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# A SYSTEMATIC APPROACH TO GEOCHEMICAL SOURCING OF OBSIDIAN ARTIFACTS

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## ABSTRACT

Chemical analysis is a proven analytical tool for obsidian provenance investigations used by archaeologists around the world. Studies of obsidian artifacts assist archaeologists in tracking human mobility patterns, revealing differential access to raw material sources, investigating prehistoric long-distance exchange, etc. In recent years, hand-held portable X-ray fluorescence (pXRF) spectrometers have become the most popular tool for provenance research on obsidian artifacts. Even so, pXRF can sometimes lead to inconclusive results. In such instances, more powerful analytical methods such as neutron activation analysis (NAA) and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) can play an important role. This work describes a systematic approach to the analysis and interpretation of geochemical data for obsidian artifacts.

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**KEYWORDS:** obsidian, geochemistry, X-ray fluorescence (XRF), neutron activation analysis (NAA), laser ablation-inductively coupled-mass spectrometry (LA-ICP-MS)

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## 1. INTRODUCTION

Obsidian is one of several lithic materials used by prehistoric humans to produce sharp-edged tools. The glassy material is shiny and attractive. Although it is relatively easy to produce tools from obsidian by pressure or percussion flaking, the sources of obsidian are limited to volcanic regions. Prehistoric obsidian procurement developed in different ways, ranging from direct acquisition to complex systems involving long-distance commerce over land or sea.

During the middle of the twentieth century, Colin Renfrew and colleagues recognized that chemical analysis was an extremely effective method by which the sources for obsidian artifacts could be identified (Renfrew *et al.*, 1965). Today, archaeologists are making extensive use of obsidian artifact compositions to identify the preferred sources of raw material, to investigate long-distance exchange, to study migration patterns, to demonstrate differential access to specific raw material sources, etc. (Cortegoso *et al.* 2020; Martin and Tykot 2019; Pitulko *et al.*, 2019; Roth *et al.*, 2019; Stern *et al.* 2019). Although obsidian research has been an outstanding success, there is the potential for additional gains by examining the overall approach more critically.

In a previous article, a systematic approach to the characterization of geologic sources of obsidian was described (Glascock *et al.*, 1998). The suggested approach involves four steps briefly summarized here.

(1). Identify potential sources by studying archaeological and geological literature, interviewing knowledgeable locals, and visiting the sources in person. Use the information gathered to create maps detailing primary and secondary source locations.

(2). Collect as many source samples as reasonably possible for analysis. An intensive collection will reveal the overall patterns of compositional variability within and between sources and subsources. Other reasons for assembling a wide-ranging reference collection are the potential to exchange samples with colleagues and to have available samples for analysis by new methods or procedures.

(3). When possible, analyze the entire collection of source samples by all methods available – X-ray fluorescence (XRF), neutron activation analysis (NAA), inductively coupled plasma-mass spectrometry (ICP-MS), and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) – in order to produce a comprehensive source database. Sources with similar chemical fingerprints but from different locations may have more obvious differences using a different technique (Glascock, 2017; Liritzis *et al.*, 2020).

(4). Finally, one can use multivariate techniques such as principal components analysis (PCA), canonical discriminant analysis (CDA), and Mahalanobis-distance based probabilities to establish the reliability of source groups and to identify the technique(s) and element(s) most likely to produce the most reliable source classifications for artifacts.

The advantages of following this approach to studies of obsidian sources are: (1) the chemical data and descriptive information will be more uniform; (2) data for newly discovered sources can be easily added to pre-existing databases; and (3) procedures offering greater efficiency and less expense for sourcing problematic artifacts may be recognized. In addition, one can go beyond the success of identifying sources for individual artifacts to understanding how obsidian was exchanged, transformed, valued, and why changes occurred (Carter *et al.*, 2006). Tykot (2002) describes the latter as the *chaîne opératoire* where all of the activities and choices involving obsidian are examined, including procurement, transport, tool manufacture, use, and disposal.

## 2. BACKGROUND

Obsidian is a super-cooled liquid that forms when the viscous lava from a volcano cools rapidly such that the process of mineral crystallization does not occur. Obsidian is usually formed at the margins of a lava flow where contact between the hot lava and colder rocks, water, or air will sometimes produce obsidian. The glass is generally black or gray in color; but other colors are possible, depending upon the composition and circumstances of formation. Obsidian can be banded or streaky. Due to a disordered atomic structure, obsidian is physically amorphous and isotropic. The latter is the main reason why obsidian makes such effective tools, since flakes can be struck from a core in almost any direction.

The sources of obsidian exploited by prehistoric humans are almost entirely restricted to geologically-recent volcanic regions. Geographically, obsidian sources are found in the Mediterranean, Central Europe, Near East, Eastern Africa, Andes mountains of South America, trans-Mexican volcanic belt, western United States, Alaska, Russian Far East, Japan, New Zealand, Indonesia, and the islands of the South Pacific.

Obsidian compositions range from about 70-75% SiO<sub>2</sub>, 10-15% Al<sub>2</sub>O<sub>3</sub>, 3-5% Na<sub>2</sub>O, 2-5% K<sub>2</sub>O, and 1-5% total Fe<sub>2</sub>O<sub>3</sub> + FeO. Peralkaline varieties of obsidian like those from the Pantelleria source are typically higher in Fe composition than are rhyolitic obsidians. The remaining elements are present in amounts below 1% and are commonly referred to as *trace elements*. The intrinsic water content of fresh obsidian

ranges from 0.1 to 0.5% by weight. Because obsidian is unstable at ambient temperatures, it will gradually hydrate through the diffusion of water into the outer surface and along cracks. As the water content increases to 3.5 wt% and above, concentric “onion-skin” cracking patterns occur that gradually destroy the glass to form perlite. As a result, the lifetime of obsidian is relatively short by geological standards. Few obsidian sources are more than 10 million years old, and many range from a few tens to hundreds of thousands of years in age.

