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Provenance of Neolithic Stone Artefacts through Minimally Invasive or Absolutely Non-Destructive Petroarchaeometric Investigations: Some Cases from Calabria (Southern Italy)

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Abstract: In the present work, more than one hundred and thirty lithic artefacts rediscovered in several archaeological sites dating from the Upper Palaeolithic to the Middle Ages from Calabria (Southern Italy) were petroarchaeometrically characterised through minimally invasive techniques. In more detail, 110 specimens were found in the Grotta della Monaca site (Sant'Agata di Esaro), and the other 23 belong to a collection kept in the Museo Nazionale Preistorico ed Etnografico "Luigi Pigorini" (Roma), coming from several localities (Longobucco, Spezzano della Sila, Cicala, Gimigliano, Roccaforte del Greco, and Bova). For preservation needs, 2 small axes in polished stone and 2 obsidians collected from Grotta della Monaca were analysed by absolutely non-destructive techniques. Optical and electron microscopic investigations, sometimes integrated with wavelength-dispersive X-ray fluorescence spectroscopy and X-ray diffraction spectrometry, allowed us to ascertain that the source area of all the lithic tools was in Calabria, except for obsidians, which come from the island of Lipari (Messina, Southern Italy). For a small number of particularly favourable cases, it was possible to define with great precision the outcrop area of the used rocks given their textural and mineralogical features. The specific source area contained a pickaxe originating from Cetraro–Fuscaldo metabasalt (lawsonite–albite facies) outcrops and two small axes in polished stone, one derived from migmatitic metapelites from Palmi and the other from meta-ultramafic rocks from Curinga. The choice of the used lithologies, harder or softer, had to be linked to the use that humans had to make of the lithic artefacts.

Keywords: lithic artefact provenance; petroarchaeometry; absolutely non-destructive techniques; WD-XRF; X-ray diffraction; SEM-EDS; Calabria

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1. Introduction

Petroarchaeometric techniques used for minimally invasive or absolutely non-destructive investigations of archaeological lithic artefacts were developed at the Dipartimento di Scienze della Terra e Geoambientali of the Bari University (Italy) in the last thirty years, with the aim of identifying their source areas. Optical microscopy (OM) and scanning electron microscopy (SEM), coupled with energy-dispersive (ED) and wavelength-dispersive (WD) spectroscopy and X-ray fluorescence spectrometry (XRF), represent the most used petroarchaeometric techniques. Dedicated laboratories are frequently equipped with the following: (i) handheld or (ii) field-portable instruments that allow in situ and very quick and inexpensive characterisations of archaeomaterials, together with initial investigations and selections of artefacts; (iii) more complex and expensive apparatuses, generally bench instruments, for very accurate quantitative analyses [1–11]. X-ray diffraction spectrometry (XRD), particularly useful for the identification of mineral phases in a sample, can be used as a non-destructive technique, but it is normally employed on powdered specimens (powdered XRD) and involves the partial destruction of a small part of the sample.

Regarding some lithoid artefacts, frequently, it is not sufficient to observe only its surface, but it is necessary to obtain a small part of its interior as well; this can be achieved by (i) taking a small fragment by breaking it along a discontinuity surface already weakened by alteration; (ii) cutting a small part of it with a diamond saw; or (iii) carrying out micro-carving to remove a representative internal part, without irreparably disfiguring it.

The extraction of a drilled portion of the sample [1] allows for the realisation of a rock thin section, which is useful for the petrographic characterisation of the artefact (Figure 1). The borehole generated in the sample during drilling operations can be easily camouflaged by filling the cavity with inert, non-hygroscopic compounds (plasticine, cement, mastic, etc.) and using a small portion of the sample itself as a plug (Figure 1, step 5).

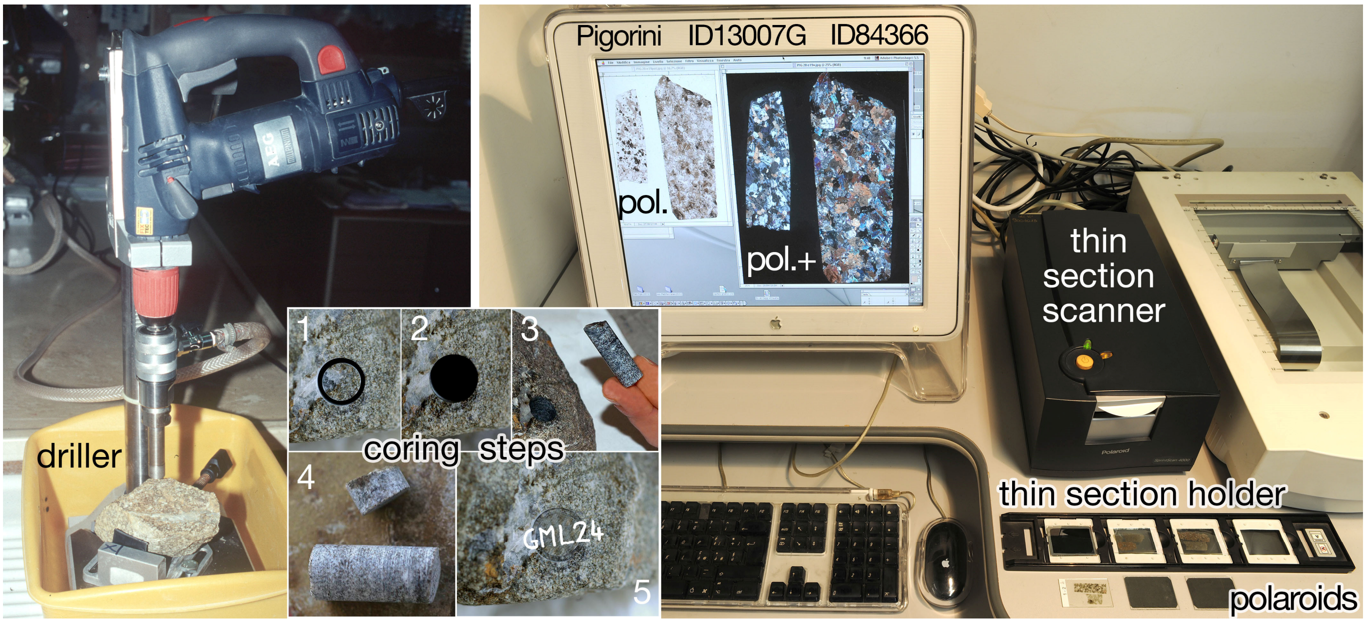


Figure 1. On the left, the sampling of a small part of the archaeological mining sample using a water-cooled diamond core driller; in the centre, drilling in five steps (see text for explanation) realised on the least important archaeological surface of the specimen. On the right, the polarised-light digital scanning of the petrographic thin section realised on the cored samples. pol. = polarised light; pol.+ = cross-polarised light.

In other cases, the small dimensions of an artefact or the importance of its preservation without the possibility of the removal of a part of it, as in the case of obsidians, must direct research toward absolutely non-destructive analytical techniques.

In some cases, investigations provide precise indications regarding the source area of the rocks used: for obsidians, not only the accurate source area but, in the luckiest cases, also the sub-source area ([1,12] and the references therein). In other favourable cases, when lithologies are not particularly widespread and, in addition, some minerals characterised by very particular chemical compositions are present, the precise attribution of the raw material source area can be formulated ([13] and the references therein). Normally, the lithologies can be correlated to different source areas ascribable to nearby rock outcrops.

