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Looking Back, Looking Forward: Materials Science in Art, Archaeology, and Art Conservation

Katherine T. Faber,[1] Francesca Casadio,[2] Admir Masic,[3] Luc Robbiola,[4] and Marc Walton[5]

[1]Division of Engineering and Applied Science, California Institute of Technology, Pasadena, California 91125, USA; email: ktfaber@caltech.edu

[2]The Art Institute of Chicago, Chicago, Illinois 60603, USA; email: fcasadio@artic.edu

[3]Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA; email: masic@mit.edu

[4]TRACES Laboratory, Université de Toulouse, CNRS UMR 5608, F-31058 Toulouse CEDEX 9, France; email: robbiola@univ-tlse2.fr

[5]Center for Scientific Studies in the Arts, Northwestern University, Evanston, Illinois 60208, USA; email: marc.walton@northwestern.edu

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Abstract

Cultural heritage materials, ranging from archaeological objects and sites to fine arts collections, are often characterized through their life cycle. In this review, the fundamentals and tools of materials science are used to explore such life cycles—first, via the origins of the materials and methods used to produce objects of function and artistry, and in some cases, examples of exceptional durability. The findings provide a window on our cultural heritage. Further, they inspire the design of sustainable materials for future generations. Also explored in this review are alteration phenomena over intervals as long as millennia or as brief as decades. Understanding the chemical processes that give rise to corrosion, passivation, or other degradation in chemical and physical properties can provide the foundation for conservation treatments. Finally, examples of characterization techniques that have been invented or enhanced to afford studies of cultural heritage materials, often nondestructively, are highlighted.

1. INTRODUCTION

Noted materials scientist Stephen Sass (1) wrote in his book *The Substance of Civilization* that "History is an alloy of all of the materials that we have invented or discovered, manipulated, used, and abused, and each has its tale to tell" (p. 6). It is impossible to fully understand society, past or present, without careful examination of the materials used to build and furnish the world around us. Our culture is seemingly shaped by and constrained by materials (2). One can go so far as to say that outside our basic biological requirements, the use of materials defines most human activity. Indeed, it is hard to imagine a modern world without the steel that girds our bridges and buildings, the ceramics that retain the heat of the food we eat, or the plastics that seem to encase all things in our current Anthropocene age. Today, almost everyone on the planet is transfixed by digital devices formed from rare-earth metals, silicon, copper, and glass. Outside these practical uses, materials are also designed for our aesthetic aspirations. Metal corrosion products, geological minerals, and plants can be transformed into pigments. In fact, from the earliest periods of human existence, we have made many choices about materials to satisfy our creative desires.

Specific to this review, how can scientific methods be used to unpack the complex cultural interactions that led to how people from the past designed, processed, and formed materials into objects and into art? Both anthropology and archaeological studies offer a deep body of literature on scientific approaches to material culture (3). Within this work, a commonly adopted framework is the *chaîne opératoire*, which essentially lays out the operational sequences that link the procurement of raw materials to their processing, formation into objects, use/trade, and finally being discarded as refuse (4)—effectively the life cycle of an object. Each of these discrete steps imparts chemical or physical features that, by analogy, can be considered part of the genetic code of the object that may be deciphered using scientific tools. Trade can be discerned through trace elemental and isotopic signatures inherited from the geological source of raw materials and linked, unaltered, to the fully formed object (5). Use can be recognized by imaging patterns of wear (6). Finally, the discarded object forms layers of corrosion products unique to its particular burial environment (7). This anthropological view of materiality shares many similarities with the materials science paradigm of processing, structure, and properties, which is the foundation for our studies (8). Conservation requires both the knowledge acquired from all of the earlier life intercessions, natural and artificial, and also how best to limit future alteration. The use of modelling has been particularly useful in advancing the field with an understanding of potential chemical reactions, their kinetics, and data reduction and analysis.

This review aims to describe cultural heritage materials science through a series of topics in the form of questions that span an object's lifetime. We make no pretense of covering the full breadth of cultural heritage materials in this review, and specifically we do not address object dating and provenance. Nonetheless, we have chosen recent examples in art and archaeology that span the role conservation science plays in metals, ceramics, polymers, and minerals, as well as organic materials from plants and animals found in art and archaeology.

We begin with the study of materials to inform the method of manufacture of ancient objects. Because past material successes help to guide us to durable and sustainable materials in the future (9), we include a segment on what might be learned from robust materials that have survived through the ages. This is followed by the characterization of the alteration of materials that occurs through their lifetime, ranging from ancient materials to contemporary materials, such as plastics. We close by looking at techniques and methodologies that have played a critical role in cultural heritage studies. In an attempt to analyze, restore, or preserve cultural heritage objects, the existing techniques of materials characterization are sometimes inadequate. This has offered opportunities for conservation scientists and their collaborators to invent new techniques or to push techniques or methods of analysis beyond their intended use or constraints. This leads not only to an iterative process in which these techniques expand their usefulness in other disciplines, but also to strategies that will guide us in the preservation of cultural heritage materials for years to come.

2. HOW DOES THE STUDY OF MATERIALS INFORM THE METHOD OF MANUFACTURE OF ANCIENT OBJECTS?

While the intention of the materials science paradigm is decidedly oriented toward the creation of new materials, it nonetheless lends itself to reverse engineering of artifacts. One can measure exactly the material properties (visual, mechanical, molecular, and elemental composition) as well as the material structure (microstructural phases and/or crystallinity) of an object and from these data infer how it was crafted or how it was intended to perform. An excellent example of reverse engineering of ancient artifacts using these principles comes from examining metallurgical microstructures that can reveal whether the material was cast, annealed, hammered, or worked by other methods. The traditional way of carrying out such analysis was to remove a wedge of metal and mount it in resin as a cross section, polish, etch, etc., before examining it optically at high magnification (10). However, these methods require a sample, which is not always possible to obtain from an intact object. Moreover, even when a sample is allowed, the object itself must retain some uncorroded metal. To supersede these obstacles, new characterization techniques are being developed for noninvasive and nondestructive analysis of metal microstructures, even if fully corroded. Bude & Bigelow (11) have pioneered the development of nanoscale X-ray computed tomography (XCT) with which the internal structure of a whole coin, for instance, can be revealed without the need for sampling. Noninvasive synchrotron XCT has also been applied to fully corroded Mesopotamian copper plate, revealing the precise distribution of the different mineralized phases (12). Similarly, by applying high-spatial-resolution photoluminescence (PL) imaging (13) on an entirely mineralized amulet dating back to 4,000 BC (14), the original as-cast metal structure was uncovered due to the luminescent properties of the semiconducting cuprous oxide formed at high temperature (**Figure 1**) (15). PL provided evidence of a eutectic Cu-Cu_2O structure surrounded with a dendrite structure formed during the cooling of this earliest known artifact made by a lost-wax casting technique.

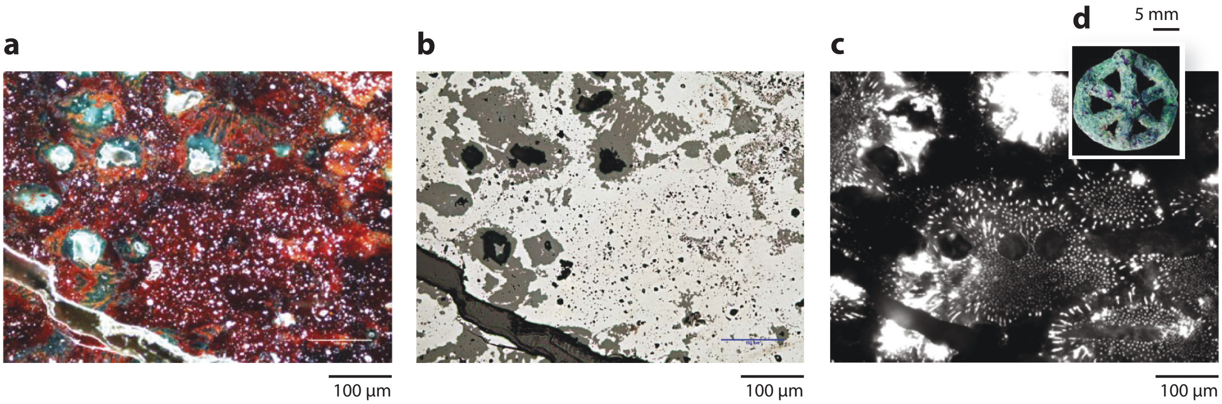

Figure 1

Photoluminescence revealing the eutectic fossil microstructure of the 6,000-year-old Mehrgarh lost-wax cast amulet (14, 15) and cross-section examination of the same area: (*a*) dark-field and (*b*) bright-field images under visible light and (*c*) photoluminescence image under 420- to 480-nm excitation and 850- to 1,020-nm bandpass emission (scale bars: 100 μm). (*d*) General view of the amulet (scale bar: 5 mm). Panel *d* adapted with permission from Reference 14; copyright D. Bagault, C2RMF.

