Chemical Fingerprinting and Source Tracing of Obsidian: The Central Mediterranean Trade in Black Gold

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ABSTRACT

Chemical fingerprinting using major or trace element composition is used to characterize the Mediterranean island sources of obsidian and can even differentiate as many as nine flows in the Monte Arci region of Sardinia. Analysis of significant numbers of obsidian artifacts from Neolithic sites in the central Mediterranean reveals specific patterns of source exploitation and suggests particular trade mechanisms and routes. The use of techniques such as X-ray fluorescence, the electron microprobe, neutron activation analysis, and laser ablation ICP mass spectrometry are emphasized in order to produce quantitative results while minimizing damage to valuable artifacts.

Introduction

The study of prehistoric exchange systems is a fundamental topic of archaeological research, as the successful reconstruction of trade may illuminate not only economic aspects of ancient societies but also the social and political climate in which it operated.[1-3] While changing theoretical emphases in recent decades have affected how archaeological data relevant to exchange systems have been interpreted, technological advancements in our ability to determine the source of archaeological materials have greatly enhanced the quantity and quality of these data. This is reflected in the goals, design, and implementation of modern provenance studies.

In the Mediterranean, provenance studies have typically focused on ceramics, ground stone tools, flint, and obsidian. A volcanic glass widely used for stone tools (Figure 1), obsidian is an ideal material for reconstructing trade since it occurs geologically in a limited number of locations, is frequently found on archaeological sites even great distances from a source, and may be chemically "fingerprinted", allowing definitive source attributions of artifacts.[4,5] The application of currently available analytical methods permits the construction of statistically significant geographic and chronological patterns of obsidian
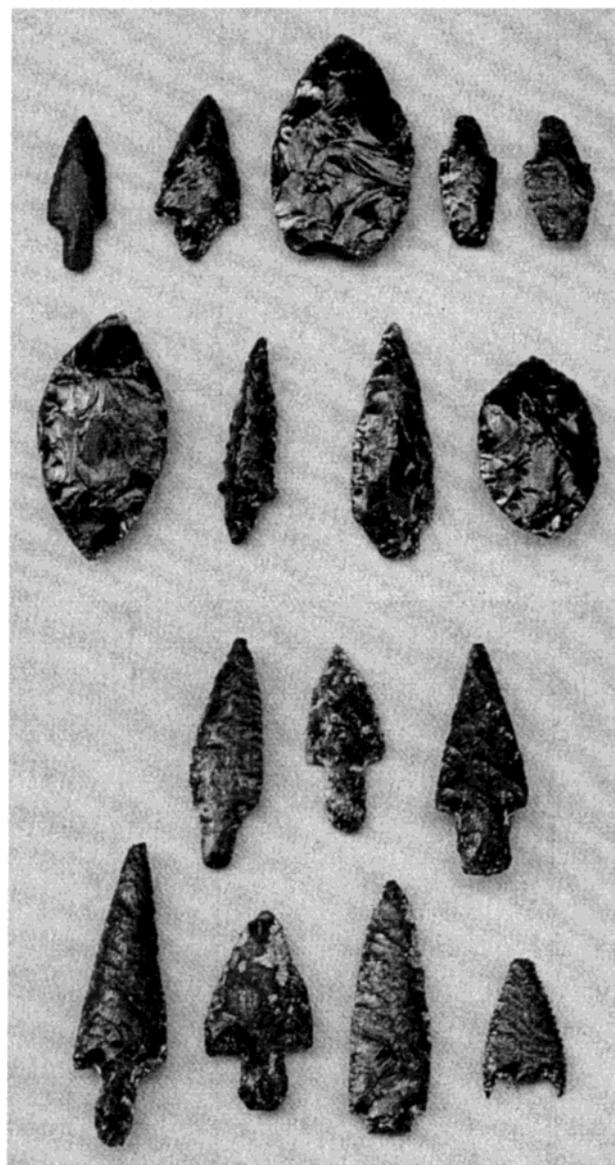
FIGURE 1. Formal obsidian tools from a Neolithic site in Sardinia. Simple flakes and blades without evidence of retouch are much more commonly found at archaeological sites.

source exploitation, and new interpretive schemes reestablish exchange as critically important for understanding all stages of the *chaîne opératoire* of lithic raw material acquisition, modification, use, and discard. As the most visible indicator of Neolithic interactions in the Mediterranean, obsidian use is also relevant to discussions of the earliest settlement of the Mediterranean islands, the transition from hunting and gathering to an agricultural way of life, long-distance exchange networks, craft specialization, and the development of social differentiation and other precursors of more complex Copper and Bronze Age societies.

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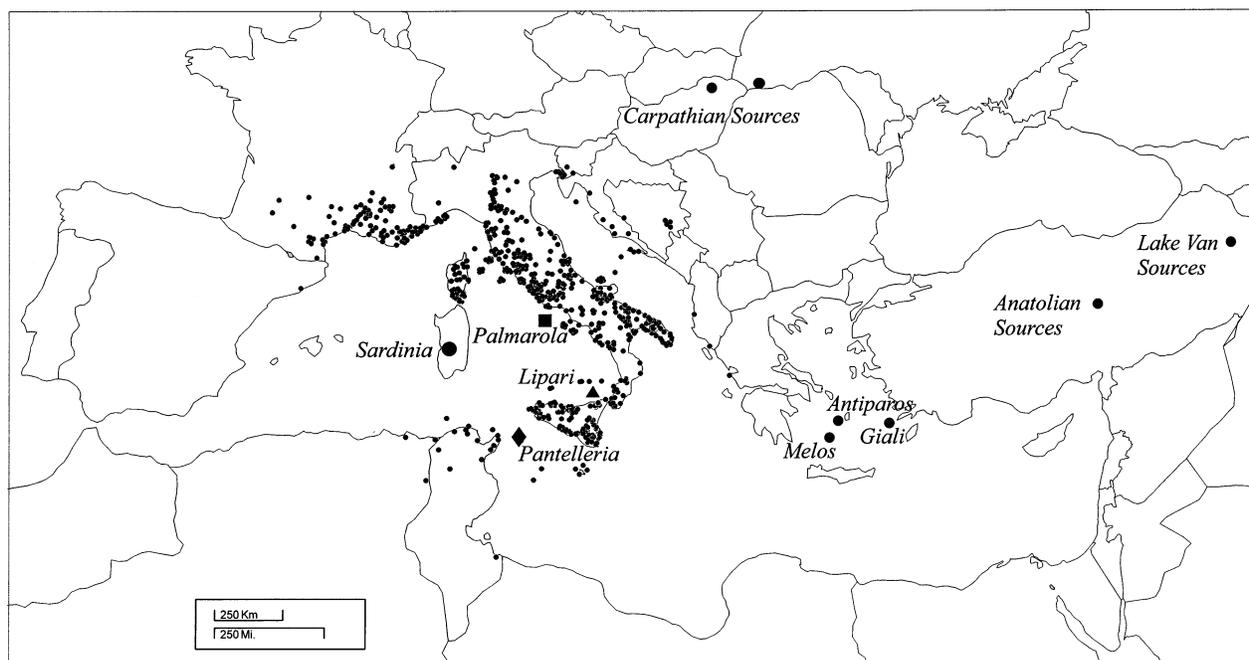* E-mail: rtykot@chuma1.cas.usf.edu. Tel.: 813 974-7279. Fax: 813 974-2668.

FIGURE 2.   Obsidian sources in the Mediterranean area and archaeological sites with obsidian artifacts in the central Mediterranean. Not shown are hundreds of sites with obsidian on Sardinia.

