Understanding the Liminal Space between Science and Archaeology: pXRF in Historical Archaeology

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Authorization to Submit Thesis

This thesis of Emma R. Altman, submitted for the degree of Master of Arts with a Major in Anthropology and titled "Understanding the Liminal Space between Science and Archaeology: pXRF in Historical Archaeology," has been reviewed in final form. Permission, as indicated by the signatures and dates below, is now granted to submit final copies to the College of Graduate Studies for approval.

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Abstract

There exists a shared space where archaeologists use techniques developed by scientists to explore archaeological questions. Portable x-ray fluorescence spectrometry (pXRF) is one such technique where archaeologists are uncovering appropriate archaeological applications. However, pXRF is currently used mainly by prehistoric archaeologists examining obsidian artifacts and is only used sparingly by historical archaeologists. This thesis sets out to explore the liminal space between science and archaeology through a case study of the use (or lack thereof) of pXRF in historical archaeological contexts. This mixed-methods qualitative study has three parts: (1) an examination of the history of the relationship between archaeology and science, (2) semi-structured interviews with eight historical archaeologists and two representatives of manufacturers experienced with pXRF, and (3) a scoping literature review of published historical archaeological research in the last two decades.

Data suggest that historical archaeologists are negotiating inclusion of their work into the boundary of 'science'; meaningful, varied, and successful research is currently being conducted, but there are negative feedback loops that prevent wider usage. Although participants spoke with enthusiasm about their own work and future applications of pXRF in historical archaeology, they described barriers with training, lack of published methodologies, and a generally negative climate surrounding historical archaeological applications of pXRF, which is reflected in the lack of peer-reviewed published literature discovered in the scoping review. However, this study suggests that pXRF is a useful tool, with limitations, that, with further research, has the ability to be applied appropriately in more historical contexts to answer interesting and novel archaeological questions. However, determining 'appropriateness' of various applications depends entirely on (re)negotiation of the boundaries between archaeology and science, which is mediated by the complicated historic relationship between the fields.

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Dedication

To my parents, Rich and Julie, and family for constantly encouraging and supporting me in all my pursuits, academic and otherwise, and especially to Matthew, for his unwavering support, confidence in me, and ability to listen while I work through my thoughts out loud.

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Chapter 1: Introduction

For the last hundred years, science has helped uncover methodological tools, like dendrochronology and radiocarbon dating, that have helped archaeologists to elucidate a number of events that occurred before written history (Wheeler 1957). However, the discipline of archaeology struggles to define its relationship with science. While natural and physical scientists often seek to not only interpret their data but also to generalize their findings to describe larger phenomena, archaeologists often seek cultural interpretations through various theoretical frameworks that are more abstract, describing things like economics, religion, and social structure through sometimes very limited data (McGovern et al. 1995, 81-2). There is also disagreement within the field about how closely the disciplines of archaeology and science are, can be, or should be aligned. Some archaeologists argue (in highly regarded scientific journals) that the field is empirically scientific in nature, and recent advances in the field allow for expanded and robust data collection that can "transform our evidence into reliable reconstructions of past social dynamics" (Smith et al. 2012, 7617). Still others are wary of aligning the field too closely with science, arguing that the field is a social science, not suited to the framework of empirical science (McGovern et al. 1995, 79).

Despite the disagreement over whether archaeology is fundamentally a scientific discipline, a subsection of archaeologists and scientists work at the junction of these two fields, such as those working with geospatial data and soil studies. The overlapping work occurring in the liminal space is often performed by individuals with varied backgrounds; however, it is important to distinguish between the backgrounds and frameworks within which these individuals work. Here, I will follow the terminology outlined by Pollard and Bray, using the terms 'scientist' to describe "a specialist who has spent most of his or her training in the physical or natural sciences" and 'archaeologist' to indicate an individual "who studies the past but is largely unfamiliar with the detail and language of chemistry, physics, or biology" (2007, 247). Work occurring at this junction is part of an interdisciplinary field that has been difficult to name, referred to as 'archaeometry', 'archaeological science', or simply 'science in archaeology'. The term archaeometry has largely fallen out of favor since its suffix emphasizes the use of precise measurements (McGovern et al. 1995, 79). The descriptor 'archaeological science' draws criticism from both archaeologists, who may consider themselves social scientists, and scientists, who might see archaeological science as a not "well-developed discipline" (McGovern et al. 1995, 79). Interestingly, this leaves the phrase 'science in archaeology', which doesn't seem to indicate a union of two fields in interdisciplinary harmony, but rather describes a situation where the overlap of the two fields falls fully within one of them. This thesis is concerned with research done at the junction of the two fields, and will thus use the term ‘archaeological science’ when generally referring to the shared space occupied by archaeologists and scientists who are using scientific techniques to probe archaeological questions. It is this space that this thesis will focus on through the use of one scientific technique, portable x-ray fluorescence spectrometry (pXRF), used both by archaeologists and scientists.

X-ray fluorescence spectrometry (XRF) is one of many currently available scientific techniques used to examine archaeological materials. Smaller, portable versions of these instruments, referred to as pXRFs, have allowed users to employ this method for data collection directly in the field rather than sending samples back to a lab for analysis. Spectroscopic analysis via pXRF gives information about elemental composition of samples. As this technology has become more accessible and easy to operate, its use in archaeological studies, particularly those investigating lithic sourcing, has dramatically increased (Ashkanani and Tykot 2013; Carter 1996; Cecil et al. 2007; Goodale et al. 2012, and many others).

For the last 15 years, archaeologists have discussed the viability of the use of pXRF. pXRF has several advantages for archaeological work, principally that it is non-destructive and is able to be used *in situ* (Rowe, Cole, and Yousuf 2013; Tykot et al. 2013). Additionally, the analysis can be performed quickly, taking less than five minutes per sample (Rowe, Cole, and Yousuf 2013, 270-271; Tykot et al. 2013, 240). Lastly, and perhaps most important for research work done on a limited budget, pXRF instruments are relatively inexpensive, starting around $20,000, and the software used to analyze the data is relatively easy to use (Goodale et al. 2012; “XRF Analyzer Price” 2020).

However, pXRF has some serious disadvantages compared to other similar technologies, including its larger, stationary counterpart. Most prominently, data measured with pXRF has variable accuracy (Cecil et al. 2007; Craig et al. 2007; Goodale et al. 2012, 882; Speakman and Shackley 2013). It is also not known how pXRF data varies with morphology, mineralogy, texture, and weather (Goodale et al. 2012, 882). pXRF is often employed by geologists; as such, there are validated calibration metrics for many geologic materials, including obsidian (Goodale et al. 2012, 882), but such calibration and validation methods are often lacking for other archaeological materials like ceramics, fabric, and metals (Tykot et al. 2013).

These disadvantages in conjunction with pXRF’s growing popularity in archaeological research have raised concerns in both the archaeological and scientific communities regarding the appropriateness of the technology’s use in archaeology. For example, a series of articles between author Ellery Frahm and authors M. Steven Shackley and Robert Speakman encapsulates the disagreement between archaeologists and scientists. In brief, Frahm published data to demonstrate that pXRF instruments can accurately source obsidian in ‘off-the-shelf’ operation, meaning no specific care was taken to calibrate the instrument for the given data set, artifacts were near the minimum size, and there was limited data correction applied to the set (2013b). Essentially, Frahm deliberately used the instrument in poor conditions, to replicate the most inexperienced of users. Speakman and Shackley however purport that Frahm’s analysis “justifies ‘internally consistent’ measurements [those taken without a calibrating to a standard] as acceptable” and that “this form of science is unacceptable,” calling for use that is more standardized, externally validated, and carried out by trained scientists (2013). Frahm’s response highlights the methodological differences between archaeological and geological uses of pXRF; he argues that sourcing need not be highly accurate in terms of raw data from a pXRF, but rather that the data allows consistent and accurate sorting of materials into types (2013a).

This ongoing discourse between scientists and archaeologists regarding appropriate uses of pXRF technology seems to involve mostly prehistoric archaeologists. In contrast, historical archaeologists seem to have mostly avoided entering the discussion (at least in published work). There are relatively few articles detailing the use of pXRF in historical archaeological contexts in refereed journals, as determined through a scoping review as part of this thesis.

This thesis is interested in uncovering possible explanations for the lack of use of pXRF in historical archaeology and tying these explanations to the larger picture—the ongoing discourse between scientists and archaeologists regarding appropriate uses of pXRF. Specifically, it seeks to answer and/or elaborate on the following questions:

1. Why is there a disparity in the type of work being done in historical archaeology with respect to pXRF? Are there missed opportunities for use of pXRF in historical archaeology?
2. What are ‘appropriate’ uses of pXRF from the archaeological and scientific perspectives?
3. How does the specific case of pXRF illuminate our understanding of the relationship between archaeological and scientific frameworks? How might this reflect back on why and how pXRF is not commonly used by historical archaeologists?

Through an exploration of these questions, this thesis will describe the shape of the liminal space between archaeological and scientific frameworks by using the case study of limited use of pXRF in historical archaeology. Chapter 2 will serve as a brief description of the history between archaeology and science and the boundaries that have historically been drawn and redrawn. Chapter 3 provides an in-depth explanation of the fundamental science behind how the instrument works, such that all readers can have a basis for understanding discussions around advantages and disadvantages. Chapter

4 will detail the methods used in semi-structured interviews conducted with historical archaeologists and representatives of pXRF manufacturers, followed by the interview findings in Chapter 5. Chapter 6 presents results from a focused scoping study investigating the use of pXRF in historical archaeological contexts in the last two decades. Chapter 7 concludes the thesis with a discussion of the findings and details responses to the research questions above.

This thesis will elucidate the reasons why historical archaeology is not using pXRF technology. It will connect pXRF's lack of use in historical archaeology to the larger discussion between archaeologists and scientists about appropriateness of pXRF in each field. This will contribute to understanding the relationship between scientists and archaeologists, and will open avenues to contemplate expanded opportunities for pXRF research in historical archaeology.

Chapter 2: Archaeology And Science, A Brief History

The analysis of archaeological materials by scientists has been occurring for hundreds of years. Some of the earliest work was performed on ancient Roman and Greek coinage in the later 18th century (Pollard, Heron, and Armitage 2017, 4). However, since this time understandings of where the boundaries between the two fields are and how they might (and should or should not) overlap have been diverse and changing. This thesis explores the space carved out in the overlap between the fields through the lens of the use of pXRF in historical archaeology. To situate the liminal space between the fields, an understanding of the historical relationship between science and archaeology is useful.

Before turning to a brief overview from the archaeological perspective, it is important to acknowledge why it is that these boundaries, and the division between the fields, may exist at all. Knorr-Cetina, a sociologist concerned with epistemology and scientific ways of knowing, describes that boundaries between fields are entrenched in institutions centered on the production and passing down of formalized knowledge: "Science and expert systems are obvious candidates for cultural division; they are pursued by groupings of specialists who are separated from other experts by institutional boundaries deeply entrenched in all levels of education in most research organizations, in career choices, in our general systems of classification" (1999, 2). While a discussion of why and how these divisions occur is beyond the scope of this thesis, it is important to recognize that archaeology and science both fit the definition of expert systems above, whose divisions are reinforced by the systems that they inhabit. However, the bounds of these systems are malleable. Researchers in the field of science and technology studies explore, among a wide variety of other topics relating to science and technology, how (and by whom) the boundaries of science are demarcated. Thomas Gieryn, one such researcher, eloquently and succinctly describes the negotiation of liminal spaces, like the one between archaeology and science.

> Boundary-work occurs as people contend for, legitimate, or challenge the cognitive authority of science – and the credibility, prestige, power, and material resources that attend such a privileged position. Pragmatic demarcations of science from non-science are driven by a social interest in claiming, expanding, protecting, monopolizing, usurping, denying, or restricting the cognitive authority of science. But what *is* "science"? Nothing but a *space*, one that acquires its authority precisely from and through episodic negotiations of its flexible and contextually contingent borders and territories. Science is a kind of spatial "marker" for cognitive authority, empty *until* its insides get filled and its borders drawn amidst context-bound negotiations over who and what is "scientific". (Gieryn 1995, 405)

These "episodic negotiations" can be seen throughout the second half of the twentieth century all the way to present in archaeology, with some archaeologists arguing for its inclusion in the space while others dispute its place. The space, at various times in history, encompasses different proportions of the field of archaeology as a whole; some argue that archaeology is an entirely scientific pursuit, while others acknowledge only that scientific techniques can be applied to archaeological questions. This brief and narrow review of the history of the relationship between archaeology and science will situate the reader in the diverse and changing perspectives of archaeologists regarding the role of science in archaeology.

We first see an early example of this space being negotiated by V. Gordon Childe in a letter to Nature in 1943. In the letter, Childe argues that archaeology should be considered a science because its methods ("accurate and dispassionate observation, systematic comparison and classification, the continual reference of explanatory generalizations to the concrete data derived from observation") are scientific by nature (1943, 23). Although Childe only begrudgingly includes historical archaeology, arguing that "comparison and classification of rusty bolts and broken tobacco-pipes from a town rubbish pit…[is] more interesting and easier to understand than lists of kings and battles, persecutions and proscriptions," the rationale behind his argument of inclusion of archaeology as science is to gain the "cognitive authority of science" Gieryn speaks about (Childe 1943, 23; Gieryn 1995, 405). Childe hopes that legitimating archaeology as a scientific pursuit will lead to "on one hand a more generous treatment of archaeology by the State and local authorities, on the other a fuller recognition of the subject's scientific status by universities and institutions" (1943, 23). With this prestige and recognition comes money and that funding will allow the field to grow, cementing its place in both academic and non-academic spaces. In a 1945 letter to Nature, Childe reiterates the importance of treating archaeology, and now also anthropology, as sciences; instead of identifying access to money as the resource afforded to scientists, he discusses another privilege afforded to scientists during the war effort—exemption from fighting. He interestingly draws a contrast between the USSR, which treats archaeologists and anthropologists as sciences, and Western nations, discussing the important research ongoing in Eastern Europe, whereas in Western Europe (and likely the United States) "archaeological research naturally suffered worse dislocation since 1941 than that in sciences more directly related to the war effort" (Childe 1945, 224). In both cases, Childe's arguments for archaeology's inclusion in science are an attempt at a renegotiation of the boundaries of science, motivated by the privileges associated with being considered scientific.

By the late1950s, "New Archaeology" was becoming generally accepted by archaeologists who were attempting to "formulate and test general laws of human behavior" (Trigger 1984, 277).

Wylie argues that the New Archaeology borrowed heavily from scientific disciplines, and practitioners "characterized their ambitions in explicitly positivist terms: the central goal of a scientific archaeology was to be [s*ic*] explanation conceived along the lines of Hempel's covering law (deductive-nomological) model of scientific explanation, and its mode of practice was to be a problem-oriented strategy of hypothesis testing, following the pattern of a hypothetico-deductive model of confirmation" (2002, 2). This framework is evident in the 1970s, where Tite describes the utility of archaeological data in testing hypotheses of socio-cultural development (1972, 1). He explains that the link between science and archaeology as being a natural extension of these goals, writing that "the natural sciences must inevitably play an extremely important role in archaeology since they can assist in the location of sites, in the provision of an absolute world-wide chronology and in the description of the bio-cultural system" (Tite 1972, 1-2). To Tite, and other archaeologists of the mid- to late-twentieth century, the frameworks of science and archaeology were relatively well aligned, making the application of scientific techniques in archaeology logical and useful.

However, by the late 1970s and early 1980s, Trigger posits that the appetite for archaeologists to make generalizations about human behavior is diminishing: "The notion that archaeological data should be used primarily to formulate and test a potpourri of universal theories about human behavior as an end in itself is increasingly being recognized as neocolonialist and insulting to the third world and to native peoples" (1984, 294). Although Trigger does not speak specifically about the application of scientific techniques in archaeology, the New Archaeology, as described by Wylie, is based in the principles of science. It was, indeed, during the 1970s that Binford, often credited with introducing New Archaeology in the 1960s, emphasized strongly that the New Archaeology was not universally generalizable, but rather that hypotheses must be tested against a specific and limited interpretation (Wylie 2002, 117-118). In Binford's words, "to be productive, a scientist must operate with a self-conscious awareness of the ideas and assumptions by which he proceeds. I have suggested that facts do not speak for themselves" (1977, 1). This would mean that data "cannot be treated as an autonomous, theory-independent empirical foundation for evaluating interpretive hypotheses" because they are context dependent and "paradigm-relative" (Wylie 2002, 118). Within twenty years of its introduction, New Archaeology and its adaptation of scientific frameworks was rejected by at least a portion of archaeological theorists.

However, the debate about the relationship between archaeology and science was still ongoing in the 1990s. Fifty years after Childe's debate over whether archaeology is a science, the field was still discussing the same issues but also adding more practical questions of how scientific research should be conducted in archaeological fields. Pollard argues that there is successful work being done at the juncture of the fields, but that they must be validated by specialists of both fields, describing that research “must be peer-reviewed by scientists from the parent disciplines, and therefore the practitioners must be competent in the parent disciplines” (1995). While this creates a distinction between archaeological practitioners of science and ‘true’ scientists, Pollard argues that archaeological scientists have a place in the liminal space between the fields, but only if they obtain scientifically-relevant education (1995).

By 1997, Killick and Young describe moving past a seemingly disastrous roundtable held at Brookhaven in 1981 where archaeologists and scientists both felt that the other could not or would not contribute to a shared field. While they identified that deliberate education of archaeology students in archaeometry helped bridge the divide in Europe, they posit that America lags significantly behind the rest of the world (Killick and Young 1997). Interestingly, in addition to limited required education they also identify the lack of funding, funding that Childe’s pleas nearly fifty years previously called for, as being partly responsible for less-than-ideal applications of scientific techniques to archaeological research (Killick and Young 1997). They specify cultural resource management (CRM) firms as driving interest in the liminal space between fields but little in the way of fundamental research necessary to successfully apply scientific techniques within archaeology (Killick and Young 1997).

The discussion over the place of science in archaeology continued through the mid-2000s. Jones situates the current liminal space between archaeology and science in relation to opposing theories that underpin the two fields. He posits that post-processualist theories that many current archaeologists ascribe to are based on a linguistic approach that separates materials from their materiality and instead treats materials as “components of abstract communicative systems” (Jones 2004, 328). This, a paradigm that is “idealist and subjectivist”, is in direct contrast to the theoretical foundation of science, based on “empiricism and objectivism” (Jones 2004, 329). However, like others, Jones describes the need to unify these fields to answer cultural questions: “at both the practical and theoretical level we are required to simultaneously consider how it is that artefacts are socially and culturally constructed, while also taking into account the physical and mechanical construction of artefacts. We do not need to study these two aspects of artefacts as separate and distinct entities” (2004, 329). In his view the physical objects are shaped by but also help to shape culture (Jones 2004, 330). This echoes the sentiments presented by Sillar and Tite four years earlier, who argued, “‘archaeological scientists’ should be encouraged to give greater consideration to the social and ideological factors that influence technological choice” (2000, 17). Jones points to the need for the theoretical frameworks to shift in order to allow archaeological science (although Jones uses the term archaeometry) "to consider how those qualities [of artifacts] are interwoven with social practices and cultural beliefs" (2004, 333). Jones goes on to describe a number of archaeological questions that archaeological science is prepared to assist in answering and gives a number of specific examples of research he believes fits this liminal paradigm, where the theoretical underpinnings of both archaeology and science generate a shared space (2004).

In a response to Jones, Gosden argues that many archaeologists are well-positioned to take up this shared space, but that the post-processualist theoretical frameworks employed by many current archaeologists prevent one from doing it with good conscience: "Unfortunately for much of the time we feel embarrassed by our urges towards typology or statistical analysis, worrying that this is a hangover from an older functionalist or empiricist stage of the discipline, one that a truly mature archaeology ought to have left behind" (2005, 183). However, at the same time as he is highlighting the current ability to bridge the theoretical gap between the fields by means of an "archaeological specialist," he falls back on unhelpful stereotypes to separate specialists from generalists who are not as well-equipped to use scientific techniques (Gosden 2005, 183). Generalists are unsuccessful because, according to Gosden, "Science is Hard. The Hard Sciences make claims to fact that the social theorist feels uncomfortable about; they are also Hard in the sense that most of us humble archaeologists don't understand them" (2005, 184). Although he immediately follows this statement by one encouraging use of the liminal space between the fields, somehow the encouragement falls flat following such exclusionary language.

However, unsurprisingly, not all archaeologists agree with the binaries and separation promoted by Jones and others. Killick, in response to Jones, argues that the binary presented "misrepresent[s] the history of interaction between archaeologists and archaeological scientists as a static rather than a dynamic relationship" (2005, 185). Killick points to Colin Renfrew, Michael Schiffer, and Lewis Binford as generating the shared space between archaeological theory and science throughout the 1960s, 70s, and 80s and that many non-British archaeologists recognized the importance of materiality long ago (2005, 186-187). He goes so far as to suggest that in order to truly engage in the liminal space Killick sees as already existing, British archaeological theorists "should stop talking down to [archaeological scientists], and try to educate themselves about what archaeological scientists actually do" (Killick 2005, 188). Killick also ties back the discussion of the liminal space between archaeology and science to fighting for relevance and a privileged position within the academic sphere: "I suggest that Jones' paper reveals more about competition for prestige and resources within British academic archaeology than it does about the relationship between archaeological theory and archaeological science" (2005, 188). Taylor, in another response, also disagrees with the historical context laid out by Jones, arguing that Jones' interpretation of the post-processual movement is "based on the work of a limited number of scholars of a particular sort" (2005, 196).

One year later, Pollard published an essay that continues to discuss the role of archaeology as a science (while also attempting to put the debate to rest). The essay begins with a reiteration of Gieryn's claims that there is a relationship between funding and "the 'scientificness' of the discipline" (Pollard 2006, 380). He distills the argument succinctly; "Perhaps [whether archaeology is a science] need not be debated seriously…Which other discipline spends so much time on internecine warfare about the very nature of itself? If it resulted in universities worldwide relocating their Departments of Archaeology into Faculties of Science, and funding them as such, then perhaps it would be worthwhile. This, however, might then mark the end of archaeology as a broadly based interdisciplinary subject attractive to students from many academic backgrounds" (Pollard 2006, 382). In this, he acknowledges that the debate has important consequences that can fundamentally change the field. He closes the essay with three points: (1) asking to put to rest the debate over whether archaeology is a science, (2) that scientific evidence cannot alone answer archaeological questions, and (3) that archaeology needs to reflect as a field on how its research priorities can interface with the many fields with which it shares a border (Pollard 2006; 394). This essay aims to shape the future of the field (although much of the space is dedicated to past successful scientific applications in archaeology) and to turn the discussion away from internal arguments about theoretical underpinnings, at least as they relate to science.

