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SILCRETE AND CHERT AS SOURCE ROCKS OF EARLY PREHISTORIC ARTIFACTS: THE CASE OF CENTRAL EVIA (GREECE)

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ABSTRACT

Silcrete and chert were used for the manufacture of stone tools in early prehistoric (Middle / Late Palaeolithic and Mesolithic) times in Central Evia island. We have undertaken an analysis of visual characteristics of prehistoric artifacts and the potential source rocks exposed in the area to provide evidence of use of locally available raw material. Field geological surveys indicate that silcrete, chert nodules in limestones, and varicolored cherts within siliceous mudstones and sandstones in the area were potential raw materials for prehistoric knappers. Geological mapping and detailed studies of the mineralogy, texture and geochemistry of critical rock types demonstrate extensive use of different silcrete facies associated with weathered ultramafic ophiolitic rocks and chert nodules occurring within Upper Cretaceous limestones. SEM, XRF, XRD and ICP-MS analytical methods were employed. The hard, massive, buff reddish-brown variety of silcrete triggered the main interest of prehistoric knappers. Provenancing of lithic tools made of silcrete is facilitated by the presence of disseminated grains of relictic chromite/spinel and serpentine, and the high Cr, Ni, Fe, Mg, Co, V contents. Chert nodules are depleted in almost all the major, minor and REE elements, except for silica and Ca. It is concluded that the chemistry of cherts alone is not considered a reliable approach to resolve the critical problem of sourcing of chert artifacts, with detailed field surveys in neighboring areas and petrographic analysis needed for compelling source to artifact correlations.

KEYWORDS: Early prehistoric artifacts, silcrete, chert, petrography, geochemistry, Artaki, Evia, Greece

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1. INTRODUCTION

Last years significant results on Palaeolithic and Mesolithic sites in the Aegean and Western Greece came out after numerous field and excavation works, e.g. Franchthi in Argolis (Perlès, 1987; 1990), Petrota - Thrace (Efstratiou and Ammerman, 2004), Artaki in Evia island (Matzanas, 2009), Kokkinopilos at Epirus (Runnels and van Andel, 2003), Maroulas at Kythnos (Sampson et al., 2010), Rhodafnidia - Lesbos (Galanidou et al., 2013), Naxos (Carter et al., 2014), Pindos Mt., Western Macedonia (Efstratiou et al., 2014), Lakonis cave (Elefanti and Panagopoulou, 2016), western Mani (Tourloukis et al., 2016) (Fig. 1). Numerous lithic objects have been found, most of which are still under investigation to characterize their precise age, the type of lithologies used, and the mode of manufacturing. Characterization of the source rocks of lithic objects is a keystone in building models for past human activities, especially for subsistence and mobility, as well as potential trading networks (Prothero and Lavin, 1990; Papoulia, 2017). Siliceous lithic objects found in Greece and especially in the Aegean are collectively characterized as made of "chert" (in greek *πυριτιόλιθος*) and flint (see Papoulia, 2017), although each group of lithic objects bears distinct petrographic and geochemical features reflecting the mode of occurrence and the formation processes of source lithologies, allowing a gross classification into certain petrographic groups. An approach to discriminate among various groups should be the identification of specific mineralogical and petrographic prints, which along with their geochemistry might help lithic specialists and archaeologists to shed light on the provenience of source rocks.

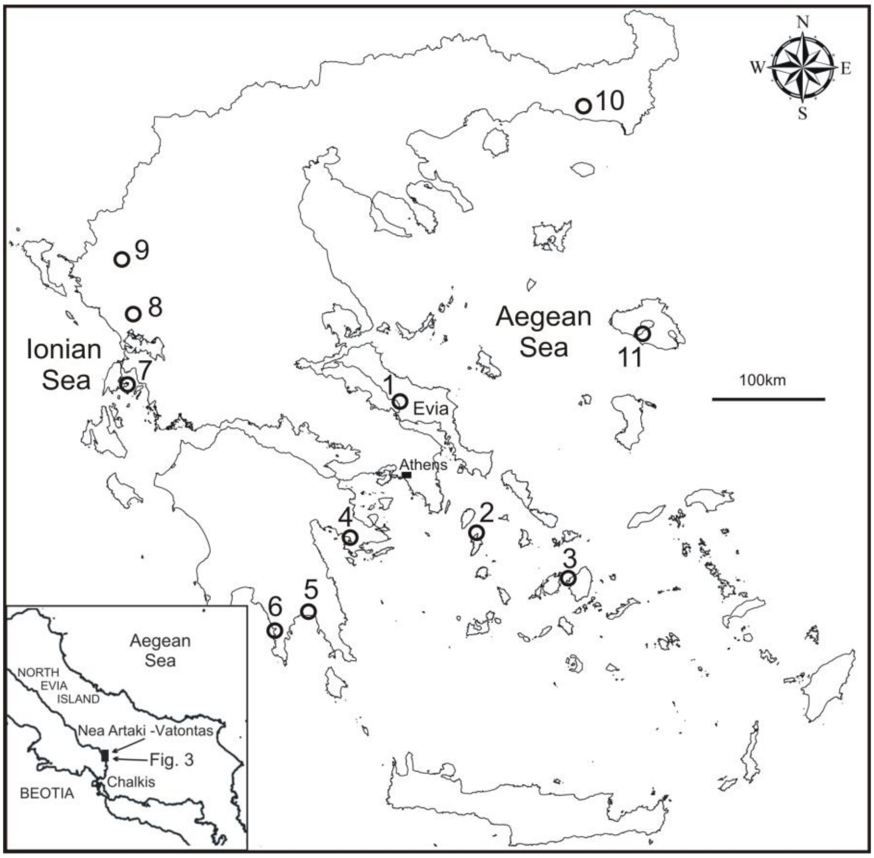

Figure 1. Map showing the main sites mentioned in the text, where lithic tools made of chert nodules, silcrete and chert (including silicified rocks) have been found. 1) Nea Artaki - Vatontas, Evia island; 2) Maroulas, Kythnos; 3) Stelida, Naxos; 4) Franchthi, Argolis; 5) Lakonis, Peloponnese; 6) Mani, Peloponnese; 7) Meganisi, Ionian Sea; 8) Kokkinopilos; 9) Pindus Mt.; 10) Petrota, Thrace; 11) Rhodafnidia, Lesbos (References in the text). Location of the Nea Artaki - Vatontas area is depicted in inset.

Despite being the second after obsidian used lithic raw material in Greece, chert (s.l.) has not received the same methodological development. Mineralogical and chemical data on chert used for the manufacture of lithic objects are still relatively sparse, while precise petrographic characterization of the siliceous material is lacking. It is concluded that the pre-historic siliceous objects are, to a major extent, composed of lithic assemblages of unknown or not well documented provenance of raw material, in agreement with the comments and statement by Tourloukis (2010, p. 50) for the Middle Palaeolithic artifacts. This omission generates a serious loss of information necessary for a better understanding of the management of lithic material, which can only be overcome through the detailed petrographic and chemical characterization of siliceous rocks. The Hellenic tectonostratigraphic terranes, extending to Anatolia to the east and to Balkan countries to the north, are characterized by abundant cherts of various petrographic and chemical characteristics as a result of diverse mode of occurrence and genesis. These cherts bear common physical characteristics that allowed knapping for production of various tools.

Chert is a very hard, dense rock, with conchoidal fracture when struck. It is a common sedimentary rock on earth and possibly the first to be exploited by man in the manufacture of tools and weaponry (Wise and Weaver, 1974). Chert is a very general term for fine-grained siliceous sediment of inorganic, biochemical, biogenic, volcanic or hydrothermal origin (Tucker, 2001). Chert is defined here, following Folk (1980), as a “sediment, essentially monomineralic, composed chiefly of microcrystalline and/or chalcedonic quartz, with subordinate megaquartz and minor amounts of impurities”. Originally chert consists of opaline silica, which transforms/recrystallizes upon diagenesis to euhedral quartz, with microcrystalline quartz as a transitional mineral phase (Thiry and Milnes, 2017). Cherts show a wide spectrum of colors, depending on their specific mineral and chemical admixtures. There are two common stratigraphic occurrences of cherts: as nodules in carbonate rocks and as bedded cherts (Blatt et al., 1980; Prothero and Lavin, 1990; Luedtke, 1992). Chert nodules are lensoid or rounded bodies, usually enclosed in carbonate or detrital sediments. The genesis of chert nodules has been much discussed. A direct chemical precipitation of silica is proposed by Folk (1980). Biological processes contributing to silica precipitation on the sediment/water interface have been proposed by other researchers (e.g. Wise and Weaver, 1974). Nodular cherts in limestones, however, contain much evidence to demonstrate a replacement and thus a diagenetic origin (e.g. Tucker, 2001; Clayton, 1986). It seems they result during early diagenesis of the host sequence after replacement (chertification) of carbonate rocks that were largely not lithified (e.g. Bernoulli, 1972; Maliva and Siever, 1989). Bedded cherts, chert layers in pelitic and fine grained detrital sediments, and radiolarites contain variable impurities of clays, biogenic radiolarian ooze and a hydrothermal Fe/Mn component (e.g. Barrett, 1981). They consist mainly of interlocking grains of microcrystalline quartz, coarser-grained recrystallized quartz of diagenetic origin, radiolarian ghosts, and traces of carbonate, iron and manganese oxides and a small fraction of clay minerals.

