Archaeological Chemistry

Archaeological Chemistry:

A Multidisciplinary Analysis of the Past

Edited by

Mary Virginia Orna
and Seth C. Rasmussen

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PREFACE

Archaeological chemistry is a topic which, when mentioned in a general public gathering, makes heads turn, eyes brighten, smiles burst forth, and questions emerge. People are very interested in archaeology, and we sometimes fear that the "chemistry" part must ride along on its coattails. Chemists are also very interested in archaeology, so much so that thirteen multi-day archaeological chemistry symposia, accompanied for the most part by published volumes, have been organized intermittently at American Chemical Society (ACS) national meetings over the course of the past 70 years. Earle R. Caley, a distinguished chemist-humanist who organized the first symposium in 1950, remarked that it was a unique experiment, the first to apply chemistry to archaeology anywhere, any time. He was also quick to point out how diverse the topic was and how it related to so many areas not thought to be even remotely related to chemistry.[1] Perusing the tables of contents of successive symposium publications[2] allows one to trace the evolution of the topic in terms of broadening disciplinary coverage and increased use of instrumental methods of analysis. However, as Curt W. Beck and Peter Oesper observed in the fifth symposium's publication, "a symposium on any rapidly growing field can only be a snapshot, showing one moment of development and not even all of that."[3] These welcome glimpses have been afforded to an ever-growing audience of this popular series in seven additional volumes published by the ACS. All of them have enjoyed the sponsorship of the ACS Division of the History of Chemistry, and from 1977 on, the sponsorship of the Subdivision of Archaeological Chemistry.

The latest of these Archaeological Chemistry symposia, the thirteenth, was generously supported by the ACS Division of the History of Chemistry and an Innovative Project Grant from the ACS Committee on

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[1] Earle R. Caley, "Symposium on Archaeological Chemistry. Introductory Remarks," Journal of Chemical Education 28, no. 2 (February, 1951): 63.

[2] A complete list of the symposia and their published proceedings is available at the Division of the History of Chemistry website at http://acshist.scs.illinois.edu/arch/arch-symposia-list.php, accessed 28 May 2020.

[3] Curt W. Beck and Peter Oesper, "Preface, Introduction," Archaeological Chemistry, Advances in Chemistry Series 138 (Washington, D.C.: American Chemical Society, 1974) vii-ix.

Divisional Activities. The collection of talks given during the symposium then became the nucleus of the present volume, now under the guidance of Cambridge Scholars Publishing. This volume continues the multidisciplinary trend with a world-class, international roster of scholars from academic institutions, museums, scientific research centers and educational research centers. It is our hope that this collection gives readers a taste of the current breadth of this exciting and growing field.

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CHAPTER 1

INTRODUCTION: ARCHAEOLOGICAL CHEMISTRY AS A MULTIDISCIPLINARY FIELD

MARY VIRGINIA ORNA[*]
AND SETH C. RASMUSSEN[†]

Abstract

Archaeological chemistry's traditional fields of interest–matter, time, and place–have been transformed due to different kinds of questions about the past that modern methods of scientific examination are in a position to shed some light on. Enhanced capabilities, for the most part multidisciplinary in nature, have revealed the limitations of confining archaeological investigations to chronological, spatial, and material areas without also considering the cultural context, the power of combined analytical techniques, and the ability of chemometrics to handle large databases to help interpret results. The chapters contained in this volume address many of these questions regarding archaeological chemistry applied to education, materials science, analysis of organic substances, and colorants. But regardless of the many advances that have been made in the field, the factors that will drive it forward in the future will be twofold: quality science combined with meaningful archaeological questions and ongoing, respectful dialogue across the many frontiers of the disciplines involved.

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Introduction

Archaeology, and by extension, archaeological chemistry, has always been concerned with three major interrogative aspects of speech: what?, when?, and where? Evolution of the discipline has been able to uncover answers to these three questions in an extremely efficient, ingenious, creative, and comprehensive manner. Analytical methods and instrumentation, from the 18th century onwards, have handled the question "what?" in an increasingly clarifying way, so much so that one seldom has to spend the time and effort to develop a new method of analysis. In fact, a roadmap for compositional analysis was put into place by the German chemist Martin Heinrich Klaproth (1743-1817) in the late 18th century, that endured until the advent of modern analytical instrumentation in the 20th century.[1] In one of the first examples of archaeological chemistry, the British chemist Sir Humphry Davy (1778-1829) (Fig. 1-1) used Klaproth's established comprehensive analytical protocols in analyzing the colors of artifacts from ancient Roman Pompeii *via* wet chemical analysis and sample comparisons.[2] Today, Davy's questions about the composition of things can not only be answered, but can also be expanded to include quantitative. as well as qualitative, information using an array of sophisticated instrumentation.[3]

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[1] Klaproth "Beitrag zur numismatische Docimasie," *Allgemeines Journal der Chemie* 6 (1801); 227-244 (later German version of the original French publication); Earle R. Caley, "Klaproth as a Pioneer in the Chemical Investigation of Antiquities," *J. Chem. Educ.* 26 (1949): 242-268; A. Mark Pollard, "Comin' in on a Wing and a Prayer": Archaeological Chemistry Since 1790," in *Archaeological Chemistry VIII,* eds. Ruth Ann Armitage and James H. Burton, American Chemical Society Symposium Series 1147 (Washington, DC: American Chemical Society, 2013), 451-459.

