3O_2^-$} and 73{$C_3H_5O_2^-$}) and a range of positive organic mass fragments between C_2 and C_6 (m/z 15, 28, 29, 41, 43, 53, 55, 57, 63, 67, 71, 73, 77, 79, 81, 83 and 85).

SIMS depth profiling indicated that the mix of species was present through the whole depth of the tarnish layer. Figure 7 shows representative profiles for silver (Ag_{107}^+), and

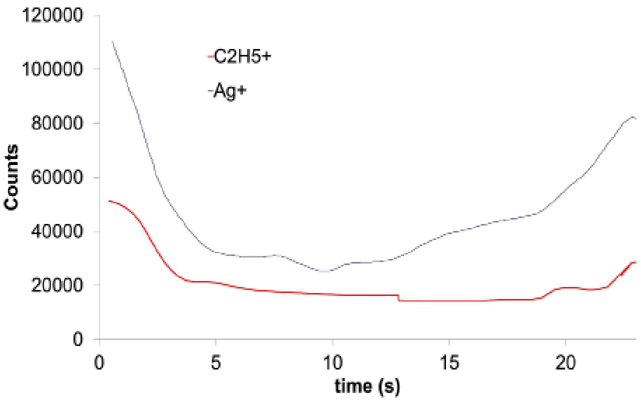

Fig. 7: SIMS depth profile

an organic species ($C_2H_3O^+$ at m/z 43). The equipment is limited to collecting three profiles at once, but the other important species were profiled separately, showing similar trends. The peak in the silver cation indicates the interface between the tarnish layer and the silver. Attempts to estimate the depth of the tarnish layer by measuring the ablation pits with a Zygo New View 200 scanning white-light interferometry microscope, were not successful because of the rough nature of the silver surface caused by the abrasive cleaning regime.

Object Examination

Neither the XPS nor the SIMS equipment used in this study are well suited for object analysis, as the sample chambers are very small. Scanning electron microscopy with energy dispersive analysis, (SEM-EDX) can provide some information about silver tarnish layers when they develop beyond a certain depth. The information is purely elemental, with no indication of the species present. Small silver objects showing tarnish accumulated over a number of years (between 2 and 25) were examined using a Joel 740 SEM with Cambridge Instruments EDX detector. The super atomic thin window on the Germaniun EDX detector allows excellent quantification of both carbon and oxygen. Analyses were taken from areas with as little dust as possible on the silver surfaces, as materials such as calcite, halite, gypsum and skin fragments would contribute carbon, oxygen, chlorine and sulfur to the analyses. Results are shown in Table 3.

The analyses followed the same trends observed from the previous XPS and SIMS results, indicating that tarnish formed over longer time periods still has a mixed composition. Of particular interest are the series of coins and medals analysed. These had ‘cabinet’ patinas, which are highly valued and had not been cleaned for over 50 years (conservation records) and are quite likely to have not been cleaned since acquisition, which was at least 100 years ago for all the examined objects. The analyses on these objects were undertaken on recessed

Table 3: SEM-EDX Analyses of Coins and Medals

Coin or medal	Sulfur	Chloride	Oxygen
A	0.40	3.74	9.72
B	0.38	4.48	6.40
C	0.47	6.01	6.01
D	0.34	4.00	4.00
E	0.30	6.11	3.06
F	2.84	3.92	3.43
G	0.04	1.44	1.44
H	0.20	1.32	0.66
I	0.58	1.47	1.23
J	0.26	2.33	6.06
K	0.78	2.57	1.29
L	0.80	3.64	5.72
M	0.36	5.03	5.03
N	0.62	2.96	7.70
O	0.48	3.86	1.93

