

Bulletin of the Geological Society of Greece

Vol. 53, 2018



Petrology and Provenance of Lithic Raw Materials used to knap stone: A Case Study From the Inner Ionian Sea

Magganas Andreas	National and Kapodistrian University of Athens
Galanidou Nena	University of Crete
Chatzimpaloglou Petros	University of Cambridge
Kati Marianna	National and Kapodistrian University of Athens
Iliopoulos Giorgos	University of Patras
Katerinopoulos Athanasios	National and Kapodistrian University of Athens

<https://doi.org/10.12681/bgsg.19655>

Copyright © 2019 Nena Galanidou, Andreas Magganas, Petros Chatzimpaloglou, Marianna Kati, Giorgos Iliopoulos, Athanasios Katerinopoulos



To cite this article:

Magganas, A., Galanidou, N., Chatzimpaloglou, P., Kati, M., Iliopoulos, G., & Katerinopoulos, A. (2019). Petrology and Provenance of Lithic Raw Materials used to knap stone: A Case Study From the Inner Ionian Sea. *Bulletin of the Geological Society of Greece*, 53(1), 277-298. doi:<https://doi.org/10.12681/bgsg.19655>



**Research Paper****Correspondence to:**

Andreas Magganas
amagganas@geol.uoa.gr

DOI number:

<http://dx.doi.org/10.12681/bgs.19655>

Keywords:

Patina, Chert, Knapped Stone, Palaeolithic, Neolithic, Bronze Age, Silica Diagenesis, Lithic Provenance, Lithology, Ionian Sea

Citation:

Magganas, A., N. Galanidou, P. Chatzimpaloglou, M. Kati, G. Iliopoulos, A. Katerinopoulos, 2019. Petrology and provenance of Lithic raw materials used to knap stone: A case study from the inner Ionian Sea. *Bulletin Geological Society of Greece*, 53, 277-298.

Publication History:

Received: 07/02/2019
Accepted: 24/02/2019
Accepted article online: 24/02/2019

The Editor wishes to thank Prof. M. Stamatakis, Prof. Hara Drinia and Ms Erietta Vlachou for editorial assistance.

©2019. The Authors

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited

Geological Society of Greece

**PETROLOGY AND PROVENANCE OF LITHIC RAW
MATERIALS USED TO KNAP STONE:
A CASE STUDY FROM THE INNER IONIAN SEA**

Andreas Magganas¹, Nena Galanidou², Petros Chatzimpaloglou¹,
Marianna Kati¹, George Iliopoulos¹, Athanassios Katerinopoulos¹

¹National & Kapodistrian University of Athens, Faculty of Geology &
Geoenvironment, Athens, Greece, amagganas@geol.uoa.gr

²University of Crete, Department of History & Archaeology, Rethymno, Greece
galanidou@uoc.gr

³University of Patras, Department of Geology, Patras, Greece,
iliopoulog@upatras.gr

Abstract

This paper examines the lithology and raw material provenance of knapped stone artifacts recovered from prehistoric sites on Meganisi in the course of the Inner Ionian Sea Archipelago survey. Research was twofold: in the field to map the geology of the island and collect raw material samples, and in the laboratory to conduct a petrological study using LM, XRD, SEM and ICP-MS techniques. The greater part of the materials used to produce stone tools consists of almost pure SiO₂, bedded or nodular cherts mainly of Malm-Turonian and Eocene ages. The cherts were collected by prehistoric knappers from local sources. Patinas present on the artifacts are relatively enriched in calcite material of incomplete silica diagenesis and subsequently a product of late weathering and alteration.

Keywords: Patina, Chert, Knapped Stone, Palaeolithic, Neolithic, Bronze Age, Silica Diagenesis, Lithic Provenance, Lithology, Ionian Sea

Περίληψη

Η μελέτη εξετάζει τη λιθολογία και την προέλευση των πρώτων υλών των λαξευμένων λίθινων τεχνέργων από προϊστορικές θέσεις στο Μεγανήσι Λευκάδος, τα οποία εντόπισε και περισυνέλλεξε η αρχαιολογική έρευνα επιφανείας στο Εσωτερικό Αρχιπέλαγος του Ιονίου. Η ερευνητική δραστηριότητα εγγράφεται στην ευρύτερη αρχαιολογική έρευνα με το διεπιστημονικό της χαρακτήρα και είχε διπλό στόχο. Στο πεδίο πραγματοποιήθηκε επιτόπια μελέτη της γεωλογίας του νησιού και συλλογή γεωλογικών δειγμάτων και στο εργαστήριο, πραγματοποιήθηκε πετρολογική εργασία χρησιμοποιώντας τις ενόργανες αναλυτικές μεθόδους LM (οπτική μικροσκοπία), XRD (περιθλασιμετρία ακτίνων-X), SEM (ηλεκτρονική μικροσκοπία σάρωσης) και ICP-MS (φασματοσκοπία μάζης με επαγωγικά συζευγμένο πλάσμα). Το μεγαλύτερο ποσοστό των υλικών που χρησιμοποιήθηκαν για την κατασκευή των εργαλείων συνίστανται σε σχεδόν καθαρό SiO₂, με μορφή στρωσιγενών ή κονδυλωδών πυριτολίθων ηλικίας κυρίως Μαλμίου-Τουρωνίου και Ηωκαίνου. Οι πυριτόλιθοι συλλέχθηκαν από προϊστορικούς λιθοξόους από τοπικές πηγές πλησίον των αρχαιολογικών θέσεων. Οι πατίνες που εμφανίζουν τα τέχνεργα είναι κυρίως περιοχές ατελούς πυριτικής διαγένεσης εμπλουτισμένες σε ασβεστιτικό υλικό, και δευτερευόντως προϊόν ύστερης αποσάθρωσης και εξαλλοίωσης.

