Ten seconds in the field: rapid Armenian obsidian sourcing with portable XRF to inform excavations and surveys

Ellery Frahm a, *, Beverly A. Schmidt b, Boris Gasparyan c, Benik Yeritsyan c, Sergei Karapetian d, Khachatur Meliksetian d, Daniel S. Adler b

a Department of Archaeology, The University of Sheffield, Northgate House, West Street, Sheffield S1 4ET, United Kingdom
b Department of Anthropology, Old World Archaeology Program, University of Connecticut, 354 Mansfield Road, Unit 1176, Storrs, CT 06269, United States
c Institute of Archaeology and Ethnography, National Academy of Sciences, 15 Charents Street, Yerevan, Armenia
d Institute of Geological Sciences, National Academy of Sciences, 24 Baghramian Avenue, Yerevan, Armenia

ARTICLE INFO

Article history:
Received 19 May 2013
Received in revised form
30 July 2013
Accepted 12 August 2013

Keywords:
Obsidian
pXRF
Field methods
Armenia
South Caucasus
Palaeolithic archaeology

ABSTRACT

Armenia has one of the most obsidian-rich natural and cultural landscapes in the world, and the lithic assemblages of numerous Palaeolithic sites are predominantly, if not entirely, composed of obsidian. Recent excavations at the Middle Palaeolithic cave of Lusakert 1 recovered, on average, 470 obsidian artifacts daily. After sourcing more than 1700 artifacts using portable XRF (pXRF) in our field house, our team sought to shift pXRF-based obsidian sourcing into the field itself, believing that the geological origins of artifacts would be useful information to have on-site during an excavation or survey. Despite increasing use of portable instruments, previous studies have principally focused on collections in museums and other archives, and as a result, obsidian sourcing has remained embedded in post-excavation studies. One critical factor in the uptake of obsidian sourcing in the field is the time needed to measure each artifact, frequently 2–6 min in previous studies. Here we report our two methods of obsidian sourcing, including source matching done automatically by the pXRF instrument’s onboard software, in only 10 s. Our tests with Armenian geological specimens and Palaeolithic artifacts demonstrate the high efficacy of our two methods, which are sufficiently fast to become syncopated with our excavation and survey activities. By reducing measurement times from a mode of 300 s in recent studies to just 10 s, here we show how (and why) to shift pXRF-based obsidian sourcing from the context of “white lab coats” to that of “muddy boots.”

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Although smaller than Belgium or the state of Maryland, Armenia has more than a dozen obsidian-bearing volcanic centers, resulting in one of the most obsidian-rich natural and cultural landscapes in the world. At numerous Palaeolithic sites, obsidian comprises the majority, if not the entirety, of the lithic assemblage. This is the case at two sites recently excavated by the Hrazdan Gorge Palaeolithic Project (Adler et al., 2012): Nor Geghi 1, an open-air Lower Palaeolithic site, and Lusakert 1, a Middle Palaeolithic cave site (Fig. 1). Their lithic assemblages are more than 99% obsidian. At Lusakert 1, in particular, after four excavation seasons (2008–2011), 13,970 obsidian artifacts have been recovered (excluding 5970 fragments smaller than 25 mm) from 11.9 m³ of sediment. That is, 1174 obsidian artifacts were recovered per cubic meter. On average, 470 obsidian artifacts were excavated daily with spatial data recorded by two Leica total stations.

In 2011, the project began a new program of obsidian studies, including artifact sourcing as well as source surveys and characterization. During the 2012 season, we analyzed over 1700 artifacts in our field house using portable X-ray fluorescence (pXRF). We established that the Nor Geghi 1 and Lusakert 1 assemblages were both approximately 93% obsidian from Gutansar (sometimes spelled as Gutanasar), the nearest volcanic center with abundant obsidian resources. The remainder came from numerous sources throughout Armenia, including Hatis, Pokr and Mets Arteni, Pokr Sevkar, Geghasar, and the Tsakhkunyats sources. Publications on these findings, included detailed source and spatial data, are currently in preparation. The focus of this paper is a methodological development that arose out of our work, specifically a desire to have obsidian source information available on-site. The methods we document here will be deployed in future seasons, becoming a...
routine component of our excavation toolkit and constituting a key strategy in our approach to site surveys and assessments.

As hundreds of artifacts were sourced in our field house during the 2012 season and the results compared to the spatial data, it became clear to us (for reasons discussed in Section 2) that an artifact’s geological origin would be useful information to have on-site during an excavation or survey. Our tests of visual classification yielded little success. Gutansar obsidian is highly variable in appearance, and as Table 1 shows, any “exotic” artifacts from other sources were overlooked and grouped into types with Gutansar artifacts. Thus, we began our efforts to develop methods for shifting pXRF from our field house into the field itself. As discussed in Section 2.4, pXRF-based obsidian sourcing has hitherto been largely conducted in laboratories, museums, and field houses. Although our colleagues are using dust- and waterproof instruments with 10-h batteries, obsidian sourcing remains embedded in post-excavation studies and is rarely, if ever, done in the field.

A critical factor in the uptake of obsidian sourcing in the field is the time needed for each measurement. In recent pXRF-based obsidian studies (Table 2), analyses took 2–6 min. The most common duration is 5 min, corresponding to 12 artifacts per hour. Our excavations at Lusakert 1 yielded, on average, 70–80 artifacts per hour. Although this suggests a need for 45-s measurements, we aimed for 10 s so that these analyses could become syncopated with the excavation activities. Additionally, we deemed it was insufficient simply to conduct a measurement in that time. After 10 s, we wanted the instrument’s built-in LCD to display an artifact’s source so excavators and surveyors could instantly know the result.

Reducing measurements from a mode of 300 s to just 10 s and having the instrument’s onboard software automatically do the data analysis is bound to raise challenging assumptions about the validity and reliability of our approach. We show that the technological capability to source obsidian artifacts rapidly on-site exists, but the methods to do so effectively were previously undeveloped. Our tests with Armenian geological specimens and Palaeolithic artifacts demonstrate the high efficacy of the two methods we report here.

2. Rationale for field-based sourcing

Obsidian artifact sourcing conducted rapidly on-site can transform the ways in which our discipline approaches subjects involving raw-material procurement, transport, and use as well as the organization of space and the identification of activity areas.
artifacts from other obsidian sources were overlooked and grouped into types with a number of Gutansar artifacts. As a result, we deemed visual sorting to be unsatisfactory in this context.

2.1. Note about “pXRF” terminology

In this paper, “pXRF” refers to the ruggedized instruments about the size and shape of a cordless drill. In contrast, some researchers (e.g., Craig et al., 2007; Liritzis and Zacharias, 2011; Speakman and Shackley, 2013) consider “pXRF” to include benchtop instruments that could be transported from an analytical laboratory to a similar context in a museum or field house. Such instruments have been used to good effect for sourcing obsidian artifacts (e.g., Cecil et al., 2007; Speakman et al., 2007; Liritzis, 2008). These systems, though, require a computer and electrical outlet, and they would not fare well outdoors. We focus on handheld analyzers designed for use in the field (e.g., geological exploration) and industrial settings (e.g., scrapyards, manufacturing).

