ARCHAEOMETRY AT THE UNIVERSITY OF MISSOURI RESEARCH REACTOR AND THE PROVENANCE OF OBSIDIAN ARTEFACTS IN NORTH AMERICA

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Descriptions of the history of the Archaeometry Laboratory at the University of Missouri Research Reactor and the procedures used for instrumental neutron activation analysis of archaeological materials are presented. The laboratory was established in 1988 to support students and faculty from the University of Missouri and other universities who were interested in archaeological research involving compositional analysis. The results obtained from the analysis of obsidian sources and artefacts from locations in the continental USA are presented for illustration.

KEYWORDS: NEUTRON ACTIVATION ANALYSIS, OBSIDIAN, CERAMICS, CHERT, GREAT PLAINS, EASTERN NORTH AMERICA

INTRODUCTION

The archaeological record is a product of human activity, a substantial portion of which is recognizable by the displacement of raw materials from their natural settings. A scientific account of this record necessitates a description of the kinds and amounts of raw materials that were displaced, along with the distance and direction of movement. Archaeologists commonly refer to this type of study as artefact sourcing or provenance determination. Provenance studies permit archaeologists to investigate such diverse topics as mobility patterns, prehistoric migrations and commerce, and they are essential to understanding cultural development.

Recognizing the importance of provenance determination to the overall progress in their field, archaeologists have long looked to the physical and chemical sciences for reliable methods to compare artefacts to raw material sources. Since the middle of the 20th century, chemical characterization has proven to be one of the most versatile and powerful approaches for sourcing artefacts. In particular, instrumental neutron activation analysis (INAA) has been employed for provenance-based research of ceramics, basalt, obsidian, limestone and other materials. The main advantages of INAA over other possible methods of chemical analysis for artefacts are ease of sample preparation, high precision and accuracy for bulk sample analysis, relative immunity to matrix effects, and the capacity to process large numbers of samples. Other strengths of INAA are its superior inter-laboratory comparability and its ability to validate new analytical methods and procedures.

THE HISTORY OF THE ARCHAEOMETRY LABORATORY AT MURR

The proposal to build a research reactor on the University of Missouri (MU) campus was conceived in the late 1950s. The primary objectives were to stimulate scientific research and educational opportunities for MU faculty and students. Funds to build the reactor were appropriated by the Missouri State Legislature and approved by the Governor in 1959. Construction of the MU-Research Reactor (MURR) was completed and the reactor was in operation by the autumn of 1966. The choice of a flexible reactor design facilitated several expansions and upgrades over the years, to accommodate changing research needs and technological advances. Today, the MURR operates on a 150-hour per week schedule at a power of 10 MW and employs more than 140 full-time staff. The MURR supports research, education and service in a variety of disciplines, including (but not limited to) agriculture, engineering, medicine, epidemiology, chemistry, physics and archaeology.

Not long after the Research Reactor began to operate, an analytical group based on the application of instrumental neutron activation analysis (INAA) was established to work with University of Missouri faculty and students from various disciplines. The first archaeometric study using INAA was performed in 1969 by a graduate student from anthropology (Sigstad 1973), who analysed a collection of catlinite and red pipestone from the Great Plains. Although several preliminary studies were made on other archaeological materials (e.g., ceramics and chert) during the mid-1970s, none of these progressed to the point of publication.

By 1979, interest in archaeological research at MURR began to regain momentum. Drs Robert Cobean and James Vogt obtained a grant from the National Science Foundation (NSF) to conduct a comprehensive characterization study for obsidian from sources in Mesoamerica. The goal of this study was to use INAA to create a trace-element database that would permit greater discrimination between the sources and subsources of obsidian so that, eventually, the sources of obsidian artefacts could be determined with high accuracy. During 1980 and 1981, Cobean and Vogt conducted an extensive sampling programme in collaboration with archaeologists from Mexico's Instituto Nacional de Antropología e Historia (INAH). The fieldwork yielded more than 800 samples (weighing a total of 710 kg) from 25 source areas located throughout central Mexico. The obsidian source samples were delivered to MURR in 1982.

While Cobean and Vogt were collecting the obsidian from Mexico, Jeremy Edward, Chris Graham and David Ives (all students of Dr Vogt) were using INAA to develop procedures and standards for the analysis of chert (Ives 1984) and obsidian (Graham *et al*. 1982; Vogt *et al*. 1982) and archaeological bone (Edward 1987). During this same time period, Michael D. Glascock (MDG), who joined MURR in 1979, was investigating archaeological applications for prompt gamma neutron activation analysis (PGNAA) to various matrices, including metals and obsidian (Glascock 1981; Glascock and Cornman, 1983; Glascock *et al*. 1984). Methods for automating data collection in INAA and PGNAA, correcting for interferences from fission products and fast neutron reactions, and monitoring quality of the collected data were also established (Glascock *et al*. 1985, 1986; Glascock and Anderson 1993).

