

Article

Obsidian at the Maddalena di Muccia (Marche, Central Italy) Archaeological Site: Evidence for Three Volcanic Sources in a Multi-Phase Context

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Abstract

This paper presents the compositional characterisation of obsidian artefacts from the archaeological site of Maddalena di Muccia (Marche, Central Italy). The assemblage, spanning the Early Neolithic to the Copper Age, was chemically and petrographically investigated using two non-destructive X-ray analytical instruments: a wavelength-dispersive X-ray spectrometer and a scanning electron microscope equipped with an energy-dispersive X-ray spectrometer. Geochemical data allow secure attribution of the artefacts to their geological sources, confirming the predominant use of Palmarola obsidian during the Early Neolithic and documenting the continued circulation of obsidian also from other sources (Lipari and Monte Arci) into the Copper Age. Significantly, the Muccia assemblage provides the first evidence in the Adriatic area for the contemporaneous presence of multiple Monte Arci obsidian sub-sources (S.A. and S.C.). This compositional pattern suggests sustained long-term exchange networks involving obsidian, and highlights the role of central Adriatic sites within broader prehistoric interaction systems of the central Mediterranean.

Keywords: obsidian; neolithic; copper age; central Italy; SEM-EDS analysis; WD-XRF analysis; non-destructive analysis



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1. Introduction

With a research history spanning more than 50 years [1–8], obsidian provenance studies have long contributed substantially to the reconstruction of prehistoric interaction networks across the Mediterranean. Nonetheless, expanding the analytical dataset remains crucial, as each new sample has the potential to reveal previously unrecognised connections and to refine existing interpretative models. The routine application of non-invasive analytical methods offers the opportunity to substantially increase the number of analysable artefacts and to generate more comprehensive and comparable datasets.

In this paper, we present the results of a study of a sample of obsidian artefacts from a key archaeological site in Central Italy, whose strategic mid-peninsular position made it a long-term hinge between the Adriatic and Tyrrhenian regions.

Obsidian provenance characterisation can be addressed using numerous minimally invasive or completely non-destructive techniques such as X-ray fluorescence (XRF) using peak intensity ratios of various elements [9,10], scanning electron microscopy coupled with energy-dispersive spectrometer (SEM-EDS) microanalysis [2,11], electron-probe microanalysis [12] and laser ablation inductively coupled plasma–mass spectrometry [13].

In recent years, the increased use of highly efficient energy-dispersive X-ray detectors has made EDS methods prevalent for identifying obsidian source areas [14–27].

Energy-dispersive XRF instruments that are particularly widespread are: (i) X-ray handguns (handheld portable XRF: HHpXRF); (ii) more complex spectrometers to be mounted on tripods (field-portable X-ray fluorescence: FpXRF); and (iii) small transportable instruments (bench-portable X-ray fluorescence: BpXRF).

However, it is worth bearing in mind that ED analyses are rapid and straightforward and particularly useful for student training [17]. In fact, they are particularly useful for initial sorting of artefacts, but one must not exclude the combination of these inexpensive, non-destructive techniques with other effective analytical methods [20,28,29].

2. Materials and Methods

2.1. The Archaeological Context of Maddalena di Muccia

Maddalena di Muccia (Figure 1) is an important stratified site in the Marche region (Central Italy) with an occupational sequence ranging from the Early Neolithic (early 6th millennium BC) to the Roman Imperial period. Following preliminary investigations conducted in the 1960s by D. Lollini, the area was subjected to systematic excavations between 2001 and 2008 by Sapienza University of Rome in collaboration with the Archaeological Superintendency of the Marche [30].



Figure 1. Central–Eastern Mediterranean obsidian source areas (in black); the red star marks the location of the Maddalena di Muccia archaeological site; the cartographic representation is from Google Earth, with modifications.

The Early Neolithic settlement identified in the 1960s consisted of numerous cavities of varying shapes, sizes, and depths and characterised by the presence of impressed pottery. Two more structures were uncovered in 2001. Among these, SU 114, topographically correlated with the area explored during the earlier campaigns, is an ovoid pit with markedly undercut walls, the morphology of which supports its interpretation as a subterranean storage structure. Three radiocarbon dates were obtained for this structure: 6637 ± 83 BP (5720–5470 BC cal 2 σ); 6638 ± 59 BP (5650–5480 BC cal 2 σ); 6440 ± 50 BP (5490–5320 BC cal 2 σ) [30]. Five obsidian artefacts were recovered from this context and analysed for provenance characterisation (Table 1).

Table 1. The analysed obsidian artefacts, their contexts of origin, their dating, and their photo (artefact orientation adjusted to accommodate the table; red scale bar is 5 mm). (?) = uncertain attribution.

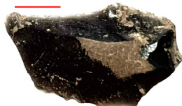
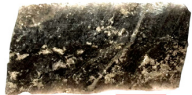
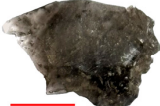
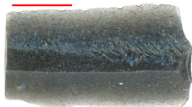
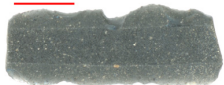
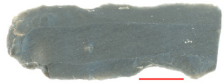
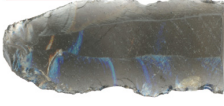
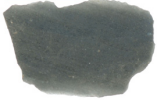
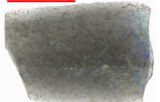
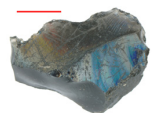
Sample ID	Year	Inv.	SU	Square	Item	Context	Chronology	Photo
MAD01	2002		114, 1/VI		Bladelet	Storage pit	EN	
MAD02	2002		114, 1/III		Flake	Storage pit	EN	
MAD03a	2002		114, 1/VI		Blade mesial fragment	Storage pit	EN	
MAD03b	2002		114, 1/VI		Bladelet	Storage pit	EN	
MAD04	2002		114, sup.		Microflake	Storage pit	EN	
MAD5	2005	4	464		Bladelet	Post hole among huts B, D, G	Copper Age	
MAD6	2003	676	212	P22	Retouched bladelet	Small pit cutting SU 213 (Copper Age)	ND	
MAD7	2003	677	270A/1		Bladelet	Foundation trench hut B	Copper Age	
MAD8	2003	678	128/1		Retouched bladelet	Pit	Copper Age	
MAD9	2003	679	210/1		Bladelet	Post hole between huts A and B, next to Palisade A	Copper Age	

Table 1. Cont.

Sample ID	Year	Inv.	SU	Square	Item	Context	Chronology	Photo
MAD10a	2008	1393	1	R32	Bladelet	Layer overlying Palisade B	Copper Age (?)	
MAD10b	2008	1394	1	R32	Bladelet	Layer overlying Palisade B	Copper Age (?)	
MAD11	2008	1398	858	R31	Retouched flake (denticulate)	Area of material concentration overlying Palisade B	Copper Age (?)	

A later Neolithic phase is attested by two pits and a large storage pit (SU 12), which contained only a single obsidian bladelet that was not selected for analysis due to post-depositional alteration. During the 3rd millennium BC, a Copper Age village developed on the site, marked by multiple episodes of construction, enlargement and internal reorganisation. The earliest phase comprises a massive curvilinear palisade delimiting the initial habitation nucleus. After roughly two centuries, following a reconfiguration of the settlement layout, five large apsidal dwellings measuring approximately 10×7 m were built. A final phase of occupation is represented by several smaller, irregularly shaped structures with variable orientations. Associated features include pits, postholes, enclosures and additional palisades. A robust series of 15 radiocarbon dates constrains the Copper Age occupation to approximately 2900–2200 BC, although none is directly linked to the structures containing the analysed obsidian artefacts [30]. The architectural scale of the settlement and the diachronic reorganisation of its internal layout indicate the long-term establishment of a demographically substantial community. The site's strategic position at the intersection of two principal trans-Appennine routes supports the hypothesis of a settlement likely intended to monitor and control movement along a major communication corridor linking the central Appennines with the Adriatic coastal zone.