The magma from which obsidian is formed occurs at high temperatures (>1000 °C). As a result, obsidian sources are for the most part chemically homogeneous with variations in composition typically a few percent or less. Different sources have compositions that reflect the compositions of their parent rocks and subsequent changes taking place in the magma chamber prior to the eruption and cooling events that produce obsidian. Although the variation in compositions for the major elements in obsidian are restricted to a relatively narrow range, the abundances of trace elements can differ by orders of magnitude between sources.

The trace elements are distributed between the liquid (obsidian) and solid (crystalline) phases. The geochemical behavior of the trace elements is governed by how easily they can substitute for other ions in crystal lattices. Several of the transition elements (i.e., Sc, Ti, V, Cr, Co, Ni) are compatible with crystallization and are easily removed from the liquid melt phase. Bulky or highly-charged elements tend to concentrate in the liquid phase because they are unsuitable by virtue of their size and/or charge to fit in the cation sites of minerals. As a result, the latter are commonly referred to as the *incompatible elements*.

The two groups of elements that have the most difficulty entering the solid phase are the light-ion lithophile elements (LILE) and the high-field strength elements (HFSE). They are the last elements to form crystals in a cooling magma. The LILE are elements with a large ionic radius such as Rb, Cs, Sr, Ba, the rare earth elements (REEs), Th and U. The LILE are too large to fit within the crystalline structure of the solid phase. The HFSE includes elements with large valences such as Zr, Nb, Hf, and Ta which have high ionic charges and these elements are unable to replace other ions in the solid. The amounts of LILE and HFSE present in different sources of obsidian are also dependent on the initial composition of the magma, thermodynamic properties (i.e., pressures, temperatures, viscosity, water content), and the age of the magma. As a result, the concentrations of incompatible elements are the most sensitive indicators of geographic origin, and analytical methods

capable of measuring these elements are preferred for obsidian provenance studies.

### 3. METHODS OF CHEMICAL ANALYSIS FOR OBSIDIAN

The first analytical method used to determine obsidian composition was emission spectrometry by Cann and Renfrew (1964) who investigated obsidian from sources in the Mediterranean and Turkey. Sample preparation and analysis by emission spectroscopy is labor intensive and the precision is limited such that other techniques became more popular. Archaeologists at the University of California-Berkeley demonstrated that higher-precision techniques such as X-ray fluorescence (XRF) and neutron activation analysis (NAA) could be used to source obsidian artifacts from Mesoamerica and California (Heizer *et al.* 1965; Stross *et al.* 1968). The first application of proton induced X-ray emission (PIXE) to obsidian from Mexico was by Nielson *et al.* (1976). The first investigations of obsidian analyses to use mass spectrometry techniques - ICP-MS and LA-ICP-MS - were by Tykot and Young (1996) and Gratuze *et al.* (2001), respectively.

During the past 20 years, portable XRF (pXRF) spectrometers have become the foremost tool for obsidian characterization studies. The pXRF is generally affordable, can be setup for use very quickly, allows non-destructive analysis, yields good resolution for several of the incompatible elements, and is transportable in a backpack. On the other hand, there have been studies where the limitations of pXRF were encountered. In such instances, methods such as NAA and LA-ICP-MS can have an important role. The following sections describe the basic principles for each method along with their advantages and limitations. In addition, a resource to calibrate obsidian analysis by pXRF developed by the Archaeometry Lab at the University of Missouri Research Reactor (MURR) is described. After describing pXRF, NAA, ICP-MS, and LA-ICP-MS, a few cases studies describing methods used to resolve the limitations of pXRF are presented.

#### A. X-ray fluorescence

X-ray fluorescence, explained in much greater detail by Jenkins (1999), is a two-step process. In the first step, an incident photon from an X-ray tube or other low-energy photon source strikes an atom and knocks out an inner-shell electron. A vacancy is created among the atom's electrons. The second step involves a rearrangement of the electrons during which an outer-shell electron fills the vacancy followed by emission of a fluorescent X-ray. The emitted X-ray has a unique energy defined by the differ-

ence in energy between the two atomic levels. Measurement of the emitted X-ray identifies the element.

If an L-shell or M-shell electron replaces the K-shell electron, the emitted X-rays are referred to as  $K\alpha$  or  $K\beta$  X-rays, respectively. If an M-shell or N-shell electron replaces an L-shell electron, the emitted X-rays are  $L\alpha$  or  $L\beta$  X-rays, respectively. Atoms with different atomic numbers have different fluorescent X-ray energies as defined by Mosley's law in which the X-ray energies for each element are proportional to  $(Z-1)^2$ .

In principal, most of the elements in the Periodic table can be measured by XRF, except those with atomic numbers below  $Z=11$  for which the low energy X-rays are difficult to measure due to absorption effects. The sensitivities for XRF range from percent for the lightest elements to a few parts per million for the high Z elements. However, these advantages bring with them several limitations where atoms from one element in the sample can influence the fluorescence output of another. Referred to as *matrix effects*, these inter-element interactions are a consequence of absorption and enhancement. They occur when some of the fluorescent X-rays induce a secondary X-ray excitation in a lower Z element. Secondary excitation is particularly strong for elements differing by one or two atomic numbers (Ni to Fe; Sr to Rb; Zr to Sr). Therefore, the number of X-rays measured for the higher Z element is reduced and the number of X-rays for the lower Z element is enhanced. Tertian and Claisse (1982) found that the errors from matrix effects can range up to 50% in extreme cases.

The rate of success when tracing artifacts to their correct sources using XRF/pXRF varies according to several factors. These include surface roughness and sample size (i.e., thickness and mass). In addition, previous knowledge of all potential sources in a particular region is important for two reasons: (1) two different sources may have similar compositions on the elements possible by XRF and (2) there may be sources not yet discovered.