2.2. Obsidian sourcing at an excavation

Obsidian sourcing at an archaeological site may yield insights that inform the excavation strategies. Consider, for instance, that most of the obsidian at our two sites originated from the nearest volcano, Gutansar; however, about 7% of the assemblages came from additional sources throughout Armenia. Some of the “exotic” artifacts are isolated finds of highly retouched tools, carried by hunter–gatherers across long distances. Others, though, occur as apparent scatter that suggest a few possibilities, including a worked nodule, a bundle or toolkit, or an occupation by a group that discarded their tools from a distant source as they made new ones. Recognizing such artifacts as they are unearthed might affect, for example, how an excavator approaches the lithic scatter, samples the stratum in that unit for dating or small finds, or interprets associated features. Such information at a subsequent time, whether years or days later, is useful but disconnected from these processes of excavation and field interpretation. The influence of excavation strategy on archaeological inquiry, especially with respect to sampling, is a matter of great significance in our discipline (e.g., Mathieu and Scott, 2004; Lyman, 2009).

There are examples of research designs in which recognizing changes in artifacts’ origins, identified as they are unearthed, may affect how a site is excavated. On-site sourcing would lend itself to such topics as the integrity of “living floors” (Dibble et al., 1997; Enloe, 2006; Machado et al., 2013; Malinsky-Buller et al., 2011) and organization of space in palimpsest occupations (Feinman et al., 2007; Adler et al., 2003). For example, at Gatecliff Rockshelter in the Great Basin, archaeologists modified their excavation strategy in light of suspected living floors (Kelly and Thomas, 2012: 86–88). Specifically, when an artifact horizon was encountered, the strategy shifted from a vertical to horizontal one, opening large surfaces and following the stratigraphic levels. This change was accompanied by greater attention to small finds (i.e., changes in sieving practice and sampling criteria for lithic, faunal, and botanical evidence), including lithic debitage and the surrounding sediments. Without indicators of a new artifact horizon, particular strata of Gatecliff Rockshelter might have been excavated differently.

This is not to suggest that, should we encounter an artifact of Hatis obsidian at Lusakert 1 among a multitude from Gutansar, we would suddenly change our overall excavation strategy for the cave. It would be a mistake to pose anything so drastic. Rather, we propose adding obsidian sourcing to the observations available to excavators as they dig. Our methods offer a new way to make field observations because, as demonstrated by our tests of visual classification, volcanic source is one tangible aspect of the material culture not apparent while excavating. As a routine component of field practice, on-site obsidian sourcing may yield insights when such information would be immediately relevant to excavators and their interpretations.

2.3. Obsidian sourcing on a field survey

We are also interested in insights from obsidian sourcing during surveys. Surveys are the principal means not only to search for and choose sites for excavation but also to reconstruct the distribution and organization of groups across the landscape. Obsidian sourcing during a survey may offer insights into settlement type, resource management, and other spatiotemporal patterns that inform how we approach surveys and document sites.

Consider Kuhn’s (1995) provisioning strategies for mobile foragers. Resource planning must account for the frequency and predictability of moves, variety and abundance of foraging opportunities, and availability of replacement raw materials. Kuhn describes two approaches to maintain tool supplies: individual provisioning and place provisioning. Individual provisioning is a

Table 1
Fifteen visual types of obsidian and 145 artifacts sorted by visual classification and by geochemical analysis. Gutansar obsidian is highly variable in appearance, so “exotic” artifacts from other obsidian sources were overlooked and grouped into types with a number of Gutansar artifacts. As a result, we deemed visual sorting to be unsatisfactory in this context.

<table>
<thead>
<tr>
<th></th>
<th>Black solid stripe</th>
<th>Coarse black</th>
<th>Coarse gray</th>
<th>Greasy black</th>
<th>Gray smooth stripes</th>
<th>Iridescent Pale gray outline red</th>
<th>Solid smooth gray</th>
<th>Smokey clear</th>
<th>Smokey clear, striped</th>
<th>Smooth black</th>
<th>Solid red</th>
<th>Tiger stripe</th>
<th>Tiger stripe, major black</th>
<th>Tiger stripe, major red</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gutansar</td>
<td>3</td>
<td>3</td>
<td>9</td>
<td>6</td>
<td>3</td>
<td>15</td>
<td>7</td>
<td>7</td>
<td>8</td>
<td>32</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Hatis</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pokr Arteni</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pokr Sevkar</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tsakhkunyats 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tsakhkunyats 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2
Measurement times in several recently published pXRF-based obsidian sourcing papers. These durations are consistent with Shackley’s (2011) claim that XRF analysts tend to measure obsidian for 150–300 s.

<table>
<thead>
<tr>
<th></th>
<th>Duration (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Golitko et al., 2010</td>
<td>60</td>
</tr>
<tr>
<td>Frahm et al., 2013</td>
<td>90</td>
</tr>
<tr>
<td>Goodale et al., 2012</td>
<td>120</td>
</tr>
<tr>
<td>Millhauser et al., 2011</td>
<td>120</td>
</tr>
<tr>
<td>Freund and Tykot 2011</td>
<td>180</td>
</tr>
<tr>
<td>Jia et al., 2010</td>
<td>180</td>
</tr>
<tr>
<td>Craig et al., 2010</td>
<td>200</td>
</tr>
<tr>
<td>Vázquez et al., 2011</td>
<td>200</td>
</tr>
<tr>
<td>Forster and Grave 2012</td>
<td>300</td>
</tr>
<tr>
<td>McCoy et al., 2011</td>
<td>300</td>
</tr>
<tr>
<td>Nazaroff et al., 2010</td>
<td>300</td>
</tr>
<tr>
<td>Tykot et al., 2011</td>
<td>300</td>
</tr>
<tr>
<td>Sheppard et al., 2011</td>
<td>300</td>
</tr>
<tr>
<td>Mean</td>
<td>208</td>
</tr>
<tr>
<td>Median</td>
<td>200</td>
</tr>
<tr>
<td>Mode</td>
<td>300</td>
</tr>
</tbody>
</table>
strategy in which there is uncertainty about mobility, resource availability, and opportunities for reprovisioning with raw materials, while place provisioning is a strategy with lower mobility and greater predictability in resource availability and distribution. Thus, raw-material transport and management strategies differ based on mobility and landscape knowledge, and strategies on a particular landscape may vary diachronically due to climatic shifts.

Therefore, the ability to rapidly identify local and non-local obsidians during surveys has great interpretive potential. At sites just a short distance from an obsidian source, artifacts from only that source may indicate a strategy primarily influenced by place-provisioning. In contrast, sites with artifacts from diverse sources could reflect a predominance of individual provisioning. In reality, both provisioning strategies were almost always at work. For example, foragers may have used individual provisioning while traveling from the Syunik region to Gutansar, but while residing near Gutansar, they shifted to primarily place provisioning. It is not a simple either-or proposition, and the palimpsest issue remains. Thus, large assemblages sourced by pXRF and with detailed spatial and stratigraphic data are key to unveiling significant patterns.

