
New challenges in the study of lithic raw materials in central Italy at the dawn of metal working societies: La Pietra and other radiolarite quarry-workshops in Tuscany

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Abstract:

In central-southern Tuscany radiolarite has been used as a lithic raw material throughout prehistory. During the Copper Age it was selected for the local production of leaf-shaped artefacts. In the area considered, the Copper Age record is almost totally restricted to burials and virtually no settlements have been investigated so far. Radiolarite artefacts are found mostly as refined arrow and, possibly javelin, heads used as grave goods.

Within this context, the discovery and recent investigation of the large radiolarite quarry of La Pietra (Roccastrada, Grosseto) and of the related workshops is of great interest. Our aim here is to integrate the record from this site with other contemporary evidence of radiolarite exploitation. A programme of surveys has thus begun on the other radiolarite outcrops of the area in order to verify the existence of further rock quarrying or working. The discovery of a previously unknown quarry-workshop and two previously unknown workshops on radiolarite outcrops is presented here for the first time. The geological and archaeological data coming from the quarry-workshops will be used, in a future stage of research, to source the radiolarite artefacts found in Copper Age graves of Central Italy. The Copper age armatures are valuable artefacts mostly kept in museums and fully non-destructive analyses must be applied to them. To tackle these challenges, we followed a methodological approach which integrates field surveys, the individuation of petrographic markers of the most exploited radiolarite horizons and geochemical analyses. For geochemical characterization, we made use of pXRF portable spectrometer and here we present some preliminary results in the light of current methodological debate.

In conclusion, even if some methodological questions remain open, we verified the feasibility of this programme of geographical, geological and geochemical characterizations and need now to increase our dataset in order to reconstruct a viable picture of Copper age lithic economy in central-southern Tuscany.

Keywords: Copper Age; radiolarite; sourcing; surveys; pXRF; quarry sites



1. Introduction

The data reported in this article concerns radiolarite exploitation and circulation in central-southern Tuscany (Figure 1) during the Copper Age. This data is to be seen in the light of the Late Neolithic and Copper Age specific raw material organized procurement and exploitation activity which are deeply entangled with socio-economic change occurring across the Mediterranean basin during the 5th and 4th millennium BCE. In the Italian Peninsula the earliest examples of quarrying and mining activity are the flint mines of the Gargano promontory (Apulia) which date back as far as the 6th millennium BCE (Tarantini & Galiberti 2011). From the 4th millennium BC, alongside the systematic quarrying and mining of siliceous rocks, also mining and quarrying of metal ores is attested (see for instance the mines of Monte Loreto, Liguria) (Campana *et al.* 2011). From the late Neolithic also the quarrying and mining of minerals used as colouring substances begins (La Rocca 2012).



Figure 1. The area of central-southern Tuscany (modified satellite pictures).

Evidence of radiolarite quarrying is found in the Liguria-Tuscany area of Tyrrhenian north-central Italy (from the eastern Riviera of Liguria to Southern Tuscany). This corresponds to an area where radiolarite is widespread. Such area of the Northern Apennines is at the same time generally very poor of good quality siliceous rocks of other kinds (Dini *et al.* 2006; Negrino & Starnini 2006; Scaramucci 2012).

The radiolarite quarry-workshop sites concentrate in the northernmost part of the area, with the large and extensively investigated site of Valle Lagorara and the close-by smaller quarry-workshop of Serra di Liciorno (Campana & Maggi 2002; Campana *et al.* 2013) (La Spezia, Liguria) and Ronco del Gatto, on the slopes of Mount Lama well within the Tosco-Emiliano Apennine (Ghiretti 2003). Another concentration is in the southern part of the area, with the major quarry-workshop of La Pietra (Gambassini & Marroni 1998) and the few minor ones which are presented here for the first time (Figure 2).

The fact that no quarry-workshop site is known between these two concentrations is due possibly to scarce research and publication rather than to a real lack of evidence. In fact, lithic industries in association with radiolarite outcrops have been reported (Stoduti *et al.* 1995) and many radiolarite outcrops are present there.

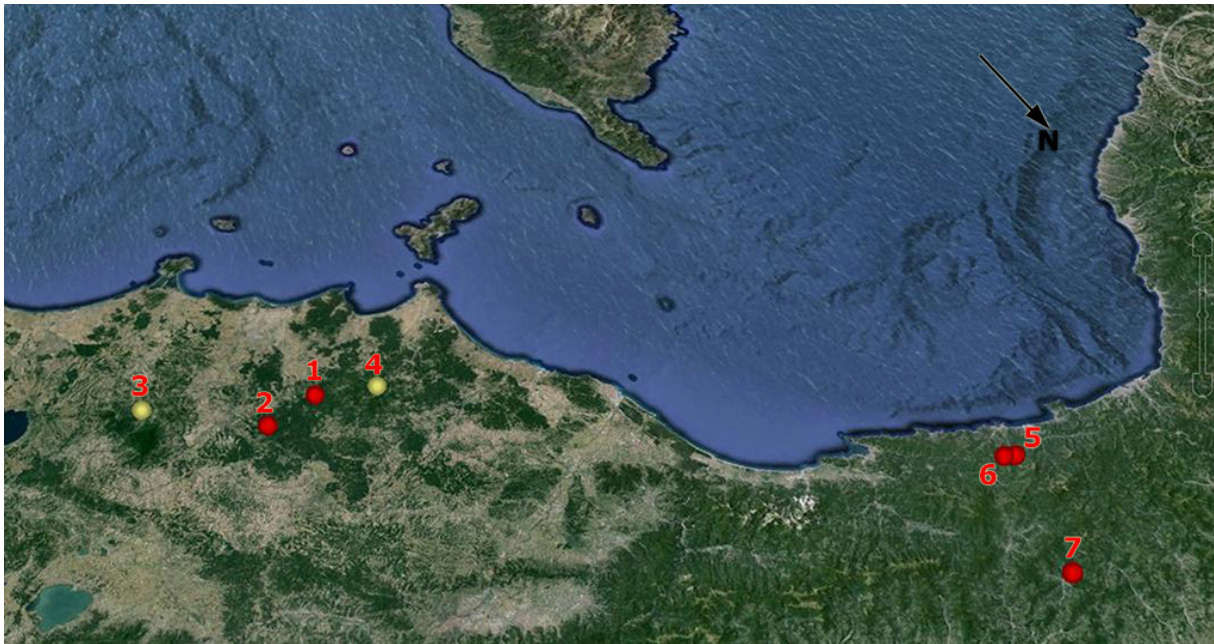


Figure 2. Location of the radiolarite exploitation sites mentioned in the text. 1-La Pietra quarry and workshop; 2-Albatreri quarry and workshop; 3-Petorsola workshop; 4-Poggio Mutti workshop; 5-Valle Lagorara quarry and workshop (Campana & Maggi 2002); 6-Serre di Liciorno quarry and workshop (Campana *et al.* 2013); 7-Ronco del Gatto quarry and workshop (Ghiretti 2003). (Satellite image: Google, Image Landsat 2015).

The long term historical factors and the geological constrains ruling the diffusion of the Copper Age radiolarite quarry-workshops are easy to see. Understanding the role of these production centres within their contemporary societies is, on the other hand, a much harder and more articulated task.

In order to carry it out meaningfully it is fundamental:

- to develop an in-depth study of the lithic industries and other records of the known quarry-workshop sites and, in particular, to look for other similar evidence in the surrounding territory. This, together with the appraisal of all other archaeological evidence for the period at issue, will help to see the main production centres within their contemporary geography.
- to trace the final destination of the raw material of this exploitation sites by sourcing the radiolarite artefacts found in contemporaneous archaeological contexts.

1.1. The site of La Pietra

The prehistoric site of La Pietra (municipality of Roccastrada, province of Grosseto, Tuscany) sits on the south-eastern slopes of the Metalliferous Hills, a mountain ridge rising in the central part of Tuscany. Mount Pietra is an isolated radiolarite outcrop (442 m a.s.l.) which forms a rock cliff rising on the left side of the Farma stream (Figure 3). The site is part of the Technological and Archaeological Park of the Grosseto Metalliferous Hills which in 2015 was also declared Tuscan Mining UNESCO Global Geopark (Casini 2015: 16). The site has also been certified as a geosite of regional interest because of its geological importance (Costantini 2015).

La Pietra has been described elsewhere in both its geological and archaeological features (Aranguren *et al.* 2013; Bucci *et al.* 2015; Gambassini & Marroni 1998; Moroni *et al.* 2015; Moroni *et al.* 2016). Here we will briefly outline some of the last outcomes from its investigation.

The rock cliff of La Pietra was used to supply raw material at least since the Middle-Upper Palaeolithic (Moroni *et al.* 2016) but it was only during the Copper Age that an

organized quarrying activity started there, accompanied by lithic workshops devoted to the production of flat retouched bifacial items (preforms for leaf-shaped armatures).