Previous Research

Long before chemical characterization studies of obsidian began in the 1960s, the Mediterranean islands of Giali, Lipari, Melos, Palmarola, Pantelleria, and Sardinia were known to have obsidian sources which likely supplied the raw material used for artifacts found at archaeological sites in the Mediterranean (Figure 2). While an ordinary wet chemical analysis of major elements had led to the surprising (and erroneous) conclusion that obsidian artifacts in Malta were of Melian origin, the seminal contribution of Cann and Renfrew demonstrated that most of the island sources could be differentiated on the basis of their trace element composition (especially barium, zirconium, niobium, and yttrium) as determined by optical emission spectroscopy.[6] During the 1970s and 1980s, further research on the Mediterranean sources using neutron activation analysis (NAA) and X-ray fluorescence (XRF) was successful not only in attributing artifacts to specific islands but also in demonstrating the existence of more than one flow on both Sardinia and Melos.[7-9] More recent applications using XRF[10-12] and PIXE[13] have utilized a nondestructive approach in which no sample is removed from the artifact. Nondestructive analysis using a scanning electron microscope equipped with energy dispersive spectrometers is sufficient to discriminate among all of the Mediterranean island sources but only some of the intraisland subsources.[14] The Mediterranean island sources can also be differentiated by their geological age, usually determined by fission-track dating, although this technique often cannot distinguish among flows of similar age and is therefore of limited value for identification beyond the island level.

The general distribution of obsidian from the Mediterranean island sources may be constructed from the elemental and fission track data.[15-17] In the Aegean region, obsidian artifacts from relatively few archaeological sites have been analyzed since it is generally assumed that Melos supplied virtually all of the obsidian utilized in mainland Greece, Crete, and the Aegean islands.[18,19] Obsidian from Melos has been confirmed at but a single site west of the Balkans,[20] and a few pieces of Anatolian obsidian have been identified in Eastern Europe and Greece.[21] The Carpathian sources[22-24] are responsible for a few artifacts found in northern Italy and some as far east as Greek Macedonia.[25] In the central Mediterranean, virtually all archaeological obsidian artifacts come from the four Italian island sources.[26] Obsidian from Lipari and Sardinia is the most widely distributed, while obsidian from Palmarola appears limited to the Italian peninsula, and obsidian from Pantelleria has only rarely been identified north of Sicily.

New Directions

Despite this long history of obsidian studies, until recently no systematic program of field survey and documentation, physical and chemical analysis, and detailed publication has been completed for the Mediterranean island sources. Significantly, the obsidian from each island has been treated by most archaeologists as deriving from a single source, when in fact it occurs as multiple primary outcrops and secondary deposits.[27] Notably, earlier analyses of artifacts made of obsidian from Sardinia[6,7] indicated that multiple, chemically differentiable sources exist, and subsequent research by several teams has resulted in the location and characterization of as many as nine chemically distinct obsidian sources in the Monte Arci region, with at least five exploited in antiquity.[9,28-31]

Recently, this author has also directed an intensive geoarchaeological survey of the obsidian sources on Lipari, Palmarola, and Pantelleria, identifying multiple flows and visual types on each island. My research program represents the only sustained effort to fully characterize the Mediterranean island sources, to analyze significant numbers of archaeological artifacts and interpret prehistoric exploitation patterns and their socioeconomic significance.[3,15,30−38]

Another advance has been the application of nondestructive or minimally destructive, relatively inexpensive analytical techniques, especially to large numbers of artifacts from single archaeological contexts. The analysis of large numbers of artifacts—even of entire site assemblages—has led to the significant revision of distribution patterns based on earlier research using limited numbers of samples. Obsidian from Palmarola, rarely documented previously in northern Italy, is actually well represented at a few sites,[39,40] while Pantellerian obsidian is continuously present in the neolithic levels of Grotta dell'Uzzo in Sicily,[41] when Lipari was previously thought to be a nearly exclusive source for Sicily. Chronological change has been documented within sites such as Arene Candide[40] and Filiestru,[15] and the work on obsidian provenance is now integrated with studies of reduction technology and use−wear.[42,43] One preliminary observation for northern Italy is that a shift occurred in the Late Neolithic toward the presence of exclusively small blades of Lipari obsidian while Sardinian obsidian was obtained as both prepared cores and larger blades. At the same time, sites in southern France employed obsidian almost exclusively from a single Monte Arci subsource (SA), suggesting selection or transport mechanisms different than those for Corsica and northern Italy.[15]

Clearly, important information about the exploitation and use of raw materials, and their economic and sociopolitical significance, can be obtained from detailed, large-scale, integrated studies of Mediterranean obsidian sources. In order for a provenance study of lithic artifacts to be successful, however, there are several prerequisites: (1) all relevant geological sources must be known; (2) these sources must be characterized for the properties (e.g., color, density, and mineralogic, elemental, or isotopic composition) which will be measured for the artifacts; (3) one or more properties must be homogeneous within a source; (4) measurable, statistically valid differences between sources must exist for one or a combination of these parameters; and (5) they must be measurable using analytical methods appropriate for archaeological artifacts. In the Mediterranean, these conditions have been met at the island level of resolution, and in some cases at the level of specific source localities.

Monte Arci, Sardinia (Figure 3)

Unlike all other Mediterranean island sources of obsidian, Sardinia is a large land mass, at approximately 25 000 km^2, and was first settled prior to the exploitation of its obsidian sources.[36] In a comprehensive survey of the Monte Arci

zone, Puxeddu[44] found 246 archaeological sites with obsidian in an area of ca. 200 km^2, several of them major workshops for the production of tools. The Monte Arci volcanic complex includes acidic lavas which often grade into a perlitic facies where obsidians are likely to occur; K−Ar and fission-track dates on geological obsidian samples have uncorrected ages of about 3.2 million years. The recognition by the 1970s that at least three chemical groups (SA, SB, SC) were represented among artifacts raised questions about which sources were utilized, since only one had been analyzed,[6,7] and both translucent and opaque obsidian had long been recognized in archaeological assemblages.

In the 1980s, several independent studies contributed to the characterization of the multiple Monte Arci obsidian outcrops. Unfortunately, results of the first study are available only in a brief conference paper;[28] no details about the obsidian deposits themselves were published with the second study;[9] and the third is an unpublished dissertation.[29] None of these studies included samples from all source localities.

My more recent survey of the Monte Arci zone located an in situ obsidian source on the northeast side of Monte Arci for the first time, as well as multiple localities with in situ obsidian on the northwestern slopes of Monte Arci, in addition to the well-known deposits at Conca Cannas.[30] Very glassy, black but highly translucent obsidian was found in situ near Conca Cannas and Su Paris de Monte Bingias, in nodules up to 40 cm in length. Less glassy and black but usually opaque obsidian was found in situ at high elevations on Punta Su Zippiri, Punta Nigola Pani, and Monte Sparau North, and in the form of bombs up to 30 cm in length on the slopes of Cuccuru Porcufurau. Very glassy obsidian, variable in transparency and sometimes with phenocrysts up to 2 mm in diameter, was found to occur in large blocks (occasionally up to 1 m in length) near Cucru Is Abis, Seddai, Conca S'Ollastu, and Bruncu Perda Crobina. Black, opaque, and less glassy obsidian, frequently with well-defined external gray bands, was found in situ along the ridge from Punta Pizzighinu to Perdas Urias on the northeastern side of Monte Arci, in blocks up to 20 cm long; in one area here was found a concentration of pieces with red streaks. Abundant obsidian in loose but natural blocks may also be found at lower elevations, from Santa Pinta to Mitza Sa Tassa. The variability in visual characteristics observed for different areas of Monte Arci suggested that it should be possible to match the previously identified chemical source groups to specific geographic localities.