[2] Humphry Davy, "Some experiments and observations on the colours used in painting by the Ancients," *Philosophical Transactions of the Royal Society of London* 105 (1815) 97-124; Mary Virginia Orna, "Historic Mineral Pigments: Colorful Benchmarks of Ancient Civilizations," in *Chemical Technology in Antiquity*, ed. Seth C. Rasmussen, American Chemical Society Symposium Series 1211 (Washington, DC: American Chemical Society, 2015), 17-69; Gabriel Moshenska, "Michael Faraday's Contributions to Archaeological Chemistry," *Ambix* 62 (2015) 266-286.

[3] Michael D. Glascock, *Compositional Analysis in Archaeology* (Oxford Handbooks Online, 2016), accessed 2 March 2020, https://www.oxfordhandbooks.com/view/10.1093/oxfordhb/9780199935413.001.0001/oxfordhb-9780199935413-e-8

Fig. 1-1. Sir Humphry Davy, 1830. Engraving on wove paper (21.5 x 14.25 in.) by G. R. Newton, after a painting by Thomas Lawrence, London. Gift of Fisher Scientific International (Science History Institute Collections. Photograph by Gregory Tobias).

The question “when?” has always been the primary concern in archaeology. When discerning what development has impacted archaeology the most over the past century, practicing established archaeologists have answered without hesitation that the increasing availability of dating techniques takes pride of place. While such investigations have been dominated by radiocarbon dating, other methods such as amino acid racemization dating, thermoluminescence, and fluorine absorption have also played critical roles.[4]

Not far behind is the answer to the third question, “where?” The growing field of “provenance studies” can allow the ability to address questions about the social and economic structure of the supply and exchange networks of materials. Because of this, these studies are considered important in shedding light on the wider geographical story through such assessment of trade routes and other commercial patterns in the ancient world.[5]

Evolution of Archaeological Chemistry

A little bit of history might help to set the modern development of archaeological chemistry in context. In response to the British Museum’s deteriorating collection while in storage during World War I, it commissioned Alexander Scott (1853-1947), a renowned chemist, to address the problem: he recommended the establishment of a science laboratory. After a slow and woefully underfunded start in 1919, it eventually became one of the most renowned museum laboratories in the world,[6] and almost every major museum in the world has followed its lead. These museum laboratories are mainly concerned with dealing with their own collections, but many other types of museums with archaeological interests can also be found in universities, private foundations, and government.

Although not many people would take exception to William Tecumseh Sherman’s (1820-1891) most famous dictum, “war is hell,” World War II turned out to be the driver of many new products, such as synthetic rubber and nylon, and the necessary labs to create and analyze these products. As a result, analytical instrumental methods grew exponentially after that war, making it possible to utilize these new devices in novel ways such as archaeology and archaeological chemistry. And as the techniques became

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[4] John F. Marra, Hot Carbon: Carbon-14 and a Revolution in Science (Columbia University Press: New York, 2019) 51-70, 116-132; A. Mark Pollard and Carl Heron, *Archaeological Chemistry*, 2nd ed. (London, The Royal Society of Chemistry, 2008), 270-301; T. Douglas Price and James H. Burton, *An Introduction to Archaeological Chemistry* (Heidelberg: Springer, 2011), 16-17; Pamela S. Zurer, "Archaeological Chemistry. Physical science helps to unravel human history," *Chemical & Engineering News* 61, no. 8 (1983) 26-44.

[5] Pollard and Heron, *Archaeological Chemistry,* 406-411.

[6] Carl Heron and Sandra Smith, *A Century of Science and Conservation* (London: The British Museum, 2019), accessed 2 March 2020.

more complex, so also did the work of archaeological chemists.[7,8] In addition to addressing the primary factors of what, when, and where, they found themselves moving into areas that involved human modes of operation, environmental conditions, and other concerns, all of which shifted chronological, spatial, and material limitations to another level. For example, in addressing the question of time, the archaeologist turned fiction author Karin Alterberg remarks: "The exploration of the past is an exercise in empathy, a way of becoming conscious of what it is to be human in another time and place."[9] There was a time when archaeology was all about finds, *i.e.* artifacts, that had shouldered their way into the present. Now it is all about the absence that emerges from what we can find out about the artifacts that announce the past's continued presence. When we "image infinity going backwards in time...there is the intimation of the enormity of everything that has gone before: a solemn procession of life in all its myriad forms moving steadily towards this present moment."[10] Few sciences can evoke this sense of presence from what we do not know about the past. Astronomy, by its very nature, peers into the past to observe events that happened lightyears ago, and forms a credible storyline that adds a bit more information to our understanding of the universe. Likewise, the archaeological sciences, when taken together and exercised using the instrumental arsenal available in the modern laboratory, are currently succeeding in filling in the blanks regarding our knowledge about past civilizations.