Pollard and Bray, more than ten years after Pollard's seeming separation of the fields in his 1995 publication and only three years after what Pollard had hoped would be the end of the debate of the nature of archaeology, seem to present a more nuanced view of the liminal space between archaeology and science (2007). Some posit that science and archaeology should not be thought of as two independent fields, but rather that the use of scientific techniques within archaeology is a field in its own right (Pollard and Bray 2007). The liminal space between the fields is a field in its own right. However, Pollard and Bray also caution against "jack-of-all-trades" practitioners that are specific to that field, emphasizing instead that specialists in each field must know enough of the other to communicate adequately for fruitful collaborations. For a successful collaboration, they posit three fundamental requirements: a common goal, shared language, and mutual respect (Pollard and Bray 2007, 255). While they continue to emphasize the need for individuals who have specialized knowledge in their own fields, it appears that the legitimacy given to those specialists with scientific backgrounds has been tempered. They emphasize the importance of "having several specialists working in the field during the excavation as equal members of the team" and call attention to the myth that scientists are better equipped to understand archaeology than archaeologists are to understand science, calling this position "simple academic arrogance" (Pollard and Bray 2007, 247, 255). Instead of emphasizing validation of the techniques used by practitioners of the parent discipline, Pollard and Bray call attention to an individual they call the "multilingual translator" who is situated at the junction of archaeology and science and can ease communication barriers (2007, 253).

Pollard and Bray use radiocarbon dating as one example of the difficulties in navigating technologies, especially new ones, that fall at the junction of archaeology and science. Pollard and Bray describe the complexities of integrating the new technique into archaeology; archaeologists had a wide range of responses to its introduction "from uncritical adulation to absolute refusal to accept anything" (2007, 249). A further hurdle had to be overcome when scientists recognized that calibration was necessary due to the variability through time of radiocarbon production (Pollard and Bray 2007, 249). Pollard and Bray describe that other forms of evidence, archaeological forms of evidence, needed to be included in order to correct for this effect; as they describe: "the wheel has therefore turned full circle, from a dating technique lauded because of its independence of the archaeological evidence, to a process that uses all the available archaeological evidence to produce the highest possible chronological resolution" (2007, 249-250). What began as two very distinct lines of evidence, one coming from the independent dating methods in science and the other coming from relevant archaeological data, eventually merged into a single form of evidence that sits squarely in the liminal space of the field. Pollard and Bray posit that this iterative process will "weave more lines of evidence into its arguments and aid the process of integration across archaeology" (2007, 250). Rather than lines of evidence coming from more and more disparate fields, the most useful lines of evidence will be born from the junction of the fields.

By the late 2000s, it seems that the discussion over appropriate usage had, at least predominantly, moved away from petty arguments over the relative advantages of each field individually and had instead turned to discussions around ways to improve and increase the work happening in the liminal space. In a discussion of the archaeological applications of synchrotron radiation (SR), Pollard and Bray argue that the "evidence shows that it took ~15 years for scientists and archaeologists to identify applications of SR that genuinely use the tool's potential to answer questions of real archaeological significance" (2007, 251). They identify that "lack of communication between the two fields" was the fundamental issue in not finding appropriate applications, and suggest that "genuine dialogue provided by good science in partnership with meaningful questions" was necessary to achieve valuable work (Pollard and Bray 2007, 252). Unlike radiocarbon dating, the archaeological uses for SR were not immediately apparent to either archaeologists or scientists. Here, focused discussion was required to not only apply the technique appropriately but to figure out how to apply it at all. In fact, Pollard and Bray identify one key piece of identifying possible applications of science in archaeology as “the ability to be broadly aware of the capabilities and limitations of other specialisms” (2007, 252). Rather than creating silos of independent fields, individuals who can understand generally what is possible and can invite meaningful collaborations are important. It is important to be clear that Pollard and Bray are not necessarily promoting archaeologists carrying out the scientific techniques themselves, but rather stating that there exists a space where archaeologists and scientists can and should collaborate to explore archaeological questions.

However, as is to be expected in such a diverse field, perspectives vary greatly. In a 2012 paper Smith et al. promote a very different viewpoint, arguing that archaeology is “a scientific discipline” but that it has only been in recent decades that “scientifically minded archaeologists” have been performing “rigorous analysis of past human societies and their changes through time” (7617). While the paper mainly focuses on the applicability of multidisciplinary archaeological research to answering broad-scale social science questions, the article seems to both diminish what others had seen as a long-standing tradition of the use of scientific techniques in archaeological research and the utility of archaeological data that the authors do not consider scientific. The authors repeatedly point to recent studies that they say show the “new relevance of archaeological data to the social sciences” and that these studies show that “archaeological data now permit systematic analysis of variation in economic, social, and political changes” (Smith et al. 2012, 7617, 7620). The emphasis on the recent nature of these multi- and trans-disciplinary data seems to ignore what many above had seen as a historical and deep connection between archaeologists and adjacent fields. Smith et al. seem to argue that without the (what they see as) recent assistance from social and natural sciences, archaeology was both non-scientific and inappropriate for answering questions of the past. They write: “…the days of fanciful speculation about the past on merely commonsense grounds or of uncritical extrapolation from the present are over. The dirt-derived findings of archaeology are now providing an empirically sound account of what people actually did, and how they organized their affairs, in the distant past” (Smith et al. 2012, 7620). In the guise of focusing on the strengths of multi- and trans-disciplinary collaborations, Smith et al. seem to situate archaeological data as useful only when performed by archaeologists who are “scientifically minded” and that these data are still secondary to natural and social scientists (2012, 7617). It’s difficult to reconcile the assertions presented in Smith et al. with those presented by others throughout the past eighty years, but this more recent paper (albeit one published in a highly regarded scientific journal, Proceedings of the National Academy of

Sciences) seems to underline the complexities associated with understanding the relationship between science and archaeology. However, one constant seems to be the privileges associated with archaeological research defined as scientific and the disunity within the field of archaeology over how that research should (or should not) be carried out or representative of the field as a whole.

In some of the most recent work published on the history of archaeology and science, archaeological science is defined simply as the use of scientific techniques in archaeological applications (Britton and Richards 2019, 4). Britton and Richards give a brief and nuanced, if perhaps slightly oversimplified, description of the history between archaeology and science. They tie the arguments over the liminal space between archaeology and science to how archaeologists most identify their research discipline, as part of the humanities, social sciences, or natural sciences (Britton and Richards 2019, 4). Britton and Richards, like many before them, focus on how to improve and increase the work happening at the junction of the field. They identify the importance of archaeological scientists understanding “the theory and practice behind the methodologies they utilise, and their caveats” (Britton and Richards 2019, 6). This simple appeal ties together eighty years of debate; those performing research in this liminal space must understand the frameworks in which they operate and how those frameworks relate to those in their adjacent fields.

The history of archaeology is complex, and an extremely wide variety of theoretical frameworks are employed by archaeologists (and those interacting with them) at any given point in time. Accurately portraying the history and understanding when and how theoretical frameworks make space for the use of science in archaeological contexts is complex and difficult. However, on a broad scale it is clear that no matter how nuanced the historical and theoretical underpinnings are, there are many archaeologists who currently believe there is utility for science within archaeology and that there is some overlap negotiated by both fields that makes up the space to do this.

As this thesis specifically explores the use of a scientific technique, pXRF, within the subfield of historical archaeology, it is useful to understand that historical archaeology is not just influenced by larger conversations about archaeology and science’s place (or lack of place) in it. Historical archaeology rose to prominence, mostly in North America, in the latter half of the twentieth century (Wylie 2002, 205). Historical archaeology is also situated at another boundary—that between history and archaeology. Historical archaeology is specifically interested in studying the recent past for which there is also historical documentation. Historical archaeologists are uniquely situated to work in the boundary of more than one field—they are already well versed in using both historical and archaeological evidence to support their conclusions. Wylie notes that historical archaeologists already use multiple lines of evidence (those from both the historical and archaeological record), where "the disunity of their sources confers epistemic advantage on their conjoint use" (2002, 208).

At its foundation, historical archaeology is a liminal space between history and archaeology, and Wylie points out that historical archaeologists "consistently emphasize the need for, and value of, substantial interfield connections. A recurrent theme in these debates is an insistence that when events and conditions of life of historic periods are at issue, vastly more can be achieved by making conjoint use of the evidential, methodological, and theoretical resources of archaeology and documentary history than can be achieved by either field working in isolation from the other" (Wylie 2002, 205). In Wylie's estimation, historical archaeologists find strength in defining the boundary of their discipline by not relying exclusively on any one form of evidence; instead they attempt to "assess the security of the sources on which they rely to address the questions they find significant (not just tractable)" (2002, 206).

Instead of insisting, like New Archaeologists did, on a unifying and logical chain of evidence, historical archaeologists exploit when lines of evidence don't match, assuming that the misalignment belies "weakness in the constituent chains of reasoning that may not be evident when the security of each is considered on its own" (Wylie 2002, 206). In this way, historical archaeologists are perhaps particularly well suited to integrate a third potential line of evidence, data based on archaeological scientific analysis, into their research questions.

This thesis will explore the shape of the liminal space between archaeology and science through the specific case of the use of pXRF in historical archaeology. This brief overview of the historic relationship between archaeology and science sets the stage for this thesis by showing that the space between the fields has been negotiated and renegotiated over the last eighty years. It also helps to describe the varied and complex space archaeologists step into and navigate when deciding to apply scientific techniques to archaeology. After a description of the specific technique at the center of this research, what follows is data collected from both participants who have negotiated the boundaries of these fields by performing pXRF research in historical archaeological contexts and a scoping review describing the last two decades of peer-reviewed literature utilizing pXRF in historical archaeology.

Chapter 3: In-Depth Description of pXRF

The following section is intended to give an overview of how XRF instruments function and how they produce the data that archaeologists use in their research from a scientific framework. I hope to give detailed enough information to provide an average archaeological researcher with a substantial grasp on the science behind the instrument without going into distracting and over-complicating minutiae. For a more detailed (especially regarding laboratory-based XRF instruments) explanation of XRF configurations and considerations, please refer to Marguí and Van Grieken 2013 and Donais and George 2018.

The Basic Science of XRF

In order to best understand when pXRF is a useful tool in archaeological research, it is necessary to understand how exactly pXRF, and XRF in general, works from a basic science perspective. First, a little must be understood about atoms. Atoms are made of a nucleus of positively charged particles (protons) and particles with no charge (neutrons). The nucleus is surrounded by a "cloud" of negatively charged particles (electrons). This cloud can be modeled as concentric circles (called shells), each of which can hold a certain number of electrons (as allowed by quantum chemistry, which we will not be getting into). The closer the shell is to the center (the nucleus), the more tightly the electrons are bound to it. This kind of interaction is similar to that of two magnets; the closer together one holds the opposing poles of two magnets, the harder it is to keep them apart.

In x-ray fluorescence, an x-ray source shoots many photons (neutrally charged particles of light) at a sample (Donais and George 2018, 2). At least some of these photons will hit atoms in the material. If the photon's energy (imparted by the x-ray source) exceeds the energy between an electron in the innermost shell of the atom and the atom's nucleus, the electron will get knocked loose. Atoms are not very stable if their energy shells are not filled as they should be (due to quantum chemistry), and this instability increases the overall energy of the atom. The atom would prefer to be more stable—at a lower energy—(thanks to quantum chemistry), so an electron from a further away shell moves in closer to create a more stable atom with a lower energy. But, that difference in energy has to go somewhere: the atom ejects a photon with an energy based on how far the electron falls (e.g., an electron falling from the third shell to the first shell will emit a larger amount of energy than an electron only falling from the second shell to the first shell) (Donais and George 2018, 2). This photon is fluorescent (thus the F of XRF) because the energy of the photon that's ejected is less than the original photon that hits the atom. These fluorescent x-ray emissions are measured by an x-ray transducer in the XRF instrument (Donais and George 2018, 2). Each of these emissions is specific for different elements because each element has a different number of protons and electrons and a different organization of those electrons into shells. This will create a unique set of possible energies for the ejected photon, with lighter elements having lower energy emissions than heavier elements (Donais and George 2018, 4). A spectrum is the resultant graph that plots all the emissions based on their energy on the x-axis with the relative intensities (proportional to the number of photons emitted at that energy) on the y-axis.

Potential Impediments for Understanding Resultant Spectra

There are, of course, certain nuances and complications. The first is that not all of the photons from the x-ray source will knock an electron loose in the sample. Some proportion of these photons will simply be transmitted through the material without ever encountering an electron (Marguí and Van Grieken 2013, 4). These will not affect the produced spectra. However, another proportion of the photons will produce 'scatter', a term that describes when the photon doesn't knock loose an electron but rather bounces off an electron (Marguí and Van Grieken 2013, 4). There are two types of scatter and these will affect the produced spectra. The first is Rayleigh scattering, when the photon interacts without losing any energy, known as an elastic collision (Marguí and Van Grieken 2013, 4). The second is Compton scattering, when the photon interacts and does lose some energy, known as an inelastic collision (Marguí and Van Grieken 2013, 4). The likelihood of these scatterings is dependent on the sample density and composition; Rayleigh scattering is more significant in higher density samples and Compton scattering is more likely to occur in lower density samples or those with a higher proportion of lighter elements (Donais and George 2018, 6-7; Marguí and Van Grieken 2013, 6). These energies show up in resultant spectra and are characteristic of the x-ray source that produced the original photon (Donais and George 2018, 6-7; Marguí and Van Grieken 2013, 4-5). What this means is that where these peaks show up in the spectra is related to the source of the x-rays and can be different for different instruments.

In addition to emissions associated with photons hitting (or scattering on) the sample, emissions associated with the creation of the x-rays that produce the incident photons can complicate the reading of spectra. The photons bombarding the sample can be created several ways, but the most common of these is via an x-ray tube. The x-ray tube, in short, works by creating a voltage differences between a cathode and anode, surfaces that conduct oppositely charged particles (Marguí and Van Grieken 2013, 10). The voltage differences in combination with a heating element near the cathode results in electrons bombarding the anode, which creates photons (the same process that happens in the sample!) (Marguí and Van Grieken 2013, 10). While these electrons hit the anode, some are slowing down, which affects the energy of the emission of the photons based on the properties of the anode (Marguí and Van Grieken 2013, 10). Photons created both by slowing and non-slowing electrons will then hit the sample as described above. The photons created by the slowed electrons will backscatter to the detector and create a characteristic peak depending on the anode material and properties of the sample (Donais and George 2018, 6; Marguí and Van Grieken 2013, 10). This peak is referred to as a Bremsstrahlung peak and is especially noticeable as a very broad peak in spectra for samples that are low density (Donais and George 2018, 6).

The second very important nuance is that XRF works better for certain elements. For instance, hydrogen and helium have so few electrons that there is only one shell (Donais and George 2018, 2). There are no electrons to fall from an outer shell if the incoming photon displaces an electron. Additionally, the relatively light elements from lithium to oxygen on the periodic table undergo a different process of electron reorganization when hit by a photon (instead of emitting energy in the form of a photon, it ejects an additional electron) (Donais and George 2018, 2-3). So, XRF is only a good technique for elements that are heavier than (further along the periodic table from) oxygen (Donais and George 2018, 3).

Another important nuance in understanding how to read an XRF spectrum is that there can be a number of ways to fill the vacancy created by the incident photon ejecting the original electron in the sample. As previously discussed, due to quantum chemistry there are certain allowable arrangements of atoms in the electron cloud. Also due to quantum chemistry, there are only certain, but often more than one, allowable ways for a vacancy in a closer-in shell to be filled by further-out shells, each of which will have a distinctive, specific energy. To distinguish between these energies and configurations, several naming conventions are currently in use. We will be using Siegbahn's notation, where each electron shell is described by a letter; the closest in shell is 'K', the second shell is 'L', the third shell is 'M', and so on. If the incident photon knocks loose an electron and creates a vacancy in the closest in shell, the energy emitted by any electron that fills the vacancy (no matter where it comes from) will be described by that shell, K. The location from where the filling electron comes is described by a subscript Greek letter; α would describe an electron that only falls a single shell (from L to K or from M to L) and β describes an electron that falls two shells (from M to K) (Donais and George 2018, 2). So, to describe the energy emitted by an electron falling from the L shell to the K shell to fill a vacancy in the K shell would be K_α. This energy is different than K_β, the energy to fill the same vacancy in the K shell with an electron form the M shell. And, as described before, the energies are also dependent on how many other electrons there are in the shell, meaning that they are specific for different elements (i.e., the K_α for lead is different than the K_α for iron). However, emitted energies can overlap; for example, the K_β for manganese has the same energy as the K_α for iron (Donais and George 2018, 6). Luckily these threads can often be untangled by the fact that both α and β processes take place, with β processes occurring with less frequency (Donais and George 2018, 4-5). This results in two peaks on the spectra that indicate the presence of one element, with the lower energy peak (α) at a higher intensity than the high-energy peak (β) (Donais and George 2018, 4). So, even if one of these two peaks overlaps with a peak characteristic of a different element, both elements should be distinguishable based on the position and intensity of the secondary peaks.

To further complicate the identification of peaks in an XRF spectra, there can also be sum and escape peaks. Both of these types of peaks are related to the transducer, which converts the radiant energy (given off the sample as photons) into an electrical signal that the computer in the instrument can understand and create a spectrum from (Donais and George 2018, 16). Sum peaks occur when two characteristic photons hit the transducer at the same time resulting in a single peak at the sum of what would otherwise be two individual peaks (Marguí and Van Grieken 2013, 22-23). These sum peaks may interfere both with the identification of the element that created the peak, but also with other elements that have energies similar to the sum peak energy (Marguí and Van Grieken 2013, 23). On the other hand, escape peaks occur when the photons coming off the sample induce fluorescence in the transducer material itself. The fluorescence of the transducer material decreases the energy of the photon coming off the sample by an amount characteristic of the transducer material (e.g., 1.74 KeV for silicon in silicon semiconductor detectors). Since this only will happen in a small proportion of the photons given off the sample for a given element, there will be a peak at the expected characteristic energy and a smaller peak at a lower energy (lower by the amount characteristic of the transducer material) than expected for the given sample emission (Donais and George 2018, 7; Marguí and Van Grieken 2013, 22). Once again, escape peaks may interfere with correct identification of the peak if the escape peak occurs at an energy expected from another element. Luckily, the software produced to work with XRF data typically has algorithms to deconvolute both of these problems, when given the correct information (e.g., the material of the detector) (Marguí and Van Grieken 2013, 22-23).

Types of XRF Instrumentation: WDXRF vs. EDXRF

There are two types of instruments used to emit the photon and to receive the resulting ejected photon. Wavelength dispersive XRF (WDXRF) instruments work by scanning a range of wavelengths of different energies until specific wavelengths are reached that match with the energy of the ejected photon (Donais and George 2018, 4). On the other hand, energy dispersive XRF (EDXRF) instruments work by simultaneously looking at all wavelengths for the ejected photons (Donais and George 2018, 4). The differences between these two types of instruments are mostly due to differences in specific components in the two systems. I will explain how and why these two types of devices are different (as well as advantages and disadvantages) without relying on detailing physical components of the instruments; for more specific information about physical components of XRF systems refer to Donais and George 2018 and Marguí and Van Grieken 2013.

WDXRF instruments were the first type of XRF instruments (Marguí and Van Grieken 2013, 73). They rely on the fact that photons of different energies have different wavelengths. Recall that XRF works by bombarding a sample with electrons that cause photons of energies specific to the elemental composition of the sample to be emitted. In WDXRF, the instrument has a physical crystal component that diffracts photons based on their wavelengths such that only certain photons of specific energies are detected at a given time by the transducer (Marguí and Van Grieken 2013, 75). The crystal component can either be physically rotated to diffract at different wavelengths (for sequential detection) or many crystal components can be oriented to specifically diffract at a different wavelength (for simultaneous detection) (Donais and George 2018, 20). Sequential detection is more time-consuming as the crystal must be rotated (typically done by a computer) for each element whereas simultaneous detection often takes less time but requires a larger and more expensive instrument as it must hold a number of crystal diffractors (Donais and George 2018, 20). Since the diffraction separates signals based on wavelength, the resolution (separation of adjacent peaks) and sensitivity (detection of peaks) of this type of instrument is often very good (Donais and George 2018, 20; Marguí and Van Grieken 2013, 74). However, these instruments either contain moving parts (in sequential detection) or are large (in simultaneous detection), fitting on a bench top or freestanding in a lab space, which makes them decidedly non-portable and more expensive, typically greater than $100,000 (Donais and George 2018, 4, 20).

EDXRF instruments work by more directly measuring the energies associated with the photons emitted from the sample (Donais and George 2018, 20). Instead of separating energies associated with photons by their wavelengths, EDXRF instruments typically use semiconductors (materials that allow some electric charge flow) to detect photons; the photons knock loose electrons in the semiconductors and because semiconductors allow charge flow within the material, the electrons move to a detector that counts them (Donais and George 2018, 18). The number of electrons knocked loose in a given ‘pulse’ is proportional to the energy of the photon precipitating the pulse (Donais and George 2018, 18). This type of detection is simultaneous because it can detect many pulses from different emitted photons at one time, although there is a limit to the total number of electrons the detector can count at a given moment (Marguí and Van Grieken 2013, 77). Saturation of the detector can be avoided through the addition of filters or secondary targets to help reduce the intensity of the signal (see Marguí and Van Grieken 2013 for further information). These filters and secondary targets can also assist with perhaps the larger issue associated with EDXRF, lower resolution for characteristic photons with similar energies (Marguí and Van Grieken 2013, 77). This lower resolution is due to the simultaneous detection of all energies; it is more difficult to separate energies that are similar in magnitude, which can lead to difficultly in definitively identifying peaks in the spectra and thus the composition of the sample (Donais and George 2018, 4; Marguí and Van Grieken 2013, 81). However, there are a number of benefits to EDXRF instruments; namely they have fewer moving parts (making them more rugged), are of a simpler design (typically allowing them to occupy a smaller footprint, including portable devices or those on a bench top), and work faster (due to the simultaneous nature of the detection) (Donais and George 2018, 4, 20-21). All these features also contribute to their typically cheaper price tag, starting as low as $20,000 (“XRF Analyzer Price” 2020). EDXRF instruments can either be laboratory-based or portable, but all pXRF instruments use energy dispersive technology.

Summary

XRF works by hurling particles of light at a material. Due to inherent properties of that material’s atomic structure, these particles will cause a chain reaction that results in particles of light with less energy ejecting from the material. An XRF instrument both creates the light particles that are shot at the material and also measures the energy of the particles that eject from the material. The energies of the ejected particles are unique for certain specific elements. pXRF devices work by using an energy dispersive detector that simultaneously measures the energies of the ejected photons, transforms them into electrical signals, and creates a spectrum, which allows a user to identify peaks characteristic of certain elements present in a given sample. There are limitations based on a number of factors, including elemental and physical composition of the sample, type of material used in the detector, and type of detection. In general, pXRF instruments have the benefit of being small and portable, although they typically do not have as good a resolution as other non-portable wavelength dispersive instruments.

Chapter 4: Interview Methods

In order to better understand how historical archaeologists are using pXRF instruments in practice, semi-structured interviews with participants were performed. The research questions guiding the thesis were also used to guide the interviews:

1. Why is there a disparity in the type of work being done in historical archaeology with respect to pXRF? Are there missed opportunities for use of pXRF in historical archaeology?
2. What are 'appropriate' uses of pXRF from the archaeological and scientific perspectives?
3. How does the specific case of pXRF illuminate our understanding of the relationship between archaeological and scientific frameworks? How might this reflect back on why and how pXRF is not commonly used by historical archaeologists?