All eight obsidian artefacts recovered from the Copper Age levels were selected for analysis (Table 1). These consist of six bladelets, two of which display use-retouch, together with a retouched flake (a denticulate). The artefact MAD10b exhibits a double patina, suggesting it may have been reworked from a piece used in an earlier period.

The obsidian artefacts derive from isolated postholes located among the Copper Age huts (MAD9, MAD5), the foundation trench of Hut B (MAD7), pits (MAD8, MAD6), layers covering Palisade B, a structure belonging to the earliest phase of the village (SU 1 in R32: MAD10a and 10b) and a concentration of archaeological materials in R31 (MAD11).

As shown in the map (Figure 2), the distribution of obsidian items is mainly in the eastern portion of the Copper Age settlement, which is also the area characterised by a dense palimpsest of structures spanning all three phases of the village. Consequently, it is not always possible to determine with certainty their precise attribution to a specific Copper Age phase. Moreover, samples MAD10a and MAD10b derive from findspots where chert cores and bladelets, attributable on technological grounds to the Early Neolithic, were recovered. The map also indicates a pit (SU 203) located in this part of the site which contained exclusively Early Neolithic material. Taken together, these observations suggest that in this area structures dating to the Early Neolithic occupation phase may have been intercepted during the construction of the Copper Age village, resulting in the admixture of archaeological materials. However, the obsidian artefacts recovered from features securely

attributable to the Copper Age, namely MAD5, MAD7, MAD8, MAD9, are not associated with earlier materials. Their stratigraphic context therefore supports their attribution to the Copper Age.

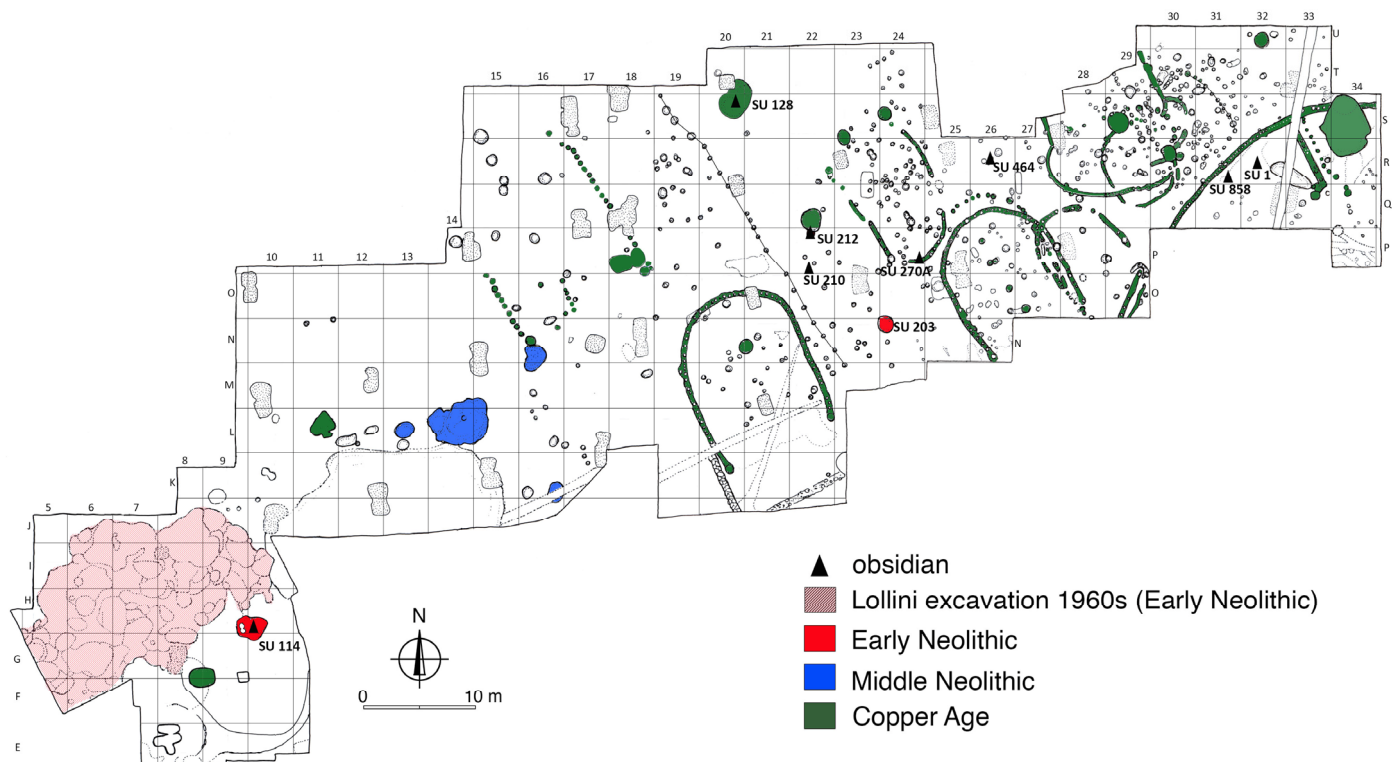


Figure 2. Plan of the Maddalena di Muccia site indicating the findspots of the analysed obsidian artefacts.

2.2. Analytical Background

Over the last 40 years, the Department of Earth and Environmental Sciences of the Aldo Moro University of Bari (Italy) has developed two completely non-destructive analytical procedures useful for obsidian petroarchaeometric characterisation: (i) microanalysis of glass and microphenocrysts of the archaeological samples [2,11]; (ii) measurement of trace element X-ray fluorescence emission from the entire obsidian sample [31].

Since the 1990s, approximately 700 obsidian samples have been characterised, most of which were found in Neolithic sites in Central and Southern Italy. In recent years, the characterisation of obsidian has been extended to Neolithic sites in the Middle East [32].

2.3. WD-XRF and SEM-EDS Protocol

Petroarchaeometric characterisation of the obsidian artefacts was performed using a wavelength-dispersive X-ray spectrometer (WD-XRF) and also a scanning electron microscope coupled with an energy-dispersive X-ray spectrometer (SEM-EDS).

The WD-XRF equipment used for the X-ray analyses is a PANalytical spectrometer (AXIOS Advanced model of PANalytical B.V., Lelyweg 1, 7602 EA Almelo, The Netherlands) equipped with a 4 kW Rh super-sharp end-window X-ray tube operating at 60 kV and 66 mA. A scintillator detector collected the Rb, Sr, Y, Zr and Nb X-ray emission lines, dispersed by a LiF 220 crystal. The obsidian samples were washed by immersing them in a glass beaker containing distilled water, which was then placed in an ultrasonic cleaning tank for about 5 min; the samples were then gently placed on a thin Mylar film that sealed the bottom of the spectrometer sample holder (Figure 3). The Rb, Sr, Y, Zr and Nb X-ray emission lines were measured according to the procedure of [31] and [33,34], particularly

taking into account that X-rays must be measured as net intensities, that is, purified from the contribution of the background and from inter-elemental interferences.