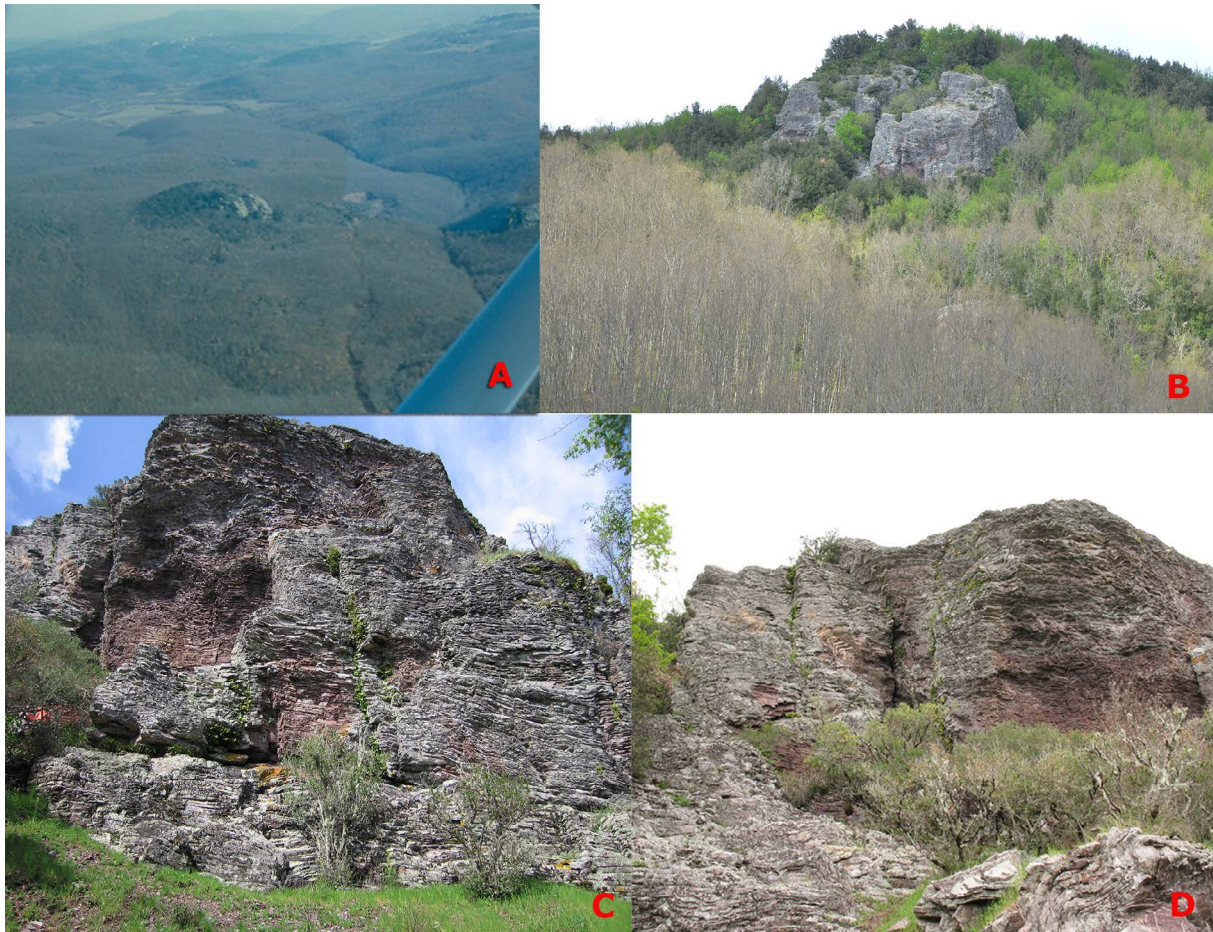


Figure 3. Different views of La Pietra rock cliff: A-air photograph with the Farma stream on the right; B-the outcrop seen from the opposite side of the Farma stream; C-detail of the south-eastern wall of the outcrop; D-detail of the southern wall of the outcrop.

La Pietra was visited, surveyed and briefly described for the first time in the nineties by Paolo Gambassini and Giuliano Marroni (Gambassini & Marroni 1998) of the University of Siena. In 2013 a research project (which is still in progress) was begun by the Archaeological Office of Tuscany and by the University of Siena.

The investigated archaeological deposit and the quarrying traces

An excavation was started in a sheltered area at the base of the outcrop. The excavation was made on four square-meters in the western sector of the ‘shelter’, attached to the radiolarite cliff. A lot of artefacts and waste material such as *débitage* and detritus was retrieved from the trench, revealing the presence of a knapping area (Moroni *et al.* 2016); this material is presently under study. Scattered charcoal samples were retrieved from every spit of the trench and a ^{14}C date was obtained which gave the result of 4226 ± 26 BP (4845-4729 - 1 sigma, 4853-4653 - 2 sigma cal. BP) (Moroni *et al.* 2016). This date confirms the attribution of the workshop activity in the shelter to the Copper Age, as already hypothesized on the bases of the lithic material technological features. Lithic remains scattered in large amounts all around the outcrop foot exclusively contain artefacts analogous to those found during the excavation of the shelter and should thus be attributed to the same chronology.

Also the abundant quarrying traces (see below) on the walls are not directly datable, but their contemporaneity to the workshop is confirmed by the retrieval in the excavation (also in the lower spits) of radiolarite slabs with the same kind of traces (Figure 4).



Figure 4. Fragment of radiolarite layer with quarrying traces and removals. From the 2014 excavation of the 'shelter' at La Pietra.

Several hammer-stones, at times fragmented, have been found on the surface around the outcrop and fragments ascribable to the same objects were retrieved in the excavation of the shelter. They are made up of large diabase, gabbro and, more rarely, quartzite cobbles, whose source can be found in the Farma stream bed (Gambassini & Marroni 1996; Moroni *et al.* 2016).

An intensively quarried area was observed on the southern side of the outcrop. Here, worked surfaces were individuated, also at heights not reachable without the employment of some sort of support (scaffoldings or ladders). At least two different kinds of extraction features were noticed: half-circles penetrating into the radiolarite layers to follow suitable levels (normally occurring where packs of layers lean out from the rock wall) and more or less wide stretches of the outcrop hammered and demolished parallel to the rock wall (Figure 5).

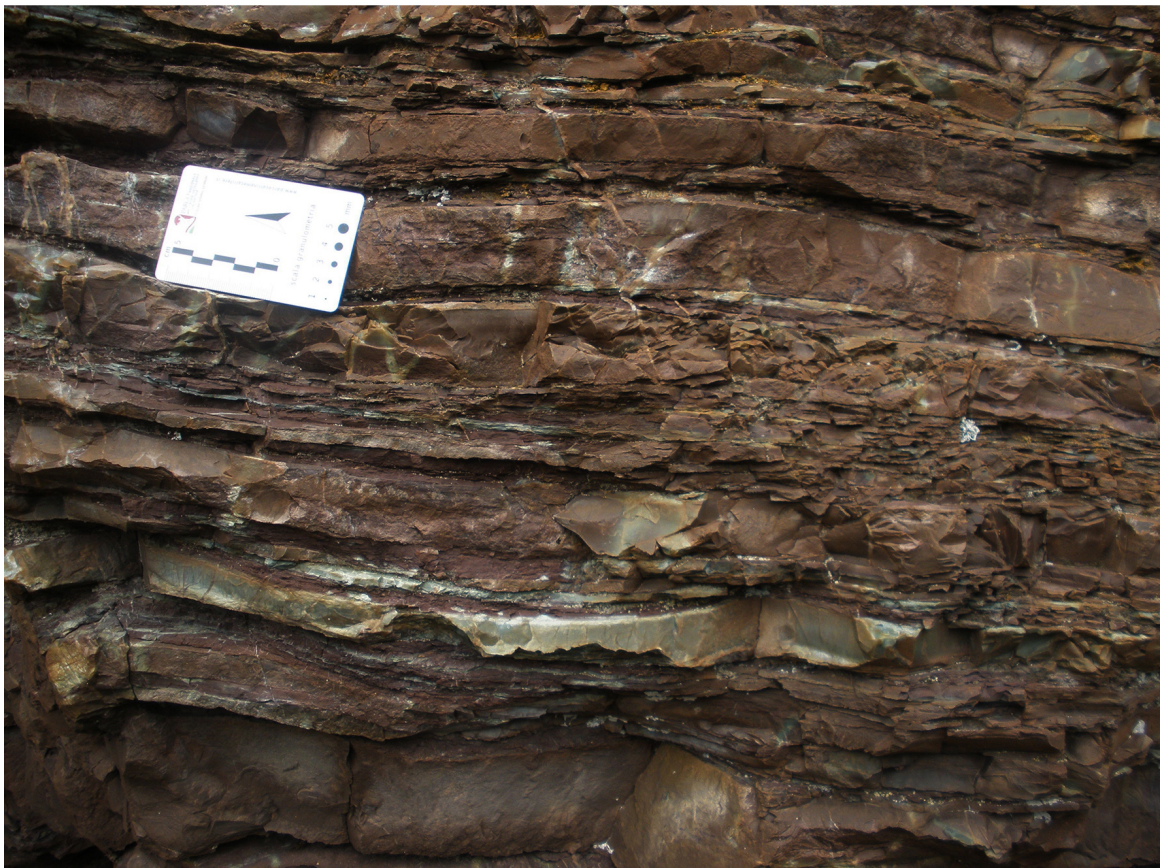


Figure 5. The quarrying traces in the south-eastern sector of La Pietra outcrop: half-circle penetrating into the rock-wall, above, and hammered flat surface, below.

1.2. The geological context of central southern Tuscany and the Diaspri formation

Some knowledge on the geological asset of central-southern Tuscany is necessary in order to clearly understand this research project and its potential. One important geological feature of this area is the coexistence of geological units from several different palaeogeographic domains which became superimposed as a consequence of the complex tectonic history linked to the Apennine orogenesis.