Chert nodules in carbonate rocks were exploited and used by Palaeolithic people for the manufacture of tools in Western Greece, e.g. Pindus Mt. (Efstratiou et al., 2014), Kokkinopilos (Kourtessi-Philippakis, 1996; Runnels and van Andel, 2003), Meganisi island (Chatzimpaloglou, 2014). Palaeolithic objects made of chert are also reported from Peloponnese (Lakonis) (Chiotis, 1997) and western Mani Peninsula (Tourloukis et al., 2016).

Rocks having been subjected to silicification by interaction with hydrothermal fluids, have also been used by Palaeolithic people in the Aegean for the manufacture of tools. Typical examples are the pervasively silicified volcanics (silica caps) of Petrota graben in Western Thrace (Efstratiou and Ammerman, 2004) dominated by opal and quartz, and the silicified sediments in Stelida area of Naxos (Carter et al., 2014; Skarpelis et al., 2017). This rock type, following strictly petrographic terminology, should be characterized as “silicification” or “silicified rock” to discriminate from chert. Silicified rocks_are typically dark to pale grey in color, cryptocrystalline to microcrystalline, and can be massive pervasive in texture. They consist of opaline silica, chalcedony, quartz, minor sulfides and sulfates. Silicification is a common feature of hydrothermal alteration of rocks in epithermal systems, and incorporates both the addition of Si and the redistribution of Si that was originally in glass or cristobalite (Henley and Ellis, 1983). Chemical elements like Ba, Cu, Zn, Pb, Sb, Tl, As and sulfur, either as sulfide or sulfate, usually participate at elevated concentrations (Hedenquist et al., 1996).

Bedded cherts and chert nodules are clearly texturally distinct relative to silicified rocks that resulted by interaction with hydrothermal fluids. Silica polymorphs generally flood the ground mass in the latter, with vugs and fractures usually infilled with slightly coarser quartz.

In contrast, silcrete (in greek “πυριτιοπαγές πέτρωμα”) is formed by geochemical processes operating at or near the Earth’s surface. Silcrete is defined here, following terminology in *The Regolith Glossary* edited by Engleton (2001), as the silicified sector of the layer of weathered rock and soil overlying bedrock, referred to as regolith. Silcretes are regarded as products of replacement or cementation of sands as well as of untramafic and granitic rocks and their weathering products by opaline silica, cristobalite or quartz (Milnes and Thiry, 1992). This process results in complete or near complete silicification of precursor regolith. Silcretes lack stratification and lamination, with their structure resembling that of textureless fine grained quartz aggregates, which are crosscut by thin quartz veinlets. The formation of silcrete usually involves silica dioxide being dissolved during weathering of silicate minerals, going to solution in groundwater and precipitated as silica polymorphs in a soil horizon or bedrock body (for details on the mode of formation of silcrete see in Trescases et al., 1981; Summerfield, 1983a, b; Milnes and Thiry, 1992; Nash and Ullyott, 2007; Taylor and Eggleton, 2017). Silcrete is extremely hard, commonly with conchoidal fracture and vitreous luster. It is resistant to weathering and erosion but eventually weathers spheroidally to produce boulders and angular fragments (Encyclopedia Britannica, 2008). The fabric, mineralogy and chemical composition may reflect those of the parent material (regolith) and hence, if residual, the underlying lithology. Thus, silcretes over granites and sandstones tend to be enriched especially in Ti and Zr, e.g. sands in the Cretaceous Antlers Formation of Oklahoma and Texas (Wyckoff et al., 2017), Paris Basin (Thiry et al., 1988; Taylor and Engleton, 2017), Australia (Senior, 1979; Thiry and Milnes, 1991; Webb and Golding, 1998) and a variety of host materials, especially playa sediments and calcrete in the Kalahari Basin (Shaw and Nash, 1998; Nash et al., 2004). Silcretes formed especially at the expense of ultramafic rocks and the overlying saprolite are characterized by the occurrence of relictic chromite/spinel, magnetite, serpentine, talc and clays, while their chemistry reflects the high concentration of Cr, Fe and Ni of the parent rocks (Trescases et al., 1981; Golightly, 1981; Valeton et al., 1987; Skarpelis 2006). Groundwater silcrete is formed when silica moves downward to the water table, resulting in deposition of silica polymorphs where physico-chemical conditions were favorable. An outline of the conditions of formation of silcretes is provided by many researchers (see for detailed discussions: Thiry and Millot, 1987; Thiry et al., 1988; Ullyott and Nash, 2006; Ullyott et al., 2015; Taylor and Eggleton, 2017). An analysis of the sedimentological context along with a study of the geochemical conditions of silcrete formation in southern Africa led Summerfield (1983b, c) to propose two distinct climatic regimes: a predominantly arid to semi-arid environment for non-weathering profile silcretes, as opposed to a much more humid climate for weathering profile silcretes. Silcretes found in Continental Greece and Evia were possibly formed under the latter climatic conditions (Skarpelis, 2006).

This paper aims to provide new data on silcrete rocks, as well as on chert nodules occurring within limestones as local raw material for the manufacture of the central Evian and especially the Nea Artaki artifacts. Characterization of the central Evian silcrete and chert nodules through petrographic and geochemical analyses aims to expand the basis of data within the various types of Aegean siliceous rocks used for the manufacture of lithic objects. Emphasis is given to identification of those petrographic, mineralogical and chemical features of silcrete and chert nodules, which help discriminate them among cherts exposed in central Evia, as well as cherts used for production of artifacts in certain Aegean and Western Greece Palaeolithic sites.

2. LITHIC TOOLS FOUND IN CENTRAL EVIA

Lithic tools of early prehistoric age have been found in central and north Evia (Sachett et al., 1967; Matzanas, 2009). Nea Artaki especially has been described as a spatially extensive open-air prehistoric site, located 7 km to the north of Chalkis city, capital of the Evia island prefecture. A big number of stone tools were recovered in the low-hill coastal area north of the Nea Artaki port (Sarantea-Micha and Mishra, 1985; Sarantea, 1986). Collection of the tools had a rescue character, to avoid their loss due to the rapid expansion of the settlement. Hand-axes, choppers, scrapers, borers, cores and denticulate scrapers were recorded among a variety of objects (Fig. 2). They are considered as remnants of local stone exploitation and processing by early prehistoric people living in the area (Sarantea, 1986; Matzanas, 2004; 2009). Previous researchers did not identify the material used for stone tool manufacturing explicitly, instead classifying it as "chert". The central Evian stone tools are made mainly of silcrete with a subordinate amount made of chert nodules. A variety of massive brick-red to dark brownish-red silcrete litho types has been used by prehistoric knappers. Rare white artifacts made of milky opal come possibly from the silica sector of vein-type microcrystalline magnesite ores in Evia. The outcrops of silcrete at "Faneromeni" and "Dyo Vouna hill - Voleri" seem to be the most significant, on the basis of the number of tools discovered (Sarantea, 1986; Matzanas, 2009). Rapid expansion of the city has limited the extent of outcrops of silcrete rocks, which were used as raw material for the manufacture of lithic tools. Only a small sector of the silcrete outcrops is now exposed at the Earth's surface at Nea Artaki and the nearby area of Vatontas, with that at Faneromeni being officially designated as an archaeological site and protected.

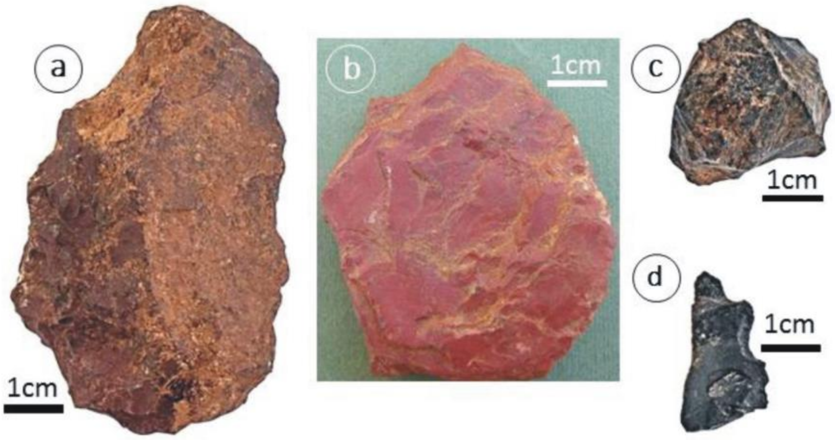

Figure 2. Representative early prehistoric artifacts made of silcrete (a and b) and black chert (c and d): (a) Side-scraper, Nea Artaki; (b) Unfinished offset point found 2.3 km to the NE of Zephyros beach; (c) Core, Nea Artaki; (d) Borer, Nea Artaki. Identifications by Dr. Ch. Matzanas (Copyright Hellenic Ministry of Culture and Sports).