Additionally, recognizing the spatial distributions of obsidians at a site could inform test pit locations or reveal different activity areas. Contrasting artifacts from the surface and levels of a test pit or trench add a temporal dimension, and correlating source data with artifact typology may uncover otherwise hidden diachronic changes in mobility between periods. At numerous open-air Palaeolithic sites in Armenia, little more is preserved than, in some instances, millions of obsidian artifacts. With a small team equipped with several pXRF instruments to cover a large area, working at such sites has become practical using the methods we report here, and the resulting datasets would be sufficiently nuanced to make meaningful behavioral interpretations.

2.4. pXRF and obsidian sourcing

Thus far pXRF-based obsidian studies have been primarily focused on sourcing artifacts at museums, universities, and archive facilities (i.e., collections previously beyond the reach of analytical techniques). Most studies have been conducted in museum labs and similar contexts (e.g., the Smithsonian’s Museum Conservation Institute in Phillips and Speakman, 2009; Craig et al., 2010; Field Museum of Natural History’s Elemental Analysis Facility in Golitko et al., 2010, 2012; Millhauser et al., 2011). For Craig et al. (2007), “in situ analysis” refers to measurements taken “where the artifacts are stored.”

Despite increasing use of pXRF, obsidian sourcing remains embedded in post-excavation studies. When artifacts are sourced, they have been detached, often distantly, in time and space from their archaeological contexts. For example, Forster and Grave (2012) analyzed 26 Near Eastern artifacts, excavated during the 1930s, at an Australian museum. This division has been the dominant paradigm since the 1960s, and obsidian sourcing has been highly productive over the last five decades. Nevertheless, use of pXRF analyzers in laboratories clearly does not take full advantage of their capacities. Our aim is to shift obsidian sourcing from the realm of “white coats” in the controlled laboratory environment to “muddy boots” in the field.

3. Background

Before reporting the development and testing of our methods for rapid obsidian sourcing, we briefly discuss obsidian studies in Armenia and two different approaches to classification in obsidian sourcing, revealing two technique-based communities of practice.

3.1. Armenian obsidian sources

Given the abundance of obsidian sources in Armenia (Fig. 1), it is beyond the scope of this paper to discuss them in detail. Badalyan et al. (2004) synthesize Armenian sourcing studies prior to 2000, including that of Blackman et al. (1998) and research never fully published. Until recently, most source characterization was done with fission-track dating and neutron activation analysis (NAA; e.g., Oddone et al., 2000; Badalian et al., 2001; Chataigner et al., 2003; Kasper et al., 2004; Cherry et al., 2010; Meliksetian et al., 2010, 2013). Rarely XRF has been used (e.g., Keller et al., 1996 used both NAA and XRF). Chataigner and Gratuze (2013a) recently studied Armenian obsidians with laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), characterizing most source complexes based on four to eight specimens each. Geologically focused studies include Keller et al. (1996) and Karapetian et al. (2001).

Relatively little archaeological data have been published regarding obsidian sourcing in Armenia, especially for the Palaeolithic. Most research has focused on the Neolithic to Bronze Age (e.g., Chataigner et al., 2003; Badalyan et al., 2004; Kasper et al., 2004; Chataigner and Barge, 2007; Cherry et al., 2010; Chataigner and Gratuze, 2013b). We are aware of obsidian sourcing at only one Palaeolithic site, Upper Palaeolithic Kalavan-1. Chataigner and Gratuze (2013b) have analyzed 18 artifacts and assigned them to Hatis (10), Gegam (4), Gutansar (3), and Satanakar in the Syunik complex (1). They also analyzed 20 artifacts from Mesolithic/proto-Neolithic Apnagugh-b (referred to by its unofficial name Kmlo-2) and attributed them to Gutansar (10), Tsakhkhunyat (4), Arteni (3), Hatis (1), Gegam (1), and a source in the Kars province of north-eastern Turkey (1). Thus, hundreds of millennia of obsidian use by modern humans and other hominins has hitherto been largely unstudied in Armenia.

3.2. Approaches to classification in obsidian sourcing

There are two schools of thought regarding classification in obsidian sourcing, and our two methods reflect these distinct approaches. Neither approach is fundamentally correct, and in instances where both approaches successfully discern sources, there is no clear reason to choose one or the other (unless there is a benefit in time or cost).

The first approach is summarized concisely by Harbottle (1982): “the more elements, the better!” (18). He sees sourcing as a form of taxonomy, applies taxonomic theory in his approach, and argues that classifications based on numerous traits are superior to those based on just a few. Harbottle cites the foundational book Numerical Taxonomy by Sneth and Sokal (1973), whose first taxonomic principle is: “the greater the content of information in the taxa of a classification and the more characters on which it is based, the better a given classification will be” (5). Thus, Harbottle claims that one tends to “get the best classifications out of the most information” (39). Similarly, Glascock (1992) maintains “it is advisable to use the information on all elements... to use the maximum amount of information” (17), citing Sneth and Sokal (1973). Consequently, Glascock and colleagues often use 20 or more elements in their source attributions (e.g., Ericson and Glascock, 2004; Glascock et al., 2007).

The second approach involves critical selection of elements. Hughes (1984) holds it “is not necessarily the case... that the inclusion of larger numbers of variables... results in a ‘better’ classification” (3). He contends poorly measured, redundant, or uninformative elements should be excluded. Citing Hughes (1984), Shackley (1988) holds “improperly chosen” elements can “covertly skew the classification analysis” and maintains “the best course is to choose elements for analysis carefully” (763). Hence,
Shackley (1995) proposes “a rule of thumb... is to use the fewest variables necessary” (546), and he frequently relies on four key elements (e.g., Ba, Rb, Sr, Zr in Shackley, 2009; Fe, Mn, Zn, Zr in Negash and Shackley, 2006).

These approaches reflect different technique-linked communities of practice. Harbottle and GlascocK are nuclear chemists who principally use NAA, while Hughes and Shackley have archaeological backgrounds and use XRF. What constitutes “standard practice” differs between the NAA and XRF communities. These differences are based on the strengths (and weaknesses) of each technique. NAA typically measures more than 20 trace elements in obsidian; however, early XRF instruments involved manually tuning a spectrometer to each element, so measuring fewer elements was desirable. By extension, methodological variations in pXRF use should be acceptable if those differences facilitate its strengths (e.g., field use).

4. Methods and materials

Our 10-s measurements take advantage of elements measured simultaneously with one X-ray filter, the development of faster detectors, and the relationship between measurement uncertainty and time. The tests we report here involved more than 500 geological specimens of Armenian obsidians and 154 Palaeolithic artifacts from Nor Geghi 1 and Lusakert 1.

4.1. Attaining 10-s measurements

Measurements in pXRF-based obsidian sourcing studies frequently take 2–6 min, and the most common duration is 5 min (Table 2). This is consistent with Shackley’s (2011) claim that XRF analysts measure obsidian for 2.5–5 min. Using 2-min measurements, Millhauser et al. (2011) analyzed about 100 artifacts in an 8-h day. This pace is still too slow for use at sites where 400–500 obsidian artifacts are recovered daily. We require a method to process up to 80 artifacts per hour. On paper, this suggests 45-s measurements, but to be fully syncopated with the excavation activities, we aimed for 10 s.