These questions were investigated using an exploratory, qualitative method, certified as exempt by the Institutional Review Board at the University of Idaho (Appendix A).

The sample was initially anticipated to be comprised of three groups, archaeologists, scientists, and representatives from manufacturers. However, once recruitment began and a wealth of archaeologists volunteered to participate and access to scientists was limited, the group consisting of scientists was dropped from the study. The sample was comprised of ten archaeologists and two representatives from manufacturers of pXRF instruments. Archaeological participants were recruited through a mix of purposive and convenience sampling. A call for participants was made through a historical archaeology listserv with approximately 1000 members (Appendix B). The researcher initially anticipated only recruiting four to six archaeologists; however, the response of potential participants was so great that the number was increased to ten, and some potential participants were turned away due to scope and time constraints. A number of participants were not directly recruited but contacted the researcher after receiving the initial email from a colleague. All ten participants had some direct experience using pXRF in their own research or were involved in collaborative research where pXRF analysis was used or is ongoing. Archaeological participants had used pXRF to investigate a wide array of archaeological questions related to: Civil War and Revolutionary War battlefield archaeology, colonial ceramics, geological samples, historic contaminants on samples, historic lead and glass identification and sourcing, modern contaminants on contemporary samples, paleontological samples, pigment identification on non-historic samples, and shipwreck archaeology. Manufacturing participants were recruited through purposive sampling. Contact forms were filled out for eight manufacturers of pXRF (Appendix B). From these contacts, two representatives, one sales representative and one product manager, reached out and agreed to participate. Both representatives had some interaction with users doing analysis of cultural materials but did not indicate experience with historical archaeologists specifically. Interview guides were developed for both groups based on a preliminary investigation of literature done by the researcher (Appendix C; Appendix D).

Interviews were conducted over Zoom at mutually beneficial times for both participant and researcher. Prior to the scheduled interview, participants, all over the age of eighteen, provided a signed informed consent form, detailing the goals of the research and explaining possible risks (Appendix E). Interviews began by turning the video of the participant off and renaming the participant with a unique alphanumeric code following the format of “Interviewee X”, where X was a number based on the order in which the participants were interviewed. Subsequent references to the participant were only based on this unique alphanumeric code, until each was given a pseudonym, assigned by random number generator based on popular names from the last century, to be referred to by for readability. Once these changes were made to protect the confidentiality of the participant, the researcher began to record the interview to be stored in Zoom’s cloud server through the University of Idaho’s business account. Interviews ranged from 29 minutes to 71 minutes in length. At the close of the interview, the interview was uploaded to Zoom’s cloud and Zoom’s audio transcription feature transcribed the audio. Subsequently, the audio and transcript files were moved to OneDrive, the University-approved storage location for low- and moderate-risk data. The video files were transferred to Microsoft Stream, the University-approved cloud storage platform for Zoom recordings. Transcripts were reviewed manually and edited by the researcher for accuracy. Transcripts were sent to participants for final approval, with an option to request an amendment to the transcript (Appendix F). Of the twelve conducted interviews, transcript approval forms were only returned by ten participants (eight archaeologists: Amanda, Anthony, Beth, James, Linda, Margaret, Michelle, and Mike, as well as two manufacturers: Jennifer and Paul). The data reported here only includes the ten participants who returned transcript approval forms. Once transcript approval forms were received, the researcher coded the transcripts by hand to identify themes. As part of the coding process each transcript was reviewed a minimum of three times. The findings detailed in Chapter 5 are organized and based on the original themes identified by coding. All data is shared with Dr. Mark Warner to ensure data preservation.

Chapter 5: Interview Findings

This chapter is divided into three large sections and analysis is based on data obtained via these interviews; firstly, I will describe the current accessibility and use of pXRF in historical archaeology by outlining common applications, exploring the hesitancy to use pXRF data in these applications, and understanding the role of the cost and marketing of the instrument in its current use. Next, I will turn to a discussion of common problems (calibrations & filters, data interpretation, feelings of intimidation, and difficulty finding published methodologies and literature) facing historical archaeologists endeavoring to use pXRF data in their research based on the data collected from research participants. Finally, I will culminate the chapter in a discussion of what historical archaeologists can do to move forward, including a discussion of training, the importance of engaging in reproducible science, and how collaborations can assist pXRF users based on data from participants.

Current Applications, Role of Skepticism, and Importance of Manufacturing in pXRF Use in Historical Archaeology

pXRF is already being used in a variety of historical archaeological applications. What follows is a discussion of its benefits and limitations as they pertain to historical archaeology, the importance of skepticism in interpreting results, and how interactions with the manufacturers of these instruments impact historical archaeologists.

Current Applications

One well-known advantage of pXRF is its portability and non-destructive nature. Nearly all participants discussed these factors as being advantageous to their work in historical archaeology. Perhaps the most obvious of these is that a user can bring the instrument into the field to test samples that can't or won't be destroyed. Unlike other techniques that might provide similar data, e.g., mass spectroscopy, samples do not need to be destroyed in any way before analysis, although flat, clean surfaces result in the best data. These advantages are best illustrated by two participants who discussed their studies concerning indigenous peoples where pXRF was the preferred tool precisely because samples did not have to be moved or removed for analysis and the analysis was completely non-destructive. One participant even noted that "the technology is understood and approved by the tribes that we were working with," which contributed to its successful use in that context. In one of these cases, the analysis was done without ever being in contact with the sample; although this situation resulted in an analysis that was not quantitative, it was done ethically and was successful in its goal of identifying the presence or absence of specific elements. In the words of Michelle "the methods were mostly developed to get the most amount of data in as much depth as possible," acknowledging that the methods were not ideal but were optimized for the circumstances. Analysis by pXRF was perfectly suited for such a study; the analysis was crucial in determining levels of pesticides on samples, which dictated the safety measures needed to repatriate them. pXRF was the only tool that could collect the necessary information in an appropriate manner. Even in cases where the non-destruction of samples is not as crucial, participants, especially those with conservation backgrounds, expressed their appreciation for its non-destructive nature. In the words of Linda: "…being able to test something and identifying something without destroying it…that just makes me so happy that we can do that." While the non-destructive and portable nature of the pXRF are universal advantages for nearly any XRF application, they are particularly useful to archaeologists working with valuable samples that may not be able to be transported to a laboratory setting.

Participants discussed a number of ways in which pXRF was well suited to use in historical archaeology. One such advantage described by a number of participants is the ability for pXRF data to help ask and answer questions about cultural materials that can't be easily identified through decorative elements. Mike noted the usefulness of using pXRF in contexts where objects visually look the same where "you wouldn't know there was a difference", including in identifying ammunition in battlefield contexts and the general sourcing of historic ceramics. Linda was able to successfully differentiate between vessel types and date vessels based on the content of specific metal elements. James identified this as an important application, explaining "there's not a lot of [historic] artifacts people would use it for, except those more nondescript ones." Margaret emphasized the kinds of information that can be gained from doing pXRF analysis on utilitarian objects, sharing that studies on utilitarian objects "adds chronological control, it adds more geographic understanding about trade and other networks that are otherwise invisible." Studying these objects that are often not investigated in great detail by historical archaeologists, which Margaret describes as "boring", can often be "valuable in terms of addressing social questions about the people who made these and used these things in the past." For example, chronologies can be created based on known changes in manufacturing as indicated by shifting elemental compositions obtained by pXRF analysis.

Data obtained by pXRF instruments can also be combined with traditional archaeological data as well as other scientific methods. A number of participants identified the combination of multiple lines of inquiry as one way to validate or strengthen pXRF data. Beth discussed the possibility of validating pXRF data with inductively-coupled plasma mass spectroscopy (ICP-MS), another type of elemental analysis, data, saying, "Being good scientists, we should have more than one form of data." Michelle agreed, "I would hope that people would be creative in how they're applying it, how they're combining it with other sources of data to not just rely on it by itself, because I think it's far more interesting to have multiple lines of data to create your interpretation." Using pXRF data in conjunction with traditional data can help untangle inconsistencies historical archaeologists wouldn't have even realized were there. A number of participants described how using pXRF data in conjunction with visual data helped them answer questions. Margaret also emphasized pXRF's utility in confirming categories based on visual identification; she uses "basic compositional analysis" to "make some connections between the decorative arts or historic terms we have for artifacts", noting that she's found discrepancies: "some of the modern definitions we use to identify these results in us identifying them incorrectly." She later argued that archaeologists relying entirely on visual identification for categorization is problematic: "we've been really hampered by the historical record into thinking we know what artifacts. And so I think that, that increasingly folks are realizing through technology like XRF that the categories that we create…are not as, maybe not as useful as we think they are, maybe not as valid as we think they are." pXRF data can be essential to understand nuances that can't be seen or are not correctly interpreted by visual analysis alone. Margaret argues that "there's been too much focus I think on things like decoration and, I don't know, different kinds of molding or different kinds of, of manufacturing or things that are visible that, that are obscuring great geographic distances or great temporal differences." A number of participants described that their research with pXRF included collecting this more typical kind of historical archaeological data, including, if applicable, Munsell colors, typology, size, weight, and other common visual data. Although historical archaeology has the advantage of using known typologies based on visual characteristics, pXRF data is a useful and sometimes novel addition.

However, participants also shared that they did not believe that all historical archaeologists share their views on the usefulness of pXRF. Mike notes, "I don't think most of them [historical archaeologists] understand it or pay a lot of attention to [pXRF]". Beth posits that historical archaeologists "have so many other sources of data that…they don't feel the need to do things that are this hard data chemistry, whereas in prehistoric archaeology, you need, you know a lot more of that" and that "a lot…more prehistoric archaeologists are open to this kind of what you could call heavy duty statistical data." She also explained, "I think people just need to, need to get used to the idea that they, that this will be useful for them."

Additionally, one noteworthy disadvantage is that the pXRF analysis only gives compositional analysis for the specific area sampled and only to a depth dependent on the density of the material. Paul describes the problems that are associated with this limitation, "The spot size of the typical XRF is…about one centimeter in diameter and it's maybe penetrating…a few microns to like a centimeter or two into the sample. So, it's not a huge volume, but, so you're always kind of biased towards the surface and you may not know what's going on inside the center of [the] sample." This limitation becomes especially problematic if the user knows that their sample is non-homogenous, like most ceramics are. Multiple readings on different spots on the sample can help average out inconsistencies, but it is important to know that if sampling a glazed object on an area with glaze the user is likely getting data representative of the glaze not the object as a whole. Paul went on to describe that if archaeologists take readings from two different places on a sample they might get unexpected results; he asserted that, "bad homogeneity is looked at as, or as the cause of someone thinking the analyzer's broken or the analyzer doesn't work." So, it is important that historical archaeologists understand and attempt to mitigate this drawback through good sampling strategies (e.g., taking readings on the flattest part of the surface, making sure that there's no glaze or occlusion on the sample, etc.).

Sourcing was one common application that a number of participants suggested as one useful and appropriate application of pXRF. However, participants also cautioned that sourcing was complex and required careful data collection and analysis. Mike described pXRF as being "good for answering questions of what's this made out of? Is it different from this, is this object similar to this one?" For example, with ceramics, Margaret described that "they're so heterogeneous and there's just so much variability inherent in the matrix of the pottery, I find that it's not at least without super, super careful, super large samples, really good controls to, to do fine-grained sourcing." She noted that other techniques were better suited for true sourcing studies, but that pXRF was appropriate for "establishing primary categories," which in some cases might give general sourcing information such as whether pottery was made locally or was imported. Amanda performed a study like this comparing ceramics to a known potter's site; she cautioned that this was "not a true sourcing study like you would do with like clays and soils, but looking at comparing ceramics." Michelle agreed that pXRF was not precise enough to do a detailed sourcing study and explained that she would turn to another technique, isotope analysis, to do that sort of study instead. Paul, when asked if sourcing would be an appropriate use of pXRF cautioned: "If you're relying on having really good quantitative data to do that…that's where it gets especially tricky and you got to really be careful that your calibration is good and that you're running standards to qualify it." He went on to describe that if the sourcing could be done through simply presence/absence quantifications that pXRF would be a better tool.

Beth answered these types of questions using pXRF data in conjunction with a collaborator; she performed a narrowly defined sourcing study, attempting to identify whether a specific ceramic piece was made domestically or was imported. James was hoping to generally source ceramic sherds, but was endeavoring to create a "shared database of information" to be able to perform more specific sourcing studies than merely binning the sherds into categories. However, as James described, even understanding patterns of more general sourcing might help answer higher level questions such as trade networks and patterns when "there are definite differences in the sherds and there are definite patterns of like okay sherds from [place A] match sherds from [place B] that are, you know, both from the colonial period." Margaret described how much of her use of pXRF was in sourcing, but cautioned that "I found that [pXRF] is most useful…for the more basic [questions,] like what is this made of rather than in a comparative framework." While sourcing was discussed by many participants, the perception of its reliability and the feasibility of the application varied.

Although using pXRF data to source materials is one application repeatedly discussed as being useful, a number of other applications were also shared: dating materials based on changes in manufacturing, mapping battlefield orientations, understanding manufacturing processes, including what raw materials were used, glass dating and identification. Participants described both general ways that pXRF was well suited specifically for work in historical archaeology and specific ways that they were and were not able to apply pXRF to their own work.

Skepticism in Utilization of pXRF to Historical Archaeology

One common theme that ran throughout discussions of applications of pXRF in historical archaeological contexts, and was seen in discussions surrounding sourcing, was that feelings of skepticism and a nuanced trust of the data were key to the successful adaptation of pXRF to their work. Participants were quick to caution that adaptation of pXRF required careful and thoughtful consideration, which they often related to a healthy sense of skepticism in analyzing data.

Nearly all the archaeologists using the instrument discussed the need to be skeptical when analyzing pXRF data. This theme was consistent from both participants who had not themselves collected pXRF data and those who were prolific users. Beth, who had formal training but had not operated the instrument for her research, described skepticism regarding the reproducibility of results: "it seems to me that every machine is calibrated a little bit differently, so can you trust the results?" These questions have led her to research in validating her current method with other scientific techniques.

However, James, who also had not operated the instrument himself, seemed to potentially have a slightly less nuanced view, explaining "the advantage of, of the XRF is it's—or at least I see it as, maybe this isn't true— but I see it as it's like hard, it's, it's science. It's hard data, you know, the, the, the XRF doesn't lie." Although mitigated by the participant's own admission that he might be incorrect, this statement does not seem to indicate a strong sense of skepticism surrounding pXRF data, analysis, and results. Interestingly, James also extended this view to other more experienced users, including those whom he collaborated with saying “you know, they, they don’t sit there and wonder like oh, am I getting bad data.” He also described his experience with other archaeologists similarly saying “I think most archaeologists that I’ve talked to and certainly me, you know, we just sort of accept it as it must work, you know, if the geologists say it works, the company selling it says it works, they’ve got data backing them up to say it works, so it must work…it never really even occurred to me to kind of question like oh, am I getting good data? I just assume, yeah it’s good data.” Interestingly, this opinion seemed to be an outlier among the group of interviewed archaeologists. However, it is important to note the plethora of peer-reviewed literature using pXRF data to source obsidian, which is fairly well-accepted and well-validated. James may be referring to these types of applications in his discussion of pXRF’s acceptance rather than its acceptance (or lack thereof) in historical archaeology.

But, most other participants highly emphasized the need for a sense of skepticism in interpreting the results as one of the most important factors in using the instrument appropriately in historical archaeological applications. And interestingly, towards the end of the interview, James also noted that “we always have to be careful we actually understand what we’re adapting…there’s always that danger of somebody reads the paper in a geology publication that says they use pXRF for this and you know, maybe an archaeologist reads that goes, I could do that for this because it works for them, and then we don’t know that no, it’s totally inappropriate for whatever this is.” So, even those archaeologists who have limited hand-on experience with pXRF instruments indicate a nuanced understanding of the potential problems on applying pXRF to new applications, even if they might not question the data collection as critically as perhaps a more experienced user. However, similarly to James, Amanda had a nuanced view of how objective pXRF data was; she described herself as choosing to do pXRF research because “I like more objective factual information” but also cautioned that she was not looking at the data uncritically, “I felt like, yeah, pXRF was going to give me these numbers, were they reliable, could I recreate this three times.” She also explained that reading training material “opened my eyes as to how difficult these processes could be if I wasn’t careful…or I didn’t take care and little steps and what matrix in effect were.”

Representatives of manufacturers also indicated that critical use was crucial for use of pXRF in historical archaeology. Paul described that one important part of training was to “try to help them see the challenges, you know, so that they can be aware and try to work with, just keep that in mind as they’re reviewing the data and maybe take extra steps to combat those problems.” He went on later in the interview to specify, "Depending on what their goals are I think it's also important to train them to be, you know, a little skeptical of what they're seeing on screen, you know, and not just take it, take it as, the right answer, the perfect answer every time, but maybe double check things somehow if you can." Feelings of skepticism can help historical archaeologists carefully examine their data to help inform accurate and data-supported interpretations.

Several participants pointed to lack of skepticism or critical analysis of pXRF as separating successful and unsuccessful adaptations of pXRF in historical archaeology. Linda noted its relatively recent use in historical archaeology as being a contributing factor, stating "I feel like, this might be incorrect…[that] not many historical archaeologists really grasp the, how complicated it is quite yet." She continues by giving a possible explanation for why it might be difficult for historical archaeologists to spend time obtaining the requisite training and background information necessary to complete a study by observing "I feel like as historical archaeologists, many of us are sort of like, get in. Get out. We're done. Move on, submit your report to the SHPO, we're done." However, she did think that if pXRF continues to be used in historical archaeology, users will "understand more the uses, of how much work it takes." These same sentiments were shared by Margaret, who shared "I think that where the issue can happen is that if someone uses it uncritically…and so I've seen, you know, erroneous— just because people know enough how to operate the instrument but don't know enough about how to interpret the results." Amanda also acknowledged that "I think that the ideas that limit archaeologists are that you can just take this instrument go, shoot, point, test and take data from it, and maybe in simplicity you can, but there's so much more to that." Amanda discussed her feelings of personal responsibility, explaining "I tried to prepare myself in the best ways to do this responsibly and accurately so that I could add something to our community."

Jennifer also cautioned a critical analysis of pXRF data. She described experiences where she's interacted with users who ask for her opinion on data: "I've had people say, what do you think of this data? And it's like, okay, yeah, you're not taking long enough reading it's—look at your error." While she emphasized that this occurs in all market segments that she interacts with, taking data at face value can be problematic when trying to make interpretations.

Margaret described the differences between people who use it critically or uncritically: "maybe that's the way that I would describe it is the difference between a scientist and a consumer. And so, a consumer just wants some kind of data out that they can interpret and, ideally, they would want it, they would probably prefer one of the other instruments that does more, this more processing and kind of spits out a result just immediately." She later shared that archaeologists who use it in this 'consumer' manner can be problematic "but it's very dependent on what they're using it for and the potential repercussions." For her, issues arise when archaeologists use it in this 'consumer' manner, but then "promulgate that information [about what a sample is made out of] as gospel." She identifies that the crucial part "is that someone has a clear idea of why they're doing it before they do it." Michelle described some similar concerns: "I usually have to sit and explain that it's not something that we can just play with. It's good to have…research questions and that helps us determine okay, will this give us the data we need, do we need a calibration curve, is this actually going to help, or are we just playing around with what looks like a ray gun?" She ties this notion back to the perception of archaeologists that the technology is easy to use and "basically can give them any answer that they need." Michelle also noted that "once people start to understand how the instrument works, why it works the way it does, and different ways that it can be applied, then the questions start getting really interesting." Not only does understanding more about the instrument and technique help archaeologists do more appropriate research, it assists them in determining even more interesting avenues of investigation. The two participants who most strongly discussed this viewpoint, of research questions being crucially important to appropriate adoption, were both squarely situated in the liminal space between the fields, one who was academically trained in a natural science and one whose professional career is centered on using scientific techniques to explore archaeological questions. To these participants, trained in the scientific method, the specific creation of a research question was essential.

Role of Cost, Marketing and Manufacturers

The process of procuring a pXRF instrument influences how and when pXRF can be used in all archaeological contexts. First it is important to understand the pXRF market. These instruments have an incredibly broad range of applications from positive material identification (PMI) in industrial sectors, to identification of soil contaminants in environmental sectors, to scrap metal sorting in the metal recycling industry. Paul estimates that for his company alloy analysis, including PMI and scrap metal, makes up 80-90% of their customers and that half of the remainder involves the mining industry. Archaeology makes up a small market segment and historical archaeology an even smaller one.

One of the predominant narratives that came up throughout interviews with both users and manufacturers is that pXRF was simply not initially designed for applications in archaeology. Anthony notes that "most of the harm that I've perceived in archaeology…[is] because they made business decisions ten years ago that don't line up with current archaeological methods, but they still want to get a sale." Mike describes a similar situation, arguing that "archaeologists aren't in the main market. So they don't give a damn about, you know…[they] aren't really looking at…archaeologists as a serious market" and that archaeologists "may always be dealing with the dregs and hand me down in terms of equipment". This thinking was also shared by Margaret who explained "archaeologists are not the primary market…the people who are using it for that aren't trying to do really heavy duty quantitative analyses the way that, that we would." There are also differences between manufacturers in terms of the options their instruments have. Jennifer describes some instruments where "there's a lot more user flexibility, especially for people who, you know, who are advanced users. And you can use them in that manner…I'd say [a specific manufacturer] is more of a point and shoot."

Anthony also discussed the impact of a representative trying to make a sale on an archaeologist's possible success of appropriately applying the instrument to historical archaeology: "I think it's like confident white guy with money to burn who typically gets the XRFs in archaeology…which I also think is also a source of a lot of the abuse from the…XRF manufacturers towards archaeology, because they understand that and recognize that as a payday ticket." However, manufacturers also had the power to really assist archaeologists in adapting the technology successfully. Anthony notes several examples of employees of manufacturers who worked hard to solve problems specific to applications and who would say no to sales "because they didn't think it was the right piece of equipment", although he acknowledged that there a small proportion of sales representatives who "very much don't care what they get as long as they get paid" and that "archaeologists need to be aware that…the person…is someone who's going to get a $5,000 check when they sign on the dotted line."

However, representatives of manufacturing companies described the benefits of providing useful and good information to archaeologists. For example, Jennifer describes that "depending on who's more active in the field with it, you know, always came up with more and better application notes to be able to demonstrate the use of it." If manufacturers are able to prove that archaeologists can be successful with their instrument, they will likely see more interest from archaeologists. Paul describes a more nuanced picture; he explains "XRF manufacturers aren't, aren't going to sell a ton of instruments in that market, so therefore they put less resources into it. That, that's, I don't know how fair that statement is, but that's kind of the feeling I get and I think it is true that the market is smaller, but on the flip side its users like that that are doing cool and new and interesting things with technology and that's always a good thing even if you sell only one a year, but if they're doing something really cool and you can make people know about it, then that's good for the manufacturer." He went on later to describe these applications as "interesting and fun" and that they help "get people thinking about the technology outside of how it's most standardly used." However, he also shared that this interest was not enough to warrant, for instance, the making of a marketing brochure specific to archaeological applications.