Preliminary age evaluation based on the typological and technological traits of the stone tools reveals that they can be attributed to the Middle and Late Palaeolithic and Mesolithic (Matzanas, 2004, p. 127; Matzanas, 2018). The view of manufacturing of "chert" at Nea Artaki during the Palaeolithic was supported by Sampson (1996) and Matzanas (2009). Details on the typological characteristics and technological variability that characterizes the Evian lithic assemblages were provided by Matzanas (2009). However, we understand that the lithic tools found in central Evia are poorly dated, whereas sequencing is not sufficiently documented. Hence we prefer referring to the lithic tools of the area as "early prehistoric" understanding the need for further systematic archaeological research to conclude on the utilization of specific rock types in each period.

3. GEOLOGY

Triassic-Jurassic carbonates and cherts, ophiolitic rocks and Upper Cretaceous limestones dominate the central and northern parts of Evia Island, as a sector of the Subpelagonian zone of the Hellenides (Chenevart and Katsikatsos, 1967). Chert is ubiquitous throughout the area. Bedded (or ribbon) cherts are abundantly exposed, that would have been readily available to prehistoric man. They are intercalated with the late Jurassic to Early Cretaceous volcano-sedimentary formation ("Diabase-chert Formation" after Baumgartner and Bernoulli, 1976; "Schist-chert Formation" after Katsikatsos et al., 1981) and the Middle-Late Triassic volcanic–derived clastic sediments ("Pagondas mélange") (Danelian and Robertson, 2001). Radiolaria-rich cherts of Middle Jurassic age overlie the previous sequence (Baumgartner, 1984). The Evian Upper Jurassic ophiolite comprises ultramafics, basaltic igneous rocks with associated siliceous sediments, and amphibolitic soles (Katsikatsos et al., 1981; Reche, 1983; Robertson, 1991). Serpentinized ultramafics as parts of the Evia ophiolite were silicified upon lateritic weathering and transformed to silcrete. They were covered by sedimentary nickeliferous iron-ores containing clasts of silcretes, possibly during the uppermost Cenomanian or at the Cenomanian / Turonian boundary (Skarpelis and Zambetaki-Lekka, 1998). The entire sequence of ultramafic rocks, silcretes and reworked ore is transgressively covered by Upper Cretaceous limestones hosting chert nodules. Chert nodules are widespread in the Upper Cretaceous transgressive limestones of the Subpelagonian zone, especially in the Cenomanian - Turonian parts of the succession (Katsikatsos et al., 1981).

Subaerial weathering of ultramafic rocks in Cretaceous times under tropical to subtropical climatic conditions resulted in the formation of extended weathering crusts, known as "Nickel lateritic weathering crusts" (Valeton et al., 1987; Skarpelis 2006). Among the critical lithologies resulting during lateritization are silcretes, as defined above. Multiple silcrete layers with massive and concretionary textures had been recognized in some profiles in Beotia (Skarpelis, 2006). Silcretes in the Cretaceous lateritic weathering crusts of mainland Greece and Evia are classified as groundwater silcretes, commonly forming layers of limited spatial extent within the lateritic profile, reflecting successive water table levels (Skarpelis, 2006). Weathered serpentine mesh textures and chlorite–talc–hematite aggregates have suffered massive replacement by microcrystalline quartz, whereas a part of the latter was recrystallized, possibly during diagenesis. In situ transformation or replacement of clays in the profile with general conservation of texture is characteristic of the groundwater silcretes. The lateritic weathering crusts were disrupted and fragmented. Fragments of the lateritic material - including silcrete - were reworked, mechanically transported and redeposited under submarine conditions, as a result of regional transgression of the Upper Cretaceous sea, forming the well-known sedimentary nickeliferous iron ores widely explored in Evia and Beotia for metallurgical processing and recovery of nickel and iron (Rosenberg, 1984; Valeton et al., 1987; Skarpelis, 1999). The fragments were transported from land, deposited under submarine conditions and cemented by spheroidal particles (peloids, pisoids and ooids) and fine grained clay- and ferruginous material of lateritic origin. The silcrete masses were the source of silcrete detritus. Detritus of silcrete are widespread within that sedimentary lithofacies. In terms of mineralogy, texture and chemistry, the detritus resemble silcretes occurring within the Nickel lateritic crusts (Skarpelis, 1999; 2006). Both the ophiolitic rocks, the relicts of lateritic weathering crusts and the sedimentary nickeliferous iron ores were transgressively covered by Upper Cretaceous (Cenomanian - Maastrichtian) limestones. Parts of the Upper Ctetaceous limestone sequence are rich in chert nodules and thin chert layers. Chert nodules are abundant also within the Kimmeridgian - Tithonian limestones at Dirfys Mt. in northeastern Evia (Katsikatsos et al., 1981). The Nea Artaki – Vatontas area shares common geological features with Sub-Pelagonian sectors in Beotia and north Evia island. A detailed geological map of the Nea Artaki area is shown in Fig. 3A, along with a lithostratigraphic column (Fig. 3B).

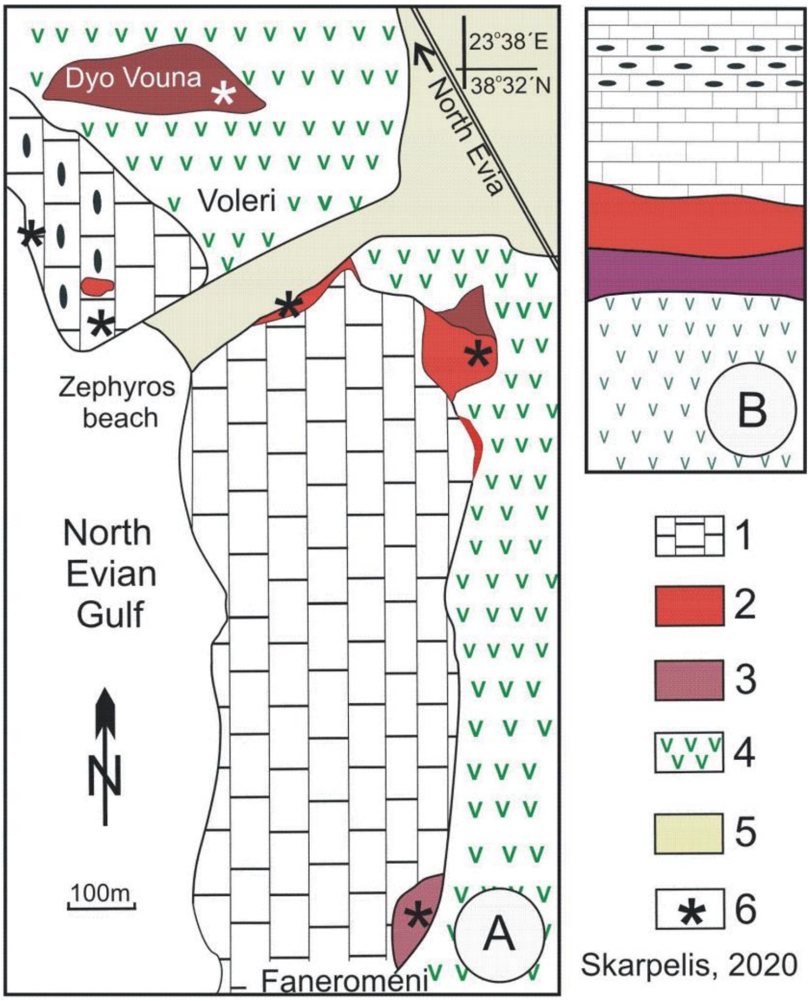

Figure 3. Geological map (A) and lithostratigraphic column (B) of the area north of Nea Artaki, where lithic tools were found: 1) Transgressive Upper Cretaceous limestones with chert nodules; 2) Sedimentary nickeliferous iron ore with silcrete detritus; 3) Silcrete; 4) Serpentinized ultramafic rocks; 5) Alluvium; 6) Sampling points.