Figure 3. On the left, the X-ray fluorescence (XRF) spectrometer with detail of the sample holder (in the light blue circle) in which the obsidian specimen seems to be suspended in the air (see text for explanation); on the right, the scanning electron microscope (SEM) equipped with an energy-dispersive spectrometer (EDS) and a detail of the sample holder (in the light blue rectangle) on which are mounted the obsidian samples and the reference standards.

SEM investigations were performed with a LEO model EVO50XVP (Zeiss, Cambridge, Cambridgeshire, UK) coupled with an energy-dispersive spectrometer (EDS) from Oxford Instruments (High Wycombe, Buckinghamshire, UK), fitted with a model X-max (80 mm²) silicon drift detector (Figure 3). SEM operating conditions included a 15 kV accelerating potential, a 300 pA probe current, an average count rate of approximately 20,000 cps across the whole spectrum, a 50 s counting time and an 8.5 mm working distance. X-ray intensities were converted into oxide concentration values using the XPP correction procedure, developed by [35,36]. Analytical data were verified using numerous reference standards from Micro-Analysis Consultants Ltd. (Ives, Cambridgeshire, UK).

Before undertaking SEM analyses, the obsidian samples were washed by immersing them in acetone in a glass beaker, which was then placed in an ultrasonic cleaning tank for about 10 min [32].

A flat part of the specimen was chosen for SEM analysis: The remaining parts of the sample were protected by covering them with a thin layer of aluminium foil (the type commonly used for cooking) to protect their more porous or fragile parts [37].

The samples were then fixed onto an aluminium stub using plasticine, to expose one of their flat surfaces to the SEM electron. The specimen was then sputtered with a 30 nm thick carbon film using a thermal evaporator (Edwards, model Auto 306, Irvine, CA, USA) to make its surface conductive; a colloidal graphite drop closed the electrical bridge between the carbon-coated surface of the obsidian and the metal stubs [32]. After SEM investigations, the carbon sputtered on the obsidian surfaces was removed by wiping the specimens with a soft cloth wetted with acetone [32,38].

3. Results

Before discussing the results, it is worth briefly describing the procedure used at the University of Bari Aldo Moro, which allows very accurate analytical data to be obtained with a completely non-destructive technique useful for identifying the obsidian source areas.

An initial characterisation is performed using WD-XRF, which allows the sample to be characterised very quickly, in 30 min [31], without having to treat the sample in any way other than washing it in a beaker containing distilled water. In this way, the glass and microphenocrysts are analysed, and the results are comparable only with laboratories that have used the same technique to measure the X-ray intensities of trace elements such as Rb, Sr, Y, Zr, and Nb.

If the results obtained leave room for doubt, further analyses are carried out using SEM-EDS, which allows analysis of both the major elements of the glass, if it is unaltered, and the microphenocrysts [2,11,32]. The analysis of microphenocrysts certifies the datum because it is not affected by glass alteration phenomena: The artefacts are normally subjected to alteration processes after burial, due to water circulating within sediments [38]. These alteration processes can affect the mobility of alkaline elements, above all Na, and promote the formation of thin carbonate film incrustations (e.g., Table 1, photo of samples MAD01-MAD03b) [[31,38] and the references therein], sometimes even enlarging the uranium-238 fission tracks [32]. The obsidian surface alteration can in some way interfere with WD-XRF analysis, even making it impossible to analyse the glass by SEM-EDS.

The precision and accuracy of analytical data were extensively discussed for the first time in 1999 [2] and in other successive papers [11,31,32].

All obsidian samples from the Maddalena di Muccia site were previously characterised using WD-XRF analysis, by measuring the net intensities of some trace elements, namely Rb, Sr, Y, Zr and Nb [31] (Table 2).

Table 2. X-ray emission and characterising ratio of some contiguous trace elements of obsidian samples from Maddalena di Muccia. The X-ray intensity values, expressed as counts per second, are background- and interference-free.

Sample	Rb	Sr	Y	Zr	Nb	Rb/Sr	Zr/Y	Zr/Nb	Y/Nb
M 1	5506.5	96.8	858.1	5309.1	1340.9	56.86	6.19	3.96	0.64
M 2	11,074.1	163.7	1852.5	10,285.0	2451.1	67.64	5.55	4.20	0.76
M 3a	11,588.2	345.2	1928.6	10,816.9	2669.6	33.57	5.61	4.05	0.72
M 3b	5795.3	156.8	884.0	5349.8	1286.5	36.96	6.05	4.16	0.69
M 4	5227.0	128.6	833.5	4506.2	1114.9	40.66	5.41	4.04	0.75
M 5	4788.0	585.5	1027.4	2663.8	1636.2	8.18	2.59	1.63	0.63
M 6	2453.4	2083.1	532.9	5489.1	708.9	1.18	10.30	7.74	0.75
M 7	10,078.8	69.4	1931.7	10,381.6	2645.8	145.18	5.37	3.92	0.73
M 8	7783.4	116.7	1463.1	8060.8	1965.3	66.70	5.51	4.10	0.74
M 9	2563.2	240.5	483.0	1614.9	787.6	10.66	3.34	2.05	0.61
M 10a	4427.0	93.9	759.4	4397.4	1087.8	47.17	5.79	4.04	0.70
M 10b	3965.1	334.8	693.7	3529.6	836.7	11.84	5.09	4.22	0.83
M 11	5522.7	290.2	1368.6	5367.7	1225.6	19.03	3.92	4.38	1.12

The source-area characterisation of the Maddalena di Muccia obsidian samples reveals three geological volcanic outcrops: Lipari, Palmarola, and Monte Arci (Figure 4), with the

latter having two sub-sources, (i) Perdas Urias (S.C.) and (ii) Conca Cannas, Canale Perdera, and Riu Solacera (S.A.).

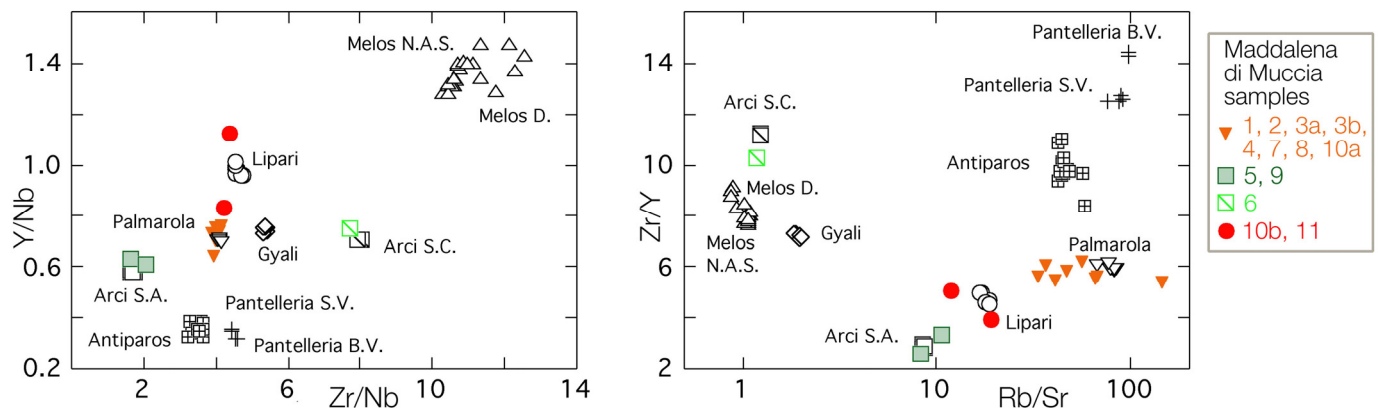


Figure 4. WD-XRF data plots of obsidian from the Maddalena di Muccia site compared with the data from other source areas in the Mediterranean (data from [2,39]); sub-source outcrops: Monte Arci, S.C. = Perdas Urias; S.A. = Conca Cannas, Canale Perdera and Riu Solacera. Pantelleria; B.V. = Bagno di Venere; S.V. = Salto la Vecchia and Balata dei Turchi. Melos; D. = Demenegaki; N.A.S. = Nihia, Adamas and Sarakiniko).