In general, the representatives interviewed seemed genuinely invested in aiding users in getting useful, accurate, and appropriate information using the instrument. Jennifer described her practice of ensuring that the instrument is the right one for the user: “So I’m really intent on learning exactly what [their] uses are and making sure it’s [a] feasible application for what they are, what do they want out of the data, you know, because I’ve had people…that it’s just not right for them, you know?” Paul concurred, saying the sales process involves “trying to understand what their problem is or what they’re trying to solve, and then trying to figure out if XRF can do it.” Both manufacturing representatives stressed the importance of determining that the tool was right for the application; this first level of review could be extremely helpful to archaeologists new to pXRF that are purchasing equipment directly from manufacturers.

Paul described his role in the company as specifically helping solve customer problems: “sometimes it’s you know figuring out how to make the software do what they want easier and faster or it might be how do we improve our analytical results by tweaking the algorithms or improving our calibrations.” Paul also shared that there are a number of factors that make pXRF analysis especially difficult for archaeologists (e.g., making calibrations, appropriate sampling strategies, accounting for matrix effects, etc.) and described that “you have to be somewhat cautious with what you’ve promised, or how you, what you promised, I guess, to the customer.” For example, one of the common marketing strategies with pXRF centers around it’s point-and-shoot capabilities, but Paul cautioned that “sample prep is one of the major things with people doing non-alloy analysis that plays the biggest part in the quality of the results.”

However, Paul also identified the feeling that representing a smaller market segment resulted in potentially less good service from manufacturers in general (although it’s important to note that he himself does not directly sell instruments). In his opinion “it takes a lot more to support customers like that. Because it’s less of a point and shoot application, you kind of have to help them through, and the training’s a little more in depth, and you need to have more, probably better software to help support them. And I think sales people may shy away from it because its funding situation’s different a lot of the time, so it’s kind of, yeah, it’s kind of complicated but pluses, minuses, I guess.” It seems unlikely that manufacturers are actually turning down a sale, but that sales and support personnel may be less familiar with the level of support that archaeologists might need in comparison with their more common users.

However, there is also a larger issue at play—cost. Nearly all participants identified cost of the instrument as being a barrier to its widespread use in historical archaeological applications. While pXRFs are often considered low cost (around $20,000), this is in comparison to laboratory-based instruments that can do similar analyses, which may cost into the hundreds of thousands of dollars ("XRF Analyzer Price" 2020). Both Mike and Beth specifically identified pXRF as being too expensive for widespread usage in cultural resource management (CRM) contexts, which are largely private-sector-based. Mike described that "drawbacks were cost, people kind of wince at…that kind of capital investment. I wouldn't think most CRM companies would jump at the opportunity to…put out a bunch of money that they're not going to…see some immediate return on." Beth also pointed out that the nature of CRM work, in which CRM companies are contracted out to a number of different entities to perform archaeological work, would make it difficult to justify the cost. She explained, "The problem with using [pXRF in CRM] would be the money, you know, who would…buy the machine, who would pay for it, who would do the analysis. And since a lot of archaeology is done in a CRM setting, the cost is going to be a limiting factor".

The cost is also possibly even a larger issue for historical archaeologists working in academic settings. Amanda had use of an instrument used across departments at her institution, and she described the benefits including the possibility of recruiting graduate students specifically interested in learning the technique, describing that "I wouldn't say every archaeology firm could go out and buy one, but maybe for universities it was a little more cost effective." Two participants described the problems with convincing their institutions to buy such a high cost instrument, both noting that sharing the instrument with others were crucial parts of their plans to obtain the instruments without having to justify the cost simply for their own research programs to use them. Margaret also added that after the initial large cost there is minimal cost in maintaining the instrument; "it's really excellent for collecting preliminary data because all it takes is someone's time." For many other instruments, there is additional cost, like those for reagents, to run the machine; however, pXRFs do not have a high cost of maintenance or materials needed to run them. One participant identified the struggle for non-profits to gain access to the technology, relating that to do pXRF work they "have to rely on like a student who has an interest who can then get support from a university or grant or something to do that sort of work." Linda identified lack of funding as being one possible factor in the robustness of the data analysis, explaining that "the only times I've ever seen some pXRF that…I'm a little on that, I would probably look into this statistic to sort of test the validity of this…are maybe not necessarily as well funded and they sort of, it's very quick and they have to sort of get in and get out and do the test." She went on to note that she's noticed that it's these same under-funded individuals that are likely to "replicate someone else's method and just go right off of that instead of doing their own research" to validate the method for their specific research goals.

However, the fact is that historical archaeologists do currently have some ability to purchase an instrument that is well enough adapted for use in historical archaeological settings. To expand this access, Anthony suggests "shifting the discussion from individual ownership because someone was able to write a grant to institutionalize ownership [to] create opportunities in fields like historical archaeology." Although it is unlikely that historical archaeologists will ever represent a substantial proportion of the pXRF market, this will at least leverage their power to increase access to the instrument.

Participants described their current applications to the field and some limitations associated with those applications. They emphasized the need for a skeptical outlook when performing measurements and analyzing pXRF data. Some also linked the role of manufacturers and the main markets of the instrument in the ways pXRF has been adapted to historical archaeological applications.

Common Problems Regarding pXRF Usage in Historical Archaeology: Calibrations & Filters, Data Interpretation, Access to Methodology, and Gatekeeping

Once a historical archaeologist determines a reasonable and appropriate use of pXRF, there are a number of hurdles to still overcome, some technical and some more intangible. Understanding how best to apply calibrations and how and when to use filters as well as the complexities of data interpretation represent technical issues that historical archaeologists need to resolve. Issues of scientific gatekeeping, including intimidations and barriers to publication, and difficulty in accessing previously developed methods are in the latter category.

Calibrations & Filters

One common obstacle associated with successful use of pXRF in historical archaeology is the ability of the users to create or use a calibration with the instrument. Calibrations essentially allow the instrument to take the raw spectral data and assign empirical values either in compositional units (ppm) or in percent composition (x% of element y). Typical empirical calibrations are created by having the instruments read samples of known composition, usually prepared by an institution like the National Institute of Standards and Technology, similar to the unknown sample. Then, the user inputs the known concentration, detailed by the institution providing the standard. As Linda explained, samples are "created…and they know exactly down to the like the, like 10^{th} decimal point exactly what elements are in that…and you scan it, use the spectrometer to scan if for, oh my gosh, I have it was like three minutes or something so it like really gets down the spectral results really, really well and then you input exact, you tell it exactly what it is." Known samples should have a similar matrix and similar composition. Calibrations are essential in obtaining accurate quantitative results, but are less important if the user is trying to obtain presence/absence measurements.

pXRF instruments often come with pre-made calibrations and many offer the user the opportunity to create their own. However, there are a number of obstacles for historical archaeologists hoping to create a calibration for a particular type of sample. Anthony describes, "Calibrations are really hard when you're dealing with historical materials [because] you're dealing with a wide array of materials, think about glasses, for example…controls are basically zip in the context of historical glasses. You can have any combination of elements. So as a consequence, it's really hard to build a calibration to report what is seen from the spectrometer in like standard international units such as you know 3% iron 2% cobalt, etc.". Paul, who works for a manufacturer, also identified that calibrations in archaeology would be difficult to make sharing, "the kind of diversity you come across in those sort of applications [where a user is looking at cultural materials] is so much bigger and I think that's also [an] important reason why it's harder to get just a good, you know, a good quantitative analysis right out of the box."

Linda had very limited access to standards to create a specialized calibration for her samples of interest: "I had only four [material] samples to create a calibration from and from a lot of our research I wasn't really necessarily comfortable building a calibration off of only four known samples." Linda instead turned to a statistical approach to validate the binning of her samples into certain categories from raw spectral values. This binning approach was mirrored by ceramic sherd research projects involving James. However, many instruments come with out-of-the-box calibration provided by the manufacturer. Several participants used these out-of-the-box calibrations, with Mike describing calibrations as "out of my job description." He went on to explain, "I don't, have never calibrated my machine. It's just it's set up like it was sold [to] me and you know I pretty much don't mess with that…I just use it for the things I know I can use it [with] the settings that I use it in." Some participants use a mix between provided calibrations and specialized archaeological calibrations. Margaret noted that she obtained a calibration from a colleague to use for ceramics that had been validated, but that "with other materials, I have mainly used the, the calibrations that come with the instrument." These pre-set calibrations are generally either empirical-based calibrations or are based on fundamental parameters.

Empirical-based calibrations are created as described above, but the process is complicated by the manufacturer. Anthony lauded empirical calibrations for their reproducibility, saying "you can refer back to, to this set of standards as to why you're getting your numbers, so that way if [a manufacturer] goes out of business…another researcher can read that paper, get an XRF, use similar materials, use the same standards, use the same regression models, and reproduce the research values." Fundamental parameter calibrations are "standardless" and use modeling to calculate composition based on relative peak intensities (Wegrzynek, Hołyńska, and Ostachowicz. 1998). Paul, a manufacturing representative, describes the benefits of these as minimizing matrix effects, the effect that the organization of the material has and the space between molecules (think the difference between compact concrete and less dense wood). The benefits are that, as Paul describes: "If you tried to measure those two different matrices with like an empirical-based calibration, one, one empirical-based calibration it'd be less likely to do well across both matrices than a calibration using fundamental parameters might be." However, they are less accurate than an empirical-based calibration calibrated for the specific sample the user is testing and because they are typically based on proprietary algorithms they are typically a black box to the user. Paul explains that the complexity of the algorithms contributes to the lack of openness with these algorithms: "There's so much, so many details that go into what that [fundamental parameters or Compton normalization] means and, kind of, different code paths and, and corrections you can apply on top of that to make it work better. So, and that's where, you know, it's never going to be completely transparent to the end user, yeah." No participants specifically identified using this type of calibration, but they are common especially on instruments designed to be easy to use.

Many users employ filters (which are placed between the sample and the instrument) that are designed to assist with identification of specific elements in specific contexts. For instance, Linda was exclusively interested in metals, so used "a yellow filter to sort of filter out all the sort of non-metallic…elements." This filter seemed to be crucial to obtaining low-background data capable of answering her specific research questions. However, as Anthony explains, "if you don't disclose what those filters are made of then the data is not reproducible, right, if a company goes bankrupt tomorrow [and] 10 years later, someone tries to reproduce research that found something interesting they might not be able to" because the researcher doesn't know the composition of the filter.

Some participants shared that some manufacturers seemed to allow better access to this kind of information; Margaret noted that she prefers working with Bruker instruments "because you can actually control the setting and see what the instrument is detecting and how it's detecting it and…what the calibrations are built on and all that sort of behind-the-scenes stuff." However, understanding how and when to use calibrations and when and why to use filters are barriers in the successful application of pXRF to historical archaeology.

Data Interpretation

One of the most complicating factors involved in analysis of pXRF research is that there are a number of levels at which the user may choose to engage with the data. The raw output of the instrument is a spectrum (a graph that plots the relative intensities of x ray emissions at a range of energies). Based on these interviews, it seems that many instruments allow users easy access to these visualizations of the data. However, not all users choose to engage with the data in this form; many manufacturers provide accompanying software that, given a calibration, will provide tabular data that gives percent composition or amount (for instance in parts per million). There are some obvious advantages and disadvantages to both of these approaches. The use of software essentially allows the user to skip the direct spectral analysis step; tabular data provided by software is easy to analyze and understand. The software analysis provides the user fast, quantitative data that they can analyze quickly and efficiently without having to look at and be able to interpret spectra for each sample.

Mike described, "You don't really have time [to look at the spectra]. You're just trying to run the object and make sure you've got good data and…that it collected data, you don't know what it really means yet." Amanda shared this same time limitation concern; she was collecting data for hundreds of samples and described that "it was just decided that we would, we could still get the answers we wanted and not have to look at that," although she retained all the spectral results. However, the disadvantages are not insignificant. To get reliable quantitative results, a user must employ or make a calibration that is appropriate for the sample that can be difficult to find for archaeological applications. If users utilize built-in calibrations, they will likely not know the details of the algorithms and refinements manufacturers employ to analyze the data. This lack of transparency makes it difficult for the user to understand what manipulations the raw data are undergoing to create the neat tabular data the software outputs. Although not fundamentally problematic, this contributes to the reproducibility problems observed in pXRF. In the view of Anthony, manufacturers have a vested interest in protecting this type of proprietary information about calibrations and algorithms used in identifying spectra "for fear that their competitors will improve their products and compete". This competition makes it difficult for users analyzing samples with instruments made by two manufacturers to have comparable and/or reproducible results. Paul, a manufacturing representative, described the difficulties of comparing results across instruments due to the nature of proprietary information typically used by manufacturers: "I could definitely see problems that even within one instrument if it's being used differently, but even more so across different vendors, you know, depending on how they, what elements they include in their calibrations and exactly how their software algorithms work. I could see issues, yeah, comparing results." This lack of comparable data contributes to downstream difficulties applying pXRF analysis to historical archaeological contexts, including creating sourcing databases.

To directly analyze a spectrum, the user must have a good working knowledge of how to interpret spectra— what peaks for what elements occur where, what interactions different elements may have, etc. Spectral interpretation is not straightforward and would likely require specific training and/or experience, both of which are time consuming. Interestingly, Jennifer, in relation to training archaeologists in spectral analysis, shared that: "I, I'd say that archaeologists are not people that shy away from the guts of it…I…haven't experienced that anyway… I've had, you know, other people…in other market segments that… they just didn't want to deal with it." Paul also shared how, in contrast to other market segments, he would likely train a researcher, a category in which he places archaeologists: "I probably would show them a spectrum through the training and try to show them like here's what a peak look like, here's some problems [that might occur]."

Jennifer emphasized the importance of examining raw spectral data, cautioning "you can completely go the wrong direction if you're relying on just the numbers you're looking at on the screen." Anthony noted that "if an individual scientist can interpret the spectra for themselves then they don't need all that calibration jumbo," although he encourages users to "calibrate some data before it's published" if possible. Anthony argues that "the closer you are to the raw output, the fewer assumptions are standing between you and what you're trying to discover".

Gatekeeping

A number of participants had experience using other scientific techniques in addition to their use of pXRF. These techniques varied widely and included laser ablation ICP-MS, a destructive mass spectroscopy technique used for elemental and isotopic analysis, UV-Vis spectroscopy, a technique used to identify specific molecules that absorb visible and ultraviolet light, and isotope analysis. However, these experiences did not preclude these participants as well as those with less experience with scientific techniques from experiences with gatekeeping. Nearly all the participants described exclusionary interactions when asked about their experiences interacting with users coming from strong natural and physical science backgrounds.

Participants described this sense of gatekeeping through interactions they had with pXRF experts with natural and physical science backgrounds. In one case, the expert upon seeing the participant's presentation in the conference packet "called [the participant] out in his keynote speech." However, upon hearing the presentation, the participant described that he apologized to her, in her memory saying "that was so presumptive of me, that wasn't very fair, your work is fantastic" and inviting her to apply to a PhD program, noting her statistical analysis of the work. In another case, a participant met with an expert who "was more into the physics of [pXRF] and how the instrumentation worked." This participant described the benefits of this interaction, sharing that he "helped guide me through some questions and what were my limitations…going to be, that kind of stuff." However, she also describes another interaction with an expert at a conference "I was a little intimidated because it wasn't my field and I openly admit that…I could not go toe to toe with somebody like that. All I could do was take heed of the warning that he would give…to make sure that I had, I had met any, any kind of those [warnings] or gone above and beyond, to get past them." In general, the same participant described, "Because… it wasn't being applied in historical archaeology settings, widely at least, that it was a little bit intimidating, I think, to see other people. They already sort of had backgrounds in different areas." Michelle has also noted this sense of intimidation that can come from archaeologists delving into pXRF research, describing "if it starts becoming not quite so much of a leap, I think that would be great. And that's, that's part of what we do now, part of the work I do now is to just make this not scary."

Margaret also shared her experiences with natural and physical scientists; she has "heard dismissive things about [the use of pXRF in historical archaeology applications], again for what I brought up about them just wanting more quantitative or more precise data." Michelle echoed the same sentiment explaining that, although nothing had explicitly been stated to her, "the perception that I have witnessed sort of having straddled the two worlds myself is that the hard scientists do not think the archaeologists have the rigor to do the work in a fully quantitative or fully…trying to find the right words here. It's, it's the perception that you're kids playing in our sandbox." This sense of gatekeeping can be exclusionary to archaeologists hoping to use pXRF research. These barriers may be less difficult to overcome for some archaeologists, especially those with a natural and physical science background; Michelle shared that "I will say that that perception of me changes as soon as I start asking good questions…going into that room unless they know you have some hard science background it is going to take a little bit of work to, to meet in the middle."

This sense of intimidation or that archaeologists are treading into others' fields can impact whether historical archaeologists choose to engage with or perform pXRF research. Linda indicated that archaeologists may not feel well-equipped to perform pXRF analyses, observing "I feel like…when [historical archaeologists] see a report they're like, cool XRF neat that's too complicated for me, I'm going to send it off to a geophysicist and they're just going to explain it to me." She went on to lament that viewpoint calling it "not really fair" to archaeologists. Michelle described her desire to "see more archaeologists feel comfortable with both even just reading the data, reading the literature, and publishing in it because I actually think that there is a bit of a…a bit of a stumbling block of 'well I can't do that'. Of course you can, if you want to you can do this." However, it is interesting to note that Jennifer, a representative of a pXRF manufacturer that sells instruments to a variety of individuals, sees the situation through a different lens. She explained "I've had folks who were like, you know, in scrap yards and stuff that didn't really, you know, they just wanted to know what to do to make it work and get done with their job, but I don't find the same attitudes with archaeologists. I think they're in the field that has, you know, is born out of curiosity. Anyway, so I find them scientific by nature, I guess." Paul agreed with this viewpoint sharing, "I would actually say that the people doing more archaeology stuff they're definitely more scientific than a lot of our customer base." He also posited that "someone specializing in archaeology is probably more equipped to deal with understanding the technology than a lot of our customer base would be, you know." This viewpoint that archaeologists are well equipped for good pXRF analysis, perhaps especially compared to other market segments, groups them with other natural and physical scientists rather than at odds with them.

However, this viewpoint does not seem to be the predominant one amongst historical archaeological users of pXRF. Mike described how his interactions with natural and physical science users of pXRF altered how he performed research. He shared an experience when was at a workshop in which the instructor was "lambasting a lot of people that get published, journal articles that don't know what the hell they're talking about…or they make some really stupid…error and they just kind of keep compounding and people cite it because it's been in press." This warning had an effect on the way that Mike conducts his pXRF research who noted "I try to be careful not to stick my foot [in] my mouth or say something really dumb, but I have made some mistakes already". Mike later discusses that his perception is that pXRF users with strong science backgrounds "look down on, kind of grimace a little bit at seeing people using the equipment that really don't, might not know how to use it correctly or haven't had it long enough."

The language used by historical archaeologists in regards to their use of pXRF can complicate the perceptions of their attitudes and use of the instrument. Margaret shared that "people are always kind of attracted to the phaser aspect of it [pXRF] that you can just shoot it and say what's in it, that is just something kind of, you know, cool about it." Michelle noted that the instruments are designed to look sci-fi-esque, describing "the new version of the Bruker, I don't know if you've seen it, has these lights that run up and down the side like a phaser from Star Trek— I'm not kidding, it's nerds who designed these things." Some participants used terms like "playing", "zapping", "toy", "whiz bang tool", and "superhuman" when referring to their use of the pXRF (Mike). In the words of

Mike, "I got taught enough to be dangerous…I can collect data and I just zap things at will." However, this language did not seem to indicate that the participant lacked understanding or knowledge of the nuances associated with using the instrument; Mike noted that the XRF "tells you factual information if you know how to interpret it or not" which emphasizes the complexities associated with data analysis. He goes on to say "I've made some mistakes and I'm not trained in any kind of nuclear chemistry…I'm kind of [a] dummy when it comes to that. So it's been dumbed down enough for people like me to be able to use it and still collect data in a systematic way, a replicable way". Mike here highlights the dichotomy seen throughout historical archaeological applications of pXRF data; the instruments are made to be easy to use and look akin to something one would see in a sci-fi movie, yet they are scientific instruments designed to take (arguably) precise measurements that are difficult to analyze successfully. In fact, Mike describes earlier work with neutron activation analysis where he performed studies that "show that it's not so, not so fast, it doesn't work nearly as good as it's getting…more objects similar that are hundred miles apart versus two, two pieces of the same object." Although Mike's use of language compares the instrument to a toy, his current and previous research demonstrates that he has a good (although self-admitted limited) understanding of the complexities of the pXRF.

Even if historical archaeologists overcome perceptions that they should not be performing pXRF research, they may find additional hurdles. Margaret described her hesitancy to publish pXRF work because she is "not comfortable with how accurate and quantitative the results are." She went on to describe that one concern was that "someone's going to knock me for trying to use XRF for this. There's so many studies that show that XRF is not the ideal technology for pottery, for example. But, it's still useful so I'm trying to, to figure out a way where I can be comfortable enough to say, these are the results, of course they're not perfect but they're still valid." This attitude is one possible explanation for the lack of peer-reviewed literature in historical archaeology. Margaret also described not only feeling a responsibility to do the research as accurately as was possible given the limitations of the instrument, but that the possibility of her colleagues having bad reactions was also a major contributor for her not publishing. If archaeologists feel so intimidated by others in the field to the point where they are not willing to publish, it is difficult to see growth in the use of the instrument in historical archaeology. She later posited that although "there are certainly plenty of us [historical archaeologists] who are very scientifically-minded, we often haven't been provided what we might think of as the necessary training to establish those guidelines" of proper use of the instrument in historical archaeological applications.

Margaret described one problem facing historical archaeologists as “innumeracy instead of illiteracy, so the unwillingness of archaeologists to get really quantitative and statistical and kind of technological. So it’s very easy for anyone to operate an XRF and see the spectra that are generated, but it is a much steeper learning curve to extract data that can be used then comparatively.” She also described that she had spoken with an individual who told her “I don’t even agree to review an XRF papers about, I forget if he was specific about ceramics or about artifacts more generally, that are not like obsidian…which does work pretty well [for pXRF analysis].” Generally, journals seek reviewers who are experts in the specific area of a paper in question; as previously discussed, there are very few individuals who might be considered ‘experts’ in historical archaeological applications of pXRF so the loss of even a single reviewer could be extremely prohibitive in the publication of historical archaeological studies. As Amanda also noted, she was hopeful that pXRF could be used in more diverse applications but that “I think there’s a little bit more pushback from other scientists and people in those communities about getting the most reliable data.” Even if researchers have the confidence to expand the use of pXRF to new applications, like Michelle, they may delay publication, which limits novel applications by other researchers.