This type of study is crucial in archaeology for tracking cultural correlations and the trade of raw materials between communities, aspects that were completely unexplored until a few years ago. Analytical studies aimed at the provenance of ancient stone artefacts are actually very common, although non-invasive techniques are not often adopted: relevant case studies that testify to the breadth and complexity of this topic are shown in [14–18].

The aim of this work is to precisely identify the provenance areas of lithic artefacts found in several archaeological sites in Calabria (Figure 2) through refined analysis using absolutely non-destructive or minimally invasive techniques. The strength of this research team in the identification of the source rocks lies in its members' profound knowledge of the petrographic characters of Calabrian rocks after many years of field and laboratory petrological investigations (e.g., [19–26]).

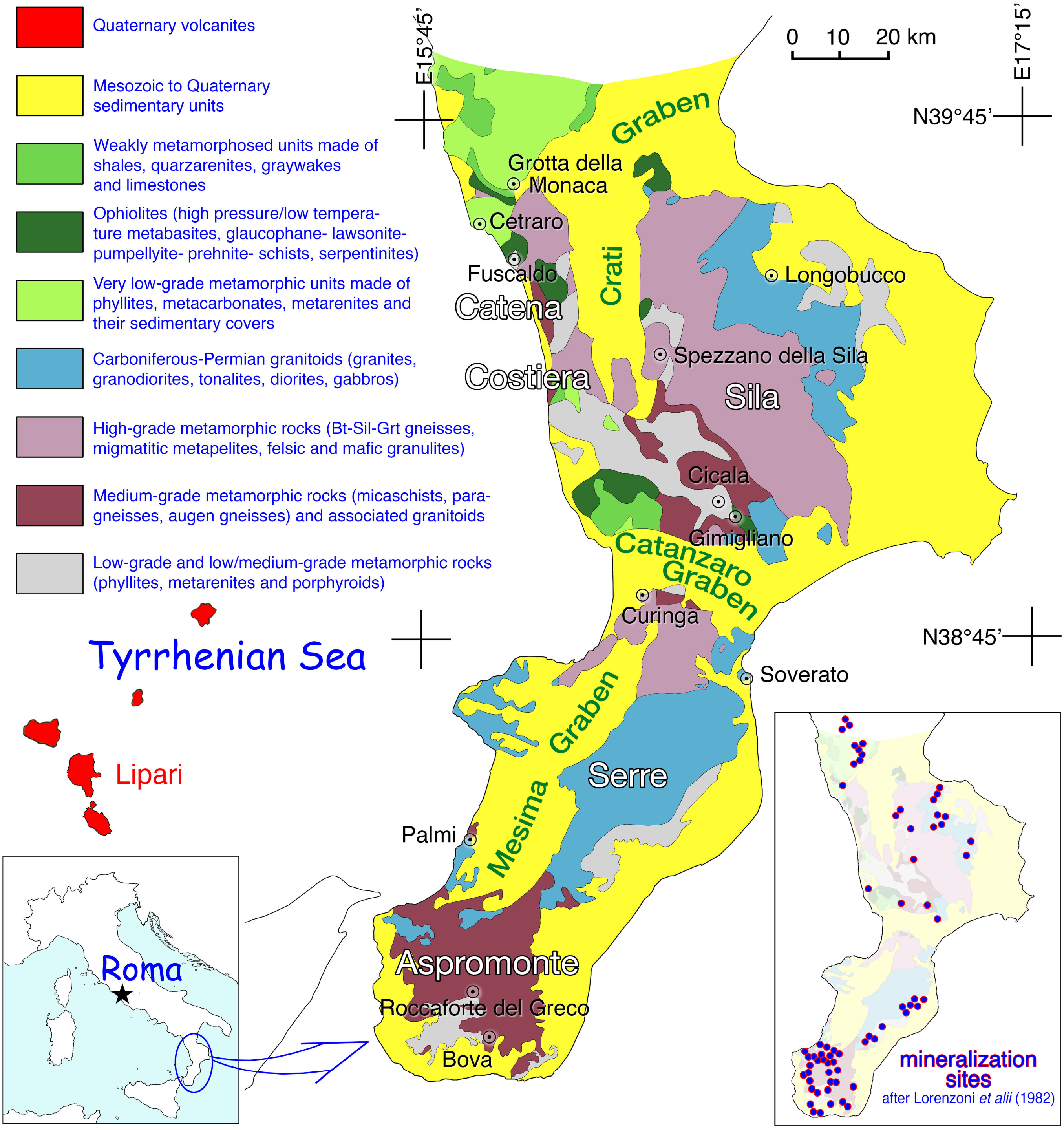


Figure 2. Geolithologic schematic map of Calabria (modified from [27]) with the archaeological localities where the samples were found; in the little bottom-right inset, the main Calabria mineralisation sites are shown (after [28]).

2. Materials and Methods

2.1. Sample Distribution and Their Geological Context

An accurate petrographic characterisation of the stone artefacts was performed using a scanning electron microscope to constrain their origin in relation to the source areas. These samples were already studied archaeologically [29,30], but their mineralogical compositions, determined through sophisticated analytical instruments, are lacking.

The majority of the studied samples (110 specimens) were found in the Grotta della Monaca site (39°37′39.5″ N, 15°58′31.9″ E), near the village of Sant'Agata di Esaro in Northern Calabria (Figure 2). The archaeological site is represented by a cave more than 500 m long, developed into impure metacarbonates and frequented by humans from the Upper Palaeolithic to the Middle Ages. The cave was used as a mine to extract Cu-Fe minerals, represented essentially by malachite [$Cu_2CO_3(OH)_2$], goethite [FeO(OH)] and azzurrite [$Cu_3(CO_3)_2(OH)_2$] [29,30], useful for pigment production. During the middle Bronze Age, moreover, the cavity was also used as a sepulchral site [31]. In the underground system of the Grotta della Monaca site, 110 artefacts related to mining activity were found, including 34 obsidian objects and 2 small axes in polished stone, the latter being related to the hypogeum sepulchral site and used as ritual objects [29,30,32].

Other lithic mining artefacts also found in Calabria, belonging to a museum collection of the Museo Nazionale Preistorico ed Etnografico "Luigi Pigorini" (Roma), were petroarchaeometrically investigated in this research. In more detail, 23 grooved samples were collected from several localities in Central and Southern Calabria (Figure 2): 2 samples from Longobucco, 1 sample from Spezzano della Sila, 5 samples from Cicala, 1 sample from Gimigliano, 8 samples from Roccaforte del Greco, 2 samples from Bova, and 3 samples from unknown areas.

Since all the studied lithic finds come from Calabria sites, an overview of the geolithological characteristics of this region is appropriately provided. The Calabria region occupies the largest part of the Calabria–Peloritani terrane [33], i.e., the "*calabro-peloritano* arc" *sensu* [34] (Figure 2), which is an Alpine nappe stack consisting of crustal rocks of continental and oceanic origin. In a plan view, the "*calabro-peloritano* arc" shows an arcuate shape and connects the reliefs of the Southern Apennines to those of the Maghrebian chain (Figure 2). It should be noted that despite the following updated geological synthesis (e.g., [24,33,35]), the regional geologic map according to [27] still remains a reference for the geolithology of Calabria (Figure 2).