The archaeological struggle between the past and the present has been summed up by the Roman senator and philosopher Boëthius (477-524): "The now that passes creates time; the now that remains creates eternity."[11] Any archaeological object is like a two-sided coin: a part that has passed and a part that remains. The part that remains can be examined for information about its role in the past, an "eternal" role that can remain

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[7] Mary Virginia Orna and Joseph B. Lambert, "New Directions in Archaeological Chemistry," in *Archaeological Chemistry: Organic, Inorganic, and Biochemical Analysis*, ed. Mary Virginia Orna, ACS Symposium Series No. 625 (Washington, DC: American Chemical Society, 1996) 1-9.

[8] Wen Chen and Mary Virginia Orna, "Recent Advances in Archaeological Chemistry," *Journal of Chemical Education* 73 (1996): 485-490.

[9] Karin Altenberg, "An Atlantis of the North Sea," *The Wall Street Journal* (9 August 2019), accessed 2 December 2019, https://www.wsj.com/articles/time-song-review-a-land-lost-beneath-the-sea-11565362615?mod=searchresults&page=4&pos=3#comments_sector

[10] Julia Blackburn, *Time Song* (New York, NY: Pantheon, 2019), viii.

[11] Boëthius (Anicius Manlius Severinus Boëthius), *De Trinitate* iv. "*Nunc fluens facit tempus, nunc stans facit aeternitatem.*"

enshrouded in mystery unless, bit by bit, the context for its fabrication and use can be pieced together from extraneous evidence. Making us aware of the continuous presence of the past in our lives is a work-in-progress of the archaeological chemist.

When the archaeological chemist addresses the question of space, it too has changed. It has transformed the question of "where?" to add the context of "why and how?" For example, changing environmental conditions will dictate how some archaeological sites might be better preserved. Conventional "do no harm" wisdom has opted for *in situ* preservation in the recent past, but this often has to be reassessed in light of modern developments. For example, the geochemistry of the Mesolithic Star Carr site in Yorkshire, UK, one of the most influential archives of human response to climate change, is contributing to the rapid, inexorable loss of valuable archaeological information. A conclusion of the study states "any bone and wood artifacts left in situ at the site are at immediate risk of increased deterioration or eventual loss."[12] Important decisions have to be made that may fly in the face of conventional protocols. Since thousands of archaeological sites are fast disappearing because of economic development, among other factors, some would say that rescue or preventive archaeology is an ethical duty.[13] This statement is certainly true in the case of Mes Aynak (Fig. 1-2), a 5000-year old culturally priceless site in Afghanistan situated at a central point along the Silk Road. It is under threat because of local looting and the government's desire to exploit the world's largest undeveloped copper deposit upon which it sits.[14] Attempts to preserve this site helped pave the way for widespread adoption of values-based management and the involvement of various stakeholder groups, and it asked fundamental questions regarding local community participation in archaeological heritage management.[15] This

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[12] Kirsty High, Nicky Milner, Ian Panter, Beatrice Demarchi, and Kirsty E. H. Penkman, "Lessons from Star Carr on the vulnerability of organic archaeological remains to environmental change," *Proceedings of the National Academy of Sciences of the United States of America* 113 (2016): 12957-12962.

[13] Jean-Paul Demoule, "We Still Have to Excavate – But not at any Price," *Archaeological Dialogues* 18 (2011):5.

[14] Mes Aynak. Sacred Land Film Project. https://sacredland.org/mes-aynak-afghanistan/. Accessed 29 May 2020.

[15] The Getty Conservation Institute. The Conservation and Management of Archaeological Sites. A Twenty-Year Perspective.
http://www.getty.edu/conservation/publications_resources/newsletters/33_1/feature.html. Accessed 28 May 2020

realization definitely shifts archaeology into the “why?” and “how?” modes of interrogation.

Fig. 1-2. Excavating the remains of a 3rd century CE Buddhist monastery at the Mes Aynak Site in Logar Province, Afghanistan. Remains of a bronze-age civilization have been found below the site (Photograph: Jerome Starkey).