La Pietra outcrop is part of the Diaspri (Jaspers) formation, a late Jurassic formation belonging to the Ophiolitic Unit of the Ligurian Domain.

The Diaspri formation is made up of thin layers of radiolarite 4 to 10 centimetres thick, usually reddish-brown with green veins but sometimes also fully green in colour. These are intercalated by centimetric levels of siltstone. Diaspri of the ophiolitic unit have a lower contact with Serpentinites, Basalts and Gabbros (thus igneous and metamorphic rocks from oceanic crust) and an upper one with siliceous limestones, shales and marls (Bucci *et al.* 2015).

The name “Diaspri” also indicates another formation almost identical in its features to the one outcropping at La Pietra but which belongs to the Tuscan Domain, and thus to a different palaeogeographical setting from that of the Ligurian formation. In fact during the Upper Jurassic (Malm Epoch), both in the Ligurian and Tuscan Domain, widespread deposits of radiolarite accumulated respectively on oceanic crust and on continental scarp. The main difference is that in Tuscan successions the Diaspri formation has a lower contact with pelagic limestone and marls instead than with ophiolitic rocks and thus both underlays and overlays limestone formations (Folk 1979; Folk & McBride 1978).

Diaspri of the Tuscan Domain are comprised of dark red radiolarite and sometimes green radiolarite layers, from 3 to 15 cm thick, with thin intercalations of siliceous siltstone. Towards the top of the formation there are 2 to 10 cm dark red marly layers. Sometimes the higher part of the formation contains rare intercalations of gray-greenish siliceous calcilutites. (Bettelli 1985:152; Bossio *et al.* 2015). During the Apennines orogeneses Ligurian and Tuscan formations became superimposed and for this reason the two types of radiolarite are found geographically very close to each other.

1.3. Copper Age archaeological evidence and settlement dynamics in central-southern Tuscany

In the area under examination virtually no Copper Age settlements have been discovered and the archaeological record is almost totally comprised of funerary evidence. The only exception is the site of San Carlo (Fedeli 1995) where, however, most of the context was lost due to the presence of a modern quarry. Here, in the only part of deposit which was spared, a curvilinear stone structure was found with abundant copper slags together with Copper Age pottery and lithic industry (Fedeli 1995: 74; Fedeli & Galiberti 2016). This site is located 40 kilometres as the crow flies west of La Pietra, on the Tyrrhenian coast.

Metals appear to have played a fundamental role in the Copper Age settlement of the area given that in central-southern Tuscany and northern Latium there concentrate some of the most important metal ores of the Mediterranean. The Metalliferous Hills have been a historic mining district and deposits of copper minerals were very important there (Giardino 1999: 54). No direct evidence of copper mining in the Metalliferous Hills during the Copper Age has been found yet but such activity is highly suggested by indirect evidence (Dolfini *et al.* 2011). The above mentioned site of San Carlo with its evidence of copper slags, is located exactly on the opposite side of the Metalliferous Hills with respect to La Pietra.

An important piece of evidence for the Copper Age geography of central-southern Tuscany is also the cinnabar quarry of Spaccasasso (Cavanna 2007; Volante 2014), which is located close to the Ombrone river mouth. A ritual and funerary site inside a small cavity lies

stratigraphically above the quarry-deposit and was radiocarbon dated to the late Copper Age–Early Bronze Age. Grave goods accompanying the human remains, buried here in secondary position, included radiolarite arrowheads (Cavanna 2007). Cinnabar mining during the Copper Age in the area is also suggested by old findings of stone mallets around some of the main deposits of this mineral on Mount Amiata (Metta 2015).

In more general terms, it has to be considered that an important role in settlement dynamics was played by river courses (Figure 6). Along all of the main rivers there is in fact Copper Age evidence (Grifoni Cremonesi 2007). This evidence marks precise tracks determined by the presence of mineral deposits (aside copper and cinnabar, also antimony silver, tin), and we should add, lithic resources. Particularly important is the Fiora River valley at the border between Latium and Tuscany where the evidence of the Copper Age burial *facies* known as Rinaldone concentrates (see below); this valley leads to the mining district of Mount Amiata (Grifoni Cremonesi 2007). The Cornia, Cecina and Bruna valleys lead from the Metalliferous Hills to the sea and the Farma and Merse valleys lead from the Metalliferous Hills to the large Ombrone valley which leads to the inner area of the region and, through the Orcia valley, to Mount Amiata.



Figure 6. Simplified map of the main water courses of central-southern Tuscany.

As mentioned above, archaeological record contemporaneous to La Pietra and to other radiolarite workshops in the area of central-southern Tuscany is almost totally made up of funerary evidence (Aranguren 2001; Aranguren *et al.* 2004; Cocchi Genick 2008; Negroni Catacchio 1993; 2006; Quagliolo 1993) and funerary contexts are also the main recipients of the finished radiolarite artefacts (Moroni *et al.* 2016).

The Copper Age in the area has in fact been defined according to the types of funerary features and two main aspects have been identified in Tuscany for this period (Cocchi Genick 2008).

The Rinaldone *facies*, evidence of which concentrate along the mid-course of the Fiora River at the border between Tuscany and Latium, is characterized by burials in artificial cavities (the so-called “tombe a grotticella artificiale”) (Negroni Catacchio 1993; 2006).

The second aspect is widespread in the whole central and northern part of the region and is characterized by collective burials in natural caves. This aspect shows a greater variability in funerary rituals than the Rinaldone one and a subdivision into four different groups has been put forward (Cocchi Genick 2008). All of the burial caves found in the province of Grosseto belong to the “Fontino group” from the name of the cave site with the highest number of burials and longest chronology. The name “Sarteano group” (or “Sienese group”) was given to the few ritual cave sites in the Sienese territory, in the Eastern sector of the region. The burial caves of north-western Tuscany have been put together under the label “Vecchiano group”. Finally the “San Giuseppe group” is comprised of a single cave burial site on Elba island (Cocchi Genick 2008; Moroni *et al.* 2016).

From a recent overview made from published data (Moroni *et al.* 2016) it emerged how radiolarite foliated points are generally absent in the Rinaldone burials whereas they are present at different degrees in the Fontino and San Giuseppe group (Figure 7). The most impressive evidence is offered by the Fontino and San Giuseppe caves comprising respectively 213 out of 364 and 42 out of 64 arrowheads made of radiolarite. (Grifoni Cremonesi 2001; Vigliardi 2001). An important aspect which emerged from this overview is the presence of arrowheads made of different lithic raw materials (often good quality flint) in sites close to the radiolarite workshops. The Copper Age funerary cave of Grotta Prato, for instance, located ten kilometres as the crow flies from la Pietra (Grifoni Cremonesi, 1983), yielded only 4 radiolarite arrowheads out of 36, whereas in the nearby site of Grotta della Spinosa, 21 out 23 points used as grave-goods were made of radiolarite (Moroni *et al.* 2016).



Figure 7. Geographical distribution of the main burial caves mentioned in the text (Fontino and San Giuseppe groups) (data from Moroni *et al.* 2016. Satellite image: Google, Image Landsat 2015).

2. Methods

2.1. The field surveys

For this research we made use of an integrated method of field surveys. In order to source the radiolarite used as raw material of protohistoric artefacts we need in fact to select possible provenance sites. The only way to do this are systematic surveys in the field. This might take quite a long time but it is a fundamental condition to make characterization easier as it allows to exclude many potential sources. Some radiolarite outcrops may have in fact no archaeological potential and so may be eliminated from the list of the possible raw material provenances of a given radiolarite archaeological artefact.

To better grasp and to manage the data we employed the geological database of the 1:10k geological maps (Regione Toscana 2015), recently made freely available on the web by the Tuscan region (Figure 8). Using this data, we are building our own geo-database with ArcGIS software.