The various nappes or tectonic units consist mainly of "crystalline" rock bodies and are representative of portions of Palaeozoic continental crust (pertaining to the European or African plates) and sectors of Mesozoic oceanic crust (related to the Alpine Tethys). Crystalline reliefs, i.e., Catena Costiera, Sila, Serre, Capo Vaticano, and Aspromonte, and Cenozoic tectonic depressions, i.e., Catanzaro, Crati, and Mesima *gräben*, in turn filled with marine sediments (Figure 2), characterise the landscape. The depressions, called Catanzaro, Crati, and Mesima *gräben*, are covered by recent deposits of the Amato, Crati, and Mesima rivers. A peculiarity of Calabrian geology is that, to the north of Catanzaro *graben,* rocks belonging to both continental and oceanic crust units outcrop, while, to the south, only continental crust units outcrop.

The oceanic crust units mainly include basaltic meta-volcanites reworked by Alpine metamorphism and serpentinites (ophiolites); the continental crust units are formed by low- to high-grade metamorphic rocks and Palaeozoic granitoids (Figure 2). These crystalline rocks are covered by sedimentary deposits dominated by limestones.

As regards the continental crust units, medium- to high-grade metamorphites (micaschists, paragneisses, augen gneisses, and minor metabasites) and Carboniferous–Permian granitoids predominate in the Sila, Serre, and Aspromonte massifs, together with phyllites and sedimentary rocks, including limestones (Figure 2). A great variety of mineralisation is associated with medium- to high-grade metamorphites and Palaeozoic granitoids, especially in the Aspromonte area [28] (Figure 2).

Geographically connected with the "*calabro-peloritano* arc" is the volcanic arc of the Aeolian Islands (Figure 2), whose volcanism also gave rise to the Quaternary rhyolitic flows that produced glassy rocks such as obsidians [31,36–42].

2.2. Petroarchaeometric Investigation Techniques

The petrographic characterisation of lithic artefacts, apart from obsidians, was performed with (i) a Polaroid (Amsterdam, The Netherlands) mod. Sprintscan 4000 (28 Mpx per inch sensor) with a diapositive sample holder, modified to accommodate polished thin sections and two Polaroid polarising filters, perpendicular to each other (Figure 1); (ii) a Zeiss Photomicroscope III Pol polarising optical microscope (Carl Zeiss, Oberkochen Germany) equipped with a EUROMEX VC 3036 (Arnhem, The Netherlands) digital camera (CCD Sony 1/2.8" and 6.0 Mpx).

Supplementary petroarchaeometric investigations of thin sections were performed with a SEM from LEO, model EVO50XVP (Zeiss, Cambridge, Cambridgeshire, UK), equipped with an X-max (80 mm^2) Silicon drift Oxford detector (Figure 3); microanalytical data were obtained under the following operating conditions: 15 kV accelerating potential, 500 pA probe current, about 25,000 output cps as the average count rate on the whole spectrum, counting time of 50 s, and 8.5 mm working distance.

Figure 3. In the left part of the figure is the scanning electron microscope equipped for microanalysis (SEM-EDS) with a Silicon Drift energy-dispersive X-ray detector (SDD); the yellow-bordered insets show two different SEM sample holders for thin-section and stub-mounted samples (**left** inset) or for the investigation of massive non sputtered specimens (in the **right** inset, two small polished stone axes). On the right side of the figure is presented the wavelength-dispersive X-ray fluorescence spectrometer (WD-XRF) used for non-destructive analyses of obsidians: in this case, the obsidian sample holder is closed at the bottom with a thin polyester film, at the centre of which is placed the specimen that appears to be suspended in the air.

X-ray intensities were converted to the concentrations of the elements by using the XPP correction scheme developed by [43,44], granted as quantitative software support by Oxford-Link Analytical (Bicester, Oxfordshire, UK); microanalytical data were checked using numerous reference materials (standards from Micro-Analysis Consultants Ltd., St Ives, Cambridgeshire, UK) for mineral phases, taking into particular account the crystal chemical formula. For pumpellyite analyses, the chemical formula was recalculated as suggested by [45]. Before SEM-EDS analyses, the thin sections were sputtered with a 30 nm thick carbon film using an Edwards Auto 306 (Irvine, California, USA) thermal evaporator.

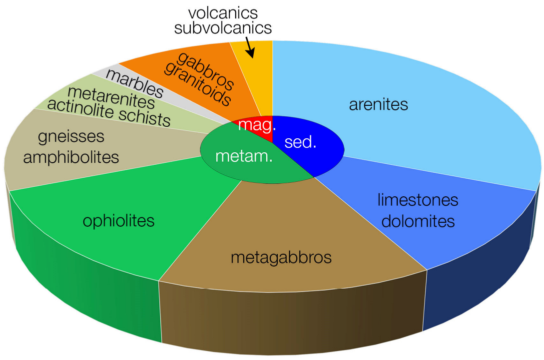
Petroarchaeometric characterisation was performed on two small axes in polished stone and on two obsidian samples. The investigation equipment was (i) SEM-EDS, without carbon-sputtering the sample (Figure 3); (ii) an X-ray diffraction (XRD) spectrometer from PANalytical, model X'Pert Pro (PANalytical B.V., Lelyweg 1, 7602 EA Almelo, The Netherlands), equipped with a Cu X-ray tube (power supply at 40 kV, 40 mA), whose CuKα radiation was partially monochromated with a Ni filter; (iii) a wavelength-dispersive X-ray fluorescence spectrometer (WD-XRF) from PANalytical, model Axios-Advanced, equipped with a 4 kW Rh super-sharp end-window X-ray tube, in which the obsidian sample was placed on a thin Mylar film, which was used to close the bottom of the spectrometer sample holder (Figure 3). The analytical conditions to measure the X-ray intensity ratio of Y, Zr, and Nb, as suggested by [46], were 60 kV and 66 mA, with an X-ray tube power supply and a scintillator detector to collect the X-ray lines dispersed by a LiF 220 crystal.

3. Results

3.1. Petrographic Features of Artefacts

The majority of the mining tools were petrographically characterised by thin-section optical microscopy; only two small axes and all the obsidian specimens were characterised with scanning electron microscopy microanalyses and X-ray diffraction spectrometry.

The petrographic observations (Supplementary Materials S1) of the lithologies of the archaeological mining samples—110 from the Grotta della Monaca site, in the surroundings of Sant'Agata di Esaro village (Figure 2), and 23 from the Museo Nazionale Preistorico ed Etnografico "Luigi Pigorini" in Roma (Figures 4 and 5)—revealed that the most common lithology is represented by metamorphic rocks (52 samples from Grotta della Monaca and 12 samples from Pigorini Museum), followed by sedimentary rocks (54 samples only from Grotta della Monaca) and, finally, magmatic rocks (4 samples from Grotta della Monaca and 11 samples from Pigorini Museum). The distribution of the various metamorphic, sedimentary, and magmatic rock types is shown in Figure 4.



	n. of sample		GdM	Pigorini	%
metamorphic	64	metagabbros (high grade)	19		14.3
		ophiolites	20		15.0
		gneiss and amphibolites (medium-high grade metam.)	10	4	10.5
		actinolite schists and metarenites (low grade metam.)		8	6.0
		marbles	3		2.3
sedimentary	54	arenites	41		30.8
		limestones and dolomites	13		9.8
magmatic	15	gabbroic and granitoid rocks	4	7	8.3
		volcanics and subvolcanics		4	3.0
total	133		110	23	100.0

Figure 4. The pie chart shows (on the (**left**)) the relative abundances of the main lithologies among the archaeological mining samples (110 artefacts from the Grotta della Monaca site and 23 artefacts from Pigorini Museum), and the table (on the (**right**)) lists the percentages of the rock types; the largest group is metamorphic (metam.) rocks, followed by sedimentary (sed.) and magmatic (mag.) rocks.