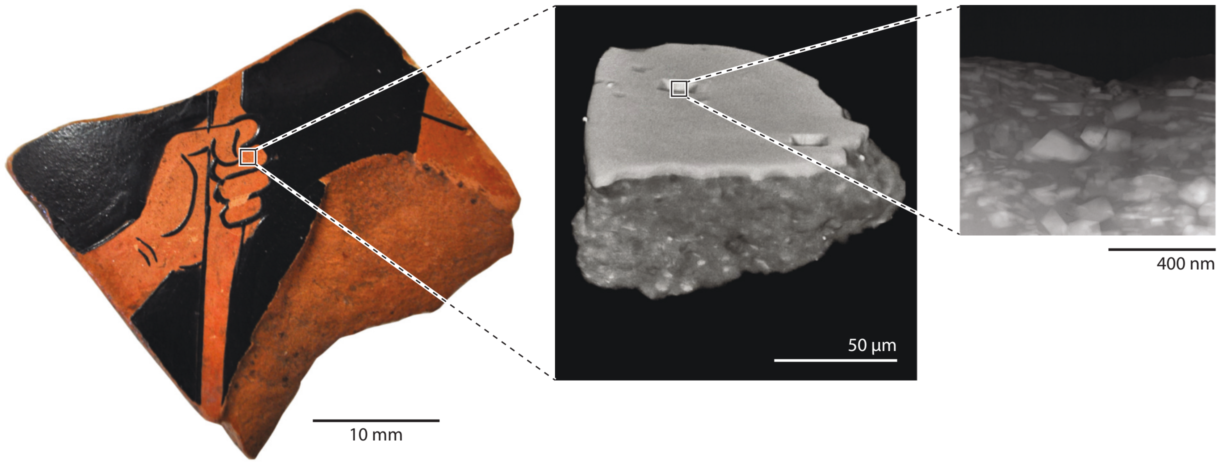

Figure 2

A red-figure style vessel fragment from fifth century BC Greece. Imaging and characterization at multiple length scales, from millimeters to microns, demonstrated that multiple firings were used to achieve this decorative effect. Vessel fragment on the left courtesy of the Getty's Open Content Program; attributed to the Kleophrades painter (J. Paul Getty Museum 95.AE.31.2).

Armed with the framework of the materials science paradigm, other questions naturally arise, such as how does the technology of a material evolve over time and how is this recognized in the archeological or historical record? One example of these discoveries relates to the shift in vase painting in fifth century BC Greece from the black-figure to red-figure styles. As has been amply documented by the history of art, there was a transformation in artistic expression at that point in time. Yet it was only recently revealed (16) through high-resolution transmission electron microscopy and synchrotron-based X-ray absorption spectroscopy studies that the single generation of potters who made these vessels also innovated new materials processing methods and firing practices to realize their creative aims (**Figure 2**). More often, material change occurs gradually over such long periods as to be entirely unrecognizable by the people making or using the material. Basing their analysis on the idea of a slow material change, Bray & Pollard (17) returned to a long-standing mystery surrounding the provenance of Early Bronze Age copper-alloy axes based on trace element analysis. Previous scholars could not convincingly tie the trace element fingerprint of the metal to any particular ore source. However, such a binary match did not account for recycling events that occurred over centuries, thus significantly depleting the metal of its original arsenic content. With this crucial insight in place, the metal source was identified as Ross Island in Ireland.

In the last two decades, the most significant technical innovations in ancient materials analysis have come from trace element and isotopic analysis. Previous generations of archaeological scientists relied on methods like neutron activation analysis to obtain sets of trace element values. Out of expedience, this time-consuming and tedious technique analyzed only a small fixed set of elements (18). However, with easy access to inductively coupled plasma mass spectrometry (ICP-MS), new trace element analyses take advantage of nearly a full periodic table of elements measured in seconds. When coupled to a laser ablation microscope, ICP-MS allows for spatially resolved trace elemental analysis that is now reaching submicron resolutions (19).

These advances opened a subfield in the analysis of ancient glass fragments that, due to their small size and extensive corrosion, could not have been analyzed by other trace element techniques. The first manufacture of glass can be traced back to Late Bronze Age Mesopotamia where the glass was refined, and the area developed into one of the most important centers for glass-making of the ancient world. Ancient Egyptians also knew how to make glass from quartz sand and natron (an alkaline substance). Shortland et al. (20) showed for the first time that ancient Mesopotamian and Egyptian glass could be differentiated from each other through comparison of rare-earth and trace metal values. Not only have these analyses led to new conclusions about the invention and origins of glass, but they have also revealed the trade of glass around the Mediterranean (21) and beyond into northern Europe (22), thus opening new perspectives on wide-scale trade in the Late Bronze Age world. Likewise, Roman glass has been an extremely active sphere of research reliant not only on trace element analysis (23), but also on isotopic analysis methods borrowed from geochemistry and made possible by the latest generation of ultrasensitive multicollector inductively coupled mass spectrometers (MC-ICPMSs). Wedepohl & Baumann (24) first used the $^{87}Sr/^{86}Sr$ ratio to identify marine mollusk shells in Roman glass, pointing toward the use of coastal sands in production. Degryse & Schneider (25) were able to determine whether a glass fragment was produced in the eastern or western Mediterranean based on the $^{143}Nd/^{144}Nd$ values of these broad tectonic zones. Most recently, Barfod et al. (26) found that $^{176}Hf/^{177}Hf$ could be used as a surprisingly specific signature to recognize glass produced near Alexandria in Egypt around the second century AD.

Glass is not the only material that has benefited from isotopic analysis. Returning to metals and extractive metallurgy, lead isotopes (^{208}Pb, ^{207}Pb, ^{206}Pb, and ^{204}Pb) have been used to link the geographic/geologic location of ores to objects as well as metal processing remains (slags, crucibles, etc.). While such analyses were met with criticism in the early 1990s on account of the poor precision of the first generation of thermal ionization mass spectrometers, a resurgence of lead isotopic analysis has occurred in recent years due to real gains in accuracy and detection limit afforded by MC-ICPMS instrumentation (27). Additional innovations in the statistical treatment of isotopic data, especially when combined with trace element analysis (28), have opened new possibilities. Furthermore, isotopic measurements of metals other than Pb, including Cu (29), Sn (30), and Fe (31), are emerging, further helping to refine the tracing of metal objects. As illustrated by Baron et al. (32), coupling the isotopic data with the content of Ag, Cu, and Pb in gold ores can be quite powerful in clarifying the provenance of Celtic gold and illuminating material ties to the economy.

Unraveling manufacturing techniques for various cultural heritage materials will become more thorough as instrumentation moves toward finer spatial resolution, and our ability to address humanistic questions will be made more specific. A glance at some recent literature shows that we are already going down this path. For instance, in studies showing the transformation of the rock lapis lazuli into ultramarine (33–35) and cobalt ore into a glass known as smalt (36–38), two materials used as blue pigments, or mullite needles forming in Hessian wares to make better refractories (39), humanistic concerns about the alchemical alteration and magical transformation of materials is a central theme. New questions arise from these studies regarding how artists or color-makers learned to manufacture these materials and what role recipes played in the transfer of knowledge across time and space. Understanding how materials processing added value and how the trade of these goods was controlled are aims of materials analysis going forward, suggesting a rich palette of future problems for materials scientists to address in close collaboration with other specialties.