Provenance, the “where?” question, used to be quite straightforward. If one could determine the geographical origin of an object, then a straight line could be drawn from that location to the place where it was found. Trace element profiles of obsidian deposits and artifacts and lead isotope ratios were excellent means of answering these questions. Now, however, advances in DNA methodologies have given rise to the possibility of solving vexing archaeological problems such as provenance of body parts. One notable example was the discovery of a desecrated tomb containing a husband-wife pair of mummies dating to about 2000 BCE at the ancient Egyptian necropolis of Deir el-Bersha. The archaeologists found dismembered body parts and a severed head – the work of tomb robbers centuries before. Mitochondrial DNA was extracted from a tooth in the head; DNA analysis determined that the head was male, but the DNA sample also corresponded most closely to a control individual from

Lebanon. It turns out that archaeological chemistry can also uncover ancient family relations![16]

Normally archaeological digs are not designed to answer the question "where?" since the excavators know perfectly well where they are when they are digging. However, if ancient documents regarding a place do not correspond to the archaeological record, this can lead to an impasse almost akin to the phenomenon of "fake news": the literal veracity of the documents is thrown into question. And the question is: do the documents reveal more about the time they were written than about the events they describe?[17]

The Multidisciplinary Nature of Archaeological Chemistry

From the examples given above, it becomes quite clear that archaeological chemistry can no longer deal with the simple ideas of time, matter, and place. It must now seriously deal with time past, time now, and time future, with respect to examination methods, cultural context, and questions of preservation. Matter must be examined now in many ways that both support and preclude excavation that is non-destructive, *in situ* when possible, and attentive to its provenance. Place has taken on a new meaning: not only provenance, but the how and why of the geographical positions of artifacts in the context of migration patterns and other factors that will convey a more nuanced understanding of the finds in question.

The chapters that apply archaeological chemistry to education explore some of these ideas. Chapter 2 on metals of archaeological interest describes the new ideas emerging from archaeometallurgy that connect with context as described in the Systems Thinking approach. Chapter 3 presents an interdisciplinary, curricular initiative, Materials Matter, that explores materials such as pigments from the perspectives of chemistry, physics, archaeology, and history. Chapter 4 presents K-12 educational activities for the introduction of alloy chemistry and processing towards the fabrication of art medals via methods developed in antiquity. Through

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[16] Odile Loreille, Shashikala Ratnayake, Adam L. Bazinet, Timothy B. Stockwell, Daniel D. Sommer, Nadin Rohland, Swapan Mallick, Philip L. F. Johnson, Pontus Skoglund, Anthony J. Onorato, Nicholas H. Bergman, David Reich and Jodi A. Irwin, "Biological Sexing of a 4000-Year-Old Egyptian Mummy Head to Assess the Potential of Nuclear DNA Recovery from the Most Damaged and Limited Forensic Specimens," *Genes* 9 (2018): 135-152.

[17] Jennifer Wallace, "Shifting Ground in the Holy Land," *Smithsonian* May (2006):58-66.

such activities, students can gain an appreciation for techniques and practices of the past, while also learning modern scientific principles.

Chapters 5 through 10, dealing with archaeological chemistry and materials science, look not only at the “what?” but also the “how?” and the all-important cultural contexts that require a multidisciplinary approach throughout. With a focus on the common materials of metal and glass, studies reveal differences in chemical composition and morphology between different archaeological samples, as well as modern materials, providing insight on chemical sources and practices used in their historical production. In addition, through the application of current materials science principles, such studies can allow prediction of how the physical properties of materials from antiquity differ from their modern counterparts, thus allowing new insight into the context of how such materials might have been utilized.

Chapters 11 and 12 explore two culturally important organic materials, wine and amber, using a multidisciplinary approach. Due to the organic nature of the species under study, these investigations require methods less common for archaeological studies and more typical for traditional studies in organic chemistry. Such methods include a greater application of wet-chemistry methods and spectroscopic methods such as nuclear magnetic resonance (NMR) spectroscopy, which find less application in most analyses of archaeological objects.

Chapters 13 through 18 survey the relationship of color to archaeological chemistry from a multidisciplinary point of view. Chapter 13 shows how a combination of biology, chemistry, physics, paleography, and linguistics can shed light on the creativity of ancient dyers in devising surprising chemical and physical combinations of an historic purple dye. Chapter 14 uses the history of medieval pigments as a framework for telling the story of another history: that of the development of infrared spectroscopy for art analysis. Chapter 15 sets the problematical dearth of historic blue pigments into the context of archaeo-synthesis utilizing a variety of disciplines from paleography to the arsenal of modern analytical methods. Although science and art diverged centuries ago, both are still intimately engaged with natural and synthetic materials that make up the archaeological trove. Archaeo-synthesis may be the new way to go, a practice that is alive and well among both bona fide archaeologists and amateurs.[18] Chapter 16 examines three of the oldest artificially produced pigments employed in the decoration of important polychrome monuments

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[18] The Making and Knowing Projects. Intersections of Craft Making and Scientific Knowing. https://www.makingandknowing.org/ , accessed 4 March 2020.