Λέξεις κλειδιά: Πατίνα, Πυριτόλιθος, Λαξευμένος λίθος, Παλαιολιθική Εποχή, Νεολιθική Εποχή, Εποχή του Χαλκού, Πυριτική διαγένεση, Προέλευση του λίθου, Λιθολογία, Ιόνιο Πέλαγος

1. The Archaeological Context

In this paper we report research on the lithology and raw material provenance of knapped stone artifacts recovered from prehistoric sites on Meganisi (Fig. 1) in the course of the Inner Ionian Sea Archipelago survey. The Archipelago consists of a cluster of islands and islets in the semi-enclosed and protected sea stretching between Lefkas and Ithaca to the west and Aetoloakarnania to the east (Fig. 2a). Between 2010 and 2014 archaeology, geology, anthropology,

architecture, ecology and oceanography specialists worked together in the field under the aegis of the ‘Inner Ionian Sea Archaeological Survey’ to reconstruct the long-term history of the northern part of the archipelago, namely the Teleboiades islands, both cultural and natural. The time frame of the cultural history was wide, from the Palaeolithic period to the 20th century (Galanidou, 2014; 2015; 2018; Galanidou et al., 2018). The backbone of the research was archaeological surface survey. In parallel, small-scale excavation, anthropological interview, geological survey, and palaeogeographic reconstruction, including sea-bed mapping, were conducted.

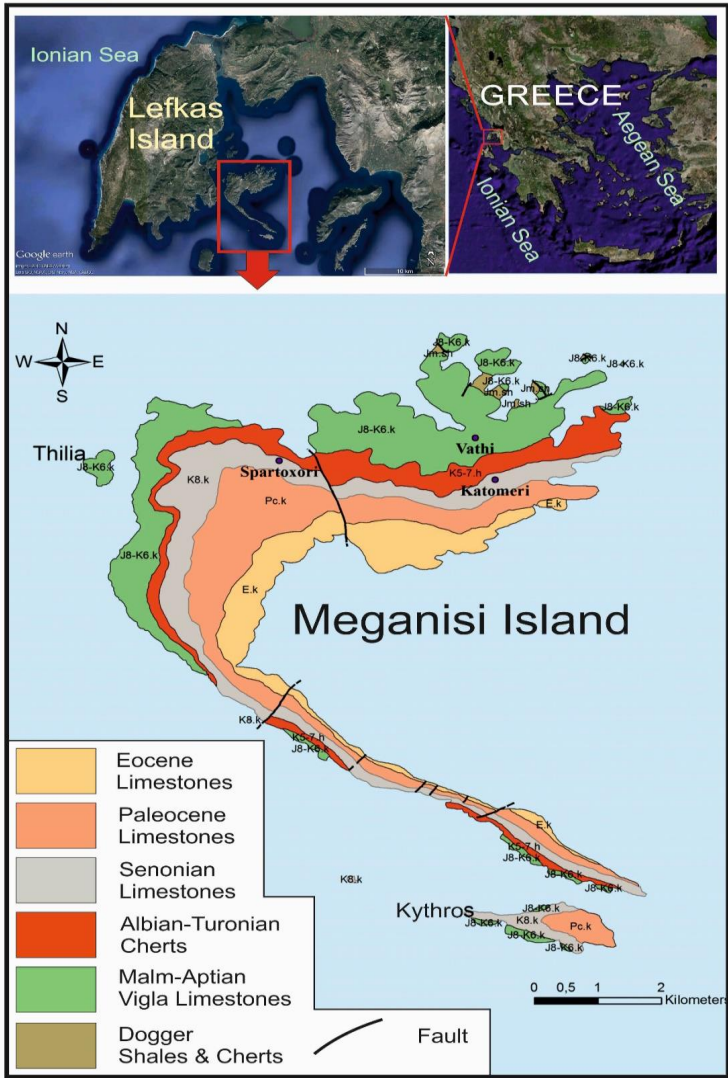


Fig. 1: Simplified geological map of Meganisi.