Analytical Methods and the Characterization of Black Gold

Continuing our systematic approach to the characterization of the central Mediterranean obsidian sources, the geological sample collection described above was followed by comprehensive physical and chemical analysis and statistical evaluation of the results. Only then were
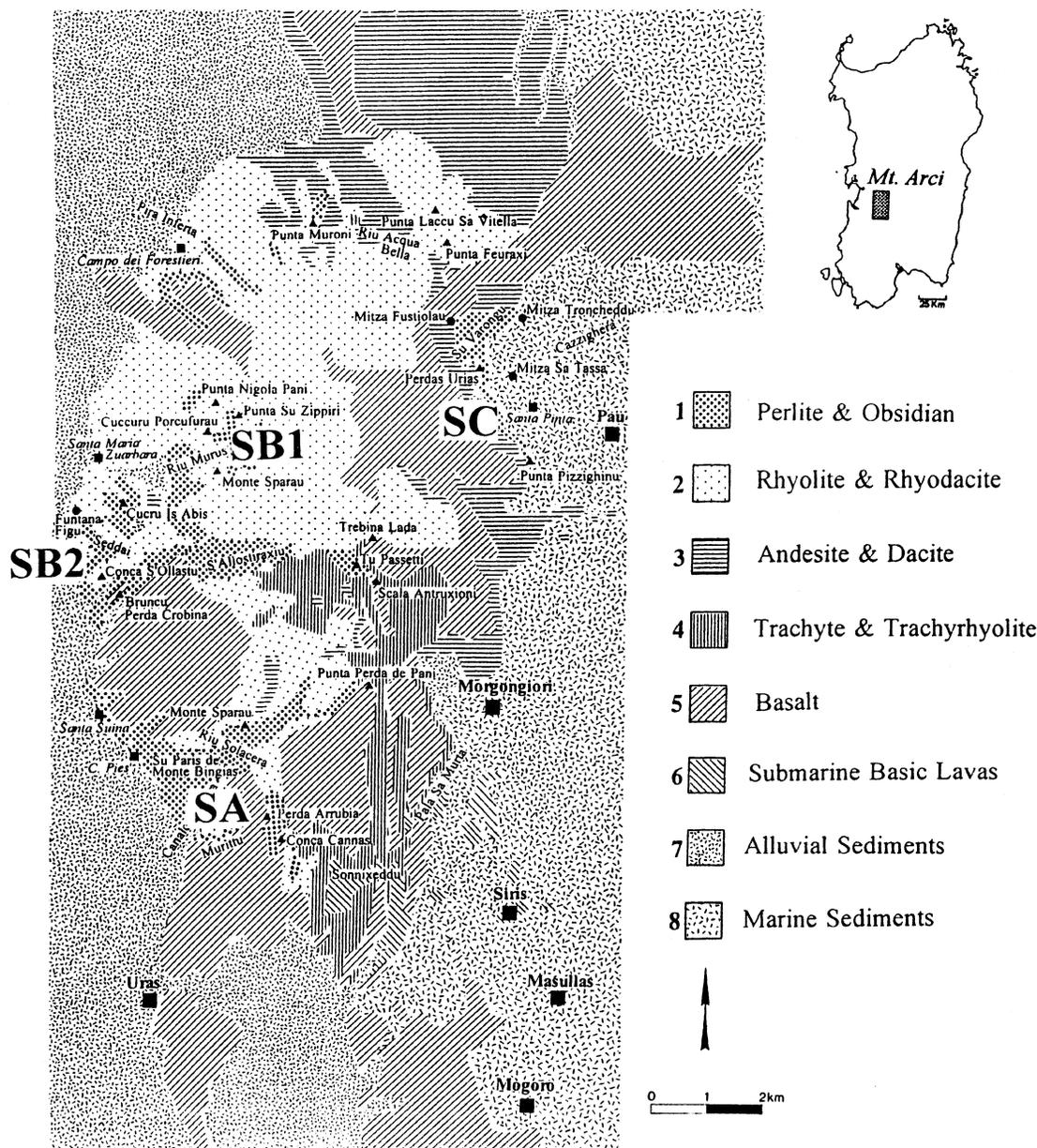
**FIGURE 3.** Obsidian sources in the Monte Arci region of Sardinia.

protocols developed which were necessary and sufficient for the provenance analysis of archaeological artifacts.[45]

A multimethod exploratory approach was designed to chemically characterize geological obsidian samples from Sardinia and, more recently, Lipari, Palmarola and Pantelleria. For the full chemical characterization of geological samples from Sardinia, a combination of electron microprobe analysis, XRF, NAA, and ICP mass spectrometry was employed.

The electron microprobe, equipped with wavelength dispersive spectrometers, is an excellent method for the quantitative determination of 10 major/minor elements and for assessing the heterogeneity of individual sources and artifacts. Only a tiny sample must be removed from artifacts, with 15–20 samples mounted and polished on a single 1-in. epoxy disk.[31,34] Mounted samples may be reanalyzed as necessary, by microprobe or by other methods including laser ablation ICP-MS. Many artifacts may be quantitatively analyzed by the microprobe at very low per-sample costs. The microprobe (or SEM) with energy dispersive spectrometers also has been used for obsidian studies in the Mediterranean and elsewhere,[14,46] but Ti, Mg, Mn, and P are typically below the minimum detection limits of EDS systems, and these are useful elements for discriminating among the Mediterranean island sources and subsources.

The principle of X-ray fluorescence is similar to that used for electron microprobe analysis, but XRF instruments achieve considerably lower (better) elemental detection limits, allowing for the analysis of a broad range of trace elements. XRF would be the preferred technique for major, minor, and trace element analysis of homogeneous materials such as obsidian if a sufficiently large (1 cm^2) and flat surface were available and the entire artifact
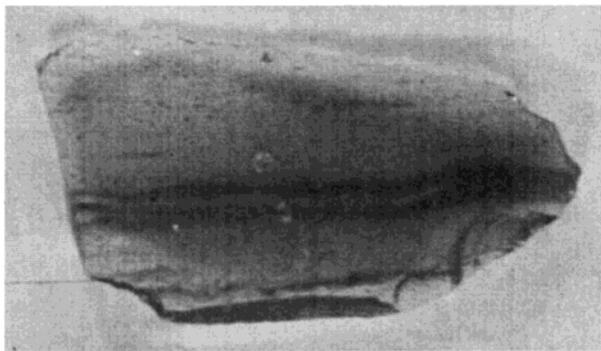
FIGURE 4. Three laser ablation craters are barely visible on this small obsidian artifact attributed to Lipari. The artifact is 2 cm in length.

could fit inside the sample chamber. While these criteria are not obstacles for the analysis of geological specimens, they can be limiting for archaeological collections. Several Mediterranean obsidian studies have used XRF, so some pre-existing data are already available.[8−10,12,28,29,47−49]

Neutron activation analysis, however, has been the workhorse of archaeological provenance studies for three decades. Some 30−35 elements can be routinely measured in a solid or powdered sample, with excellent precision for rare earth elements, although NAA is not appropriate for determining bulk chemical composition in silicate rock samples. The results of several hundred obsidian analyses are available for the Mediterranean region.[7,8,21,29,39,40,50−52] Unfortunately, the unsubsidized cost of analysis by NAA is high, and access to research reactors is expected to decrease significantly in the near future.

ICP-MS is now an established method of trace element analysis with applications in a number of fields including archaeology.[38,53] Compared to NAA, ICP-MS has greater sensitivity for many elements, especially those found in silicate rocks,[54,55] and is probably the best single technique for initially evaluating which trace elements may be useful in an archaeological provenance study. The preparation of silicate samples for solution analysis, however, is both time-consuming and destructive. Solid samples may be introduced using a laser ablation device, but this results in somewhat reduced sensitivity and precision.[56] If this precision is nevertheless sufficient for the separation of all archaeologically significant source groups, though, then LA-ICP-MS becomes an excellent technique for the analysis of obsidian artifacts since samples need not even be removed from whole artifacts and the tiny holes left by the laser (as small as 10 μm in diameter) make this microanalysis technique virtually nondestructive (Figure 4). Another advantage of ICP-MS is that isotope ratio data are also produced, with precisions approaching those of thermal ionization mass spectrometers (at least for multicollector instruments), and strontium,[57] lead, and neodymium isotope ratios are likely to be good discriminators of Mediterranean obsidian sources.