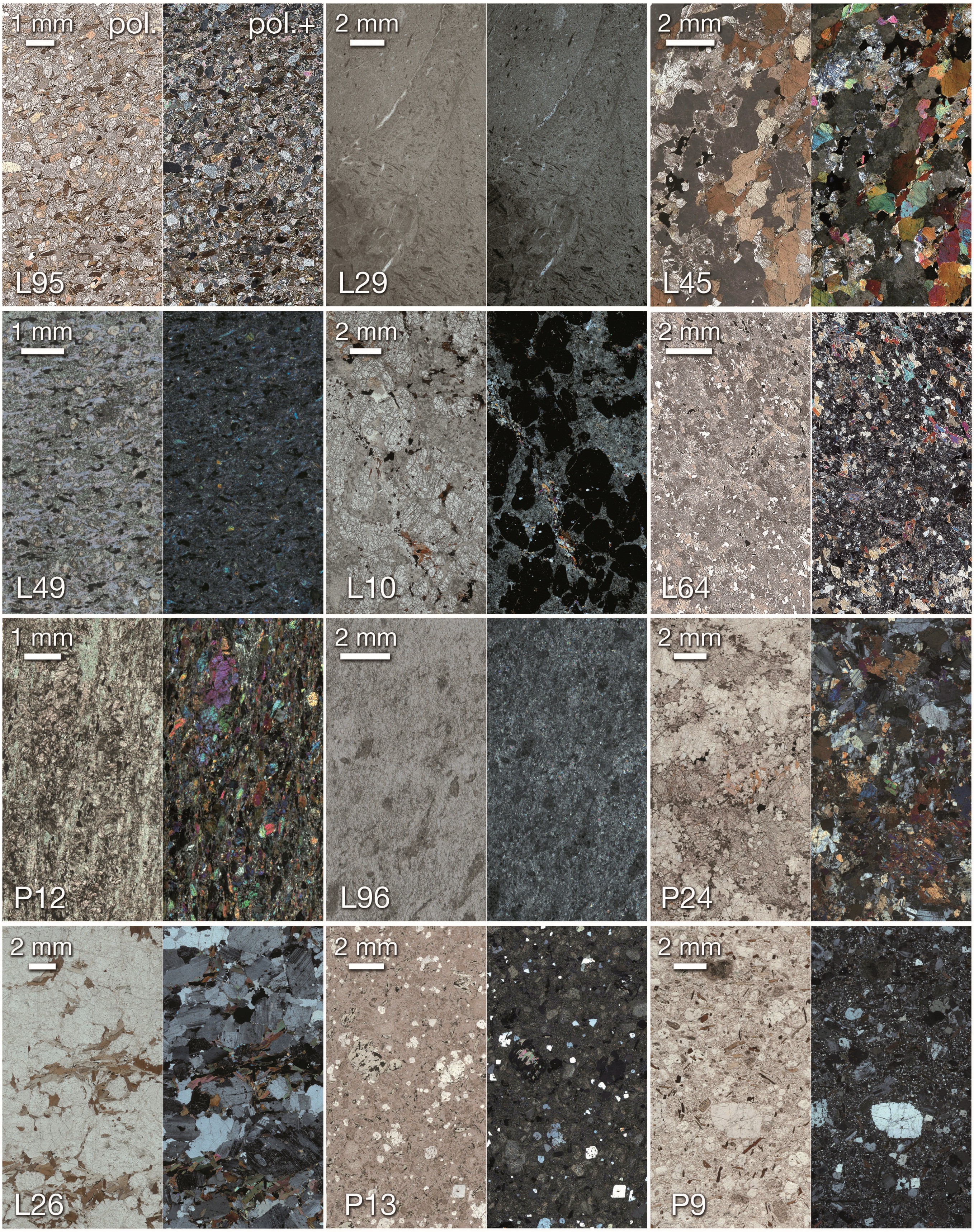


Figure 5. Polarised-light digital scan of the petrographic thin section of the samples representing each rock group (refer to Figure 4). Arenites: L95, litharenite. Limestones and dolomites: L29, fossiliferous limestone. Metagabbros: L45, pyroxene–amphibole metagabbro. Ophiolites: L49, glaucophane–lawsonite

scist. Gneisses and amphibolites: L10, garnet–sillimanite–plagioclase gneiss; L64, amphibolite. Metarenites and actinolite schists: P12 (Pigorini ID 84459), actinolite–chlorite schist. Marbles: L96, marble with rare silicates. Gabbros and granitoids: P24 (Pigorini ID 84443), amphibole-bearing gabbro; L26, biotite-bearing tonalite. Volcanic and subvolcanics: P13 (Pigorini ID 84456), rhyolite; P9 (Pigorini ID 84418), dacite. The labels L and P indicate the samples from Grotta della Monaca and Museo Pigorini, respectively; pol. = polarised light; pol.+ = cross-polarised light.

Metamorphic processes evolved on pre-existing rocks and induced the recrystallisation of the mineralogical association, forming a stable paragenesis under the new P-T conditions. The stone artefacts are mainly metamorphic rocks affected by recrystallisation on magmatic, metamorphic, or sedimentary protoliths. The studied samples can be classified on the basis of equilibrium paragenesis: (i) under high-temperature conditions, some samples can be classified as metagabbros, mafic granulites, felsic granulites, meta-ultramafics, amphibolites, and garnet–biotite–sillimanite gneisses; (ii) low- to medium-grade metamorphic rocks belonging to ophiolitic suites affected by high-pressure (HP) and low-temperature (LT) metamorphic conditions, such as glaucophane–lawsonite–pumpellyite–prehnite schists, have also been recognised; (iii) actinolite schists, meta-arenites, and marbles recrystallised under low-P-T conditions.

Table 1 shows the mineralogical associations and metamorphic grades of the metamorphic rocks, which account for 48% of the artefacts, while 41% are sedimentary rocks (Figure 4).

Table 1. Petrographic characteristics of the main lithologies recognised among the artefacts (mineral abbreviations according to [47]).

Metamorphic rocks				
Name	**Protoliths**	**Mineralogical association**	**Metamorphic grade**	**Provenance of sample**
Metagabbro	Igneous	Pl, Cpx, Opx, Amph, Grt, Bt	High grade	Grotta della Monaca
Mafic granulite	Igneous	Pl, Opx, Kfs, Cpx, Qtz, Amph, Grt	High grade	Grotta della Monaca
Felsic granulite	Igneous/sedimentary	Qtz, Pl, Kfs, Opx/Sil, Grt	High grade	Grotta della Monaca
Meta-ultramafite	Igneous	Ol, Px, Pl, Amph, Phl, Spl, Srp, Opq	Low grade	Grotta della Monaca
Amphibolite and amphibole-bearing gneiss	Igneous/sedimentary	Amph, Bt, Pl, Qtz	High/medium grade	Grotta della Monaca/ Museo Pigorini
Garnet-biotite-sillimanite gneiss	Sedimentary	Qtz, Pl, Kfs, Bt, Sil, Grt, Crd	High grade	Grotta della Monaca/ Museo Pigorini
Glaucophane-lawsonite- pumpellyite-prehnite- schists	Igneous	Gln- Lws- Pmp- Prh, Ep, Qtz, Pl, Chl	Low grade(HP-LT)	Grotta della Monaca
Actinolite schist	Igneous/sedimentary	Amph, Chl, Qtz, Pl, Ep, Px, Opq	Low grade	Museo Pigorini
Metarenite	Sedimentary	Qtz, Pl, Kfs, Grt, Amph, Chl, Ep, Cal	Low grade	Museo Pigorini
Marble	Sedimentary	Cal, ± Qtz	Low grade	Grotta della Monaca