Research has shown that the insular picture seen today in this part of west Greece results from the climatic change brought about by long-term variations in the planet's orbital path and position, and distortion of the earth's crust by the weight of ice. These, combined with vertical changes caused by tectonic activity, control the local relative sea-level change (Flemming et al., 2014; Sakellariou and Galanidou, 2016). The islands of the archipelago are the higher parts of a Pleistocene terrestrial landscape, much of which now lies submerged beneath the sea due to the postglacial sea-level rise (Zavitsanou et al., 2015; Sakellariou and Galanidou, 2017). Investigations were framed in such a way as to reconstruct the dynamic change which the Inner Ionian area has undergone through time and the responses and interaction of human populations to the changing landscape (Galanidou, 2018). In glacial periods the majority of the islands were connected to the neighbouring landmasses. During these periods the presence of Palaeolithic groups was achieved by walking rather than sea-crossing. Some of the attractions to prehistoric hunter/gatherers are still visible today: wetlands, karstic cavities and raw materials of superb quality suitable for making stone tools. During interglacial periods, however, sea levels rose and sea-crossings, albeit over small distances within a closed and fairly safe sea, would be required to access the islands. Was the same set of resources equally attractive to the agro-pastoralist communities of the Neolithic, the Bronze Age or later historical periods, by which time the landscape had become fragmented into small islands? The deep-time perspective of the settlement history of the Inner Ionian Sea has made imperative an approach to island archaeology that is founded on interdisciplinary collaboration to examine the human responses to the changing landscape. Such collaboration also allowed research on Palaeolithic maritime activity in this inner and protected sea. Lacking the winds, currents and dangers of crossing the open Ionian and Adriatic Seas, it offered better conditions for early maritime ventures. Palaeogeographic reconstructions suggest that Atokos, an island situated in the centre of the Archipelago and highly visible from various viewpoints, namely Lefkas, south Meganisi, Kythros, Arkoudi and the Akarnanian coast due to its prominent relief (Fig. 2a), always invited exploration throughout the period examined. Archaeological research on the Archipelago examined whether the early Palaeolithic groups met the challenge

of crossing small distances to reach Atokos (Galanidou, 2018; Galanidou et al., 2018).

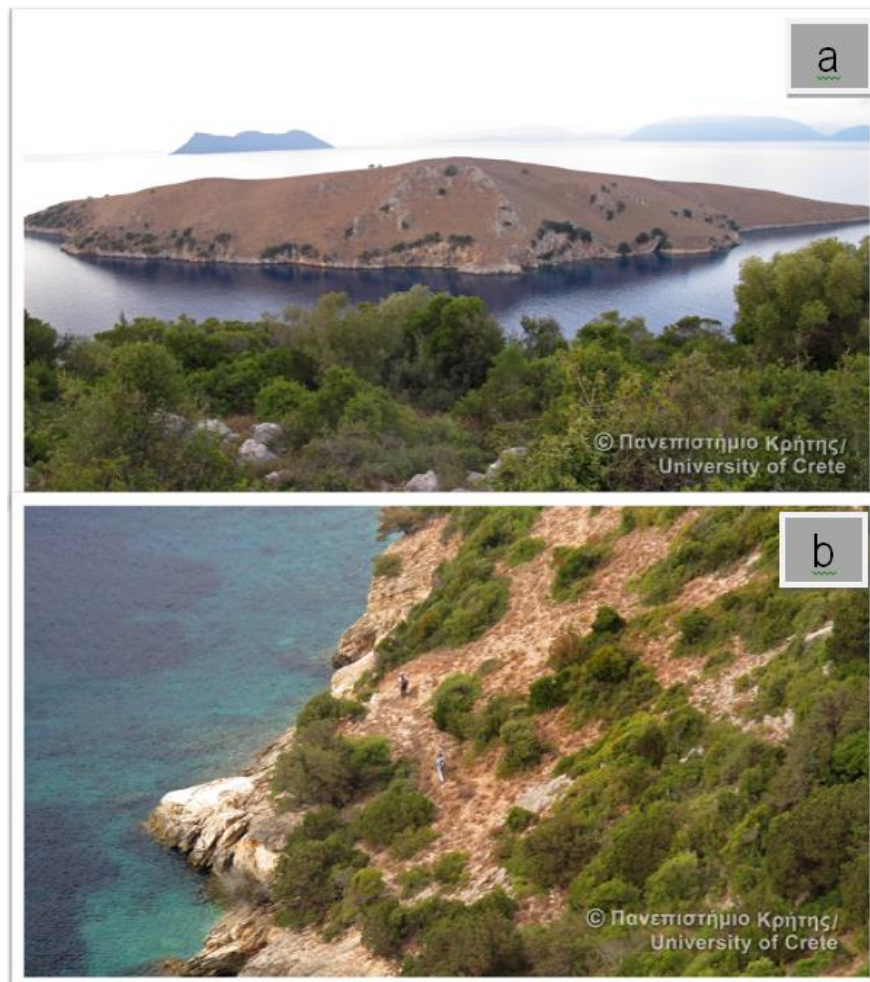


Fig. 2: (a) A view of the Inner Ionian Sea Archipelago from south Meganisi. In the centre is Kythros, with Atokos in the background left and Lefkas and Arkoudi in the background right. (b) Surface surveying on the steep slopes of southwest Meganisi.

The archaeological investigation explored a surface area of approximately 7 km² (Fig. 2b) and brought to light 20000 small finds from Meganisi, Kythros, Thilia, Atokos, Arkoudi, Madouri, and the islets of Formikoula, Petalou and Nisopoula (Galanidou, 2014; 2015; 2018; Galanidou et al., 2018) (Fig. 1). The lion's share consists of knapped-stone artifacts, that is tools, cores, debitage and knapping debris (Fig. 3), dated from the Middle Palaeolithic to the

Neolithic and the Bronze Age. These objects were manufactured from the locally available cherts. Quantitative analysis suggests that the presence or absence of lithic artifacts is directly related to surface karstic geological structures. Most of the sites yielding lithic artifacts are found on the relatively thicker bedded limestones. They were also discovered on top or within red earth deposits in karstic depressions. The present study examines lithic material recovered from Meganisi, the largest island of the Archipelago and the one which yielded the largest number of prehistoric sites.