4. MATERIALS AND METHODS

Because destructive analysis of cultural objects is not an option we categorized lithic objects using petrographic criteria by visual inspection of artifacts kept in the private collection of Mrs E. Sarantea-Micha (Chalkis) with the aid of a binocular microscope. In addition we studied lithic objects stored in the Archaeological Museum of Chalkis using High Resolution photographs provided by the Ephorate of Antiquities of Euboea. A geological field survey of the central Evia with emphasis on geological units in which cherts have been reported, and geological mapping of the Nea Artaki area was followed at the next stage. Detailed mineralogical, textural and geochemical analyses of rock samples visually matching prehistoric artifacts was carried out. The mineralogy and petrography of the rock samples was studied by combined optical microscopy, X-Ray Diffractometry (XRD) and Scanning Electron Microscopy/Energy Dispersive X-Ray Spectroscopy (SEM/EDS). Mineralogical and petrographic investigation was carried out on thin and polished thin sections of the rock by conventional Plane Polarized Microscopy. Emphasis was given to the textural features of the rock and the identification of critical accessory minerals. In describing the colors of the rocks we used the "Rock-Color Chart" of the Geological Society of America (Munsell® Color Chart, revision 2009). For description of rock texture, microcrystalline quartz is defined after Folk (1980) as massive quartz aggregates made of equidimensional grains usually ranging from a fraction of a μm to 20 μm, whereas the term megaquartz is used for quartz overgrowths and vein fillings, composed of equant to elongated grains larger than 20 μm. For XRD, a Siemens D-5005 diffractometer was used. X-ray diffractograms were evaluated with EVA software, version 2.0. Back-scattered imaging of samples were performed using a SEM JEOL JSM-5600 with energy dispersive spectroscopy (SEM-EDS) Oxford Link Isis 300 system at the Laboratory of Economic Geology and Geochemistry, National and Kapodistrian University of Athens, Greece. Excitation potential was 20 KV, the beam current 0.5 nA. The data were reduced with the aid of the ZAF program. Rock chips were crushed and pulverized using a tungsten carbide mill, the resultant grain size of pulps being -75 μm at 99.1%. Major elements were analyzed by X-Ray Fluorescence spectrometry (XRF) at ALS Labs in Ireland. Lithium borate was added to calcined sample, then the mixture was fused between 1050 and 1100 °C. A glass disc was prepared and then analyzed. For trace- and Rare Earth Elements (REE) a prepared sample was digested with perchloric, nitric, hydrofluoric, and hydrochloric acids and analyzed by Inductively coupled plasma mass spectrometry (ICP-MS). Results were corrected for spectral inter-element interferences. Loss on ignition was measured at 1000°C.

5. RESULTS

5.1. Chert nodules within Upper Cretaceous limestones.

Chert nodules are enclosed into the Late Cretaceous platform limestones exposed all along the coast to the west of Zephyros beach (Fig. 3). The host limestones are bituminous, thick to medium bedded, grey to dark grey in color. The chert nodule bodies are boudinaged, ellipsoidal to ameboid in shape, black to black-grey in color, ranging in size between 5 and 40 cm (Fig. 4a). Chert bands occurring as planar bodies are rare. A brown-grey colored cortex transitional to the enclosing limestones (Fig. 4b), ranging in thickness between 1 and 3 cm, consists mostly of calcite and quartz. The chert nodules are featureless in texture, consisting of quartz with minor calcite as proved by microscopic and X-Ray diffractometry study (Fig. 5). The chert nodules are composed mainly of interlocking grains of microcrystalline quartz. Microscopic spherical to subspherical pyrite aggregates of a size <10 μm (pyrite framboids), calcite rhombohedra, and organic matter are subordinate mineral constituents (Fig. 4c and 4d). Calcite fillings of fractures of nodules are lacking. Parts of the pyrite micrograins have been altered to goethite. The grain size of quartz in cherts ranges from less than 0.3 to 10 μm, the most common size being 0.5 to 4 μm. Pyrite framboids in sediments were claimed to have been precipitated via iron monosulfide intermediates from porewaters supersaturated with respect to both pyrite and iron monosulfides (Roberts and Turner, 1993).

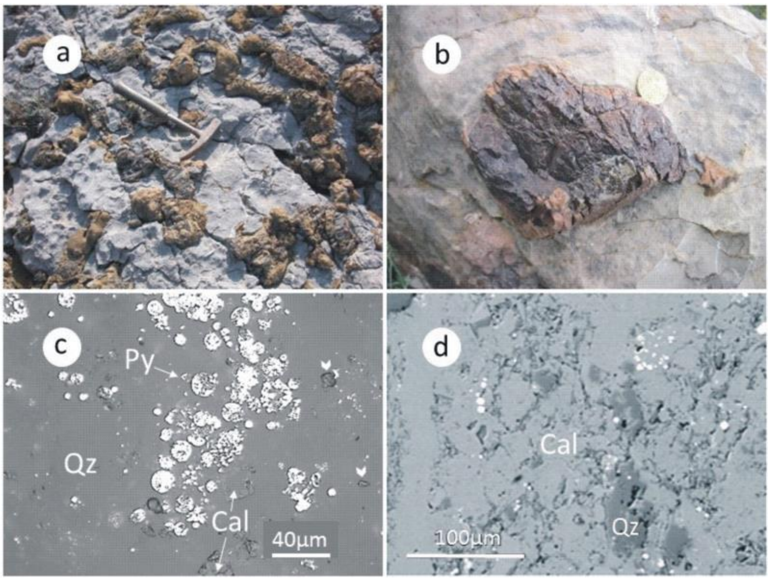

Figure 4. Photographs of outcrops and micrographs of chert nodules: (a) and (b) Chert nodules within limestone; (c) Micrograph of chert nodule showing disseminated pyrite framboids (Py) and calcite rhombohedra (Cal); Arrows depict spots of organic matter (reflected plane-polarized light image); (d) Micrograph of quartz and calcite aggregates in the cortex of a chert nodule (crossed polarized light image)

Table 1. Chemical analyses of chert nodules

	A 2A	A 2B	A 2C	A 2D	A 2E	A 2F	DSDP 62 (†)	NASC (‡)	Chert (§)
SiO_2	90.5	88.8	89.6	90..2	89.8	91.8	96.17	64.8	91.4
TiO_2	0.01	0.01	0.01	0.01	0.01	0.02	0.03	0.78	0.02
Al_2O_3	0.14	0.17	0.11	0.16	0.12	0.15	0.69	16.9	0.9
FeO^T	0.22	0.32	0.11	0.13	0.31	0.04	0.21	5.7	0.5
MnO	0.01	0.01	0.01	0.01	0.01	0.01	0.001	0.06	n.a.
MgO	0.06	0.06	0.08	0.08	0.09	0.03	0.01	2.85	0.8
CaO	5.04	5.62	5.64	5.14	5.2	4.1	0.3	3.56	2.7
Na_2O	0.02	0.02	0.01	0.01	0.02	0.01	0.07	1.15	0.1
K2O	0.03	0.04	0.02	0.01	0.02	0.01	0.04	3.99	0.05
P_2O_5	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.11	0.03
LOI	4.2	4.67	4.33	4.12	4.31	3.7	2.91		3.6
Total	100.24	99.73	99.93	99.88	99.9	99.89			
Ba	1	1.1	1.1	1.1	2	2	10	636	n.a.
Cr	9	11	8	8	7	8	1	124.5	n.a.
Ni	4	3	7	7	6	5	3	58	n.a.
Co	2	5	4	4	3	3	n.a.	25.7	n.a.
Zr	2	4	2	2	4	3	n.a.	200	n.a.
Rb	0.9	1.1	0.2	0.2	0.7	0.6	n.a.	125	n.a.
Sr	3	4	1	1	3	4	2	142	n.a.
Ta	1.2	0.9	1.3	1.3	0.8	1.5	n.a.	1.12	n.a.
Th	0.01	0.01	0.01	0.01	0.01	0.01	n.a.	12.3	n.a.
V	6	7	4	4	5	4	n.a.	n.a.	n.a.
Nb	0.3	0.2	0.2	0.2	0.3	0.3	n.a.	n.a.	n.a.
La	0.2	0.1	0.1	0.1	0.1	0.2	n.a.	31.1	n.a.
Ce	0.4	0.5	0.2	0.4	0.5	0.5	n.a.	66.7	n.a.
Pr	0.03	0.04	0.04	0.03	0.05	0.04	n.a.	7.5	n.a.
Nd	0.1	0.1	0.2	0.1	0.2	0.2	n.a.	27.4	n.a.
Sm	0.06	0.04	0.05	0.03	0.04	0.05	n.a.	5.59	n.a.
Eu	0.02	0.01	0.02	0.01	0.01	0.01	n.a.	1.18	n.a.
Gd	0.05	0.05	0.05	0.05	0.05	0.05	n.a.	4.9	n.a.
Tb	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	n.a.	0.85	n.a.
Dy	0.05	0.05	0.05	0.05	0.05	0.05	n.a.	4.17	n.a.

Ho	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	n.a.	1.02	n.a.
Er	0.03	0.03	0.03	0.03	0.03	0.03	n.a.	2.84	n.a.
Tm	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	n.a.	0.48	n.a.
Y	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	n.a.	n.a.	n.a.
Yb	0.05	0.04	0.03	0.04	0.05	0.03	n.a.	3.06	n.a.
Lu	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	n.a.	0.46	n.a.