Table 1. *Cont.*

Sedimentary rocks				
Name	**Mineralogical composition/fossils**			**Provenance of sample**
Litharenites	Lithic label fragments, Qtz, Fsp, Mca, fossils			Grotta della Monaca
Hybrid sandstone	Cal, Qtz, Mca, Fsp, fossils			Grotta della Monaca
Quartzarenites	Qtz, Kfs			Grotta della Monaca
Limestones and marl-limestone	Cal, fossils			Grotta della Monaca
Dolomites	Dol, fossils			Grotta della Monaca
Magmatic rocks				
Name	**Mineralogical composition**	**Type**	**Texture**	**Provenance of sample**
Gabbro-diorite	Pl, Px, Amph	Intrusive	Holocrystalline	Grotta della Monaca /Museo Pigorini
Granite	Qtz, Pl, Kfs, Bt	Intrusive	Holocrystalline	Grotta della Monaca /Museo Pigorini
Tonalite	Qtz, Pl, Bt, Amph	Intrusive	Holocrystalline	Grotta della Monaca
Rhyolite	Qtz, Fsp, Bt	Effusive	Porphyritic	Museo Pigorini
Dacite	Qtz, Pl, Bt	Effusive	Porphyritic	Museo Pigorini

Among the sedimentary rocks, sandstones consisting of litharenites, hybrid sandstones (formed by silicate and carbonate materials), and quartzarenites predominate, and carbonate rocks such as limestones, marly limestones, and dolomites with microfossils may also be present (Table 1). The remaining 11% consists of magmatic rocks, both intrusive, such as gabbros, diorites, and tonalites, and volcanites or subvolcanites, such as rhyolites and dacites, with a porphyritic texture (Figure 5, Table 1).

3.2. Mineral Chemistry of Artefacts

Three samples of artefacts formed by metamorphic rocks and containing peculiar minerals, such as pumpellyite, dark mica, and aluminosilicate, were analysed to establish the mineral chemistry of these phases and to compare their compositions with those of possible candidate natural sources.

The mineralogical association of the L34 artefact found at Grotta della Monaca consists of plagioclase, glaucophane, lawsonite, pumpellyite, epidote, and opaque; this paragenesis is stable around temperatures of 200–300 °C and at pressures of ~5–6 kbar in metabasite affected by HP-LT metamorphism during the burial or subduction process. These rock types are found in geological settings characterised by ophiolitic suites representing basaltic products forming the oceanic crust, covered by sedimentary deposits of the oceanic environment involved in subduction-related tectonic processes. In Italy, schists with pumpellyite occur along the Alpine chain (in the Alps and in Calabria) and are part of the ophiolitic suites exhumed after the Alpine orogeny; the areas of occurrence are shown in Figure 6. Pumpellyite chemistry in metabasites was detected in the Alps and Calabria by [25,48]. The chemical composition of the pumpellyite from the L34 ophiolite artefact was determined using SEM-EDS. The chemistry of pumpellyite was compared with that in the literature to propose the source area of the archaeomaterial. The chemical comparison based on the Al, Fe^{2+}, and Mg contents of pumpellyite (Figure 6) allowed us to identify its provenance as ophiolite rock types outcropping in Catena Costiera, precisely from the Cetraro–Fuscaldo area (Figure 2), as shown by the tighter overlap with pumpellyites from this area (outcrop SA-215 in Figure 6).

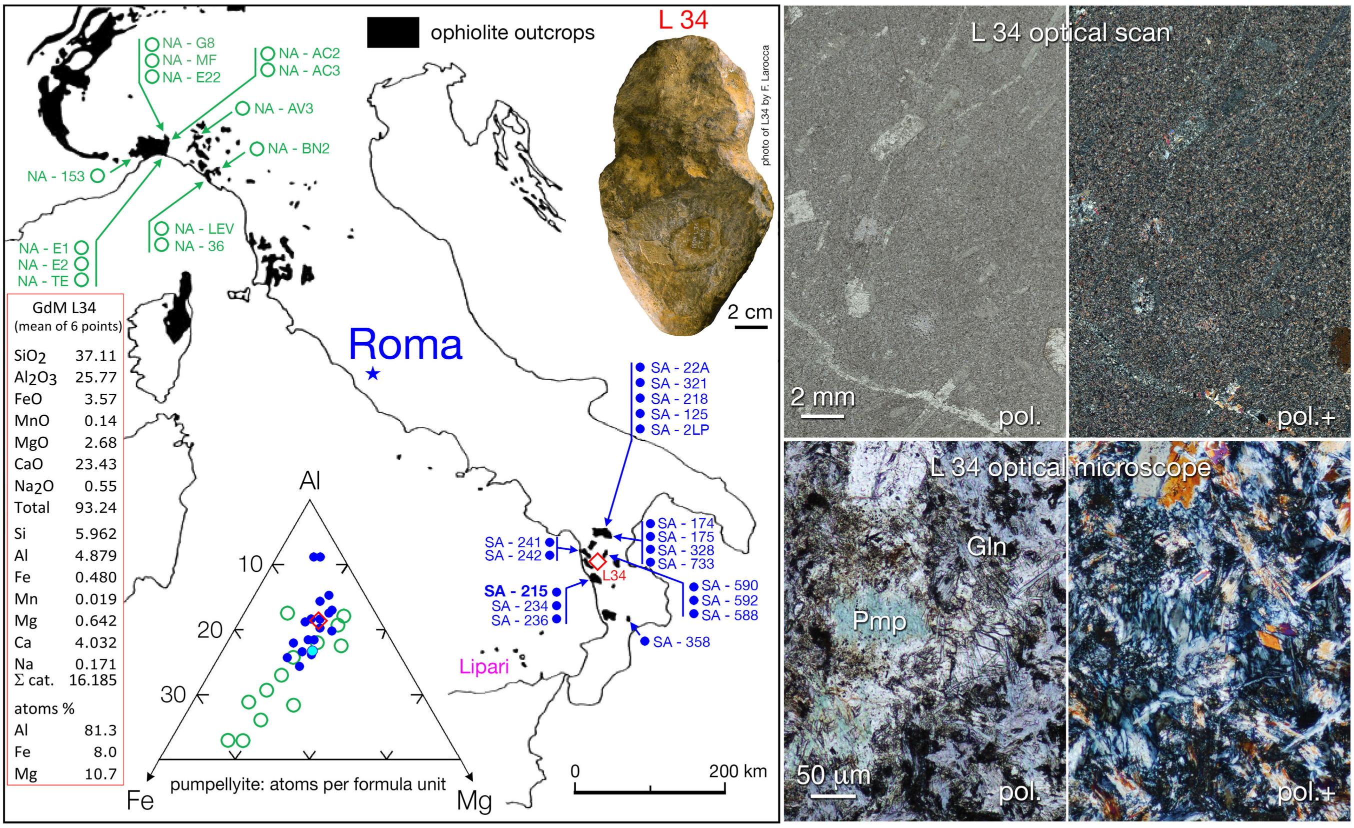


Figure 6. On the left, the main ophiolite outcrops and related collected samples in the Ligurian Alps (in green) and in Calabria (in blue) are shown (modified from [48]). In the triangular plot (Al-Fe-Mg), the microanalyses of pumpellyites from Ligurian Alps (green circle) and Calabria (blue dots) are shown [48]; pumpellyites of Catena Costiera (Calabria) [25] are reported as light-blue dots along with the mean (red rhombus) of six SEM-EDS microanalyses (data in the bordered red rectangle) of pumpellyites from the L34 grooved pickaxe (Grotta della Monaca). The composition of pumpellyite from the L34 sample seems similar to that of the SA-215 (bold font in the figure) sample from Cetraro–Fuscaldo. On the right are the transmitted-light optical scan of the L34 petrographic thin section and the transmitted-light photo showing pumpellyite (Pmp) and glaucophane (Gln) under the optical microscope. pol. = polarised light; pol.+ = cross-polarised light.

