MRS Advances © 2017 Materials Research Society
DOI: 10.1557/adv.2017.148

A Decade of Portable (Hand-Held) X-Ray Fluorescence Spectrometer Analysis of Obsidian in the Mediterranean: Many Advantages and Few Limitations

Robert H. Tykot[1]
[1]Department of Anthropology, University of South Florida, Tampa, FL 33620, U.S.A. Email: rtykot@usf.edu

ABSTRACT

Starting in 2007, a portable, hand-held X-ray fluorescence spectrometer was used to elementally analyze and determine the geological source of obsidian artifacts in the Mediterranean, effectively replacing the instruments used in my previous research studies - INAA, LA-ICP-MS, ED-XRF and an electron microprobe with WDS. Approximately 400 geological obsidian samples from the Mediterranean area, and 8500 obsidian artifacts from prehistoric sites in Italy, France, Croatia, Malta, Tunisia, Greece, Cyprus, Turkey, Israel, and Egypt have been analyzed non-destructively by pXRF. Overall, the pXRF can distinguish all of the individual sources, based on the composition of Fe and trace elements Rb, Sr, Y, Zr, and Nb, as well as assign most artifacts to specific subsources and thus addressing archaeological research hypotheses about trade and exchange in many different time periods.

INTRODUCTION

Obsidian, a volcanic rock, has been used for making stone tools for nearly two million years. In the Mediterranean, the only geological sources are on the Italian islands of Lipari, Palmarola, Pantelleria, and Sardinia, the Greek islands of Melos and Giali, and in central Anatolia, while by the Neolithic period obsidian artifacts often are found at archaeological sites hundreds of kilometers away (Figure 1). The study of prehistoric trade and exchange, and its implications about socioeconomic practices, transportation capabilities over land and sea, the movement of people and material culture, and how these changed over time, has been a major part of archaeological research for a long time. The development of instrumental methods of elemental analysis first led to studies showing that obsidian sources in the Mediterranean could be distinguished starting in the 1960s [1]. Since then, many different analytical methods have been developed and used successfully on archaeological obsidian [2, 3, 4], with instrumental neutron activation analysis (INAA) [5], electron microprobe analysis (EPMA) [6], X-ray fluorescence (XRF) spectrometry [7, 8, 9], scanning electron microscopy with an energy dispersive spectrometer (SEM-EDS) [10], and laser ablation ICP mass spectrometry (LA-ICP-MS) [11, 12, 13] the most commonly used in the Mediterranean. While scientifically sound, there are however four key aspects regarding the analysis of archaeological artifacts:

(1) is the analysis destructive to the artifact?
(2) where can the analysis be conducted?
(3) how much does it cost for the instrument and its use?
(4) how much time and labor cost are involved?

Most analytical methods are destructive (e.g. taking a powder sample, or a small chip to fit in the instrument chamber), yet more and more countries do not allow destructive analyses and/or for the artifacts to be taken elsewhere for analysis. In addition, analysis of archaeological materials

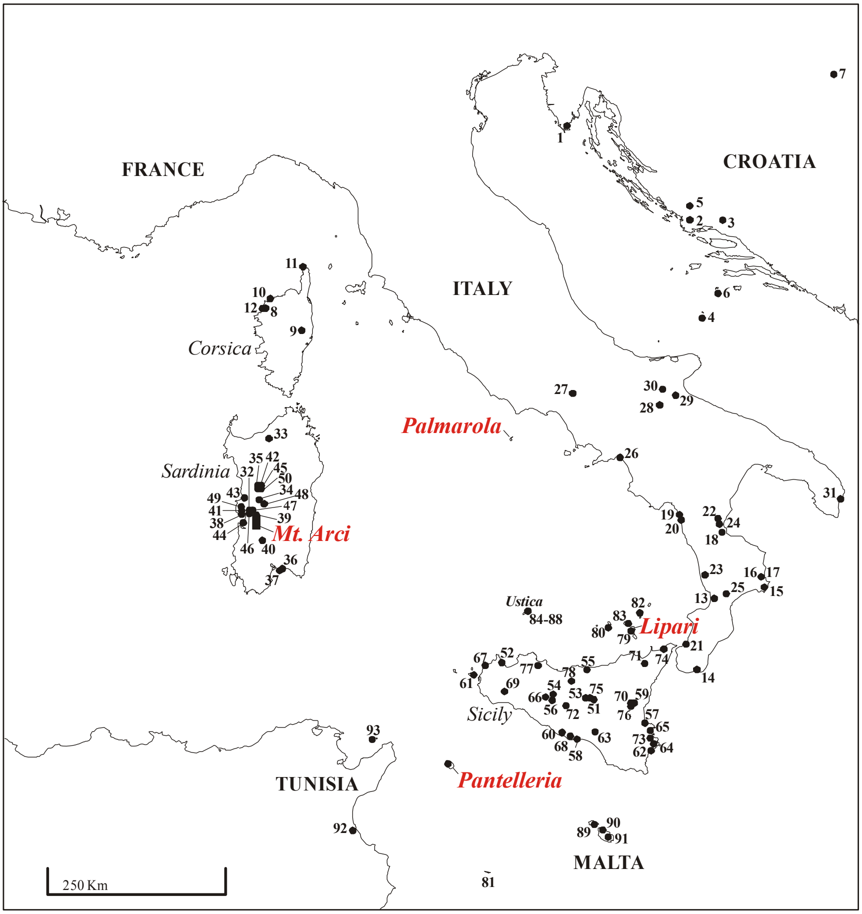

Figure 1. Map of central Mediterranean sources and sites with 10 or more obsidian artifacts tested by pXRF. Sites are listed in Table 2.

has typically been done using expensive instrumentation operated in geochemistry laboratories, while funding for archaeological research has always been limited.