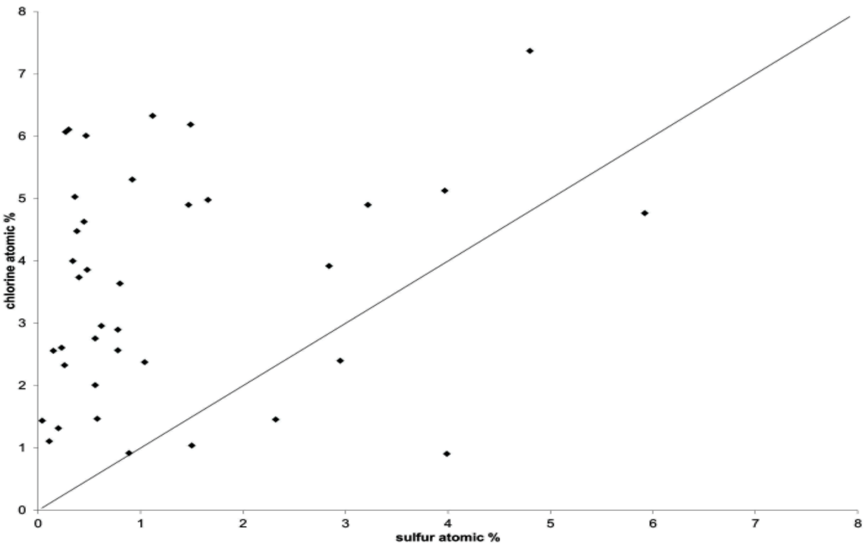

Fig. 8: *Cl versus S for small silver objects*

areas, where the patina was well preserved. Figure 8 shows a graph of the analysed chlorine concentration against the sulfur concentration. The line at 45° marks a one to one ratio of these two species and, as can be seen, the majority of analyses are above this line, as the patinas are predominantly chlorine based.

Species extending through the whole depth of the tarnish layer that had accumulated over 25 years on display.

The very long term tarnish formed on several objects was also analysed using potentiodynamic stripping (Palmsens 3 potentiostat, silver/silver chloride reference electrode, 0.1M sodium nitrate electrolyte) (Capelo et al 2013). Table 4 shows the estimated period (from conservation records) since last cleaning of the object, the calculated depth of silver sulfide, silver chloride, silver oxide and the full depth of the tarnish layer calculated from summing the three values.

Table 4: Potentiodynamic stripping analyses of tarnishes formed over long periods

Minimum period of exposure since last cleaning (years)	Equivalent layer depth (µm)		
	sulfide	chloride	Oxide
31	0.33	0.50	0.50
32	0.26	0.46	0.72
36	0.36	0.55	0.55
38	0.39	0.77	0.39
22	0.40	0.79	0.40
29	0.42	0.35	0.91
29	0.51	0.68	0.68
28	0.54	0.72	0.72
34	0.37	0.66	1.03
35	0.59	0.49	1.28
21	0.64	0.96	0.96
26	0.68	0.56	1.47
33	0.68	0.57	1.48
28	0.33	0.50	0.50

The tarnishes were all found to contain significant chloride and oxide, as-well as silver sulfide, Table 4. The technique is reported to have a very low sensitivity to sulfate (Sanders et al 2015). The tarnish layer thickness ranged from 1.4 to 2.7μm, despite the (up to) thirty five years of environmental exposure. This would place them in category IC2, – low according to the standard ISO11844-1 (ISO 2005).

A related project involved examination of a large number of silver objects from display showing unusual tarnish patterns. Examination with visual microscopy revealed particles with tarnish or discoloured halos around them. These were found to extend up to 1mm beyond the edge of the particles. In only one instance was the object sufficiently small to be examined in the SEM chamber and the halo was found to be rich in sulfur, chlorine, carbon and oxygen compared to the unaffected silver surface. Several of the particles were removed and analysed with SEM-EDX. This indicated that the particles responsible were of several different types, including clay particles (aluminium and silicon detected), fly ash, organic particles and one instance of sodium chloride. Such particles are thought to attract and hold humidity and pollutant gases onto the metal surface. Micro Raman spectroscopy of sodium chloride crystals has identified organic species absorbed onto the crystal surfaces. Particles have been shown to play a role in the atmospheric corrosion of several metals (Vernon 1935, Leygraf et al 2016). Recent research has shown deposited dust has a significant impact on silver tarnish rates in heritage buildings (Thickett and Costa ICOM CC 2014).

Environmental Sources of Chloride

The source of the chloride detected in the tarnish was further investigated.