Shortly after the arrival of the obsidian samples from Mexico, Dr Vogt was diagnosed with an illness that led to his death in 1985. Dr Vogt's prolonged illness and Dr Cobean's acceptance of a permanent position in Mexico delayed progress on analysis of the obsidian collection. After Dr Vogt's death, MDG and J. Michael Elam (JME) revived the obsidian projects such that analysis of the entire Mesoamerican obsidian source collection was completed by 1988 (Glascock *et al*. 1988; Cobean *et al*. 1991).

Building upon the success of the obsidian project, MDG and JME formally established the Archaeometry Laboratory at MURR in 1988, with support from the National Science Foundation and the University of Missouri. The operating plan for the Archaeometry Laboratory borrowed heavily from the earlier archaeometric INAA programmes at Brookhaven (Harbottle and Sayre) and Berkeley (Asaro and Perlman). Both Brookhaven and Berkeley had operated under the auspices of the US Department of Energy (US-DOE) until the mid-1980s, when the mission of the DOE changed and support for archaeometry within the DOE was discontinued. The Archaeometry Laboratory at MURR operates by: (1) selecting projects based on peer review of mini-proposals; (2) employing uniform procedures for sample preparation, standardization, and automated sample counting (Glascock 1992); (3) adopting multivariate procedures for data interpretation (Bieber *et al*. 1976; Neff 2000); and (4) training archaeologists in the methods used to interpret their data.

By 1990, projects and samples were arriving to the Archaeometry Laboratory in ever-greater numbers, and MDG recognized the need for an additional staff member. Dr Hector Neff (HN), who had been working at the Smithsonian Institution with Ronald Bishop, was persuaded to join the Archaeometry Laboratory in June 1990. MDG, JME and HN worked to establish a tradition of preparing written reports of the compositional data that would be easily adaptable for journal publication. With the help of students and other technical staff, additional detectors and sample changers, and continued support from the NSF and the University of Missouri, the Archaeometry Laboratory gradually expanded its capacity, to the point that approximately 5000 samples per year can now be analysed by INAA.

In 2000, MDG and HN recognized that many of the university research reactors were facing closure within the next 20 years and that techniques such as inductively coupled plasma–mass spectroscopy (ICP–MS and LA–ICP–MS) were becoming more accessible to archaeologists (Kennett *et al*. 2001). In addition, there was a concern that as this shift from INAA to other techniques took place, the valuable INAA data that had been collected over the years would be lost or rendered incompatible with more recent data collected by newer methods. Consequently, a grant was obtained from the NSF to purchase a high-resolution inductively coupled plasma–mass spectrometer (ICP–MS) and a laser ablation system. We immediately began investigating applications of LA–ICP–MS (Neff 2002; Speakman and Neff 2002, 2005) and developing analytical procedures and reference standards to facilitate the exchange of data between laboratories using various analytical techniques. One important aspect to note is the continued viability of INAA as the primary refereeing technique to validate new methods or procedures as they are being developed.

In 2002, HN left MURR to assume a tenured position at California State University-Long Beach, where he currently directs a laboratory using laser ablation time-of-flight ICP–MS (LA–TOF–ICP–MS) as its primary analytical technique for archaeological studies. The MURR and CSULB laboratories are collaborating on a number of projects, most importantly those that create standards and establish analytical procedures for routine analysis of archaeological materials. Following the departure of HN from MURR, Robert J. Speakman (RJS) was promoted from within. RJS supported data interpretation and management of the ceramics database until late 2006, when he left MURR to assume a position at the Smithsonian's Museum Conservation Institute (formerly the Smithsonian Center for Materials Research and Education). MDG continues to manage the ceramic, obsidian and chert databases.

Recognizing that certain applications of INAA and ICP–MS are limited due to the destructive nature of sample preparation or the difficulty of removing archaeological specimens from their home country, the Archaeometry Laboratory purchased a portable X-ray fluorescence (PXRF)

spectrometer in early 2005, and we are using this instrumentation both in the laboratory and in the field. Samples of metal and obsidian artefacts from South America were successfully analysed during the summer of 2005 (Speakman *et al.* 2006; Craig *et al.* n.d.).