Specifically, samples 1, 2, 3a, 3b, 4, 7, 8 and 10a originate from Palmarola, samples 10b and 11 originate from Lipari, and samples 5, 9 (sub-source S.A.) and 6 (sub-source S.C.) originate from Monte Arci.

The peculiarity of three distinct source areas within the same archaeological site, one even represented by two sub-sources, suggested that SEM-EDS investigations should be performed in order to further constrain the analytical data obtained using WD-XRF. EDS microanalysis of the obsidian glass (Table 3) shows that the samples were quite altered during the period of their burial. In fact, the value of alkaline elements, in particular Na₂O, is relatively low, less than 4%, and sometimes below 2%.

Table 3. SEM-EDS microanalyses of obsidian glass from Maddalena di Muccia (oxides expressed in wt%); the values reported in the table represent the mean of three determinations. C.I.A. is the Chemical Index of Alteration [$\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$ in mol.%].

Sample	SiO ₂	Al ₂ O ₃	FeO	CaO	Na ₂ O	K ₂ O	C.I.A.
M 5	76.00	13.46	1.02	0.67	3.27	5.54	51.66
M 6	74.29	14.25	1.02	1.03	1.99	7.14	52.54
M 9	75.60	13.67	1.13	0.67	3.58	5.35	51.45
M 10b	75.51	12.86	1.48	0.83	3.99	5.33	48.16
M 11	75.45	12.92	1.42	0.77	4.16	5.27	48.09

In some cases, however, glass analysis confirmed that samples 10b and 11 originated from Lipari and that samples 5, 6 and 9 originated from Monte Arci, and it attributed samples 5 and 9 to sub-source S.A. and sample 6 to sub-source S.C. (Figure 5).

Unfortunately, for the samples ascribed to Palmarola geological outcrops using WD-XRF, it was not possible to confirm their origin solely through glass analysis, due to both the surface alteration of the artefacts and the presence of thin carbonate concretions (e.g., Table 1, photo of samples MAD01–MAD03b). Fortunately, the presence of pyroxene crystals (Figure 6), although very small and often with a skeletal texture, allowed the attribution of some samples to the Palmarola source area (Figure 7, Table 4).

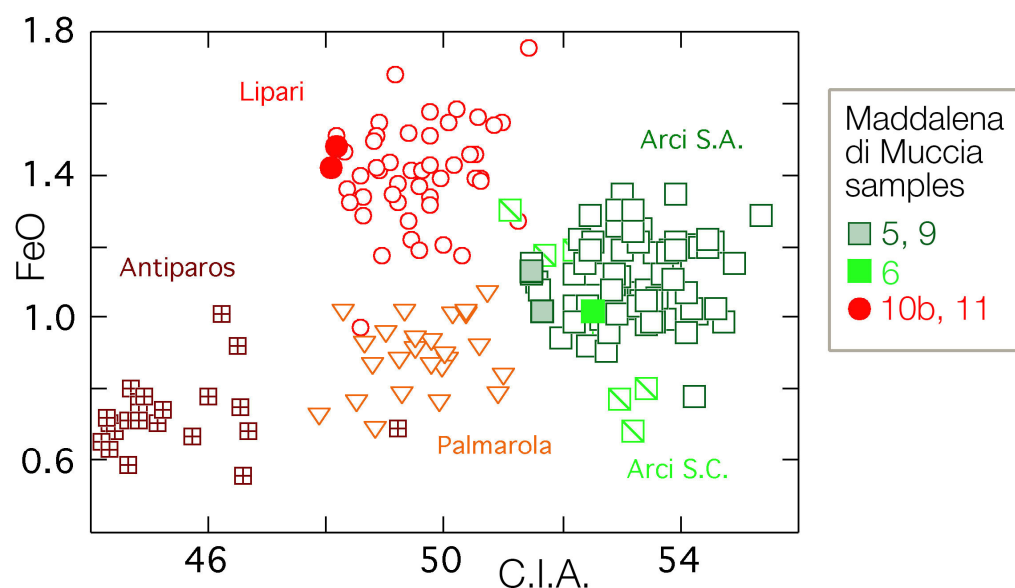


Figure 5. SEM-EDS microanalyses of the major obsidian source areas in the Mediterranean basin (data from [2,39]); obsidian samples 5 and 9 (green squares), 6 (light green square) and 10b and 11 (red circles) from the Maddalena di Muccia site (glass analyses, representing the mean value of five microanalyses) are also plotted. Sub-source outcrops: Monte Arci, S.C. = Perdas Urias; S.A. = Conca Cannas, Canale Perdera and Riu Solacera.

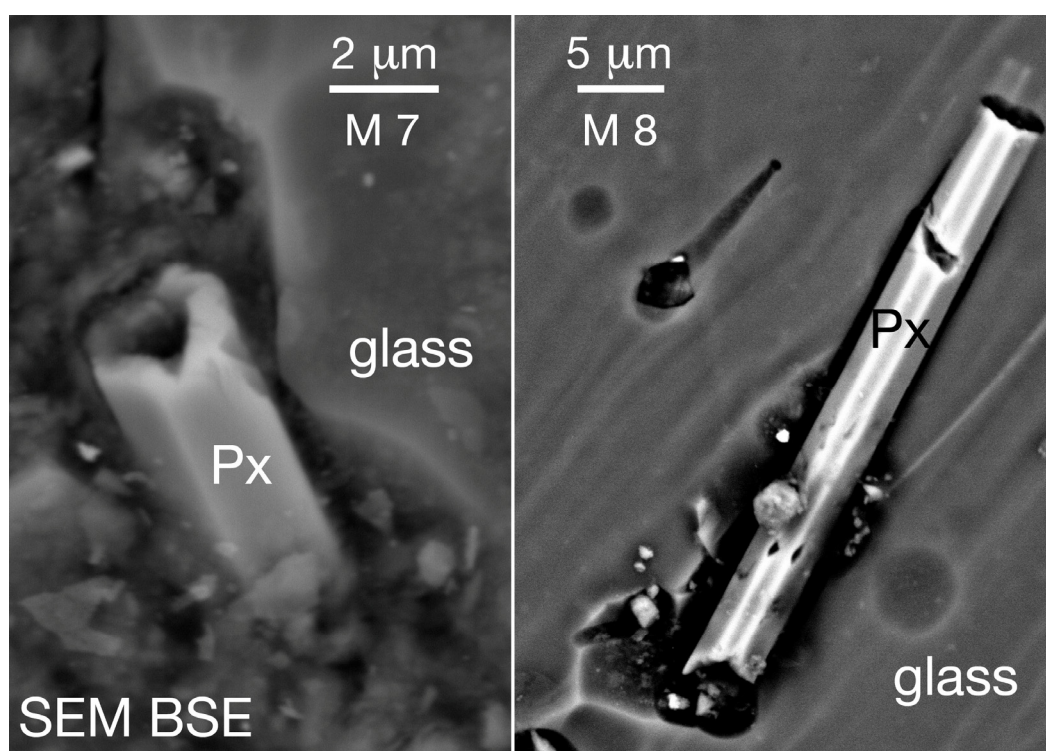


Figure 6. Backscattered SEM images of pyroxenes in obsidian samples M7 and M8; the pyroxene of the M7 sample shows a skeletal texture, an indicator of rapid crystallisation.

