CAMBRIDGE
Cambridge University Press & Assessment
978-1-009-59219-2 — Retrospective and Prospective for Scientific Provenance Studies in Archaeology
A. M. Pollard
Excerpt
More Information

At the 1928 meeting of the British Association for the Advancement of Science in Glasgow, the ‘Sumerian Committee’ of the BAAS made its first report, including the analysis of 34 bronze objects (Desch, 1929). The Committee, constituted of leading British archaeologists and metallurgists, was established to ‘report on the probable source of the supply of copper used by the Sumerians’. Thus was born one of the first interdisciplinary projects carrying out the chemical analysis of archaeological copper alloy objects, with the express aim of provenance. Nearly 100 years later, it is perhaps time to reflect on such activity.

This Element seeks to chart the development, degrees of success, and suggests a possible re-focussing for one of the major activities in scientific archaeology – the use of chemical and isotopic measurements on archaeological artefacts to determine the origin of the raw materials used to make these objects, commonly referred to as provenance studies. The focus here is on inorganic materials, particularly copper alloys, ceramics, and lithic materials, since several hundred thousand analyses have been published on these categories; numerically, studies on other materials generally pale into insignificance. Organic materials, particularly amber, have been historically important, and others, such as textiles, the production and trade of which have been key economic activities, are under-represented in the provenance literature because of poor survival and also the need for more specialized analytical techniques such as proteomics and light stable isotope ratios.

Inorganic provenance studies were widely adopted from the 1960s onwards because in principle they can elucidate trade and exchange patterns in the ancient world, and, therefore, contribute to studies of contact between societies, either in terms of trade in materials or other forms of social transfer of goods. Perhaps even more significantly, it can provide proxy evidence for the exchange of ideas. The rise of provenance was facilitated by two parallel developments – the increasing availability of instrumental methods of chemical analysis, and changing theoretical concepts of the role of material culture within archaeology. The growing scepticism in some quarters towards provenance studies from the 1980s onwards was partly the consequence of a gradually increasing recognition of the complexity of the production processes for all but the simplest of artefacts, including a growing appreciation of the potential for recycling in some materials, particularly glass and metals. However, rather than signalling the end of materials analysis as a tool for provenance studies, these potentially confounding features can present interesting new challenges and unexpected opportunities for the modern archaeologist. In fact, they transform the concept of provenance from the apparently simple question of ‘where does this object come from?’ to the much more interesting one of ‘how did humans manage and

Cambridge University Press & Assessment
978-1-009-59219-2 — Retrospective and Prospective for Scientific Provenance Studies in Archaeology
A. M. Pollard
Excerpt
More Information

use the raw materials at their disposal to produce these artefacts?' Given that the ultimate aim of archaeology is to understand past human societies, this seems to provide a very fruitful and important avenue for future research.

1 The Provenance Hypothesis

Provenance in this context means identification of the source of the raw materials used to make archaeological objects. For ceramics, this corresponds to the source of the clay used, and perhaps the temper added. For copper alloys, it can be interpreted as the mine from which the copper ores are extracted, but it might involve multiple mines if alloying metals (tin, zinc) are added. Archaeologically, the term can be extrapolated from the direct identification of source to include the matching of a set of artefacts (the unknown group) with another set (the control group), the *implication* being that they come from the same place, without necessarily identifying the specific geological source(s). The former exercise can be considered as *provenance-to-source*, and the second *provenance-to-match*. This definition is very different to that used in art history, where provenance means the lifehistory (biography) of the artefact, ideally documenting the sequence of all owners (and hence locations) of a particular work of art since its creation. Some authors, particularly in the USA (e.g., Price and Burton, 2011: 213), have promoted the use of the term *provenience* to define the 'birthplace' of the object, and *provenance* to signify the 'resume' (biography) of the object. Although this is an important distinction, and embraces the art historical definition, the majority of archaeologists simply use the term *provenance* to cover both of these definitions, perhaps taking the view that 'birthplace' is part of 'biography'.