<div align="center">ANALYTICAL PROCEDURES AND STANDARDS</div>

The analytical procedures used for INAA at MURR represent a superset of the methods employed by most other archaeometric-INAA laboratories (Glascock 1992). Specifically, two separate irradiations are performed (i.e., short and long), permitting as many as 33 elements to be measured in most ceramics, basalt and cryptocrystalline silicates, and 28 elements to be measured in obsidian. The short-irradiation samples, which weigh about 100 mg each, are encapsulated in clean polyethylene vials. A pneumatic tube shuttle-rabbit system transports the samples in pairs to an irradiation position with a neutron flux of 8×10^{13} n cm^{-2} s^{-1}, where the samples undergo a 5-second irradiation. The pneumatic-tube system returns samples to the laboratory and, after 25 minutes of decay, the radioactive samples are measured by high-purity germanium (HPGe) detectors for 12 minutes each. The short-lived elements measured include Al, Ba, Ca, Cl, Dy, K, Mn, Na, Ti and V.

Samples for long irradiation are prepared by weighing 150–200 mg of sample material into high-purity quartz vials. For the long irradiation procedure, archaeological samples numbering between 35 and 50 samples, along with seven reference standard and quality control samples, are bundled together. Each week, two sample bundles are irradiated together for 24 hours (ceramics, basalt) or 70 hours (obsidian, cryptocrystalline silicates), using a neutron flux of 5×10^{13} n cm^{-2} s^{-1}. Following irradiation, the samples are allowed to decay for 7–8 days prior to a first measurement by two HPGe detectors coupled to sample changers. The samples are counted for 30 minutes each in order to measure eight medium-lived elements: As, Ba, La, Lu, Nd, Sm, U and Yb. After an additional 3–4 weeks decay, the long-irradiation samples are recounted for approximately 3 hours each to measure 17 long-lived elements: Ce, Co, Cr, Cs, Eu, Fe, Hf, Ni, Rb, Sb, Sc, Sr, Ta, Tb, Th, Zn, and Zr. Typical measurement uncertainties range from 2% to 5% for most elements, except for As, Ba, Cl, Nd, Sr and Zr, which range from 5% to 10%, and Ti and Zr, which range from 10% to 20%.

The primary standard reference materials employed at MURR include SRM 1633a Fly Ash, SRM 688 Basalt and SRM 278 Obsidian Rock issued by the National Institute of Standards and Technology (NIST). An in-house reference material (Ohio Red Clay) is included with each irradiation batch involving ceramics. Because the standard SRM 1633a is now becoming scarce, INAA laboratories are switching to a newer reference material, SRM 1633b Fly Ash, as their primary standard. Inter-calibration measurements between SRM 1633a, SRM 1633b and other standards have been established by MURR such that we can readily compare data from other laboratories with our own. Our standard values for SRM 1633a, SRM 1633b, SRM 688 and SRM 278, and Ohio Red Clay are listed in Table 1.

<div align="center">ARCHAEOLOGICAL DATABASES AT MURR</div>

The INAA data (as well as the more recent data by ICP–MS, LA–ICP–MS and XRF) for archaeological specimens analysed at MURR are merged with descriptive data for the samples (e.g., analytical ID, name of person submitting samples, site name, geographical coordinates, sample type, colour, form etc.) into a separate comprehensive database for each material type. The data for individual samples or groups of samples can be easily extracted for inspection,

Table 1 *Concentrations of elements in reference materials used by the Archaeometry Laboratory at MURR (in ppm unless otherwise indicated)*

Element	SRM 1633a	SRM 1633b	SRM 688	SRM 278	Ohio Red Clay
Al (%)	14.1	14.8	9.25	7.51	9.45
As	145	132	2.4	4.7	14.1
Ba	1320	683	198	970	668
Ca (%)	1.11	1.61	8.69	0.71	0.45
Ce	168	184	13	60	110
Cl	<69	<70	34	620	<100
Co	44.1	48.6	48.0	1.8	20.2
Cr	193	197	321	6.6	90.7
Cs	10.4	10.5	0.26	5.2	10.6
Dy	14.6	15.5	3.3	6.3	7.4
Eu	3.58	3.93	1.00	0.78	1.54
Fe (%)	9.38	7.71	7.16	1.45	5.33
Hf	7.29	6.76	1.55	8.50	7.16
K (%)	1.89	2.00	0.168	3.46	3.55
La	79.1	85.5	5.3	32.0	50.9
Lu	1.075	1.050	0.326	0.770	0.640
Mn	190	143	1250	397	253
Na (%)	0.165	0.194	1.58	3.56	0.140
Nd	75.7	82.0	8.9	30.0	42.3
Ni	130	116	152	9	76
Rb	134	139	5.0	14	184
Sb	6.15	4.85	0.26	1.79	1.39
Sc	38.6	40.2	36.6	4.8	19.0
Sm	16.8	18.6	2.4	5.9	8.0
Sr	835	1036	169	64	66
Ta	1.93	1.84	0.31	1.29	1.65
Tb	2.53	2.73	0.52	1.06	1.06
Th	24.0	24.4	0.3	12.6	15.1
Ti (%)	0.823	0.730	0.700	0.141	0.594
U	10.3	8.8	0.32	4.55	2.96
V	300	300	238	9	211
Yb	7.50	7.43	2.03	4.60	4.27
Zn	220	206	81	53	101
Zr	240	223	59	290	170