3. WHAT CAN ANCIENT MATERIALS TEACH US ABOUT DESIGNING SUSTAINABLE MATERIALS TODAY?

Since the Industrial Revolution, our use of engineering materials has increased exponentially. With the substantial rise in demand, there are growing concerns about the sustainability of our current practices. Materials processing technologies have played a key role in the cultural history of human civilizations. The ancient remains of the Romans, Egyptians, Mayans, and many others testify to these peoples' extraordinarily sophisticated knowledge of both structural and decorative materials. While much of the research into ancient materials is for historical and preservation purposes, some studies are starting to approach such research with durability in mind (9). We maintain that ancient materials processing technologies are a powerful source of inspiration for the innovative design of modern materials. What we call antiquity- or paleo-inspired materials are those that naturally possess extraordinary, long-term mechanical, structural, or chemical durability. In contrast to studies that seek to recreate such ancient solutions, this approach aims to design new materials suitable for modern applications. There are many archaeological materials around the world that can be used as model materials for this antiquity-inspired approach. Roman concrete, Egyptian blue (EB) and Mayan blue, or even the cuprous oxide in corroded copper discussed earlier, to name a few, show remarkable durability.

Concrete, with its main ingredient being ordinary Portland cement (OPC), is the most widely used modern construction material with an expected lifetime not exceeding 150 years. It currently accounts for over 7% of global CO_2 emissions, and its production is expected to at least double by 2050 (40). As is well known, concrete is prone to degradation. The consequences of these processes are huge in terms of maintenance costs and public safety. Long-term, energy-related applications of cementitious materials, combined with continued pressure for rehabilitation and reconstruction of infrastructure, motivate the exploration of more durable solutions. Ancient Roman concrete structures have lasted thousands of years through a variety of seismic and climate zones. The formula for Roman concrete, or *opus cæmenticium*, in itself was not new and had been used to varying levels of success by the Greeks and Phoenicians. However, the Romans' addition of local *pozzolana* (pozzolan or volcanic ash) to the mixture represented a breakthrough in the creation of binding mortar (41). Pozzolan, which is native to the areas surrounding Mount Vesuvius in Campania, possesses a unique chemical composition that gives the resulting mortar a substantial compressive strength and allows it to set in aqueous environments. The mortar of Roman concrete is considered to be the prototype for modern concretes that partially replace OPC with natural pozzolans to reduce embodied CO_2 and produce a resilient calcium-aluminum-silicate-hydrate (C-A-S-H) binder (42) and has been recently studied (43) using a combination of energy-dispersive X-ray spectroscopy (EDS) and Raman spectroscopy (**Figure 3**). The ancient Roman technology for creating cement features three important characteristics that have significant implications for inspiring sustainable modern solutions: lower carbon and energy footprint, intrinsic self-healing properties, and use of recycled materials.

First, the embodied energy of the ancient Roman cement formula is significantly lower compared to that of OPC because of the lower temperatures required to calcine limestone. OPC is based on clinker that is produced by calcining limestone and clay at temperatures that reach 1,450°C, a process that requires a significant amount of energy generally supplied through burning fuels. As a consequence, the total carbon footprint comes from carbonates associated with limestone (about 50%) and the rest from the composition of the burning fuels. The calcining of limestone to produce lime, the essential starting ingredient for Roman concrete, is associated with temperatures not exceeding 1,000°C. Integrating this to the relatively longer useful life of Roman concrete, this property could be fundamental in the design of more durable and environmentally friendly construction materials (44–47).

Second, the low permeability characteristics of the Roman mortar and the autogenous self-healing processes are critical for the long-term chemical and mechanical resilience of concrete structures. The extreme durability of ancient Roman concrete can be associated with the postpozzolanic reactions of fluids supersaturated in calcium, silicon, aluminum, sodium, and potassium in

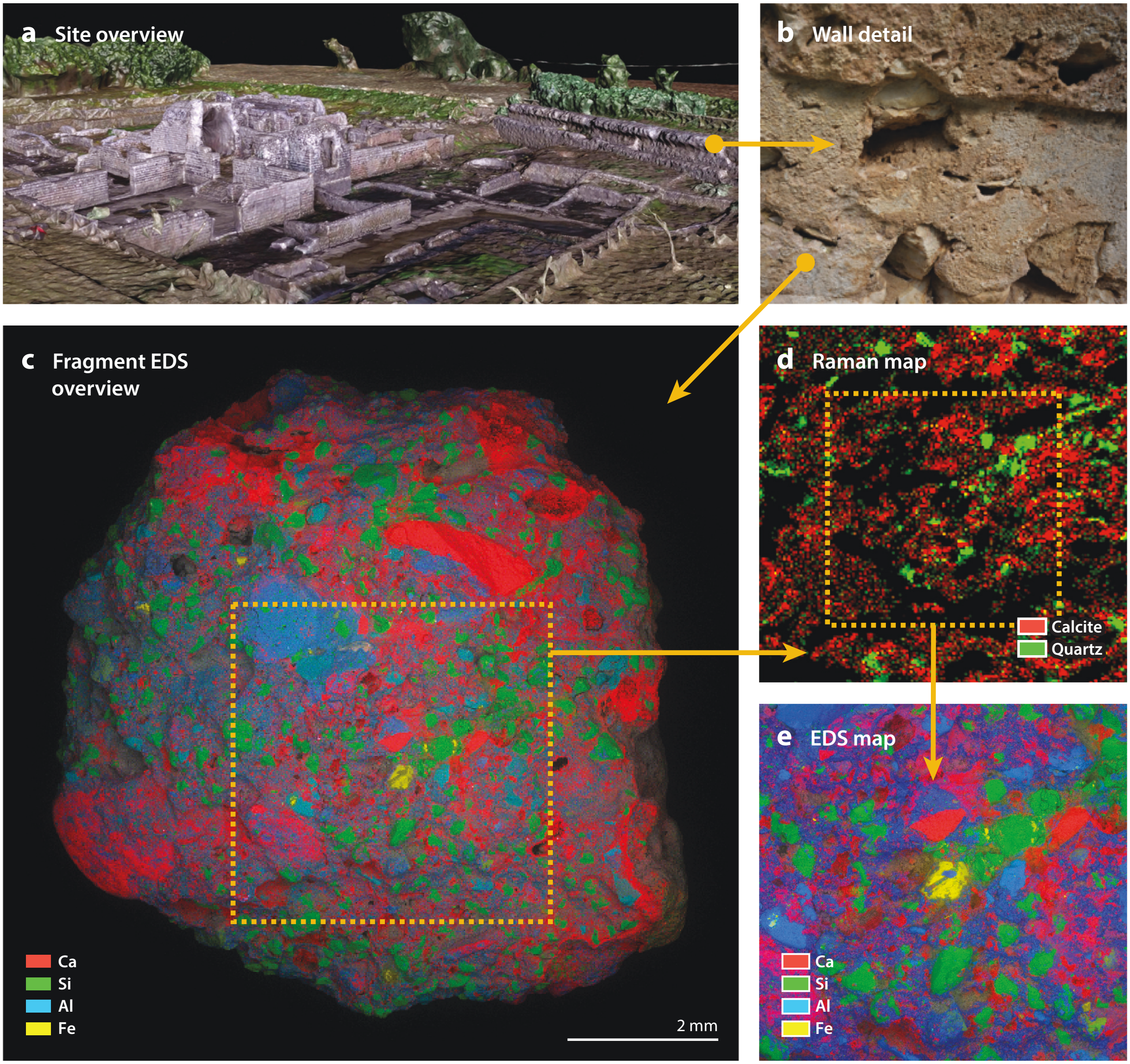

Figure 3

Correlative energy-dispersive X-ray spectroscopy (EDS)/Raman study of an ancient Roman concrete sample from the Privernum archaeological site in Italy. (*a*) 3D reconstruction of the archaeological site, collected using drone photogrammetry, and (*b*) a photograph of the wall surface. (*c*) The multidetector EDS element map of the entire concrete sample and (*d*) the 3D Raman phase map with detail in panel *e* allow the correlative mineral phase mapping of irregular pristine samples. Figure adapted from Reference 43 (CC BY).

the vesicles (relict gas bubbles), interfacial zones, and pore spaces of concrete and mortars. These processes eventually lead to the formation of crystalline analogs of C-A-S-H, namely, strätlingite in the case of open-air structures and Al-tobermorite in marine environments (45, 48). Recent findings reveal that Al-tobermorite also occurs in the leached perimeters of feldspar fragments, zeolitized pumice vesicles, and in situ phillipsite fabrics in relict pores (49). Recent research has posited that the fine interweave of sulfur-rich fibers in the mortar matrix enhances aggregate bonding, which further contributes to the durability of Roman concrete (50). Understanding the continued development of rock-forming minerals in situ is one of the key challenges and motivations for exploring Roman concrete as the inspiration for a self-healing, durable modern cement.