The ideal sample of obsidian for pXRF analysis is one with a clean flat surface covering the entire area of the incident X-ray beam. If the surface of an artifact is not uniform, incident X-rays may be scattered instead of creating fluorescent X-rays. The result will be a reduced signal measured in the spectrometer (Potts *et al.* 1977).

The thickness and area of an artifact analyzed by pXRF are critically important factors. The term "infinite thickness" describes the minimum thickness a sample must have to absorb all of the incident X-rays from source and return a characteristic fluorescent X-ray signal to the spectrometer. In other words, infi-

nite thickness is the same as the escape depth. If the fluorescent X-rays are produced deeper than the escape depth, they will not reach the spectrometer. For example, approximately 99% of the  $K\alpha$  and  $K\beta$  X-rays measured for all low-Z elements thru mid-Z elements (i.e., Rb, Sr, Y, Zr, and Nb) originate from within the first 3 mm of the surface. For the barium K-lines, infinite thickness is greater than 1cm.

When the artifacts are too thin or small in diameter, the uncertainties in composition will increase because a greater proportion of the incident X-rays will pass through or around the sample without interaction. As a result, measurements for a thin artifact sample compared to a thick source sample will have a smaller proportion of fluorescence X-rays for the higher Z elements (i.e., Zr and Nb) than for the lower Z elements (i.e., Rb and Sr). Prior to the development of pXRF, most XRF laboratories would avoid studying small or thin artifacts.

Quantitative analysis of geological and archaeological materials by XRF is challenging because the concentrations of individual elements can vary widely. Most manufacturers of XRF and pXRF spectrometers provide an instrument calibration based on the fundamental parameters (FP) approach (Sherman 1955). The FP calibration is based on the theoretical relationship between X-ray intensities, mass absorption coefficients, fluorescence yields, corrections for matrix effects, etc. However, the results using FP are sometimes widely inaccurate when concentrations are extreme. Therefore, empirical calibrations specifically designed for obsidian are more popular (Liritzis and Zacharias, 2010).

An empirical method for quantitative calibration employed by Shackley (1995) involves measuring a series of geological materials certified by international agencies such as the United States Geological Survey (USGS), the National Research Council (NRC) of Canada, the Geological Survey of Japan (GSJ), the US National Institute of Standards and Technology (NIST), and others. Because the mass/volume of the calibration sample is not directly known, count rates for the fluorescent X-rays are normalized by a portion of the spectrum background (e.g., the Rayleigh peak). Calibration curves for the elements are generated by plotting concentration versus the normalized count rates.

The geological reference materials mentioned above are only available in powdered form and are relatively expensive. Very few are as high in silica content as obsidian or rhyolite, and they do not cover the entire range of concentrations observed in some obsidian sources. As a result, the Archaeometry Lab at MURR created an obsidian calibration suite with solid samples from 40 different geologic

sources. We selected obsidian sources covering as wide a range concentration as possible for the mid-Z elements (i.e., Rb, Sr, Y, Zr, and Nb), since they are the most sensitive indicators of provenance. An advantage to using solid samples instead of ground powders for calibration is that they are more similar to non-destructively analyzed artifacts. See Glascock and Ferguson (2012) for a complete description.

The obsidian calibration suite was prepared from geological samples previously analyzed by NAA, ICP-MS, and LA-ICP-MS at MURR. We required the original geological samples to be large enough such that plenty of sample material would remain to create samples for multiple XRF calibrations. We also required the calibration samples to be at least 1 cm

thick and without visible inclusions. The subsamples for NAA and LA-ICP-MS were analyzed as small fragments without grinding to powder. Subsamples for ICP-MS were powdered prior to acid digestion, and used as a secondary check on the NAA and LA-ICP-MS analyses. In addition to selecting sources with a wide range (low and high) of concentrations, we required the combined NAA, ICP-MS, and LA-ICP-MS analyses of five or more geological specimens from the source to have standard deviations of <3% for the mid-Z elements (Rb, Sr, Y, Zr, and Nb). Table 1 lists the names of sources used and the mean concentration for each source used to calibrate the XRF and pXRF instruments at MURR.