The artefact L138 (Figure 7) is a small axe, very dark green in colour, from Grotta della Monaca. It can be classified as dark-mica-bearing meta-ultramafite (Table 1) and was chosen for the occurrence of dark mica, which is a rather uncommon mineral in ultramafic rocks such as peridotites. Furthermore, ultramafic rocks outcrop in a few areas in Italy. In fact, peridotites are typical mantle rocks that can be exhumed in orogenic areas where the deep continental crust or the younger oceanic crust outcrops. In Italy, outcrops of dark-mica-bearing meta-ultramafic rocks are found in the Alps, at Finero massif, and in Southern Calabria at Serre massif, near Curinga village ([49] and the references therein). Serre meta-ultramafic rocks are interbedded with metagabbros and mafic and felsic granulites (Figure 2). The chemical composition of the dark micas differs between the two sites due to distinct abundances of sodium: the Calabrian dark micas have a higher average K/(K + Na) ratio (>0.91 [49]) than those from the Finero peridotite massif in the Alps (<0.91 [50]).

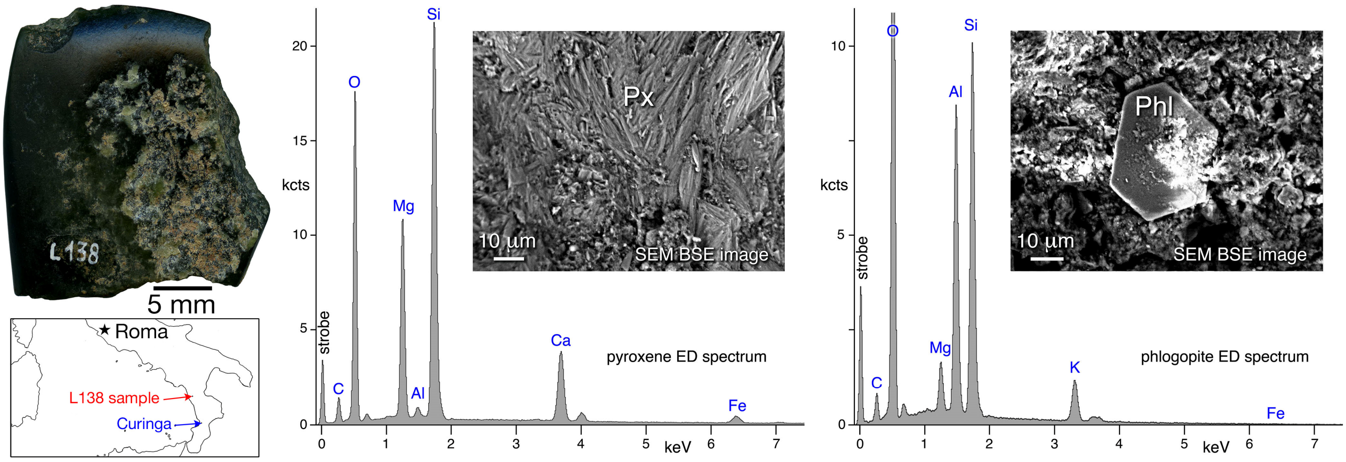


Figure 7. On the left, a macro-photo of a small axe (L138 sample from Grotta della Monaca) and the location of the meta-ultramafic rock outcrop (Curinga, Calabria) from which the sample originates; in the centre and on the right, the SEM backscattered electron (BSE) images of the axe surface showing the presence of pyroxenes (Px) and euhedral phlogopite (Phl). The ED X-ray spectra of pyroxene and phlogopite are also reported.

The quantitative elemental analyses of dark mica in the small axe were not carried out using SEM investigations, as the surface of the find would have been permanently modified by the carbon coating. However, a qualitative analysis shows a spectrum of elemental abundances in which relevant peaks are observed for Mg and K, and no peaks are detected for Na and Fe, suggesting a very high value of the K/(K + Na) ratio and a typical composition of phlogopite (highly Mg-rich dark mica). In addition, qualitative analyses of other dark minerals reveal abundances of Ca- and Mg-rich pyroxenes that are typical of ultramafic rocks. The small axe made of peridotite was found together with other artefacts classified as mafic and felsic granulites (Table 1). Consequently, it is reasonable to think that these artefacts made of high-grade metamorphic rocks and of phlogopite-bearing peridotite derive from the Curinga area rather than the Alps, in agreement with the provenance of the L34 artefact (pumpellyite-bearing schist).

In the Grotta della Monaca site, another small white axe made of polished stone (L2 sample) was discovered. It has been analysed by SEM-EDS and X-ray diffraction techniques. The prevailing chemical component in the axe is an aluminosilicate (Al_2SiO_5), whose morphology, observed with SEM-BS electrons, indicates the sillimanite polymorph (Figure 8). Confirmation that the sample consists of an aggregate of sillimanite crystals was also provided by X-ray diffraction investigation: the surface of the sample furnished an X-ray spectrum that fit with the ASTM reference lines of sillimanite (Figure 8).

Sillimanite is a polymorph of Al_2SiO_5, stable in metapelitic rocks under high-temperature conditions; frequently, it is found in migmatitic gneisses forming the lower continental crust affected by partial melting [20,23]. These rock types are present both in the Alps and Calabria; however, in Southern Calabria, they are often associated with felsic and mafic granulites, metagabbros, and phlogopite-bearing peridotites [19,22,24]. The pluricentimetre size of the sillimanite in the small axe suggests that its provenance is the Calabrian outcrops, and, in particular, coarse-grained sillimanite crystals even larger than 4 cm are found in the Palmi area (Figure 2) in migmatitic rocks near the coastline (Figure 8). Ultimately, it can be assumed that the origin of the white axe, because of the large size of the sillimanite, is Calabrian rock, specifically in the Palmi area.