Some measurement times in Table 2 involve the use of multiple X-ray filters inside the analyzer to measure different portions of the X-ray spectrum. The 90-s measurements in Frahm et al. (2013), for example, were two sequential 45-s measurements using different filters. One way to reduce measurement times is to focus on elements measured well using only one filter. For Niton instruments, it must be the “main” filter (i.e., the primary filter, which has a proprietary composition), which is used to fluoresce transition elements and measure a series of X-ray phenomena (e.g., Rayleigh and Compton scattering) to adjust for various physical effects (e.g., morphology, density) from a particular material or specimen.

Recent technological advancements in pXRF analyzers also enable shorter measurement times. Most important is the development of silicon drift detectors (SDD), which can attain the same precision 2–10 times faster than older silicon p-n diode (PN) detectors. The majority of prior studies have used analyzers with PN detectors (e.g., Craig et al., 2010; Golitko et al., 2010; Jia et al., 2010; Nazaroff et al., 2010; Millhauser et al., 2011; Sheppard et al., 2011; Vázquez et al., 2011; Forster and Grave, 2012). Therefore, our use of an SDD instrument enabled shorter counting times than those in previous studies.

Additionally, the relationship between the time and uncertainty of a measurement is not linear. Instead, uncertainty is inversely proportional to the square root of the number of X-ray counts and, thus, measurement time (Fig. 2). To cut uncertainty in half, measurement time must be quadrupled. Decreasing error from 10% to 2% necessitates a measurement 25 times longer. Precision quickly incurs a considerable time cost. To attain an average precision of 2.3% for six elements (Fe, Rb, Sr, Y, Zr, Ba), Giauque et al. (1993) measured for 1000 s (i.e., 16.7 min). If 10% relative error had been acceptable, each artifact could have been measured in less than a minute.

4.2. Materials: instrument, artifacts, and geological specimens

Our tests used a Niton XL3t GOLDD+ pXRF analyzer. This instrument generates X-rays via a 50-kV tube with a silver anode, and it is outfitted with a silicon drift detector (SDD) that, as mentioned in Section 4.1, is 2–10 times faster than PN detectors. We have found that the XL3t GOLDD+- has, in practice, an X-ray resolution better than 155 eV (versus 180 eV, in practice, for the PN-based XL3t). Like other XRF instruments, Niton pXRF analyzers automatically monitor and adjust their tube currents (to a maximum of 200 μA for the GOLDD+-) as a means to attain optimal X-ray count rates for a particular specimen or material. Additionally, when operated at 50 kV with the “main” filter, this instrument yields an X-ray flux about 60% greater than that of 40-kV tubes (flux increases with the square of voltage). With a higher flux, more X-rays enter a specimen and, in turn, excite more characteristic X-rays to measure.

More than 500 geological specimens of Armenian obsidians were used in these tests, and the majority was collected from the sources by our team. The tests also included 154 artifacts from Nor Geghi 1 (Lower Palaeolithic) and Lusakert 1 (Middle Palaeolithic). Artifacts were chosen prior to knowing their origins, which were identified before these tests.

All geological specimens and artifacts were previously analyzed using pXRF with more conventional procedures, including two-minute analyses, a test stand, and operation via a laptop. Analyses were conducted in “mining” mode, which uses fundamental parameters (FP) correction to adjust measurements for X-ray emission, absorption, fluorescence, and other phenomena. To convert the data into element concentrations, we initially used the factory-set calibration factors and subsequently applied linear-regression calibrations based on 24 obsidians analyzed by NAA and XRF at the University of Missouri’s Research Reactor (MURR) and by electron microprobe analysis (EMPA) at the University of Minnesota. These data will be detailed in a publication, currently in preparation, regarding obsidian sources important at sites along the Hrazdan River.
5. Method 1: spectrum matching and $\chi^2$ fits

Our first method makes use of the pXRF algorithms to automatically identify metal alloys, and it follows Harbottle’s approach to classifying obsidian artifacts. Specifically, 24 elements are compared in a specimen and reference library using $\chi^2$ fits calculated in realtime.

5.1. Using the “Spectral Fingerprints” algorithms

One of the most common uses of pXRF is automated identification of alloys and metal grades in as little as 3–5 s. These instruments are routinely used in metal scrapyards to quickly identify, for example, different grades of stainless steel. In some manufacturing fields, including the aerospace and petrochemical industries, pXRF is used for alloy verification of every component as part of their quality assurance measures. The onboard software compares measurements to an integrated library of more than 400 alloys and displays the closest match in realtime on the built-in LCD. This process is known as positive material identification (PMI). Every day thousands of pXRF analyzers are used in commercial PMI applications, and a single worker can take as many as 1000 measurements during an eight-hour shift.

These algorithms can also be used with other materials and custom libraries. In the Niton software, this is called Spectral Fingerprint mode. First one uses the Teach Fingerprint routine to record spectra from reference materials and create a custom library. Each measurement takes 60 s. Then one measures a specimen using Match Fingerprint, and the built-in screen shows the closest matching reference in realtime. To identify a matching reference material, the algorithms use a Pearson’s chi-squared ($\chi^2$) test as a means to determine goodness of fit between the spectrum from a specimen and those in the library (Hejzlar and Pesce, 2009). This statistic is one of the most common metrics for “best fits” in spectrometry.

Specifically, the Niton software uses measured X-ray intensities from 24 pre-set elements to calculate the mean squared distance (MSD) between measurements from a specimen and each reference material within the library. If the spectra from a specimen and a reference material perfectly match, the MSD is zero. As differences increase, the MSD increases as well. As soon as one starts measuring a specimen, the LCD displays the names of the one or two best matches from the library and the MSD for each. Thus, calculated and displayed in realtime, is a statistical metric of the matches between a specimen and the reference population.

5.2. Limitations of the “Spectral Fingerprints” method

One weakness of this method is the pre-set list of 24 elements: Sb, Sn, Pb, Ag, Al, Mo, Nb, Zr, Bi, Re, Pb, Se, W, Ta, Zn, Hf, Cu, Ni, Co, Fe, Mn, Cr, V, and Ti. These elements allow identification of over 400 metal alloys, but many are not particularly useful for obsidian. Nb and Zr are very useful for obsidian sourcing. Ta and Hf, for example, can be useful for obsidian but occur at concentrations that require the sensitivity of NAA. Sr and Rb, however, are missing, and elements such as W and Ni are unlikely to yield much discriminating power. At present, elements cannot be added or removed to the Spectral Fingerprint mode (but this may change in the future). Nevertheless, we felt that this method was worth exploring due to unforeseen applications, however, we are willing to consider a method based on X-ray intensities rather than elemental data, and as noted in Section 3.2, there already are distinct technique-based communities of practice in obsidian sourcing. Thus, while we are interested in the long-term utility of our raw data, our primary goal is producing correct source identifications useful to our team during excavations and surveys.

Lastly, metal identification commonly involves flat surfaces and, for alloys like stainless steel, minimal surface alteration. It was unknown at the outset of this study how the curvature and weathering of artifacts would affect our results. Using ceramics, pXRF tests by Forster et al. (2011) demonstrate that elements are not equally affected by surface effects. Light elements, like Si, Ca, and Ti, are strongly affected by convex, concave, and grooved surfaces, whereas heavy elements like Rb, Sr, and Zr are largely immune. The same trend was reported for surface coatings. Therefore, if suitable elements dominate the fingerprint in Spectral Fingerprint mode, the results could be largely unaffected by surface irregularities.