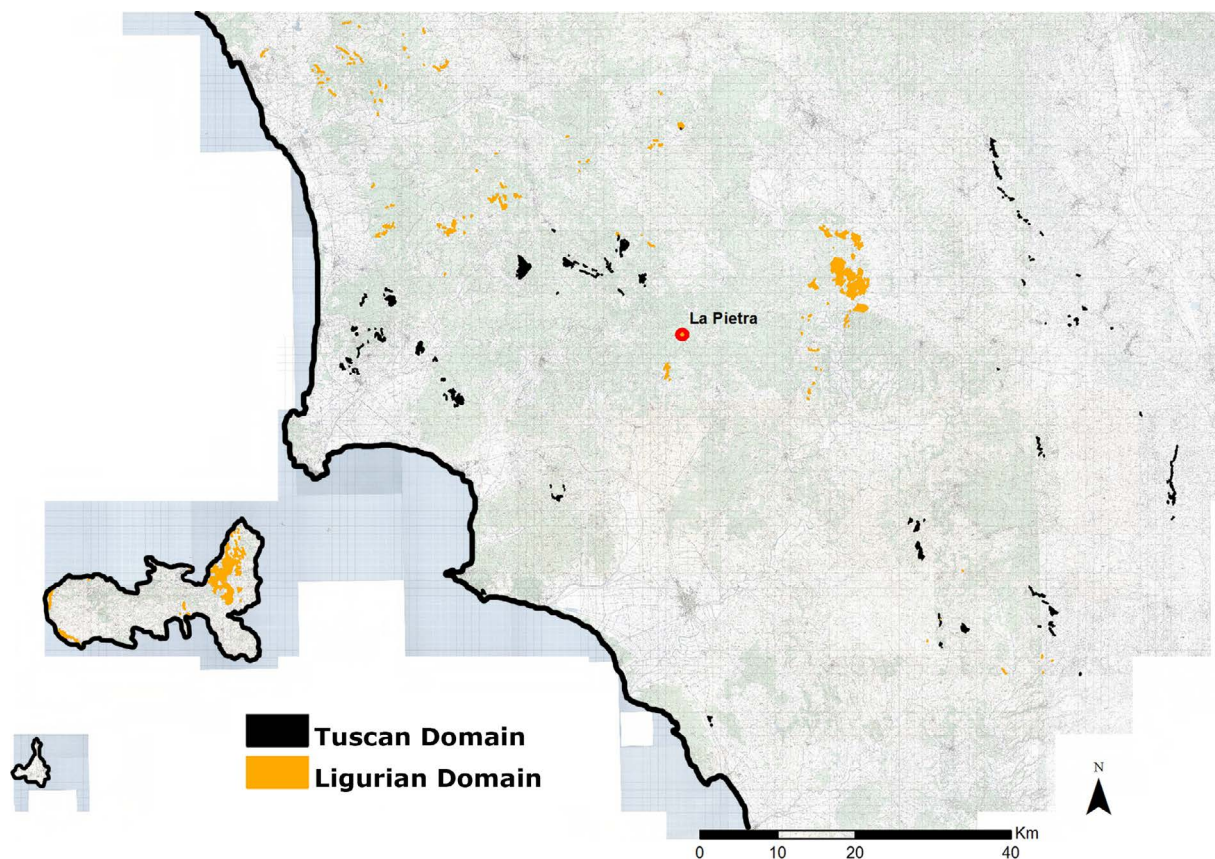


Figure 8. The radiolarite (“Diaspri”) outcrops of the Tuscan and Ligurian domains in the area of central-southern Tuscany with La Pietra. Map created with ArcGIS software. Data from Geodatabase of Tuscany (Regione Toscana 2015).

The outcrops were surveyed thoroughly in all accessible points. We took samples of all portions of radiolarite layers which appeared to be suitable for knapping. We also took samples of those horizons which, by their specific characteristics, could be classified as separate lithotypes.

For this first step of research we decided to survey two sample areas: the first one includes all radiolarite outcrops which can be found moving radially away from La Pietra towards the coast, the inner part of the Metalliferous Hills and the Ombrone River valley, whereas the second one is the area around the volcanic complex of Mount Amiata and the upper Fiora Valley.

2.2. Geochemical analyses

Geochemical characterization for the sourcing of sedimentary siliceous rocks has been a fundamental scientific tool for research on prehistoric life-ways based on the study of lithic assemblages. This research has been successful only in as much as it was integrated with other techniques and as far as it was able to bring together different levels of analyses, from the macroscopic downwards (Arzarello *et al.* 2011: 93; Brandl *et al.* 2014; Turq 2005:11).

For what concerns geochemical sourcing of siliceous sedimentary rocks, difficulties arise because of the high heterogeneity in their chemical and lithological compositions which makes the sources difficult to define and to distinguish one from the other (Newlander *et al.* 2015).

Geochemical characterization of radiolarite is a recent acquisition of lithic raw material studies, which has developed mostly in central Europe in response to new data and challenges which arose from geological surveys of outcrops and from the study of raw material exploitation sites (Elekes *et al.* 2000: 502).

Sourcing of radiolarite artefacts at the site of Krems-Wachtberg (Austria) (Brandl *et al.* 2014) was done by LA-IPC-MS analyses. This proved to be a valid tool for distinguishing radiolarite of different geological regions (*i.e.* Northern Alpine and Carpathian radiolarites). Variations in light elements Ba and Mg were found to be the most diagnostic for distinguishing between the Northern Alpine and Carpathian sources, although it was not possible to make well distinct groups within the same regions. Also, Sr, Rb and V allowed some distinctions to be made between the two main regions (Brandl *et al.* 2014, 15).

In the Italian Northern Apennines (Liguria and Emilia), Bietti and colleagues (2006) made chemical analyses of radiolarite geological samples by ICP-EOS (induced coupled plasma-optical emission spectroscopy). The study was aimed at the individuation of trace elements which could be used to create “types” specific of a single geological formation or of a part of it. These analyses were only made on Ligurian type radiolarites and, as far as we know, were never brought forward.

In our own research, we made use of pXRF for a preliminary characterization of radiolarite samples and archaeological artefacts from central-southern Tuscany.

Portable X-ray fluorescence spectrometry (pXRF) allows non-destructive analyses of the elemental composition of archaeological artefacts also outside the labs (*e.g.*, in museums) (Newlander *et al.* 2015) and is thus very useful when it comes to analyse valuable archaeological collections, as in the here presented case of the Copper Age arrowheads.

pXRF was rarely used on sedimentary siliceous rocks and results of such analyses have only very recently started to be published (Tykot *et al.* 2016; Pereira *et al.* 2016; Newlander *et al.* 2015). Newlander and colleagues (2015), analyzed chert sources, together with obsidian, fine grained volcanic and metamorphic rocks, used by the prehistoric inhabitants of central and eastern Nevada. These authors argue that, differently from other rocks, chert sources are more difficult to isolate, due to their highly variable lithological and chemical compositions and that a larger sample needs to be analyzed in order to fully define the variation in the elemental composition of each source. They could also notice, however, that the elemental data obtained with pXRF reflect the macroscopic variability exhibited by these types of stones, mostly for what concerns colour and Fe content. They finally suggest that cherts may require longer count time than other stones in pXRF measurements (Newlander *et al.* 2015: 544).

Our pXRF analyses on radiolarite was performed using an Olympus DELTA-Premium handheld pXRF analyzer, equipped with a 40kV tube, a “large area SDD detector”, accelerometer and barometer for atmosphere pressure corrections of light elements measurements. The laboratory measurements were done with the instrument mounted on the fixed station. Data were acquired with the “Soil Mode” (3-beam) of the instrument which

utilizes Compton Normalization for low concentrations (PPM to 3%) of elements in light matrices.

pXRF analyses are aimed at:

- characterizing radiolarite of different geological sources in the region to see if it is possible to make distinct groups between Ligurian and Tuscan Domain radiolarite and between different outcrops within each of the two domains.

- Assign archaeological radiolarite arrowheads to the different radiolarite groups.

For this scope we analysed: geological radiolarite samples coming from different horizons of the La Pietra and Albatreti outcrops and which could be grouped macroscopically into different lithotypes; archaeological radiolarite artefact from the surface collections and from the excavation of La Pietra; geological and archaeological samples from a Tuscan Domain radiolarite outcrop and a Ligurian one with evident geological differences from La Pietra.

Finally, pXRF measurement was also performed on a typical Copper Age radiolarite elongated arrowhead (probably a javelin-head) coming from an unknown locality of central Italy and belonging to a private collection, the Lanfredini collection, held at the University of Siena.

3. Results

3.1. Field surveys and advances in the definition of radiolarite geo-diversity

As explained above, radiolarite of the Tuscan Domain is present in Tuscany alongside the Ligurian Domain one. By using the geo-database we were able to draw a thematic map of radiolarites belonging to this two different palaeo-geographic domains and which offers for the first time a complete view of the quantity and type of radiolarite available in the territory around the Copper Age quarry of La Pietra (Figure 8).

In the area sampled so far, however, most of the outcrops of both Domains appeared to be highly affected by tectonics and a great number among them showed only very fractured and unworkable radiolarite layers and did not show any anthropic trace (Figure 9).

In the area around La Pietra several Ligurian Domain radiolarite outcrops were surveyed. An interesting case is that of the area of Bagni di Petriolo, on the Farma stream, 16 kilometres downstream from La Pietra. Here there exist four small outcrops only one of which was found to have clear traces of workshop activities. At Roccatederighi, 7 kilometres SW of La Pietra, there is a large area of radiolarite outcrop but exposed layers and detritus show no knapping suitability. Similar negative results come from the outcrop of Monte Acuto, 3 km South of the Petriolo area.

For what concern Tuscan Domain radiolarite in this area, we visited the outcrops of Poggio Mutti and Cornate Mts. (see below), 17 km NW of La Pietra. On the Northern slope of Cornate Mt. radiolarite forms a high rock cliff here however there appear to be virtually no knappable material. On Poggio Mutti, on the other hand, good quality green radiolarite was individuated and is linked to clear workshop traces.

In the area of Mount Amiata and the upper Fiora Valley most radiolarite outcrops belong to the Tuscan Domain Diaspri and show very similar characteristics to those observed at Cornate (strongly fractured and unworkable layers even where there exist a large variety of lithotypes).

Only one outcrop (Triana) of Ligurian Domain radiolarite is recorded in geological maps of the Mount Amiata area and shows very fractured and totally unworkable material. Geological literature (Bettelli 1985) and notes to geological maps, however, describe the presence of radiolarite as olistoliths.