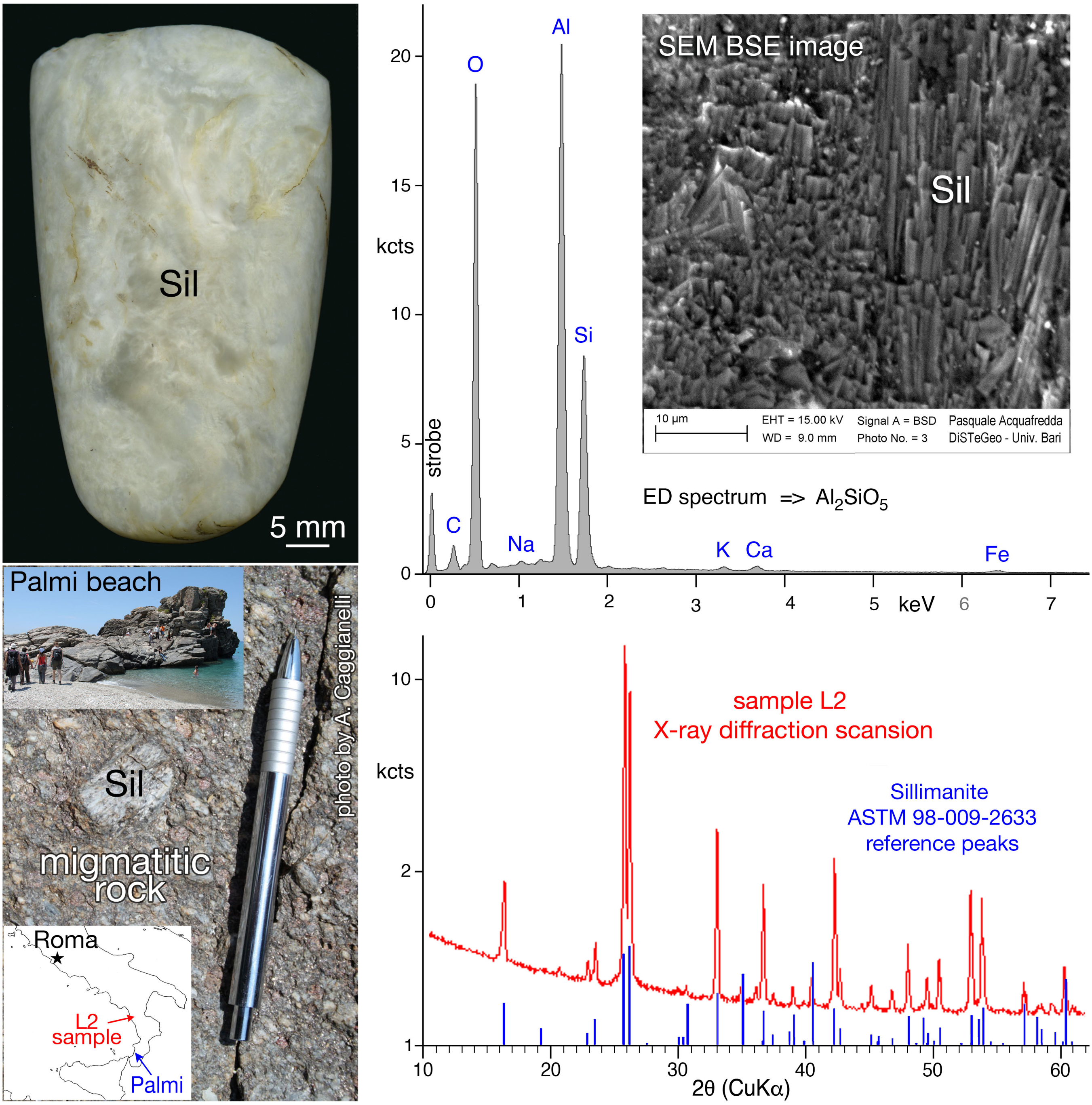


Figure 8. In the upper part, the macro-photo of the small white axe (artefact L2 from Grotta della Monaca) and SEM backscattered electron (BSE) image of its surface with the related ED X-ray spectrum (Al_2SiO_5) are shown. In the lower part, a photo of a migmatitic rock outcrop (Palmi area, Reggio Calabria) with large sillimanite (Sil) crystals from which the sample originates is shown, and the X-ray diffraction spectrum of the axe surface matching the ASTM sillimanite reference peaks is also shown.

3.3. Chemistry of Obsidians

The samples identifiable as obsidians were analysed by [24] using the non-destructive SEM-EDS technique (Figure 9); two fragmentary bladelets (L152 and L163 samples) among the 34 samples show anomalous chemical compositions, having SiO_2 < 68.5 wt%, CaO > 0.9 wt% (Figure 9), and Na_2O > 11 wt%. Furthermore, assuming that the chemical anomaly was related to the surface alteration, SEM-EDS analyses performed after with acetic acid treatment still showed compositions outside of the range of usual values, with high Na contents (Figure 9).

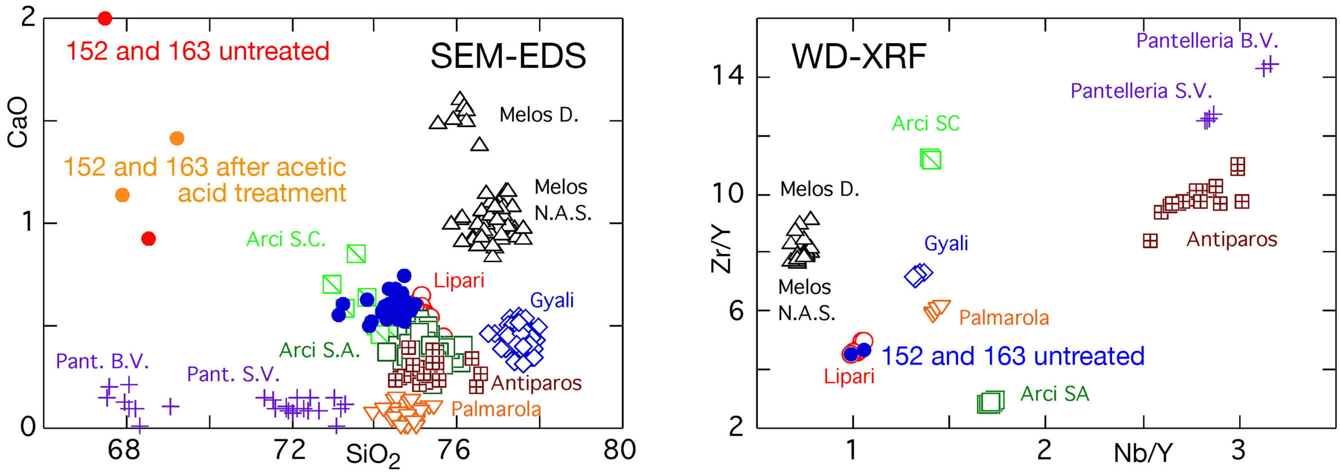


Figure 9. On the left, SiO_2 vs. CaO contents (using SEM-EDS technique) of the obsidians from Grotta della Monaca (blue, red, and orange dots) compared with the composition of different geological obsidians from the Mediterranean basin (modified from [31]). On the right, Nb/Y vs. Zr/Y ratios in obsidians, measured as the WD-XRF peak intensity ratio [46]. The L152 and L163 samples from Grotta della Monaca (blue dots), also after acetic acid treatment of their surfaces, show an outsider composition according to SEM-EDS analysis, while they are quickly connected to the Lipari source area using the WD-XRF technique (diagram on the right). Obsidian source area in the Mediterranean basin: Arci S.C. = Perdas Urias; Arci S.A. = Conca Cannas, Canale Perdera, and Riu Solacera (Sardinia); Pantelleria B.V. = Bagno di Venere; Pantelleria S.V. = Saltò la Vecchia and Balata dei Turchi (Sicily); Melos D. = Demenegaki; Melos N.A.S. = Nihia, Adamas, and Sarakiniko (Greece).