Finding Published Methods & Literature

One of the main inconsistencies that drove this research was understanding the lack of peer-reviewed published literature of pXRF use in historical archaeological contexts. All eight archaeological participants had participated at some level in research using pXRF in historical archaeology. Anecdotally, at least one participant noted that “within the last couple years I’ve seen so much more and more I feel like coming out or I hear about it or this person is working on something.” However, this is not born out in the literature and the majority of participants have not published in peer-reviewed journals. Participants described a number of circumstances that contributed to the lack of formal publication: several participants published reports online, the work of a number of participants resulted in reports for governmental agencies or the private sector. Linda suggested the lack of pXRF literature could be linked to the detailed typologies available to historical archaeologists, explaining that her suspicion is that historical archaeologists “only really sort of touch into XRF or touch into geophysics or other sort of avenues when they’re, sort of, their traditional avenues don’t necessarily work for them.” Lack of peer-reviewed published methodologies was identified as a bottleneck to further publishing by Linda, who posited that research is “going to pick up immensely into the future as people publish more” noting that “once it hits sort of that critical mass, people will find it much more amenable to sort of digest because it’s, they’re more used to it.” Anthony added that one possible reason for the publishing discrepancy in pXRF between archaeological fields is that “I think a lot of historical archaeologists don’t feel as comfortable as other fields of archaeology in being able to incorporate [pXRF]" because they don't have the "physics, chemistry, and statistics background." Some participants also explained that research couldn't be published, "Anything with regard to NAGPRA will not be published." Michelle also shared another possible reason for a lack of peer-reviewed literature in historical archaeological use of pXRF: null results typically are unable to be published. This means that if, for instance, a researcher found that they were unable to successfully source some particular samples of pottery, many journals would not accept a paper based on that premise. An additional factor may be that a number of participants were not involved in the academic sphere, a space where peer-reviewed publications is crucially important to career advancement. Some of these participants publish on personal or institutional websites, which can be hard to track down.

This lack of centralized data was identified by several participants as being one reason they struggled to find vetted methodologies and comparable pXRF data. Mike noted that "there's no central location" for pXRF data or other elemental analysis data done on historic objects. Michelle also noted that the same was true for finding methodologies: "it's so scattered in the literature, there is no good consistent place to go looking for it, shall we say." Amanda shared similar sentiments, describing that one difficulty was determining the best methodology for answering her question, "as far as gleaning the right information for what your projects were geared towards…I think that that took more work. You know, because different people were using it for different items and different materials and those kinds of questions of what's appropriate for your work and your material would just vary." Amanda tried to overcome this hurdle by extensively reading existing literature, which she noted was limited for her specific historical archaeological application, but acknowledged that the time involved in developing her methodology might be a barrier to some.

Some participants created or are attempting to create archaeological specific documentation and methodologies when they couldn't find it elsewhere. One participant had noted the lack of formal documentation for archaeologists, so she "wrote a manual" specific to the instrument she is most familiar with that is being used by others for training purposes. The need for established methodologies was shared by Margaret who explained, "I think we do need real best practices. We need some, some kind of established guidelines." She went on to link the lack of best practices to both the fact that pXRF is not as heavily used by academic scientists which results in "no one's told us like this is exactly how you do it to get the kind of data that you need to say this" and that there aren't archaeologists "who are really engaging with that literature and trying to, to promote the use in, I think, the way that we need to do so." However, Michelle asserted that "if we do start getting the methodologies published in a way that people can find and follow, I think that you'll see the use increase as well as the publishability of the data." Some participants were actively pursuing publishing standardized methodologies. Mike noted that "working toward…a standardized method for [a] particular class of objects, I think that's going to be crucial…to develop some sort of baseline setting and just consistent things so that you can compare". He is working with colleagues to "come up with a standardized approach" for looking at ammunition, but that they "hadn't quite gotten there yet".

One participant described the importance of published methodologies, saying "that is the first place I look when trying to develop something is what have other people done. That being said, I have had huge amounts of trouble finding what other people have done so I can't actually repeat their experiment." She also linked lack of published methods with "semi problematic or less preferred" usage of the instrument in historical archaeological contexts.

Margaret suggested two reasons why literature and available methods might be limited in historical archaeology. She suggested that historical archaeologists using pXRF in a new application "have to produce the initial sort of validation of the XRF data to say, to use an established technology like ICP-MS or like neutron activation or something like that to, to verify that the results you think you're getting are actually the results that you're getting." Many historical archaeologists may not have the expertise or access to these kinds of instruments to perform validations and, of course, one of the main benefits of pXRF is its relatively ease of use. She also pointed out that one problem in historical archaeology is that "our sample size is not always as good as it should, you know that we have much more, much greater limitations on the quality or our samples, the size of our samples, the ability to perform destructive analysis on our samples."

A number of hurdles face historical archaeologists once they decide to incorporate pXRF analysis into their work. Participants described varying relationships with the use of filters and/or calibrations and their perception of the need to employ them or create their own. The same was true for analysis of spectral data. Participants described varying degrees of perceptions about what was appropriate for their own applications. Many also described exclusionary practices, actions, and ideas from natural and physical scientists (and possibly from their own community) and the difficulty of finding methodologies in the limited published data. However, these are all hurdles they negotiated in exchange for uniquely interesting pXRF data.

Moving Forward: Training, Reproducible Science, and Collaborations

While a good proportion of the interview time was dedicated to problems, participants also discussed ways historical archaeologists could move forward. In the words of Paul: "I'm guessing as you've seen there's a lot of issues you can run into with, you know, um, but there's also a lot of power there and potential." To best harness this power and potential, a discussion of training, commitment to reproducible science, and the benefits of collaborations follows.

Training Problems

Most participants described their training on pXRF as a combination of workshops (some multi-hour or even multi-day sessions) put on by manufacturers or other experts, reading literature and the manual provided with the instrument, and one-on-one training with an experienced user. A number of participants noted the importance of these one-on-one connections; Linda described her pXRF mentor saying he "was really, really adamant about helping me through the first like, like two weeks of literally holding my hand every single day and walking me through it. And then after when he was like, no, you can do this like you, you will be able to understand this, I asked him questions…and bothered him a whole bunch." She noted the importance of her continued access to him as a resource, noting that "if I were to continue [using pXRF in another context], I would definitely want him or one of my other conservator friends to sort of help me with the initial process." Linda also suggested that "a two-week training course" providing instruction, documentation, and recorded webinars might be an efficient way to train archaeologists new to the technique.

Margaret had a similar experience, sharing that having "a lot of conversations one-on-one with [manufacturer] representatives as particular questions came up that really clarified things for me." Amanda similarly benefited from one-on-one connections with other pXRF users in addition to other written training materials and workshops, although she cautioned that "depending on your material and your research questions and how those varied would depend on how you need to set up the machine." Michelle also similarly described her gratitude for the connections her institution provided to users of pXRF knowledgeable in historical archaeological applications explaining, "it also has really, really helped to have colleagues or contacts who are experts with the use and application of the XRF so that if I get stuck I can ask." She described a situation in which such a contact was able to help her design an experiment to answer a specific research question.

Only one historical archaeologist participant described having taken a chemistry class in college, which she explained as "extraordinarily, extraordinarily helpful". However, she, along with other participants, argued that coursework in physical sciences wasn't necessary for an archaeologist to successfully use the instrument simply noting that "it's going to take personal investment and a lot of time" if an archaeologist doesn't come into the research with background knowledge. Michelle was in a similar position, she had a bachelor's of science degree in chemistry and "that helped tremendously to understand you know how the instrument works, what is it doing when it's giving x ray energy, and what are the, what is the reading giving out— that helped a lot, I will not deny that." Michelle argues that "there is absolutely no reason why an archaeologist can't learn to use a pXRF," but notes that "it may take a little bit of effort and work" to learn the necessary information. In her opinion, the most important question an archaeologist needs to be able to answer before using pXRF is "is it a tool that will provide data that is useful for the question."

One crucial problem is a lack of resources that are targeted at the historical archaeological community. The lack of specific training programs, formal or informal, by historical archaeologists was one puzzling aspect of this research. There are limited programs that do exist, although the only two generally available in person trainings (offered at conferences or institutions and available for the interested users) were specific to those using pXRF in conservation settings, not for archaeological applications. Anthony identifies one criticism of an emphasis on highly trained pXRF users as "using an XRF shouldn't be the same as becoming an expert in XRF." This same criticism is mirrored in the lack of training material targeted towards archaeologists. Mike explained "there's not a pXRF for Dummies book on the subject…or just kind of a for the layman or the for the non-specialist archaeologist use…I glean when I can off the internet and different little classes and workshops." Anthony identified a lack of "physics, chemistry, and statistics background needed to properly interpret XRF" as a major problem facing historical archaeologists. Margaret, who conducted training for archaeologists and other interested users at her academic institution, described the importance of "trying to talk about it in terms that they would understand that the expectation that they probably hadn't had a physics class since high school…that analytical chemistry and archaeometry was probably not something that they necessarily engaged with on a daily basis but they were interested in."

Another barrier to providing such training is, as Michelle explained, "time and opportunity." Although some participants, including Michelle seemed to be good candidates to lead such a training, at least two participants specifically rejected the term "expert". Mike, who, based on descriptions of his work, seemed to be one of the most experienced pXRF users of the archaeological participants, argued, "Some people might consider me an expert but, I'm nowhere near an expert." However, there are benefits to leading such a training. Margaret shared that a crucial part of her own training occurred when she was creating training for others, describing that "the onus was on me since I was conducting trainings…that's when I really got it was when I had to explain it to someone else." However, the lack of appropriate opportunity or venue to provide such training seemed to be more problematic, with trainings typically being in person and in small groups, often run by a manufacturer that the group purchased an instrument from. This opportunity disappears, for example, if a user has purchased an instrument second-hand or has been temporarily loaned an instrument by a colleague.

However, it's important to note that a number of participants indicated the importance of informal training. Anthony emphasized that archaeologists should not "be afraid to experiment with this technology…in a way that teaches you the basic scientific concepts" as opposed to users saying "okay, we've got it for a week. We're only going to measure these objects and that's it." Mike also noted that pXRF is in its infancy with users "using it kind of cavalierly and zapping anything you want" but that "people are still kind of stuck in…a university mode where they got only so much time…with the machine". Margaret added that informal experimenting was also crucial to assisting her in learning to use the instrument, sharing that "having the opportunity to, to create a calibration, fiddle with it, fiddle with it again, fiddle with it again and see how it affected the results was really useful."

Representatives of manufacturers, who often help provide training to historical archaeologists who purchase instruments from them, described some of the process of the current training they provide. It is, however, important to note that some archaeologists never have direct experience with a manufacturer; at least one of the participants described buying an instrument from a third party and in the case of shared instruments, it is unlikely that all users would have access to a representative. Jennifer's training process with new users seemed extensive and well rounded, however she described herself as "not your normal sales person, to be honest." She described that when she trains individuals she will "look to them [the user] to be the expert in their field, and then I'd come with, you know, the technology and go through theory of how XRF works." However, she also explained that she tailors the training experience based on the specific application: "I make sure that I have, I learn about it so I can be successful in it." Jennifer notes that she likes to make her training specific to the types of research questions the user is hoping to answer, but not so specific that the user has no ability to generalize the training to other potential applications: "One thing I really like to do is to just make sure that they have a full understanding of the capabilities of the instrumentation, so that they can apply it to new things that they may bring to the table." Once again, this participant describes the importance of a good fundamental understanding of the instrument to most successfully use the instrument. She also described the importance of continued interaction with the user: "I spend a lot of time with follow up so that, you know, I'm sure they're using it correctly. There's nothing worse for me." However, Jennifer describes her general interactions with archaeologists as limited; she typically only interacts with archaeologists who contact her company seeking to purchase an instrument; in limited cases (she estimates fewer than 50 total in comparison with weekly for more common applications) she interacts with individuals via workshops if "connected to a university where I'm doing a presentation on the XRF in their specific field or, or in their classroom."

The amount of training necessary to operate an instrument also varies based on the capabilities of the instrument. As Jennifer describes there are two points of view on training: "But, it's also, you know, if they rely on knowing that you can be trained, you know. They're the ones who really believe in people about, you know, you can be trained and I think the other companies I think they don't have, most of them have more fundamental parameters calibration, which is more along the lines of point shoot and then data interpretation's like a whole another field." Jennifer links differences in manufacturing as limiting the amount of training necessary or useful to archaeologists. If a historical archaeologist only has access to an instrument where creating a calibration is not an option, they might find a training that emphasizes creating calibrations less useful.

However, some training provided by manufacturers would be useful regardless of the actual instrument used. For example, Jennifer describes the importance of radiation safety, collecting sufficient data, and using a long enough sample time. She described her desire for "making sure their sampling protocol fits what they're trying to learn."

While participants described having different training experiences, they all identified the training they received or sought out as being important to their successful use of the instrument. Many had a combination of in-person formal training (provided either by a manufacturer or experienced user in a workshop format) and informal one-on-one training. Many identified the one-on-one training as being especially useful when determining how to perform novel measurement and analyses.

Reproducible Science in Historical Archaeology

A number of participants described the importance of conducting their research in a reproducible way. Reproducible science involves not only a careful and consistent methodology that can be replicated in the same context but also information that would allow users anywhere in the world to obtain similar results. Anthony was a vocal proponent of the application of the tenets of reproducible science to historical archaeology, but a number of other participants described similar sentiments.

In order to engage in reproducible science, a pXRF user must describe the methodology employed in detail; Anthony suggested including all possible information on filters, energy and current of the instrument, calibrations, algorithms used in the analysis, and spectral data. Interestingly, Anthony noted, "In the field of archaeology there's just a lot of frowning on the use of spectral data to support hypotheses, which I find absolutely ridiculous". He noted that editors of peer-reviewed publications might seek quantitative results as opposed to "qualitative spectral data". Even participants with less direct pXRF experience agreed that adequate description of methodology is important; Beth described that in published results she expects that "they back up their data and say exactly what's going on…you just have to be pretty detailed." Margaret noted that this kind detailed methodology is crucial for answering questions; she shared experiences where other pXRF users would get in contact with her for assistance in analyzing data and they were unable to answer methodological questions. She explained "they're just collecting data that's not actually very useful because it wasn't planned out in advance." Amanda provides a good counter example of these users. She described the process of her research in detail. Although her question was fairly general in trying to determine different categories of ceramics, she went through a detailed process to ensure she was able to answer questions about whether groups of ceramics were similar or different from one another. She began by reading the existing literature, including methodology. She described that "some people were saying with the study of ceramics that — you know, they're non-homogenous— that it was going to be very difficult to get reliable data." So, after she "whittled down the elements that we were looking at also from the literature", she "went through different methods of testing the machine" by preparing samples in a number of ways after thoroughly cleaning them. Once her preliminary data was collected and her method was validated, she extended the study to a relatively large sample size with replicate measurements. Even though the study was performed several years ago, she was able to recall a number of specific details that would have made it relatively easy for another archaeologist to reproduce her work.

The importance of reproducible science is to allow for consistency and reliability across the field of pXRF usage in historical archaeology. A number of participants discussed the possibility of databases of information that would allow for a number of independent groups to do research like sourcing more efficiently. As James describes, "the only way to get that [sourcing] data is going to be lots of archaeologists collecting the data so that eventually we can say oh look we found this giant clay source in southeast China, here's the elemental composition and then we can go back to all that data from the sherds [collected previously] and go oh type b matches that perfectly." However, this sort of schema only works if all the research going into creating and comparing the sourcing data is collected in a reproducible and reliable manner otherwise the data will not be comparable. Michelle agreed that you would "have to use the exact same methodologies to collect the data for comparability" in a sourcing study.

Reproducible science was discussed by several participants as being one important way for historical archaeologists to collect and publish methodologies that can be adapted by other researchers. Reproducible methods might also expand the utility of current applications, allowing for archaeologists to share and compare data sets, as might be done for sourcing studies.

Collaborations

Engaging with pXRF analysis at this level might seem overwhelming. Successful collaborations are a key piece in the successful adaptation of pXRF to historical archaeology. These collaborations, in the experiences of the participants, can take many forms. However, use of collaborations was another prominent theme referenced by a majority of the participants. As Linda noted, "often we're set into silos in different sort of specialties, and different, different science…and I feel like [pXRF] is a good way for us to break down some of those silos…I think that's a good benefit, too, of opening that…line of communication."

The collaborations discussed in the interviews seemed to fall into two categories: formal and informal. Amanda used a formal collaboration with several statisticians at her institution which she described was born out of the fact that she "did not have a strong math background, not in this kind of statistical work that I really wanted to do." She credited her collaborators explaining, "If it hadn't been for them, I would not have gleaned the information that I got…really getting the answers came from their help." Paul also described the importance of complex statistical analyses saying: "Then as a whole you look at that through one of these multivariate techniques and you get a more, you might get a more complete understanding of the sample that way." As he understood, the research team able to perform this analysis was an interdisciplinary collaboration at an institution. Amanda also described informal collaborations with other archaeologists, describing that "there were multiple people I met at conferences doing pXRF" and that these contacts resulted in a trip to another institution where she collaborated by doing pXRF for another archaeologist.

Two participants had no direct experience with handling a pXRF instrument, but both had seen pXRF instruments being used by others (in one case by a chemist and the other by hazardous materials specialist and another archaeological collaborator) and had incorporated pXRF data into their research. While both these participants described these collaborations as being successful and informative, both participants did not receive spectral data, only a spreadsheet with percent compositions. Both participants recalled that their pXRF collaborators were enthusiastic, explained the process of data collection, and collected repeated measurements on multiple places on the sample with guidance from the archaeologists. The participant collaborating with the hazardous materials specialists described the interactions: "I can say, can you analyze this artifact for me and tell me what elements are in it and generally they're like sure, you know, we'd love to, why, what's the artifact, what do you want to see, you know what, what are you trying to figure out." Collaborators brought their expertise in handling the instrument and appropriately collecting data; for example, in one case the sample was not totally homogenous and the hazardous materials specialist explained "we need to get a reading where the concrete on has flaked off because the concretion is a whole separate, you know, it's, it's going to have a completely different elemental makeup than the base metal." As previously discussed, the non-homogeneity of samples has a potential to be overlooked by inexperienced or not well-trained archaeologists, so it is noteworthy and important that this collaboration resulted in the successful communication of that information and proper data analysis of a non-homogenous sample.

Interestingly, in both cases the semi-quantitative or quantitative results aligned with identifications made by the archaeologists based on a visual examination of the samples. One participant expressed relief that the pXRF data agreed well with her identification, saying that if her identification was wrong "I'm not gonna do this ever again…not the XRF, but the, you know, just [identifying]." While neither of these projects were published in academic journals (one analysis was performed for the private sector and the other for a governmental agency), these historical archaeologists did not see spectral data and may not have been able to include it even in report form. Collaborations like these may make it more challenging to perform reproducible science. Although neither of these participants remembered many specific details (e.g., what instrument was used, how was the data calibrated, what filters may have been used), the pXRF user should be able to provide this data. However, when asked how one of these participants vets the data given back to them, they replied "I mean actually when you say that question out loud I realized that really nothing to sort of trust that— it's kind of one of those, I just assume that people giving me the data know what they're doing. Um and are above board, and maybe that's partly because, like I said, the, the [specific archaeological] community is fairly small, um, so I know these people and trust them." This attitude is tricky to unpack; on one hand, the purpose of a collaboration is to work with those who have areas of expertise beyond the researcher's own, however, when your analysis relies heavily on the validity of the data it can be troubling that a researcher doesn't have a good idea of how the data was collected or analyzed nor know the extent of the collaborator's expertise.

James also described an informal collaboration to build a database of a specific material type, explaining that a member of his research community "contacted me and said hey we're building this database…can we look at the ones you guys have? And we were like you know sure that would be great, tell us where to send them and we'll send them to you kind of thing." This collaboration was especially lucrative as James did not have experience using a pXRF instrument himself, but was interested in being able to compare pXRF data he had access to to such a database. Collaborations can also include those with undergraduate researchers. Margaret shared that one benefit she saw in pXRF was that she will "train my undergrads [to use the instrument] and then to sit down with the data that are produced and say what can we do with these." This type of collaboration is especially valuable because it helps educate the next generation of potential pXRF users through collaborative research rather than a more formal training program.

Participants described several aspects of their experiences with pXRF as potentially helpful to moving the field forward. They discussed the importance of some kind of formal or informal training as being important for appropriate application to various historical archaeological contexts, the potential utility of reproducible science for increasing publishable and adaptable methods to increase research being done in the field, and that collaborations were key in their current and future successes.

Summary

Data collected from participants in semi-structured interviews were a rich source for understanding attitudes and perceptions of the current state of pXRF research being done by historical archaeologists. Participants were eager to share successes and cautionary accounts that helped situate their perceptions of their research in the larger context of the field. These experiences were diverse, as were the applications described, which hopefully speaks to the potential generalizability of the findings related here to other research being performed. The data conveyed in this chapter will be analyzed in conjunction with understandings of the history of the intersection between archaeology and science briefly described in Chapter 2 and a scoping review that follows in Chapter 6.

Chapter 6: pXRF In Historical Archaeology, A Scoping Review

A scoping literature review was performed in conjunction with interviews to better understand the current state of peer-reviewed literature using pXRF in historical archaeology. From preliminary research and through the interviews, it seemed that there was very little peer-reviewed research that used portable instruments. However, historical archaeologists are often involved in applied work, namely archaeologists employed by federal or state governments or cultural resource management (CRM) firms in the private sector. Such work typically does not result in journal submissions but rather technical reports (so-called "grey literature) that are submitted to clients and state or federal agencies. Initially, sources of grey literature, mined from state agencies or obtained by CRM firms, were going to be examined in conjunction with peer-reviewed literature. However, it became clear that the grey literature search was outside of the scope of the current project, as much of this work is difficult to access.

To examine state resources, the Idaho, Oregon, and Washington state historic preservation offices (SHPO) were contacted. Access was gained to the online records search systems for Oregon and Washington (OARRA and WISAARD, respectively) and a representative from the Idaho SHPO performed a query search of their system. However, these systems did not seem well adapted to search for reports that included the use of pXRF data. A preliminary search including terms like "pXRF", "XRF" and "fluorescence" of these databases provided few, if any results. This seemed to be related to how the databases were queried with the searches. The OARRA database only queried title keywords of bibliographic items. WISAARD searched metadata fields of records and scanned PDFs of reports. While the Idaho SHPO does not specify how it searches, based on the two results provided it appears that it is also a title keyword search. The identification of pXRF use as part of work done for a state agency is simply unlikely to make it into the title of the final report submitted to the SHPO, which made these records difficult to track. A full examination of grey literature submitted to the state would either entail physically examining hundreds of thousands of, in some cases non-digitized, records or would need to wait until records had been digitized if database querying could search all digitized material, not just selected metadata. In any case, based on the scope of this thesis project, grey literature from state agencies was not examined.