Fig. 3: Prehistoric artifacts from Meganisi manufactured on chert. (a) Blades and points. (b) Cores. All exhibit traces of patina.

2. The Geological Context

From a geological point of view, Meganisi preserves a near complete sedimentary record of the Ionian Zone, with formations spanning the Middle Jurassic to the recent (Bornovas, 1964; Manakos, 1985). During geological survey on Meganisi the lithologies of the island have been studied in detail and the geological map of the island has been improved and updated (Iliopoulos and Kousis, in prep.). The pre-Miocene formations cover most of the island. They consist of Posidonia shales of Middle Jurassic (Dogger) age, followed successively by Upper Jurassic (Malm) to Aptian limestones of the Vigla Formation, Albian–Turonian bedded cherts, Coniasian to Maastrichtian (Senonian) limestones with calciturbidites of mixed pelagic and benthic fauna, and Paleocene and Eocene resedimented limestones (Figs 1, 4). Very restricted in extent are the clastic deposits, consisting of Miocene sands and silts and Quaternary sediments; these top the Meganisi stratigraphic column (Iliopoulos and Kousis in prep.).

The pre-Miocene formations on Meganisi are deep-water limestones showing variable thicknesses. Besides being found in the Albian–Turonian beds, cherts are also found intercalated in Posidonia shales, as well as within limestones or marly limestones of all the other formations (Fig. 4). Usually, they appear as grey, yellow and brown to white thin beds (usually 5–40 cm in thickness) and occasionally as nodules (usually 10–20 cm in diameter), the latter increasing in quantity and thickness the higher they are located in the stratigraphic column. The Albian–Turonian formation comprises thin and multi-coloured chert layers, alternating with thin marly limestones (Figs 4c–d). The individual chert layers are about 20cm thick, while their colour changes gradually from the bottom to the top of the formation from red, to green and grey, and finally to black. Eocene micritic limestones enclose only nodular cherts, relatively large in diameter and arranged at certain stratigraphic levels.

Similar geological, stratigraphic and sedimentological features in the Middle Jurassic shales of Meganisi and its equivalent formation located elsewhere in the Ionian Zone (Karakitsios, 2003) suggest that they were probably formed in

an extensional syn-rift environment. Also, analogous comparison of the Upper Jurassic to Eocene sedimentary rocks indicates that these early formations from Meganisi were deposited in a post-rift deep axial basin, which was formed by differential subsidence between the central areas and margins of the Ionian basin, while after the Maastrichtian it became shallower and clastic material from the margins was deposited (Skourtsis-Coroneou, Solakious and Constantinidis, 1995).



Fig. 4: (a) Slumped thin bedded limestones with cherts of Vigla Formation. (b) Nodular cherts in Vigla limestones. (c) Albian-Turonian cherts. (d) Black-coloured cherts in the Albian-Turonian Formation. (e) Grey cherts interlayered in Posidonia Shales. (f) Chert nodules forming discontinuous layers in between thin limestone layers on Kythros.

3. Objectives and Methods

We use mineralogy and petrology to characterize and classify the raw materials of artifacts made on chert. Based on this classification we then explore the possible sources and the provenance of the used lithic raw materials. Alteration features and mineralogy of the artifacts' patinas are also discussed. We also focus on the rock formations associated with the artifacts' sources, pointing out their geological origin, depositional setting and subsequent evolution.

The mineralogy, texture and chemistry of three different groups of samples are examined: (a) prehistoric *artifacts* made of chert; (b) *unworked cherts*, i.e. raw materials, found as loose pieces within the archaeological sites or in close proximity to them; and (c) siliceous rocks occurring in the wider region of Meganisi. The samples of unworked cherts, group b, cover different artifact rock types and show comparable macroscopic to mesoscopic characteristics with the examined artifacts of group a. These samples of unworked materials are assumed to represent the gamut of raw materials used to manufacture the prehistoric artifacts. The samples of siliceous rocks, named here '*geological samples*' or group c, were extracted from outcrops and road cuts of original, unweathered bedrock of known stratigraphic position, geological age and formation, occurring on Meganisi within walking distance of the archaeological sites. The geological samples were collected from all pre-Miocene formations and included both bedded and nodular cherts.

In total, over 600 specimens were studied (belonging to all three groups). Four hundred of these were archaeological specimens, i.e. artifacts, and were only subjected to macroscopic and mesoscopic examination. The remaining 200 objects, consisting of samples of groups b and c, were analysed using the analytical techniques presented below. During the summers of 2010 and 2011 work was conducted in the field and comprised sampling, macroscopic description of geological formations and their respective rocks, and geological mapping. In the laboratory the analytical methods employed were: i) petrographic analysis under polarized light microscopy (PLM); ii) X-ray diffraction (XRD); iii) scanning electron microscopy with an energy dispersive

analytical system (SEM-EDS) and iv) inductively coupled plasma–mass spectrometry (ICP-MS). The latter two techniques were employed to identify the geochemical composition in major and trace elements of minerals and rocks (Chatzimpaloglou, 2014; Chatzimpaloglou et al., in prep.). Analytical work using the first three techniques took place at the National and Kapodistrian University of Athens Laboratory of Mineralogy and Petrology, involving the analyses of 100, mainly chert, samples. ICP-MS analyses of 16 chert and siliceous limestone samples were performed at ACME Laboratories in Ontario, Canada.