*Table 1. XRF calibration suite in parts per million.*

ANID	Source Name	Ba	Ca	Fe	K	Mn	Nb	Rb	Sr	Th	Ti	Y	Zn	Zr
OBS-01	Timber Butte, Idaho	37,1	4903,2	3762,0	35904,0	754,0	32,2	176,4	13,0	12,0	252,3	36,3	59,0	45,8
OBS-02	Guadalupe Victoria, Mexico	907,2	3367,7	4275,0	33539,0	516,0	9,3	91,5	59,5	7,6	575,9	9,9	27,3	55,6
OBS-03	Little Glass Buttes, Oregon	1140,5	5151,9	6202,0	36044,0	326,0	6,9	94,7	62,0	8,5	626,6	16,7	28,0	95,9
OBS-04	Blue Mountain, California	1085,2	998,9	28255,0	29190,0	1706,0	16,1	58,8	1,0	6,2	1156,3	65,4	160,4	386,6
OBS-05	West New Britain(5), Papua New Guinea	319,2	8648,2	8894,0	19554,0	610,0	2,2	33,5	191,0	1,5	1145,4	24,7	49,9	120,9
OBS-06	Big Southern Butte(1), Idaho	2,6	3212,8	11825,0	40582,0	306,0	281,5	275,8	1,0	19,0	518,2	201,7	253,0	306,3
OBS-07	Mono Craters, California	23,4	3832,7	7730,0	38853,0	353,0	20,3	181,0	5,9	18,8	368,5	23,5	43,0	104,1
OBS-08	RS Hill, New Mexico	3,2	2544,0	7165,0	35950,0	441,0	237,9	361,5	1,0	42,7	155,6	76,9	134,2	155,7
OBS-09	Whitewater Ridge, Oregon	1581,7	6324,2	6869,0	35538,0	235,0	8,4	113,4	82,7	9,2	820,6	19,7	32,3	123,9
OBS-10	Casa Diablo (Sawmill), California	1065,1	6092,4	9160,0	44769,0	279,0	12,1	143,7	117,0	15,3	1122,1	12,7	33,3	189,3
OBS-11	Tucker Hill, Oregon	272,4	5443,4	4544,0	37590,0	510,0	10,1	98,1	47,4	7,6	265,8	19,6	31,1	65,0
OBS-12	East Medicine Lake, California	720,2	6297,0	10328,0	36636,8	271,0	8,7	140,1	70,0	15,1	1428,6	23,2	33,8	199,7
OBS-13	Grasshopper Group, California	759,8	5844,3	9015,0	37577,7	274,0	9,7	134,7	68,1	13,0	1286,4	23,8	31,9	184,8
OBS-14	Inman Creek-A, Oregon	855,2	7116,7	11045,0	27242,0	545,0	8,2	80,1	147,5	6,7	464,5	14,9	52,2	96,3
OBS-15	Burns Green, Oregon	43,0	1321,7	17743,0	38905,0	507,0	42,1	102,1	2,0	7,7	954,1	77,6	126,4	643,2
OBS-16	La Joya, Jalisco, Mexico	3,7	1213,8	19030,0	33457,0	572,0	60,6	157,4	1,0	15,8	837,0	66,4	129,0	804,6
OBS-17	GsJj Rift, Kenya	26,1	1483,9	46000,0	33147,3	1775,0	605,6	512,0	6,1	82,9	1556,9	395,1	591,6	3489,3
OBS-18	Kedong Road Rift, Kenya	261,4	5669,3	23364,4	41436,2	1076,7	275,8	203,2	51,5	35,8	3081,3	83,3	139,5	1156,7
OBS-19	Mule Creek(1), New Mexico	55,0	3859,2	6906,0	40290,0	387,0	25,9	228,0	11,7	28,6	419,2	37,1	39,1	103,2
OBS-20	Basaltic Plateau, Russia	137,1	49864,4	70000,0	2036,2	1082,4	3,7	11,2	360,0	0,8	7842,1	16,3	123,1	75,9
OBS-21	McDaniel Tank, New Mexico	1107,3	6877,3	9943,0	38973,0	632,0	35,9	157,0	195,0	17,9	1589,5	32,6	64,0	243,7
OBS-22	Cannonball Mtn(1), Oregon	4,2	1816,8	23735,0	39568,0	465,0	118,6	345,0	0,9	40,7	1007,5	107,5	212,4	1118,6
OBS-23	Witham Creek, Oregon	6,5	870,0	25159,0	34972,3	648,9	89,8	205,1	1,5	26,1	813,7	90,7	175,1	1152,6
OBS-24	El Paraiso, Queretaro, Mexico	1,3	1088,6	19544,0	36652,0	237,0	58,0	223,0	0,4	29,8	793,3	175,3	242,2	1227,3
OBS-25	Volcan Navajas, Nayarit, Mexico	55,9	984,4	44190,0	30633,0	1361,0	117,5	185,4	8,8	21,5	688,9	126,3	277,8	1216,7
OBS-26	Chickahominy, Oregon	1388,3	4248,9	11473,0	36589,0	429,0	19,0	102,4	21,6	7,7	1078,8	50,3	64,2	299,0

OBS-27	Davis Creek, California Cerro del Medio, New Mexico	618,7	5755,7	5328,0	37960,0	388,0	10,9	104,9	57,7	9,6	530,3	15,5	27,7	87,9
OBS-28	Mexico	27,0	2500,3	7376,0	40412,0	424,0	50,9	151,0	3,4	16,2	527,8	39,5	57,0	149,5
OBS-29	Cougar Mtn, Oregon Sierra de Pachuca(1), Hidalgo, Mexico	1298,3	4745,1	7945,0	31334,0	312,0	10,9	88,8	32,4	6,9	332,9	49,9	69,8	122,8
OBS-30	Polvadera, New Mexico	10,7	784,6	15820,0	37841,0	1147,0	88,1	192,0	2,1	18,7	1127,8	105,8	211,7	988,2
OBS-31	Mexico San Leonel, Nayarit,	11,0	3066,6	3823,0	39483,0	450,0	42,4	144,4	3,8	16,4	447,0	18,7	33,4	57,1
OBS-32	Mexico Zacualtipan, Hidalgo,	5,9	1689,9	12343,0	37880,0	258,0	32,7	146,5	0,3	14,4	612,6	50,6	108,0	453,5
OBS-33	Mexico Paredon, Puebla,	278,4	4778,1	10522,0	44340,0	174,0	17,2	280,4	33,9	35,8	1174,9	43,9	38,8	206,0
OBS-34	Mexico Archibarca, Salta,	62,1	2554,3	8484,0	40288,0	359,0	38,5	161,0	4,6	17,4	818,5	44,7	57,2	193,5
OBS-35	Argentina	876,2	10804,0	8655,0	33035,0	549,0	18,4	112,3	355,0	14,9	807,1	15,4	48,5	108,1
OBS-36	Meydan Dağ, Turkey Sarikamis(South),	58,2	2858,8	9500,0	34571,7	543,0	31,0	198,4	15,5	23,7	454,9	49,6	73,5	269,2
OBS-37	Turkey	519,1	3234,9	5523,0	38300,0	351,0	13,1	129,0	20,9	16,4	525,1	21,0	29,9	91,1
OBS-38	Gregory Creek, Oregon Obsidian Cliffs,	2287,3	8209,1	6549,0	37568,0	661,0	10,7	74,8	147,0	3,8	221,7	20,3	42,0	58,1
OBS-39	Oregon El Peceno, Mendoza,	875,8	5886,7	7988,0	28707,0	314,0	7,3	74,7	100,0	6,9	564,1	12,1	30,0	88,3
OBS-40	Argentina	1179,0	8090,3	5861,0	37917,0	878,0	22,8	222,0	330,0	11,5	548,5	9,2	52,7	110,5