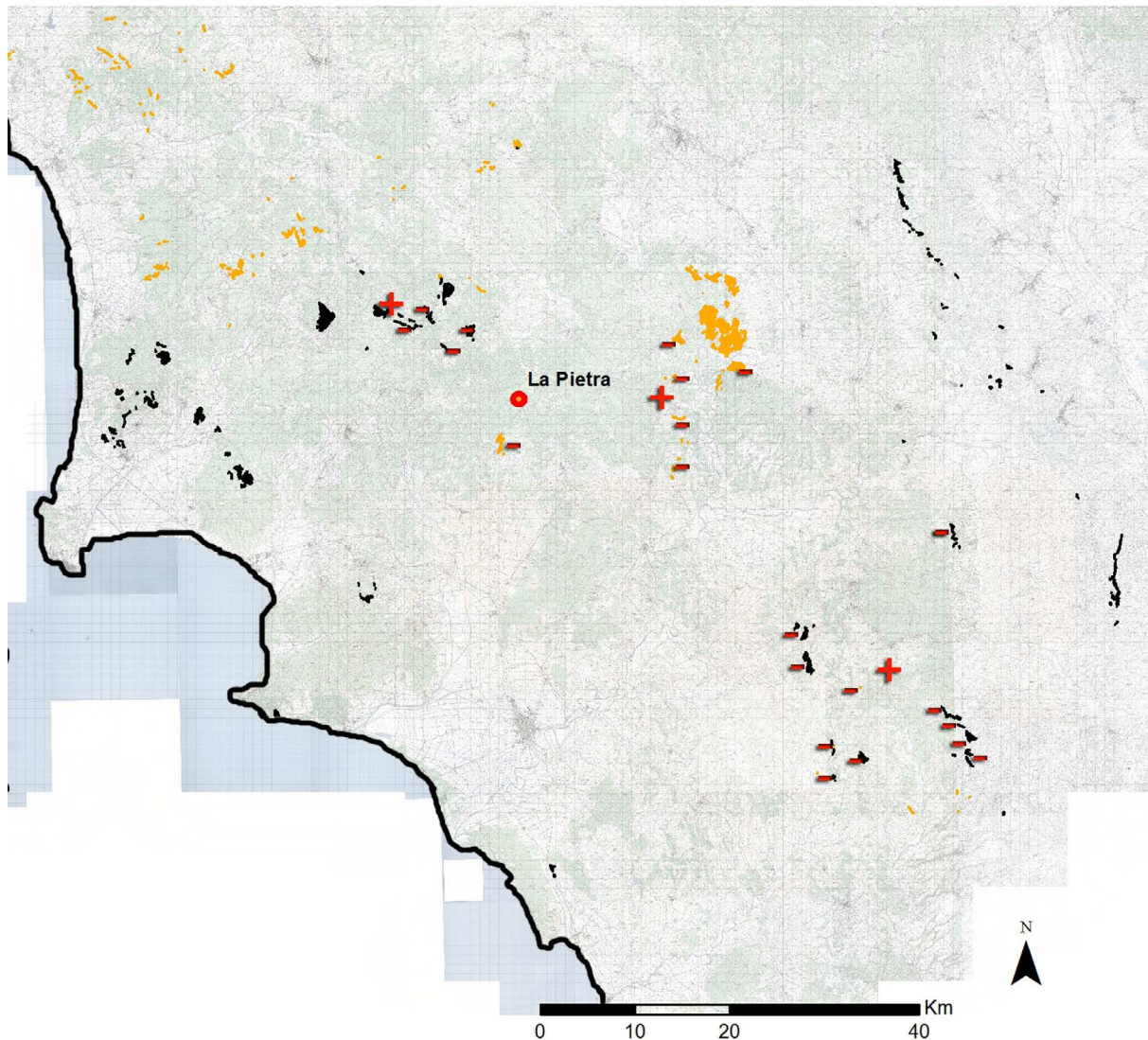


Figure 9. Presence of anthropic traces in the radiolarite outcrops surveyed (“-” no traces; “+” traces). Modified from map created with ArcGIS software. Data from Geodatabase of Tuscany (Regione Toscana 2015).

Good quality radiolarite resembling the Ligurian Domain one can in fact be found quite abundantly in the gravels of the Fiora River (Figure 10). This led us to look for more outcrops, not indicated in geological maps. A good proxy for the presence of radiolarite is that of ophiolitic rocks of which radiolarites represent the earliest sedimentary cover (Folk & McBride 1978). We thus visited some ophiolitic rock outcrops in the vicinity of the Fiora River. In one of these (Sasso di Petorsola) very close and to the Fiora springs, radiolarite was found both attached to the base of the ophiolitic rock spur and two hundred meters away from it where a small outcrop sits within the Cretaceous Palombini Shales formation. The radiolarite outcrop at Petorsola is not mapped nor described in geological literature.

The general features of radiolarites belonging to the Ligurian Domain have been described in some detail in geological studies dedicated to ophiolites (Cortesogno *et al.* 1987; Folk & McBride 1978; Principi *et al.* 2004) and the different horizons and lithotypes of the Ligurian radiolarites are also well described in relation to the large Copper Age quarry of Valle Lagorara (Campana & Maggi 2002).

Tuscan Domain radiolarites, on the other hand, have never been described before in detail in relation to pre-proto-historic lithic technology. In the area surveyed they show similar characteristics across the different outcrops and can be grouped in the following litho-

typological groups. This grouping is for the scope of archaeological study only and does not entail any geological interpretation.



Figure 10. Fragment of radiolarite layer (indicated with white dot) in the gravels of the river Fiora.

Three main groups were individuated:

Red radiolarite: This group comprise radiolarites which are bright red or reddish-brown in colour with rare yellow or whitish zonations. They are most abundant in the outcrops south-west of Mount Amiata. This lithotype is however seldom workable as it is found in very fractured layers which divide up in small prismatic blocks.

Varicoloured radiolarite: This group comprises radiolarite which varies in colour from white to grey, brown or varicoloured. A common characteristic to these layers is the very strong fracturing. They are found abundantly in the eastern and southern area of Mount Amiata and at Cornate and Poggio Mutti.

Green radiolarite: They can be found in different hues of green and are generally medium or coarse grained. They often show orange, brown, red or black veins and flames. These lithotype is definitely less abundant than the others described for the Tuscan Domain. It is found at Poggio Mutti and was observed in outcrops east of Mount Amiata.

3.2. The new archaeological evidence of quarry-workshops Petorsola

As mentioned above, an unmapped outcrop of radiolarite was individuated in the upper Fiora Valley, at the foot of the volcanic cover of Mount Amiata. This is very close to the rock spur of Petorsola which is an ophiolitic olistolith included in the formation of the Palombini Shales (lower Cretaceous) (Figure 11). Here we individuated clear evidence of workshop activity which appear Holocene in age.

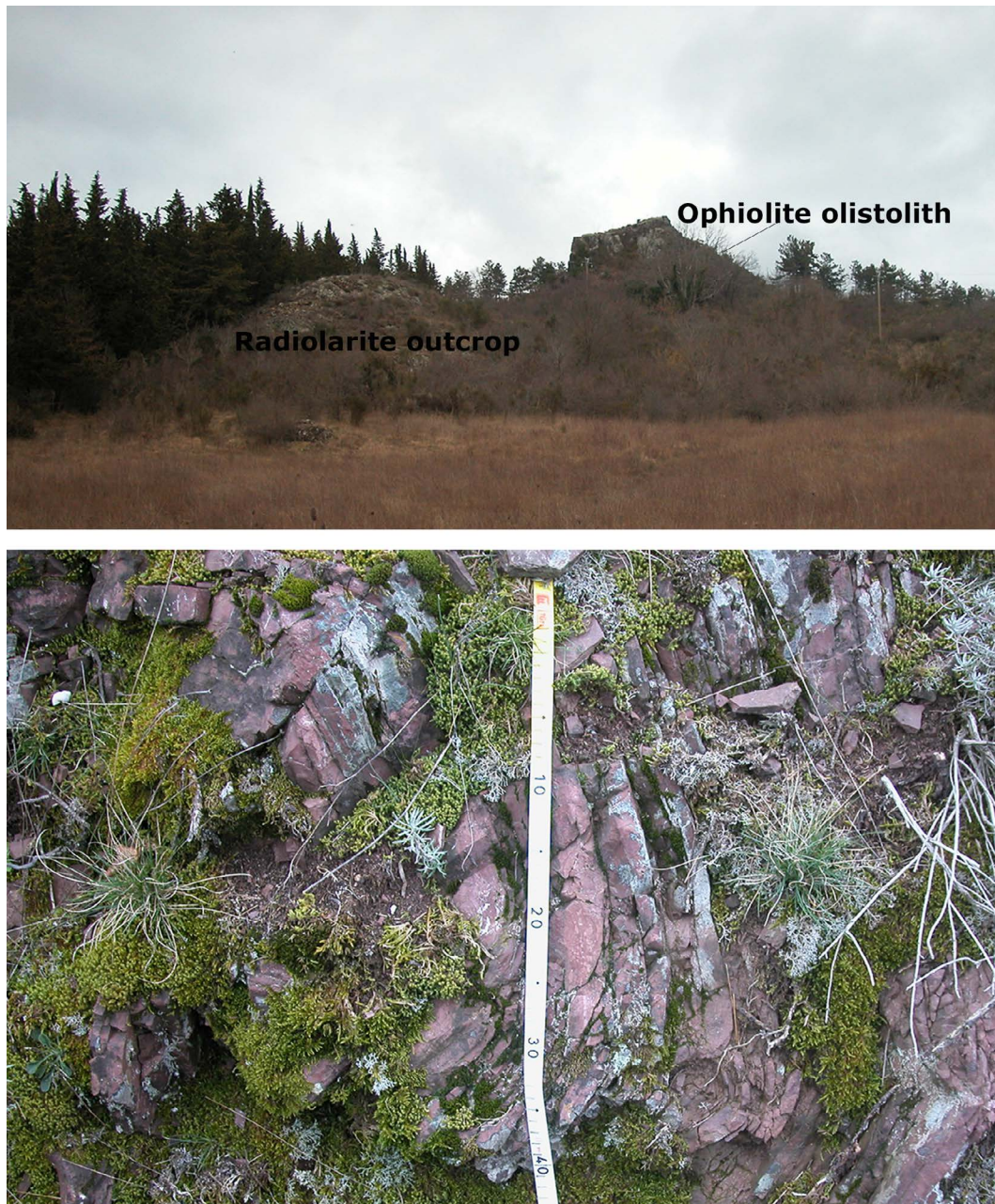


Figure 11. Petorsola ophiolite olistolith and radiolarite outcrop.