It is important to emphasize that 'provenance-to-match' has a much longer history in archaeology than scientific provenance studies. Similarities in material culture rapidly became one of the key markers for defining cultural groupings, and particular forms of ceramics, such as Roman transport amphorae, or red-gloss Samian ware, arranged into intricate typologies, have been key indicators of trade and exchange across the empire from Spain to India. These parallels are deduced from visual study of form – careful classification of shape, manufacturing details, and decorative features – often supplemented by visual examination of fabric – the colour and texture of the ceramic paste. Thus, the framework for studying provenance was already in place when Weigand *et al.* (1977) observed that 'in many instances there will exist differences in chemical composition between pottery from different sources that will exceed, in some recognizable way, the differences observed within pottery from a given source'. They termed this the 'provenience postulate', and suggested that it was the basis

Cambridge University Press & Assessment
978-1-009-59219-2 — Retrospective and Prospective for Scientific Provenance Studies in Archaeology
A. M. Pollard
Excerpt
More Information

of all studies involving provenance attribution using chemical analysis. In 2001, Wilson and Pollard (2001: 507–508) attempted to clarify and systematize the assumptions behind the scientific provenance of archaeological materials by setting out six criteria for the 'provenance hypothesis':

i) The prime requirement is that some chemical (or isotopic) characteristic of the geological raw material(s) is carried through (unchanged, or predictably relatable) into the finished object.
ii) That this 'fingerprint' varies between potential geological sources available in the past, and that this variation can be related to the geographical (as opposed to perhaps a broad depositional environment) occurrences of the raw material. *Inter*-source variation must be greater than *intra*-source variation for successful source discrimination.
iii) That such characteristic 'fingerprints' can be measured with sufficient precision in the finished artefacts to enable discrimination between competing potential sources.
iv) That no 'mixing' of raw materials occurs (either before or during processing, or as a result of re-cycling of material), or that any such mixing can be adequately accounted for.
v) That post-depositional processes either have no effect on the characteristic fingerprint or that such alteration can either be detected (and the altered elements or sample be discounted) or that some satisfactory allowance can be made.
vi) That any observed patterns of trade or exchange of finished materials are interpretable in terms of human behaviour. This presupposes that the outcome of a scientific provenance study can be interfaced with an existing appropriate socio-economic model, so that such results do not exist *in vacuo*.

The first requirement reflects the idea of the 'fingerprint' – a characteristic element, set of elements, or isotopic composition which passes through from the source material to the object, ideally with no change. The possibility of a quantifiable change to the fingerprint through the various steps of the processing (depending on material) has to be acknowledged, but presents significant challenges in reality – it would require considerable supporting evidence to conclude that the difference observed in the fingerprint between source and product is due to processing (e.g., volatilization of certain elements at high temperatures) rather than signifying something else. The crux of the hypothesis is captured in points (ii) and (iii), particularly if the aim is provenance to source. Different geological sources (of ore, clay or rock, and so on) can only be distinguished if the fingerprint varies between alternative sources, if the internal variation in the fingerprint is less than that between sources, and the measurement technology is capable of measuring these differences. It also relies on the assumption that sources are geographically discrete. It might be of limited use archaeologically if a geological source of clay consists of a large chemically homogeneous river valley or flood plain (e.g., the Nile, or the Indus), rather than specifically located clay deposits (although it might be the case that what appears to be a chemically homogeneous deposit using one set of indicators (e.g., major elements) might show significant trends when a different set (e.g., trace elements) is used). Point (v) requires that what is measured as a fingerprint is (ideally) unaffected by post-depositional factors such as selective corrosion or contamination from groundwater.

Point (iv) – no mixing or recycling – is perhaps the issue that has dominated theoretical discussions of provenance. It is self-evident that, at least for provenance-to-source, any mixing of material from sources with different fingerprints will make it more difficult to assign an object to a specific source. Depending on the number of potential sources involved, and the magnitude of diversion in the measured fingerprint, it could simply result in less confidence in the assignment of object to source, or it could give rise to the creation of an entirely 'fictitious source' – the mixture resulting in data which, when plotted on an appropriate graph, appear to form a coherent source group, but which do not actually correspond to any real source. This is a case where provenance-to-match has a distinct advantage – if the characteristics of the unknown objects match those in the control material, then a common source can be proposed, even if it is itself unknown. The issue of mixing and recycling is discussed further next.