## B. Neutron activation analysis

Neutron activation analysis (NAA) is one of the most sensitive and versatile techniques available for elemental analysis of geological materials. The technique was discovered by Hevesy and Levy (1936). It involves exposing a sample to neutrons, followed by one or more measurements of the emitted gamma rays following radioactive decay. Since the gamma rays for each element have unique energies, a trained analyst can use the gamma rays to identify individual elements and their amounts present in the sample. Detailed descriptions of NAA are available in a number of publications (De Soete *et al.*, 1972; Ehmann & Vance, 1991; Glascock, 1998).

Using neutron activation one can measure up to fifty different elements in most geological matrices by employing multiple irradiations, decays, and measurement times. With routine procedures for obsidian at MURR, we conduct two different irradiations and three measurements (i.e., short, medium, and long) to generate results for thirty elements. Most importantly for obsidian, these measurements produce high precision data for several of the incompatible elements (i.e., Rb, Cs, Sr, Ba, Hf, Ta, Th, and the REEs).

At MURR, we do not require samples of obsidian to be ground into a powder before analysis. Grinding samples can induce contamination from elements not part of the original sample (Boulanger *et al.* 2013). Samples are typically crushed to produce a collection of interior fragments that fit inside our high-purity quartz vials (4 mm inner diameter). Samples are handled with teflon tweezers to avoid

metal contamination. Although the recommended sample mass is 200 mg, we have successfully analyzed samples of obsidian as small as 5 mg. The standard reference material for NAA is SRM-278 Obsidian Rock from NIST. The best data on obsidian comes from our long irradiation times – but those samples are permanently radioactive and cannot be returned. However, an abbreviated NAA procedure using short five-second irradiations, has been demonstrated to solve source identification conflicts in several instances (Glascock *et al.* 1994). With NAA, we are capable of analyzing about 120 artifacts per week by the short irradiation procedure. If long irradiations are necessary, the turn-around time for sixty obsidian samples is approximately five weeks.

## C. Inductively coupled plasma-mass spectrometry

Inductively coupled plasma-mass spectrometry (ICP-MS) is a type of mass spectrometry in which an inductively coupled plasma ionizes the atoms from a sample. An argon gas transports atoms from the sample to the plasma chamber after digestion in acid (i.e., ICP-MS) or after laser ablation (LA-ICP-MS). Both methods enable detection of different isotopes from the same element, which makes them versatile techniques for both elemental and isotopic analysis.

Using LA-ICP-MS, the laser ablates the surface of a sample to create particles for ionization by the ICP torch (Gratuze *et al.* 2001). In obsidian, LA-ICP-MS is capable of measuring concentrations from as low as 10 ppb. One of the greatest advantages of LA-ICP-MS is that the sample is not destroyed and it does

not become radioactive which means the sample can be analyzed by a second method such as NAA. At MURR, we can analyze approximately thirty obsidian samples per day by LA-ICP-MS.

#### 4. A SYSTEMATIC APPROACH TO SOURCING OBSIDIAN ARTIFACTS

For the vast majority of obsidian studies relying on pXRF, the rate of success for assigning sources is very high. The sensitivity to several key elements, along with the availability and low-cost of pXRF all contribute to this success. Even so, the results from pXRF can fail to provide an unambiguous source assignment for reasons described below. If this happens, there are certain methods that will help answer the questions regarding most unassigned artifacts.

When assigning artifacts to specific sources, one of the most powerful methods is visual inspection of scatterplots. The method is simple, yet highly effective. Using scatterplots of the artifact compositions in either two dimensions or three dimensions, one can identify clusters of compositionally related artifacts, recognize clusters of artifacts that differ from one another, and detect unrelated outliers. Multiple scatterplots should be inspected such that all possible variation within the artifact data set is realized.

After identifying artifact clusters, the artifacts are compared to scatterplots of the source samples. A best-practice strategy is that the comparisons should be against the distributions for geological samples previously analyzed with the same pXRF spectrometer. Comparisons to singular geological samples or to published data from another laboratory are not recommended. Either of the latter comparisons will increase the probability for errors: (1) if sources are chemically similar on the limited number of elements measured by pXRF; (2) if unknown sources are present; or (3) if artifacts have size, surface, or shape issues.

Source distributions contain the data for collections of source samples with similar compositions surrounded by individual confidence ellipses in two-dimensions (or ellipsoids in three-dimensions). By removing extreme outliers, source distributions are conservatively defined. For instance, a 90% confidence ellipse is the boundary inside which at least 90% of the samples with the "same" composition will plot. With exceptions for the tiny artifacts and unknown sources, the artifact clusters should overlap known source distributions on all combinations of scatterplots. When making the comparisons, the first step is to eliminate all sources that are obviously different from the artifacts. With fewer source groups to investigate, the scatterplots become easier to interpret. There will be fewer possible sources to consider for each artifact cluster – hopefully just one.

#### *A. When the pXRF results suggest the presence of previously unknown sources*

Although hundreds of obsidian sources were discovered, mapped, and studied chemically over the past 50+ years, there are still regions where a new chemical fingerprint for artifacts may appear that suggests the presence of a new source, but the location is unknown. When the Archaeometry Lab at MURR encounters data suggesting a new source, we submit a few of the artifacts for a comprehensive analysis by NAA and/or LA-ICP-MS. Unless the artifact is extremely small (i.e., <100 mg), a portion of the artifact will be saved for other analyses.