Starting in the early 2000s, the development of less expensive, low maintenance, non-destructive, and portable X-ray fluorescence (pXRF) spectrometers has fundamentally changed the analysis of archaeological materials, in particular obsidian given its geologically homogeneous nature and no significant difference in composition between the surface and interior of worked artifacts [14]. In the central/western Mediterranean, the 7100 artifact analyses conducted starting in 2007 using a hand-held pXRF account for approximately two-thirds of all the chemical analyses ever done on obsidian in that region. The analysis of such a large number of artifacts, including 50 or more from nearly 40 different archaeological sites, allows for statistical comparison between individual sites and their contexts (e.g. residential, burial/ritual, other), geographic areas (e.g. coastal/inland, highland/lowland) and distance from geological sources, and changes over time (socioeconomic, technological). The frequency of transport between island sources and mainland sites is suggestive of maritime capabilities also for the transport of domesticated animals, ceramics, and other materials.

pXRF INSTRUMENTATION AND ANALYTICAL METHODS

Just like full- or desktop-sized lab-based energy-dispersive X-ray fluorescence (ED-XRF) spectrometers, there are at least several different brands and models of portable hand-held XRF (pXRF) spectrometers, with characteristics and features that also change over time. In the studies discussed here, a Bruker III-V+ model was used from 2007-2012, and the III-SD model since then [15]. The III-V+ has a Si-Pin detector and a typical resolution of 190 eV at 10,000 cps while using an X-ray tube with an Rh target, maximum voltage of 40 kV, and filament current of 10-11 μA. The collimator produced a beam of about 5 x 7 mm, an area smaller than most obsidian artifacts, while tiny debitage fragments could also be analyzed. For producing quantitative results for trace elements, analyses were conducted for 180-300 seconds, measuring 1024 channels while using a filter (76 μm Cu, 25 μm Ti, 305 μm Al) that reduces the background and increased the precision for the K-alpha peaks for Rb, Sr, Y, Zr, and Nb in the range 5-18 kV. The III-SD differs in its detector, which is a 10 mm^2 peltier cooled XFlash® silicon drift detector (SDD), with typical resolution of 145 eV at 100,000 cps while measuring 2048 channels. This greater sensitivity allows for the same precision in much less time, with most obsidian analyses done at 90-120 seconds. For both models, the detection limits for the trace elements mentioned are in single-digit parts per million (ppm).

Analyses were conducted in many different museums and storage facilities [16, 17, 18, 19]. The easy transport (in a regular backpack) of the pXRF, which runs on batteries for several hours and may be placed on a plastic stand while connected to a laptop or run with an attached PDA, greatly facilitated the analyses in this study (Figure 2).

The raw count data produced are calibrated using a special Excel file that includes many obsidian standards analyzed in several different laboratories. While theoretically that should allow direct comparison of results from different instruments, different calibration software and profiles are often used, so that there are offsets in the results. This may be resolved by conducting analyses on each instrument of the same standards or other samples. In early uses of the pXRF, issues were raised about accuracy and compatibility, but this is now resolved [20, 21, 22, 23, 24, 25, 26].

For this study in the Mediterranean, each pXRF model was used on a large number of geological obsidian samples from each of the island sources and subsources that had been collected as part of extensive surveys [6, 27, 28, 29]. Therefore, no recalibration was necessary when assigning newly analyzed artifacts with older model geological sample data.

It should be pointed out that other analytical instruments are able to provide concentrations on additional elements known to vary between sources. Neutron activation analysis in particular provides precise results for many elements, including Co, Ba, La, Ce, Sm, Th, and U, among others. So are there any potential archaeological problems in using a portable XRF and its more limited detection capabilities of trace elements? For the Mediterranean in


Figure 2. Conducting pXRF analyses of obsidian within a museum in Croatia

particular, the pXRF easily distinguishes each of the island sources (Figure 3), and the important subsources for Lipari (Figure 4), Sardinia (Figure 5), and Melos (Figure 6) (Table 1). It will not, however, distinguish all of the subsources for Palmarola and Pantelleria (Figure 7), but does that impact archaeological research on obsidian usage from these small islands?

ARCHAEOLOGICAL BACKGROUND

Obsidian was utilized in the Mediterranean as early as the later Upper Paleolithic, was widely used during the Neolithic (ca. 6000-3000 BC) when domesticated animals and plants first arrived, and its use continued into the Bronze Age. But chert and other stone tool material was also available and utilized, while there were changes over time in territorial control, transportation and tool production technology (direct/indirect percussion, artifact type and size), selection of specific obsidian material in comparison to other lithics for certain tool types, and socioeconomic and political practices [30, 31, 32]. In addition, there are several differences between each of the obsidian sources and subsources, including quantity, size, accessibility, knapping quality, brittleness, and visual characteristics including color, translucency, and the presence of phenocrysts.