and artifacts during Classical and Late Antiquity by integration of direct scientific knowledge from the analysis of material culture with seminal texts of ancient writers and contemporary alchemical manuals, exploring not only the intrinsic optical, chemical and microstructural properties of these pigments, and how they contributed to the paintings' qualities, aesthetics and function but also how these properties could provide fingerprint markers as trace evidence in archaeological forensic investigations for authentication, classification, dating and attribution – a quintessentially multidisciplinary project. Chapter 17 presents new applications of portable X-ray fluorescence spectroscopy to the study of rock paintings, with particular focus on paint layer stratigraphy. This ability to see underneath surface paint layers shows great promise in answering stratigraphic ambiguities and highlights the potential applications of this non-destructive technique to rock art sites around the world. Typically, scientific examination of pigments has traditionally been carried out for four purposes: objective description of method, restoration, conservation, and authentication. Do these purposes need to be rethought? Do they need to be broadened out to other types of artifacts? What other purposes might the modern archaeologist have in mind?[19] In Chapter 18, we see the analysis of pigments and inks for the purpose of artifact conservation linked strongly with cultural heritage.

Beyond the examples reported in the current volume, a recent example of multidisciplinarity broadened the four purposes of pigment examination to structural characterization. For over a thousand years, a mysterious blue pigment called "folium," used to illuminate medieval manuscripts, has eluded identification. Only a multidisciplinary approach, including conservation scientists, biologists, chemists, and paleographers able to transliterate Hebrew characters into Portuguese, were able to solve the problem. The source of the pigment are the ripe berries of a plant native to Portugal, *Chrozophora tinctoria*; the multidisciplinary team was able to determine the structure of the major colorant, chrozophoridin (Fig. 1-3).[20,21]

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[19] Mary Virginia Orna, "Chemistry, Color, and Art," *Journal of Chemical Education* 78 (2001): 1305-1311.

[20] P. Nabais, J. Oliveira, F. Pina, N. Teixeira, V. de Freitas, N. F. Brás, A. Clemente, M. Rangel, A. M. S. Silva and M. J. Melo, "A 1000-year-old mystery solved: Unlocking the molecular structure for the medieval blue from *Chrozophora tinctoria*, also known as folium," *Science Advances* 6, (2020): eaaz7772.

[21] Maria J. Melo, Rita Castro, Paula Nabais, and Tatiana Vitorino, "The book on how to make all the colour paints for illuminating books: Unravelling a Portuguese Hebrew illuminators' manual," *Heritage Science* 6 (2018): 44.

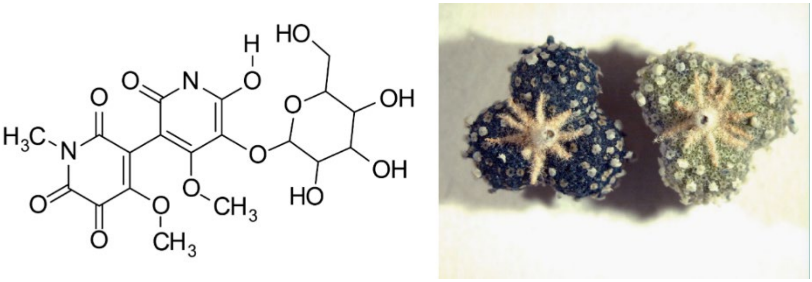

Fig. 1-3. Structural formula of chrozophoridin(left); Ripe berries of *Chrozophora tinctoria* (right, NOVA University Lisbon, Creative Commons License).

As the methods to delve more and more deeply into the chemical characteristics of species being examined become more sophisticated, the information gained will only give rise to more questions and more possibilities for collaboration across the disciplines. Not only will this bring new methods and techniques to bear on both new and old questions, but this will bring fresh perspective. That is, new ways of thinking about questions of archaeological interest without the restraints of long-held viewpoints.

Conclusion

Where do we expect to see the most important advances in archaeological chemistry in the next decade? Some would say in the improved and broader use of Raman spectroscopy both in the laboratory and in the field. The increasing importance of Raman spectroscopy applied to art and archaeology has led to numerous conferences on this subject as well as the growth of databases for spectral comparison and chemometrics techniques.[22] The multidisciplinary dialogue between Raman spectroscopists, archaeologists, and conservationists, especially those involved with preventive conservation, have been found most fruitful.[23] While there is no

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[22] Peter Vandenabeele, Howell G. M. Edwards and Luc Moens, “A Decade of Raman Spectroscopy in Art and Archaeology,” *Chemical Reviews* 107 (2007): 675-686.

