

## Flipping materials analysis on its head: what materials science can learn from archaeology

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**Summary:** Materials scientists are trained to understand that high-quality data requires high-quality samples. Archaeology shows a different and very powerful way to approach the analysis of materials.

Early in my training as a materials scientist, I learned that my data could be only as good as the quality of my samples. When I had a single-crystal diffraction data set that was difficult to analyze, the most expedient fix was to collect data on a different crystal. When my scanning tunnelling microscope images showed a dirty surface, the safest strategy was to re-clean the substrate. There is great value in striving to make the perfect sample, especially when trying to understand the fundamental structure and physical properties of a material. In fact, I teach my own students from this gospel. However, I now also show my students that this is not the only way to approach materials analysis -- and I have archaeology to thank for this.

Unlike a laboratory-produced sample, an archaeological specimen doesn't come with its own notes on how it was produced, when it was created, or the environment in which it was stored. One must work using a forensic approach to extract clues about how and why a specimen was made. Each sample is unique, and there is rarely an opportunity to go back and extract another, better example. Instead, one must adapt the type and scope of the analysis methods to match the sample. In this way, the study of archaeological materials affords an opportunity to flip the standard materials science approach on its head (Figure 1). Simply put, the choice of analysis techniques must be tailored to the archaeological specimen, since it is usually impractical to tailor archaeological specimens to suit a fixed range of analysis methods.

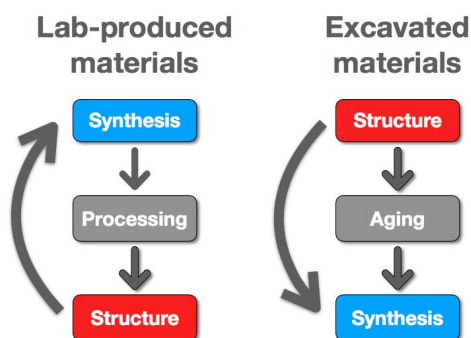


Figure 1. A schematic illustration emphasizes that laboratory-produced materials begin with knowledge of the synthesis conditions, while excavated archaeological materials begin with structural analyses.

If you picture archaeological specimens as pieces of pottery, jewelry, or coins that are reminiscent of a museum -- or an Indiana Jones movie -- then you aren't seeing the full range of what archaeological science encompasses. It helps to recognize that radiocarbon

( $^{14}\text{C}$ ) dating is the cornerstone of archaeology because it provides the best way to assess ages. This means that datable, carbon-rich materials are highly sought at excavations. For example, charred seeds and wood contain graphite, which is the most widely dated form of carbon. It is an active area of research to develop dating strategies for other carbon-rich materials such as lime plasters and mortars (calcium carbonate), bones (collagen), sediments (humins and pedogenic carbonates), and plant-based phytoliths (carbon-containing silica).<sup>1</sup> Although many of these carbon-based specimens are unlikely to appear in a museum exhibit, they build the essential stratigraphic context that enables accurate radiocarbon dating.

Even the best archaeological specimens produce relatively messy data. Predictably, there are challenges with heterogeneous compositions, amorphous components, fluorescence, dissolution, recrystallization, and contamination.<sup>2</sup> Similar to biogenic and geogenic samples, archaeological specimens often appear different from their as-produced form as they are changed by the environment in which they have existed, whether in open-air, buried, or submerged under water. For this reason, it is often helpful to compare excavated specimens with lab-produced samples that attempt to simulate the kinds of structural and compositional changes that could occur as specimens age in different kinds of environments.

Despite the distinct differences between lab-produced and field-sourced samples, many subfields of materials science overlap well with archaeological investigations. A few of these include:

- **High-temperature solid-solid state chemistry.** Since graphite is one of the more stable allotropes of carbon, archaeological sites that have been exposed to fires or other high temperature events tend to yield a larger quantity of graphitized -- and thus readily datable -- specimens. Anthropogenic production of materials such as metal blades, lime plasters and mortars, and cooking vessels also involves high temperatures. In this way, understanding how solid materials crystallize and decompose as a function of temperature is very valuable.<sup>3</sup>
- **Spectroscopy.** Due to the prevalence of poorly crystalline materials, diffraction-based structural characterization methods are not always suitable for archaeological investigations. Infrared spectroscopy is becoming an increasingly popular sample screening method, in large part to the availability of portable instruments that can be used on-site during an excavation.<sup>2</sup> While some of the spectroscopy is "routine" phase screening, ample opportunities also exist for expanding the limits of what IR spectroscopy can say about structural disorder in solids.<sup>4</sup>
- **Environmental chemistry.** Because archaeological samples have been exposed to the elements for long periods of time, knowledge of the atmospheric, ground, and water chemistry of a region plays a key role in the interpretation of material changes. For example, deviations in radiocarbon levels in a sample can be caused by interactions with groundwater, which means that the radiocarbon content of a sample no longer corresponds to its true age. In principle, such deviations could be used to

understand more about the environmental history of an archaeological specimen and its surroundings.<sup>1</sup>