4. Results

Petrography shows that the Meganisi artifacts, unworked cherts and geological samples (groups a, b and c) consist mainly of crypto-, micro- and macro-crystalline quartz and chalcedony (Fig. 5) (Chatzimpaloglou, 2014). At the macroscopic scale, crypto- and micro-crystalline quartz has a dense and compact translucent to opaque appearance, waxy to dull lustre and a uniform, usually white or yellowish, colour (the latter hues due to impurities of iron oxides). Crypto- and micro-crystalline forms of silica show pure quartz XRD patterns, without any opal peak or curvature (Fig. 6).

Under polarized light microcrystalline quartz is birefringent, whereas macro-crystalline quartz and chalcedony show granular and radiated-fibrous structures respectively. Macro-crystalline quartz and chalcedony are limited types of quartz and are commonly observed within pores and/or microfossils. Inside the microcrystalline quartz groundmass of some Palaeocene cherts a few silicified clast fragments have been observed.

Microcrystalline calcite is the next most common mineral, occurring in almost all types of sample. It usually comprises their groundmass, but it is also found as a major constituent of tests and the interior of some microfossils (Fig. 5c). Moreover, microcrystalline calcite is replaced gradually by crypto- to micro-crystalline quartz toward the core of some layers or nodules of cherts (Fig. 6b).

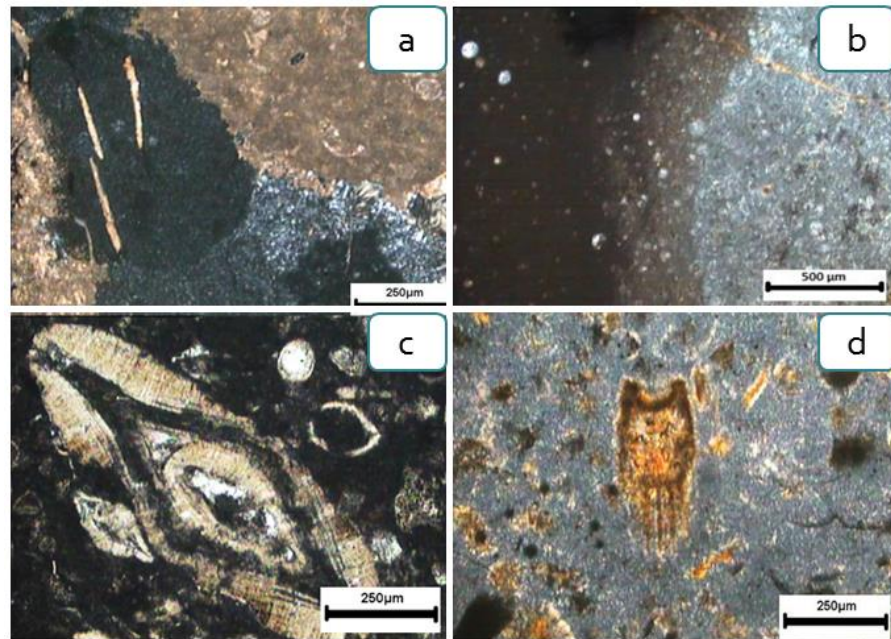


Fig. 5: (a) Carbonate grains cemented by micro-crystalline quartz and chalcedony. (b) Gradual transition from micro-crystalline quartz to siliceous carbonate material. (c-d) Partly or totally silicified radiolaria and foraminifera in crypto- and micro-crystalline quartz in Paleogene cherts.

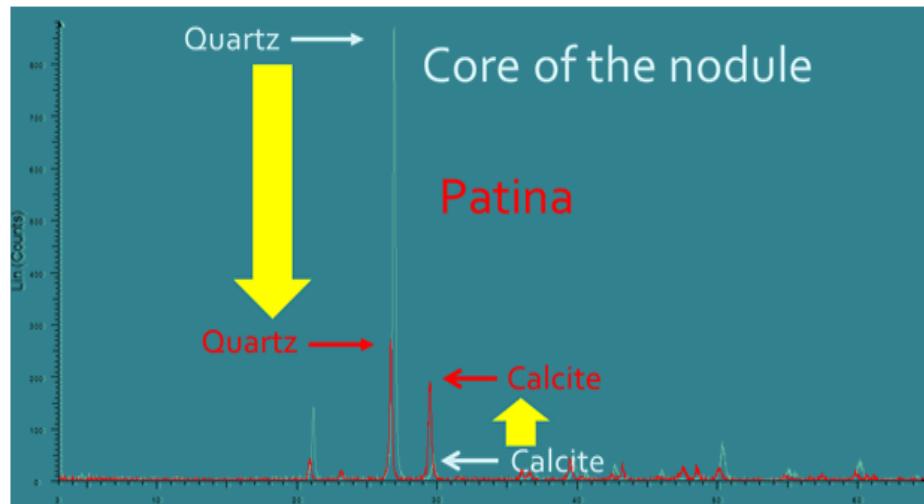


Fig. 6: Increase of calcite/quartz ratio from patina to core of a nodule of Vigla Formation is revealed by comparison of their XRD patterns.