Nearly 200 geological obsidian samples from 20 collection localities in Sardinia were analyzed for 38 major and trace elements using a Fisons PQ 2 Plus quadrupole ICP mass spectrometer. Since the purpose of these initial analyses was to determine how many subgroups could be chemically distinguished, rather than to characterize them quantitatively, calibration curves were generated for only some elements, and the data produced should not be considered indicative of the actual composition of the samples, although in most cases they are reasonably close.[31] Exploratory multivariate statistical analysis initially identified five source groups of workable obsidian (SA, SB1, SB2, SC1, SC2), but it did not seem archaeologically significant to distinguish between two of them (SC1 and SC2) since they are visually indistinguishable and co-occur in the same secondary deposits.[34] A re-examination of the data now shows that the SB1 subgroup may be further subdivided into three discrete sub-subgroups (SB1a, SB1b, SB1c), but it is unlikely that distinctions at this tertiary level are archaeologically significant.

For the quantitative characterization of the Sardinian sources, 125 geological obsidian samples from Monte Arci were analyzed using a Cameca MBX electron microprobe. Samples were excited by a relatively wide (40 μm) 15 keV electron beam, and the X-radiation was measured by WDS with counting times of 10−80 s per element. Samples from Lipari and Pantelleria, and a standard reference material, were also analyzed in order to enable comparison with results from other laboratories and by other methods.[34] The results confirm Francaviglia's finding that the central Mediterranean island sources can be easily distinguished from one another by their major/minor element composition,[9] which is also sufficient for distinguishing at least four Sardinian flows,[31,34] two on Melos, and five on Pantelleria,[47] using simple bivariate plots (Figure 5).

A subset of 60 geological obsidian samples from Sardinia was then quantitatively analyzed for 27 elements by INAA using the 10 MW light-water-moderated Missouri University Research Reactor. Gamma rays were measured at different points during the decay period after irradiation using a high-purity germanium detector. The same set of 60 samples was also analyzed for 15 elements by XRF using a Spectrace 5000 spectrometer at the Northwest Research Obsidian Studies Laboratory. Depending on the elements analyzed, samples were scanned in air or vacuum paths for 200−600 s, with X-ray tube settings of 12−50 kV. The NAA and XRF results confirmed the initial findings by ICP-MS of the existence of seven chemically distinguishable groups (Figure 6). The microprobe, NAA, and XRF data are presented in Table 1. The differing chemistries of the relatively coeval Monte Arci obsidian sources are best explained by variable crustal contamination rather than fractional crystallization.[58,59]

Following the assessment that it was archaeologically unnecessary to further subdivide the SB1 and SC sources, the electron microprobe was selected for the analysis of nearly 700 obsidian artifacts from dozens of prehistoric sites, doubling the total number of artifacts analyzed in the central Mediterranean. In addition to the use of bivariate plots of the major elements, robust multivariate statistical analysis was used to attribute each artifact to a specific source. Discriminant functions determined from the geological data were applied to each unknown (ar-
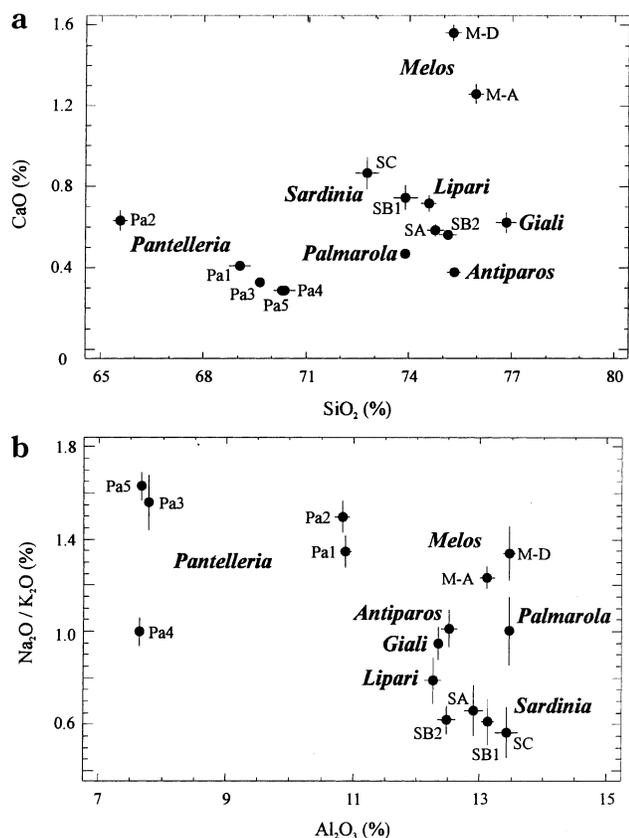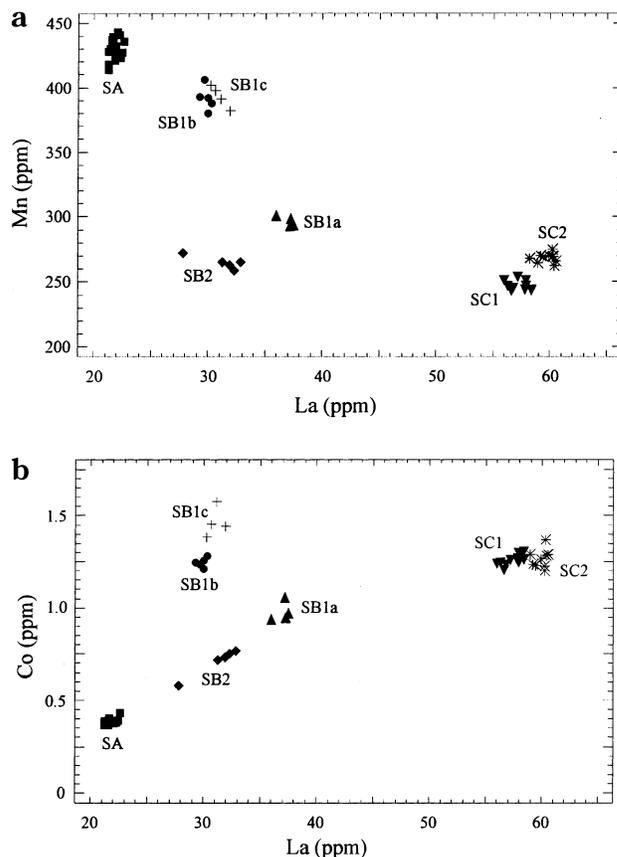
FIGURE 5. Characterizing Mediterranean island obsidian sources. (a) SiO_2 vs CaO; (b) Al_2O_3 vs Na_2O/K_2O. Data adapted from Francaviglia[9,47] and Tykot.[15]

FIGURE 6. High-resolution characterization of the Monte Arci, Sardinia, obsidian sources. Two additional subsources, not illustrated, contain obsidian only in tiny nodules unsuitable for tool use. (a) La vs Co; (b) La vs Mn.

chaeological) sample using the jack-knifing option in the software program BMDP 7M. More than 95% of the artifacts were attributed to an individual subsource with greater than 95% probability.