[23] Olivier Berger, Pascale Bonnard Yersin, Jean-Marc Bonnard Yersin, Chantal Hartmann, Erwin Hildbrand, Vera Hubert, Katja Hunger, Marianne Ramstein and Marie Worle, “Applications of Micro-Raman Spectroscopy in Cultural Heritage – Examples from the Laboratory for Conservation Research of the Collections Centre of the Swiss National Museums,” *Chimia* 62 (2008): 882-886.

doubt that the entry of archaeological chemistry into “big science,” necessitating expensive equipment, expertise in handling the increasing amount of automatically generated data, and multivariate statistical approaches necessary to analyze these data, is essential, there are also the more human considerations that are often overlooked. We would tend to agree with the view that although we are very good at practicalities, we might be more remiss at engaging in quality thinking. As affirmed by Pollard and Heron, “[c]areful construction of relevant archaeological questions, and intelligent interpretation of results within a sound theoretical framework, should lead to further a better integration of chemical studies within archaeology.”[24] Of course, modern chemical studies are no longer simply pure chemistry and incorporate aspects of biology, physics, engineering, and materials science. As such, it can be expected that archaeological chemistry will also continue to incorporate and apply this multidisciplinary approach to chemical research, while also reinforcing traditional overlaps with history and archaeology.

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[24] Pollard and Heron, *Archaeological Chemistry*, 410.

ARCHAEOLOGICAL CHEMISTRY AND APPLICATIONS TO EDUCATION

CHAPTER 2

METALS OF ARCHAEOLOGICAL INTEREST: NEW DIRECTIONS

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Abstract

Two major archaeological eras, and one sub-era, take their names from metals: the Copper Age, the Bronze Age, and the Iron Age. Bronze, an alloy of copper and tin (and often smaller amounts of other materials), enjoyed widespread use from the third millennium BCE onwards due to its greater hardness with respect to pure copper or any other hard materials of the time, such as ceramics or gold. Weapons, tools, armor, and decorative and building materials made of bronze were therefore more durable and useful than any previously known material. Bronze artifacts also seem to have been used as valuable materials of trade. Its widespread use was only superseded in the 1300s BCE by iron, ushering in the Iron Age, a technological breakthrough marked by the widespread production of carbon steel, enabling the manufacture of tools and other objects superior to those made of bronze. This paper will review this history in terms of the advent of archaeometallurgy in the mid-20th century which applied the techniques of modern science along with archaeological methodologies to numerous studies of the impact of this technology on societies and cultural heritage. Since metals today play an important role in our personal lives just as they did in antiquity, this chapter will also address the chemistry curriculum in terms of pedagogical applications that will help incorporate the teaching of metals in elementary and secondary school courses.

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Archaeological Metals

Metals are all around us and almost everything we touch in the modern world has some kind of metal component including furniture, housing, eating utensils, jewelry, appliances, entertainment modules, and many other objects that we would be hard put to do without. Although we have many different types of metals at our disposal today (77% of the periodic table consists of metals), their abundance and availability could not always be counted on in archaeotime. In fact, there were only eight widely known metals in the ancient world, and these are listed in Table 2-1.

The historical sequence for metal usage can be linked directly to the free energy of formation of the metals' oxides. Gold does not form a stable oxide and can be found in its native state. Silver, lead, and copper can sometimes be found in the native state or in weakly bound oxide and sulfide ores.[1] Mercury occurs rarely in its native state: only as tiny globules in association with its principal ore, cinnabar (HgS). It is easily recoverable from its silver and gold amalgams, however, with slight heating. Iron occurs in its native state only in meteors. The earliest known copper metal work has been found in eastern Turkey and dated to the 9th millennium BCE.[2] Even though gold is much more easily found in its native state, the archaeological record situates the earliest gold finds to the mid-5th millennium BCE, about four thousand years after copper.[3] A glance at Table 2-1 provides an explanation of gold's late appearance: it is much less abundant than copper.

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[1] James A. Charles, "The Coming of Copper and Copper-Base Alloys and Iron: A Metallurgical Sequence," in *The Coming of the Age of Iron*, eds. Theodore A. Wertime and James D. Muhly (New Haven, CT: Yale University Press, 1980), 151-181.

[2] Thomas Birch, Thilo Rehren and Ernst Pernicka, "The Metallic Finds from Çatalhöyük: A Review and Preliminary New Work," in *Substantive Technologies at Çatalhöyük: Reports from the 2000–2008 Seasons*, ed. Ian Hodder, *Çatalhöyük Research Project series 9; BIAA Monograph 48; Monumenta Archaeologica 31* (Los Angeles, CA: Cotsen Institute of Archaeology, 2013), 307-318.

[3] David Killick and Thomas Fenn, "Archaeometallurgy: The Study of Pre-Industrial Mining and Metallurgy," *Annual Review of Anthropology* 41 (2012): 559.