Other subordinate mineralogical constituents that were found only in some geological samples of certain ages comprise barite, apatite and Fe-oxides, normally in association with calcite (Fig. 7). Moreover, barite, apatite and hematite mostly occur in the lower layers of the Albian–Turonian bedded cherts, while in their top layers only barite has been verified. A few barite crystals along with calcite have also been recognized in the chert samples from the Senonian formation. Only a small number of the examined artifacts and unworked cherts actually contain barite and apatite.

The cherts of all studied sample groups contain siliceous or calcareous microfossils, which are mostly Radiolaria and planktonic foraminifera (Figs 5b-d, 7e). Reworked benthic fossils were only recognized in a number of samples collected from Eocene cherts. The original calcite of their tests has been partly or totally replaced by crypto- and micro-crystalline quartz and chalcedony during diagenesis. One rare occasion is a fish tooth preserving its original apatitic composition (Fig. 7c). Palaeocene and Eocene cherts, as well as some artifacts, are quite enriched with partly or totally preserved Radiolaria and silicified foraminifera.

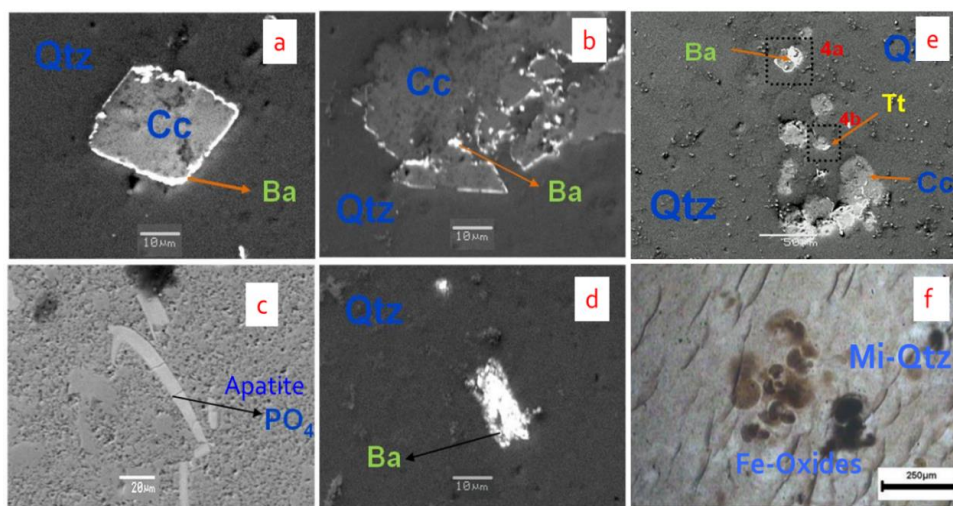


Fig. 7: BSE - SEM microphotographs from Meganisi cherts: (a-b) Idiomorphic calcite (cc) rimmed by barite (Ba) within crypto-crystalline quartz (Qtz). (c) Apatite within a fossil fragment. (d) Isolated barite crystal within crypto-crystalline quartz. (e) Barite replacing foraminifer tests. (f) Fe-oxides within micro-crystalline quartz (Mi-Qtz).

Several artifacts are partly or totally covered with patina, mostly of the white, red-brownish or multi-coloured type. Glossy patina is seldom observed. Usually, it is more calcitic than the core of the artifact, which is enriched in microcrystalline silica; the transition between the two parts is either gradual or immediate. The same type of “patina” is usually found in nodular cherts. Rarely, impressive rose-coloured patinas could develop around black nodules. The change in calcite/quartz ratios between the patina and the core of the nodules was also revealed by XRD analyses (Fig. 6).

The geochemical analyses of representative artifacts, unworked cherts and geological samples show that their silica content ranges from 79.44 %wt. to 98.57 %wt. and is inversely correlated with CaO and Sr. Conversely, K₂O is positively highly correlated with Al₂O₃, Rb and Zr, thus suggesting that they were hosted in the same mineral phase, probably of detrital K-feldspar or clay minerals. The systematic differences in major and trace elements between samples of different ages, colour, texture and archaeological or geological origin are quite few. The most important seems to be the relatively very high Ba values of the geological samples of Albian–Turonian and Senonian age (up to 465 ppm) and of two artifacts (up to 300 ppm), as well as the high Sr content of Malm–Aptian and Senonian cherts (up to 56 ppm) and of some artifacts.

In contrast, REE content in both artifact and geological samples shows remarkable differentiations and variable depletions relative to the Post Archean Australian Shale (PAAS) of Taylor and McLennan (1985) (Fig. 8). The most obvious REE anomaly in all samples is in Ce, while significant Eu anomaly is observed in the samples of Palaeogene age.