Beyond handling and conservation treatments, the obvious airborne deposition routes are via particles and gases. Glass slides were exposed horizontally to collect particles, initially in the showcases tested, and then also in showcases at a series of sites across the UK. The slides were exposed for 28 days, after this time the surface was extracted with 10ml of 18.2MΩ cm-1 water and the extract filtered (50μm) and analysed with ion chromatography for anions.Long term deposition rates were also estimated from fabrics used to dress showcases. A 5cm by 5cm piece was cut from the fabric and analysed as for dust. The three fabrics analysed had been in situ for over 20 years.

Figure 9 shows significant chloride deposition in most locations. Those from maritime locations are higher, but there is a measurable rate at locations measured.

Chloride containing gas concentrations were analysed using Palmes diffusion tubes and the method developed for acetic acid (Gibson 1998) and the diffusion co-efficient quoted by (Dimmock and Marshall, 1987). The diffusion tubes are exposed vertically with the open end down and a 10μm dust filter fitted.

Some airborne species detected as chloride were analysed in all the showcases measured as shown in Figure 10. Without deposition velocities it is not possible to determine the likely deposition rates to the surface from the gas species. However, the dust deposition levels are high and likely to be the predominant source.

Discussion and Conclusions

The exposure experiments showed no clear correlation between tarnish rate and hydrogen sulfide or carbonyl sulfide concentration in showcase environments. This is a different behaviour than that exhibited in room environments. The tarnish rate is generally related to the air exchange rate of the showcases.