Discussion and Conclusion

The provenance results now available provide a much more detailed view of the distribution of obsidian from the central Mediterranean island sources (Figure 7). While the distribution map indicates that obsidian from Sardinia and Lipari was much more widely used than obsidian from Palmarola and Pantelleria, it does not quantitatively describe the relative importance of each source or subsource at each archaeological site, nor does it suggest particular transport routes or mechanisms. In particular, it disguises the fact that outside of the results of my own research, only a dozen of the 200 sites shown represent 10 or more analyses. When significant numbers of artifacts are analyzed from individual sites, it is possible to demonstrate real temporal and spatial differences in source exploitation.[37] At Filiestru Cave in northwest Sardinia, for example, the chemical analysis of 86 artifacts indicated that the use of source SB obsidian steadily decreased over the course of the Neolithic period, to be replaced primarily by obsidian from source SC.[15] At Arene Candide on the coast of Liguria, the analysis of 53 artifacts also shows a decrease during the Neolithic in the use of

source SB obsidian and the increasing importance of obsidian blades from Lipari.[40] Factors which result in differential exploitation may include variation in accessibility, quantity, quality, and appearance of the raw material, as well as social, political, and/or technological variables which may control the timing and frequency of access, lithic reduction techniques, transportation routes and mechanisms, and ultimately the function of obsidian artifacts in particular regions and time periods.

Perhaps most interesting is a comparison of the relative source frequencies by region (Figure 8). As expected, Palmarola obsidian is never dominant, accounting for just over 20% of obsidian assemblages in central Italy. Obsidian from Pantelleria surprisingly accounts for nearly 40% of the analyzed obsidian in Sicily but only 20% of the obsidian in Malta, which is much farther from the Lipari source.[60] Obsidian from Lipari dominates assemblages throughout southern and central Italy but tapers off in frequency with distance, comprising about 30% of the obsidian tested from sites in northern Italy and only 17% in southern France. This falloff is characteristic of down-the-line exchange systems in which obsidian would have been traded from one village to the next in ever decreasing quantity.[1] That no obsidian from Lipari has been identified in Corsica (or Sardinia) would support the hypothesis that obsidian was transported northward from Lipari primarily

Table 1. Elemental Composition of Obsidian Subsources, Monte Arci, Sardinia

	SA	SB1a	SB1b	SB1c	SB2	SC1	SC2
SiO_2[a]	74.72 ± 0.26	73.77 ± 0.26	74.01 ± 0.09	74.14 ± 0.48	75.05 ± 0.33	72.48 ± 0.19	72.68 ± 0.39
Al_2O_3	13.40 ± 0.15	13.68 ± 0.05	13.61 ± 0.05	13.56 ± 0.12	12.97 ± 0.15	14.03 ± 0.10	14.01 ± 0.11
MgO	0.08 ± 0.01	0.13 ± 0.04	0.11 ± 0.01	0.10 ± 0.04	0.11 ± 0.02	0.25 ± 0.03	0.18 ± 0.07
CaO	0.59 ± 0.04	0.75 ± 0.02	0.74 ± 0.02	0.74 ± 0.05	0.57 ± 0.02	0.88 ± 0.05	0.87 ± 0.05
Na_2O	3.44 ± 0.16	3.34 ± 0.07	3.39 ± 0.03	3.43 ± 0.12	3.34 ± 0.22	3.28 ± 0.05	3.30 ± 0.12
K_2O	5.26 ± 0.22	5.63 ± 0.12	5.49 ± 0.06	5.48 ± 0.12	5.51 ± 0.35	5.96 ± 0.10	5.94 ± 0.15
TiO_2	0.09 ± 0.01	0.18 ± 0.01	0.15 ± 0.00	0.16 ± 0.04	0.13 ± 0.02	0.28 ± 0.02	0.26 ± 0.04
MnO	0.08 ± 0.01	0.11 ± 0.02	0.09 ± 0.00	0.09 ± 0.01	0.08 ± 0.01	0.13 ± 0.01	0.14 ± 0.01
Fe_2O_3	1.25 ± 0.09	1.31 ± 0.27	1.33 ± 0.10	1.21 ± 0.10	1.17 ± 0.17	1.57 ± 0.13	1.47 ± 0.24
P_2O_5	0.06 ± 0.01	0.04 ± 0.01	0.05 ± 0.01	0.04 ± 0.01	0.04 ± 0.01	0.03 ± 0.01	0.03 ± 0.01
Cl[b]	860 ± 54	584 ± 39	765 ± 27	771 ± 44	691 ± 34	541 ± 35	540 ± 45
Sc	3.9 ± 0.1	3.3 ± 0.1	3.8 ± 0.1	4.0 ± 0.1	3.2 ± 0.0	3.3 ± 0.1	3.3 ± 0.0
Co	0.38 ± 0.01	0.98 ± 0.05	1.24 ± 0.02	1.45 ± 0.07	0.74 ± 0.02	1.26 ± 0.03	1.27 ± 0.05
Zn	75 ± 2	62 ± 2	73 ± 2	72 ± 2	48 ± 3	58 ± 2	73 ± 12
Ga	23 ± 4	25 ± 2	24 ± 3	25 ± 1	24 ± 4	2± 2	23 ± 5
Rb	249 ± 3	235 ± 4	237 ± 4	238 ± 3	242 ± 8	173 ± 3	172 ± 1
Sr	31 ± 2	84 ± 7	76 ± 16	82 ± 11	56 ± 7	130 ± 4	131 ± 5
Y	37 ± 2	29 ± 3	33 ± 3	31 ± 4	26 ± 1	27 ± 1	28 ± 1
Zr	121 ± 10	198 ± 8	166 ± 17	176 ± 12	161 ± 9	247 ± 10	245 ± 7
Nb	49 ± 3	36 ± 4	40 ± 2	38 ± 6	30 ± 3	29 ± 3	29 ± 3
Sb	0.21 ± 0.01	0.16 ± 0.01	0.17 ± 0.01	0.18 ± 0.01	0.33 ± 0.01	0.11 ± 0.01	0.11 ± 0.01
Cs	4.1 ± 0.1	3.7 ± 0.1	3.8 ± 0.1	3.8 ± 0.1	6.7 ± 0.2	2.0 ± 0.0	2.0± 0.0
Ba	152 ± 9	470 ± 6	320 ± 20	345 ± 11	298 ± 6	936 ± 12	907 ± 20
La	21.8 ± 0.4	37.0 ± 0.6	29.9 ± 0.3	30.9 ± 0.6	32.1 ± 0.6	57.3 ± 0.8	59.7 ± 0.7
Ce	51 ± 1	77 ± 1	65 ± 1	67 ± 2	66 ± 2	116 ± 2	124 ± 3
Nd	23 ± 1	32 ± 1	28 ± 1	31 ± 2	28 ± 1	52 ± 1	50 ± 2
Sm	6.7 ± 0.1	7.6 ± 0.1	7.3 ± 0.1	7.4 ± 0.3	6.2 ± 0.1	9.8 ± 0.1	9.6 ± 0.2
Eu	0.32 ± 0.00	0.70 ± 0.05	0.59 ± 0.01	0.63 ± 0.02	0.56 ± 0.02	1.14 ± 0.02	1.13 ± 0.01
Tb	1.07 ± 0.02	0.89 ± 0.01	1.00 ± 0.02	0.96 ± 0.10	0.76 ± 0.01	0.93 ± 0.02	0.87 ± 0.03
Dy	5.9 ± 0.3	4.6 ± 0.2	5.7 ± 0.4	5.8 ± 0.6	4.3 ± 0.3	4.8 ± 0.2	4.9 ± 0.3
Yb	2.8 ± 0.1	1.9 ± 0.0	2.4 ± 0.1	2.2 ± 0.3	1.7 ± 0.1	1.8 ± 0.1	1.7 ± 0.1
Lu	0.42 ± 0.01	0.32 ± 0.01	0.40 ± 0.01	0.37 ± 0.03	0.32 ± 0.01	0.29 ± 0.01	0.29 ± 0.01
Hf	3.7 ± 0.1	5.1 ± 0.1	4.7 ± 0.2	5.0 ± 0.4	4.4 ± 0.1	6.8 ± 0.1	6.8 ± 0.1
Ta	3.6 ± 0.1	2.3 ± 0.0	2.9 ± 0.1	3.0 ± 0.0	2.3 ± 0.0	1.9 ± 0.0	1.9 ± 0.0
Pb	32 ± 3	31 ± 3	28 ± 2	31 ± 4	32 ± 1	30 ± 3	31 ± 4
Th	16.0 ± 0.2	20.4 ± 1.0	18.5 ± 0.3	18.9 ± 0.6	19.1 ± 0.5	24.9 ± 0.5	25.1 ± 0.2
U	5.7 ± 0.5	5.8 ± 1.7	4.0 ± 0.2	4.2 ± 0.3	5.1 ± 0.4	2.5 ± 0.1	1.7 ± 0.5