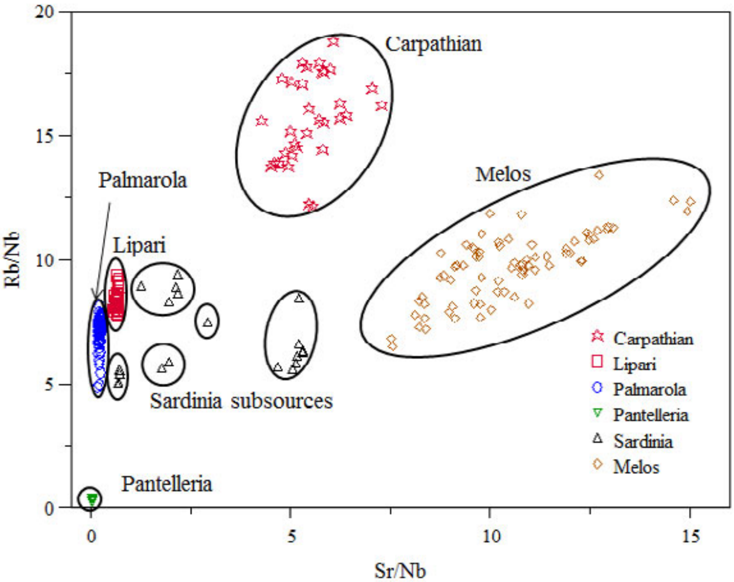

Figure 3. Graph distinguishing major geological sources using trace element ratios. The ellipses are boundaries for the geological samples tested.

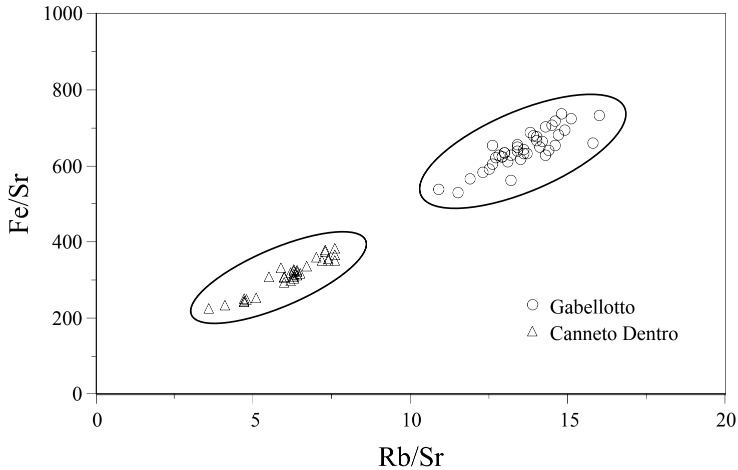

Figure 4. Graph distinguishing Lipari subsources using element ratios. The ellipses are boundaries for the geological samples tested.

https://doi.org/10.1557/adv.2017.148 Published online by Cambridge University Press

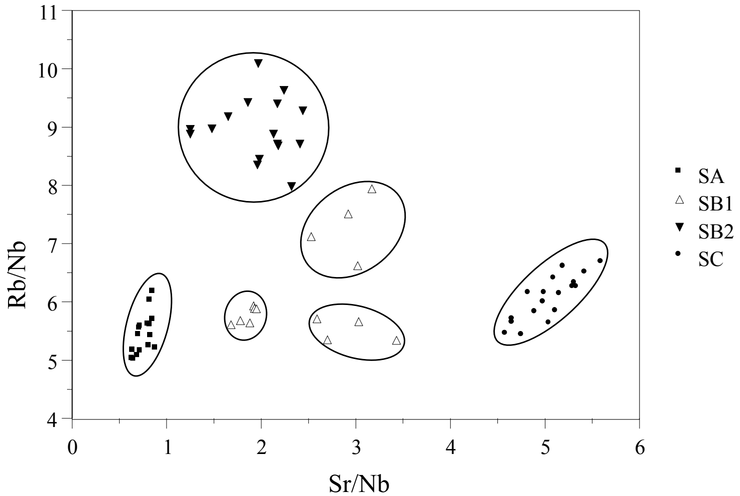

Figure 5. Graph distinguishing Monte Arci (Sardinia) subsources using element ratios. The ellipses are boundaries for the geological samples tested.

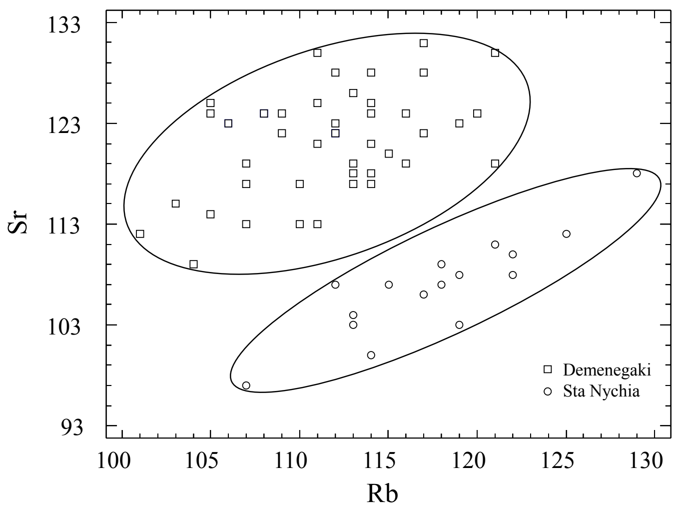

Figure 6. Graph distinguishing Melos geological obsidian subsources. The ellipses are boundaries for the geological samples tested.