The final point was effectively a plea to interpret the results of any provenance study in terms of real human behaviour, rather than relying on abstract arrows on maps showing the movement of objects, apparently without the aid of human intervention. Trivially, this might involve thinking about how objects can move – as trade, gifts, tribute, war booty, and so on – and also about the mode of transport – maritime, riverine, or land. However, we must avoid the trap of assuming that human activities in the past carried the same meaning as they do today. Uniformitarianism is not a reliable guide in archaeology. Trade and exchange do not necessarily reflect purely commercial activities or 'market forces'. Marcel Mauss (1872–1950) showed how in many societies gift exchange was at the heart of creating and maintaining relationships both within and between social groupings (Mauss, 1923–1924). Karl Polyani (1886–1964) proposed that there were three modes of exchange: reciprocity, redistribution, and market exchange (Polyani, 1944), although not necessarily mutually exclusive. Gift exchange is a form of reciprocity; redistribution implies some centralized control of distribution, often via a central depot, and market

Cambridge University Press & Assessment
978-1-009-59219-2 — Retrospective and Prospective for Scientific Provenance Studies in Archaeology
A. M. Pollard
Excerpt
More Information

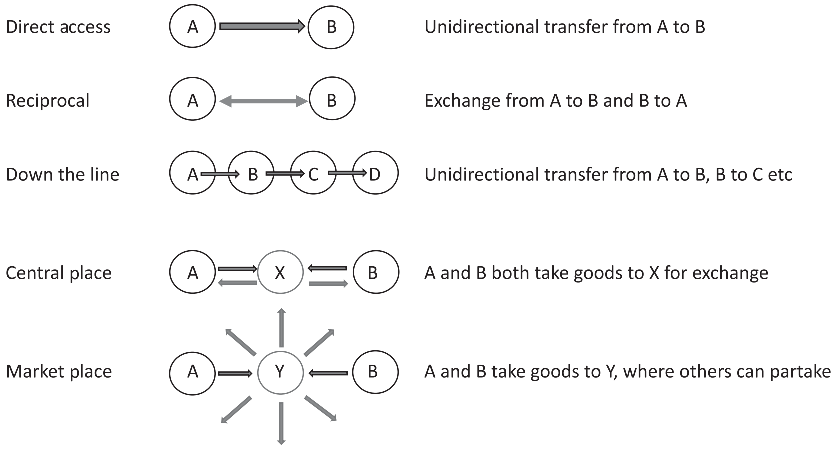

Figure 1 Some simple models of trade and exchange, redrawn from Renfrew and Bahn (2020: 371)

exchange involves a specific central location, but not necessarily a financial transaction. The particular mode of exchange is clearly linked with considerations of scale and organization – trading is very different in the context of a centralized imperial economy such as China or Rome, compared with differently regulated trading between independent tribal groups, or between traders working across the borders of settled sedentary populations and nomadic pastoralists. Renfrew and Bahn (2020: 371) have combined these social and economic considerations with various forms of settlement organization to produce a series of models for the exchange of physical commodities, some of which are redrawn in Figure 1. These range from direct contact between A and B to intermediate markets (A to market, market to B) to down-the-line trade (A to B to C to D, and so on). The form of exchange has an important influence on the distribution of particular objects, and also on how we should interpret provenance – as discussed in Section 7.1, in down-the-line trade, time taken to travel could be a factor in understanding the significance of finding objects from A at site D.