Table 2-1. The Metals Known from Antiquity[4,5]

Metal	Z	Average Crustal Abundance (ppm)	Melting Point (K/°C)	Principal Ores	Formula
Iron, Fe	26	50,000	1808/1534.9	Hematite Magnetite Goethite Siderite	Fe_2O_3 Fe_3O_4 α-FeO(OH) $FeCO_3$
Zinc, Zn	30	70	692.7/965.8	Sphalerite Smithsonite	ZnS $ZnCO_3$
Copper, Cu	29	55	1356.6/1083.5	Chalcopyrite Chalcanthite	$CuFeS_2$ $CuSO_4 \cdot 5H_2O$
Lead, Pb	82	13	600.7/327.55	Galena Cerussite	PbS $PbCO_3$
Tin, Sn	50	2	505.1/232.0	Cassiterite	SnO_2
Silver, Ag	47	0.07	1235.1/962.0	Acanthite Stephanite	Ag_2S Ag_5SbS_4
Mercury, Hg	80	0.05	234.3/-38.9	Cinnabar	HgS
Gold, Au	79	<0.01	1337.6/1064.5	Gold	Au

A quantitative rationale for the sequence described above can be deduced by an examination of Figure 2-1, an Ellingham Diagram[6] for all of the archaeologically important metals except mercury and gold.

This plot of the free energy of formation of metal oxides (ΔG_f^o) against temperature (K) indicates, first of all, that the ΔG itself becomes less negative with increasing temperature, implying that at some very high temperature, the metal oxide will become unstable. However, given the fact that three millennia intervened between the initial use of copper (in its native state) and clearly smelted copper, it is evident that a whole series of innovations were necessary to make that quantum leap. These included the use of carbon as charcoal, a reducing atmosphere, an enclosed system to

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[4] John Emsley, *The Elements, 3rd ed.* (Oxford: Clarendon Press, 1998).

[5] David Killick and Thomas Fenn, “Archaeometallurgy: The Study of Pre-Industrial Mining and Metallurgy,” *Annual Review of Anthropology* 41 (2012): 559.

[6] Harold J. T. Ellingham, “Reducibility of Metal Oxides and Sulphides in Metallurgical Processes,” *Journal of the Society of Chemistry and Industry, London* 63, no. 5, (1944): 125.

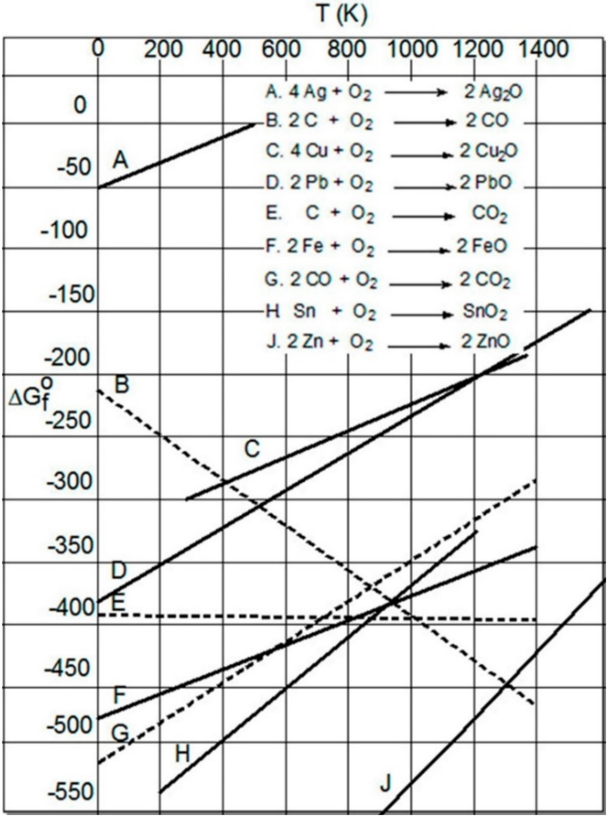

Figure 2-1. Ellingham Diagram for Metals Used in Antiquity superposed on three carbon/charcoal reactions (dashed lines), normalized to consumption of one mol O_2. Diagram: Authors' own work.

prevent loss of volatiles, the development of bellows and blowpipes to achieve higher temperatures, and fireproof ceramic materials to make proper containers, such as crucibles. In fact, though evidence for crucible smelting of copper in the 6th millennium BCE has been found in Anatolia, furnace smelting did not appear in the area until the very end of the Chalcolithic period, three millennia later.[7]

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[7] Paul T. Craddock, "From Hearth to Furnace: Evidences for the Earliest Metal Smelting Technologies in the Eastern Mediterranean," *Paléorient* 26, no. 2, (2000): 151; doi : https://doi.org/10.3406/paleo.2000.4716, (accessed July 16, 2019).

As the ΔG_f^o for oxidation of all the metals becomes less negative with rising temperature, reduction of the metal from its ore becomes more likely by simply heating it. This is obvious in the case of silver (Reaction A). For the other metals (Reactions C, D, F, H, and J), when a line intersects with one of the dashed carbon lines (Reactions B, E, or G), we see that in the presence of carbon or carbon monoxide, the metal can be reduced more easily as shown by the equations in Table 2-2.