The small radiolarite outcrop, measuring about 20 meters in diameter and 2 metres in height, does not show any trace of quarrying activity. Surface lithic industry is scattered abundantly at the foot of the outcrop, on the edge of a small alluvial terrace and in a wooded area immediately west of it.

The lithic industry observable on surface is made in large part of cortical flakes and blades and of tested radiolarite slabs. Only two pre-forms were found and collected during our surveys. These point to a Copper Age attribution of the workshop activity, based on analogies with the lithic industries from the other workshops described above.

The radiolarite available at Petorsola appears to be of mediocre quality. Almost certainly usable slabs were selected and picked by knappers from the natural detritus. It needs to be considered that, even if scarce, the quality of this radiolarite is among the best which can be found in the area of Mount Amiata and the upper Fiora Valley.

The presence of a white opaque chalcedony paste which replaces radiolarian tests and other inclusions is a feature which appears to be characteristic of this radiolarite and which was also observed on samples from radiolarite pebbles from the Fiora River bed. This could be a micro-*facies* characteristic of this radiolarite horizon, useful for sourcing artefacts made of radiolarite coming from this area.

In the territory of the upper Fiora Valley, Copper Age evidence comprise sparse findings which include: a hammer-stone with central groove and bearing traces of cinnabar found at the historic mine of Cortevicchia (Giardino & Steiniger 2011); two copper daggers; a copper halberd with the back shaped as a hammer which is ascribable to the Rinaldone *facies* (Metta 2015).

Albatreti

As explained above, around the locality of Bagno di Petriolo there are several small radiolarite outcrops belonging to the Ligurian Domain.

The outcrop that we dubbed Albatreti (Civitella Paganico) (because of its proximity to a stream bearing that name) has yielded plenty of evidence of workshop and quarrying activity (Figure 12). The radiolarite outcrop forms a small dome on the right side of the Albatreti stream. The outcrop develops along a NS axes and is about 300 meters long and 100 meters wide.



Figure 12. Albatreti quarry-workshop: A & B. outcropping radiolarite layers with traces of hammering; C. radiolarite detritus and debitage waste along the slope of the Albatreti stream; D. a preform of probable Copper Age date.

Radiolarite layers outcrop only for less than one meter on the summit and on the northern slope and are for the rest buried under soil.

From observation of the surface lithic industry it is clear that the workshop activities there were particularly intense and started already in the Pleistocene. Débitage elements from

different stages of laminar reduction sequences are present where the soil is eroded. An Upper Palaeolithic site (Le Caldanelle) is known less than one km downstream (Arrighi *et al.* 2007; Galiberti & Ronchitelli 1979).

Traces of quarrying are observable on a little area of exposure (about 2 square meters) of the radiolarite layers on the northern slope of the outcrop and along the Albatreti stream. Clear impact stigmata are visible on the layers and are almost identical to those observable at La Pietra.

Lithic industries from the workshops are visible on surface on the whole area of the outcrop and on the Albatreti stream bed: they comprise thousands of cortical flakes and large waste flakes. Many fragmented preforms at an initial stage of working were observed and also some preforms abandoned at an advanced stage of working were recovered.

The site of Albatreti appears to be strongly linked to and could share the same chronology with the quarry-workshop of La Pietra.

Poggio Mutti

Poggio Mutti (807 m a.s.l.) is part of small mountain ridge which reaches the height of 1060 meters with the peak of Cornate, the highest peak of the Metalliferous Hills.

The site is located 17 km as the crow flies from La Pietra. Poggio Mutti is also a geosite and contains a significant geo-diversity (Buracchi *et al.* 2015). The presence of lithic workshop here was communicated to the Archaeological office of Tuscany in 2005.

The radiolarites outcropping at this locality belong to the Diaspri formation of the Tuscan Domain.

The Diaspri formation covers the summit of Poggio Mutti and the whole of its northern slope. The radiolarite layers of this formation are mostly of the red and varicoloured type with a very poor knapping quality.

Radiolarites of the green type, homogeneous and with a matt texture, only outcrop halfway along the northern slope of Poggio Mutti and to a smaller amount along the southern one.

The green radiolarites are the only one to bear clear traces of lithic workshop activity.

On the northern slope of Poggio Mutti in fact a great amount of knapping waste was observed, among which two artifacts which can be considered to be part of a Copper Age preforms reduction sequence. The lithic industry is almost totally affected by a thick whitish patina. No *in situ* layers are exposed and small pits were possibly excavated to retrieve the raw material. This is suggested by some round depressions which were observed on the ground.

3.3. Results of geochemical analyses

We took as starting point for our geochemical characterization the work by Brandl and colleagues (2014) where variations in trace elements Ba, Mg and, to some extent, Sr, Rb and V were found to be the most diagnostic for distinguishing between radiolarite outcrops of different geological areas (Brandl *et al.* 2014: 15). We focused on Sr and Rb only as Ba could not be detected by the pXRF device we employed and Mg was detected only in a small number of our samples. V, although present, was not found to vary significantly across the different samples we measured, whereas a good response was observed for Zr. Results of pXRF analyses are reported in Table 1. For these preliminary analyses, we simply plotted in scatter diagrams the variations of the couples Sr vs Rb and Rb vs Zr.

In the first place, we verified the possibility of distinguishing between radiolarite outcrops of the same geological domain. This is especially important for Ligurian Domain radiolarite as the outcrops of this rock have yielded most of the evidence for Copper Age raw material exploitation.

Table 1. Elemental concentration (mg/kg) from the pXRF analyses for each sample. Abbreviations: LD - Ligurian Domain; TD - Tuscan Domain.

Sample	Type	Provenance	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Rb	Sr	Zr	Ag
LP2-2a	red radiolarite	La Pietra (LD)	1660	376	147	0	6	33	2339	7	7	0	11	12	2	50
LP2-2b	red radiolarite	La Pietra (LD)	3370	61	264	20	5	47	1944	0	0	8	19	13	18	25
LP2-2c	red radiolarite	La Pietra (LD)	3122	1019	266	0	8	97	3204	0	18	0	22	15	15	23
LP2-2d	red radiolarite	La Pietra (LD)	2842	500	253	16	18	103	4842	10	0	0	20	14	15	38
LP2-2e	red radiolarite	La Pietra (LD)	2797	418	253	24	19	135	3643	0	17	0	17	12	11	14
LP2-2f	red radiolarite	La Pietra (LD)	4305	550	337	13	16	160	4937	24	12	10	24	13	16	33
LP2-2g	red radiolarite	La Pietra (LD)	2460	308	229	0	15	183	2901	11	0	6	14	10	14	0
LP2-2h	red radiolarite	La Pietra (LD)	2321	643	224	12	0	70	2076	0	7	6	17	12	12	40
Alb. 1	red radiolarite	Albatreti (LD)	2083	399	208	12	15	196	2952	11	6	0	12	11	11	65
Alb. 2	red radiolarite	Albatreti (LD)	2280	580	231	0	14	189	2193	0	12	0	14	16	10	41
Alb. 3	red radiolarite	Albatreti (LD)	3582	445	310	33	22	144	3184	32	0	9	18	13	14	15
Alb. 4	red radiolarite	Albatreti (LD)	2849	515	201	24	12	190	3816	12	20	0	14	12	10	57
Alb. 5	red radiolarite	Albatreti (LD)	3695	660	369	21,5	18	136	4642	14	11	0	22	12	22	0
DV 1	green radiolarite	Poggio Mutti (TD)	6635	0	797	54	24	216	4692	0	0	18	51	27	33	54
DVPM1	green radiolarite	Poggio Mutti (TD)	9109	1240	949	54	39	445	8646	0	61	30	64	29	42	0
DV 31	green radiolarite	Poggio Mutti (TD)	4884	323	479	52	23	25	2183	0	26	0	25	105	29	61
DV 2	green radiolarite	Poggio Mutti (TD)	7008	0	741	0	25	298	5947	0	0	122	60	13	40	9
14P02	green radiolarite	La Pietra (LD)	2914	0	300	0	19	124	2591	0	20	0	14	15	13	52
VLP 1	green radiolarite	La Pietra (LD)	2277	0	239	25	15	24	1493	0	17	0	13	14	14	54
VLP 2	green radiolarite	La Pietra (LD)	3348	0	429	0	0	209	3698	30	20	0	17	16	15	70
PT1	red radiolarite	Petorsola (LD)	2882	277	367	0	23	120	5909	0	18	0	20	15	26	50
PT2	red radiolarite	Petorsola (LD)	4495	0	386	36	25	134	7390	0	0	11	27	16	24	0
PT3	red radiolarite	Petorsola (LD)	4913	312	509	36	28	160	7500	28	0	11	32	17	21	47
LE n.39	red radiolarite	Fiora River gravels near Petorsola (LD)	6379	386	472	46	31	208	8291	63	21	0	31	14	24	49
Arch.1	red radiolarite arrowhead	Lanfredini Collection	2780	749	245	16	33	147	3532	17	9	7	12	11	10	0