Investigations of artifacts suggesting the presence of unknown sources have occurred a number of times. Thorough examinations of pXRF data for artifacts from the San Martin Jilotepeque, Guatemala, Glass Buttes, Oregon, and Nemrut Dağ, Turkey sources facilitated the discovery of multiple sub-sources. Colleagues with whom we were working, were provided information suggesting where unknown sources might be present. They were encouraged to visit and collect additional geological samples to enhance completeness of the obsidian database. Six sub-sources were identified at San Martin Jilotepeque (Braswell and Glascock, 1998), eight sub-sources at Glass Buttes (Ambroz, *et al.* 2001), and six sub-sources at Nemrut Dağ (Frahm *et al.* 2012).

#### *B. When the artifact surface, size, or thickness are not ideal*

For many years, XRF laboratories with lab-based XRF instruments have recommended that obsidian artifacts submitted for analysis have a clean flat surface and be >1cm in diameter and > 3 mm in thickness. Artifacts with rough or dirty surfaces or those that are small and thin generate less accurate and less precise data.

Artifact with uneven surfaces will scatter the primary X-rays such that the number of fluorescent X-rays is reduced. Artifacts with surface contamination (e.g., dirt, ink, fingernail polish) produce signals for elements that are not part of the sample. In particular, elements such as Ca, Ti, and Zn are often found in the materials used to mark an identification on an artifact. These markings should be removed with water, alcohol or acetone. One should always have the best side facing the pXRF.

The most frequent problem that an archaeologist using a pXRF is likely to encounter is the temptation to analyze every piece of obsidian in sight no matter how small or thin. This is especially true when traveling in a foreign country where exporting artifacts to the home laboratory may be impossible. When the artifact does not meet the infinite thickness require-

ment, it creates inaccuracies because the calibration curves are based on samples that absorb all fluorescent X-rays originating from atoms within the “infinite thickness” of thick geological samples.

As artifacts become smaller and thinner, measurements are no longer proportional to the concentrations but are influenced by thickness. The distributions for thinner artifacts become “stretched” such that the shapes of artifact distributions are much different from source distributions.

Hughes (2010) describes a solution to the tiny artifact problem. Because adjacent elements (i.e., Rb and Sr, Y and Zr, Zr and Nb) are least affected, Hughes demonstrates that scatterplots based on ratios of the incompatible elements (i.e., Sr/Rb, Y/Zr, Nb/Zr) reduce the stretching problem and fewer opportunities for erroneous assignments will occur.

A region from which the Archaeometry Lab receives a large number of tiny artifacts from collaborators is northwestern Iran (Abedi *et al.* 2018; Khazaee *et al.* 2014). More than 90% of the artifacts from northwestern Iran analyzed in our laboratory were assigned to three different sources. These are Meydan Dağ and Nemrut Dağ in southeastern Turkey and the Syunik source in southern Armenia. The map in Figure 1 shows the major sources known the region. Figure 2 shows a scatterplot of Rb versus Zr where a series of tiny artifacts plotted with three elongated 90% confidence ellipses. The elongated artifact distributions become a serious problem when comparing the artifacts against a greater number of sources with similar compositions. After converting the artifact data to ratios for Sr/Rb and Nb/Zr, the scatterplot shown in Figure 3 greatly reduces the problem with tiny artifacts and makes assigning artifacts to their proper source less uncertain.

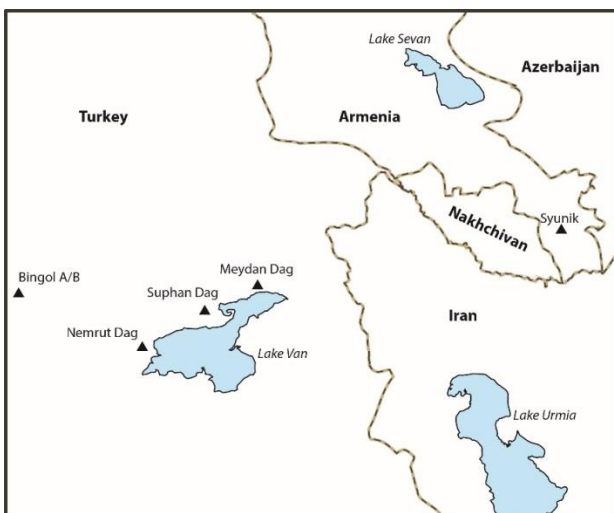


Fig. 1. Map of most important sources in southeastern Turkey and southern Armenia supplying archaeological sites in northwestern Iran.

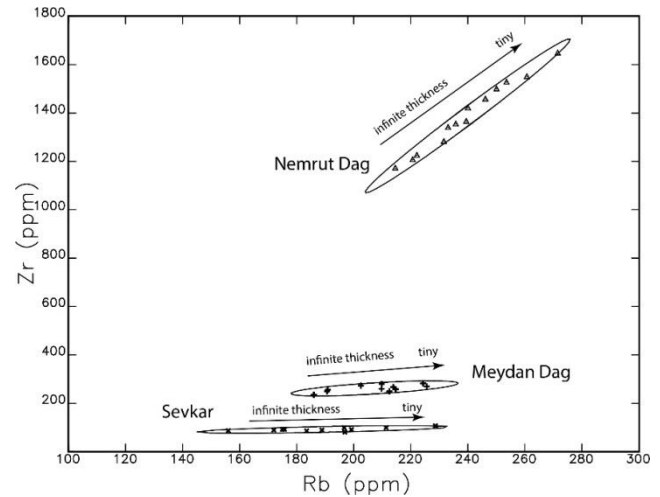


Fig. 2. Scatterplot of Rb versus Sr showing the elongated distributions for tiny artifacts from the three most important obsidian sources for archaeological sites in northwestern Iran. The ellipses are shown at the 90% confidence interval.