Finally, Roman builders also used recycled construction materials to enhance their concrete's durability (51). For example, their *opus caementicium* consisted of diverse kinds of aggregates, such as pebbles and irregular gravel, brick and tile fragments, and other terracotta goods, like broken pieces of amphorae. Collectively, the crushed, recycled ceramic fragments, also known as *cocciopesto*, are frequently associated with structures that are in continuous or frequent contact with water, such as cisterns, aqueducts, and pavements (52). The fascinating long-term success of mortars utilizing fired ceramic fragments is attributed to the development of a reaction rim in which the fired clay particles chemically bond with the binder, improving the mechanical properties of the mortar (53). Having both the environmental benefit of recycling materials and the structural benefit of improved performance, such ancient strategies can provide insights into durable design and incentivize recycling in modern construction.

The utilization of ancient insights to produce durable materials can be generalized to many other materials, including ancient alloys, glasses, or pigments. EB is the oldest known synthetic pigment dating to the fourth dynasty in Egypt and possibly earlier to replace the very valuable lapis lazuli (blue stone) (54). EB was used for millennia all around the Mediterranean basin, in the Middle East, and in Europe. However, its use decreased during the late Roman period and the Middle Ages, and, as such, knowledge about this technology was lost (55, 56). In ancient times, EB was prepared by heating a mixture of a calcium-rich compound (e.g., the powder of calcareous rock), a source of copper (copper alloy or copper ore, such as malachite), silica powder (sand), and natron to between 850 and 1,000°C (57). Described by Vitruvius in his *De Architectura* and reverse engineered in the late nineteenth century, EB has always attracted attention and curiosity for its beauty and durability. Developing intense blue, inorganic pigments that are environmentally benign, earth abundant, and durable is a key challenge in pigment and dye design. As demonstrated by archaeological evidence, EB is indeed very stable in almost any condition; it is made using simple and inexpensive methods of production; and its constituents are readily available, abundant, and safe. Furthermore, EB is famous for the near-infrared PL properties of its main crystalline component, cuprorivaite (58, 59). These exceptional properties are currently being studied for applications that range from forensic science to nanotechnology (60–62).

As another example, Maya blue, a pigment seen in Central American wall paintings and statues from the eighth to fifteenth centuries AD, exhibits remarkable durability and chemical resilience. The ancient Mayans boiled a clay (palygorskite) and organic colorant (indigo) to create the first permanent organic pigment (63). Its color and high stability against chemical aggression in the form of strong acid and base treatments can be explained by a hydrogen-bonded organic/inorganic complex in which indigo molecules are dispersed inside the nanochannels and grooves of the palygorskite mineral (64, 65). The Mayans heated the raw materials in the range of 70–130°C (66), allowing the indigo to penetrate the palygorskite tunnels and paving the road for a series of ultrastable synthetic organic pigments in a clay host used in a variety of applications (67–70). One of these applications is the methyl red@palygorskite that uses a similar method of production except that the indigo is substituted by the organic molecule methyl red to obtain a purple-colored host/guest supramolecular complex (71).

The above-mentioned examples rely on acquiring a fundamental understanding of the underlying physical and chemical mechanisms responsible for the remarkable properties of ancient engineering materials. The core feature of our interest in these materials is their enduring behavior over long temporal scales. We maintain that ancient materials processing technologies and the diagenesis-related processes are a powerful source of inspiration for innovative design of modern materials. Such utilization of ancient insights to produce new materials can be generalized and potentially lead to solutions with proven sustainability.

4. WHAT CAN WE LEARN ABOUT ALTERATION PHENOMENA AND THEIR PREVENTION FROM THE STUDY OF CULTURAL HERITAGE MATERIALS AND VICE VERSA?

Alteration phenomena of cultural heritage materials are complex. Not only is the original state and original condition of cultural heritage materials undefined, but the impact due to human activities and the environment over time is also poorly known. Studying the alteration of cultural heritage materials first involves the characterization of the present state of the material through use of noninvasive or minimally invasive techniques. A second, often necessary step involves the use of modern materials to experimentally determine, validate, or mimic the alteration process or phenomenon revealed from ancient materials studies. By iterating between studies of ancient and modern materials (artificially aged), a preventive approach for conservation of these materials may be formulated. Such studies are particularly challenging given that ancient materials are often of limited quantity, precious, and frequently characterized by a complex state of degradation due to multiple sources of alteration. A clear objective is to adopt a multiscale and multipronged approach for learning about the degradation of properties of ancient materials, including not only (bio)chemical (with elemental and functional groups identification) but also structural and physical characterization.

Regarding metals and alloys, degradation (mainly corrosion) studies not only provide information on the current state and its stability, but they can also inform the fundamental processes involving either significant reactivity with the atmosphere or, conversely, demonstrate a remarkably passivating behavior. A typical example is bronze (Cu-Sn alloys). Under certain corrosive environments, such as with chlorides in seawater or sulfide compounds in anaerobic soils, the corrosion products within the bronze patina are found to be unstable when exposed to the ambient atmosphere, which induces a dramatic surface exfoliation (cf. **https://skfb.ly/6OPOC** in 72). In contrast, bronze patinas can provide remarkable protective properties in most natural environments. By coupling chemical and structural characterization of ancient archaeological artifacts (73) or outdoor monuments (74) with modern electrochemical investigations in aqueous electrolytes (75, 76), researchers acquired evidence of a fundamental corrosion phenomenon. These unique properties of tin in a copper solid solution lead to the preferential dissolution of copper (decuprification), improving bronze corrosion resistance, as evidenced by focused ion beam scanning electron microscopy (FIB-SEM) studies (77). Because tin atoms are tetravalent (similar to carbon or silicon), nanocrystallites of tin (IV) hydroxyl-oxide species (**Figure 4**) can form a stable solid network within the patina, through which other species may percolate between the surface and bulk (73, 75, 78). As a result, the original surface of the bronze appears fossilized and a pseudomorphism prevails, preserving the original shape of the artifact if no corrosion resumption occurs in the atmosphere (72–74). Identified in most common natural environments (soil, water, air), this process has been observed in all tin bronzes since the Bronze Age. Consequently, the corrosion of bronze can serve as a source of historical data, e.g., revealing old polishing grooves and signs of use, or can provide the archaeological abandonment conditions prior to water submersion (72). Moreover, the bronze patinas may inspire the development of new protective and eco-friendly coatings (79).

Degradation also may affect the support materials of ancient artifacts, such as collagen in parchments. A notable example is the collection of ancient texts well known as the Dead Sea Scrolls,