From the combination of these reactions, we can see that as the temperature rises in the presence of carbon with a limited supply of air (a reducing atmosphere), it becomes easier to reduce a copper ore (Figure 2-2) to elemental copper. In fact, this can be accomplished at a mere 400 K (127 °C), which is a rationale for why copper ushered in the age of metals prior to the Bronze Age.

Table 2-2. Reaction of Copper with Carbon at 400 K

Reaction	Reaction Equation	ΔG_f^o (kj/mol)
B	$2\ C + O_2 \rightarrow 2\ CO$	-280
-C	$2\ Cu_2O \rightarrow 4\ Cu + O_2$	+280
B-C	$2\ C + 2\ Cu_2O \rightarrow 4\ Cu + 2\ CO$	0

Figure 2-2. Copper Ore from the Timna Valley, Israel. Copper has been mined at this site since the 5th Millennium BCE (Courtesy of Sana Shilstein, Weizmann Institute of Science, Israel).

In 1825, the Danish antiquarians, Christian Jürgensen Thomsen (1788-1865) and Jens Jacob Worsaae (1821-1885)[8] defined three archaeological periods based upon artifact usage/technological development: the Stone Age, the Bronze Age, and the Iron Age.[9] Over the past two centuries, these demarcations have been refined such that the term "Stone Age" is no longer used, but is sometimes referred to as the Archaic Age, or several divisions of Paleolithic and Neolithic periods (2.5 million – 3000 BCE). Furthermore, a Chalcolithic Age (6000 – 2000 BCE) is often inserted prior to the Bronze Age (3000 BCE – 500 CE) to signify the evolution from stone as the primary tool to the development of copper tools. Our present age, the Iron Age, is estimated to have its start date at about 1000 BCE. Since technological development differed from place to place, any dates assigned to the beginning and ending of these ages must be very broad, overlapping approximations.

In addition to the obvious functionality of metals, their acquisition and use have driven social and political change for millennia: their availability in one society has often enabled that society, due to superior tools and weapons, to exercise hegemony over others, either through war, hostile incursions, or economic sanctions. Their symbolic uses in monuments, jewelry and other art forms have bestowed noteworthy cultural meanings that have influenced neighboring societies in no less a fashion.

Evolution of Metal Usage through the Ages

When early craftsmen first discovered metals we will never know. Possibly flint knappers found some "rocks" that behaved quite differently from normal minerals in that they did not cleave along fixed planes. Or perhaps their behavior when heated yielded a fluid substance that hardened when cooled and had a shiny appearance. Whatever the event, or series of events, the native metals, copper, silver, and gold, were the earliest metals to be worked and used in ancient societies. Gradually, metalworkers made the paradigm shift from working found metals to extracting them from their ores, *i.e.*, smelting them, "an intellectual and technical landmark in

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[8] Worsaae's subsequent use of stratigraphy in excavation work was crucial in demonstrating the three-age system.

[9] Vera V. Mainz, "The Metals of Antiquity and Their Alloys," in *Chemical Technology in Antiquity, American Chemical Society Symposium Series 1211*, ed. Seth C. Rasmussen (Washington, D.C.: American Chemical Society, 2015), 139-180.

the history of the human race."[10] Smelting led to availability of additional metals, along with the development of smithing, annealing, forging, alloying, casting, and all the other metalworking arts. Copper became alloyed in turn by arsenic, tin, and lead, forming bronzes of which the most common was copper-tin with a percentage of about 10-12% tin, often with small amounts of other metals and semi-metals present by default. Bronzes were a great discovery because of their lower melting points, therefore making it easier to work with them, and superior hardness, as well as other desirable properties. By the 13th century BCE, the Bronze Age was at its technical and artistic height with large, highly embellished artifacts, both useful and decorative (Figure 2-3), that entered the archaeological record.

Figure 2-3. Great bronze cauldron from Tylissos, Crete; ca. 1600-1300 BCE. Archaeological Museum of Heraklion. Wikimedia Commons Image. On the outer surface of the vessel there are clearly outlined foundry seams that demonstrate the technique of manufacture.

Iron followed copper as the metal of choice once smelting was in place. Since iron's melting point is 1800 K (1540 °C), well beyond the capabilities of a Bronze Age hearth, it was probably discovered when it was inadvertently added, possibly as native meteoric iron, to the smelt mix along with charcoal. According to Figure 2-1, iron ores can be reduced at temperatures slightly higher than 800 K (ca. 525 °C) in the presence of carbon. If we look more closely at the Ellingham Diagram, we see that in

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[10] Joseph B. Lambert, *Traces of the Past: Unraveling the Secrets of Archaeology through Chemistry* (Reading, MA: Addison-Wesley, 1997), 173.