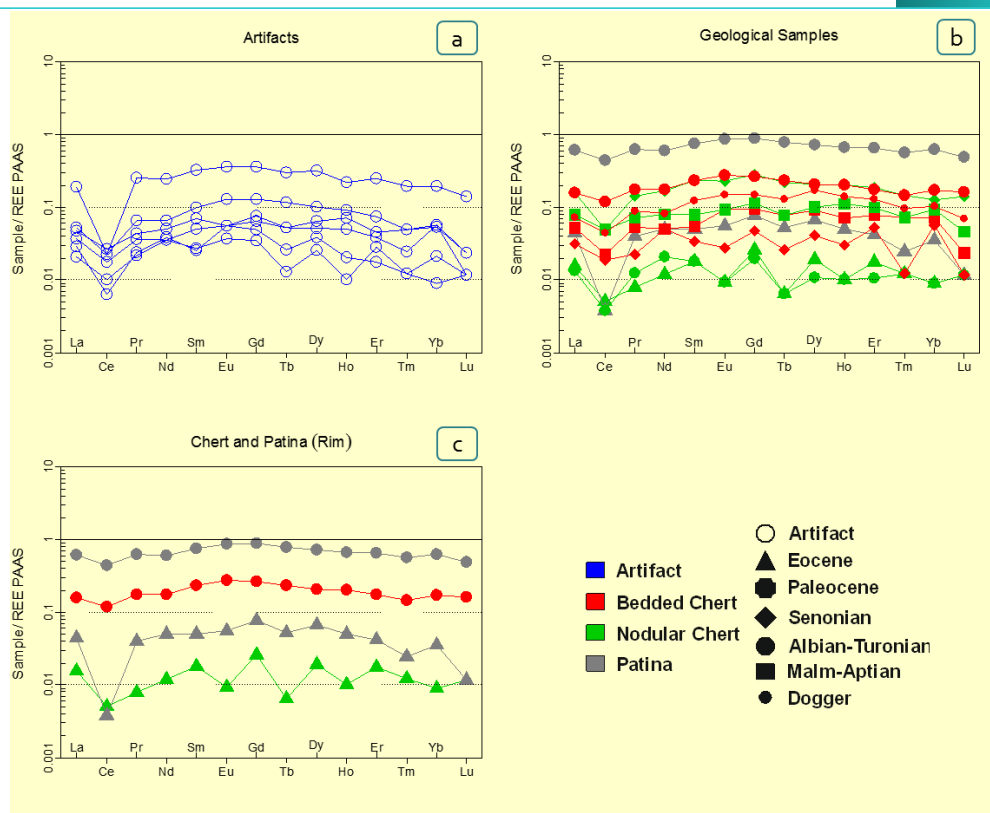


Fig. 8: REE/PAAS spidergrams of artifacts (a) and geological samples (b). Chert and patina REE/PAAS pattern comparison (c).

5. Chert Petrogenesis and Artifact Provenance

The above described observations and analytical results suggest that the artifacts and unworked cherts recovered from Meganisi share many mineralogical, textural and geochemical features with the geological samples collected from local sources of cherts. It is very difficult or even impossible to localize the quarries or the exact extraction locales of the rocks used to make prehistoric tools. A more realistic research target is the determination of the geological formation that the raw materials of the artifacts were taken from. To this end the petrological processes, through which the nearby occurring siliceous rocks were formed, have to be reviewed.

The similar light grey to brown colour of the samples, the presence of crypto- to micro-crystalline quartz indicating the same diagenetic grade, similar fossils, comparable index minerals like barite and apatite, and the analogous

geochemical patterns of the artifacts, the unworked cherts and the geological material, all clearly suggest that the examined artifacts originated from local sources of chert. In order to obtain a more specific determination of the provenance of the cherts, the quartz/calcite ratio, as well as the quantity and type of the microfossils, were additionally examined. Our study has shown that cherts from two geological periods, namely Malm–Turonian and Eocene, seem to have been mostly used for the knapping of the studied artifacts. More specifically, the majority of the artifacts were manufactured on white, grey and light brown cherts from the Vigla Formation. Dark-coloured, barite-bearing cherts from the Albian–Turonian formation and fossiliferous cherts from the Eocene formation were rarely used. These observations were further confirmed by the similar chemical composition of artifacts and source rocks, in particular from the relatively immobile rare earth elements (REE). We used REE contents as a discriminating tool for the provenance of the artifacts (Fig. 8a-b). This analytical approach further confirms that the analysed artifacts were taken from the local, Meganisi, sources and mostly from the cherts of the Malm–Aptian Vigla Formation and to a lesser degree from Albian–Turonian cherts. So, the most prominent places from where artifacts were extracted are located in the northern and north-western parts of the island (Fig. 1).