(†) Average chert DSDP 62 (n=10) (Hein et al., 1981); (‡) North American Shale Composite (NASC) (Gromet et al., 1984; Haskin and Haskin, 1966); (§) Average chert nodules and chert (Cressman, 1962). n.a.: not available. Major elements in wt%, Minor and REE elements in ppm.

Chemical analyses of major, minor and REE elements of chert nodules are included in Table 1. For the sake of comparison, chemical data on chert samples from Deep Sea Drilling Project (DSDP) Leg 62 (Hein et al., 1981), the North American Shale Composite (NASC) (Gromet et al., 1984; Haskin and Haskin, 1966) and the "average of chert nodules and chert" by Cressman (1962) are also given. The chert nodules have lower SiO_2 (average 90.1 wt%) and higher CaO contents (average 5.12 wt%) relative to the DSDP Leg 62 cherts, associated with their lower percentage of cryptocrystalline quartz and higher percentage of calcite respectively. They are within the range of major element contents of nodular cherts and chert layers in carbonate rocks of diverse ages from numerous outcrops in the world (see Table 7 and Fig. 2 in Cressman, 1962). Mg and Mn are very low, explaining the chemical purity of calcite, as indicated by SEM work. Fe is related to the presence of disseminated pyrite framboids or their oxidation product (goethite). All other elements, especially REE, Cr, Ni, Fe and Co, are strongly depleted relative to DSDP Leg 62 cherts. They are also depleted in most, except for Ca, elements compared to forty nodular cherts sampled by the DSDP and Ocean Drilling Project (ODP) in the Pacific, Atlantic and Indian basins as recorded by Murray et al. (1992), possibly as a result of the lack of a detrital aluminosilicate fraction. Their chondrite normalized REE pattern (Fig. 6) is comparable to NASC, characterized by a LREE enrichment, HREE depletion and a very weak negative Eu anomaly. They are depleted in REE by roughly 220 orders of magnitude, relative to NASC. They show comparable REE concentrations and rather similar overall REE patterns with a set of samples of chert nodules of various ages from North America given by Luedtke (1992). They are grossly similar in REE chemistry to the Stelida (Naxos) cherts (Skarpelis et al., 2017). In relation to REE contents of chert nodules used for manufacturing of lithic objects in Meganisi island (Chatzimpaloglou, 2014), they are depleted by 1 to 2 orders of magnitude for most of them.

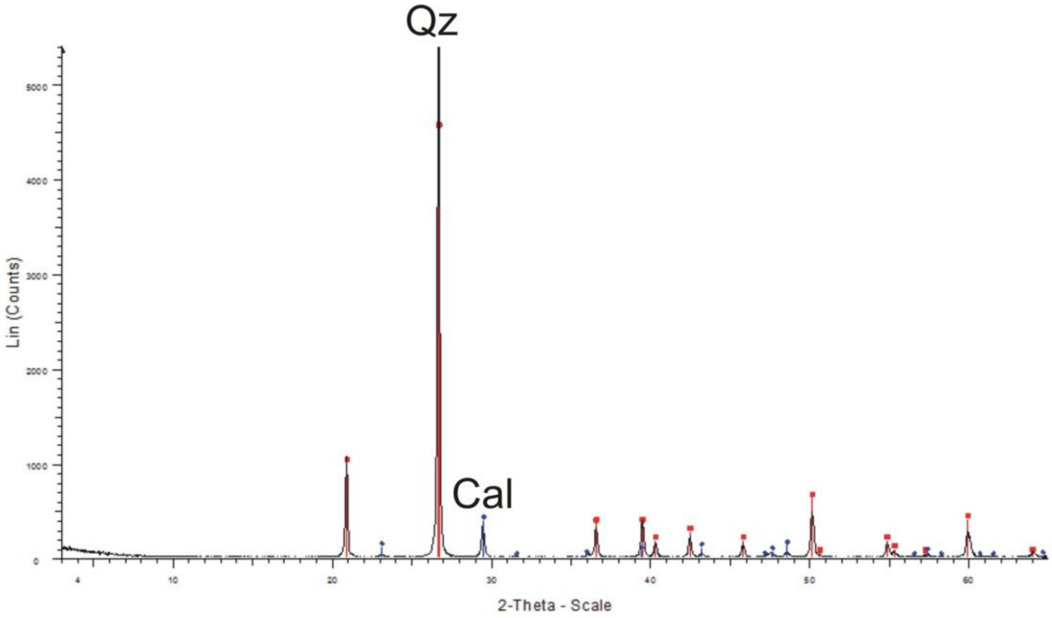

Figure 5. X-Ray diffraction pattern of chert nodule (Qz: quartz, Cal: calcite).

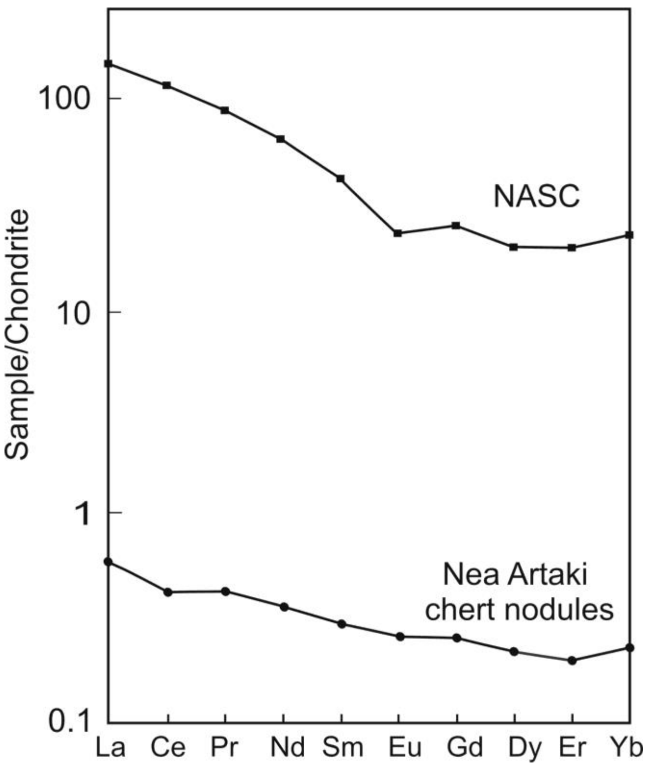

Figure 6. Chondrite-normalized REE pattern of average of Nea Artaki chert nodules compared to North American Shale Composite (NASC). Normalization values after Sun and McDonough (1989).

5.2. Silcrete

Silcrete varies in color from buff reddish-brown to pale grey with a red hue. Light grey to whitish grey and white silcretes are rather rare. Lithic objects made of white silcrete may be erroneously characterized as consisting of quartzite. Silcrete has a markedly conchoidal fracture. Weathering profiles at Faneromeni and Dyo Vouna are restricted to silcretes, resulted by massive silicification of the underlying serpentinized ultramafic bedrock, indicating erosion and removal of the overlying saprolitic material. Photographs of silcrete specimens from Nea Artaki and Vatontas are given in Fig. 7a to 7f. Combined microscopic and X-ray diffractometry studies prove that weathered serpentine mesh textures and chlorite-talc aggregates have suffered massive replacement by quartz, whereas a part of the latter was recrystallized, possibly during diagenesis. Several generations of megaquartz characterize veins, which are probably fillings by silica of once-open fractures (Fig. 7a, 8a, b, c). Disseminated relictic chromite/spinel grains or aggregates of anhedral crystals are observed (Fig. 8d), even by visual inspection (Fig. 7c). Hematite dispersions within the siliceous matrix are usual in reddish to brownish colored samples. The matrix of silcrete is composed almost entirely of microcrystalline quartz (Fig. 8a, b). In the case of central Evian silcretes the formation model, which invokes silicification of the ultramafic rock or products of weathering by relative accumulation of silica released by weathering of the minerals in overlying parts (Golightly, 1981; Skarpelis, 2006), should be accepted.