[a] Major elements (in oxide %) obtained by electron microprobe using wavelength dispersive spectrometers. [b] Trace element results (in ppm) from INAA, except for Ga, Sr, Y, Nb, and Pb (XRF).
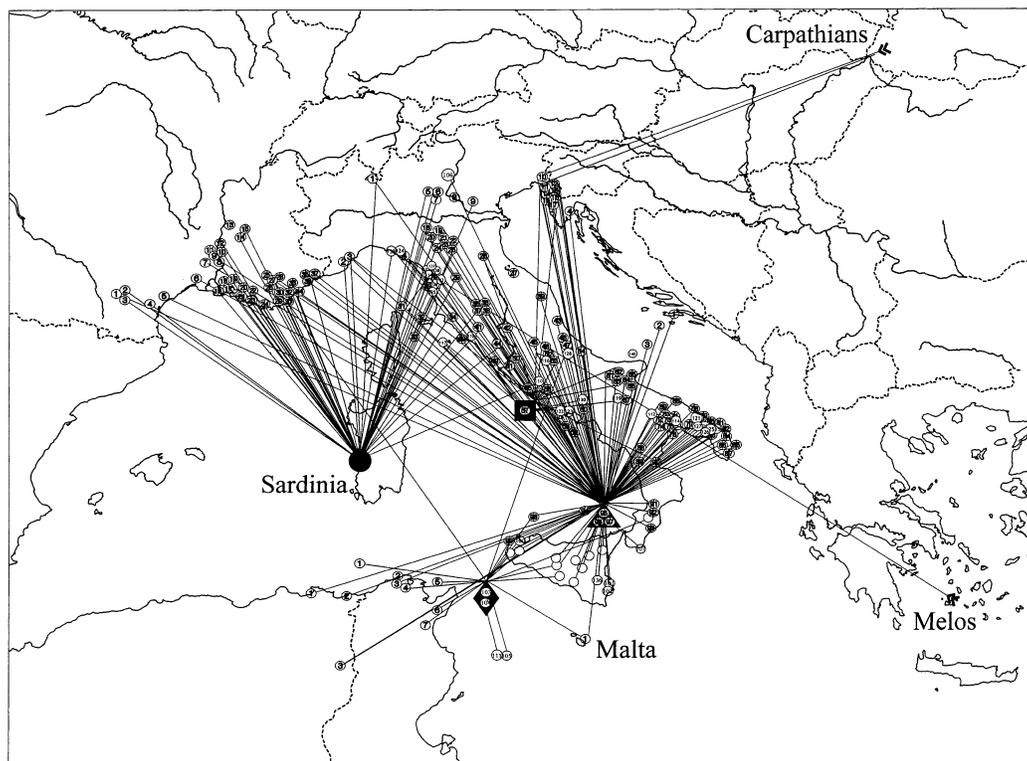
FIGURE 7. Central Mediterranean archaeological sites with provenienced obsidian artifacts. Numbered sites have been published elsewhere;[17,15] specific data for unnumbered sites have not yet been published.[60]
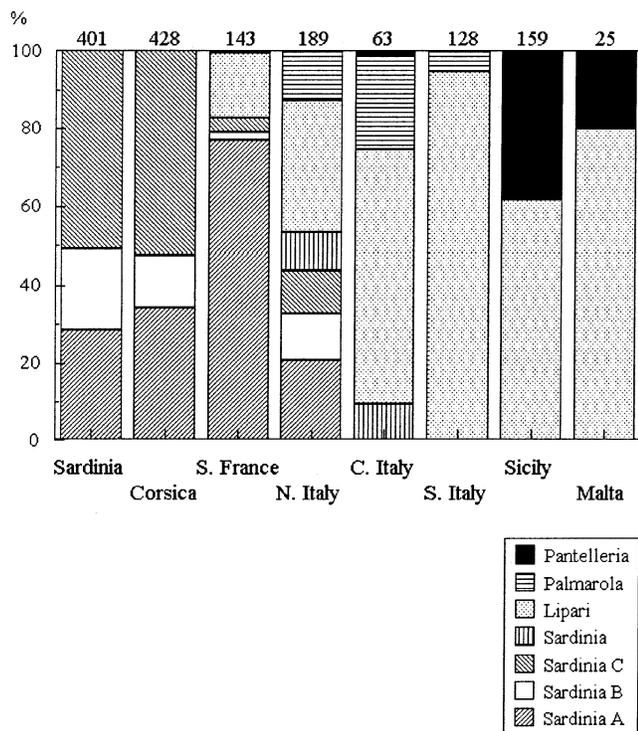
FIGURE 8. Frequency of obsidian source usage in different regions of the central Mediterranean, based on a compilation of published artifact analyses. Fission track analyses attribute obsidian to Sardinia (Monte Arci) without differentiating between subsources. The number of artifacts analyzed is shown at the top of each bar.

by land or along coastal routes and around rather than across the Ligurian Sea to southern France.

The Sardinian sources account for all of the obsidian found at hundreds of archaeological sites in Sardinia and Corsica (not shown in Figure 6), as well as more than 80% of the obsidian found in southern France and more than 50% of that in northern Italy. Sardinian obsidian is found at several sites north of the Po River but apparently did not reach the shores of the Adriatic Sea, and there is no evidence of any Sardinian obsidian in North Africa, to which it is closer than Lipari. Particularly informative is the relative usage of the three major Monte Arci subsources, which clearly demonstrates that in Sardinia differential exploitation of the individual obsidian flows occurred, resulting in significantly different geographic and chronological distribution patterns.[15,31,34,35] Locally, these differences may be correlated to the quantity, quality, and accessibility of obsidian in each source zone.

In Sardinia and Corsica, source SC accounts for more than half of all assemblages, followed by SA at about 30–35%. In northern Italy, the relative proportion of source SC is greatly reduced, while in southern France source SA comprises more than 95% of the Sardinian obsidian found there. If one examines relative usage at specific archaeological sites in these regions, one finds that there is a similar pattern of source representation at many sites in Sardinia, Corsica, Tuscany, and Liguria, which is also consistent with a down-the-line trade mechanism. The predominance of source SA obsidian in southern France

and at a few northern Italy sites, however, suggests either a different trade route or specific selection of one obsidian type over another, perhaps because of cultural preferences, perceived differences in obsidian quality or symbolic value, or the substitution of alternative materials for the functions served specifically by SB and SC obsidian.

Similar detailed characterization studies have now been extended to the obsidian sources on Lipari, Palmarola, and Pantelleria, with several thousand geological samples collected during intensive field surveys in 2000−2001. Two visual types were identified on both Lipari and Palmarola, and at least four distinct source localities were documented on Pantelleria. Unlike Sardinia, it is anticipated that trace element analysis will generally be necessary to reliably distinguish the multiple flows on these islands. A single method will then be selected for the analysis of more significant-sized assemblages of artifacts from prehistoric sites in the central Mediterranean, virtually revolutionizing the archaeological documentation of prehistoric trade and interaction networks and their cultural interpretation in this region. When integrated with typological, technological, and use−wear studies, a more complete understanding of human behavior in the Neolithic central Mediterranean will result. The scientific methodology employed and the interpretive integration of geochemical, archaeological, and other data may be used as a model for lithic provenance studies in other world regions.