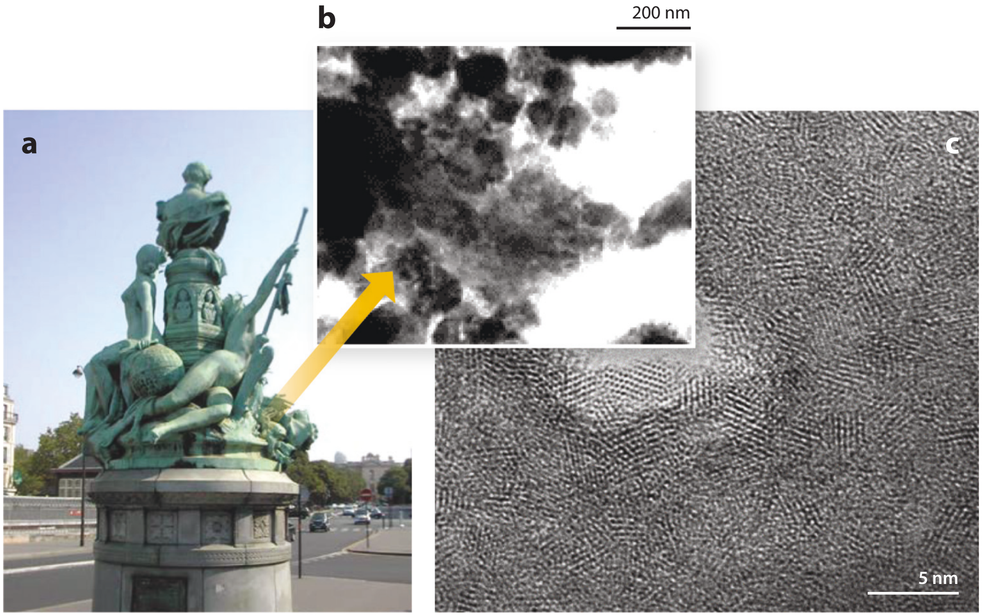

Figure 4

Tin-containing nanoprecipitates in bronze patina (74). (*a*) Bronze monument of Francis Garnier (Paris, 1898). (*b*) Transmission electron microscopy observation of pale-green patina compounds (scale bar: 200 nm) and (*c*) high-resolution transmission electron microscopy lattice image of tin-species nanoprecipitates (scale bar: 5 nm).

discovered in the mid-twentieth century. Miraculously preserved in the natural limestone and man-made marl caves of the Judean desert, the scrolls can today be found in many institutions and private collections around the world. Studies of the Dead Sea Scrolls using advanced analytical techniques show that questions about their production methods, their provenance, and whether the fragments can be traced to a single scroll can be addressed with materials science tools (80, 81). Using polarized Raman spectroscopy, Schütz et al. (82) were also able to measure the level of disorder of protein molecular units in collagen fibers, effectively developing a noninvasive and nondestructive methodology to infer the relative degree of degradation of the scrolls. Latour et al. (83) investigated ancient parchments and references (untanned skin and pure collagen), mainly composed of dermal fibrillar collagen, at different length scales by implementing noninvasive correlative nonlinear optical imaging and nanoinfrared measurements. Coupling morphological and chemical information provided unambiguous collagen and gelatin signatures. New insight into the understanding of the irreversible denaturation of collagen to gelatin (gelatinization) allows advancements in the preservation of collagen-based materials in museum and archival collections. In addition, this study opens avenues for a broad range of applications regarding such widespread biological materials.

Another support for cultural heritage materials of importance is wood (deadwood) composed primarily of cellulose, lignin, hemicellulose, pectin, and other water-soluble and insoluble extractives. This complex biomaterial widely used by humans most often suffers serious degradation calling for extensive restoration treatments and preventative conservation. Walsh-Korb & Avérous (84) provide an overview of the chemistry and biochemistry of wood degraded by numerous chemical, biological, and environmental agents and propose how degradation phenomena influence materials properties. The understanding of degradation processes affords critical discussions of conservation treatments, including newly developed biomaterial consolidants.

The investigation of alteration processes of cultural heritage materials requires a genuine knowledge of the degradation process. This leads to research focused on controlling the kinetics of the decay phenomena and developing specific methods for reproducing them. Model samples can be produced according to ancient recipes, such as in panel paintings (85), or using a standard, such as wood panel (86), but often controlled aging tests are carried out in simulated environments allowing monitoring of the degradation process. For example, Krzemień et al. (85) demonstrated that the cracking mechanism of panel paintings is related to brittle-to-ductile transitions of the gesso layer applied on the wooden support at high relative humidity levels. On this basis, laboratory-controlled craquelure patterns have been realistically produced to mimic the historical ones, offering a precise classification of crack formations on historical paintings.

A typical example of accelerated aging with heat as reported by Franzoni et al. (87) proved to be a fairly effective and reproducible method to cause artificial weathering in stone samples (i.e., near-surface damage). This thermal aging approach was validated for testing consolidants (88). In this study, decayed stone samples with features similar to naturally weathered marble were efficiently produced and tested. A predictive mathematical model coupling alteration depth and dynamic elastic modulus variations was also tested and could be tailored to other lithotypes or ceramics. Stone can also be affected by crystallization damage induced by the evolution of sodium sulfate phases, which cause internal stresses due to pronounced precipitation within pores (89). In this case, another specific aging process based on cyclic impregnation and drying rather than constant capillary uptake has shed light on this corrosion phenomenon, even though the artificial aging environment does not necessarily correlate with real exposure conditions in which supersaturated solutions within pores can be produced by evaporation. For ancient metals, artificial aging methods remain essential to validate theories on actual corrosion processes or to test treatments such as those for determining the effectiveness of protective coatings. Aging tests may lead to the design of international aging standards in which corrosive conditions and environments are standardized. However, for conservation applications, standards are not always adequate and more effective methodologies must be developed. For example, as reported in Reference 77 concerning testing protective coatings for outdoor bronzes, aging runoff effects were simulated by dropping equivalent acid rain solutions on bronze coupons to develop altered standard surfaces that could mimic the real patina of ancient bronze. This approach allowed for a correct assessment of new conservation treatments in accordance with valuable engineering practices. Conversely, alteration studies of ancient materials offer a unique perspective for understanding fundamental processes not easily revealed in the laboratory and for appraising the impact of time on aging of materials.

Degradation studies have also been used to elucidate both beneficial and harmful roles of metal soaps in paints. Metal (primarily lead, copper, and zinc) carboxylates are formed by reaction of metallic pigments and driers with the oil-based media used for paintings. A typical example of this was reported by Cotte et al. (90) for lead soaps, observed from ancient to modern periods, responsible for processes that influence color as well as structure of the paint stratigraphy or external varnish. This work shows how fundamental it is to determine both the origin(s) and the role(s) of metal soaps in paints for answering the simple question, Are metal soaps (systematically) associated with degradation? By comparing data collected via micro Fourier transform infrared (FTIR) and micro X-ray diffraction spectroscopies on ancient artifacts and on model paints according to historical recipes, the present components in historical paintings may be found to differ markedly from those originally used or prepared by the painter. A case in point is the unusual presence of plumbonacrite (lead carbonate hydroxide oxide) observed both on a degraded painting by Van Gogh as well as on laboratory-aged samples. For these studies of complex degradation processes affecting paint layers on different supports, investigating cross sections, which couple observation and analytical methods to draw precise analytical imaging, becomes paramount (91).

In addition to the chemical and structural alteration of materials illustrated above, degradation from mechanical damage is also of fundamental importance for diagnosing the conservation state of heritage objects and planning appropriate conservation strategies. Structural degradation is typically the case for oil paints that embrittle by polymerization as reported in Reference 92, a study that correlates mechanical and chemical properties. For oil paintings (92), a permanent transformation of the oil paint film occurs over time, affecting the physical properties of naturally aged paint films. The identification of degradation processes induces development of conservation strategies in which modeling of the degradation behavior and monitoring damage risk are more integrated. An example of this was reported by Oakley et al. (93), who constructed a microkinetic model for the curing and aging of oil-based systems, specifically for the autoxidation of ethyl linoleate catalyzed by cobalt(II) 2-ethyl hexanoate as a function of catalyst concentration and temperature.

Although these long-term mechanical changes due to aging are often minor, they reveal that reactivity and susceptibility to degradation can continue over hundreds of years. The role of temperature and relative humidity variation on mechanical behavior was reported in the foundational research of Mecklenburg & Tumosa (94) and reviewed by G. Depola, K. Shull & M. Walton (manuscript in review). From computational studies on model paintings, stresses in the paintings were assessed, which has had a direct impact on the risk assessment for transportation of works of art. On the macroscopic scale, mechanical testing methods have recently been used to examine the damaging effects of vibrations during the transport of works of art. For instance, Sauvage et al. (95) examined how pastel drawings couple to sound waves and assessed what frequencies are most damaging, providing us with new avenues for damage investigation.

5. WHAT CHALLENGES ARE PRESENTED BY THE RECENT USE OF PLASTICS AND POLYMERS IN CULTURAL HERITAGE?

Plastics entered the market in the late nineteenth century and were immediately incorporated into the canon of art making. All classes of polymers—thermosets, thermoplastics, and elastomers—have been widely adopted by artists and designers for functional objects, for objects of design, and for making of works of art. Plastics are pervasive in museum collections encompassing not only works of modern and contemporary art and design, but also historical artifacts of the aviation industry (96) and prosthetics documenting the history of medical science (97), to name a few. Their quick development and proliferation are matched only by the rapid decay of their material, structural, and aesthetic properties. With plastics, timescales of degradation are measured in decades, not centuries.