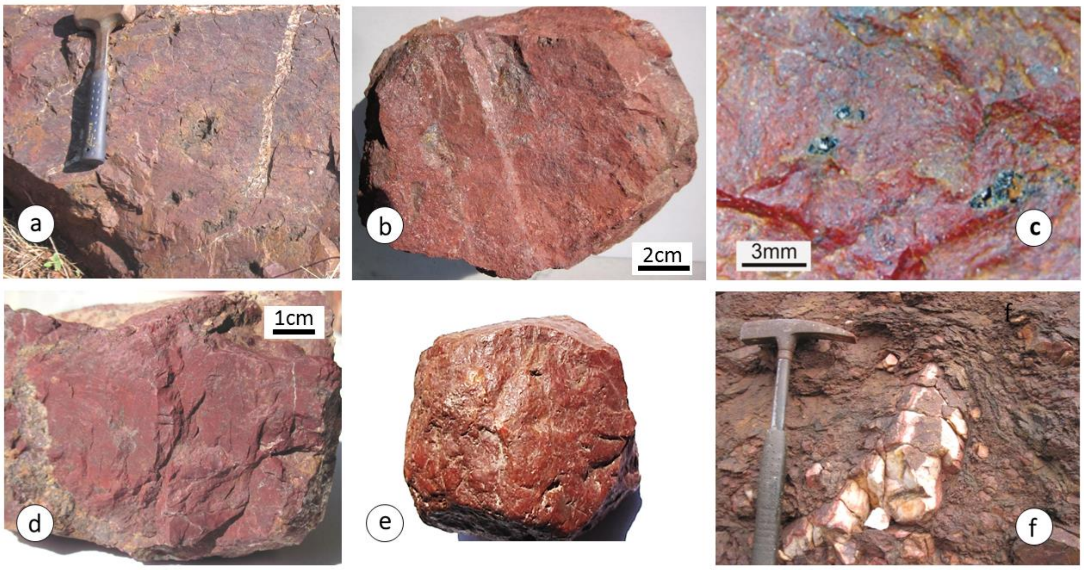

Figure 7. Photographs of silcrete rocks: (a) Silcrete crosscut by quartz veinlets (Faneromeni); (b) Massive silcrete from Vatontas, (c) Close-up view of silcrete with disseminated relictic chromite aggregates (black spots); (d) Red to violet colored massive silcrete (SE of Voleri); (e) Abraded cobble of silcrete in sedimentary nickeliferous iron ore (Faneromeni) (Ø 8cm); (f) Boulder of white massive silcrete within sedimentary nickeliferous iron ore (SE of Voleri). This rare silcrete lithotype should be misinterpreted as quartzite.

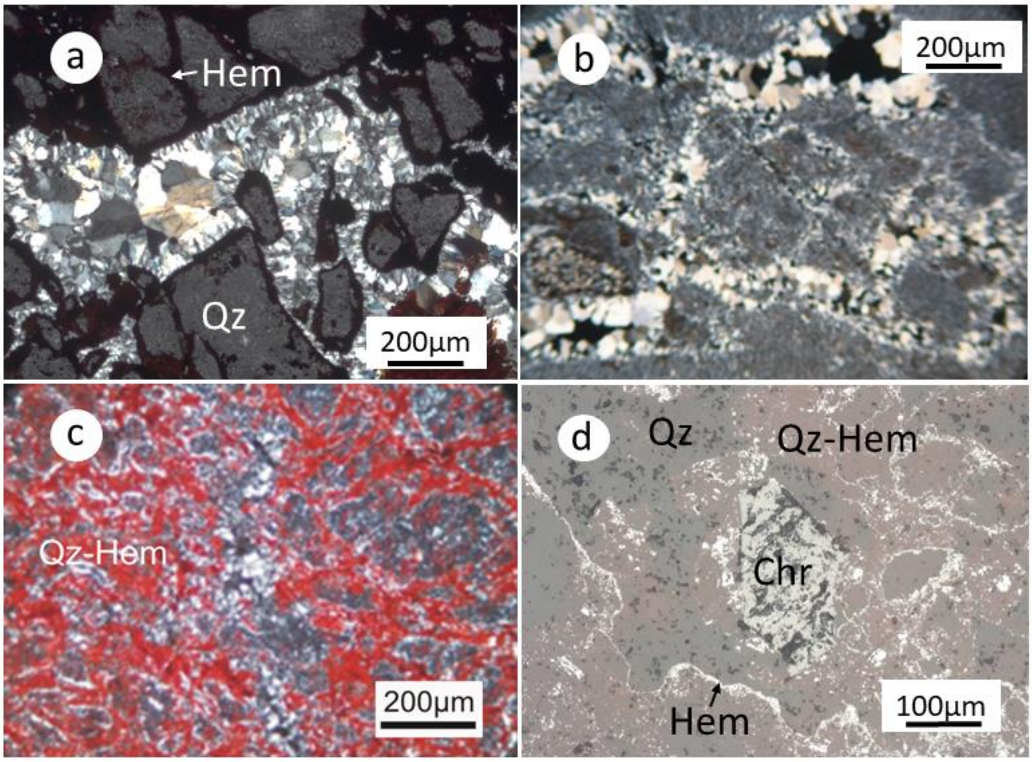

Figure 8. Micrographs of silcrete rocks: (a) Pervasive fine grained replacement of ultramafic rock transformed to silcrete. Late stage veinlets and voids filled with quartz (Qz) and hematite (Hem) (Faneromeni silcrete) (crossed polarized light image); (b) Massive replacement of the weathered ultramafic rock by quartz, with grain size of individual grains ranging between 2 to 15µm. Voids filled with quartz (Dyo Vouna hill)) (crossed polarized light image); (c) Fine grained quartz intermixed with fine grained hematite (Qz-Hem, reddish matrix) with crosscuting quartz veinlets (crossed polarized light image); (d)) Relictic chromite aggregate (Chr) within silcrete. Note the very fine grained quartz (Qz), the quartz + hematite (Qz-Hem) aggregates and the late stage hematite veinlets (Hem) (reflected plane-polarized light image).

Table 2. Major and minor elements analyses of silcrete

	A 1	A 1-2	A 3	A 1-B	A 3 -2	A 6	A 4	B 14	B 15	B 19	B 1	B 2	Sav†	Sav‡	SrR§	SUB¶	SavEǂ	SavQ#
SiO_2	87.5	86.8	87.7	87.2	85.8	97.6	99.3	92.5	86.3	87.4	89.7	88.5	89.69	92.04	84.1 - 98.6	85.7	96.98	96.32
TiO_2	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.02	0.04	0.01	0.01	0.01	0.01	0.05	0.01 - 0.1	n.a.	0.53	1.35
Al_2O_3	0.24	0.11	0.19	0.02	0.3	0.37	0.06	0.9	1.01	0.09	0.4	0.35	0.29	0.65	0.1 - 2.62	0.95	0.68	0.74
FeO^T	9.6	10.5	10.9	10.5	11.8	1.37	0.34	0.6	5.1	7.8	3.1	3.45	6.53	3.51	0.08 - 5.84	6.8	0.43	0.08
MnO	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.03	0.18	0.09	0.03	0.03	0.02	0.78	0.01 - 0.18	n.a.	0.01	0.01
MgO	1.41	1.9	0.08	1.6	1.38	0.2	0.13	4.1	5.5	3.1	2.9	4.7	3.05	1.8	0.5 - 8.13	2.4	0.09	0.23
CaO	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.2	0.16	0.1	1.8	1.1	0.55	0.1	0.02 - 0.18	n.a.	0.1	0.09
Na_2O	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.1	0.05 - 0.1	n.a.	0.1	0.04
K_2O	0.01	0.01	0.01	0.01	0.01	0.05	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.07	0.01 - 0.09	n.a.	0.07	0.03
P_2O_5	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.05	0.04 - 0.1	n.a.	0.02	0.58
LOI	0.92	0.3	0.41	0.82	0.61	0.61	0.27	1.51	1.65	1.3	1.5	1.25	1.08	0.95	0.04 - 2.06	2.8	0.48	2.14
Total	99.73	99.69	99.35	100.2	99.95	100.25	100.16	99.89	99.98	99.92	99.47	99.42				98.65		
Ba	1.7	2.3	4.6	3.5	2.8	6.5	1.9	2.8	4.2	2.9	3.2	2.1	3.21	18	1 - 35	n.a.	n.a.	n.a.
Cr	2860	3155	3350	4855	3680	700	470	3952	4379	5475	3272	3079	2969	1411	26 - 6052	1299	n.a.	n.a.
Ni	2850	1690	2341	1832	3593	327	258	4160	3375	2669	3611	3690	3270	1304	107 - 3368	3454	n.a.	n.a.
Co	103	201	152	102	98	98	79	67	89	123	165	129	116	76	5 - 340	267	n.a.	n.a.
Zr	45	67	84	31	76	39	52	78	69	82	79	54	49.5	60	50 - 89	n.a.	n.a.	n.a.
Rb	0.6	0.5	0.4	0.4	0.6	1.3	0.4	0.5	0.9	0.8	0.6	0.4	0.5	3.2	1 - 11	n.a.	n.a.	n.a.
Sr	0.7	0.3	0.9	0.6	0.5	1.7	0.6	1.2	1.5	1.8	1.1	1.1	0.9	44	33 - 88	n.a.	n.a.	n.a.
Ta	0.7	0.4	1.2	0.5	1.1	2	1.2	1.3	1.2	0.7	0.4	0.9	0.8	n.a	n.a.	n.a.	n.a.	n.a.
Th	0.08	0.05	0.05	0.04	0.03	0.09	0.05	0.06	0.04	0.06	0.02	0.05	0.06	n.a	n.a.	n.a.	n.a.	n.a.
V	28	18	5	45	68	55	5	32	23	87	9	17	22.5	20	1 - 59	n.a.	n.a.	n.a.
Nb	0.3	0.1	0.2	0.3	0.4	0.3	0.2	0.5	0.2	0.4	0.5	0.2	0.25	n.a	n.a.	n.a.	n.a.	n.a.