References

(1) Renfrew, C. Trade and culture process in European prehistory. *Curr. Anthropol.* **1969**, *10*, 151−160.

(2) Perlès, C. Systems of exchange and organization of production in neolithic Greece. *J. Mediterranean Archaeol.* **1992**, *5*, 115−164.

(3) Tykot, R. H. Determining the source of lithic artifacts and reconstructing trade in the ancient world. In *Written in Stone: The Multiple Dimensions of Lithic Analysis*; Kardulias, P. N., Yerkes, R., Eds.; Lexington Books: Maryland, 2002.

(4) Shackley, M. S. Gamma rays, x-rays and stone tools: some recent advances in archaeological geochemistry. *J. Archaeol. Sci.* **1998**, *25*, 259−270.

(5) Shackley, M. S. Current issues and future directions in archaeological volcanic glass studies: an introduction. In *Archaeological Obsidian Studies: Method and Theory*; Shackley, M. S., Ed.; Plenum: New York, 1998; pp 1−14.

(6) Cann, J. R.; Renfrew, C. The characterization of obsidian and its application to the Mediterranean region. *Proc. Prehistoric Soc.* **1964**, *30*, 111−133.

(7) Hallam, B. R.; Warren, S. E.; Renfrew, C. Obsidian in the Western Mediterranean: chacterisation by neutron activation analysis and optical emission spectroscopy. *Proc. Prehistoric Soc.* **1976**, *42*, 85−110.

(8) Shelford, P.; Hodson, F.; Cosgrove, M. E.; Warren, S. E.; Renfrew, C. The sources and characterisation of Melian obsidian. In *An Island Polity: The Archaeology Exploitation in Melos*; Renfrew, C., Wagstaff, J. M., Eds.; Cambridge University Press: Cambridge, 1982; pp 182−192.

(9) Francaviglia, V. Characterization of Mediterranean obsidian sources by classical petrochemical methods. *Preistoria Alpina—Museo Tridentino di Scienze Naturali* **1986**, *20*, 311−332.

(10) Crisci, G. M.; Ricq-de Bouard, M.; Lanzaframe, U.; de Francesco, A. M. Les obsidiennes du midi de la France. *Gallia Préhistoire* **1994**, *36*, 299−327.

(11) Petrassi, L.; Zarattini, A. Il valore dell'ossidiana e le vie terrestri. Ipotesi dopo i primi risultati della fluorescenza ai raggi X. In *Casale del Dolce. Ambiente, economia e cultura di una comunità preistorica della Valle del Sacco*; Zarattini, A., Petrassi, L., Eds.; Baioni Stampa: Roma, 1997; pp 191−208.

(12) De Francesco, A. M.; Crisci, G. M.; Lanzafame, U. Nuovi sviluppi del metodo analitico non distruttivo in fluorescenza X per risalire alla provenienza di ossidiane archeologiche. In *Le Scienze della Terra e l'Archeometria*; D'Amico, C., Livadie, C. A., Eds.; CUEN: Napoli, 1998; pp 141−145.

(13) Poupeau, G.; Bellot-Gurlet, L.; Brisotto, V.; Dorighel, O. Nouvelles données sur la provenance de l'obsidienne des sites néolithiques du Sud-Est de la France. *C. R. Acad. Sci. Paris, Sci. Terre Planètes/Earth Planetary Sci.* **2000**, *330*, 297−303.

(14) Acquafredda, P.; Andriani, T.; Lorenzoni, S.; Zanettin, E. Chemical characterization of obsidians from different Mediterranean sources by non-destructive SEM-EDS Analytical Method. *J. Archaeol. Sci.* **1999**, *26*, 315−325.

(15) Tykot, R. H. Obsidian procurement and distribution in the central and western Mediterranean. *J. Mediterranean Archaeol.* **1996**, *9*, 39−82.

(16) Williams-Thorpe, O. Obsidian in the Mediterranean and the Near East: A Provenancing Success Story. *Archaeometry* **1995**, *37*, 217−248.

(17) Bigazzi, G.; Radi, G. Prehistoric Exploitation of Obsidian for Tool Making in the Italian Peninsula: A Picture From A Rich Fission-Track Data-Set. In *XIII International Congress of Prehistoric and Protohistoric Sciences,* Forlí, Italy, 8−14 September 1996; Arias, C., Bietti, A., Castelletti, L., Peretto, C., Eds.; A.B.A.C.O.: Forlí, 1996; Vol. 1, pp 149−156.

(18) Torrence, R. *Production and Exchange of Stone Tools*; Cambridge University Press: Cambridge, 1986.

(19) Obsidian characterization in the Eastern Mediterranean. In *Archaeological Chemistry*; Pollard, A. M., Heron, C., Eds.; Royal Society of Chemistry: London, 1996; Chapter 3, pp 81−103.

(20) Bigazzi, G.; Meloni, S.; Oddone, M.; Radi, G. Provenance studies of obsidian artifacts: trace elements analysis and data reduction. *J. Radioanal. Nucl. Chem.* **1986**, *98* (*2*), 353−363.

(21) Renfrew, C.; Aspinall, A. Aegean obsidian and Franchthi Cave. In *Les Industries Lithiques Taillées de Franchthi (Argolide, Grèce). Tome II. Les Industries du Mésolithique et du Néolithique Initial*; Perlès, C., Ed.; Indiana University Press: Bloomington, 1990; pp 257−270.

(22) Williams-Thorpe, O.; Warren, S. E.; Nandris, J. The distribution and provenance of archaeological obsidian in Central and Eastern Europe. *J. Archaeol. Sci.* **1984**, *11*, 183−212.

(23) Biró, T. K.; Pozsgai, I.; Vladar, A. Electron beam microanalyses of obsidian samples from geological and archaeological sites. *Acta Archaeol. Acad. Sci. Hung.* **1986**, *38*, 257−278.

(24) Bigazzi, G.; Marton, P.; Norelli, P.; Rozloznik, L. Fission track dating of Carpathian obsidians and provenance identification. *Nucl. Tracks Radiat. Meas.* **1990**, *17*, 391−396.

(25) Kilikoglou, V.; Bassiakos, Y.; Grimanis, A. P.; Souvatzis, K. Pilali-Papasteriou, A.; Papanthimou-Papaefthimiou, A. Carpathian obsidian in Macedonia, Greece. *J. Archaeol. Sci.* **1996**, *23*, 343−349.

(26) Pollmann, H.-O. *Obsidian im Nordwestmediterranean Raum: Seine Verbreitung und Nutzung im Neolithikum und Àneolithikum*; BAR International Series 585; Tempus Reparatvm: Oxford, 1993.

(27) For similar problems in the American southwest, see: Shackley, M. S. Intrasource chemical variability and secondary depositional processes: lessons from the American southwest. In *Archaeological Obsidian Studies: Method and Theory*; Shackley, M. S., Ed.; Plenum: New York, 1998; pp 83−102.

(28) Mackey, M.; Warren, S. E. The identification of obsidian sources in the Monte Arci region of Sardinia. In *Proceedings of the 22nd Symposium on Archaeometry*, University of Bradford, Bradford, U.K., 30 March−3 April, 1982; Aspinall, A., Warren, S. E., Eds.; University of Bradford: Bradford, 1983; pp 420−431.

(29) Herold, G. Mineralogische, chemische und physikalische Untersuchungen an den Obsidianen Sardiniens und Palmarolas. Grundlagen zur Rekonstruktion Prähistorischer Handelswege im Mittelmeerraum. Ph.D. dissertation, Universität (TH) Fridericiana Karlsruhe, 1986.

(30) Tykot, R. H. The sources and distribution of Sardinian obsidian. In *Sardinia in the Mediterranean: A Footprint in the Sea*; Tykot, R. H., Andrews, T. K., Eds.; Sheffield Academic Press: Sheffield, 1992; pp 57−70.