sorting and interpretation by a variety of multivariate statistical programs, including a series of program modules written by HN (e.g., Neff 2002) and based on the original Brookhaven programs (Sayre 1975; Bieber *et al*. 1976; Harbottle 1976). We usually collaborate with the submitter of the samples on the task of data evaluation and occasionally invite students or faculty to visit our laboratory for training in the use of our interpretive software. These methods seem to work well, and since 1988 have helped more than 85 graduate students from MU and other universities to complete their degrees using data generated in the Archaeometry Laboratory at MURR.

Since 1988, we have worked on hundreds of archaeological projects, analysed many thousands of archaeological samples, and collaborated with archaeologists on more than 350 publications

and over 300 presentations at national and international conferences. Because it is not possible to list all of the projects, publications, presentations and graduate student degrees within the limits of this article, we summarize our work below by describing the accumulated databases. Interested readers should consult our website for comprehensive lists of publications, presentations and graduate student degrees supported by the Archaeometry Laboratory at MURR. Data from a number of completed projects are available for download, along with our license-free software. The primary URL is http://archaeometry.missouri.edu.

The obsidian database

In the beginning, our focus was on obsidian from sources in Mesoamerica (Mexico, Guatemala and Honduras), but over the years interest has grown to include other regions. Unlike the obsidian sourcing studies of the 1960s and 1970s, for which the numbers of analysed specimens were as few as two or three samples per source (Cobean *et al.* 1971), archaeologists and geologists are encouraged to collect large numbers of samples for each source and to provide geographical coordinates and maps of primary outcrops and secondary deposits (Glascock *et al.* 1998). The obsidian source specimens are analysed comprehensively by all available methods (INAA, XRF and LA–ICP–MS) in order to (1) establish the most detailed characterization possible for each source, (2) discover the most discriminating elements for each geographical region, (3) identify the most economical method for sourcing obsidian from a particular geographical region, and (4) increase the overall accuracy of provenance studies of obsidian artefacts. The identification of specific sub-sources as small as a few square metres has promoted better understanding of changes in source procurement patterns by prehistoric peoples (Braswell and Glascock 1998; Glascock *et al.* 1999; Ambroz *et al.* 2001).

   The differences in element concentrations between obsidian sources are influenced by the compositions of the rocks that melted to produce the magma, the melting conditions and changes taking place in the magma chamber, such as fractional crystallization and removal of elements as the magma cools immediately prior to eruption. Although compositions for the major elements in obsidian are constrained within relatively narrow limits, the trace elements can differ by orders of magnitude between sources. As a result, trace elements have proven to be more useful for differentiating between sources in support of archaeological work. The differences are most pronounced for elements that happen to be incompatible with the solid magmatic phases. The incompatible elements that tend to have higher concentrations in the liquid magma are Ba, Sr, Rb, Cs, Y, Zr, Hf, Nb, Ta and the REEs. Fortunately, INAA has proven to be very sensitive to a majority of these elements.

   The most popular regions for obsidian research are Mesoamerica, South America, the western United States, Alaska and the Mediterranean. More recently, we have been collaborating with Russian archaeologists and geologists to characterize obsidian from northeastern Asia, including the regions of Primorye, Korea and the Kamchatka Peninsula (Kuzmin *et al.* 2000; Speakman *et al.* 2005; Glascock *et al.* 2006). The number of analysed samples in the MURR obsidian database is rapidly approaching 20 000 artefacts and source samples, from more than 400 different sources around the world (Table 2).