Obtaining grey literature directly from CRM firms was also attempted. Representatives from the Society for Historical Archaeology (SHA) and from the American Cultural Resources Association (ACRA) were contacted. The representative from SHA recommended contacting several faculty members who were involved in the CRM field in several different states; both of these individuals were unable to provide any suggestions for systematic ways to search grey literature from CRM firms. The representative from ACRA, a member-based organization providing information and support to CRM firms, suggested posting on their blog with a request for information directly from members. A short post was written and was shared via ACRA's social media channels (Appendix B). However, this garnered no responses. There is no centralized database for CRM reports, which may be submitted to the government or other organizations and may contain confidential information. Once again, based on the scope of this thesis project, grey literature directly from CRM firms was not examined.

Peer-reviewed literature, however, is relatively easy to locate systematically and can give a sense, albeit a limited one, of how pXRF is being used in historical archaeological contexts. A semi-systematic literature review was performed to answer the following questions: (1) where are archaeologists doing pXRF research, (2) approximately how much XRF research is done with portable versus laboratory-based instrumentation, (3) on what kinds of materials are researchers performing pXRF methods, (4) with what instruments are the analyses being done, (5) what kinds of methodological information are included in historical archaeological pXRF literature, (6) what kinds of analysis is being done with the pXRF data (quantitative, semi-quantitative, presence/absence), and (7) how is the data being presented to readers.

Criteria for inclusion in the literature review are subsequently described. Eight journals were selected based either on the criteria that they were journals specifically focused on historical archaeological research (Historical Archaeology and International Journal of Historical Archaeology), were focused on the junction between science and archaeology (Archaeometry, Archaeological and Anthropological Science, Journal of Archaeological Science, and Journal of Cultural Heritage), or were leading archaeological journals (American Antiquity and Advances in Archaeological Practice). Online archives of each journal, through their publisher's website as accessed via the University of Idaho's library catalog, were queried with Boolean search terms. The Boolean search terms were: "pXRF" OR "XRF" OR "x ray fluorescence" OR "EDXRF" OR "WDXRF" OR "x-ray fluorescence". This Boolean should catch the large majority of papers that included reference to pXRF research by including both abbreviated and non-abbreviated terms as well as several possible variations. Based on results, these online searches were conducted on the full text of the article, which either appeared in digital or digitized form on the publisher's site.

The Boolean search was then filtered by date, including only papers with a publication date from 2000-2021 (see Table 1). An important note is that Archaeological & Anthropological Sciences has only been in print since 2009 and Advances in Archaeological Practice only since 2013; no results were filtered by date of publication for these two journals. Articles were then assessed for exclusion. Firstly, any article that was not historical archaeology was excluded; criteria for exclusion were pre-1500 CE for Europe and Asia and pre-European contact for the Americas, Africa, and Oceania. Next, articles were excluded based on the instrumentation used; all laboratory-based instruments were excluded, as were modified XRFs (e.g., total reflection x-ray fluorescence and macro x-ray fluorescence scanning). Micro-XRFs were also excluded, even if they were portable instruments; although the technology is functionally the same, they sample a much smaller area of an object, which alters substantially the discussion about its appropriate uses. If an article did not specify an instrument and did not specifically indicate that the analysis was done *in situ* or that the instrument was portable, it was excluded. Literature reviews and meta analyses that included discussion of pXRFs were excluded. Articles using pXRF to analyze experimental archaeological samples (samples produced by present-day archaeologists to investigate questions related to material culture) were excluded. Table 1 summarizes the number of articles fitting the above criteria for each journal.

Table 1 Summary of proportion of articles fitting the scoping review criteria by journal.

Journal	Number of initial, time-filtered search results	Number of results fitting all criteria	Percent of initial results fitting all criteria
Advances in Archaeological Practice	5	1	20.0%
American Antiquity	90	1	1.1%
Archaeological & Anthropological Sciences	210	4	1.9%
Archaeometry	453	15	3.3%
Historical Archaeology	12	0	0.0%
International Journal of Historical Archaeology	10	4	40.0%
Journal of Archaeological Science	525	9	1.7%
Journal of Cultural Heritage	272	27	9.9%
Total	1577	61	3.9%

Once the sixty-one articles fitting the criteria were found, I identified features relevant to the study, including site location, time period, type of material being analyzed, whether the analysis was performed *in situ* or in a laboratory setting, the instrument used, the type of analysis undertaken, the level of detail in which the authors described any filters or calibration they used, whether the analysis was destructive (samples taken from object), and if the authors included spectral data. A summary of these results is presented in Appendix G in Table A1 and the references to the articles given in Appendix H.

The goal of this scoping review is not to present an exhaustive accounting of each of these articles to evaluate their merit nor is it meant to provide any sort of statistical power. The purpose of the review is, instead, to provide the reader with a general sense of what, where, when, and how historical archaeologists have been publishing pXRF results since the turn of the 21st century. The following is a discussion of general trends observed in this scoping review.

Firstly, and perhaps most obviously, is the uneven distribution of the publication of these articles through time. In the first ten years of the period examined, only six articles were published using pXRF in historical archaeology. This trend is not particularly surprising; the first true pXRF (there were early instruments that were 'field portable' in that the components could fit on a large cart that could be operated independently) was not introduced until 1994 ("X-Ray Fluorescence (XRF) Glossary" 2012). However, the increase has not been steady as the instrument became better known and validated in archaeological contexts; there was a large increase in the late 2010s, with more than half the articles in this review published since 2018. There have not been particular advances made with the instrumentation in the last decade, so this sharp increase must be due to other factors.

Another stark trend can be discerned when looking at the locations of the sites where pXRF is being employed. At a broad level, the majority of work was done on European sites (33 of the articles), followed by Asian sites (13), North American and African (7), South American (3), and finally Oceanic (1). Studies including multiple sites on more than one continent were counted in each category. The small number of North American sites is noticeable given the fact all the interview participants were based in North America and their experiences with pXRF were predominantly (although not exclusively) based on North American artifacts.

Another interesting feature was the time period of the artifacts analyzed. More than half of the publications (36) included objects from the 19th and 20th centuries, although a much smaller number of publications (17, ~28%) included only objects from the 19th and 20th centuries, which represented about 40% of the historical time period (although this varied based on time of European contact in the Americas, Africa, and Oceania). Just about a third of the articles examined objects that spanned more than three hundred years and over half included more than a century, though it is important to note that the time period is indicative of the time being investigated in the article not necessarily the period of the objects that were specifically studied with pXRF. It is hard to deconvolute exactly the distribution of the time periods investigated, but researchers using pXRF seemed to be interested in investigating materials both from a narrow time range (as specific as a single painting from a single year) and a broad time range (as wide as 2400 years).

The types of materials analyzed by pXRF also varied widely across the articles. I binned the specific material analyzed into one of five categories (the number of articles follows the category in parentheses): ceramic (13), geologic (14), glass (2), metal (14), and paint/ink (18). Generally, the articles were evenly distributed across these categories, with the exception of glass, which was only analyzed in two articles. Given the extensive and well-validated use of pXRF for geologic materials in prehistoric archaeology, the wide variety of applications was surprising; however, it mirrors the wide variety of applications discussed by participants. As with the types of materials being analyzed, there was also a wide array of instrumentation used in the studies; 17 of the articles used Bruker-manufactured instrumentation, 18 used Thermo Scientific instruments, and 14 used homemade instruments or those of an undetermined manufacturer. The remaining articles used instruments manufactured by various other companies. The number of homemade instruments was surprising, and in these cases authors typically described in detail the specifications of the instrument, including the manufacturers of the individual parts.

Interestingly, although all the instruments used were portable, the split between analyses in the lab or *in situ* (either in a museum, private collection, or at an excavation) was fairly even. Twenty-three articles performed the work *in situ* in comparison to 32 that performed the work in a laboratory or *ex situ* setting; the remaining articles analyzed both in the lab and field or did not specify. This is consistent with the descriptions of participants; some had or were planning on using an instrument in the field, while other exclusively used the instrument in a lab setting.

The remainder of the features investigated in the scoping review involve the types of pXRF analysis performed by the investigators and the details regarding the methods employed. The decision to include an analysis of these was informed by information both provided by participants and the literature (see Frahm 2013a; Frahm 2013b; Speakman and Shackley 2013). I first identified whether the analysis provided was quantitative (data provided was in ppm, percent composition, etc.), semi-quantitative (data indicated major versus minor elements or data was provided in ratio form), or presence/absence (data simply indicated whether a given element was found in a sample). The selected articles were split between these three analysis types; 27 articles were quantitative, 19 were semi-quantitative, and 14 were presence/absence, with the remaining articles seeming to not include the data they indicated they collected in their methods. Quantitative analysis was done on all identified material types except for paint or ink, but most of the analysis done on metal and geologic samples was quantitative. Ceramic materials were investigated fairly evenly by semi-quantitative and quantitative measurements; paint/pigments were also fairly split between semi-quantitative and presence-absence. Overall, based on visual analysis of the tabulated data there did not seem to be any overarching trends about analysis type.

I also indicated whether researchers in the body of the article or in supplemental material provided information about whether they used a filter or calibration and whether they described the filter or calibration ('ND' indicates that the article did not include any specified information, 'Yes' indicates it did, 'No' indicates it specifically indicated that the article did not employ a filter/calibration). I also identified whether the article (or supplemental information) included a figure showing one or more pXRF spectrum. Most articles did not include information about the use of filters; only about 15% of the articles included that they used a filter and these same articles also described the filters used in some way. This information did not seem to be specific to a single journal, representing four of the eight examined. Interestingly, all but one article that specified the use of a filter also specified and described a calibration used. In general, articles that specified use of calibration were more common, representing just fewer than 40% of all articles examined in the review. The large majority (~90%) of these also described either the pre-set calibration used or how they created the calibration. There was no obvious relationship between the specified use of a calibration and material used, however these articles were more likely to employ quantitative analysis; only five of the 25 articles that used calibrations did not employ quantitative analysis. Interestingly, articles that did not specify use of a calibration also employed quantitative analysis, although this was a relatively small proportion (7 of 36 that did not specify use of or did not use a calibration). The inclusion of spectral data was, in general, relatively uncommon; only approximately 25% of the articles included spectral data. Spectral images appeared in only three of the eight journals examined, Archaeometry (4 articles), Journal of Cultural Heritage (12 articles), and Journal of Archaeological Science (1 article). There was no obvious relationship between inclusion of spectra to any other feature examined. However, only one of the articles describing both the use of a filter and a calibration included spectral data. While no overarching trends can be established regarding the inclusion of information about filters or calibrations or the addition of spectral data, there did not seem to be a direct relationship between specified use of filters/calibrations and inclusion of spectra.

It is important to note that this review has a number of limitations. Due to the scope of this thesis, this review only included results from eight prominent journals targeting archaeology, specifically historical archaeology, or the juncture of archaeology and science. The inclusion of additional journals could change the trends seen in this review. Additionally, one possible limitation is the inconsistency in editor dependent decisions; for example, editors of certain journals may be more or less willing to include raw spectral data in an article or its supplementary material. Rather than being artifacts of an author's choice, these features may be more related to differences between journals. Perhaps most prominently, and discussed above, is that peer-reviewed literature is not necessarily representative of the actual work of historical archaeologists. As was the case with some participants, the nature of their work (for the government or a private CRM firm) is simply not conducive to peer-reviewed published literature. The population of archaeologists who choose to publish in refereed journals will also influence the content and data of the article. However, this review is representative of what is publicly (albeit not generally freely) available to historical archaeologists who are interested in or already performing archaeology using pXRF. Grey literature is not as accessible because it is not always publicly available and it is not easily queried if it can be found at all. As previously stated, this review is not meant to have any statistical power nor be completely representative of the use of pXRF in historical archaeology, but rather to supplement interview data with a semi-systematic investigation of the literature.

In general, it seems that pXRF usage in the eight journals examined focused on European materials. The studies often included materials from a large span of time and the pXRF data collection was mostly not performed in the field. Researchers performed all types of analyses, but material type seemed to influence the type of analysis done. Less than half of the articles included detailed information about calibrations and/or filters used in the analysis, and less than a third of articles included spectral data. A discussion of these findings along with the findings of the interview data will attempt to clarify the current state of pXRF usage in historical archaeology, as well as tie this space to the larger liminal area between archaeology and science.

Chapter 7: Discussion

This thesis aims to describe the shape of the liminal space between archaeological and scientific frameworks by using the case study of limited use of pXRF in historical archaeology by exploration of the following questions:

1. Why is there a disparity in the type of work being done in historical archaeology with respect to pXRF? Are there missed opportunities for use of pXRF in historical archaeology?
2. What are ‘appropriate’ uses of pXRF from the archaeological and scientific perspectives?
3. How does the specific case of pXRF illuminate our understanding of the relationship between archaeological and scientific frameworks? How might this reflect back on why and how pXRF is not commonly used by historical archaeologists?

In order to investigate these questions, eight historical archaeologists involved in pXRF research and two representatives from companies that manufacture pXRF instruments were interviewed. In this final chapter, synthesized analysis of this data, in conjunction with a scoping review examining peer-reviewed historical archaeology literature published in the last twenty years using pXRF, will explore these questions.

One overwhelming theme identified by these data is the utility of pXRF analysis in historical archaeology. While elemental analysis, as is done with pXRF, nearly always gives a user information that they are not able to determine by sight alone, this is especially advantageous in historical archaeology. Historical archaeologists are often examining non-descript or otherwise utilitarian materials or choose to spend less time analyzing these objects because they are non-descript and cannot be easily analyzed through traditional archaeological methods. Participants identified these cases as being especially conducive to historical archaeological applications, but a wide variety of applications were demonstrated in the scoping review, ranging from applications to metals to ceramics to paints and pigments, among others. As evidenced both by the exponential growth in peer-reviewed literature in recent years and by the enthusiasm of participants, the appetite to understand and successfully utilize pXRF to answer archaeological questions is present and increasing.

However, the use of pXRF was consistently problematized by participants, they themselves users of the technology, and it seems that this attitude is mirrored in the lack of peer-reviewed published literature. Participants, archaeologists and manufacturers alike, identified that uncritical use of the instrument as one big problem currently facing the field and that a sense of skepticism was fundamentally important to the appropriate application of pXRF to archaeological material. While interview data suggested that the eight archaeological participants were critical users of the instruments, their views were nuanced and at times seemed to verge on uncritical. For example, a number of participants expressed that a benefit of pXRF data is that it is objective, factual, or truthful, and they contrasted this to other types of archaeological data. This viewpoint is complex in itself; participants were careful to stress the importance of contextual understandings of pXRF data. For example, an instrument that reads a high level of rhodium for a given sample may either indicate that the sample is composed of rhodium or that there is rhodium present in the pXRF detector that is being detected through escape peaks. It is important that an archaeologist critically analyze such a result, which may be more difficult if their perception is that pXRF data is infallibly accurate. However, the view that pXRF data is objective, factual, or truthful is reinforced by the "cognitive authority of science" which is tied up in the historical relationship between archaeology and science discussed in Chapter 2 (Gieryn 1995, 405). The view that scientific data is non-subjective is crucially important to its privileged position, a position that pXRF users may want to benefit from by its use.

This untenable dichotomy, of the very benefits of pXRF research being tied directly to its disadvantages, was seen throughout this research. One oft-repeated benefit of pXRF is how relatively easy it is to use. Three participants described how the instrument is designed to look like a sci-fi-esque ray gun. The very form of the instrument seems to emphasize just how easy it is to use this as a 'point and shoot' tool. However, archaeologists using instruments in this manner is a sparking point for controversy (Frahm 2013a; Frahm 2013b; Speakman and Shackley 2013). This dichotomy is frustrating; many portable XRF instruments are built to be easy to use but archaeologists who take advantage of this are using the instrument outside of the standards of the field. This controversy is also informed by what some see as improper use by archaeologists operating the pXRF as a "black box". Speakman and Shackley describe this as when "the inner working of the XRF instrument are not understood by the user, nor does the user care to learn how and why the instrument functions—the only importance is that the sample is analysed and that numbers are generated" (2013, 1435). Speakman and Shackley use this criteria to draw a boundary around scientific versus non-scientific use of the instrument; the advent of portable XRF systems has led to a situation in which they say, mockingly, "everyone can be a *scientist*" (2013, 1435). In his response, Frahm identifies that "their concerns are ultimately due to the proliferation of an analytical technique to which specialists like themselves previously held the reigns [*sic*]" (2013a, 1447). In this series of articles, there is an obvious and active negotiation of the boundary between archaeology and science, one that is tied to the fundamental power given to (or negotiated by) science. Frahm emphasizes that there is a difference in determining appropriate methodology (which he believes can include "black box" uses) for archaeological applications and traditional methods used by geochemists (2013a). This discussion shows a negotiation for the expansion of the boundaries of science outside of traditional or historic uses of the technique. Frahm also connects the influence that funding has in continually reinforcing the *status quo* in science; in describing the fundamental differences in the types of questions archaeological research employing pXRF is asking, Frahm quips, “I look forward to a time when archaeologists have sufficient funding to subsidise geochemists’ research” (2013a, 1445). Here Frahm identifies, within the microcosm of pXRF use in archaeology, the difficulty of renegotiating the boundaries of what is considered appropriate scientific research with a system based on retaining a privileged position. It is important to note that Speakman, Shackley, and Frahm are specifically discussing the application of pXRF technology to sourcing prehistoric lithic material. However, historical archaeologists are cognizant of this negotiation of power as played out by these articles; at least two participants identified Speakman and Shackley by name and discussed how they perceived Speakman and Shackley’s views as predominantly negative.

It is important to note here the relationship between the design of the instrument itself and what Speakman and Shackley find to be inappropriate use. These pXRF instruments are not designed for archaeologists or their applications but rather industries like mining, positive material identification, and scraping; manufacturing participants described archaeologists are representing a small portion of the sales of pXRFs. Archaeologists representing a small market segment also has a great impact on the future. Anthony points out “a lot of the big changes aren’t driven necessarily within the field of archaeology or conservation but rather by what we can manufacture.” Archaeologists have a limited ability to influence future technological advances that might make pXRF better suited for work in historical archaeology both because the ability to manufacture those advances may be limited but also because archaeologists simply do not have the economic pull to influence the manufacturers. Although looking like a ray gun does not fundamentally affect the pXRF’s ability to be successfully applied to historical archaeological applications, it is important to understand that there is a relationship between marketing, how the instrument is built to be operated, and how archaeologists practically use the instrument. Both representatives of manufacturers noted that they see archaeological applications as different from most uses their customers have. The instrument is built to be easy to use and to be used a “black box” and is marketed as such because these qualities are unqualifiedly favorable in the majority of their markets. Speakman and Shackley argue that these qualities lead to improper use by historical archaeologists, although they don’t comment on its utility or appropriateness for use in other market segments.

However, it’s important to emphasize that even Speakman and Shackley do not argue outright that pXRF is fundamentally inappropriate to use in archaeological contexts, only that individuals who do not understand the instrument cannot properly use it. However, the data suggest that, based on a small sample, archaeologists are concerned with using the instrument properly and do care about "how and why the instrument functions" (Speakman and Shackley 2013, 1435). The archaeological participants had an extremely wide range of specific scientific knowledge that would allow them to uncover the "black box". One piece of knowledge that was specifically investigated pertained to the use of spectral data. As previously discussed, spectral data allows a user a peek inside the black box; the spectrum is closer to the unmanipulated raw data than a table an instrument might provide given a calibration. However, spectral analysis on its own does not provide any quantitative data. A number of participants felt that they had neither the time nor expertise to make spectral analysis worth it, and less than a third of the articles investigated in the scoping review included pXRF spectral data in the article body or supplementary information. Investigating spectral data is potentially less impactful if a matrix-matched calibration is used. Understanding and/or creating one's own calibration would be another point of knowledge that would uncover the "black box". However, obtaining appropriate calibrations are, as previously discussed, difficult. If a careful calibration is not possible, historical archaeologists must understand that tabular data provided by the instrument is simply the instrument's best guess, and the further away the sample is from the calibration (e.g., the instrument is calibrated on obsidian and the user is analyzing glass samples), the worse the guess will be.

While examining spectra and having a good understanding of calibrations helps to uncover the "black box" condition of many commercially available pXRF instruments, the data suggests that spectral analysis is not a prerequisite for successful application of pXRF to historical archaeological data. Like Frahm suggests, the data indicates that methodology need only be sufficient to answer the types of questions being asked (2013b). If, for example, the archaeological question being explored can be investigated by presence/absence measurement, there is little reason for an archaeologist to create their own calibration and carefully investigate each spectrum for potential inconsistencies. Most participants indicated that they did not analyze spectral data nor create a specialized calibration specifically suited to their sample material. However, all of them, except perhaps one who did not have direct pXRF experience, indicated that they understood the limitations of the instrument when they didn't have such best-practices approaches in place. A number of participants discussed the potential for pXRF to be used in sourcing studies; however, all of them recognized the limitations of the instruments provided the methodologies they were using, and in most cases they identified that true sourcing studies were not possible. However, a number of them found that sourcing studies involving categorizing samples based on statistical analysis of elemental composition similarities was appropriate given their methods. A similar picture is drawn in the literature examined in the scoping review: most articles that employed quantitative analysis described using a calibration and no articles that employed only presence/absence analysis described using a calibration. This indicates that archaeologists understand the relationship between a good calibration and accurate quantitative data, and that, in situations that don't require accurate quantitative data, archaeologists are less likely to describe those methodologies.

This is not to suggest that Speakman and Shackley do not identify some potential problem areas, but rather that the use of pXRF instruments in a "black box" manner is more related to the marketing and design of the instrument and the types of questions archaeologists are asking rather than an unwillingness to learn or ignorance to these potential problems. Rather, I would argue that there are systemic barriers, those related to science's exclusionary boundary setting, that are preventing robust application of pXRF to historical archaeology.

Participants described examples of the structures that bolster the privileged position of scientific knowledge. There are two examples, both described in detail previously, that stand out in this regard. The first is the experience of the participant who interacted with an expert with a natural or physical science background at a conference. The expert, identified as such by both the participant and based on his position giving a keynote address, took an opportunity speaking to the entire conference to undermine the work done by a graduate student, work that the expert later admitted was well done. Here, the power negotiated by his position as a scientist (and likely academic hierarchy, student-teacher norms, and possibly gender inequities) was used to reinforce the boundaries of science and its privileged position. While the participant described his apology at the end of her talk, her voice, not amplified by her position as a scientist, expert, or academic authority, was minimized, accessible only to those who attended her talk whose views were likely influenced by the comments of the expert. The second example is that of the participant who described her hesitancy to publish her work due to the climate of the field. When describing her situation, she indicated that she thought her work was valid but that she felt there would be a negative reaction to it. While she did not specify that these individuals would be natural or physical scientists, she later referenced Shackley in the context of his well-known views on pXRF application in archaeology. Although there are a number of reasons that users may choose not to publish data, there seems to be a perception that those trained in the natural or physical sciences should continue to be the arbiters of good pXRF research. This is echoed in the many self-deprecating comments, especially those by Mike, placing the research and knowledge of archaeologists below those of scientists based on nothing other than the "cognitive authority of science", which most of the archaeologists who participated in the study did not seem to claim for themselves (Gieryn 1995, 405). While the example of the participant whose research was devalued at the conference was slightly different, the same principles can be applied to that situation;

the participant's voice was quiet compared to, and made quieter by, the expert who asserted his ability to determine the boundaries of science. While examining the effects of gender in contributing to the negotiation of the boundary between archaeology and science was outside the scope of the current study, it may be important here to note that gender may play a large role in interactions between scientists and archaeologists.