What do all of these examples have in common? They highlight a strong interplay between structural changes in a material and its life-history. A considerable amount of archaeological science research emphasizes how solids can undergo changes to their chemical compositions and crystal structures over time.<sup>2</sup>

Fruitful intersections between archaeology and materials science are particularly evident in explorations of non-traditional materials for radiocarbon dating. In such cases, materials science plays a key role in developing rational strategies to identify and extract specimens that are suitable for dating.

- **Carbonate minerals.** Lime-based plaster and mortars are historic building materials in many parts of the world. This means that distinguishing these kinds of anthropogenic sources of calcite and aragonite from carbonate minerals produced in other ways (such as pyrogenic ash, biogenic shells, or and geogenic limestone) can be very important for archaeological interpretation. Vibrational spectroscopy, X-ray diffraction, and microscopy methods are often used to help pre-screen for datable specimens.<sup>2,4,5</sup>
- **Graphenic carbon materials.** There is an enticing -- and largely unrecognized -- parallel between the well-established cleaning protocols for graphitic radiocarbon samples and more recent research that focuses on producing and separating graphene oxide from other highly oxidized graphenic debris.<sup>6</sup> It may be possible to utilize graphene oxide chemistries to adapt radiocarbon sample cleaning protocols to accommodate a broader range of poorly preserved (partially oxidized) specimens.
- **Silicates.** Phytoliths are glassy, silica-based structures inside plants that persist long after cellulose, lignin, and other plant components decay away. Recent studies indicate that these silicates encapsulate carbonaceous material that can have an accurate radiocarbon signature.<sup>7</sup>
- **Metals.** Blades or jewelry that have been worked and fired can have graphitic inclusions that are datable. Knowledge of microstructural changes that occur in different metals and alloys as they are formed and shaped is valuable.<sup>8</sup>

Although links between archaeology and materials science are ever-growing, there are also incongruous aspects that require more effort to integrate. When one's lab is an excavation site, research has to happen differently (Figure 2). I believe that there are things that laboratory-based materials science can learn from archaeological science.

- **Statistics.** Even though it is usually possible to produce a large number of replicate samples in a lab, we as a materials science community do not usually insist on rigorous statistical analyses related to reproducibility assessments.<sup>9</sup> On the other hand, archaeology has a strong tradition -- and robust method development -- of

statistical analyses, especially as it relates to radiocarbon date modelling and interpretation.<sup>10</sup> Bayesian statistics are powerful, yet materials science has yet to embrace them.

- **Interdisciplinarity.** Working across disciplines is more than just reading different journals and using different jargon. Science talks are practiced to appear off-the cuff; archaeology talks are papers that are read from a script. Science prefers to have short, frequent publications; archaeology often prefers books and long reports. Science provides dates as numbers with error bars; archaeology places value on extracting dates from texts, often in translation. When people come from disciplines that have very different expectations for what constitutes good and productive scholarship, they need to work together -- early and often -- to define what a fruitful and successful collaboration looks like.
- **Public participation.** Large excavations often survive because of valuable contributions of volunteer labor from people with no prior experience with archaeology. Members of the public volunteer their time (and often pay their own expenses) to have the experience of participating in an archaeological investigation. This often turns into a very memorable experience for the volunteer, and incredible public-relations opportunities for the excavation leaders. Could versions of this approach help improve public science awareness?



Figure 2. Archaeological excavation at Phillips Garden, Port au Choix (Newfoundland), Canada.

Flipping my understanding of materials analysis on its head, by working with archaeological materials, has been stimulating, challenging, and rewarding. This is just one example of how the problem solving strategies in laboratory-based materials science can be translated to very different kinds of research questions. I encourage others to give it a try.

Acknowledgements: Thanks to Prof. Steve Weiner and Prof. Elisabetta Boaretto, the past and current directors (respectively) of the Kimmel Centre for Archaeological Science at the Weizmann Institute of Science (Israel), for igniting and fueling my interest in archaeological science over the past ten years. The author declares no competing interests.

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