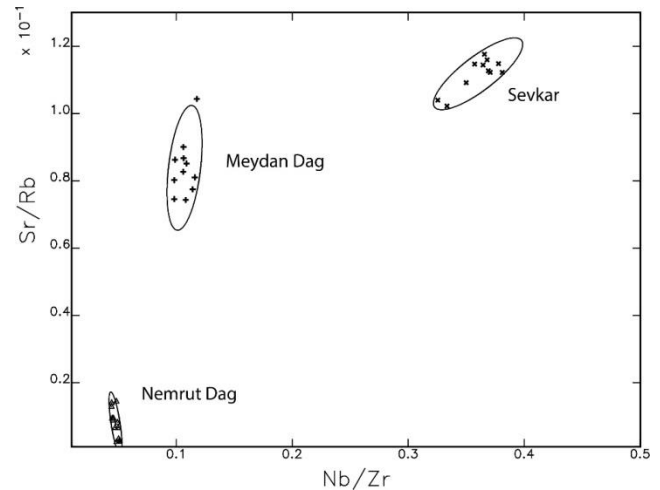


Fig. 3. Scatterplot of Sr/Rb versus Nb/Zr for the tiny artifacts from Fig. 2. The ellipses are shown at the 90% confidence interval.

### C. When artifacts are from chemically similar sources

In order to satisfy the provenance postulate of Weigand *et al.* (1977), it is necessary to identify at least one or more elements showing the differences between sources is greater than the variation within sources. For obsidian, it is rare when two geographically distinct sources have almost identical compositions, especially when a large number of elements are measured. However, there are a few examples for which similarity creates problems assigning artifacts.

One of the most familiar cases of nearly identical compositions involves using pXRF to distinguish between the nearly identical Bingöl A and Nemrut Dağ B sources in southeastern Turkey. The sources



are located more than 120 km apart but multiple researchers have noted the difficulty in assigning artifacts to either source. Some of the different methods used include: (1) assumptions dependent on maximal efficiency by Gratuze *et al.* (1993) and Khalidi *et al.* (2009); (2) peralkalinity (i.e., ratios among Al, Ca, Na, and K) by Poidevin (1998); and (3) high precision measurements of Al, Fe, Ti, and Zr by Frahm (2012). However, none of these methods are highly reliable because the differences between concentrations for low Z elements are small and hard to measure accurately, artifact surfaces are rarely flat, and small artifacts can exacerbate the problem.

A solution to differentiating between Bingöl A and Nemrut Dağ was recommended to the author by Jim Blackman in a private communication. Blackman suggested that the element Br which can be measured with high accuracy and precision by routine NAA is quite different for the two sources. To investigate his suggestion, NAA was used on all available geological samples from Bingöl A and the Nemrut Dağ subsources. The results are shown in Table 2 and Figure 4 where in addition to Br, two other elements Cl and Cs were found to be significantly different. The differences are greater than those reported by any of the previously proposed analytical methods and can be measured with high accuracy and precision. In addition, samples as small as 5 milligrams are adequate for making these measurements by NAA.

Table 2. Comparison of Bingöl A and Nemrut Dağ sources.

Source	Br (ppm)	Cl (ppm)	Cs (ppm)
Bingöl A (11 samples)	15.1 ± 0.9	1455 ± 70	14.4 ± 0.3
Nemrut Dağ subsources (n = 22)	2.5 to 7.4	380 to 1045	7.1 to 10.6

In west-central Argentina (i.e. Mendoza province), a pair of chemically similar artifact clusters were discovered by pXRF (Cortegoso, *et al.* 2020). The source area in the Andean highlands known as Laguna del Diamante has two geochemical types locally available - Laguna del Diamante and Arroyo Paramillos. A map of the region along the Argentina-Chile border is shown in Figure 4. Analyses of more than 1200 artifacts, discovered that the Arroyo Paramillos type is chemically similar to obsidian from the Las Cargas source located 100 km south of Laguna del Diamante. With pXRF, the difference between the Arroyo

Paramillos and Las Cargas sources is slight and only observable for the element strontium.



Figure 4. Map of obsidian sources along the Argentine-Chile border.

To seek additional elements supporting differences between the sources, NAA was used to study source samples from all three locations (i.e., Las Cargas, Laguna del Diamante, and Arroyo Paramillos). Although differences between Las Cargas and Arroyo Paramillos were observed, they were not very robust. The best element by NAA was also strontium. The means and standard deviations for strontium measured by NAA were as follows: Las Cargas (Sr = 206 ± 22 ppm), Laguna del Diamante (Sr = 70 ± 9 ppm), and Arroyo Paramillos (Sr = 230 ± 19 ppm). The overlap between Arroyo Paramillos and Las Cargas is significant.

Because of the similarity between Las Cargas and Arroyo Paramillos on both pXRF and NAA, identifying a method to differentiate between the sources is challenging as shown in Figure 5, especially for smaller artifacts. Similar to the approach used for tiny artifacts, the most successful approach involves use of element ratios. In Figure 6 a scatterplot of Sr/Rb versus Nb/Zr found that the separation between artifacts from Arroyo Paramillos and Las Cargas is slightly greater. Thus, making a decision regarding the correct source for artifacts from these sources can be done with improved confidence.