5.3. “Teach Fingerprints” protocols

The instrument was “taught” twelve obsidian spectra for this test (Fig. 1): Pokr Arteni, Mets Arteni, Gutansar, Hatis, Geghasar, Syunik-1 (Pokr and Mets Sevkar), Syunik-2 (Mets Satanakar and Bazenik), Tsakhirunyats-1 (Arkaysar/Kamak), Tsakhirunyats-2 (Tvvakar), and Tsakhirunyats-3 (Damlik). Each type was represented by one polished specimen characterized by NAA, XRF, and EMPA. Although the software has the capability to store hundreds of fingerprints, we used one specimen per obsidian type for two reasons. The first was speed. Obsidian sources are, with few exceptions, geochemically homogeneous (e.g., Glascock et al., 1998: 18, Hughes, 1998: 107, Shackley, 2008: 198), and with one specimen each, we taught the software all twelve obsidians in less than 20 min. We could pick up a new instrument and use this method in minutes. Second, the software reports only the two best matches, so using two or more specimens would mean not knowing the second-best match.

When the fingerprints are plotted (Fig. 3), our data suggest that most elements provide a degree of discrimination. This might be due partly to the uncorrected nature of these data (i.e., they are unadjusted for interferences from other elements). This is sometimes due to an element already in the fingerprint. For example, Co appears to vary considerably, but the measurements likely reflect interferences from Fe X-rays. In contrast, the Bi data likely include...
interferences from Ba, an element useful in obsidian sourcing. Thus, fingerprints include subtle contributions from elements beyond the pre-set list, and such interferences become fortuitous (e.g., Ba is not included in the pre-set list of elements, but it nevertheless contributes to the overall fingerprint due to its uncorrected contributions to the Bi X-ray intensity measurements).

5.4. Testing protocols for geological specimens and artifacts

First, 485 geological specimens were analyzed once for 10 s. Of these specimens, 459 corresponded to the twelve Armenian obsidians for which the software had fingerprints in its reference library, and 26 came from Georgia and Turkey. All specimens were analyzed on unprepared surfaces, which varied from smooth flake scars to weathered exteriors. This test used a cardboard stand, designed to be lightweight and duplicated anywhere in the world.

Second, the 154 artifacts were measured for 10 s, and the instrument was used as it would be in the field. Operation was entirely handheld without a laptop, electricity, or test stand. Analyses were started by the trigger and ended automatically after 10 s. Positioning was aided by the instrument’s internal camera. The artifact surface selected for analysis was simply the one considered least likely to puncture a film over the measurement window. Analyses were conducted outdoors in conditions that varied from direct sunlight to light rain.

5.5. Results for geological specimens and artifacts

Fig. 4 demonstrates what the pXRF displays. For Gutansar and Hatis, the match was sufficiently definitive that only the best fit and its \( \chi^2 \) value were displayed. For the Pokr Arteni specimen, the correct source is marginally better than the B-ranked Mets Arteni. For a Syunik-Sevkar specimen, Syunik-Satanakar is a close second-best fit. The Tsakhkunyats-2 specimen is correctly identified, and Tsakhkunyats-3 is ranked as the next-best match.

Table 3 summarizes the A- and B-rank matches and their \( \chi^2 \) values for the 459 Armenian geological specimens, and Supplementary Table S1 gives specimen-by-specimen results. Only seven were misidentified. Five specimens from Mets Arteni were matched to Pokr Arteni, just 3 km away (with Mets Arteni as close B-rank matches). A Syunik-Sevkar specimen was matched to Syunik-Satanakar, and vice versa. For both, the \( \chi^2 \) values were virtually identical.

To establish how the software would handle obsidians not in the library, we analyzed 26 specimens from Georgia and Turkey. Table 4 summarizes the A- and B-rank matches and their \( \chi^2 \) values for these specimens, and Supplementary Table S2 gives specimen-by-specimen results. The Nemrut Dağ specimen yielded \( \chi^2 \) values so high that the screen displayed “No Match,” and the Bingöl B specimens had \( \chi^2 \) values above 1, indicating poor matches. The other nine Turkey specimens had \( \chi^2 \) values between 0.43 and 0.92, and their A- and B-rank matches are anomalous compared to Table 3. For example, the Sarıkamış specimen had an A-rank match of Syunik-Sevkar, but the B-rank was Pokr Arteni, not Syunik-Satanakar. Hence, A- and B-rank matches that make little geochemical sense can suggest a mismatch. Georgian specimens were matched to Tsakhkunyats-3 and Hatis, not Chikiani, and their \( \chi^2 \) values may be too small to be recognized as erroneous. Therefore, we propose including a Chikiani fingerprint in future work.

Table 5 summarizes the A- and B-rank matches and their \( \chi^2 \) values for the 154 artifacts, and Supplementary Table S3 lists artifact-by-artifact results. Generally the artifacts have higher \( \chi^2 \) values than the geological specimens. This is likely due to a combination of artifacts’ uneven, weathered surfaces (i.e., hydration on a sub-millimeter scale) and handheld operation adding small geometric errors (i.e., less-than-ideal geometric alignments of X-ray tube, artifact, and detector). Nevertheless, all 154 artifacts were correctly matched to their sources.

6. Method 2: discriminant functions with pass/fail mode

Our second method uses two software features: (1) “pass/fail” mode for testing consumer products and (2) “pseudo-elements,” commonly used to automatically calculate percent oxide or
element ratios. This method follows Hughes’ approach to classification, and it remedies the key weakness of our first method: a lack of quantitative elemental data.

6.1. Using the pass/fail and pseudo-element algorithms

pXRF is often used to test consumer products for compliance with regulatory limits. For example, the software can be used with pass/fail criteria for the European Union’s Restriction of Hazardous Substances Directive (RoHS). RoHS prohibits, for example, Pb above 1000 ppm. A Pb concentration over 1300 ppm results in the measurement highlighted in red to mark a “fail.” If Pb is below 700 ppm, the result is a green “pass.” A yellow “inconclusive” results if the level falls in the intermediate range. Thresholds may be set for any element; however, the algorithms are rather simple. The software assumes “pass” is below a low threshold and “fail” is above a high one. There is no way to define an intermediate range as “pass.”

Another issue is illustrated by Fig. 5. Suppose one wishes to distinguish two obsidians based on Elements A and B. Neither source can be defined by ranges of Elements A and B due to overlaps. There is, though, an axis on which the two populations are perfectly differentiated: line c-d. This axis combines Elements A and B in a discriminant function (line e-f). With more elements, discriminant analysis (DA) derives the best discriminating axes in higher dimensions. These functions can also classify new observations (i.e., analyzed artifacts).

The general form of a discriminant function is:

\[ D = c_1X_1 + c_2X_2 + c_3X_3 + \ldots + c_iX_i + A \]

where \( D \) = discriminant function; \( c \) = discriminant coefficients; \( X \) = original variables (e.g., elements); \( i \) = number of variables; \( A \) = constant.