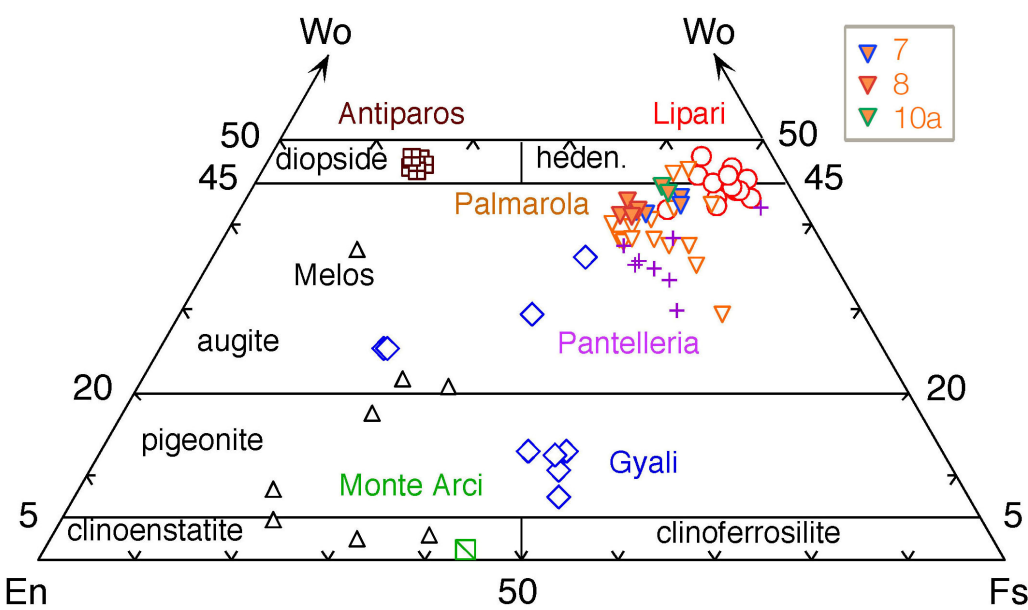


Figure 7. Compositions of pyroxenes according to the [40] nomenclature for the major obsidian source areas in the Mediterranean (data from [11,39]); pyroxenes from samples 7, 8 and 10a of the Maddalena di Muccia site are plotted as solid symbols. En: enstatite; Fs: ferrosilite; Wo: wollastonite; Aug: augite.

Table 4. Pyroxene microanalyses (oxides expressed in wt%) of the Maddalena di Muccia obsidian samples; formula based on 6 oxygens. En: enstatite; Fs: ferrosilite; Wo: wollastonite.

Sample	M7-1.1	M7-1.2	M7-2.1	M7-2.2	M8-1.1	M8-1.2	M8-2.1	M8-2.2	M10a-1.2	M10a-4.1
SiO ₂	48.57	48.58	49.69	50.55	50.59	49.79	50.17	50.45	48.46	49.41
TiO ₂	0.27	0.31	0.31	0.00	0.00	0.27	0.32	0.25	0.35	0.27
Al ₂ O ₃	3.15	3.18	3.92	4.12	1.40	1.47	1.24	1.30	7.20	6.95
FeO	23.51	23.65	21.56	20.75	22.27	22.68	21.80	21.94	20.61	20.79
MnO	2.48	2.36	2.01	1.95	2.24	2.23	1.95	1.96	1.76	1.43
MgO	3.50	3.62	4.69	4.87	5.40	5.19	5.33	5.86	3.54	3.46
CaO	17.67	17.46	16.52	16.33	17.46	18.01	18.51	17.73	16.92	16.58
Na ₂ O	0.91	1.01	1.00	1.05	0.63	0.66	0.66	0.79	0.77	0.72
K ₂ O	0.00	0.12	0.47	0.58	0.13	0.00	0.19	0.16	0.86	0.79
Total	100.07	100.28	100.17	100.21	100.12	100.31	100.18	100.43	100.47	100.41
Si	1.944	1.941	1.955	1.975	2.002	1.977	1.988	1.989	1.893	1.922
Ti	0.008	0.009	0.009	0.000	0.000	0.008	0.010	0.007	0.010	0.008
Al	0.149	0.150	0.182	0.190	0.065	0.069	0.058	0.060	0.332	0.319
Fe	0.787	0.790	0.709	0.678	0.737	0.753	0.722	0.723	0.673	0.676
Mn	0.084	0.080	0.067	0.065	0.075	0.075	0.066	0.065	0.058	0.047
Mg	0.209	0.216	0.275	0.284	0.318	0.307	0.315	0.344	0.206	0.201
Ca	0.758	0.747	0.696	0.684	0.740	0.766	0.786	0.749	0.708	0.691
Na	0.071	0.078	0.076	0.080	0.048	0.051	0.051	0.061	0.059	0.055
K	0.000	0.006	0.024	0.029	0.007	0.000	0.010	0.008	0.043	0.039
Σ cat	4.009	4.017	3.995	3.984	3.993	4.006	4.004	4.007	3.982	3.958
En	11.9	12.3	16.4	17.2	17.7	16.8	17.3	19.0	13.0	12.8
Fs	44.9	45.1	42.2	41.2	41.0	41.2	39.6	39.8	42.4	43.1
Wo	43.2	42.6	41.4	41.6	41.2	41.9	43.1	41.2	44.6	44.1

SEM-EDS microanalysis of biotite microphenocrysts present in the glass of obsidian artefacts, easily recognisable using backscattered electron images (Figure 8), confirms

that samples 5, 6 and 9 were collected from Monte Arci geological outcrops, specifically sub-source S.A. for samples 5 and 9 and sub-source S.C. for sample 6 (Figure 9, Table 5).