2 The Origins of Chemical Analysis in Archaeology

All of the examples discussed in this Element are predicated on the chemical analysis of inorganic objects. This application of the art of chemical analysis to archaeological artefacts has a long prehistory. The traditional methods of assay for gold – by separating the gold from silver by fire, or using the touchstone – have been known since at least the 2nd millennium BCE (Pollard, 2016). It is undoubtedly the case that miners and metalworkers were able to assay ores and precious metals long before the advent of analytical chemistry, and, indeed, the need for such assay provided an impetus for the development of chemistry (Greenaway, 1962, 1964). Cuneiform tablets from Mesopotamia (from the early 2nd millennium BC) describe the quantitative assay of gold by fire (Levey, 1959). For example, one 1st millennium BCE text says ‘2 minas 2 shekels of gold were put into the furnace, 10 1/2 shekels of them were lost in the furnace, 1 mina 51 1/2 shekels of dark gold came out of the furnace’ (Levey, 1959: 33). Since 60 shekels = 1 mina, we can calculate that the original purity of this gold was around 91.4%. The Medieval Arab scholar Geber (Abu Mūsā Jābir ibn Hayyān, c. 721–c. 815 CE) shows a knowledge of the purification of gold, referring to gold ‘sustaining the Tryal of the cupel, and cement’ (Holmyard, 1928: 63), and his works were translated into English by Richard Russel in 1678. From at least the late 13th century CE, the Royal Mint (established within the Tower of London around 1279 CE) has routinely assayed the fineness of English gold and silver coinage (Watson, 1962). The gold coinage of Henry III was certified as ‘fine’ (i.e., 24 carat, or 100% gold) in 1257 CE, and Edward III established a gold currency at 99.48% purity in 1343. This declined over the next two centuries, until the ‘Great Debasement’ of Henry VIII when it declined to 83.33%, to be reinstated to 99.45% by Edward VI in 1550. Such evidence comes from the results of an ancient ceremony known as the ‘Trial of the Pyx’ carried out at the Mint since the late 13th century, in which the *Miles Argentarius* (Assay Master) certifies the fineness of the coinage, the method of which is ‘differing but little from the modern fire-assay of silver’ (Watson, 1962: 6). Hence, the assay of precious metal precedes modern chemical analysis by many centuries.

Many surviving medieval European texts give increasingly clear descriptions of the process of precious metal purification, and also for assaying base metal ores. Theophilus’ *On Divers Arts*, written c. 1110–1140 CE, probably by the Benedictine monk Roger of Helmarshausen in Hesse, central Germany (Hawthorne and Smith, 1963), describes in Book III (Chapter 23) how to refine silver in a porous ash-lined cupel, using added lead to promote the oxidation of impurities. He also describes (Chapter 33) how to cement gold in order to purify it using a process which involves creating a ‘sandwich’ of thin sheets of gold alternating with layers of a mixture of recycled ground ceramics or burnt clay (two-thirds) with common salt (one-third) moistened with urine, heated in a fire-tested ‘casserole dish’. Heating the casserole for 24 hours causes the salt to remove impurities, and, after a number of repetitions of the process, pure gold is obtained. The fineness of the original gold can be established by comparing the weight of the refined gold with that of the original. Further chapters (69 and 70) describe how to separate gold from copper in gilded

Cambridge University Press & Assessment
978-1-009-59219-2 — Retrospective and Prospective for Scientific Provenance Studies in Archaeology
A. M. Pollard
Excerpt
More Information

scrap metal by cupellation in a bone-ash crucible, and how to separate gold from scrap gilded silver by heating with sulfur, which allows both gold and silver to be recovered.

The first European book to give a very clear description of assaying is the *Probierbüchlein*, possibly first published in Germany in 1518, although Annaliese Sisco and Cyril Stanley Smith (1949), the translators of this text into English, believe that the first edition is that of 1534 printed in Maydeburg. It was produced in numerous editions through the 16th and 17th centuries, and contained clear practical instructions for the purification of gold and silver by cementation, but also procedures for dissolving metals and ores in mineral acids for parting or assay, much as is still done today. It was the main source of such information in Europe until Lazarus Ercker's *Beschreibung allerfürnemisten mineralischen Ertzt und Berckwercksarten* (1574) (Sisco and Smith, 1951), which provided the first widely available European textbook for miners on assaying ores. This was extensively translated across Europe, including an English version published by Sir John Pettus (1683) as *Fleta Minor, or, the Laws of Art and Nature in Knowing, Judging, Assaying, Fining, Refining and Inlarging the Bodies of Confined Metals*. According to Pettus' translation, Ercker's introduction says:

> 'To learn and understand the way of Assaying, Proving and Refining of Metals, is an Excellent, Noble science, and an Antient and profitable Art, long since found out by the Art of Alchimy and Chimistry, as also all other Works of the Fire, by which not only the nature of Oars and Mines, and what Metalls contained in them are known; . . .'.