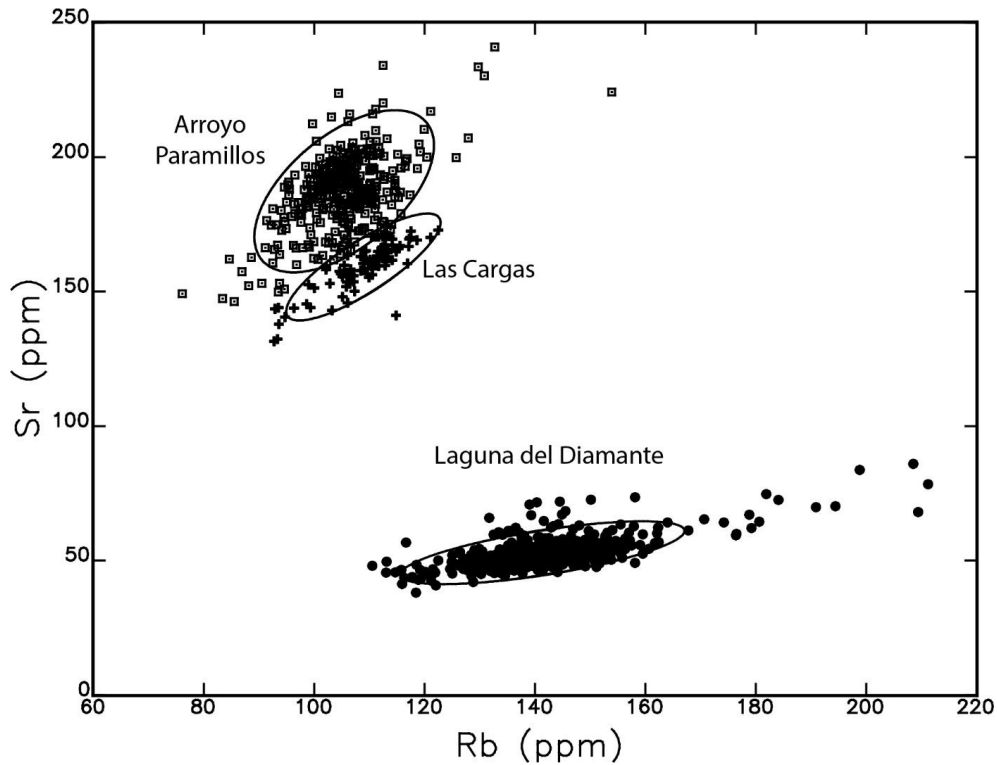


Figure 5. Rb vs Sr all artifacts.

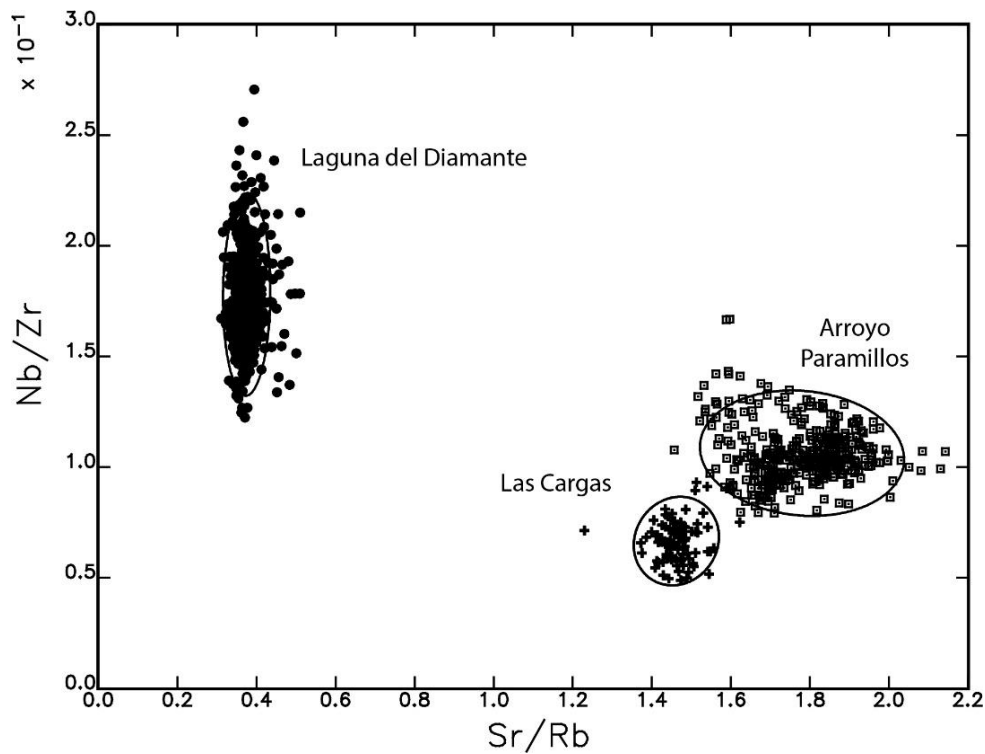


Figure 6. Ratios for artifacts from Mendoza.

An interesting finding from this study has been the fact that artifacts in Chile are mainly from Arroyo Paramillos. In Argentina, the Laguna del Diamante and Las Cargas sources are dominant. This is probably due to greater accessibility of Arroyo Paramillos from the Chilean side.

Another method we have discussed, but have not investigated would be to analyze lead isotope ratios in samples from Las Cargas and Arroyo Paramillos. However, if the method were successful, it would be prohibitively expensive.

## 5. CONCLUSIONS

In recent years, portable XRF spectrometers have become the leading instrumentation for obsidian provenance studies. pXRFs have the advantages of portability, low cost, and are sensitive to several of the key elements useful for determining the source. Methods for identifying the sources to obsidian artifacts presented here will help archaeologists place source specimens in their proper groups while rejecting outliers or discordant specimens. Important questions that archaeologists using pXRF should be

able to answer are: (1) Is your instrument properly calibrated for obsidian? (2) Do you have data for a sufficient number of geological samples to establish distributions for sources of interest when comparing artifacts? (3) Do you know how to handle the data tiny artifacts? (4) Do you have access to a secondary analytical technique (e.g., NAA, LA-ICP-MS) to resolve artifacts that give ambiguous results? By following some of the strategies described here, the rate of success at assigning provenance will be increased when encountering some of the challenging situations.

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