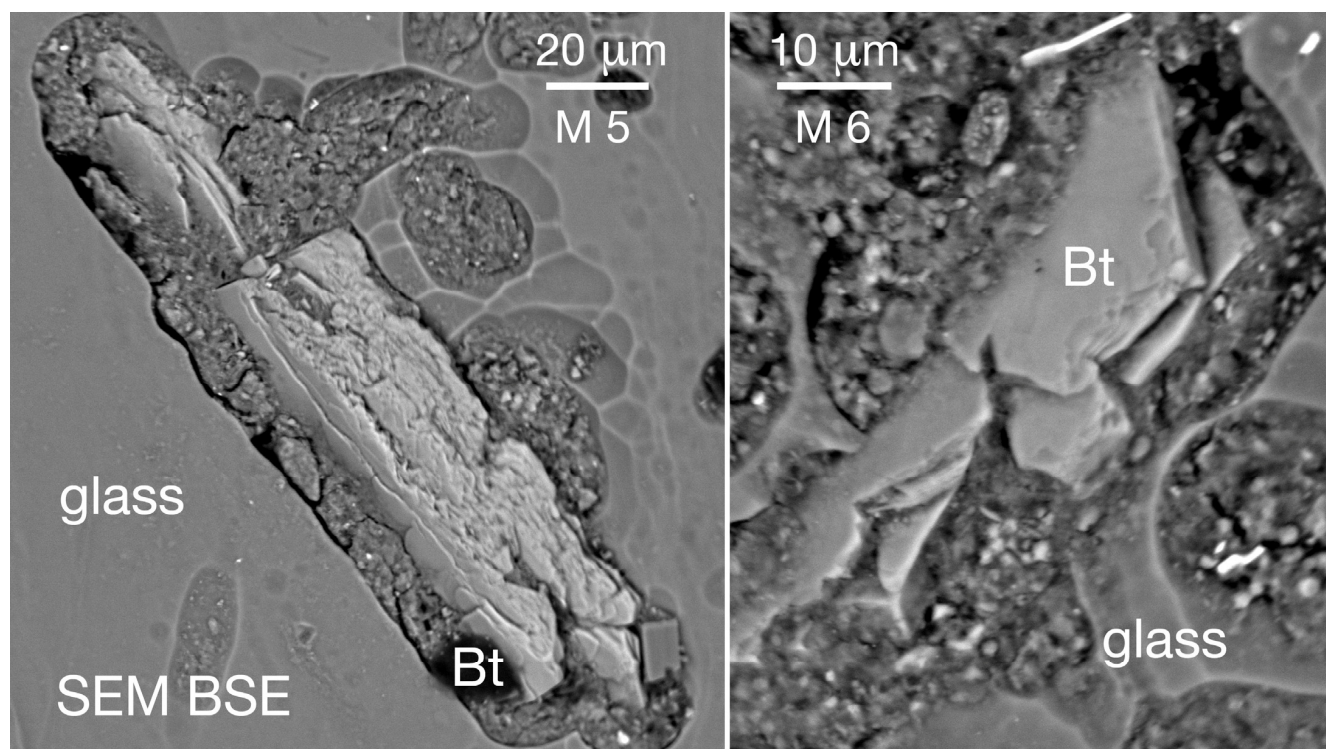


Figure 8. Backscattered SEM images of biotites in the M5 and M6 obsidian samples; the surface of the glass of the samples often shows widespread alteration minerals.

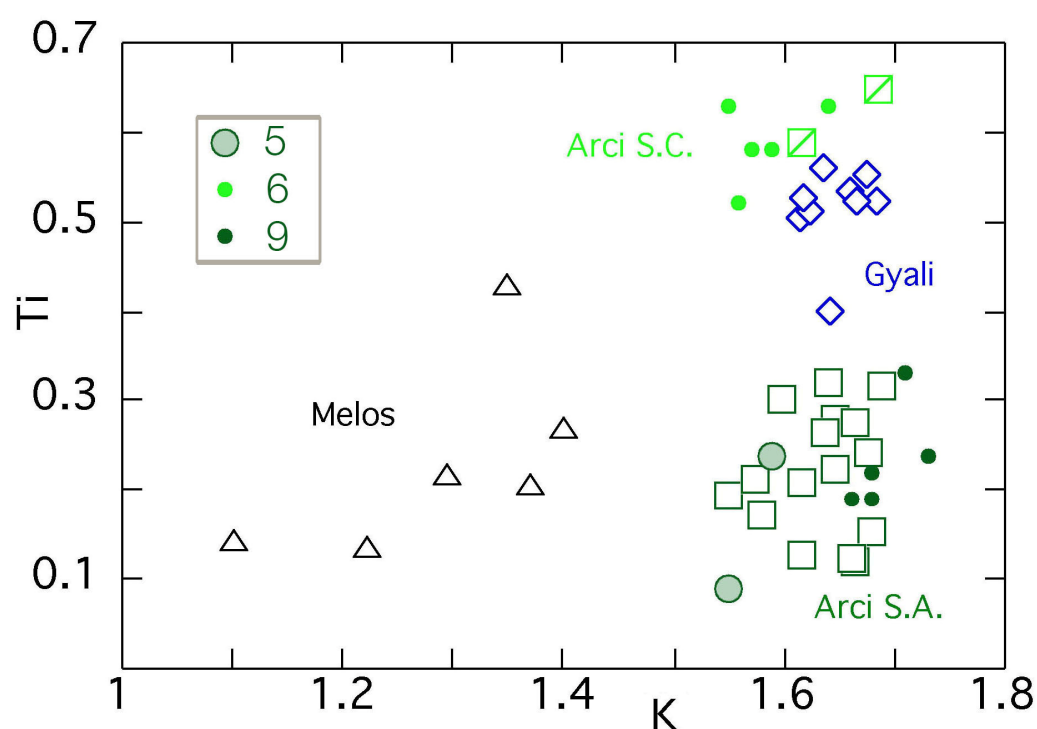


Figure 9. Composition of biotites plotted on a K vs. Ti diagram for the major Mediterranean obsidian source areas (data from [11]); biotite from samples 5, 6 and 9 of the Maddalena di Muccia site are plotted as solid symbols. Sub-source outcrops: Monte Arci, S.C. = Perdas Urias; S.A. = Conca Cannas, Canale Perdera and Riu Solacera.

Table 5. Biotite microanalyses (oxides expressed in wt%) of the Maddalena di Muccia obsidian samples; formula based on 22 oxygens.

Sample	M5 1	M5 2	M6 2a	M6 2b	M6 2c	M6 3a	M6 3c	M9 1a	M9 1b	M9 1d	M9 1e	M9 1f
SiO ₂	39.31	37.46	38.01	39.06	39.94	38.84	39.14	36.33	38.38	39.87	40.56	36.17
TiO ₂	0.81	2.13	5.65	5.31	4.81	5.76	2.67	2.04	1.62	2.94	1.97	1.59
Al ₂ O ₃	15.86	16.02	14.51	14.53	14.64	14.54	16.98	14.18	16.11	15.66	17.31	14.82
FeO	22.56	22.15	14.94	14.031	2.72	15.13	21.28	28.67	24.48	20.09	19.38	27.47
MnO	0.00	0.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.23	0.29
MgO	8.00	8.43	13.47	13.98	15.03	13.41	7.12	5.30	5.98	8.48	7.24	6.10
CaO	0.71	0.66	0.30	0.35	0.47	0.25	0.55	0.87	0.84	0.51	0.67	0.83
Na ₂ O	0.38	0.57	0.73	0.77	0.67	0.56	0.42	0.00	0.32	0.24	0.38	0.36
K ₂ O	7.98	8.15	8.75	8.54	8.49	8.30	7.61	8.56	8.51	9.02	8.88	8.39
Total	95.60	95.81	96.35	96.57	96.77	96.81	95.77	95.95	96.25	96.81	96.63	96.02
Si	5.969	5.716	5.599	5.693	5.758	5.666	5.875	5.748	5.876	5.934	6.003	5.691
Ti	0.092	0.245	0.626	0.582	0.521	0.632	0.301	0.242	0.186	0.329	0.220	0.189
Al	2.839	2.881	2.519	2.497	2.487	2.500	3.004	2.643	2.906	2.747	3.020	2.747
Fe	2.865	2.825	1.841	1.710	1.534	1.846	2.670	3.792	3.134	2.500	2.399	3.614
Mn	0.000	0.031	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.029	0.039
Mg	1.811	1.917	2.958	3.038	3.230	2.916	1.593	1.251	1.365	1.882	1.597	1.432
Ca	0.116	0.107	0.047	0.054	0.073	0.039	0.088	0.147	0.138	0.081	0.106	0.140
Na	0.111	0.168	0.210	0.219	0.187	0.159	0.123	0.000	0.095	0.070	0.109	0.109
K	1.546	1.586	1.644	1.588	1.561	1.545	1.457	1.728	1.663	1.712	1.677	1.684
Σ cat	15.347	15.477	15.442	15.380	15.351	15.304	15.112	15.552	15.364	15.255	15.160	15.644

Ultimately, the petroarchaeometric characterisation of obsidian using WD-XRF and SEM-EDS shows that the obsidian samples from the Neolithic and Copper Age phases of Maddalena di Muccia are attributable to three different source areas: Lipari, Palmarola and Monte Arci (Table 6). Two sub-sources within the Monte Arci source area are identifiable: Perdas Urias (S.C.) and Conca Cannas, Canale Perdera and Riu Solacera (S.A.).