The ceramic database

Ceramic artefacts, clays and additives represent the largest category of archaeological materials subjected to analysis by INAA and other compositional methods. Ceramic objects ranging

Table 2 *A summary of the obsidian samples analysed by INAA at MURR*

Region	Number of sources analysed	Numbers of specimens analysed by INAA	
		Source	*Artefacts*
Mesoamerica	77	2 347	9 950
South America	42	562	1 405
Western United States	166	1 949	543
Alaska and western Canada	24	75	381
Mediterranean	17	596	16
Northeastern Asia	27	185	510
Japan	14	110	130
Oceania	8	96	66
East Africa	31	43	0
Total	406	5 963	13 001

from utilitarian and decorative vessels to roof tiles, sculptures, ornaments and children's toys are common to almost every archaeological site and encompass a large portion of human history. Because ceramics are the first materials produced by humans that did not already exist in nature, they can tell us much about the development of technology, human interaction, and practical and artistic expression.

That INAA has remained one of the most popular methods for studying ceramic materials is due especially to (1) ease of sample preparation, (2) the fact that hazardous acids for sample digestion are not required, (3) its excellent precision and accuracy, and (4) the large number of elements measured. Although some have advocated analysis of ceramics by weak-acid extraction procedures (Burton and Simon 1993) combined with ICP, direct comparisons of the ceramic samples analysed by the weak-acid procedure with analyses by INAA (Neff *et al.* 1996; Triadan *et al.* 1997) have proven that significant problems exist. As such, these studies demonstrate the fallacy of promoting unproven analytical procedures until after proper validation studies have been performed in conjunction with well-accepted refereeing techniques such as INAA.

Table 3 lists the numbers of ceramic samples, clays and temper materials analysed at MURR from several different regions. The total number of such analyses is currently more than 42 000 samples. The regions of Mesoamerica and the American Southwest have been by far the most popular, but analyses of ceramic materials from areas such as the Mediterranean and South America have also been numerous. More recently, neglected regions such as the Caribbean, sub-Saharan Africa and South-West Asia have grown in importance.

Chert and flint

Chert, flint and other cryptocrystalline silicates represent another archaeological matrix often studied by INAA. Due to the greater heterogeneity of individual sources of cryptocrystalline silicate, larger bulk sample sizes (e.g., 1 g), which are easily possible by INAA, are typically analysed to obtain as many elements as possible (*c*. 30 elements). INAA has met with great

Table 3   *A summary of the ceramic, clay and temper samples analysed by INAA at MURR*

Region	Number of samples analysed by INAA
Mesoamerica	13 636
South America	3 078
American Southwest	11 228
American Midwest	2 745
American Great Plains	1 705
American West Coast	1 080
American East Coast and Southeast	666
Caribbean	637
Eastern Mediterranean	3 700
Western Mediterranean	1 144
South-West Asia	506
Sub-Saharan Africa	693
Oceania	925
Miscellaneous	461
Total	42 204

Table 4   *A summary of the chert samples analysed by INAA at MURR*

Region	Number of samples analysed by INAA
Great Plains	250
American Midwest	510
American East and Northeast	810
American Southwest and West	920
Alaska	650
Mesoamerica	360
Europe	130
Russia	60
Total	3690

success in areas such as the Brooks Range of Alaska, where the sources are quite distinct (Malyk-Selivanova *et al.* 1998), but in other regions such as France the heterogeneous nature of raw materials makes discrimination between outcrops of chert almost impossible (Blades *et al.* 1997). Table 4 lists the numbers of samples analysed at MURR from each of the major regions.

Other materials

A number of other archaeological materials have also been studied by INAA at MURR. Among these are basalt, steatite, limestone, marble, turquoise, ochre, catlinite, glass beads, copper, bones, teeth and tree rings. Table 5 gives a complete listing of the various types of archaeological materials and the number for each type analysed at MURR.

Table 5 *A summary of the other archaeological materials studied at MURR*

Archaeological material	Number of samples
Basalt	905
Soapstone	451
Copper ores and artefacts	313
Ochre and hematite	460
Glass beads	1033
Limestone	1551
Marble	100
Bones and teeth	400
Turquoise	50
Wood	80
Miscellaneous	360
Total	5703

One important aspect of our databases (and those generated at other laboratories) is that data we generate today are fully compatible with those that we generated 20 years ago. Consequently, researchers can draw upon earlier research without having to go through the lengthy and expensive process of duplicating reference and source groups. This is particularly true with obsidian and pottery: a researcher can submit a few artefacts for analysis that can then be compared to known reference groups, and, if materials of similar composition are in our database, source determinations are possible without any source sampling and without any investment in building reference groups. For illustration, recent provenance studies on obsidian artefacts from different sites in North America are presented below.