Clearly, the arts of assay were well-known long before analytical chemistry, and also that these methods all involved trial by fire – essentially a smaller-scale version of the processes required to reduce metals from their ores, or separate gold from silver, and therefore requiring access to metallurgical furnaces and facilities. It was not until the late 18th century CE that a different method emerged in Europe, ultimately giving rise to quantitative gravimetric analytical chemistry. This consisted of precipitating a known compound of a particular element out of a solution created by dissolving the sample in a suitable solvent. By employing a sequence of specific precipitations, a series of different elements can be quantified from the same solution. By weighing the amount of sample dissolved, and weighing the dried precipitate(s), the proportion of the precipitated element in the sample can be calculated, providing allowance can be made for the form in which the element is precipitated – for example, if tin (Sn) is precipitated as tin oxide (SnO_2), it would require correction by a factor of $(119/(119 + 2 \times 16))$, or 0.79, to reflect the proportion of oxygen in the compound. This could not have been calculated in this way until the atomic weights of the elements had been established, which began with John Dalton's '*New System of Chemical Philosophy*' (Dalton, 1808; 1827). Before that, an empirical observation would have been made (by fire) to calculate the proportion of metallic tin in the oxide precipitate.

Thus, at least in the chemical laboratory, trial by fire gradually gave way to gravimetric analysis, originally known as the 'humid method'. The first systematic exposition was that of Torbern Bergman (1735–1784) at the University of Uppsala, Sweden, who published a protocol for the aqueous gravimetric analysis of gemstones entitled '*Disquisitio chemica de terra gemmarum*' (Bergman, 1777). The big advance here was the use of an alkali fusion to bring the gemstone into solution, but Bergman's precipitation protocol was not very rigorous, and was subsequently improved by Martin Heinrich Klaproth (1743–1817) in Berlin (Klaproth, 1792/3) and Nicolas-Louis Vauquelin (1763–1829) in Paris (Vauquelin, 1799). These three analytical protocols have been re-published and compared by Oldroyd (1973).

The earliest report of the quantitative gravimetric chemical analysis of a metal appears to be that of Gustav von Engeström (1738–1813), who published a paper in 1776 on the composition of the imported white copper alloy paktong from China, which he found to contain approximately 29% nickel (with some cobalt). A year previously, von Engeström (1775) had published an analysis of imported zinc oxide from China, thus showing that he was engaged in understanding the nature of these imports – 'industrial espionage' to allow Europe to compete with Chinese technology. Bergmann himself published '*Dissertatio Chemica de Analysi Ferri*' in 1781. Given these dates for the early chemical analyses of metals in the late 1770s, it is remarkable to note that the earliest published chemical analyses of archaeological metal artefacts can be traced to 1777 by Johann Christian Wiegleb (1732–1800), read to the Kurmainzische Akademie Nutzlicher Wissenschaften, Mainz, on 2 April 1777 (Wiegleb, 1777; Pollard, 2018). He used nitric acid to dissolve the metal, but only measured tin, and assumed that the rest was copper. A few years later, Michel Jean Jérome Dizé (1764–1852) published the tin content of five Roman, one Greek, and two Gallic copper alloy coins (Dizé, 1790). Klaproth, in his better-known publication dated to 1792/3 (but actually read to the Royal Academy of Sciences and Belles-Lettres of Berlin on 9 July 1795, and published in 1798), reported the chemical analyses of six Greek and nine Roman coins, measuring directly copper, lead, and tin, and, in some samples, iron and silver – thus providing the earliest realistic analyses of ancient coins, justifiably earning him the title of the first archaeological chemist (Caley, 1949; Pollard, 2016), in addition to his renown as a mineral chemist.