As can be seen in Figure 13, with the pXRF device a distinction of this kind does not appear to be feasible. We in fact tried to plot possible differences in elemental composition between the La Pietra and Albatreti radiolarites. These two sources largely overlap. Of course, this might change with an increase in sample size, but these preliminary and non-statistical data, is all the same in line with what was found in previous studies on radiolarite sourcing which have shown only feeble possibilities of making distinctive groups on geochemical bases within radiolarite belonging to the same geological region (Brandl *et al.* 2014). Nonetheless, some positive result came from comparing the outcrops of La Pietra and Petorsola (Figure 14). Here the examined sample is very small, nonetheless a distinctive cluster does emerge for the Petorsola radiolarites, especially when observing the distribution of the Rb/Zr values. This may open a line of research on the geochemical distinction between radiolarite belonging to the Ligurian Domain around La Pietra and those of the small outcrops of the same domain but found as olistoliths. Increasing the number of measurements on radiolarite samples from the area of the Upper Fiora valley will help to better verify this last group which may be helpful for sourcing radiolarite arrowheads in the area of southern Tuscany and northern Latium.

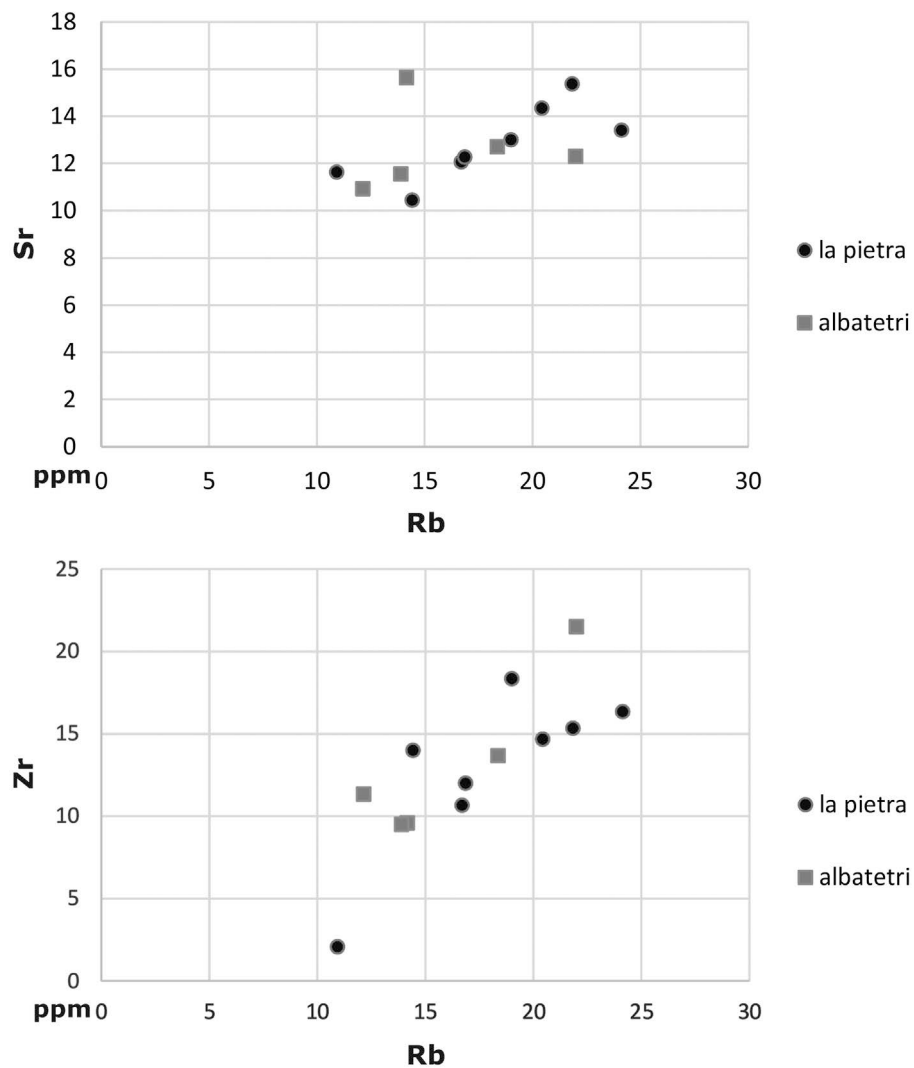


Figure 13. Scatter diagrams showing the values of Rb/Sr and Rb/Zr in radiolarite samples from the outcrops of La Pietra and Albatreti.

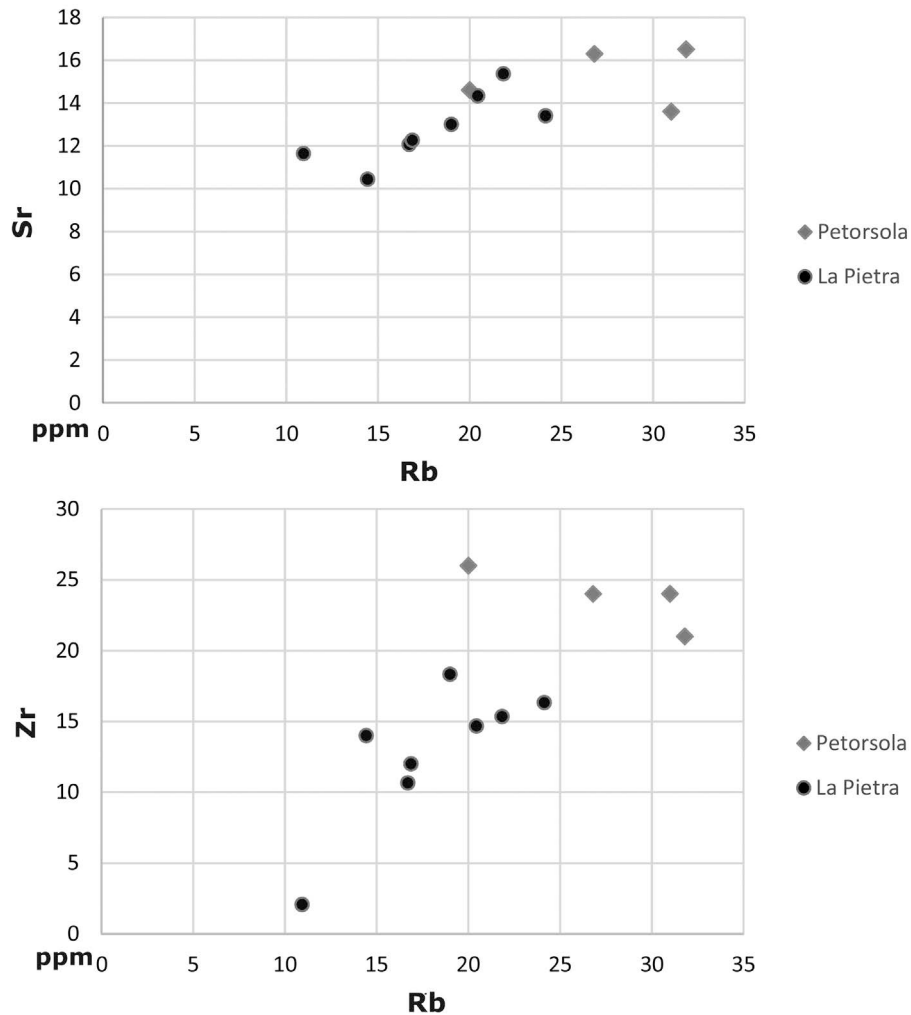


Figure 14. Scatter diagrams showing the values of Rb/Sr and Rb/Zr in radiolarite samples from the outcrops of La Pietra and Petorsola.

The attempt of distinguishing geochemically the radiolarite of the Ligurian Domain from that of the Tuscan one was done in this preliminary analysis only with samples coming from the outcrop of Poggio Mutti. The green type radiolarite of Poggio Mutti, the only one on which traces of exploitation were found, was compared with green radiolarite samples of La Pietra. These radiolarites are macroscopically similar. The results of these measurement are quite encouraging as it is possible to see a that elemental values of the green radiolarite of the two different Domains fall quite apart and tend to form two distinct groups (Figure 15).

As the final scope of these analyses is the sourcing of archaeological artefacts made of radiolarite we performed pXRF measurements also on the above mentioned Copper Age arrowhead.

The raw material of this artefact is macroscopically very similar to the radiolarite of La Pietra and Albatreti. The pXRF results (Figure 16) show how its Rb/Sr and Rb/Zr values fall within the lower range of the Ligurian radiolarites group of La Pietra and Albatreti type, and very distant from the range of the Petorsola group.

4. Discussion and conclusions

La Pietra quarry-workshop was the starting point for a research on Copper Age radiolarite exploitation in central-southern Tuscany. Our surveys allowed to identify another intensively exploited quarry and workshop and two minor workshops. These discoveries are

already giving us a better detailed image of the Copper Age geography in the area of central-southern Tuscany, the knowledge of which was until now largely restricted to funerary evidence.