PROVENANCE STUDIES OF OBSIDIAN ARTEFACTS FROM ARCHAEOLOGICAL SITES IN NORTH AMERICA

Obsidian sources in the western USA and Alaska

In addition to studying the obsidian sources in Mesoamerica, more than 175 obsidian sources located in the western USA and Alaska have been characterized by INAA in detail. All obsidian sources in the USA are located in the western states. Not surprisingly, obsidian artefacts found in archaeological contexts east of the Rocky Mountains can be traced to a small number of sources, as shown in Figure 1, including Obsidian Cliff, Bear Gulch, Malad, Black Rock, Mineral Mountains and three sources in the Jemez Mountains (El Rechuelos, Cerro del Medio and Obsidian Ridge). A plot of Cs versus Hf, shown in Figure 2, demonstrates the success of INAA at discriminating between these sources.

Archaeological sites in the Great Plains and Midlands

The discovery of obsidian artefacts at North American prehistoric sites to the east of the Rocky Mountains is a rare occurrence that invokes ideas of long-distance exchange. At the few sites where obsidian artefacts are found, the numbers are typically quite small. Because the numbers of artefacts are limited, archaeologists often find it challenging to envision meaningful relationships
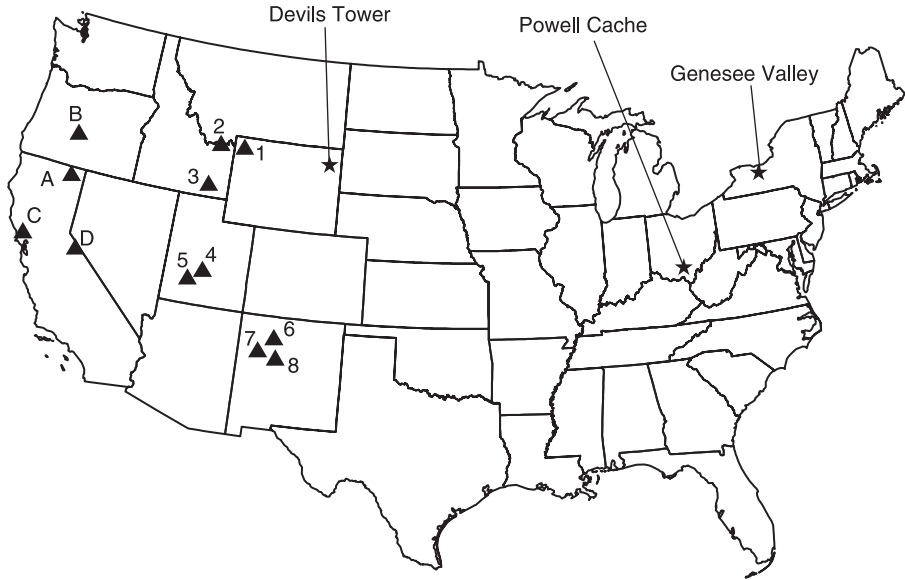
Figure 1 *A map showing the obsidian sources and archaeological sites mentioned in this study. The obsidian sources are labelled as follows: 1, Obsidian Cliff; 2, Bear Gulch; 3, Malad; 4, Mineral Mountains; 5, Black Rock; 6, El Rechuelos; 7, Cerro del Medio; 8, Obsidian Ridge—see also A, Blue Mountain; B, Newberry Volcano; C, Annadel; D, Bodie Hills.*
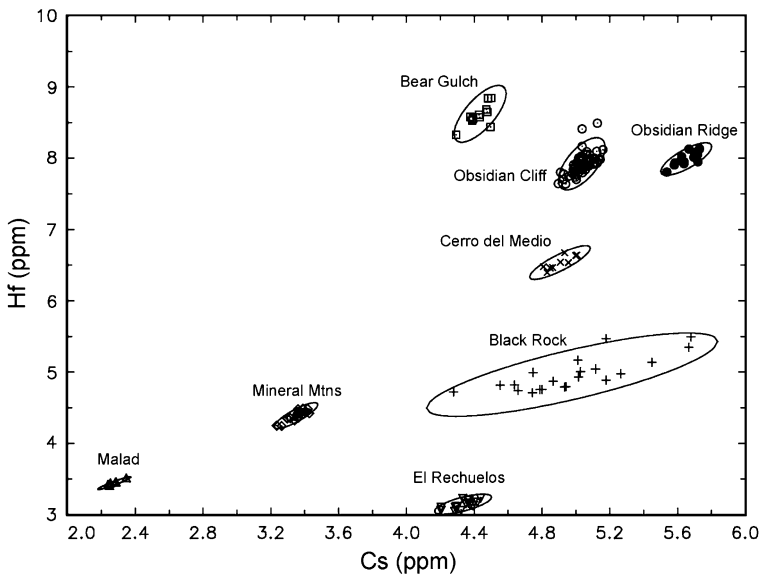