The high concentrations of sodium are due to the migration of this element towards the outermost parts of the sample during the burial period; however, by cutting a small portion of the specimen, the unaltered part of the glass can be analysed, making it possible to determine the rock source area, identified as the volcanic island of Lipari [31]. The attribution of all obsidian samples to the island of Lipari was obtained through the Fe vs. C.I.A. diagram (C.I.A. = chemical index of alteration [$Al_2O_3/(Al_2O_3 + CaO + Na_2O + K_2O)$ in mol.%]), which perfectly distinguishes the source of Lipari from that of Monte Arci [31].

With the aim of perfecting the used technique, the two samples with anomalous chemical compositions (L152 and L163) were analysed for some trace elements using WD-XRF equipment, with which the peak intensity ratios of Zr/Y and Nb/Y were detected (see [38] for the procedure). In the binary diagram in Figure 9, the composition of these samples falls exactly in the obsidian field from Lipari, confirming their provenance and validating once more the technique of using WD-XRF peak intensity ratios.

4. Discussion

The petrographic study, along with testing using non-destructive techniques, of lithic artefacts used as mining tools constrains the provenance of the used rock types. The analysed lithic objects had multiple uses depending on their shape, density, toughness, tenacity, and size. Most were used as percussion instruments, beating masses, or grooved pickaxes; others were used to make grindstones and pestles, and still others were ritual objects (such as the small axes). These artefacts were extensively used from the Upper Palaeolithic to the Middle Ages, as, at that time, considerable mining activity in Calabria was occurring, especially to obtain minerals (malachite, goethite, and azzurrite) to be used as pigments [29,30].

The choice of different types of rocks employed for the production of the artefacts depended on the specific use for which they were intended. The most commonly quarried rocks, found in Grotta della Monaca and/or preserved at the Museo Pigorini, are metamorphic in origin and generally do not have the highest toughness. However, humans in the past chose, among the raw materials, the most tenacious specimens already selected by natural erosion processes, i.e., by taking the more rounded pebbles along rivers within the Catanzaro, Mesima, and Crati *gräben* or on beaches (such as Palmi beach) in areas close to the place of their manufacture. In fact, among the metamorphic artefacts, high-pressure metabasites or high-grade schists (Grt-Bt-Sil gneiss and felsic or mafic granulites) with isotropic textures were selected, being the toughest and most available in the nearby Catena Costiera massif or in Sila and Serre. The basic rocks were preferred for their mineralogical composition, having been formed by Fe-Mg minerals with a higher density (>3.0 g/cm^3) and greater hardness. In addition, the high-grade metamorphic rocks, although derived from sedimentary rocks (Grt-Bt-Sil gneiss), acquired a quite isotropic texture and greater grain size due to recrystallisation under high-temperature conditions.

Following this approach, the artefacts that do not require the highest tenacity were also realised with sedimentary rocks (41%) or low-grade marbles available in neighbouring areas, selecting well-cemented fine-grained sandstones or micritic limestones. They were essentially used to make grindstones and pestles, the use of which favoured lithotypes with a not-too-high specific weight (about 2.5), such as sandstones, rather than extremely tough rocks with a fairly high specific weight (about 3.0), which were used to make mining tools. Similarly, the choice of magmatic rocks, such as granites and tonalites or rhyolites–dacites, is related to their isotropic texture, which makes these rocks suitable for mining exploration.

The optical microscopy, SEM-EDS, XRD, and WD-XRF techniques allowed the acquisition of textural and chemical data on the artefacts, which were compared with similar data from Italian rocks. For some samples, the comparison with petrographic and chemical data in the literature also indicates a precise provenance. Glaucophane–lawsonite–pumpellyite–prehnite-schists, actinolite schist, meta-arenite, and marble affected by HP-LT metamorphism are typically related to the ophiolitic suite exhumed during the Alpine orogenesis (70 Ma ago); these rock types are present in the western Alps and in Catena Costiera. The detailed comparison of the pumpellyite chemistry from sample L34 indicates a clear provenance in Catena Costiera, particularly in the Cetraro–Fuscaldo area. Similarly, the petrographic features and the phlogopite chemistry of meta-ultramafite, as well as the aggregate of sillimanite in a small white axe (sample L2), suggest a provenance in Northern–Central Serre (Curinga and Palmi areas in Calabria).

The artefacts studied derive mainly from areas adjacent to the Grotta della Monaca site; in particular, objects of the appropriate size and shape are found along the rivers that collect detritus from the erosion of Calabria’s crystalline rocks in Sila, Catena Costiera, and Serre. In fact, the geological and petrographic features of the crystalline basement correspond to the found lithologies. In Catena Costiera, mainly metabasites (e.g., glaucofane-bearing schists, pumpellyite-bearing schists, actinolite schist) and metasediments (metarenite and marble) forming a Mesozoic oceanic crust affected by HP-LT metamorphism during Alpine orogenesis with Cenozoic sedimentary covers (limestones and fine/coarse-grained sandstones) are present. The Sila and Serre massifs are mainly formed by Carboniferous and Permian granitoids, including gabbros and diorites intruded in lower, middle, and upper continental crusts consisting of metagabbros with small bodies of peridotites, Grt-Bt-Sil gneisses, micaschists, porphyroids, Bt-bearing paragneisses, and phyllites [19,21,22].

A specific case is that of obsidians, also related to their high cutting capacity, having been formed by volcanic glass; the exceptional properties of obsidians induced humans of the past to seek more easily accessible areas of supply. The X-ray peak intensity ratios of some trace elements, such as Zr/Y and Nb/Y, measured in two obsidian samples (L152 and L163), confirm beyond doubt that the provenance of the obsidian artefacts is on the island of Lipari among the volcanic products dispersed in the Mediterranean domain, as already indicated by [31].

5. Conclusions

Minimally invasive and/or absolutely non-destructive techniques allowed us to identify the source areas of more than 130 lithic artefacts, used primarily as tools for mining and the primary extraction and processing of metal ores, collected in Calabria (Southern Italy) from several archaeological sites dating from the Upper Palaeolithic to the Middle Ages.

All mining samples (110 artefacts from the Grotta della Monaca site and 23 grooved lithic artefacts preserved at the Museo Nazionale Preistorico ed Etnografico "Luigi Pigorini" in Roma), petroarchaeometrically characterised by optical microscopy on thin sections, are attributable to rocks outcropping in Calabria.

In particular, the pumpellyite analyses performed using the minimally invasive SEM-EDS technique on a grooved pickaxe (sample L34) from Grotta della Monaca allowed us to identify a specific outcrop from the Cetraro–Fuscaldo ophiolitic suite (Figure 2).

Moreover, for two small axes in polished stone, used as ritual objects, and two obsidians collected in the Grotta della Monaca, the source outcrops were identified using absolutely non-destructive techniques (SEM-EDS, WD-XRF using peak intensity ratios of trace elements, and XRD): of the two small axes, one (L2 sample, a migmatitic paragneiss) is traced to migmatite outcrops in the Palmi area, and the other (L138 sample, a phlogopite-bearing meta-ultramafic rock) is traced to meta-ultramafic rocks from the Curinga area; for the two obsidian specimens (L152 and L163 samples), WD-XRF analyses certify the island of Lipari as the area of origin.

The petrography of all lithic artefacts confirms a local provenance, with the exception of the obsidians. The choice of lithologies, harder or softer, had to be linked to the use that humans had to make of the lithic artefacts.

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