Table 1. Average, minimum, and maximum values of selected elements and element ratios for 316 geological samples from the Mediterranean island sources and subsources

Source/Subsource	No.	Stats	Fe	Th	Rb	Sr	Y	Zr	Nb	Sr/Nb	Rb/Nb	Rb/Sr	Fe/Sr
Lipari - Canneto	33	avg	14827	41	284	52	39	155	29	1.6	9.6	6.2	313
		min	13471	33	258	38	36	147	27	1.3	8.4	3.6	226
		max	17630	48	311	78	43	167	33	2.7	11.4	7.6	383
Lipari - Gabellotto	41	avg	14042	45	299	22	45	171	32	0.7	9.6	13.6	645
		min	12290	38	278	21	41	155	26	0.5	8.0	10.9	531
		max	14850	55	312	24	48	185	35	0.9	11.6	16.0	738
Melos - Demenegaki	45	ave	12325	12	111	121	19	119	9	13.6	12.5	0.9	102
		min	11267	9	101	109	15	107	6	11.0	9.8	0.8	92
		max	15382	16	121	131	21	129	11	20.4	18.3	1.0	125
Melos - Sta Nychia	17	ave	10479	13	118	106	19	109	10	11.2	12.5	1.1	99
		min	9385	11	107	93	16	101	8	8.6	10.1	1.0	88
		max	16145	16	129	118	22	117	11	12.8	14.3	1.3	149
Palmarola	39	avg	14503	77	453	14	62	261	57	0.3	8.0	32.1	1022
		min	12834	66	383	12	53	238	49	0.2	6.9	20.5	799
		max	26251	95	509	19	72	284	64	0.3	9.1	41.4	1404
Pantelleria - Balata dei Turchi	57	avg	30886	23	170	15	139	1523	548	0.0	0.3	11.6	2111
		min	27678	18	151	11	123	1312	459	0.0	0.3	8.3	1520
		max	33580	31	191	20	166	1622	651	0.0	0.3	16.0	2931
Pantelleria - Lago di Venere	28	avg	31213	18	125	13	95	1124	341	0.0	0.4	9.5	2383
		min	22209	14	114	10	84	995	301	0.0	0.3	7.9	1674
		max	34497	22	136	16	104	1266	386	0.1	0.4	12.6	3535
Sardinia - SA	21	avg	11860	16	244	31	33	90	39	0.8	6.2	7.8	380
		min	10849	12	232	28	27	80	32	0.7	5.6	7.1	348
		max	12642	21	262	34	36	108	43	0.9	7.2	8.5	430
Sardinia - SB2	22	avg	14176	18	232	76	26	145	30	2.6	7.9	3.3	195
		min	11304	13	203	36	20	109	22	1.6	6.1	1.8	131
		max	16419	26	244	113	31	288	39	5.2	10.1	6.3	319
Sardinia - SC	13	avg	16552	21	173	135	23	229	24	5.7	7.3	1.3	123
		min	14196	15	151	121	19	201	20	5.0	6.2	1.1	100
		max	23031	29	187	157	28	250	27	6.7	8.5	1.4	171

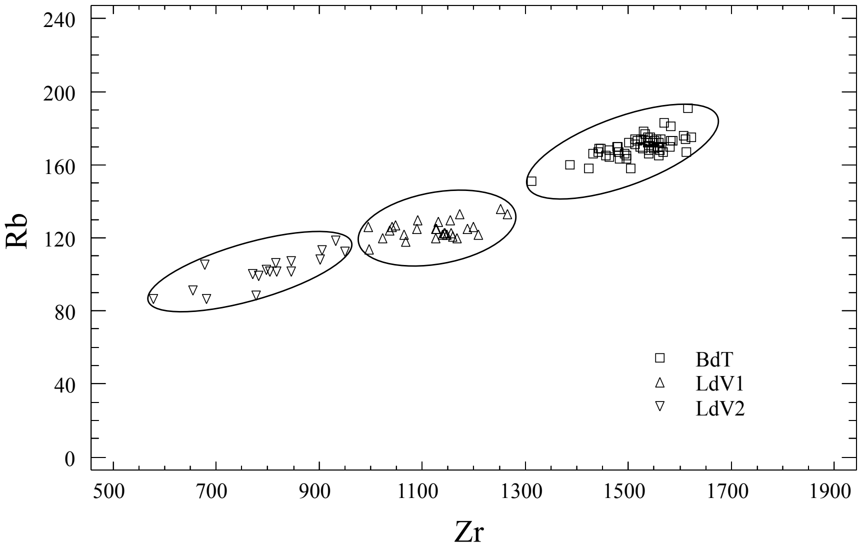

Figure 7. Graph distinguishing Pantelleria subsources (Balata dei Turchi, Lago di Venere 1 & 2). The ellipses are boundaries for the geological samples tested.

At archaeological sites, different contexts may have been representative of production or use areas, ritual activities, burial offerings, or trash deposits. The presence of cores, debitage, blades and other tools (Figure 8) indicates local production, while the absence of primary reduction waste flakes suggests the main preparation of cores closer to the geological source, probably by lithic specialists. The distribution of obsidian over great distances, over sea and land, was likely to have been embedded with other materials. In general, obsidian artifacts are not found in special contexts, even at sites hundreds of kilometers from their sources. It appears that cores were likely produced close to the geological sources and transported over great distances, with blades and other tools then produced on a local basis.