(31) Tykot, R. H. Prehistoric Trade in the Western Mediterranean: The Sources and Distribution of Sardinian Obsidian. Ph.D. dissertation, Harvard University; University Microfilms: Ann Arbor, MI, 1995.

(32) Tykot, R. H. Appendix I: obsidian provenance. In *Ustica I. The Results of the Excavations of the Regione Siciliana Soprintendenza ai Beni Culturali ed Ambientali Provincia di Palermo in Collaboration with Brown University in 1990 and 1991*; Holloway, R. R., Lukesh, S. S., Eds.; Providence and Louvain-La-Neuve; Archaeologia Transatlantica, 1995, Vol. XIV, pp 87−90.

(33) Tykot, R. H. The geological source of an obsidian ear (04.1941) from the Museum of Fine Arts, Boston. *Rev. Égyptol.* **1996**, *47*, 177−179.

(34) Tykot, R. H. Characterization of the Monte Arci (Sardinia) obsidian sources. *J. Archaeol. Sci.* **1997**, *24*, 467−479.

(35) Tykot, R. H. Mediterranean islands and multiple flows: the sources and exploitation of Sardinian obsidian. In *Archaeological Obsidian Studies: Method and Theory*; Shackley, M. S., Ed.; Plenum: New York and London, 1998; pp 67−82.

(36) Tykot, R. H. Islands in the stream: stone age cultural dynamics in Sardinia and Corsica. In *Social Dynamics of the Prehistoric Central Mediterranean*; Tykot, R. H., Morter, J., Robb, J. E., Eds.; Accordia Research Institute: London, 1999; pp 67−82.

(37) Tykot, R. H.; Ammerman, A. J. New directions in central Mediterranean obsidian studies. *Antiquity* **1997**, *274*, 1000−1006.

(38) Tykot, R. H.; Young, S. M. M. Archaeological applications of inductively coupled plasma-mass spectrometry. In *Archaeological Chemistry V*; Orna, M. V., Ed.; American Chemical Society: Washington, DC, 1996; pp 116−130.

(39) Ammerman, A. J.; Cesana, A.; Polglase, C.; Terrani, M. Neutron activation analysis of obsidian from two neolithic sites in Italy. *J. Archaeol. Sci.* **1990**, *17*, 209−220.

(40) Ammerman, A. J.; Polglase, C. R. Analyses and descriptions of the obsidian collections from Arene Candide. In *Arene Candide: A Functional and Environmental Assessment of the Holocene Sequence (Excavations Bernabo Brea-Cardini 1940−50)*; Maggi, R., Ed.; Il Calamo: Roma, 1997; pp 573−592.

(41) Francaviglia, V.; Piperno, M. La repartition et la provenance de l'obsidienne archeologique de la grotta dell'Uzzo et de Monte Cofano (Sicile). *Rev. Archéom.* **1987**, *11*, 31−39.

(42) Hurcombe, L. New contributions to the study of the function of Sardinian obsidian artifacts. In *Sardinia in the Mediterranean: A Footprint in the Sea*; Tykot, R. H., Andrews, T. K., Eds.; Sheffield: Sheffield Academic Press: 1992; pp 83−97.

(43) Hurcombe, L.; Phillips, P. Obsidian usage at the Filiestru cave, Sardinia: choices and functions in the Early and Middle Neolithic periods. In *Sardinian and Aegean Chronology: Towards the Resolution of Relative and Absolute Dating in the Mediterranean*; Balmuth, M. S., Tykot, R. H., Eds; Oxbow Books: Oxford, 1998; pp 93−102.

(44) Puxeddu, C. Giacimenti di ossidiana del Monte Arci in Sardegna e sua irradiazione. *Studi Sardi* **1958**, *14−15*, 10−66.

(45) Glascock, M. D.; Braswell, G. E.; Cobean, R. H. A Systematic Approach to Obsidian Source Characterization. In *Archaeological Obsidian Studies: Method and Theory*; Shackley, M. S., Ed.; Plenum: New York and London, 1998; pp 15−66.

(46) Merrick, H. V.; Brown, F. H. Rapid chemical characterization of obsidian artifacts by electron microprobe analysis. *Archaeometry* **1984**, *26*, 230−236.

(47) See also: Francaviglia, V. Ancient obsidian sources on Pantelleria (Italy). *J. Archaeol. Sci.* **1988**, *15*, 109−122.

(48) Giardino, C.; Guidi, G. F.; Moioli, P.; Negri, P. Correlazione mediante spettrometra XRF di reperti di ossidiana provenienti da Capri con ossidiane del bacino del Mediterraneo. In *Le Scienze della Terra e l'Archeometria*; D'Amico, C., Livadie, C. A., Eds.; CUEN: Napoli, 1997; pp 295−298.

(49) De Francesco, A. M.; Crisci, G. M. Provenienza delle ossidiane dei siti archeologici di Pianosa (Arcipelago Toscano) e Lumaca (Corsica) con il metodo analitico non distruttivo in fluorescenza X. In *Il primo popolamento Olocenico dell'area corso-toscana*; Tozzi, C., Weiss, M. C., Eds.; Edizioni ETS: Pisa, 2000; pp 253−258.

(50) Williams-Thorpe, O.; Warren, S. E.; Barfield, L. H. The sources and distribution of archaeological obsidian in Northern Italy. *Preistoria Alpina—Museo Tridentino di Scienze Naturali* **1979**, *15*, 73−92.

(51) Williams-Thorpe, O.; Warren, S. E.; Courtin, J. The distribution and sources of archaeological obsidian from Southern France. *J. Archaeol. Sci.* **1984**, *11*, 135−146.

(52) Randle, K.; Barfield, L. H.; Bagolini, B. Recent Italian obsidian analysis. *J. Archaeol. Sci.* **1993**, *20*, 503−509.

(53) Halliday, A. N.; Der-Chuen, L.; Christensen, J. N.; Rehkamper, M.; Yi, W.; Luo, X.; Hall, C. M.; Ballentione, C. J.; Pettke, T.; Stirling, C. Applications of multiple collector-ICPMS to cosmochemistry, geochemistry, and paleoceanography. *Geochim. Cosmochim. Acta* **1998**, *62*, 919−940.

(54) Parry, S. J. *Activation Spectrometry in Chemical Analysis*; John Wiley: New York, 1991.

(55) Moens, L.; Dams, R. NAA and ICP-MS: a comparison between two methods for trace and ultra-trace element analysis. *J. Radioanal. Nucl. Chem. Articles* **1995**, *192,* 29−38.

(56) Gratuze, B. Obsidian characterisation by laser ablation ICP-MS and its application to prehistoric trade in the Mediterranean and the Near East: Sources and distribution of obsidian within the Aegean and Anatolia. *J. Archaeol. Sci.* **1999**, *26*, 869−881.

(57) Gale, N. H. Mediterranean obsidian source characterisation by strontium isotope analysis. *Archaeometry* **1981**, *23*, 41−51.

(58) Montanini, A.; Barbieri, M.; Castorina, F. The role of fractional crystallisation, crustal melting and magma mixing in the petrogenesis of rhyolites and mafic inclusion-bearing dacites from the Monte Arci volcanic complex (Sardinia, Italy). *J. Volcanol. Geotherm. Res.* **1994**, *61*, 95−120.

(59) Montanini, A.; Villa, I. M. ^{40}Ar/^{39}Ar chronostratigraphy of Monte Arci volcanic complex (Western Sardinia, Italy). *Acta Vulcanol.* **1993**, *3*, 229−233.

(60) Nicoletti, F. Il commercio neolitico dell'ossidiana nel mediterraneo ed il ruolo di Lipari e Pantelleria nel più antico sistema di scambio. In *Prima Sicilia: alle origini della società siciliana*; Tusa, S., Ed.; Ediprint: Siracusa, 1997; pp 259−269.

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