Faneromeni: A 1, A 1-2, A 6; Dyo Vouna: A 3, A 1-B, A 3-2; Triada mine - detritus: A 4; Beotia: B 14, B 15, B 19, B 1, B 2 (Skarpelis, unpublished); Sav†: Average silcrete (this study); Sav‡: Average silcrete (Rosenberg, 1984, n=13); SrR§: Range silcrete (Rosenberg, 1984); SuB¶: Silcrete on ultramafics, Brazil (Trescases et al., 1981); SavEǂ: Average silcrete-Europe (Nash and Ullyott, 2007); SavQ#: Average silcrete, SE Queensland (Senior & Senior, 1972). n.a.: not available

Table 3. Rare Earth Elements analyses of silcrete

	A 1	A 1-2	A 3	A 1-B	A 3 -2	A 6	A 4	B 14	B 15	B 19	B 1	B 2	Sav†	Sav‡	SrR§	SuB¶	SavEǂ	SavQ#
La	0.2	0.4	0.6	0.3	0.2	0.9	0.1	0.3	0.2	0.6	0.3	0.5	0.38	98	20 - 193	n.a.	n.a.	n.a.
Ce	0.2	0.7	0.9	0.5	0.3	1.9	0.1	1.2	1.6	0.9	0.4	0.8	0.5	n.a.	n.a.	n.a.	n.a.	n.a.
Pr	0.03	0.02	0.15	0.12	0.14	0.14	<0.03	<0.03	0.03	0.12	0.15	0.12	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Nd	0.2	<0.1	0.5	0.3	0.2	0.5	<0.1	0.1	<0.1	0.1	<0.1	0.1	n.a.	23	10 - 54	n.a.	n.a.	n.a.
Sm	0.07	0.03	0.12	0.14	0.12	0.07	<0.03	<0.03	0.11	<0.03	0.13	<0.12	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Eu	<0.03	<0.03	<0.03	<0.03	0.03	0.03	<0.03	<0.03	0.03	<0.03	<0.03	<0.03	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Gd	<0.05	<0.05	0.13	<0.05	<0.05	0.08	<0.05	0.05	<0.05	0.05	<0.05	<0.05	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Tb	0.01	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	0.01	<0.01	<0.01	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Dy	<0.05	0.1	0.1	<0.05	0.05	0.05	<0.05	0.05	<0.05	<0.05	<0.05	<0.05	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Ho	0.01	0.02	0.03	0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.03	<0.01	0.02	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Er	<0.03	<0.03	0.07	0.04	0.03	<0.03	<0.03	0.05	<0.03	<0.03	<0.03	0.04	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Tm	<0.01	<0.01	0.02	<0.01	0.01	0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.01	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Y	0.2	0.2	0.8	0.5	0.2	0.4	0.1	0.4	0.3	0.5	0.3	0.5	0.36	2.4	1 - 8	n.a.	n.a.	n.a.
Yb	0.03	<0.03	0.12	0.03	<0.03	0.04	<0.03	<0.03	0.04	<0.03	0.05	0.04	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Lu	0.01	0.01	0.02	0.02	0.03	<0.01	<0.01	0.02	<0.01	<0.01	0.02	<0.01	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

Faneromeni: A 1, A 1-2, A 6; Dyo Vouna: A 3, A 1-B, A 3-2; Triada mine - detritus: A 4; Beotia: B 14, B 15, B 19, B 1, B 2 (Skarpelis, unpublished); Sav†: Average silcrete (this study); Sav‡: Average silcrete (Rosenberg, 1984, n=13); SrR§: Range silcrete (Rosenberg, 1984); SuB¶: Silcrete on ultramafics, Brazil (Trescases et al., 1981); SavEǂ: Average silcrete-Europe (Nash and Ullyott, 2007); SavQ#: Average silcrete, SE Queensland (Senior & Senior, 1972). n.a.: not available

Chemical analyses of silcrete from the Nea Artaki outcrops are included in Tables 2 and 3, along with chemical analyses of silcretes of Beotia (Skarpelis, unpublished). Available chemical data on silcretes from Beotia and Evia given by Rosenberg (1984) and Brazil (Trescases et al., 1981), as well as the "Average silcrete of Europe" (Nash and Ullyott, 2007) and the "Average silcrete of Queensland" (Senior and Senior, 1972) are also included for comparison. It is obvious that the silicification process has led to an absolute enrichment of silica, which averages 89.7 wt%. By major and minor element chemistry the silcrete of Nea Artaki is comparable to the silcretes of Beotia and those from other outcrops in Evia, as reported by Rosenberg (1984). They are also comparable in chemistry to silcretes formed in weathering profiles on ultramafic rocks in Brazil (Trescases et al., 1981). Characterization of the studied rock by chemistry as silcrete is justified following Summerfield (1983a), who claimed that silcretes should contain at least 85% SiO_2 with particularly pure silcretes containing in excess of 95% SiO_2. Most true silcretes in Australia have SiO_2 >90 wt%, Al_2O_3 <1wt%, while Fe_2O_3 is highly variable but generally <1.0 wt% except in 'red' silcretes where values can be as high as 5.0 wt% (Taylor and Eggleton, 2017). Compared to the "Average Europe silcrete" (Nash and Ullyott, 2007), and the silcretes in Queensland (Senior and Senior, 1972; Senior, 1979; Taylor and Eggleton, 2017), the central Evian silcretes are characterized by high Cr, Fe, Ni, Mg and Co concentrations, whereas they are depleted in other elements, especially Ti. The relatively high titanium content is a characteristic of most silcretes in Australia (e.g. Senior, 1979; Taylor and Eggleton, 2017), in southern Africa (Summerfield, 1983c) and western Europe (Ullyott and Nash, 2006). This is reasonable because of the different bedrocks (ultramafics in the case of Evia and Brazil, and quartzo-feldspathic sandstones in the areas mentioned above), the type of the silcrete and the possible differences in the prevailing climatic conditions at the time of formation (for details see Summerfield, 1983a; Senior, 1979; Taylor and Engleton, 2017).

5.3. Cherts

They occur intercalated as boudinaged layers within siliceous mudstones and sandstones of the so-called "Schist-chert Formation" of central Evia (Katsikatsos et al., 1981). These rocks occur along a narrow strip extending from a point to the east of Nea Artaki city up to the south and east of the Vatontas village. They range in color from grey to greenish grey, red, brick-red with a brownish tint (Fig. 9). Microscopic examination of representative samples collected from the area of Vatontas indicates they are composed of fine grained quartz, clay minerals, Fe-oxides and minor calcite. Quartz veining and voids filled with megaquartz are usual. By their color, texture and mineralogy they are clearly discriminated from silcrete and chert nodules. Although individual beds of cherts and radiolarites of Evia are usually intensely brecciated due to tectonism, they are locally massive and have a conchoidal fracture. Therefore, the prehistoric knappers were possibly able to find locally suitable material for the production of stone tools. However, the cherts do not appear to have been as important a resource as the silcrete lithologies, possibly due to their inferior quality for lithic tools manufacture.

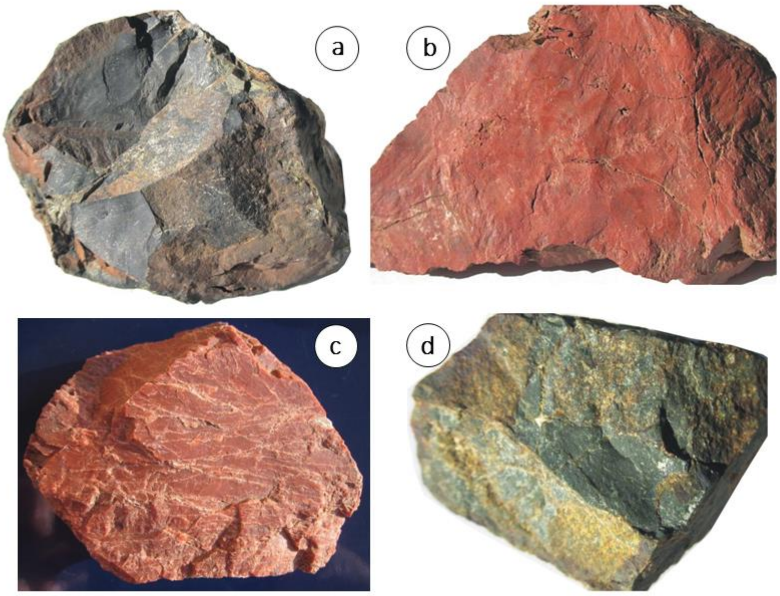

Figure 9. Hand specimens of cherts from outcrops of the "Schist-chert Formation" exposed to the east of Nea Artaki and Vatontas area: (a) and (b) Massive grey and brick-red chert respectively, (c) Red chert with quartz veining, (d) Grey-greenish massive chert.