Figure 8. Examples of obsidian artifacts tested: core, blade, flakes

ARTIFACT ANALYSES

Analyses using the pXRF have been conducted on more than 7200 obsidian artifacts from the central/western Mediterranean. These come from about 175 different archaeological sites, although many were survey rather than formal excavation sites. In most cases, the entire obsidian assemblage was analyzed, and only in a few cases were there so many artifacts that a random selection was analyzed. Ten or more obsidian artifacts have been found and analyzed at nearly 100 of the sites, and 50 or more at 40 of the sites, sufficient for statistical comparisons (Table 2). In nearly all cases, the entire archaeological assemblage has been analyzed by the pXRF, while in just a few cases with several hundred artifacts that a random sample was selected. Visual characteristics and descriptive information were also recorded, and along with contextual information (if any), will be incorporated in the overall interpretations of obsidian use for different geographic areas and in different time periods. Results have been published for some sites [16, 17, 18, 19, 31, 32, 33], while most of the analyses were conducted within the last few years and reports are in various stages of preparation, submission, and review.

DISCUSSION

Sourcing analyses conducted over the last 40 years, including with the pXRF in the last decade, show that in the Neolithic period (ca. 6000-3000 BC), obsidian from Lipari and Sardinia (Monte Arci) was the most widely used in the central and western Mediterranean. Obsidian from Lipari reached as far as southern France, northern Italy, and Croatia, while obsidian from Sardinia reached eastern Spain, southern France, and from northern to southern peninsular Italy [33]. Palmarola obsidian was used with less frequency, but also made its way to much of peninsular Italy and even across the Adriatic; Pantelleria was the most restricted, used mostly in western Sicily, Tunisia, and Malta. During the Neolithic, small numbers of Carpathian obsidian reached the Dalmatian coast, but surprisingly no Lipari obsidian has been found in Albania or Greece, and no Melos obsidian has been found in southern Italy. Only in the Copper Age did some Melos obsidian make its way to an Adriatic island. Obsidian was still regularly being used in the Copper and Early Bronze Ages in Sardinia, and in and near Sicily.

Regarding the need for identification of specific obsidian subsources, it has been shown that the use of the Monte Arci (Sardinia) subgroups clearly changed between the Early and Late Neolithic, with type SA decreasing, and the use of SB2 becoming nearly absent at sites in both Sardinia and Corsica [34, 35]; this is in contrast to the clear dominance of type SA in southern France, with multiple sites suggesting different selection criteria and/or direct acquisition, in particular at Terres Longues where the more than 4000 artifacts found suggests it might have been a redistribution center [36]. The much larger number of analyses by pXRF has only reinforced the chronological change in Monte Arci subsource usage.

For Lipari, the Gabellotto Gorge subgroups account for ~99% of all artifacts analyzed, while only a small number have been assigned to the Canneto Dentro subsource, and mostly at sites in Sicily rather than in peninsular Italy. This may suggest more direct visits to Lipari from Sicily, rather than from Calabria. For Pantelleria, seemingly not regularly occupied during the Neolithic, Balata dei Turchi (which has three layers representing different formation episodes, but not distinguishable with this pXRF) is far more dominant than the two Lago di Venere subsources, and this is likely due to the much greater quantity and size of the raw material and its

Table 2. Central/western Mediterranean sites with 10 or more obsidian artifacts tested by pXRF

Country	Region	Site No.	Site	No. of Artifacts
Croatia	Istria	1	Kargadur	21
Croatia	Dalmatia	2	Danilo	58
Croatia	Dalmatia	3	Loc. Musa	33
Croatia	Dalmatia	4	Palagruza	49
Croatia	Dalmatia	5	Pokrovnic	17
Croatia	Dalmatia	6	Susac	64
Croatia	Slavonia	7	Samatovci	28
France	Corsica	8	A Fuata	17
France	Corsica	9	Castellare	21
France	Corsica	10	La Pietra	44
France	Corsica	11	Lumaca	20
France	Corsica	12	Monte Ortu	22
Italy	Calabria	13	Acconia	170
Italy	Calabria	14	Bova Marina	197
Italy	Calabria	15	Capo Alfiere	150
Italy	Calabria	16	Crotone	331
Italy	Calabria	17	Crotone Mandria Vituso	14
Italy	Calabria	18	Favella	44
Italy	Calabria	19	Grotta del Romito	11
Italy	Calabria	20	Grotta dellla Madonna	29
Italy	Calabria	21	Piani della Corona	141
Italy	Calabria	22	Saracena	467
Italy	Calabria	23	Serra D'Aiello	130
Italy	Calabria	24	Sibari	253
Italy	Calabria	25	Tiriolo	59
Italy	Campania	26	Ausino	21
Italy	Campania	27	Venafro	132
Italy	Puglia	28	Masseria La Lamia	13
Italy	Puglia	29	Passo di Corvo	12
Italy	Puglia	30	Santa Cecilia	14
Italy	Puglia	31	Zinzulusa	16
Italy	Sardinia	32	Cantoniera Frumini	10
Italy	Sardinia	33	Contraguda	155
Italy	Sardinia	34	Domus de janas di Triarzu	10
Italy	Sardinia	35	Duos Nuraghes	244
Italy	Sardinia	36	Grotta San Bartolomeo	40
Italy	Sardinia	37	Grotta Sant'Elia	10
Italy	Sardinia	38	Mes'e Arrius	10
Italy	Sardinia	39	Nuraghe Tiria	10
Italy	Sardinia	40	Ortu Comidu	147
Italy	Sardinia	41	Palas de Casteddu	10
Italy	Sardinia	42	San Sergio	19
Italy	Sardinia	43	Santa Caterina di Pittinuri	126
Italy	Sardinia	44	Sant'Anna	15
Italy	Sardinia	45	Serbine	35
Italy	Sardinia	46	Serra de Castius	10
Italy	Sardinia	47	Simaxis	10
Italy	Sardinia	48	Su Casteddu Becciu	11
Italy	Sardinia	49	Su Cuccuru de Is Arrius	20
Italy	Sardinia	50	Urpes	45