One fascinating facet of this discussion is that it seems to present the view that those with natural or physical science backgrounds have great authority in deciding what is or is not good science, or is science at all. However, in discussing how to evaluate the appropriateness of pXRF data, participants identified the need to be skeptical or critical of the data presented to them by the instrument. Margaret, for example, described problematic usage as when users are uncritical of their data and then "promulgate that information [about what a sample is made out of] as gospel." Yet here, participants consistently buy into the system that places scientific knowledge in a privileged position, even when arguments can and have been made that their expertise is not directly related to the knowledge sought by archaeologists (Frahm 2013a). The complex interplay between a need for skepticism in using a pXRF instrument and analyzing its data and the trust placed in the system that prioritizes scientific knowledge would be a rich topic for further research and is one that's been explored in other contexts (Knorr-Cetina 1999; Latour and Woolgar 1986).

The data also suggest that systematic barriers are also preventing future work that may improve, at least in the eyes of scientific frameworks of knowledge as described by Speakman and Shackley, the research being done in the field of historical archaeology using pXRF. Most participants described or echoed my sentiment that there was a lack of peer-reviewed literature involving pXRF in historical archaeology. This is confirmed by the results of the scoping study. The method of the scoping study allowed for a comparison of the proportion of work done with portable instruments in historical contexts as opposed to other archaeological settings (experimental, prehistoric, etc.) and laboratory instruments; the initial Boolean search terms should have isolated most XRF work published in the journals and the exclusion criteria isolated pXRF in historical archaeology. As seen in Table 1, less than 4% of the articles initially isolated via Boolean search matched the criteria for inclusion in the scoping review. This demonstrates that not only are there very few papers (only 61 articles were included in the scoping review), but that XRF in archaeology and pXRF in other archaeological contexts are being successfully used and published on. Participants indicated a few possible reasons for both the disparity specific to historical archaeology and also the small number of articles out there. Many participants described what I was initially concerned might be the entire story—historical archaeology is unique in that there are already a number of lines of evidence, namely documentary evidence, that can assist archaeologists answering questions, and as such there are often well-defined typologies that may make chemical analysis of artifacts simply unnecessary. Participants posited that in other subfields of archaeology, lack of defined typologies or other supporting evidence may make elemental analysis like pXRF a more necessary and widely accepted technique. While this seems like one logical and likely reason for a relatively small proportion of pXRF work to be done in historical archaeology, Margaret shared that she was told by an expert trained in natural and physical sciences that he limits what kinds of articles he will review based on the perception that pXRF is only a validated method for certain kinds of archaeological artifacts, mainly obsidian. As previously discussed, reviewers are an essential step in publishing in refereed journals and the loss of even a single reviewer in a field this small could have large effects on the amount of work published. Based on participant data, research is being done in historical archaeological contexts with pXRF; however, it seems as though the research done is not proportional to the research published. A number of factors may influence this, but the comments of Margaret raise the question of how much of the research is being weeded out in the publishing pipeline and what proportion of that might be based not on the merit of the research but rather preconceived notions, based on traditional scientific frameworks, of the possible validity of the method.

While no other participants directly discussed this kind of obvious exclusionary barrier, many described their perceptions of scientists not taking their work or the application of pXRF research to archaeology seriously. Michelle described her perception of scientists looking at archaeologists engaging in pXRF research: “It’s, it’s the perception that you’re kids playing in our sandbox.” Here, Michelle demonstrates the boundary drawn by scientists to exclude archaeologists from participation in science and diminishes the contributions of archaeologists, again not based on their individual merit, but rather writ large based on previous boundary negotiations that leave archaeology on the outside of science. While many archaeological participants seemed to accept and generally not be particularly bothered by this perception, a problem can and likely does arise if the perception of scientists impacts the ability of archaeologists to publish methods that can be used by other researchers. Nearly all archaeological participants discussed the need for, and current lack of, validated methodologies to be widely and publicly available. However, even excluding systematic barriers facing historical archaeologists doing this kind of work, it is challenging to create and publish a detailed, validated (according to some kind of discipline-based standard) method that could be adapted by others. Participants described difficulty in locating appropriate literature, which is substantiated by the scoping review. Participants in the study were all based in North America and predominantly studied archaeological materials found in the United States; the scoping review revealed that, in its limited scope, most of the materials are based in Europe and many studies included materials older than would fit the definition of historical archaeology in the U.S. While methods may not be specifically location-based, differences in composition between goods found in the U.S. in historic times and those found in other countries may require some adjustment or may not be directly comparable (however, these data could be of great use if trying to compare American-made goods with British-made ones). Until archaeologists are able to determine and negotiate the shape of the intersection between historical archaeology and pXRF usage, both scientists and archaeologists (many of whom participants described as not understanding the utility of pXRF research) may continue to have the perception that the work happening at the intersection is lacking; this will lead to continued difficulties in publishing methods and data that may help to advance the field.

Work described by participants and found in the scoping review was varied, interesting, and demonstrated a desire from historical archaeologists to continue to find successes in applying pXRF to their research. However, archaeological participants indicated that there were difficulties in applying pXRF that went above and beyond difficulties in securing funds to purchase or share an instrument, learn to use it properly, and successfully carry out research. Participants consistently indicated that there were higher-order changes that would help apply pXRF to historical archaeology, which included increasing publications (to share methods), creation of shared databases (for use in potential sourcing studies), and generally finding ways to gain validation both from the fields of archaeology and science. I posit that these higher order problems can be addressed through an arbitration of the space of science, which "acquires its authority precisely from and through episodic negotiations of its flexible and contextually contingent borders and territories" (Gieryn 1995, 405). These episodic negotiations are already occurring, as seen in the discourse between Frahm and Speakman and Shackley, but it seems that these negotiations are occurring much more slowly, or not yet at all, in historical archaeology.

One of the easiest ways for archaeology to expand the boundary between science and archaeology, so that pXRF research might become more accepted and methods may be better validated by those operating in the liminal space, is to participate in reproducible and open science, a suggestion shared by Anthony. The application of open and reproducible science to archaeology has been suggested recently and the conversation is happening in other disciplines as well (Chen et al. 2019; Marwick et al. 2017; Watson 2015; Woelfle, Olliaro, and Todd 2011). While aligning the space of the liminal field with this scientific paradigm validates the power structure of science, it may be necessary to work within the system in order to eventually move past it. Participants indicated that they often felt looked down upon by those they regarded as experts in the field (often individuals who were trained natural or physical scientists), even if they felt that their research was successful, interesting, and/or adding substantially to the field. Continuing to operate under the traditional structures of science may allow negotiated entry into the scientific space; once within it may be easier to negotiate an expansion like the one Frahm seems to be looking for.

However, the idea of reproducible science, if palatable given the complex history between archaeology and science, does have some obvious benefits aside from the eventual possible restructuring of what science is from within. The importance of reproducible science goes beyond allowing for consistency and reliability across the field, it also contributes to 'open science', a concept used in a variety of disciplines to describe transparency and accessibility of research including "data stewardship instead of data ownership, transparency in the analysis process instead of secrecy, and public involvement instead of exclusion" (Marwick et al. 2017, 8). It is this second norm that that can be hard to reconcile with pXRF data, as manufacturers typically don't provide the proprietary information encoded in their calibrations, filters, and software analysis. In the eyes of Anthony, open science is crucial if archaeologists are using publicly funded grants to support their research, as archaeologists "have a fiduciary obligation then as public servants…to ensure that the methods they're using are open and reproducible. Because that also democratized what we're doing as scientists."

pXRF is a relatively easy tool that can help answer questions in historical archaeological contexts. However, the tool must be well understood and its precise use detailed to others for a truly successful application. It is difficult to tell if most historical archaeologists are currently engaging in reproducible and open science due to an overall lack of literature. Based on the scoping review, a minority of articles described using a calibration, one piece of information that would be vital to engaging in reproducible and open science. However, it is difficult to untangle the role that standards specific to different journals might have to play on inclusion of data that would help make the research open and reproducible (i.e., publication of spectral data if it was used to determine presence/absence of specific elements). Regardless, performing pXRF analysis in this manner is no easy task—as described previously there are a number of barriers. Writing a detailed methods section would necessitate an archaeologist to understand what kind of calibration they're using, it would require a consistent and known sampling time, and archaeologists would have to include spectral data. However, it behooves archaeologists to engage in their research at this level. It gives some validity to the methods, is transparent for others to adapt the method, and is a direct response to gatekeepers who don't believe historical archaeologists capable of appropriately conducting this kind of research. These benefits are in addition to any statistical power or comparative work that might become possible when historical archaeologists engage in reproducible science. If an archaeologist can detail and understand their methodology to this level, it is very likely that their application is an appropriate one—they have taken care and consideration into how to answer a specific research question through XRF analysis. Anthony adds that this critical thinking aspect is crucial: "It is extremely important that if you're going to use this equipment to learn something that you have to do it in a way that others can learn from too because if you don't, it's not science it's a company's word for it."

Committing to reproducible science ensures that historical archaeologists are performing well thought out research that can be independently validated. It will help to move the field toward being more accepted by others in the scientific community and will allow archaeologists to perform research of interest to them, like some sourcing studies. Achieving a level of support from the scientific community through a renegotiation of the liminal space between the fields will allow archaeologists access to some of the power and privilege that comes with doing 'science', which may (or may not) help them gain acceptance within their own field.

There are two main ways historical archaeologists may practically begin to negotiate these bounds, both of which were identified by archaeological participants as crucially important: training and collaboration. All participants were asked what kinds of trainings they felt were necessary for archaeologists to be able to successfully use the instruments; these answers varied greatly but generally included both formal training, like workshops and those offered by manufacturers when purchasing a new instrument, and more informal training, like guidance from graduate students or other collaborators. Participants described trainings that varied as widely as their backgrounds did, and this is one obvious disadvantage; archaeologists have different academic and research experiences that might assist them, and they also have very heterogeneous applications that may necessitate different levels of training. As Michelle describes, "if you are someone who is looking specifically at different types of metal from historic sites, the calibration may already have been created for you, you don't need to know how to make one." If the training is too narrow and focused on details that aren't important to all applications, there may be a high proportion of people who decide that the training isn't right for them. This is similar to the case of Beth, who attended the first day of a two day training: "After the first day, which was the basics, I decided…this wasn't something that came naturally to me to understand, and there were other things that I wanted to put my time into and understanding." Not all trainings will be relevant to all users and some, like Beth, may find that the technique simply doesn't align with their research plans. However, good training is a hugely limiting factor in the appropriate use of pXRF in historical archaeological contexts, so determining appropriate guidelines for training such that it is as accessible to as many historical archaeologists as possible is important.

Participants identified training as being crucial to their successes with the instrument. Participants were hesitant to identify specific training plans, which is perhaps reflective of their myriad and winding training journeys. However, beyond trainings in how to physically operate the instrument safely, it seems that the most important aspect is having a one-on-one relationship with an experienced user. Some of these relationships seemed to be born from more formal institutional-level training events (e.g., Linda and Amanda), while other evolved in other ways (e.g., Michelle's long-standing institutional connections). Workshops at national conferences (or held virtually, a practice becoming more common in a post-2020 pandemic world) led by experienced users and/or manufacturers would be one way to democratize trainings and for new users to cultivate these all-important one-on-one connections with both other new users and experienced ones.

Collaborations may also assist historical archaeologists in negotiating the boundaries of archaeology and science. While collaborations were generally discussed as useful, some participants had difficulty finding funding opportunities needed to solidify such formal collaborations. Beth described her desire for a formal interdisciplinary (involving archaeologists and chemists) and multi-institutional collaboration funded by a federal grant; unfortunately, their first grant application was not funded which has meant that the project has "sort of languished since then." As with solving training problems, it is difficult to suggest specifics in making successful collaborations. One opportunity could come from more established and available training opportunities as discussed before. As with the availability of methods, finding and creation collaborations will likely become easier if more work is published and/or available; individuals can connect more easily with users with similar applications.

Collaborations are a critical opportunity for historical archaeologists. They can connect individuals who are interested in incorporating pXRF data but who don't want to engage with pXRF at such a detailed level—their collaborators will bring expertise in how to use the instrument and integrate the data successfully or they can assist with the statistical analysis necessary to interpret complex data. Likewise, the more experienced collaborators will have access to data and the creativity of questions asked by individuals who might not limit research questions based on perceived limitations of the instrument or who can expand their interdisciplinary research. Collaborations, especially with those who may already have successfully negotiated the liminal space, may be one opportunity for historical archaeologists to more successfully negotiate a space for their research with pXRF.

This field is rich for further study, including both studies using pXRF in archaeological contexts and studies using pXRF to understand larger relationships. While touched on briefly here, more research is merited on the creation of scientific knowledge and the frameworks of science. Of specific interest is the role science communication might play in complicating the creation and maintenance of interdisciplinary fields. In brief, Latour and Woolgar explain, "In other words, the fact that scientists often change the manner and content of their statements when talking to outsiders causes problems both for outsiders' reconstruction of scientific events and for an appreciation of how science is done" (1986, 28). There may be relationships between explanations of pXRF and its possible applications by scientists and manufacturing representatives and the work that archaeologists understand to be possible and appropriate. Themes explored through the scoping analysis would also benefit further research. The physical location where pXRF data is collected varies, with more papers performing analysis in laboratory settings rather than *in situ*. This finding was somewhat surprising, although a similar trend was also observed from participant data, given that one of the main stated benefits of pXRF is the portable aspect of it. One possible theory is that portable instruments, in part due to their compact nature and their main markets, are more accessible (both from a cost and training standpoint) to archaeologists. Further research on why certain research settings are used and how different research settings influence the types of archaeological questions asked and how well they are able to be answered is needed. These are just two possible avenues for further study, but there are many more rich topics to study both in understanding the current state of the field and with the intention to expand or further legitimate the field.

This thesis set out to explore questions, reiterated at the beginning of this chapter, surrounding the use of portable x-ray fluorescence spectrometry in historical archaeology through an examination of the historic relationship between archaeology and science, a detailed explanation of how pXRF works, interviews with eight historical archaeologists and two representatives of manufacturers experienced with pXRF, and a scoping review. This data suggests that the disparity in work being done in historical archaeology in comparison to other fields of archaeology is ascribable to a number of factors, including a sense that elemental composition analysis is not as necessary to this field as it is to others and that appropriate methodologies do not already exist to ease future research. However, based on information provided by participants, the climate of the current field as described by Frahm and Speakman and Shackley, and the historic relationship between science and archaeology, there are systemic factors related to the negotiable but defined borders of what is considered science that impact the ability for historical archaeologists to successfully engage in and publish research with pXRF (Frahm 2013a; Frahm 2013b; Speakman and Shackley 2013). There are certainly missed opportunities, like the possibility of some types of sourcing studies referenced by various participants, that might be attainable should these boundaries be negotiated more successfully. However, this is not to suggest that these boundaries are not being negotiated on a small scale; participants described varied, interesting, and successful research. However, with reference to the second guiding question of the thesis, understanding what is or is not considered 'appropriate' use complicates how the research currently being conducted by historical archaeologists with pXRF is received and disseminated. Here again, the influence of the science's privileged position and the complex history negotiating the boundaries between archaeology and science creates complexity in understanding what is or is not appropriate. Participants indicated their belief that pXRF is currently a useful tool with limitations, but that it is likely to be, with further research, appropriate to use in more historical contexts to answer interesting and novel archaeological questions. However, this is in some conflict with the small amount of currently published literature as seen in the scoping review and the climate of the field both as described in the literature and relayed by participants. Determining 'appropriateness' once again will depend on negotiation and renegotiations of the boundaries between archaeologists, particularly in historical archaeology, and scientists. In reference to the third guiding question, the case of pXRF as indicated throughout this thesis is a microcosm that shows the nuances and difficulties of operating at the junction of archaeological and scientific frameworks. The liminal space occupied by the research and those doing it is governed by changing definitions of science and scientific work and is informed by the challenging past relationship between archaeology and science.

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Appendix A: Institutional Review Board Certified Exempt Letter

University of Idaho
Office of Research Assurances
Institutional Review Board
875 Perimeter Drive, MS 3010
Moscow, ID 83844-3010
Phone: 208-885-6162
Fax: 208-885-6014
Email: irb@uidaho.edu

December 10, 2020

To: Mark Steven Warner

Cc: Emma Altman

From: University of Idaho Institutional Review Board

Approval Date: December 10, 2020

Title: Understanding the Liminal Space between Science and Archaeology: Utilization of pXRF in Historical Archaeology

Protocol: 20-171, Reference: 011371

Exempt under Category 2 at 45 CFR 46.104(d)(2).

On behalf of the Institutional Review Board at the University of Idaho, I am pleased to inform you that the protocol for this research project has been certified as exempt under the category listed above.

This certification is valid only for the study protocol as it was submitted. Studies certified as Exempt are not subject to continuing review and this certification does not expire. However, if changes are made to the study protocol, you must submit the changes through VERAS for review before implementing the changes. Amendments may include but are not limited to, changes in study population, study personnel, study instruments, consent documents, recruitment materials, sites of research, etc.

As Principal Investigator, you are responsible for ensuring compliance with all applicable FERPA regulations, University of Idaho policies, state and federal regulations. Every effort should be made to ensure that the project is conducted in a manner consistent with the three fundamental principles identified in the Belmont Report: respect for persons; beneficence; and justice. The Principal Investigator is responsible for ensuring that all study personnel have completed the online human subjects training requirement. Please complete the *Continuing Review and Closure Form* in VERAS when the project is completed.

You are required to notify the IRB in a timely manner if any unanticipated or adverse events occur during the study, if you experience an increased risk to the participants, or if you have participants withdraw or register complaints about the study.

IRB Exempt Category (Categories) for this submission:
Category 2: Research that only includes interactions involving educational tests (cognitive, diagnostic, aptitude, achievement), survey procedures, interview procedures, or observation of public behavior (including visual or auditory recording) if at least one of the following criteria is met: i. The information

University of Idaho
Office of Research Assurances
Institutional Review Board
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Moscow, ID 83844-3010
Phone: 208-885-6162
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obtained is recorded by the investigator in such a manner that the identity of the human subjects cannot readily be ascertained, directly or through identifiers linked to the subjects; ii. Any disclosure of the human subjects' responses outside the research would not reasonably place the subjects at risk of criminal or civil liability or be damaging to the subjects' financial standing, employability, educational advancement, or reputation; or iii. The information obtained is recorded by the investigator in such a manner that the identity of the human subjects can readily be ascertained, directly or through identifiers linked to the subjects, and an IRB conducts a limited IRB review to make the determination required by .111(a)(7).

Appendix B: Participant Recruitment Materials

Recruitment Email to Historical Archaeology Listserv

Subject: pXRF in Historical Archaeology: Recruiting Interviewees

Hi-

My name is Emma Altman, and I'm currently an anthropology master's student at the University of Idaho. My research is focused on defining the appropriateness of the use of pXRF in historical archaeology. I'm currently seeking individuals (both archaeologists and natural scientists) who have first-hand experience using pXRF to participate in a 45-60 minute Zoom interview (with possible follow up interview upon mutual agreement) discussing their experiences and attitudes using pXRF in historical archaeology. Please reach out to me if you have any questions and/or are interested in participating in this research, and feel free to forward this request to any colleagues you have that might be interested in participating.

Thank you so much for your time-

Emma Altman

M.A. Candidate Anthropology

University of Idaho

ealtman@uidaho.edu

Contact Form Example for Recruitment of Manufacturing Representatives

Hi- I'm currently an anthropology master's student at the University of Idaho. My thesis research is focused on the appropriateness of the use of pXRF in historical archaeology and I'm interested in speaking with representatives of manufacturers of pXRF. I'm hoping to interview representatives who have had direct contact with archaeologists who use pXRF for 45-60 minutes via Zoom. If such an interaction is not possible, I would appreciate any sales or technical materials you might give an archaeologist interested in purchasing a pXRF instruments. Thank you so much for your time and please feel free to reach out with any questions.

Blog Post on American Cultural Resources Association ACRAsphere

Title: pXRF in CRM: Research Literature Request

ACRA Community-

The use of scientific techniques like portable X-ray fluorescence spectroscopy (pXRF) is becoming more common in historical archaeology. Research focusing on how and why archaeologists use these techniques is important to ensuring the future effective and appropriate use of them. I'm currently an anthropology master's student at the University of Idaho (under the advisement of Mark Warner), and my thesis research is focused on the appropriateness of the use of pXRF in historical archaeology.

As part of this research, I'm interested in looking at grey literature (site reports and other documents) for historic sites that include the use of pXRF so I might understand the contexts that pXRF is currently being used in. Any shared materials would not be reproduced in the thesis; all data would be analyzed in non-identifiable aggregate. In the unlikely scenario that I would like to include specific details, I will directly request permission from your firm.

If you or your firm have any documents or reports that you would be willing to share with me for this research project, please contact me at ealtman@uidaho.edu.

Best,

Emma Altman

ACRA Student Member

Appendix C: Interview Guide Archaeologists

Introductory

- What is your name, gender, job title, and institution you work for?
    - How many years have you been working in your field of study?
    - How do you identify yourself in terms of your discipline?

Context of pXRF in their research

- Please tell me a little about your experience and/or knowledge of pXRF
    - Tell me how you have used pXRF in your own research
        - Could you describe the context of that research a bit for me?
        - Could you tell me about the actual instrument you used?
        - How do you prepare objects for study?
        - How do you analyze the data?
        - Why did you decide to use pXRF in this context?
        - What other kinds of data did you use in conjunction with pXRF?
        - How did the results of your pXRF study help you complete the picture you were seeing with the rest of your data?
        - Overall, could you please characterize your experience with pXRF?

Attitudes towards pXRF

- What do you see as the benefits and drawbacks of pXRF?
- How do you feel when you read papers/site reports/other materials or publications where others use pXRF?
- What is your general sense of the archaeological community's attitudes towards pXRF?
    - How, or in what ways, do you agree or disagree with these attitudes?
- What is your general sense of the scientific community's attitudes towards archaeologist's use of pXRF?
- When might you suggest students/colleagues/others use pXRF? Have you ever done so? How was it?

Training in pXRF

- Could you describe how you were trained to use a pXRF?
    - How sufficient did you feel your own training to be to use the pXRF instrument successfully?
- What do you feel is necessary for an archaeologist to successfully use pXRF in terms of training in use of the instrument or analysis of data?
    - How do you think archaeologists should receive this training (field school, graduate/undergraduate coursework, on-the-job training)?

Future of pXRF in archaeology

- What do you feel is the most appropriate way to utilize pXRF in historical archaeology? What are your beliefs about its current level of use?
- Could you describe how you see the future of pXRF in historical archaeological research?
- In ten years, how do you think that pXRF will be used? Can you imagine it will be used more or less than it is being currently?

Other than the questions I asked, is there any additional information that you think might be useful to me as I continue this research?