Figure 2 *A bivariate plot of Cs versus Hf for obsidian sources commonly linked to artefacts found in the Great Plains and the Midwest. Confidence ellipses at the 95% level are drawn around each source group.*
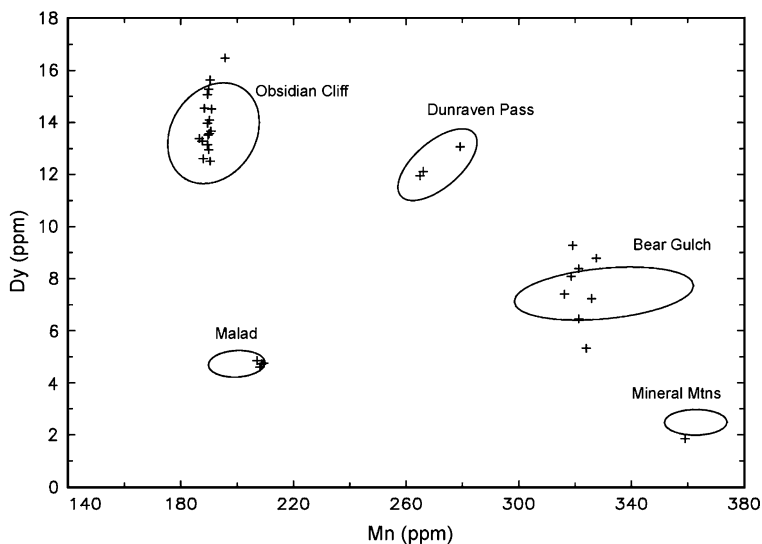
Figure 3 *A bivariate plot of INAA data for obsidian artefacts from Devils Tower National Monument mentioned in this study. Samples are projected against 95% confidence ellipses for the INAA reference groups.*

between the sources and the archaeological site. One notable exception is a recent study of obsidian artefacts from the site of Devils Tower National Monument in northeastern Wyoming. What makes the Devils Tower obsidian significant is the high concentration of obsidian artefacts found at a single landscape feature.

Thirty-three obsidian artefacts from sites in the vicinity of Devils Tower were submitted for INAA by Dr Brian Molyneaux. Although the initial report on this work has been published elsewhere (Molyneaux 2002), the results are interesting because they demonstrate movement of obsidian from multiple sources to a single archaeological site. The INAA results determined that 17 of the 33 artefacts came from the source at Obsidian Cliff, eight came from Bear Gulch, Idaho (also known as Big Table Mountain), four came from the source at Malad, Idaho, one artefact came from the Mineral Mountains source in central Utah, and three artefacts came from Dunraven Pass (a lesser known source within Yellowstone National Park).

A bivariate plot showing the short-lived elements Mn and Dy is shown in Figure 3, and illustrates the use of INAA to source these artefacts. The dominance of obsidian from the Obsidian Cliff and Bear Gulch sources is not surprising in light of the shorter distance to these higher-quality obsidian sources and the frequency with which obsidians from these sources have been found previously at sites east of the Rocky Mountains (Hughes 1995; Wright and Chaya 1995). Dunraven Pass obsidian has only been found within Yellowstone National Park and at Devils Tower.