Table 2 (continued)

Country	Region	Site No.	Site	No. of Artifacts
Italy	Sicily	51	Aidone	41
Italy	Sicily	52	Capreria	12
Italy	Sicily	53	Casa Bastione	68
Italy	Sicily	54	Casalicchio	77
Italy	Sicily	55	Castelbuono	100
Italy	Sicily	56	Casteltermini (Loc. La Grazia)	35
Italy	Sicily	57	Cava Canabarbara	10
Italy	Sicily	58	Contrada Caduta (Licata)	52
Italy	Sicily	59	Contrada Orto del Conte	70
Italy	Sicily	60	Fontanazza Monte Grande	50
Italy	Sicily	61	Grotta d'Oriente	26
Italy	Sicily	62	Isola di Ognina	140
Italy	Sicily	63	La Muculufa 1	20
Italy	Sicily	64	Matrensa	124
Italy	Sicily	65	Megara Hyblea	127
Italy	Sicily	66	'Npisu	14
Italy	Sicily	67	Paceco Grotta Maiorana	19
Italy	Sicily	68	Palma di Montechiaro (Licata)	44
Italy	Sicily	69	Partanna	18
Italy	Sicily	70	Poggio Rosso	22
Italy	Sicily	71	San Basilio	16
Italy	Sicily	72	Serra del Palco	42
Italy	Sicily	73	Stentinello	133
Italy	Sicily	74	S. Martino	142
Italy	Sicily	75	TRB (Tornambe')	51
Italy	Sicily	76	Tre Fontane	62
Italy	Sicily	77	Valdesi	42
Italy	Sicily	78	Vallone Inferno	74
Italy	Sicily islands	79	Contrada Diana	204
Italy	Sicily islands	80	Filo Braccio (Filicudi)	50
Italy	Sicily islands	81	Lampedusa	58
Italy	Sicily islands	82	Pta. Milazzese (Panarea)	45
Italy	Sicily islands	83	Rinicedda 1	205
Italy	Sicily islands	84	Ustica - Faraglioni	307
Italy	Sicily islands	85	Ustica - Parrish C.G. Seminara collections	129
Italy	Sicily islands	86	Ustica - San Bartolicchio quarter	11
Italy	Sicily islands	87	Ustica - Spalmatore	28
Italy	Sicily islands	88	Ustica - Villaggio Cardoni	96
Malta	Gozo	89	Brochtorff Circle	60
Malta	Malta	90	Skorba	296
Malta	Malta	91	Tas-Silg	29
Tunisia	Sousse	92	Hergla	13
Tunisia	Nabeul	93	Zembra	33

availability along the southern coast. Palmarola is a tiny island with no drinkable water source; most of the geological obsidian is found in the Tramontana area at the northern end, with some also found at the southeastern tip (also not distinguishable with this pXRF). The protected bay on the northwest side would likely have been the main stop during the Neolithic.

The most significant discoveries from the analysis of such large numbers of obsidian artifacts are the directions and greater distances than expected that are now documented. In particular the reach of Sardinian obsidian into central and southern Italy, and of Lipari as well as Palmarola obsidian across the peninsula to the Adriatic and Croatia, is at first surprising [19]. The quantity of obsidian found at many sites suggests that maritime travel was fairly regular from the beginnings of the Neolithic, while the eastward directions are the opposite of that for the spread of the agricultural package of animal husbandry, crop cultivation, year-round settlement, and ceramic production. Obsidian from these island sources was used regularly, continuing until the Copper Age, if not later in some areas. The absence of preserved boats or other vessels (other than later period inland canoes) and artistic depictions has led to a broad range of ideas about their size and type (with sails?), and the seasonal/annual frequency of large open-water travel.

Pantelleria is the furthest from the mainland, 100 km southwest of Sicily, yet accounts for nearly 40% of the abundant obsidian assemblage at Uzzo Cave on the northwest coast of Sicily, an extra 60 km further (as the crow flies). On the small island of Ustica, yet another 70 km north of Palermo into the Tyrrhenian Sea (total >225 km), Pantelleria obsidian was still regularly used at several different sites, even if only 16% of the obsidian assemblage. Ustica is still more than 150 km from Lipari, but the much greater dominance of Lipari obsidian on Ustica suggests direct contact with Lipari, rather than travel from the Aeolian Islands to northeast Sicily, then by land or sea westward along the north coast to Palermo, and lastly by sea to Ustica.

The complexity of obsidian transport and distribution is exemplified by the inland site of Casalicchio in west-central Sicily where Pantelleria obsidian is >55%, far more than other western Sicily sites (second is 24% at nearby Serra del Palco), and with lithic assemblages from sites in central and eastern Sicily almost entirely Lipari obsidian. While the geological sources of obsidian artifacts are fairly easily identified by pXRF, interpretations of the transport and exchange of obsidian is more difficult, as it was likely accompanied by other materials including ceramics, textiles, animals, food, etc. that are either not preserved and/or their origins cannot easily be tested.