Material identification is the first essential step toward advancing our knowledge of degradation phenomena in complex systems, as many of these objects come into museum collections with the generic label of plastics. Composition (including the constituent macromolecules as well as the myriad additives such as plasticizers, colorants, and fillers), microstructure, and manufacturing processes all play a role in the kinetics and pathways of decay. However, they are often shrouded in trade secrets or largely forgotten due to rapid technical obsolescence.

Optical techniques provide fast and noninvasive identification of polymers used in artworks just as reliably as for industrial applications in commercial packaging or for the study of marine microplastics pollution (98). When analyzing art objects, especially those with plastics that may be degraded or easily scratched, contactless, portable methods of in situ analysis are preferred. FTIR spectroscopy in reflectance and attenuated reflectance mode (99, 100), near-infrared spectroscopy

(101), and Raman and Fourier transform Raman spectroscopy (102) are widespread methods of identification that have been used to establish expansive databases of plastics of relevance to art and design. Among these polymers, cellulose esters (103), polyurethane (PUR) (104), and plasticized polyvinyl chloride (PVC) (105) are the most readily and catastrophically degraded.

Celluloid, developed in the 1860s and 1870s from modified natural materials, was the first synthetic polymer. Manufactured from cellulose nitrate and camphor, this early thermoplastic polymer had attractive features: It could be molded and shaped with temperature, and it was transparent. Redolent of modernity, celluloid was most notoriously adopted by Russian avant-garde artists Naum Gabo (1890–1977) and Antoine Pevsner (1886–1962). Because it could be extruded into thin, strong, and flexible sheets, it became popular as a support for photographic and motion-picture film. However, cellulose nitrate undergoes autocatalytic degradation leading to denitration, depolymerization, and emission of nitrogen oxide gases. Combined with loss of the camphor plasticizer, these processes lead to embrittlement, cracking, crazing, warping, yellowing, and loss of structural strength (106). This rapid deterioration, combined with extreme flammability, has led in the 1920s to the substitution of cellulose nitrate with cellulose acetate as a support for motion picture film and photographic negatives (107).

Cellulose acetate esters degrade via hydrolysis, deacetylation, and loss of plasticizers, a process that is accelerated by temperature, humidity, and UV light. While industry can exploit this fast degradation by engineering consumer products with lower environmental impact (108), for works of art and design, physical and chemical deterioration may lead to total loss of the artwork, depending on composition and storage conditions. Naum Gabo's *Construction in Space: Two Cones*, 1927, is a famous example of complete material failure: Forty years after its completion, it was crumbling and deemed unexhibitable (**Figure 5**). Sutherland et al. (109) analyzed the sculpture at the Philadelphia Museum of Art to find that the cellulose acetate was so degraded after 90 years that FTIR spectra showed only the fingerprint of regenerated cellulose. The authors were able to identify cellulose acetate with pyrolysis gas chromatography mass spectrometry and classified the progressive stages of degradation of different elements by monitoring deacetylation products. Because sculptural elements that had been pigmented black were less degraded than transparent sheets, the researchers suggested that the addition of pigments may have had an inhibitory effect. Similarly, Salvant et al. (110) correlated the remarkable state of preservation of two large blue/black sheets of cellulose nitrate used by Bauhaus artist László Moholy-Nagy (1895–1946) to their fillers and plasticizer.

PUR esters and ethers have been widely used in modern sculpture (104). Degradation of PUR foams is now well understood to occur mostly through photo-oxidation and cross-linking of ethers, hydrolysis of ester chains, and depolymerization of esters. The consequent loss of mechanical properties—going from a ductile to a fragile regime—and eventual failure of the structure through crumbling have been demonstrated in both historical and artificial aged PUR samples. Visible change can occur after only 20 or 30 years. Data from compression force deflection tests show an inverse correlation between relative humidity during aging and the compressive strength of the material (112). Surprisingly, at later stages of aging, Young's modulus increases; cross-polymerization and the accumulation of adipic acid crystals in the inner cells have been correlated to increased rigidity.

Rather than being a simple materials science problem, interventions aimed at recovering lost structural integrity for art objects also need to abide by the conservation principles of not changing the appearance of the work and possibly assuring reversibility or retreatability. Pellizzi et al. (113) tested two aminoalkylalcoxysilanes that had already shown promising reinforcing results on unaged PUR ester foams on already degraded polymer; during testing, colorimetric measurements accompanied stress/strain tests when determining a successful treatment. The ability of the reinforcement polymer to penetrate the foam structure and bond with or coat the

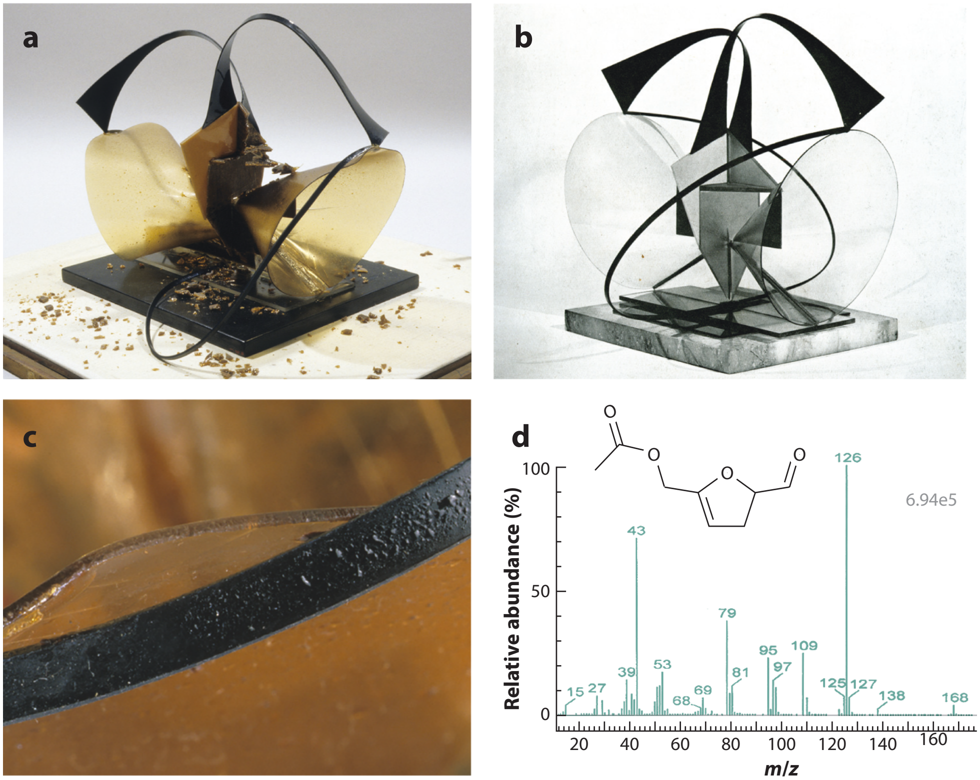

Figure 5

Naum Gabo's *Construction in Space: Two Cones*, 1927 (Philadelphia Museum of Art, A.E. Gallatin Collection, Acc. 1952-61-7): (*a*) the sculpture in 2001 and (*b*) as reproduced in Reference 111. (*c*) Detail of one of the cones showing exudation of plasticizer on the black elements and warping of the clear cellulose acetate sheet in the conical forms. (*d*) Electron ionization mass spectrum of 5-acetoxymethylfurfural, an acetylated pyrolysis product of cellulose acetate that was used by Sutherland et al. (109) to identify the original, now highly degraded, material as cellulose acetate. Abbreviation: *m/z*, mass-to-charge ratio. Photo in panel *a* by Joe Mikuliak and provided by the Philadelphia Museum of Art. Works of Naum Gabo (panels *a* and *b*) copyright Nina & Graham Williams and reproduced with permission. Panels *c* and *d* provided by Ken Sutherland.

structure without occluding the pores completely (to preserve flexibility) is compatible with principles related to polymeric consolidants and water repellents used for stone in the conservation of historic architecture (114). However, the aging and durability of experimental consolidation treatments for PUR plastics still need to be evaluated for performance over time (113, 115).