Table 6. The provenance, contexts and dating of the analysed obsidian artefacts. (?) = uncertain attribution.

Sample ID	Year	SU	Item	Source	Context	Chronology
MAD01	2002	114, 1/VI	Bladelet	Palmarola	Storage pit	EN
MAD02	2002	114, 1/III	Flake	Palmarola	Storage pit	EN
MAD03a	2002	114, 1/VI	Blade mesial fragment	Palmarola	Storage pit	EN
MAD03b	2002	114, 1/VI	Bladelet	Palmarola	Storage pit	EN
MAD04	2002	114, sup.	Microflake	Palmarola	Storage pit	EN
MAD5	2005	464	Bladelet	Arci S.A.	Posthole among huts B, D, G	Copper Age
MAD6	2003	212	Retouched bladelet	Arci S.C.	Small pit cutting SU 213 (Copper Age)	ND
MAD7	2003	270A/1	Bladelet	Palmarola	Foundation trench hut B	Copper Age
MAD8	2003	128/1	Retouched bladelet	Palmarola	Pit	Copper Age
MAD9	2003	210/1	Bladelet	Arci S.A.	Posthole between huts A and B, next to Palisade A	Copper Age
MAD10a	2008	1	Bladelet	Palmarola	Layer overlying Palisade B	Copper Age (?)

Table 6. Cont.

Sample ID	Year	SU	Item	Source	Context	Chronology
MAD10b	2008	1	Bladelet	Lipari	Layer overlying Palisade B	Copper Age (?)
MAD11	2008	858	Retouched flake (denticulate)	Lipari	Area of material concentration overlying Palisade B	Copper Age (?)

4. Discussion

We can now compare our results with previously published data (Table 7) on the provenance of obsidian from Early to Late Neolithic sites in the Marche region [37,41–47] and, more broadly, the middle Adriatic regions of Italy from Emilia-Romagna to Abruzzo [24,45–51]. The data presented in Table 7 derive from studies carried out over an extended period of time and within different analytical and research frameworks; consequently, the proportion of characterised artefacts relative to the total assemblages cannot always be established, and the resulting datasets should not be regarded as statistically comparable. Nevertheless, when considered collectively, these data provide valuable evidence for reconstructing the spatial extent and diachronic development of the circulation of different obsidian sources over time.

Table 7. Summary of obsidian provenance data from archaeological sites in the middle Adriatic regions of Emilia-Romagna, Marche and Abruzzo (EN = Early Neolithic; MN = Middle Neolithic; RN = Recent Neolithic; FN = Final Neolithic; CA = Copper Age). n.d. = not determined.

Site	Chronology	Total	Lipari	Palmarola	Pantelleria	Sardinia	n.d.	Bibliographic Ref.
Fornace Cappuccini (RA)	EN	14	4	10				[48]
		18	8	10				[52]
Santa Maria in Selva (AN)	FN	32	31				1	[45–47]
		61	61					[42]
Portonovo (AN)	EN	2	2					[37]
Coppetella di Jesi (AN)	FN	5	5					[42,46,47]
Ripabianca di Monterado (AN)	EN	5	5					[42,46,47]
Donatelli di Genga (AN)	FN	2	2					[42,46,47]
Saline di Senigallia (AN)	FN	2	2					[42,46,47]
Maddalena di Muccia (AN)	EN-RN	8	6	2				[42,46,47]
	EN-CA	13	2	8		3		this paper
Fontenoce di Recanati (MC)	RN	1	1					[42,46,47]
Esanatoglia (MC)	EN	12	12					[53]
Monte Tinello (AP)	FN	1	1					[42,46,47]
Villa Panezia (AP)	RN	1		1				[42,46,47]
Colle Santo Stefano (AQ)	EN	9	3	6				[49,50]
		24		24				[45–47]
Settefonti (AQ)	RN	4	2	2				[50]
		10	3	6			1	[45–47]
Fonti San Callisto (AQ)	MN	1	1					[50]
Ripoli (TE)	MN	1	1					[50]
Paterno (TE)	FN	2	2					[50]

Table 7. *Cont.*

Site	Chronology	Total	Lipari	Palmarola	Pantelleria	Sardinia	n.d.	Bibliographic Ref.
Colle Cera (PE)	MN	35	29	4			2	[46,47]
	MN	53	46	7				[43]
Catignano (PE)	MN	3	3					[50]
		183	168	13			2	[44–47]
Villa Badessa (PE)	MN	4	2	2				[50]
Grotta dei Piccioni (PE)	RN		X					[43]
Marcianese (CH)	EN	2		2				[50]
Fossacesia (CH)	RN	4	4					[50]
		44	36	5	1		2	[45–47]

To enhance clarity without implying statistical comparability, Table 8 summarises the absolute number of characterised artefacts by source and chronological phase. In fact, in Table 7, the proportion of characterised artefacts relative to the original assemblages is not consistently known; therefore, the data should not be considered statistically representative.

Lipari appears to have been the primary source of obsidian in the central Mediterranean area and clearly has the widest distribution throughout Italy [51,54,55]. Our results, therefore, are in line with those from many other Early to Late Neolithic inland and coastal sites in the Marche [56]: Obsidian from Lipari is predominant and, at times, the only source present across all Neolithic periods.

Table 8. Absolute number of characterised artefacts by source and chronological phase referring to sites in the Central Adriatic region of Italy. The table aggregates only the analysed materials reported in Table 7 and is intended as a descriptive overview. (EN = Early Neolithic; MN = Middle Neolithic; RN = Recent Neolithic; FN = Final Neolithic; CA = Copper Age). n.d. = not determined.

Chronology	Lipari	Palmarola	Mount Arci	Pantelleria	n.d.	Total
EN	40	59				99
MN	250	26			4	280
RN	46	14		1	3	64
FN	103				1	104
CA	2	3	3			8

The exclusive presence of obsidian from Lipari at the Early Neolithic sites of Portonovo, Ripabianca di Monterado and, more recently, at the Esanatoglia site (unpublished analytical data reported in [53,57]) suggests the existence of consolidated strategies for procuring raw materials. An Early Neolithic spread of Pontine obsidian, alongside that from Lipari, through trans-Appennine routes to the west, covering significant distances, between the Tyrrhenian and the middle Adriatic coasts, is suggested by the predominant presence of obsidian from Palmarola [58] at the northern Early Neolithic site of Fornace Cappuccini in Emilia-Romagna ($n = 20$, 62.5% of the analysed samples [51,59–61]), with artefacts from Lipari, and at the southern Early Neolithic sites of Marcianese ($n = 2$, without artefacts from Lipari) and especially Colle Santo Stefano ($n = 20$, more than 70% of the samples analysed [62]).