The socioeconomic nature of Neolithic cultural groups is well established, yet long-distance transport appears to vary considerably; by the end of the Neolithic, however, there may have been more territorial control, both over the sources (especially on Lipari and Sardinia) and for land-based transport [33]. The particular selection of obsidian types is best illustrated by the burial and ritual site of Xaghra (Brochtorff Circle) on the island of Gozo when compared with the residential and ritual site of Skorba on Malta, less than 15 km away. Pantelleria dominates (72%) the Xaghra obsidian artifacts, while is less than 25% at Skorba. Extensive examination of potential use-wear traces and lithic techno-typology would yield stronger hypotheses for this selection.

On Sardinia and in Corsica, the chronological change in subsource selection has been well-established. In the Early-thru-Middle Neolithic, SA, SB, and SC were regularly used at almost all sites tested, while by the Late Neolithic the lithic assemblages are dominated by SC with little use at all of SB [34]. By that time, major production sites near Sennixeddu (SC) were established, and the SC obsidian continued to dominate lithic assemblages through the Bronze Age Nuragic period [16, 31].

CONCLUSIONS

The use of a non-destructive, portable XRF to analyze thousands of archaeological obsidian artifacts has revolutionized the data now available for making interpretations about prehistoric trade and exchange in the central and western Mediterranean, in particular variations based on particular contexts and site locations as well as changes over time. The pXRF provides a highly beneficial "package" of analyzing great numbers of artifacts non-destructively and rapidly without needing to export them from museums and facilities in many countries. Archaeologist users of the pXRF must nevertheless be educated consumers and fully understand its limitations. Future pXRF instruments are likely to have even lower detection limits, expanding the number of trace elements that may be used for distinguishing obsidian sources and sources.

ACKNOWLEDGMENTS

I thank many colleagues and administrators in Italy, France, Malta, Croatia, and other countries for arranging the permission to analyze obsidian artifacts in many different museums and storage facilities. I also appreciate the assistance from two colleagues in particular in conducting the analyses over the last several years, Andrea Vianello and Kyle Freund. Some funding for this research has been provided by the University of South Florida.

REFERENCES

1. J.R. Cann and C. Renfrew, The characterization of obsidian and its application to the Mediterranean region, *Proceedings of the Prehistoric Society* **30**, 111-33 (1964).

2. R.H. Tykot, Chemical fingerprinting and source-tracing of obsidian: the central Mediterranean trade in black gold, *Accounts of Chemical Research* **35**, 618-627 (2002).

3. R.H. Tykot, Scientific methods and applications to archaeological provenance studies, in *Physics Methods in Archaeometry. Proceedings of the International School of Physics "Enrico Fermi"*, edited by M. Martini, M. Milazzo and M. Piacentini (Società Italiana di Fisica, Bologna, 2004) pp. 407-432.

4. R.H. Tykot, Obsidian in Prehistory, in *Encyclopedia of Glass Science, Technology, History, and Culture*, edited by P. Richet (John Wiley & Sons, Inc., 2017).

5. B.R. Hallam, S.E. Warren, C. Renfrew, Obsidian in the western Mediterranean: characterisation by neutron activation analysis and optical emission spectroscopy, *Proceedings of the Prehistoric Society* **42**, 85-110 (1976).

6. R.H. Tykot, Characterization of the Monte Arci (Sardinia) obsidian sources, *Journal of Archaeological Science* **24**, 467-479 (1997).

7. G.M. Crisci, M. Ricq-De Bouard, U. Lanzafame, A.M. De Francesco, Nouvelle méthode d'analyse et provenance de l'ensemble des obsidiennes neolithiques du Midi de la France, *Gallia Préhistoire* **36**, 299-327 (1994).

8. V. Francaviglia, Characterization of Mediterranean obsidian sources by classical petrochemical methods, *Preistoria Alpina* **20**, 311-332 (1986).

9. A.M. De Francesco, G.M. Crisci, M. Bocci, Non-destructive analytic method using XRF for determination of provenance of archaeological obsidians from the Mediterranean area: A comparison with traditional XRF methods, *Archaeometry* **50**, 337-350 (2008).

10. F.-X. Le Bourdonnec, G. Poupeau, C. Luglie, SEM-EDS analysis of western Mediterranean obsidians: a new tool for Neolithic provenance studies, *C. R. Geoscience* **338**, 1150-1157 (2006).

11. B. Gratuze, Obsidian characterization by laser ablation ICP-MS and its application to prehistoric trade in the Mediterranean and the Near East: Sources and distribution of obsidian with the Aegean and Anatolia, *Journal of Archaeological Science* **26**, 869-881 (1999).

12. D. Barca, A.M. De Francesco, G.M. Crisci, Application of Laser Ablation ICP-MS for characterization of obsidian fragments from peri-Tyrrhenian area, *Journal of Cultural Heritage* **8**(2), 141-150 (2007).

13. R.J. Speakman, M.D. Glascock, R.H. Tykot, C. Descantes, J.J. Thatcher, C.E. Skinner, K.M. Lienhop, Selected applications of laser ablation ICP-MS to archaeological research, in Archaeological Chemistry: Analytical Methods and Archaeological Interpretation, edited by M.D. Glascock, R.J. Speakman, R.S. Popelka-Filcoff (ACS Publication Series 968, American Chemical Society, Washington, DC, 2007) pp. 275-296.

14. R.H. Tykot, Using non-destructive portable X-ray fluorescence spectrometers on stone, ceramics, metals, and other materials in museums: advantages and limitations. *Applied Spectroscopy* **70**(1), 42-56 (2016).

15. Bruker, Tracer series pXRF spectrometer, https://www.bruker.com/products/x-ray-diffraction-and-elemental-analysis/handheld-xrf/tracer-iii/overview.html [accessed November 15, 2016].