Beyond structural effects, gas emissions due to the degradation of plastics have been studied not only as markers for the possible inception of grave degradation and ultimately material failure, but also for the potential harm to other objects stored in their vicinity. One example is the emission of acetic acid from degrading cellulose esters, which accelerates degradation in nearby objects in a process referred to as vinegar syndrome for the characteristic vinegar odor of these degraded materials. In addition to measuring cross-infection rates (116), the response to this challenge paves the way for the development of sensors that can alert collection managers of the state of degradation of their plastics and guide confinement of certain objects in separate storage areas. A commercial, low-cost, paper-based sensor (the photographic activity test) has been developed to detect the presence and amount of acetic acid emitted by the degradation of cellulose acetate supports for film and photographic materials (117). More sophisticated and sensitive methods based on solid-phase microextraction (SPME) have been tested for assessing the emission of volatile organic compounds (VOCs) in magnetic tapes and their relative degree of degradation in the laboratory, on storage shelves, and in operando conditions during playback (118). Sensors first developed as wearable bio-integrated systems (119) that do not require expensive gas chromatography mass spectrometry equipment to analyze the specific VOCs that are harmful to art objects (as is required by SPME fibers) are an encouraging new area of application. As plastics and adhesives are pervasive in consumer residential and commercial buildings, such sensors would also have wide applicability to detect VOCs that are harmful to humans.

In addition to VOC analyses, research into plastics made for artistic and design purposes can overlap with environmental research; Shashoua (120) suggested that studying cycles of plastics degradation in marine and terrestrial environments might offer insights into the long-term degradation of plastics conserved in museums. Conversely, because studies of biodegradable plastics have shown limited transferability from laboratory tests to in-field observations (121), museum artifacts may in turn provide insights into degradation processes that have extended over relatively long timescales.

While most researchers currently rely on point analysis of surfaces to address deterioration of museum objects, future directions should focus on detecting degradation at multiple length scales. Saviello et al. (122, 123) used synchrotron radiation FTIR for depth profiling of degradation products and UV stabilizers inside acrylonitrile–butadiene–styrene (ABS) following photo-oxidative degradation. They also correlated mechanical properties with chemical aging through nanoindentation scratch tests on ABS, PVC, polypropylene, high-density polyethylene, and linear low-density polyethylene. Several imaging techniques can provide a comprehensive assessment not only of the chemical composition but also of structural features of polymer objects; these can alert researchers to areas most likely to degrade in composite materials. For example, 3D terahertz pulsed imaging has shown promise in highlighting structural features such as coatings and pores in foams as well as cracks, circular voids, and delamination in degraded polymers (124). Fluorescence lifetime imaging has been successfully used to map the presence and localization of fluorescent photo-oxidative degradation products of ABS in reference and design objects (125).

Nanotechnology is only in its infancy in its application to the challenges posed by plastics in art, from diagnosis to conservation intervention. Gómez et al. (126) recently described a minimally invasive technique to sample degradation products off the surface of ABS and polyvinyl acetate (PVAc) plastics and subsequently to analyze the chemicals on nanostructured substrates that are surface-enhanced Raman active, thus achieving high sensitivity and a complementary approach to the analysis of off-gassed VOCs.

Restoring mechanical strength and cohesion through functionalized nanoparticles, or possibly the reinsertion of lost plasticizers, are areas of future research. Repairing cracks, for example, in objects made of transparent acrylic plastics with adhesives, poses stringent requirements. The repair must be invisible; it cannot be carried out in a solvent that can cause craze stresses and must have the same refractive index as the joins (127). These repairs could also benefit from developments in self-healing polymers to prevent repeated failure at break points.

At the moment, promising applications of nanotechnology are mostly limited to surface cleaning. Bartoletti et al. (128) successfully cleaned a sculpture by Eva Hesse (1936–1970) containing a PVAc and acrylic coating with a tailor-made polyvinyl alcohol/polyvinylpyrrolidone–based hydrogel. The treatment aimed at the containment and targeted release of cleaning solutions through optimal shape conformation to the surfaces to be cleaned, leaving behind no residues of the applied materials.

Artists like Eva Hesse, who made seminal sculptures with rubber latex, fiberglass, polyester, and epoxy resins in the 1960s, have explicitly sought out plastics for their ephemeral duration. Consequently, the concept of the patina of age should be as accepted for modern materials as for ancient bronzes, and scientists need to continue to research methods to diagnose, repair, and mitigate plastics deterioration in museum collections. With constant and rapid development in polymer research and commercialization, the field is still developing. Nowadays biodegradable plastics and polymers used in additive manufacturing and rapid prototyping (129) are already entering museum collections; how these materials will degrade beyond their intended lifetime once they are used for artistic production is still largely unknown, and museums and collectors will have to contend with their long-term preservation, leaving many exciting challenges in materials science.

6. WHAT CULTURAL HERITAGE MATERIALS QUESTIONS MOTIVATE THE DESIGN OF NEW ANALYTICAL OR IMAGING TECHNIQUES?

Cultural heritage materials studies span multiple length scales from nanoparticles in Böttger lusterware to the metallurgy of the Titanic. Moreover, heterogeneities in chemistry and structure, either intended or caused by natural alteration, provide added complexity. In some instances, existing techniques and protocols of the various characterization probes are inadequate or require destructive testing. We highlight here examples that have motivated enhancements to existing techniques, new techniques, and new analytical or computational methods.

6.1. Spectroscopic Methods

Given the desirability and sometimes necessity of in situ examination of cultural heritage objects, the development of a portable X-ray fluorescence (XRF) spectrometer some 50 years ago provided an important advancement for conservation scientists. Historically, the largest fraction of these studies was conducted using single-spot analyses (130). With the improvement of X-ray optics, composition as a function of position could be discerned using confocal XRF with depth resolution in tens of microns (131). Dik et al. (132), however, were first to employ scanning macro-XRF, in which the sample of interest, in this case, Van Gogh's *Patch of Grass*, is locally irradiated while being moved through a focused or collimated X-ray beam, thus allowing the entire sample surface to be scanned sequentially. In current practice, areas as large as 1,500 cm^2 are analyzed, affording, in some cases, identification of the distribution of chemical elements over an entire painting and through the stratigraphy of paint layers for visualization of hidden paintings, e.g., a detailed view of the underpainting of a woman's head in *Patch of Grass* (132). More recently the technique has been employed in the study of underdrawings in twelfth to fifteenth century illuminated manuscripts to provide insight into workshop practice (133).

Hyperspectral imaging, previously known as multispectral imaging, made its way to conservation science over the last 20 years as an outgrowth from astrophysical and geophysical remote sensing (134). Spectral reflectance, from the visible to the mid-infrared, allows for the evaluation of color and composition, as shown in **Figure 6**, in concert with XRF spectra. Other studies include underdrawings, palimpsests, colored grounds, evaluation of conservation treatments (e.g., in-depth and surface chemical modifications), and, as was the case in some of the early conservation studies, differentiation of similar-appearing pigments, as reported by Delaney et al. (135). Furthermore, hyperspectral imaging can be used to guide and optimize sampling procedures when invasive techniques are required.