Very limited obsidian from Palmarola had previously been identified by [42,46,47] at the inland multi-phase site of Maddalena di Muccia ($n = 2$, 25% of the analysed samples), albeit without any secure attribution to the Neolithic and/or Copper Age phases here

attested, and at the Recent Neolithic settlement of Villa Panezia ($n = 1$, 100% of the samples analysed). By contrast, the predominance of Palmarola obsidian from securely stratified Early Neolithic contexts at Maddalena di Muccia ($n = 5$ from SU 114, 38.5% of the analysed samples) documented by the present study confirms the widespread circulation of Pontine obsidian during the Early Neolithic. These new data highlight how, at the beginning of the 6th millennium BC, communities in central Adriatic Italy were fully integrated into wide-ranging exchange networks, capable of overcoming apparent physical barriers such as the Apennine chain.

During the subsequent phases of the Neolithic, circulation certainly intensified and became systematic. Obsidian from Lipari became the predominant type, sometimes to the exclusion of all others, from Mid-Neolithic phases onwards, as at Santa Maria in Selva ($n = 93$, 100% of the samples analysed [63]). Obsidian from Palmarola is attested, together with artefacts from Lipari, in many Middle to Late Neolithic villages in Abruzzo [64] such as Catignano ($n = 13$, 7% of the samples analysed [65]), Colle Cera ($n = 11$, 12.5% of the samples analysed), Villa Badessa ($n = 2$, 50% of the samples analysed), Fossacesia ($n = 5$, 10% of the samples analysed), not distant from the Adriatic coast, and at the inland settlements of Settefonti ($n = 8$, 57% of the samples analysed [66]), confirming overland trans-Apennine exchange networks.

The provenance from the island of Pantelleria of one specimen found in the Recent Neolithic site of Fossacesia (Table 5.3 [46]; Table 9.2 [47]) has hitherto not been confirmed by edited analytical data (it is not reported in [45]: 540, Figure 3), nor has the related sub-source been identified. In any case, the sample from Pantelleria at the Late Neolithic necropolis of Galliano (sub-source of Salto la Vecchia and Balata dei Turchi [67]), in a chronologically well-defined context (T5 dated to LTL15556A: 5628 ± 45 BP, 4543–4357 BC), significantly expands its known distribution area toward the Adriatic regions during the second half of the 5th millennium BC, compared to the previously recognised, more restricted distribution limited to Western Sicily, Malta and the northern coast of Tunisia [68].

The three obsidian samples from Monte Arci [69] documented at Maddalena di Muccia from two different sub-sources (S.A. and S.C. types) currently represent the only evidence of multiple Sardinian obsidian sub-sources identified along the Adriatic coast. The presence of a Sardinian obsidian in the Marche is reported in two previously cited papers (Table 5.3 [46]; Table 9.2 [47]), but its archaeological provenance is not further specified, except for the presumed date of sampling of “Mar 02”, nor has the related sub-source been identified.

The discovery of one tiny bladelet from Sardinia (S.C. type) in Puglia, in the karstic doline of Pulo di Molfetta on the Adriatic coast [38], has already expanded the geographical range of Monte Arci obsidian exploitation and distribution from Sardinia to Southern Italy during the Neolithic. More recently, obsidian artefacts from the S.A. and SB2 sources have been recovered from the Late Neolithic layers (Spatarella facies) of the cave at San Michele Arcangelo di Saracena [70]. An exclusive presence of obsidian from Monte Arci (without indication of the intra-island sub-sources) was identified by [46,47] (tab. 5.5 and tab. 9.4 respectively) at the otherwise unknown site of Masseria di Gioia (Brindisi province, Puglia), documented only by surface materials from archaeological surveys.

On the Tyrrhenian side, Sardinian sources account for all of the obsidian found in Sardinia and Corsica, and, until now, have been documented only in Central Italy (Tuscany and Lazio) and Northern Italy (Liguria and several sites north of the Po River) [52,71–73].

Obsidian from Sardinia, frequently in association with that from Lipari, is well-documented in northern Tuscany at Grotta all’Onda, Neto di Bolasse, Podere Casanova, Spazzavento and Neto-Via Verga [45,51,71]. In southern Tuscany (as at La Consuma and La Chiarentana), a more significant role of contact with the south of Italy is confirmed by the presence of obsidian from Palmarola. Obsidian from Monte Arci is rarely attested south

of the Tiber River; in southern Lazio, it is so far documented only at the sites of Casali di Porta Medaglia (Rome [74,75]) and Casale del Dolce (Anagni [76]).

Obsidian circulation declines after the end of the Neolithic, but, although episodic, it continues throughout the Copper Age. In the Rome area, where numerous settlements and necropoleis span a broad chronological range between the 4th and 3rd millennia BCE, obsidian is attested in the form of cores, débitage, and tools in Middle Copper Age contexts associated with the Gaudio facies (Casetta Mistici, Tor Pagnotta), as well as in Late Copper Age contexts corresponding to the Laterza and Ortucchio facies (Casale Massima, Osteria del Curato-Via Cinquefrondi, Quadrato di Torre Spaccata) [77,78]. Obsidian artefacts are also found in graves of the Middle Copper Age Rinaldone facies (Lucrezia Romana t.67, Ponte delle Sette Miglia t.6, Osteria del Curato t.7 [79]). Notably, two large obsidian cores were included among the grave goods of a Rinaldone burial at Sgurgola-Casali, also in Lazio [80,81]. At Maddalena di Muccia, obsidian appears to enter the site primarily as finished products, mostly in the form of bladelets. Nevertheless, the assemblage is numerically too small to allow robust conclusions about the modalities of the raw material's introduction to the site.

One of the key contributions of the present study is the documentation of obsidian use at Maddalena di Muccia during the final phases of the Copper Age, a period for which evidence has been comparatively scarce. Notably, three of the eight analysed artefacts are attributed to Monte Arci, including multiple sub-sources, indicating a continued circulation of obsidian from different primary sources into the late Copper Age. The presence of Sardinian obsidian could reflect embedded procurement potentially linked to other high-quality raw materials, such as silver. No direct evidence of silver is documented at Maddalena di Muccia, nor at other Copper Age sites in the Adriatic regions of Italy; except for a silver sheet fragment recovered from the cemetery of Celletta dei Passeri (Emilia-Romagna) [82]. Nevertheless, silver from Sardinian sources is geochemically attested at contemporary sites in the Rome area [83,84]. Inland communities of Central Italy, located along natural trans-Appennine communication routes, may have acted as intermediary nodes facilitating these broader exchange networks. Taken together, our results highlight the complexity and continuity of resource circulation and provide new insights into the role of central Italian communities within long-distance interaction systems during the late Copper Age.

5. Conclusions

Petroarchaeometric characterisation of obsidian artefacts of the Maddalena di Muccia site, performed using non-destructive techniques on both the glass matrix and the microphenocrysts, allowed the identification of three different volcanic source areas in the Mediterranean region (i.e., Palmarola, Lipari, and Monte Arci) and, for one of these, even two different sub-sources (i.e., Monte Arci S.A. and Monte Arci S.C.). The study provides, in particular, the first evidence in the Adriatic region of the significant and simultaneous presence of obsidian artefacts originating from multiple sub-sources of Monte Arci, suggesting a lasting and long-term exchange of Sardinian obsidian along with that coming from other Mediterranean sources.

The assemblage of Maddalena di Muccia provides significant data for several reasons. First, they confirm the predominant use of Palmarola obsidian in the Early Neolithic. Second, they show the continued use of obsidian into the Copper Age. Although some artefacts may represent the reuse of materials from older structures, as suggested by double patina, others are clearly associated with the Copper Age settlement phase. Consistent with observations in the Roman area, the quantity of obsidian increases in the final Eneolithic phases.

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