16. R.H. Tykot, Sourcing of Sardinian obsidian collections in the Museo Preistorico-Etnografico 'Luigi Pigorini' using non-destructive portable XRF, in *L'ossidiana del Monte Arci nel Mediterraneo. Nuovi apporti sulla diffusione, sui sistemi di produzione e sulla loro cronologia Atti del 5°Convegno internazionale (Pau, Italia, 27-29 Giugno 2008),* edited by C. Lugliè (NUR, Ales, 2010) pp. 85-97.

17. R.H. Tykot, L. Lai, C. Tozzi, Intra-site obsidian subsource patterns at Contraguda, Sardinia (Italy), in *Proceedings of the 37th International Symposium on Archaeometry, 13th-16th May 2008, Siena, Italy*, edited by I. Turbanti-Memmi (Springer, 2010) pp. 321-328.

18. R.H. Tykot, K.P. Freund, A. Vianello, Source analysis of prehistoric obsidian artifacts in Sicily (Italy) using pXRF, in *Archaeological Chemistry VIII. ACS Symposium Series* **1147**, 195-210 (2013). Edited by R.A. Armitage and J.H. Burton.

19. R.H. Tykot, Obsidian use and trade in the Adriatic, in *The Adriatic, a sea without borders: communication routes of populations in 6000 BC*, edited by P. Visentini and E. Podrug (Civici Musei di Udine, Museo Friulano di Storia Naturale, 2014) pp. 171-181, 224-225.

20. N. Goodale, D.G. Bailey, G.T. Jones, C. Prescott, E. Scholz, N. Stagliano, C. Lewis, pXRF: a study of inter-instrument performance, *Journal of Archaeological Science* **39**, 875-883 (2012).

21. N. Forster and P. Grave, Non-destructive PXRF analysis of museum-curated obsidian from the Near East, *Journal of Archaeological Science* **39**, 728-736 (2012).

22. A.N. Shugar, Portable X-ray fluorescence and archaeology: Limitations of the instrument and suggested methods to achieve desired results, in *Archaeological Chemistry VIII. ACS Symposium Series* **1147**, 173-195 (2013). Edited by R.A. Armitage and J.H. Burton.

23. I. Liritzis and N. Zacharias, Portable XRF of archaeological artifacts: Current research, potentials and limitations, in *X-ray Fluorescence Spectrometry (XRF) in Geoarchaeology*, edited by M.S. Shackley (Springer, New York, 2013) pp. 109-142.

24. E. Frahm and R.C.P. Doonan, The technological versus methodological revolution of portable XRF in archaeology, *Journal of Archaeological Science* **40**, 1425-1434 (2013).

25. E. Frahm, R. Doonan, V. Kilikoglou, Handheld portable X-ray fluorescence of Aegean obsidians, *Archaeometry* **56**, 228-260 (2014).

26. M. Milič, PXRF characterisation of obsidian from central Anatolia, the Aegean and central Europe, *Journal of Archaeological Science* **41**, 285-296 (2014).

27. V. Francaviglia, Ancient obsidian sources on Pantelleria (Italy). *Journal of Archaeological Science* **15**, 109-22 (1988).

28. R.H. Tykot, T. Setzer, M.D. Glascock, R.J. Speakman, Identification and characterization of the obsidian sources on the island of Palmarola, Italy, *Geoarchaeological and Bioarchaeological Studies* **3**, 107-111 (2005).

29. R.H. Tykot, M.R. Iovino, M.C. Martinelli, L. Beyer, Ossidiana da Lipari: le fonti, la distribuzione, la tipologia e le tracce d'usura, in *Atti del XXXIX Riunione Scientifica dell'Istituto Italiano di Preistoria e Protostoria: Materie prime e scambi nella preistoria italiana, Firenze, 25-27 November 2004*, 592-597 (2006).

30. R.H. Tykot and A.J. Ammerman, New directions in central Mediterranean obsidian studies, *Antiquity* **71**(274), 1000-1006 (1997).

31. K.P. Freund and R.H. Tykot, Lithic technology and obsidian exchange networks in Bronze Age Nuragic Sardinia (Italy), *Archaeological and Anthropological Sciences* **3**, 151-164 (2011).

32. K.P.Freund, R.H. Tykot, A. Vianello, Blade production and the consumption of obsidian in Stentinello period Neolithic Sicily, *Comptes Rendus Palevol* **14**, 207-217 (2015).

33. R.H. Tykot, Obsidian finds on the fringes of the central Mediterranean: exotic or eccentric exchange?, in *Exotica in the Prehistoric Mediterranean*, edited by A. Vianello (Oxbow Books, 2011) pp. 33-44.

34. R.H. Tykot, Obsidian procurement and distribution in the central and western Mediterranean, *Journal of Mediterranean Archaeology* **9**, 39-82 (1996).

35. R.H. Tykot, L'esatta provenienza dell'ossidiana e i modelli di diffusione nel Mediterraneo centrale durante il Neolitico, in *L'ossidiana del Monte Arci nel Mediterraneo: recupero dei valori di un territorio*, a cura di P. Castelli, B. Cauli, F. Di Gregorio, C. Lugliè, G. Tanda & C. Usai (Tipografia Ghilarzese, Ghilarza, 2004) pp. 118-132.

36. V. Lea, The diffusion of obsidian in the northwestern Mediterranean: toward a new model of the Chassey culture? *Journal of Mediterranean Archaeology* **25**, 147-173 (2012).