Appendix D: Interview Guide Manufacturing Representative

Introductory

- What is your name, job title, and institution you work for?
    - How many years have you been working in your field of study?
    - How do you identify yourself in terms of your discipline?
- Please tell me a little about your experience and/or knowledge of pXRF.

Information about sales of pXRF

- Could you tell me about your role in [insert company name] as it relates to pXRF?
- Can you tell me about the breakdown of your customers? Are they mostly archaeologists or mostly 'scientists'?
- Could you discuss the ways that these types of customers are different in terms of what they ask you or what you tell them about the instrument?

Attitudes towards pXRF in archaeology

- Could you describe what interaction you've had (if any) with archaeologists, specifically historical archaeologists, using pXRF?
- Have you read any literature or publications where archaeologists use pXRF?
    - What are the thoughts and/or feelings that come to mind when you read these publications?
- What is your general sense of the attitudes of pXRF manufacturers towards pXRF being used in historical archaeology or fields that might not be seen as science?
    - How, or in what ways, do you agree or disagree with these attitudes?
- When might you suggest archaeologists use pXRF? Have you ever done so? How was it?

Training in pXRF

- What do you feel is necessary for an archaeologist to successfully use pXRF in terms of training in use of the instrument or analysis of data?
    - How do you think archaeologists should receive this training (field school, graduate/undergraduate coursework, on-the-job training)?

Future of pXRF in archaeology

- What do you feel is the most appropriate way to utilize pXRF in historical archaeology? What are your beliefs about its current level of use?
- Could you describe how you see the future of pXRF in historical archaeological research?

Other than the questions I asked, is there any additional information that you think might be useful to me as I continue this research?

Appendix E: Initial Participant Consent Form

Understanding the Liminal Space between Science and Archaeology: Utilization of Portable X-ray Fluorescence (pXRF) in Historical Archaeology
Informed Consent for Interviews

Emma Altman and Dr. Mark Warner, from the Department of Sociology and Anthropology at the University of Idaho are conducting a research study. The purpose of the research is to understand appropriate uses of pXRF in historical archaeology and how these uses inform our understanding of the liminal space between science and archaeology. You are being asked to participate in this study because you are a scientist or archaeologist that is familiar with pXRF or you are a representative of a company that sells pXRF instruments.

Your participation will involve a recorded Zoom interview. The interview should take about 45-60 minutes to complete. Upon mutual agreement with the research team, a follow-up interview may take place. The interview includes questions about your experience with pXRF, your thoughts on historical archaeologists' using pXRF, and what you foresee as the future of pXRF research in historical archaeology. Your involvement in the study is voluntary, and you may choose not to participate. You can refuse to answer any of the questions at any time. There are no known risks in this study, but some individuals may experience discomfort or loss of privacy when answering questions. The interview will be recorded in Zoom and subsequently transcribed using Zoom's audio transcription feature in conjunction with manual transcription. Zoom's terms of service can be found at https://zoom.us/terms and its privacy statement can be found at https://zoom.us/privacy. Transcripts of interviews will be provided to you with a two- week window for approval or requests for revision. Data, only accessible to Dr. Warner and Ms. Altman, will be located in a University- approved cloud server. All identifying information will be carefully screened and removed from any publications, and you will only be referred to by a non-identifying pseudonym.

The findings from this project will provide information on appropriate uses of pXRF in historical archaeology, including possible suggestions for appropriate training, and will help illuminate the liminal space between the fields of science and archaeology. If published, results will be presented in summary form only.

If you have any questions about this research project, please feel free to contact Emma Altman at ealtman@uidaho.edu or Dr. Mark Warner at (208) 885-5954 or mwarner@uidaho.edu. If you have questions regarding your rights as a research subject, or about what you should do in case of any harm to you, or if you want to obtain information or offer input you may call the Office of Research Assurances at (208) 885-6340 or irb@uidaho.edu.

By printing this form, signing below, taking a photograph/scanning the document, and returning it via email to Emma Altman, you certify that you are at least 18 years of age and agree to participate in the above described research study.

______________________	______________________________	____________
Name of Adult Participant	Signature of Adult Participant	Date
______________________	______________________________	____________
Name of Research Team Member	Signature of Research Team Member	Date

Appendix F: Participant Transcript Approval Form

Understanding the Liminal Space between Science and Archaeology: Utilization of Portable X-ray Fluorescence (pXRF) in Historical Archaeology
Final Consent Form

This form gives Emma Altman and Dr. Mark Warner final authorization to use material from your interview. A draft of these materials has been presented to you for your review, correction, or modification for a period of two weeks (provided on ___/___/___, to be returned by __/__/__). You may grant rights for this draft as is, or with the modifications you specify, if any.

I, ____________________________, hereby grant the right to use information from recordings and/or notes taken in interview of me, to Emma Altman and Dr. Mark Warner. I understand that the identities and any identifying information for respondents will remain confidential. All files and associated data will be located in a University- approved cloud server. All identifying information will be carefully screened and removed from any publications, and you will be referred to by a non-identifying pseudonym.

If you have any questions about this research project, please feel free to contact Emma Altman at ealtman@uidaho.edu or Dr. Mark Warner at (208) 885-5954 or at mwarner@uidaho.edu. If you have questions regarding your rights as a research subject, or about what you should do in case of any harm to you, or if you want to obtain information or offer input you may call the Office of Research Assurances at (208) 885-6340 or irb@uidaho.edu.

By printing this form, signing below, taking a photograph/scanning the document, and returning it via email to Emma Altman, you agree to allow the use of the data contained in the transcript provided to the research team

_____ with no changes

_____ with the corrections/modifications attached to this form

____________________	____________________________	__________
Name of Adult Participant	Signature of Adult Participant	Date
____________________	____________________________	__________
Name of Research Team Member	Signature of Research Team Member	Date

Appendix G: Scoping Review Table

Table A1 Data extracted during scoping review and analyzed in Chapter 6.

Short Title	Year	Journal Abbr[a]	Site Continent	Analysis location	Time Period	Material Category	Manufacturer	Analysis[b]	Use filter?[c]	Describe filter?[c]	Use calibration?[c]	Describe calibration?[c]	Show spectra?
"Not All That Is White Is Lime"	2019	Arch	Europe	in situ (museum)	20th c CE	geologic	Ametek	P/A	ND	ND	ND	ND	No
"St. Joseph with the Child" by Gian Lorenzo Bernini	2020	JCH	Europe	in situ (museum)	1663	paint/ink	homemade	P/A	ND	ND	ND	ND	No
20th century artists' oil paints	2014	JCH	Europe	lab	1960s	paint/ink	Bruker	P/A	ND	ND	ND	ND	Yes
A Box Containing Carpenter's Accessories from The Akko 1 Shipwreck, Israel	2016	Arch	Asia	lab	19th c CE	metal	Thermo Scientific	Q	ND	ND	ND	ND	No
A comparative study of two icons representing the "Coronation of the Virgin by the Holy Trinity"	2017	JCH	Europe	in situ	18th - 19th c CE	paint/ink	Oxford	P/A	ND	ND	ND	ND	Yes (Supp)

Short Title	Year	Journal Abbr[a]	Site Continent	Analysis location	Time Period	Material Category	Manufacturer	Analysis[b]	Use filter?[c]	Describe filter?[c]	Use calibration?[c]	Describe calibration?[c]	Show spectra?
A cost surface model of volcanic glass quarrying and exchange in Hawai'i	2011	JAS	North America	lab	14th-19th c CE	geologic	Bruker	Q	Yes	Yes	Yes	Yes	No
A polychrome Mukozuke (1624-1644) porcelain offers a new hypothesis on the introduction of European enameling technology in Japan	2018	JCH	Asia	ND	1624-1644	ceramic	homemade	S	Yes	Yes	ND	ND	Yes
Analysis of lapideus materials from the columns of the cathedral of St Maria in Randazzo (Catania, Italy) and from their ancient origin quarries	2001	JCH	Europe	in situ	13th-19th c CE	geologic	homemade	Q	ND	ND	Yes	No	No
Archaeometric study of 17th/18th century painted pottery from the Belgrade Fortress	2018	JCH	Europe	lab	17th-18th c CE	ceramic	homemade	Q and P/A	ND	ND	Yes	Yes	Yes

Short Title	Year	Journal Abbr[a]	Site Continent	Analysis location	Time Period	Material Category	Manufacturer	Analysis[b]	Use filter?[c]	Describe filter?[c]	Use calibration?[c]	Describe calibration?[c]	Show spectra?
Assessing the Diversity of Mission Populations through the Comparison of Native American Residences at Mission Santa Clara de Asís	2014	IJHA	North America	ND	18th-19th c CE	geologic	Bruker	ND	ND	ND	ND	ND	No
Changes in the body, glaze and enamel compositions of early Meissen porcelain, 1723-c.1740	2020	Arch	Europe	lab	18th c CE	ceramic	Bruker	S	ND	ND	ND	ND	Yes (non-portable)
Characterization Of Archaeological And In Situ Scottish Window Glass	2013	Arch	Europe	both	12th-20th c CE	glass	Thermo Scientific	Q	ND	ND	Yes	Yes	Yes
Characterization of the artist's palette from the polychrome decorations of the El Bahia Palace doors (Marrakesh, Morocco)	2018	JCH	Africa	lab	19th c CE	paint/ink	Bruker	P/A	ND	ND	ND	ND	No

Short Title	Year	Journal Abbr[a]	Site Continent	Analysis location	Time Period	Material Category	Manufacturer	Analysis[b]	Use filter?[c]	Describe filter?[c]	Use calibration?[c]	Describe calibration?[c]	Show spectra?
Coade, Blashfield or Doulton? The in situ identification of ceramic garden statuary and ornament from three eighteenth and nineteenth century manufacturers	2016	JCH	Europe	in situ	18th-19th c CE	ceramic	Thermo Scientific	S	Yes	Yes	Yes	Yes	No
Determining the Provenance of Cayo Pottery from Grenada, Lesser Antilles, Using Portable X-Ray Fluorescence Spectrometry	2018	Arch	North America	lab and in situ (private collection)	13th-17th c CE	ceramic	Bruker	S	No	No	No	No	No
Disclosing glittering and sparkling effects in 20th-century reverse glass paintings	2020	JCH	Europe	in situ (museum)	1912-1954	metal	Bruker	S	ND	ND	ND	ND	Yes

Short Title	Year	Journal Abbr[a]	Site Continent	Analysis location	Time Period	Material Category	Manufacturer	Analysis[b]	Use filter?[c]	Describe filter?[c]	Use calibration?[c]	Describe calibration?[c]	Show spectra?
Does Carneiro's circumscription theory help us understand Maori history?	2014	JAS	Oceania	lab	15th-19th c CE	geologic	Bruker	Q	Yes	Yes	Yes	Yes	No
Early Production Recipes For Lead Antimonate Yellow In Italian Art	2005	Arch	Europe	in situ (museum)	14th-16th c CE	paint/ink	Tracor	P/A	ND	ND	ND	ND	No
EDXRF analysis of blue pigments used in Valencian ceramics from the 14th century to modern times	2006	JCH	Europe/Asia	lab	14th-20th c CE	ceramic	homemade	S	ND	ND	ND	ND	Yes
Enlightening the use of materials and techniques in earthen architecture in southeast Brazil during the first coffee cycle (19th century)	2018	JCH	South America	lab	19th c CE	geologic	Bruker	Q	ND	ND	Yes	Yes	No
Export Chinese blue-and-white porcelain	2017	JAS	Asia	lab	16th-17th c CE	ceramic	Thermo Scientific	Q and S	Yes	Yes	Yes	Yes	No

Short Title	Year	Journal Abbr[a]	Site Continent	Analysis location	Time Period	Material Category	Manufacturer	Analysis[b]	Use filter?[c]	Describe filter?[c]	Use calibration?[c]	Describe calibration?[c]	Show spectra?
First insights into Chinese reverse glass paintings gained by non-invasive spectroscopic analysis	2019	AAS	Asia	in situ (museum)	19th-20th c CE	paint/ink	Bruker	P/A	ND	ND	ND	ND	No
From Landscapes of Meaning to Landscapes of Signification in the American Southwest	2017	AA	North America	lab	14th-17th c CE	geologic	Bruker & Thermo Scientific	Q	ND	ND	Yes	Yes	Yes
Heavy Metals in Archaeological Soils: The Application of Portable X-Ray Fluorescence (pXRF) Spectroscopy for Assessing Risk to Human Health at Industrial Sites	2021	AAP	South America	in situ	17^{th} c CE	geologic	Olympus	S	Yes	Yes	Yes	Yes	No

Short Title	Year	Journal Abbr[a]	Site Continent	Analysis location	Time Period	Material Category	Manufacturer	Analysis[b]	Use filter?[c]	Describe filter?[c]	Use calibration?[c]	Describe calibration?[c]	Show spectra?
How do you say "Bocour" in French? The work of Carmen Herrera and acrylic paints in post-war Europe	2019	JCH	Europe	lab	1948-1952	paint/ink	Bruker	P/A	ND	ND	ND	ND	No
How traces of pollutants in the environment modify bioremediation efficiency performed with Desulfovibrio vulgaris, and the advantage of an optimization protocol using soft chemicals	2018	JCH	Europe	in situ (museum)	17th-18th c CE	geologic	Thermo Scientific	Q	ND	ND	Yes	No	No
Identification of iron-gall inks in historical drawings by Fibre Optics Reflection Spectroscopy	2017	JCH	Europe	lab	16th-19th c CE	paint/ink	Skyray	P/A	ND	ND	ND	ND	No

Short Title	Year	Journal Abbr[a]	Site Continent	Analysis location	Time Period	Material Category	Manufacturer	Analysis[b]	Use filter?[c]	Describe filter?[c]	Use calibration?[c]	Describe calibration?[c]	Show spectra?
Identifying American native and European smelted coppers with pXRF	2015	JAS	North America	lab	17th-18th c CE	metal	InnovX	Q	Yes	Yes	Yes	Yes	Yes
Investigation of a naturally patinated bronze artifact originating from the outdoor statuary group of Mathias Rex	2014	JCH	Europe	lab	1902	metal	InnovX	Q	ND	ND	ND	ND	No
Iron artefacts from the Akko Tower Wreck, Israel, and their contribution to the ship's characterization	2017	AAS	Asia	lab	19th c CE	metal	Thermo Scientific & Oxford	Q	ND	ND	Yes (Oxford)	Yes (Oxford)	No
Japanese or Chinese? Non-invasive analysis of East Asian blue-and-white porcelain	2019	AAS	Asia	lab	16th-20th c CE	ceramic	Thermo Scientific	Q	ND	ND	ND	ND	No

Short Title	Year	Journal Abbr[a]	Site Continent	Analysis location	Time Period	Material Category	Manufacturer	Analysis[b]	Use filter?[c]	Describe filter?[c]	Use calibration?[c]	Describe calibration?[c]	Show spectra?
Multi-analytic characterization of colorants in two impressions of an Utagawa Toyoharu perspective print	2020	JCH	Asia	lab	18th-19th c CE	paint/ink	Bruker	S	ND	ND	ND	ND	Yes
Multi-analytical investigation of panel, pigments and varnish of The Martyirdom of St. Catherine by Gaudenzio Ferrari (16th century)	2020	JCH	Europe	in situ	15th-16th c CE	paint/ink	Assing	S	ND	ND	ND	ND	No
New insights regarding the Akko 1 shipwreck	2010	JAS	Asia	lab	19th c CE	metal	Thermo Scientific	Q	ND	ND	ND	ND	No
Nineteenth Century Gunflints from the Nepalese Armory	2019	IJHA	Asia	lab	19th c CE	geologic	ND	Q	ND	ND	ND	ND	No

Short Title	Year	Journal Abbr[a]	Site Continent	Analysis location	Time Period	Material Category	Manufacturer	Analysis[b]	Use filter?[c]	Describe filter?[c]	Use calibration?[c]	Describe calibration?[c]	Show spectra?
Non-destructive characterization of Della Robbia sculptures at the Bargello museum in Florence by the combined use of PIXE and XRF portable systems	2004	JCH	Europe	in situ (museum)	15th-16th c CE	ceramic	homemade	Q	ND	ND	Yes	Yes	Yes
Non-invasive spectroscopic methods for the identification of drawing materials used in XVIII century	2020	JCH	Europe	in situ (museum)	18th c CE	paint/ink	homemade	S	ND	ND	ND	ND	Yes
On the blue and green pigments of post-Byzantine Greek icons	2020	Arch	Europe	lab	15th-19th c CE	paint/ink	homemade	P/A	ND	ND	ND	ND	No
On the Metal-Leaf Decorations of Post-Byzantine Greek Icons	2018	Arch	Europe	in situ (museum)	15th-19th c CE	metal	homemade	P/A	ND	ND	ND	ND	Yes

Short Title	Year	Journal Abbr[a]	Site Continent	Analysis location	Time Period	Material Category	Manufacturer	Analysis[b]	Use filter?[c]	Describe filter?[c]	Use calibration?[c]	Describe calibration?[c]	Show spectra?
Parameters in the use of pXRF for archaeological site prospection	2013	JAS	North America	depends	18th c CE	geologic	Thermo Scientific	Q	Yes	Yes	Yes	Yes	No
Physico-chemical characterization and conservation issues of photographs dated between 1890 and 1910	2008	JCH	Europe	lab	1890-1910	paint/ink	EIS	S	ND	ND	ND	ND	No
Physico-Chemical Characterization of Pigments and Binders of Murals in a Church in Ethiopia	2016	Arch	Africa	in situ	17th c CE	paint/ink	Thermo Scientific	S	ND	ND	Yes	Yes	Yes (Supp)
PIXE, ED-XRF and optical analysis to authenticate the Garvăn gold monetary treasury	2020	Arch	Europe	lab	19th c CE	metal	Bruker	Q	ND	ND	ND	ND	No
Pre-Industrial Iron Smelting and Silver Extraction in North-Eastern Greece	2016	Arch	Europe	lab	4th-19th c CE	geologic	Thermo Scientific	Q	ND	ND	Yes	Yes	No

Short Title	Year	Journal Abbr[a]	Site Continent	Analysis location	Time Period	Material Category	Manufacturer	Analysis[b]	Use filter?[c]	Describe filter?[c]	Use calibration?[c]	Describe calibration?[c]	Show spectra?
Provenancing Central African copper croisettes	2019	JAS	Africa	lab	9th-18th c CE	metal	Bruker	P/A	ND	ND	ND	ND	No
Seal the deal	2020	JAS	Europe	lab	13th-17th c CE	metal	Thermo Scientific	Q	ND	ND	Yes	Yes	No
Spanish Colonial Networks of Production	2019	IJHA	South America	in situ	18th-19th c CE	ceramic	Thermo Scientific	Q	ND	ND	Yes	Yes	No
Stratigraphic EM-EDS, XRF, Raman and FT-IR analysis of multilayer paintings from the Main Altar of the St. James Church in Levoča (Slovakia)	2018	JCH	Europe	in situ	early 16th c CE	paint/ink	Oxford	ND	ND	ND	ND	ND	No
Strontium, a new marker of the origin of gypsum in cultural heritage?	2014	JCH	Europe/Africa	depends	7th c BC - 17th c CE	paint/ink	Assing	S	ND	ND	Yes	Yes	Yes

Short Title	Year	Journal Abbr[a]	Site Continent	Analysis location	Time Period	Material Category	Manufacturer	Analysis[b]	Use filter?[c]	Describe filter?[c]	Use calibration?[c]	Describe calibration?[c]	Show spectra?
Testing the accuracy of portable X-ray fluorescence to study Aztec and Colonial obsidian supply at Xaltocan, Mexico	2011	JAS	North America	lab	**10th-17th c CE**	geologic	InnovX	Q	ND	ND	Yes	Yes	No
The Chronology of Insiza Cluster Khami-Phase Sites in South-Western Zimbabwe	2019	Arch	Africa	lab	15th-19th c CE	glass	Thermo Scientific	S	ND	ND	Yes	Yes	No
The Dor C shipwreck, Israel	2017	AAS	Asia	lab	19th c CE	metal	Oxford & Thermo Scientific	Q	ND	ND	ND	ND	No
The Origin of overglaze-blue enameling in Japan	2019	JCH	Asia	lab	17th-18th c CE	ceramic	homemade	S	No	No	ND	ND	Yes
The Production, Distribution and Consumption of Metals and Alloys at Great Zimbabwe	2016	Arch	Africa	lab	9th-19th c CE	metal	Thermo Scientific	Q	ND	ND	ND	ND	No

Short Title	Year	Journal Abbr[a]	Site Continent	Analysis location	Time Period	Material Category	Manufacturer	Analysis[b]	Use filter?[c]	Describe filter?[c]	Use calibration?[c]	Describe calibration?[c]	Show spectra?
The Reliquary Bust of Saint Lambert from the Liège Cathedral, Belgium	2020	Arch	Europe	in situ (museum)	1512	metal	Thermo Scientific	Q	Yes	Yes	Yes	Yes	No
The Twentieth Century Invention of Ancient Mountains	2021	IJHA	Europe	in situ	15th-19th c CE	geologic	ND	S	ND	ND	ND	ND	No
The wall paintings in the former Refectory of the Trinità dei Monti convent in Rome	2004	JCH	Europe	in situ	17th-18th c CE	paint/ink	homemade	S	ND	ND	ND	ND	No
Toward a fast non-destructive identification of pottery	2015	JCH	Asia	lab	14-16th c CE	ceramic	Bruker	S	ND	ND	ND	ND	Yes
Unveiling the art of René Lalique with XRF and Raman spectroscopy	2018	JCH	Europe	in situ (museum)	20th c CE	metal	homemade	Q	ND	ND	Yes	Yes	No
Violon. Céret by Pablo Picasso	2019	JCH	Europe	in situ (private collection)	20th c CE	paint/ink	Bruker	P/A	ND	ND	ND	ND	No

Short Title	Year	Journal Abbr[a]	Site Continent	Analysis location	Time Period	Material Category	Manufacturer	Analysis[b]	Use filter?[c]	Describe filter?[c]	Use calibration?[c]	Describe calibration?[c]	Show spectra?
XRF Characterization Of 18th Century Piedmontese Porcelains From The Palazzo Madama Museum (Torino, Italy)	2016	Arch	Europe	in situ (museum)	18th-19th c CE	ceramic	Thermo Scientific	Q	Yes	Yes	Yes	Yes	No

[a] Journal abbreviations used are as follows, with parenthetical giving abbreviation: Advances in Archaeological Practice (AAP), American Antiquity (AA), Archaeological and Anthropological Sciences (AAS), Archaeometry (Arch), International Journal of Historical Archaeology (IJHA), Journal of Archaeological Science (JAS), Journal of Cultural Heritage (JCH).
[b] Levels of analysis are abbreviated as follows, with parenthetical giving abbreviation: quantitative (Q), semi-quantitative (S), presence/absence (P/A).
[c] No data is abbreviated "ND", specifying there was insufficient data in the paper to definitively indicate whether a filter or calibration was used or described. Values of "Yes" or "No" indicate that there was sufficient data to determine these parameters.

Appendix H: Scoping Review Bibliography

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