The presence of obsidians from the Malad and Mineral Mountain sources indicates the attraction of a widely recognizable geographical feature. Devils Tower was undoubtedly a gathering place for many of the nomadic peoples of the Great Plains, who were probably also using the site for multiple purposes, including sacred ceremonies. The rare occurrence of such a large number of obsidian artefacts at a single location is clearly an indication of the familiarity of Devils Tower as a landmark and waypoint.
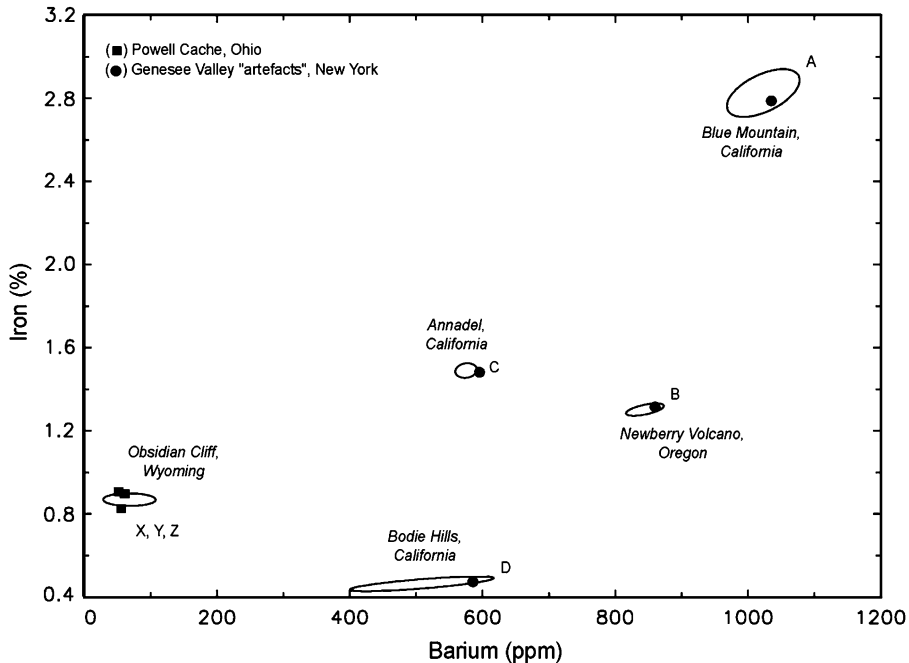
Figure 4 *A bivariate plot of INAA and XRF data generated for the Powell Cache (X–Z) and Genesee Valley (A–D) artefacts. Samples are projected against 95% confidence ellipses for the INAA reference groups.*

Midwestern and Eastern sites

In 2001, Richard M. Gramly submitted seven obsidian tools to the MURR Archaeometry Laboratory for provenance determination. Three of the tools were from the Powell Cache, a Middle Woodland period cache from a site in southern Ohio. The authenticity and provenance of the Powell samples were well established. The remaining four samples were from an extant private collection and were purportedly recovered from Middle Woodland period sites in the Genesee Valley of western New York (Gramly 2003).

The seven artefacts were initially analysed by X-ray fluorescence (XRF) in an attempt to determine their sources using a non-destructive method. Previous obsidian artefact sourcing studies (Hatch *et al*. 1990; Hughes 1995) have shown that most of the obsidian artefacts found at Middle Woodland sites in the mid-continent and eastern USA can be sourced to the Obsidian Cliff source in Yellowstone National Park, Wyoming, or to other nearby sources (e.g., Griffin *et al*. 1969; Hatch *et al*. 1990). Not surprisingly, our XRF data indicated that the Powell Cache artefacts could be attributed to the Obsidian Cliff source.

By contrast, source identification of the four Genesee Valley artefacts using XRF was inconclusive. The XRF data clearly demonstrated that these artefacts did not originate from Wyoming or Idaho sources, and even suggested that the samples were from more than one source. Therefore, we analysed the four artefacts by INAA in order to obtain a better chemical fingerprint for comparison to our more comprehensive INAA database of obsidian sources from North America. Examination of the INAA data unequivocally demonstrated that the four artefacts originated from sources located in California and Oregon (Fig. 4).

To date, no Hopewell artefacts have been reported from the California and Oregon sources in question. However, Dillian *et al*. (2005) recently reported that an obsidian biface reportedly discovered in Gloucester County, New Jersey, probably originated from a source in the Warner Mountains of northern California. As with the Genesee Valley artefacts, the Gloucester County artefact was discovered by a private individual (in 1960) and was stored in a private collection until the time of analysis. Although Dillian *et al*. maintain that the provenance of this artefact is secure, we believe that additional research is necessary before such a claim can be validated. In the Genesee Valley case, it is intriguing that one individual could have discovered four artefacts, made from four relatively obscure West Coast obsidian sources in New York. Because the original collector of the artefacts is deceased, we are unable to obtain additional information about the artefacts. However, it is worth noting that the four obsidian sources are located at or near major recreational areas in California and Oregon that are easily accessible by automobile (as are the Warner Mountains). We believe it more likely that the Genesee Valley artefacts were obtained directly from California by the purported 'discover' of the artefacts, or that they were purchased and inserted into his collection. The Genesee artefacts may or may not be authentic; that is yet to be determined. One thing that does seem apparent to us is that the artefacts were unlikely to have been recovered from archaeological sites in New York's Genesee Valley.

CONCLUSION

During the past 50 years, remarkably productive collaborations between archaeologists and physical scientists have clearly demonstrated the power of NAA as a means of determining prehistoric diet and material sources, and of tracing the movement of people, stone tools, ceramic vessels and other archaeological materials. Although other analytical techniques such as XRF and ICP–MS are available to researchers, NAA at MURR continues to be one of the strongest methods available for chemical characterization studies of archaeological materials—now and in the foreseeable future.

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