Such an equation is compatible with the software’s “pseudo-elements.” For example, a geologist may be more interested in the ratio of CuO to NiO in a rock outcrop than the absolute Cu and Ni contents. The software can report a pseudo-element defined as \((Cu \times 1.252)/(Ni \times 1.273)\), and the calculations are done automatically and displayed onscreen. If that geologist is interested in identifying rocks above a particular ratio, pass/fail thresholds could be defined (and quantitative data for Cu and Ni would still be acquired to calculate the pseudo-element).

Consequently, we derived discriminant functions, entered them as pseudo-elements, and calculated thresholds for six Armenian obsidian source complexes. It must be emphasized that, to calculate the pseudo-elements, fully quantitative elemental data (i.e., data...
corrected for matrix effects, calibrated, and converted into element concentrations) are acquired simultaneously.

6.2. Selecting elements for discriminant analysis

Five elements were selected for DA: Zr, Sr, Rb, Nb, and Fe. For two reasons, these are among the elements most frequently used for obsidian sourcing (e.g., Seelenfreund et al., 2002; Silliman, 2005; Negash and Shackley, 2006; Carter and Shackley, 2007; De Francesco et al., 2008; Phillips and Speakman, 2009; Shackley, 2008). First, their concentrations vary little within obsidian flows but can vary as much as three orders of magnitude among volcanoes (Rapp and Hill, 2006:225). Second, due to X-ray physics, elements in “mid-Z” portion of the periodic table are measured especially well with XRF (e.g., Giaque et al., 1993). Shackley (2008) notes these elements are “some of the most sensitive” for sourcing (203). Therefore, this method follows a Hughesian approach: using the best-measured, most-discriminating elements.

These elements are also measured using the “main” X-ray filter and, therefore, can be simultaneously quantified. Other elements, including Ba and Ti, have proven useful in prior obsidian sourcing studies. However, Ba must be measured using Niton’s “high” filter, which would increase the measurement duration. Similarly, Ti can be detected using the main filter; however, precise quantification at its concentrations in obsidian requires the “low” filter.

As noted in Section 4.1, measurement uncertainty is inversely proportional to the square root of the measurement time. Fig. 6 shows the results of our tests regarding this relationship for Zr, Sr, Rb, and Fe. For all five elements, uncertainties are below 10% (at the 2σ-level) after 10 s. In fact, for Sr and Rb, the uncertainty is 6% after 10 s, and for Zr and Fe, it is 4%. Consider that NAA has uncertainties of 10% for Sr and 5% for elements such as Rb and 5–10% for Sr and Zr (Glasscock et al., 2007:346). After 10 s, these elements have uncertainties comparable to NAA data, and there is little point in longer measurements.

6.3. Weaknesses of DA with pseudo-elements

With a limit of 15 pseudo-elements, defining populations using two to three discriminant functions restricted us to five to seven
groups. Using the XLSTAT Pro statistical package, we derived three discriminant functions based on more than 1800 analyses from six obsidian source complexes (Fig. 1): Arteni (n = 356), Geghasar (n = 58), Gutansar (n = 886), Hatis (n = 330), Syunik (n = 81), and Tsakhkunyats (n = 78). Therefore, as a trade-off for fully quantitative elemental data, the distinction between, for example, Pokr and Mets Arteni obsidians would not be evident in the field with this configuration, but subsequent data analyses could discern them. If distinguishing Pokr and Mets Arteni was important, newly derived functions could do so.

6.4. Using discriminant functions

We derived three discriminant functions using Nb, Zr, Sr, Rb, and Fe, and since pseudo-elements are assumed to yield positive numbers, the functions’ constants were increased so that all results are positive. The final equations are:

\[
F1 = 2.36 \times Nb + 2.07 \times Zr - 2.86 \times Sr + 0.064 \times Rb + 0.011 \times Fe + 80
\]

\[
F2 = 2.42 \times Nb + 0.43 \times Zr + 0.39 \times Sr + 0.032 \times Rb + 0.007 \times Fe - 80
\]

The first two functions account for 94.6% of the variability in the dataset, and all three functions account for 98.3% of the variability. Fig. 7 shows the transformation of our elemental data to maximize separation among the six source complexes and how the five elements contribute to each function. Based on our a priori knowledge of Armenian obsidians, these functions can be used to assign newly analyzed artifacts to their most likely sources.

Each complex was defined by the first two or all three functions as pseudo-elements, and thresholds were based on our 1800 analyses of Armenian geological obsidian specimens (Table 6). The functions were identical for all six complexes; only the thresholds differed, derived from the maximum and minimum values for the geological specimens. An alternative approach could use distinct functions for every complex, and each set of functions could be specially derived to maximize the differences between one particular complex and all others.

Each series of thresholds defined the “intermediate” range for each complex. When the value for a discriminant function (as a pseudo-element) falls in the range for a particular source complex, that value turns yellow onscreen, corresponding to the “intermediate” range in pass/fail mode. Too low a value is green; too high is red. When the two or three functions that define a complex all display yellow values onscreen, it is a match. Fig. 8 shows examples. Gutansar, Hatis, and Tsakhkunyats are each defined by two functions, and when both of their respective functions display yellow values, it is a match. Arteni and Syunik are defined by all three functions, and a match occurs when all three display yellow values.

6.5. Testing protocols for geological specimens and artifacts

First, 499 geological specimens were analyzed three times each for 10 s: 467 from the six obsidian source complexes included the DA and 31 from Georgia, Turkey, and Armenian sources excluded from the DA. Analyses were conducted in the “DA” method, which uses FP correction to adjust measurements for X-ray emission, absorption, and other phenomena. The conditions were otherwise the same as the first method. Second, the 154 artifacts were measured for 10 s. Again the analyzer was operated in handheld mode, and weather conditions varied from direct sunlight to light rain.

6.6. Results for the geological specimens and artifacts

Table 7 summarizes the matches for the 467 specimens from the six source complexes, and Supplementary Table S4 gives analysis-by-analysis results. Of the 1391 analyses, only one analysis of a
Gutansar specimen yielded no match, but its quantitative elemental data (collected simultaneously) could still be readily matched to the proper volcano. All other analyses match the correct volcanic complex.

We analyzed 31 specimens to determine what happens when “unknown” specimens are encountered. Table 8 summarizes the findings for these specimens, and Supplementary Table S5 reports analysis-by-analysis results. All ten specimens from

Fig. 6. Our tests show the inverse square relationship between measurement uncertainty and time for Zr, Sr, Rb, Nb, and Fe for a Gutansar obsidian specimen. The specimen was measured multiple times for a series of durations between 1 and 40 s. After 10 s, these five elements have measurement uncertainties comparable to NAA data.

Gutansar specimen yielded no match, but its quantitative elemental data (collected simultaneously) could still be readily matched to the proper volcano. All other analyses match the correct volcanic complex.