6. DISCUSSION

Identification of source rocks of lithic objects is critical in building models for prehistoric life in various parts of the world. Research concerning petrographic and chemical characterization of cherts in an archaeological context in Greece is a recent endeavor. It is obvious that the chert nodules and silcrete described above have a significant mineralogical and chemical feature in common with siliceous rocks from other sites in Greece, which had been utilized for manufacturing of early prehistoric tools: they consist almost entirely of silica polymorphs (especially quartz) and hence their major chemical constituent is SiO_2. However, minor differences in the type of subordinate rock forming minerals, the chemical features related to concentration of minor and REE elements, and also in specific rock textures should be used as diagnostic characteristics for a discrimination among cherts (s.l.) of various genetic origins and possibly different provenience.

Cherts: Little geo-archaeological work on the non-obsidian lithic resources of Greece has been done, despite the fact that there are extensive outcrops of chert and chert nodules in the various lithostratigraphic - tectonic units of the Hellenides (Jacobshagen, 1986). These include chert nodules and bedded cherts, usually rich in radiolaria, of the Pindos, Ionian, Subpelagonian and Vardar geotectonic zones, as well as bedded cherts capping oceanic ophiolitic lithologies (e.g. Othrys, Koziakas, Evia, Argolis) (Jacobshagen, 1986), and pervasively silicified volcanics (silica caps) in Thrace (Efstratiou and Ammerman, 2004). However, difficulties arise in attempts to identify source rocks of lithic tools made of chert due to the lack or paucity of petrographic and analytical data, as well as the very low concentration of several REE elements, being below detection limits of ICP-MS techniques. Visual morphological characteristics such as color, luster, fracture, patina and inclusions are different amongst cherts. Cherts and chert nodules in the Aegean are far less homogenous than obsidian, due to their different mode of formation, mineral impurities and geological history. The chemistry of bedded cherts and radiolarites especially reflects the relative proportion of three mineral components: biogenic ooze, clays, and hydrothermal metal precipitates (e.g. Barrett, 1981). Therefore, chert is difficult to chemically characterize, due to the large heterogeneity that is possible within a single outcrop (e.g., Barrett, 1981; Luedtke, 1992; Robertson and Varnavas, 1993). As stated by Luedtke (1992) "any attempt to match an artifact to its source can be successful only if the differences among sources are greater than the variability within each source". Hence, detailed petrographic - in addition to geochemical - studies of outcrops may allow the identification of the geological sources of material used for the manufacture of artifacts. The data on Nea Artaki chert nodules indicate that chemically they do not differ considerably from other chert types for which data are available (e.g. Stelida - Naxos, Meganisi - Ionian islands). However, they can be distinguished by visible properties (those observable with the unaided eye). As an example, the Nea Artaki chert nodules, and accordingly the lithic tools, are characterized by black to grey color relative to the very light grey to white, locally light grey with a honey hue of the Stelida cherts, as described by Skarpelis et al. (2017). In addition, mineralogical and textural properties visible only through the microscope are typically distinct: (a) Mineralogical properties: microcrystalline quartz with subordinate calcite + framboidal pyrite + spots of organic matter in Nea Artaki chert nodules, and zircon + anatase + hematite + barite at Stelida and (b) Textural properties: the Nea Artaki nodules are structureless relative to the microcrystalline quartz texture, with "abundant cavities + quartz crystals projecting into cavities + thin crosscutting quartz veinlets" of Stelida cherts.

Silcrete: Silcrete, with good conchoidal fracture, was one of the most preferred rock-type by hunters, who produced bifacial and unifacial tools, projectile points, scrapers and other finely knapped tools worldwide (Thiry and Milnes 2017). The use of silcrete as a knapped stone is extensively studied in archaeological terms in regions where it is widely available, in particular in Australia, South Africa and North America. Silcrete outcrops, often associated with sites where manufacturing of lithic objects has been described, are distributed throughout a significant part of Australia, South Africa, South and North America and a few European countries (Wragg Sykes and Will, 2017; and references therein). Because of its hardness and extensive occurrence, silcrete was used by primitive people, who employed impact and pressure flaking techniques to make stone tools and weapons (Stephens, 1971; Thiry and Milnes, 2017; Wragg Sykes and Will, 2017). In the Aegean, outcrops of silcrete and sedimentary nickeliferous iron-ores containing fragments of silcrete are restricted to central Evia and Beotia and have a very limited extent also in Attica. Mineralogical and geochemical criteria (concentration of Cr, Ni, Fe, Mg, Co, V), are useful for discrimination between various chert types and silcretes. In the case of silcrete tools, the complex of silica textures and association with chromite/spinel, serpentine and iron-oxide minerals would pose a rather easy task for identification and provenance. Chemical analyses of silcretes formed in lateritic weathering crusts on ophiolitic rocks in the Aegean are limited to those given by Rosenberg (1984) and this study. However, it should be noticed that the data on La, Nd and Y given by Rosenberg (1984) have to be treated with caution due to the analytical method applied (X-Ray Fluorescence). The high La, Nd and Y values of Rosenberg (1984) are much higher than those obtained by ICP-MS techniques (this study). Hence, discrimination patterns based on REE elements are difficult to discern and the conclusions based solely on chemical data must remain tentative. Critical chemical features of silcretes, and accordingly lithic tools made of silcrete, based on major and minor elements concentrations, should be highly helpful in any attempt to discriminate among rocks featuring similar macroscopic visual characteristics and lithic objects from other localities, especially if geological information on actual local and regional source materials exists.

Non-destructive Portable X-ray Fluorescence (PXRF) techniques are now widely applicable for detection of certain chemical elements, aiming to identify the geochemical print of the lithic objects. PXRF can be useful for distinction of silcretes from cherts, owing to the high Cr, Ni, Fe, Mg, Co, V contents of the former over the latter, in conjunction with the common occurrence of disseminated chromite/spinel grains, usually identifiable with the aid of a lens. Since non-destructive methods have to be applied for those mineralogical, petrographic and geochemical studies of lithic objects, and taking into consideration the still little available relevant methodologies and laboratory techniques, we conclude that careful visual inspection of lithic objects by experts in the subject and an evaluation of their chemistry by PXRF complemented by Portable X-ray diffractometer analysis for a rough mineralogical testing are currently useful tools.

7. CONCLUSIONS

From the data presented above we come to the following conclusions:

1. Local silcrete rock and chert nodules occurring within Upper Cretaceous limestones were extensively used for the manufacture of artifacts in early prehistoric times in Nea Artaki - Vatontas area, Evia island. The pattern from this study indicates a primarily local procurement of raw material, although other potential sources do exist in central and north Evia. Varieties of silcrete lithotypes were used for the manufacture of lithic tools. There is an absolute similarity between the lithological types from which these tools are manufactured with the various lithological types of silcrete and chert nodules exposed in the area, so that the hypothesis of local exploitation and processing on site for tool making is justified. Chert nodules were used in low proportions, possibly due to inferior knappability relative to silcrete.

2. Chert nodules are black to black-grey in color, characterized by equigranular quartz aggregates and subordinate calcite rhombohedral grains, pyrite framboids, pseudomorphs of goethite after pyrite and spots of organic matter. They are depleted in almost all the major, minor and REE elements, except silica

and Ca. However, the chemistry of the various types of chert and chert nodules alone is not considered a reliable approach to resolve the critical problem of sourcing of a chert artifact, since usually the chemistry of a rock type varies within the macro- and mesoscale. Additional data from outcrops of cherts (s.l.) and chert nodules representative of various stratigraphic and geological settings are necessary.

3. Silcretes are buff reddish-brown in color to pale grey with a red hue. Light grey to whitish grey silcretes are rather rare. Relictic mesh serpentine texture and aggregates of chromite/spinel grains as well as clay minerals are inherited from the original serpentinized ultramafic rocks. Typical replacement of the ultramafics by microcrystalline quartz and late veining and filling of voids by megaquartz are critical microscopic textural features. They are enriched in Cr, Ni, Fe, Mg, Co and V relative to cherts and chert nodules. Hence these are useful distinctive chemical criteria. It is worth to be noticed that these elements should be detected by PXRF in lithic objects featuring similar macroscopic characteristics (e.g. color, fracturing, luster). They are of superior quality relative to chert nodules and cherts occurring within various geological units exposed in the nearby area. That observation explains the predominance of lithic objects made of silcrete over those made of chert and chert nodules.

4. The fact that artifacts found elsewhere in the Aegean and Western Greece visually are not easily identifiable to chert types of various geological settings and origin is evidence of the need for detailed petrographic studies. These studies involve identification procedures requiring a comparison of lithic tool petrographic features with those of source rock samples. Detailed petrographic attributes of lithic objects made of chert are reliable criteria of origin and potential provenance, especially if geological information on actual local and regional source materials exists. However, the chemical criteria described here are not intended to be an easy panacea; their greatest power is realized when they are complemented by thorough geological, petrographic and mineralogical studies.

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