A drawback to hyperspectral imaging is that data sets of a single sample might include a million spectra. A number of recent advancements in hyperspectral imaging have occurred in the data

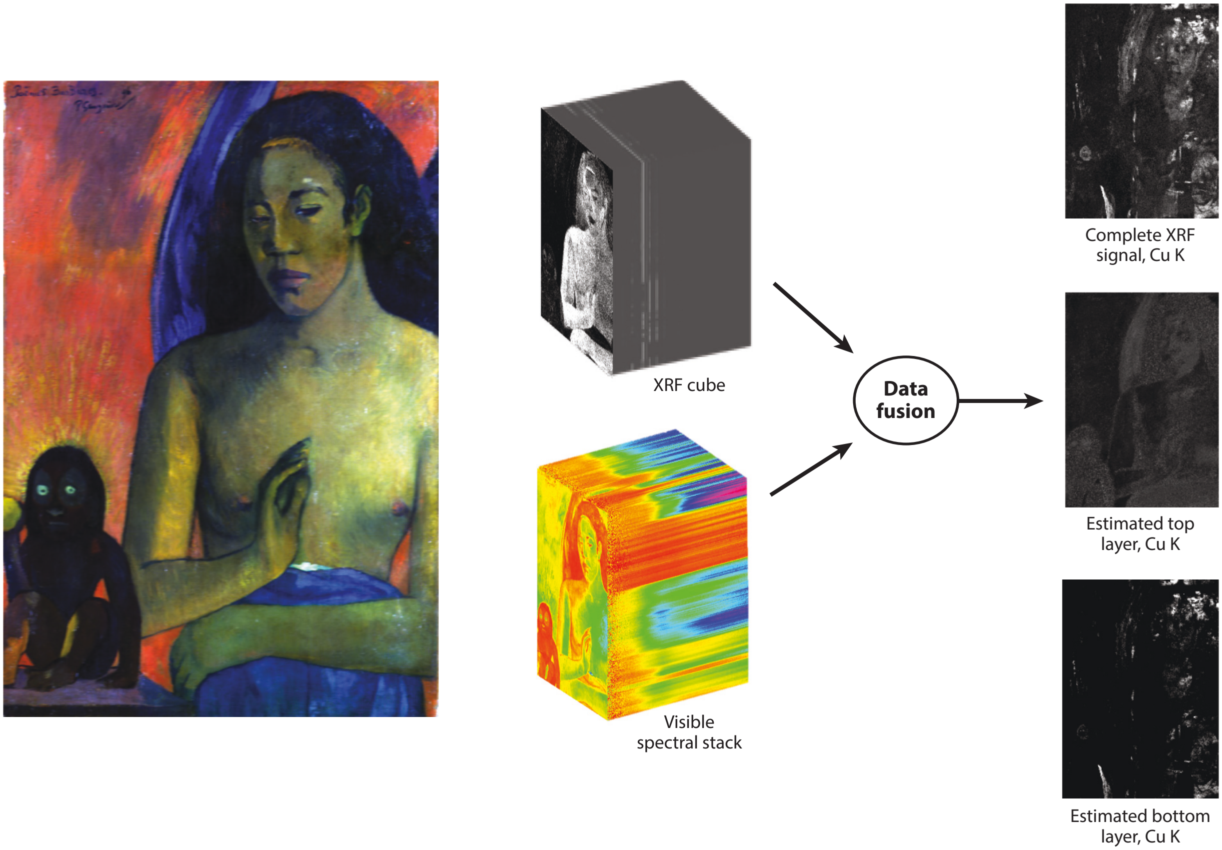

Figure 6

XRF and spectral imaging of Paul Gauguin's *Poemes Barbares*, 1896 (Harvard Art Museums/Fogg Museum). A current trend is to register such data sets on a pixel-by-pixel basis for better pigment identification and also to delayer hidden scenes based on the different penetration depths of X-rays and visible light. Abbreviation: XRF, X-ray fluorescence.

reduction and analysis subfield to ease and expedite visualization and classification from 3D data sets. For example, Pouyet et al. (136) describe an improved data reduction technique in which a statistical embedding method provides a nonlinear representation of the spectra in 2D space. The technique overcomes some limitations of prior methodologies, such as the selective examination of only several 3D projections, which ultimately limits the accuracy of the analysis. Using mock-up paint samples and a historical artifact, the statistical embedding method was found to surpass prior methods (136) and has been extended to other communities that use hyperspectral imaging (137).

6.2. Electrochemical Methods

Though they have been practiced for more than a century, among the newest analytical tools emerging for the study of cultural heritage materials are electrochemical techniques. Usually used for treatments such as the dechlorination of metallic artifacts under polarization, the new developments afford a micro- or nondestructive approach for the identification of raw materials as well as validation of conservation treatments, mainly on metallic materials. Doménech-Carbó &

Doménech-Carbó (138) demonstrate that electrochemical measurements offer valuable information for identifying and quantifying components, tracing provenances and manufacturing techniques, and providing new tools for authentication and dating of metallic artifacts (139). These measurements could be very powerful when coupled to other characterization methods, such as FIB-SEM with EDS (140). Two main approaches have been widely applied to cultural heritage materials: One is voltammetry of immobilized particles, and the other is electrochemical impedance spectroscopy applied to corrosion studies. Cano et al. (141) illustrate the interest in the latter to evaluate protective treatments on different metals. More recently, the development of a gel polymer electrolyte (142) enhanced the development of in situ conservation applications (143) for the study of corrosion kinetics and repair. A compelling in situ example by Letardi et al. (144) assesses the impact of laser cleaning treatments on two bronze monuments exposed to atmospheric conditions. In addition, the development of electrochemical methods for preventive conservation in the field includes specific sensor devices (145, 146), which were revealed to be more accurate than the usual approaches for monitoring the alteration of indoor and outdoor metal artifacts (145, 147).

6.3. Mechanical Probes

Described originally as a mechanical properties microprobe, the nanoindenter has become a common tool to assess the hardness and elastic properties of thin films (148) or polycrystals that exhibit property changes across interphase boundaries. By virtue of the size of the indenter, the probe is particularly useful in studying the mechanical properties of painting stratigraphy, as first demonstrated by Salvant et al. (149) on submillimeter samples of Van Gogh's oil paints. The technique proved useful to document the aging of paints due to autoxidative processes followed by polymerization of unsaturated fatty acids. Nanoindentation of zinc oxide–filled alkyd model systems combined with dynamic mechanic analysis and quartz crystal rheometry revealed that the disparate techniques are in good agreement if the timescales of the three techniques are considered (150).

A major challenge of nanoindentation of small volumes with rough surfaces is that the required indentation depth is influenced by the stiffness of the embedding medium. Fujisawa & Łukomski (151) have developed a data analysis method that accounts for the elastic discontinuity in such systems. More recently, the nanoindentation technique has been adapted by Tiennot et al. (152) to be nondestructive. They replaced the conventional sharp-pointed Berkovich indenter tip with a microsphere glued to a millimeter-sized cantilever. Upon contact with the sample of interest, an optical fiber–based interferometer monitors the deflection of the cantilever to assess the viscoelastic properties of the paint without damage to the sample. It is conceivable that this technique could be extended to in situ investigations by mounting the probe to a robotic arm, thus allowing for in-gallery examinations.

7. FUTURE ISSUES

While the body of knowledge of archaeological and ancient materials is substantial, as new twentieth century and contemporary materials are used by artists, our research needs to adapt to characterize, predict, and protect them in a proactive manner. For example, compared to the literature about ancient bronzes and other historical cuprous and ferrous alloys, conservation of light metals, including the various typology and surface treatment of aluminum base metals and Mg and Ti alloys, is still little explored. Despite the extensive literature on composite structures for architecture, transportation, communication, or spatial applications, the literature on light metals used for sculpture or other artistic applications is scarce.

In terms of analytical techniques, as the spatial resolution of physical, chemical, and imaging probes continues to improve, one can envision being able to interrogate cultural heritage materials down to individual pigment grains, nanoscale metal phases, or even atoms and thus gather new insights into both material and historical questions.

Climate change accompanied by sea level rise, tidal flooding, and storm and temperature intensification is likely to have a serious impact on objects of cultural heritage, accelerating their alteration. New conservation treatments will likely be needed, posing new challenges for materials scientists in the design and application of protective treatments. Similarly, as museums grapple with issues of sustainability and, in the western world, attempt to move away from carbon fuel dependence to feed their HVAC systems, which allow tight temperature and relative humidity controls, there will be a need for epidemiological studies harvesting big data and high-resolution imaging techniques (such as laser- or acoustic emission–based techniques coupled to advanced image processing techniques). These would capture the actual response of complex, hierarchical art objects to fluctuations in temperature and relative humidity. Modeling will play an increasingly important role, for example, in determining damage functions on cultural heritage objects calculated from humidity fluctuations or in predicting how aged oil paint will react when exposed to such fluctuations.

By allying themselves with cultural heritage professionals and turning their research to questions about materials processing, design, performance, and failure in heritage collections, buildings, and sites as highlighted in this review, materials scientists can contribute to the preservation of material culture, which is key to the well-being of communities.

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