We analyzed 31 specimens to determine what happens when “unknown” specimens are encountered. Table 8 summarizes the findings for these specimens, and Supplementary Table S5 reports analysis-by-analysis results. All ten specimens from

Fig. 7. The transformation of our elemental data (a) using discriminant analysis to maximize the separation among the six Armenian source complexes (b) and how the five elements contribute to each of the three discriminant function (c).
Turkey had no match. For the Georgian obsidian, 40 of 42 analyses had no match, and two analyses matched Hatis (and other analyses for these specimens had no match). One specimen from Khorapor was matched to the Syunik complex. Khorapor is geographically and geochemically close to Syunik, so the result is neither unexpected nor detrimental. Khorapor obsidian is chemically distinguishable from the Syunik sources, so refinements to or rederivations of the

<table>
<thead>
<tr>
<th>Source Complex</th>
<th>F1 Max (Fail)</th>
<th>F1 Min (Pass)</th>
<th>F2 Max (Fail)</th>
<th>F2 Min (Pass)</th>
<th>F3 Max (Fail)</th>
<th>F3 Min (Pass)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arteni</td>
<td>366</td>
<td>283</td>
<td>74</td>
<td>143</td>
<td>125</td>
<td>69</td>
</tr>
<tr>
<td>Geghasar</td>
<td>379</td>
<td>355</td>
<td>390</td>
<td>437</td>
<td>125</td>
<td>69</td>
</tr>
<tr>
<td>Gutansar</td>
<td>445</td>
<td>365</td>
<td>460</td>
<td>382</td>
<td>130</td>
<td>50</td>
</tr>
<tr>
<td>Hatis</td>
<td>228</td>
<td>214</td>
<td>230</td>
<td>214</td>
<td>130</td>
<td>50</td>
</tr>
<tr>
<td>Syunik</td>
<td>437</td>
<td>382</td>
<td>450</td>
<td>370</td>
<td>130</td>
<td>50</td>
</tr>
<tr>
<td>Tsakhkunyats</td>
<td>125</td>
<td>109</td>
<td>130</td>
<td>115</td>
<td>130</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 6
Pass/intermediate/fail thresholds for the discriminant functions for the six Armenian source complexes. “Actual” denotes the empirically derived boundaries for each function and complex based on more than 1800 analyses of geological specimens using conventional pXRF methods. “Threshold” denotes the values used in the pXRF software and subsequently tested with 10-s analyses of geological specimens and Palaeolithic artifacts.

Fig. 8. These screen captures of the pXRF instrument’s built screen demonstrate how a matching source is displayed to a user after 10 s using the discriminant analysis method. Gutansar, Hatis, and Tsakhkunyats are each defined by two discriminant functions, and when both of their respective functions display yellow values, it is a match. Arteni and Syunik are defined by all three functions, and a match occurs when all three display yellow values.
discriminant functions may reduce or eliminate this misidentifi-
cation in the future.

A problem is that two Spitakasar specimens were matched to
the Arteni complex. These obsidians are also similar chemically, so
the overlap is unsurprising. It is unclear whether this result is
archaeologically troublesome. Our team identified no Spitakasar
artifacts, and recent studies of Armenian obsidians (e.g. Badalyan
et al., 2004; Chataigner and Gratuce, 2013a,b) analyzed no Spita-
kar obsidian. We anticipate that discriminant functions could be
rederived, perhaps including additional elements (cf. data in Keller
et al., 1996), to account for Spitakasar obsidian and reduce or
eliminate the overlap with the Arteni complex.

Table 9 summarizes the matches for the 154 Armenian artifacts,
and Supplementary Table S6 gives artifact-by-artifact results. All
but two artifacts had matches, and all 152 matches were correct.
Two Gutansar artifacts yielded no match, but their quantitative
elemental data (collected simultaneously) would still be readily
attributed to the proper volcano.

7. Discussion and conclusions

Here we demonstrate two methods of sourcing obsidian arti-
facts in just 10 s while in the field. A claim of automated, on-site
source identification in only seconds may be met with skepti-
cism; however, through tests of both geological specimens and
archaeological artifacts, we have established the validity and reli-
ability of both methods. The technological ability to source obsidian
artifacts rapidly on-site clearly exists, but the methods to do so
effectively were hitherto undeveloped. The methods perform so
well that there is no clear reason to recommend one over the other.
For a particular application, a preference for either quantitative
data or more exact source identi-
cation will determine
which one to use. Ultimately, both methods are so fast that they
could be used together for a combined approach at a site or on a
survey. For example, at a site where Gutansar obsidian dominates,
artefacts can be initially identified using the Spectral Fingerprint
method and immediately reanalyzed using the DA method.

Two points are worth stressing. First, our methods are not
intended to replace traditional sourcing procedures in the field
house (using pXRF) or laboratory (using stationary instruments).
Rather, they are intended to offer information previously unavai-
liable in the field and to optimize resources (e.g., time, money) in
subsequent sourcing efforts. Second, our methods have been
developed only after considerable foundational research, including
surveys and sampling of obsidian sources, source characterization
by multiple techniques, and analyses of more than 500 geological
specimens and 1700 archeological artifacts. As such, our approach
critically depends on, rather than undermines, conventional
obsidian sourcing procedures.

The situation is analogous to that regarding the different ap-
proaches to obsidian sourcing with EMPA. To precisely analyze
numerous elements in obsidian source specimens, researchers have
used measurement durations of a few minutes (e.g., Tykot, 1995;
Weisler and Clague, 1998; Frahm, 2012). Merrick and Brown
(1984), however, were interested in rapid sourcing of Kenyan
obsidian artifacts. After characterizing geological specimens using
XRF and wet chemistry, they identified three elements able to
discern most sources: Ca, Ti, and Fe. With additional analytical
choices made to optimize for speed, each artifact was measured for
10–12 s. If Merrick and Brown (1984), using a 1960s-vintage elec-
tron microprobe, were able to acquire sufficiently precise mea-
surements in 10 s for obsidian sourcing, it should be unsurprising
that a state-of-the-art pXRF analyzer could do the same. As recently
pointed out by Speakman and Shackley (2013), the newest gener-
pation of pXRF instruments has better detectors and electronics than
lab-based XRF systems manufactured just five years ago.

Regarding chert sourcing, Luedtke (1992) argued that a “good
source analysis is usually complex and expensive, and should not be
initiated merely as a fishing expedition in the vague hope that you
might find something interesting” (117). Our approach to on-site

Table 7
Summary of the matches for 467 Armenian geological obsidian specimens included in our discriminant analysis. One erroneous identification is italicized. See Supplementary Table S4 for analysis-by-analysis results.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Source</th>
<th>Specimens</th>
<th>Analyses</th>
<th>Match</th>
<th>Analyses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arteni</td>
<td>Metz Arteni</td>
<td>43</td>
<td>129</td>
<td>Arteni</td>
<td>129</td>
</tr>
<tr>
<td></td>
<td>Pokr Arteni</td>
<td>54</td>
<td>162</td>
<td>Arteni</td>
<td>162</td>
</tr>
<tr>
<td>Gegham</td>
<td>Geghasar</td>
<td>9</td>
<td>17</td>
<td>Geghasar</td>
<td>27</td>
</tr>
<tr>
<td>Gutansar</td>
<td>–</td>
<td>249</td>
<td>747</td>
<td>Gutansar</td>
<td>746</td>
</tr>
<tr>
<td>Hatis</td>
<td>–</td>
<td>89</td>
<td>267</td>
<td>Hatis</td>
<td>267</td>
</tr>
<tr>
<td>Syunik</td>
<td>Syunik-1: Sevkar (Mets and Pokr Sevkar)</td>
<td>7</td>
<td>21</td>
<td>Syunik</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>Syunik-2 (Mets Satanakar and Bazienik)</td>
<td>8</td>
<td>24</td>
<td>Syunik</td>
<td>24</td>
</tr>
<tr>
<td>Tsakhkunyats</td>
<td>Tsakhkunyats-1 (Arkasayar/Kamakar)</td>
<td>2</td>
<td>6</td>
<td>Tsakhkunyats</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Tsakhkunyats-2 (Tvakan)</td>
<td>4</td>
<td>12</td>
<td>Tsakhkunyats</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>Tsakhkunyats-3 (Damlik)</td>
<td>2</td>
<td>6</td>
<td>Tsakhkunyats</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 8
Summary of the matches (or lack thereof) for 31 geological obsidian specimens excluded from our discriminant analysis. The erroneous identifications are italicized. See Supplementary Table S5 for analysis-by-analysis results.