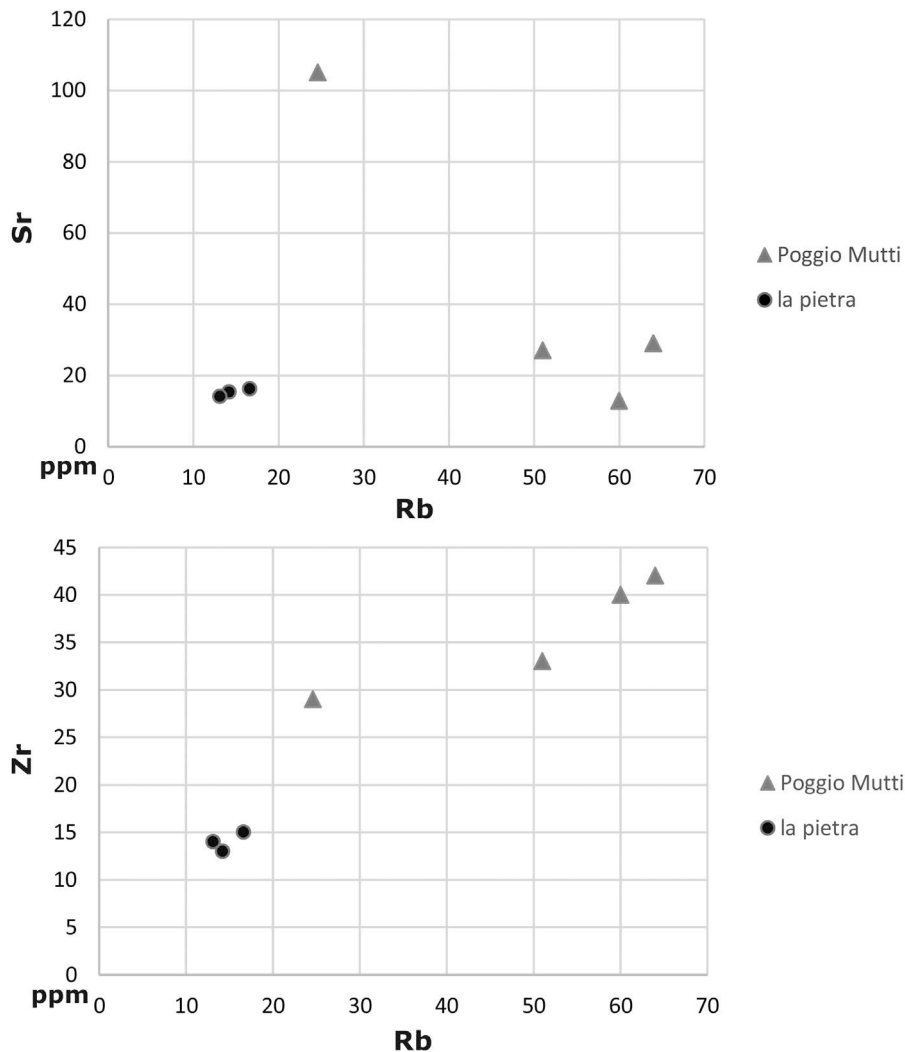


Figure 15. Scatter diagrams showing the values of Rb/Sr and Rb/Zr in radiolarite samples from the outcrops of La Pietra and Poggio Mutti.

The results of our surveys are also helping to better detail radiolarite geo-diversity. The territory under study is characterized by the superimposition of radiolarite formations from two different palaeo-geographic domains (Tuscan and Ligurian). To this context, we can add the presence of radiolarite olistoliths in different formations. The here presented data on the Petorsola outcrop draws attention to the importance of their study.

In order to bridge the gap between the radiolarite exploitation sites and the coeval archaeological evidence it is pivotal to source the radiolarite arrowheads used as grave-goods in burial sites and to attempt to assign their raw material to the different production centres.

Elemental composition analyses through pXRF has shown the potential of using such method for the sourcing of radiolarite, especially in cases like ours in which we are dealing mostly with museum artifacts which can only be studied by totally non-invasive techniques. The application of pXRF to sedimentary siliceous rocks is quite new and we hope to contribute further to the debate on its usefulness in sourcing studies by increasing the size of our sample and by performing multivariate and statistical analyses.

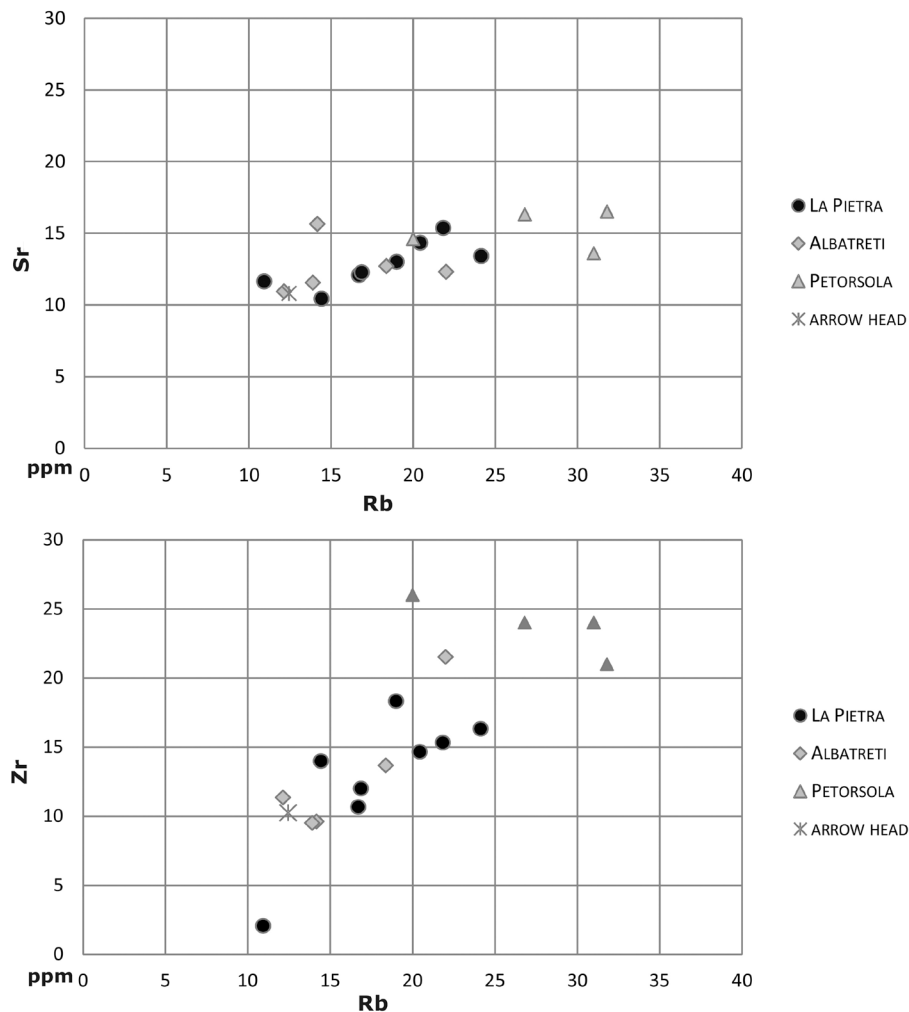


Figure 16. Scatter diagrams showing the elemental of Rb/Sr and Rb/Zr for the Copper Age radiolarite arrowhead of the Lanfredini collection against those of the La Pietra, Albatreti and Petorsola outcrops.

We are currently working on defining geochemically the group of Tuscan Domain radiolarites and see if they can be distinguished from the Ligurian ones, following the preliminary results obtained in distinguishing the Tuscan green radiolarite of Poggio Mutti from the Ligurian green radiolarite of La Pietra. This last result is particularly important as some of the burial sites (Grotta Prato, Grotta della Spinosa) at issue are located virtually halfway between these two workshops. The fact that the Ligurian Domain radiolarites from an olistolith (Petorsola) seem to be distinguishable by their chemistry from the main formation found inside the Ligurian sequence is also encouraging, especially because the area where the Petorsola outcrop sits is near the core area of the Copper Age Rinaldone *facies*.

The fact that the radiolarite from the main new quarry-workshop individuated so far (*i.e.* the site of Albatreti) does not appear to be distinguishable from that of La Pietra on geochemical bases calls for the integration with other methodologies of raw material attribution.

In this sense, through extensive surveys in primary outcrops it is possible to reduce the number of the potential provenance sites. It is also possible to individuate which horizons are represented in each of the outcrops and which were most exploited.

Characterizing macroscopically or at low magnifications a specific radiolarite horizon can help to recognize those same characteristics in radiolarite artefacts. A horizon in fact may be present in one quarry-workshop but be subordinate or absent from another. Even when a same horizon is present across different exploited outcrops there may be portions of it

characterized by peculiar micro-facies which define specific lithotypes. For this reason, we are building up a reference collection of the different lithotypes of radiolarite we can individuate.

The area of radiolarite quarry-workshops distribution defined at the beginning of this paper is much wider than the one here considered in detail. After we complete our work of field surveys and raw material characterization in the area of central-southern Tuscany, it is our intention also to collaborate to the characterization of the evidence from Liguria and Emilia Romagna where surveys have already been carried out (Campana *et al.* 2013). This extended perspective will necessarily include the understanding of the limits of the influence areas of those which appear, so far, to be the major production centres of radiolarite preforms for arrowheads and other foliated artefacts during the Copper Age of Tyrrhenian northern-central Italy: La Pietra and Valle Lagorara.

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