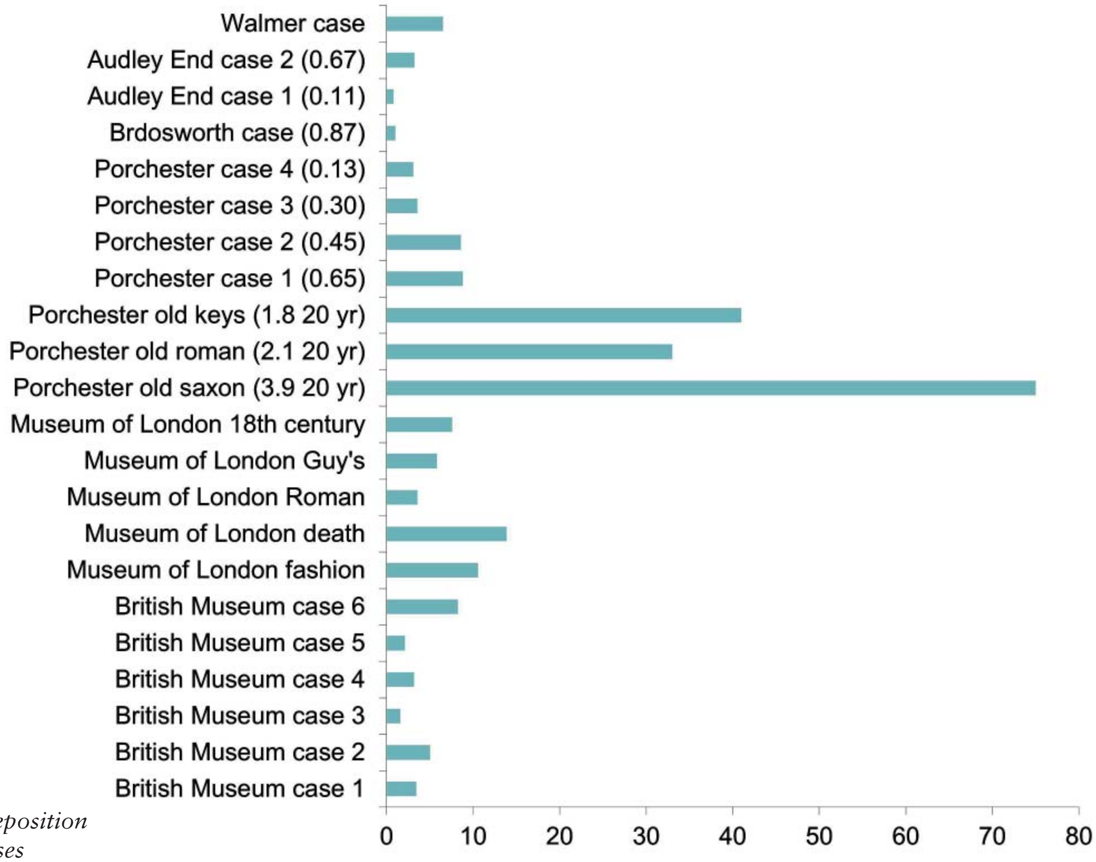

Fig. 9: *Anion deposition rates in showcases*

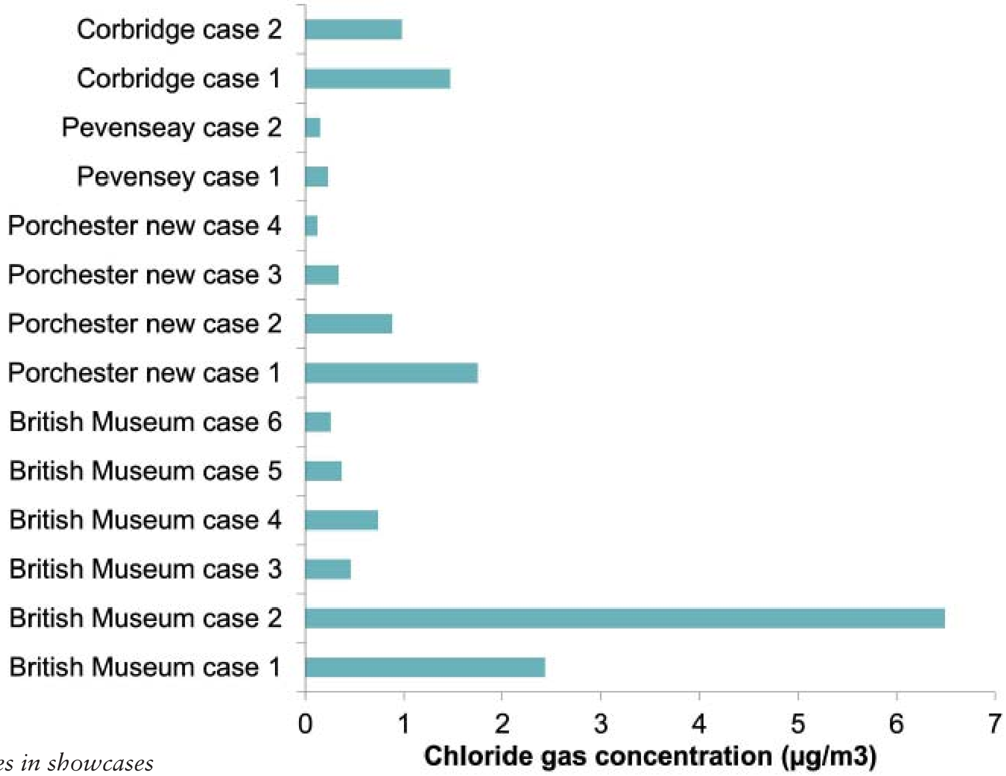

Fig. 10: *Airborne chlorides in showcases*

Some differences in tarnish rate were observed in some showcases. A possible explanation is the low air flow in showcases, combined with the very high reactivity of silver surfaces results in tarnish rates being controlled by fluxes as opposed to concentrations.

The tarnish formed was mixed and not predominantly silver sulfide, both in the short term exposures and in tarnishes examined that had formed over several decades. Chloride and oxide were almost always present along with a range of unidentified organic compounds. It is likely sulfate was also present in many instances, but only XPS and SIMS could distinguish it from sulfide. All compounds were found throughout the tarnish layer and not just at the surface. Industrial research has recently identified similar mixed tarnishes (Sanders et al 2015). Significant care had been taken to ensure showcase environments did not cause tarnish through emission from the construction and dressing materials used in the showcases. However, internal sources from mixed media objects were observed in one instance. Chloride deposition by both particles and from the gas phases was observed, the particles appear to be the main route.

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