<table>
<thead>
<tr>
<th>Region</th>
<th>Complex</th>
<th>Source</th>
<th>Specimens</th>
<th>Analyses</th>
<th>Match</th>
<th>Analyses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Armenia</td>
<td>Khorapor</td>
<td>–</td>
<td>1</td>
<td>3</td>
<td>Syunik</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Gegham</td>
<td>Spitakasar</td>
<td>2</td>
<td>6</td>
<td>Arteni</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>Kechut</td>
<td>Aghvorik</td>
<td>4</td>
<td>12</td>
<td>No match</td>
<td>12</td>
</tr>
<tr>
<td>Georgia</td>
<td>Chikiani</td>
<td>–</td>
<td>14</td>
<td>42</td>
<td>No match</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>–</td>
<td>Hatis</td>
<td>2</td>
<td>5%</td>
<td>No match</td>
<td>3</td>
</tr>
<tr>
<td>Turkey</td>
<td>Kars</td>
<td>Arpaçay</td>
<td>1</td>
<td>3</td>
<td>No match</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Meydan Dağ</td>
<td>5</td>
<td>15</td>
<td>No match</td>
<td>15</td>
<td>100%</td>
</tr>
<tr>
<td></td>
<td>Tendürek Dağ</td>
<td>3</td>
<td>9</td>
<td>No match</td>
<td>9</td>
<td>100%</td>
</tr>
<tr>
<td></td>
<td>Sarıkamu'</td>
<td>–</td>
<td>1</td>
<td>3</td>
<td>No match</td>
<td>3</td>
</tr>
</tbody>
</table>
sourcing might be seen, at least by some, as a fishing expedition. We would reply to such a view in two ways. First, the research here is based on our a priori knowledge of Armenian obsidians, including the important obsidian sources at sites for which we have done sourcing and our initial exploration of spatiotemporal patterns in their use at those sites. Furthermore, our work in the field house to source artifacts excavated or collected on surveys just days earlier established the desirability of this information in the field. By the time volcanic sources were identified for recently recovered artifacts, excavations had proceeded, and a chance for any specialized sampling of the artifacts’ contexts, if so desired, had passed. Additionally, by the time we had sourcing results for a few artifacts collected during a survey, our team had since moved on to a different area or site, providing no opportunity for feedback regarding, for example, possible occupation phases at the site. Second, because pXRF can source artifacts rapidly and inexpensively, we can commit less time and money to more targeted and speculative modes of inquiry. With reduced financial and time constraints, we should be more willing to pursue new approaches that, for example, employ obsidian sourcing to characterize sites at high spatial resolution.

By displacing obsidian sourcing from the context of “white lab coats” to that of “muddy boots,” pXRF becomes a facilitating technology, removing physical (and temporal) barriers that have previously segregated archaeological practice between the field and the distant analytical laboratory (i.e., the traditional context of obsidian sourcing studies). The portability of handheld instruments can bring together field and laboratory practices in a common setting. Observations regarding obsidian artifacts, traditionally available only after the artifacts have been detached in both space and time from their archaeological contexts, can now be made in the field, providing almost immediate insights that can inform excavation and survey strategies.

Acknowledgments

The authors thank Pavel Avetisyan, Director of the Institute for Archaeology and Ethnography, Armenia, for his support of this project. We recognize the generous financial support for the Hrazdan Gorge Palaeolithic Project provided by the Norian Armenian Programs Committee (University of Connecticut, 2008–2013), a Large Faculty Grant (University of Connecticut, 2012), and the L.S.B. Leakey Foundation (2010 and 2011). Niton UK and Thermo Scientific are thanked for their insights and suggestions regarding spectral fingerprints and pseudo-elements. Additional Armenian obsidian specimens came from the Smithsonian Institution, specifically the collections of M. James Blackman and the late James F. Luhr. Obsidian specimens from Turkey were collected by George “Rip” Rapp, University of Minnesota and the late Tuncay Erkan, Directorate of Mineral Research and Exploration of Turkey. Georgian obsidian specimens came from Nino Sadradze and Givi Maisuradze, Institute of Geology, Georgian Academy of Sciences. Roger Doonan is thanked for his thoughts and insights on the topic at hand. Two anonymous reviewers made comments that led to clarifications of the final manuscript. This research was also supported by the Department of Archaeology at the University of Sheffield and the Marie Curie Network FP7-PEOPLE-2010-ITN: New Archaeological Research Network for Integrating Approaches to Ancient Material Studies (NARNIA).

Appendix A. Supplementary data

Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.jas.2013.08.012.

References

Chataigner, C., Gratuze, B., 2013b. New data on the exploitation of obsidian in the southern Caucasus (Armenia, Georgia) and Eastern Turkey, part 2: obsidian procurement from the Upper Palaeolithic to the Late Bronze Age. Archaeometry. http://dx.doi.org/10.1111/arcm.12007.

Table 9
Summary of the matches for 154 Palaeolithic artifacts using the discriminant analysis method. See Supplementary Table S6 for artifact-by-artifact results.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Source</th>
<th>n</th>
<th>Match</th>
<th>n</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arteni</td>
<td>Pokr Arteni</td>
<td>1</td>
<td>Arteni</td>
<td>1</td>
<td>100%</td>
</tr>
<tr>
<td>Gutsansar</td>
<td>—</td>
<td>1</td>
<td>Gutsansar</td>
<td>149</td>
<td>99%</td>
</tr>
<tr>
<td>Hatis</td>
<td>—</td>
<td>1</td>
<td>Hatis</td>
<td>2</td>
<td>100%</td>
</tr>
<tr>
<td>Syunik</td>
<td>Syunik-1: Sekvar (Mets and Pokr Sekvar)</td>
<td>1</td>
<td>Syunik</td>
<td>1</td>
<td>100%</td>
</tr>
<tr>
<td>Tsakhkunyats</td>
<td>Tsakhkunyats-1 (Arkaysar/ Kamara)</td>
<td>1</td>
<td>Tsakhkunyats</td>
<td>1</td>
<td>100%</td>
</tr>
<tr>
<td></td>
<td>Tsakhkunyats-3 (Damlık)</td>
<td>1</td>
<td>Tsakhkunyats</td>
<td>1</td>
<td>100%</td>
</tr>
</tbody>
</table>