From a geological point of view, the Meganisi cherts are siliceous rocks of biogenic origin. This was implied by the abundance of siliceous test remains, mostly radiolarians, the deep-water pelagic limestones that host the cherts, and the absence of any hydrothermal, other magmatic or high heat flow source in the vicinity (or even further off), as the lithologies of all the Ionian zone successions indicate. The biogenic origin of the silica of the studied artifacts, unworked cherts and geological materials is likewise suggested by the major and trace chemical element content of the rocks, and especially the high $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ ratios and the low MgO contents (He et al., 2011; Chatzimpaloglou, 2014; Chatzimpaloglou et al., in prep.). The low $\text{Fe}_2\text{O}_3/\text{SiO}_2$ and $\text{Fe}_2\text{O}_3/\text{TiO}_2$ ratios also rule out silica deposition in a mid-ocean ridge environment, favouring a pelagic or a continental slope one (Murray 1994). The setting of silica deposition is further clarified using the Ba, Sr and REE contents of the cherts. These chemical elements and especially some REE

ratios, such as La_n/Ce_n and Lu_n/La_n , as well as the absence of a positive Eu anomaly and the noticeable negative Ce anomaly, designate a clear pelagic origin, far from any continental margin and any hydrothermal source (Murray, 1994; Chatzimpaloglou, 2014; Chatzimpaloglou et al., in prep.). Moreover, REE are more depleted in chert layers than nodules, and in recent formations than in older ones (Fig. 8b). Moreover, the samples from the Albian-Turonian Formation are the most enriched in REE, show almost flat patterns and have contents approaching PAAS values. The Ce anomaly is more intense in the younger formations, suggesting high depletion of Ce^{3+} in the seawater of that time (Piper and Bau, 2013).

The presence of micro- and mega-quartz and chalcedony and the absence of opal polymorphs in the Meganisi cherts are indicative of a high diagenetic grade, probably causing modifications during mesodiagenesis. Thus, the most probable factors seem to be the high burial depth and time, especially for the older aged cherts of the Mesozoic era. The overburden for the younger and less buried Eocene cherts has been calculated to be greater than 2300 m (the thickness of Oligocene flysch and Neogene deposits). This burial depth for the Eocene cherts and the even greater subsidence for all the other cherts that underlie them are generally considered factors that could increase the chance of diagenesis, without the involvement of other factors (Riech and Von Rad, 1979; Hesse and Schacht, 2011). Another argument in support of the idea that the burial depth was the main cause controlling the silica diagenesis in Meganisi is that the major diagenetic factor even in the younger Miocene siliceous rocks of the Paxi Zone in the adjacent islands of Lefkas, Zakynthos and Kefallonia is also their burial depth (Stamatakis et al., 1988; Stamatakis et al., 1989; Magganas et al., 1993; 1996-1997). In addition to the burial depth, time would also have played an important role in the silica diagenesis. The time of burial since the Eocene Epoch on its own covers at least 30 Ma, which is considered more than adequate for diagenetic transformations.

The diagenetic mechanisms that occurred include compaction, silica transformation, dissolution/reprecipitation and recrystallization processes because of the complete or partial siliceous test destruction of micro-organisms (mostly radiolaria). However, it is presently believed that the final silica phase

may have formed by a solid status process, after a dissolution–reprecipitation mechanism in which the primary diagenetic silica content in the interstitial pore fluid is equal to the solubility of quartz (Cady, Wenk and Downing, 1996). The discretionary enrichment of barite in the cherts of Albian–Turonian age and the textures that it forms (barite mainly replaces the calcareous and siliceous skeletal elements of the microfossils and develops epitaxially over euhedral calcite crystals) clearly suggest that it was crystallized as an authigenic mineral during diagenesis. This selective barite appearance, as mentioned above, makes it a very useful index mineral with implications for the provenance of the artifacts.

Though the oxidation conditions appear to be relatively constant during the deposition and diagenesis of the chert-hosted formations in Meganisi, an important exception probably exists during the Albian–Turonian. The differences in the above-described textural, mineralogical and chemical characteristics between the Albian–Turonian bedded cherts and the cherts of other ages indicate a change in the redox conditions during their deposition, signifying an important anoxic event towards the end of this period. This is in accordance with studies in the Ioannina area further north, where analogous siliceous rocks and carbonates point to an anoxic episode of similar age (Karakitsios, Kafousia and Tsikos, 2010; Danelian et al., 2004).

The patina present in many studied geological samples, unworked cherts and artifacts seems to have been mainly formed during geological processes (e.g. diagenesis, chemical weathering) rather than being related to anthropogenic activity (e.g. exposure to fire). One possible interpretation argues that patina represents the transitional zone between the newly formed chert and the original carbonate material. For this option the best possible mechanism that we can suggest for the patina formation is the incomplete mobilization of chemical elements, especially silicon, and the partial or gradual replacement or dissolution/reprecipitation of the initial calcium carbonate by silica during diagenesis. A second interpretation regards the usually found white or rusty-coloured patina, identified when the cherts were exposed to weathering conditions, either on the surface or a small distance below in the soil or

subsoil. The rarely observed secondary patina (e.g. of glossy type) on certain artifacts may have been created by humans during their intensive use. With regard to REE, patinas are always more enriched in them compared to the respective chert samples from the same formation (Fig. 8c), which means that REE prefer to concentrate in the carbonate fraction rather than the silica one.

6. Conclusions

The present study departs from the archaeological question of provenance of the lithic artifacts discovered on Meganisi in the course of the Inner Ionian Sea Archipelago survey and has addressed the petrogenetic evolution of their siliceous source rocks.

The quartz/calcite ratio, as well as the quantity and type of the microfossils of the cherts, the presence of certain index minerals such as barite, and their geochemical profile show that the lithics chosen to make stone tools were taken from local sources, primarily from the cherts of the Vigla Formation and secondly from the Albian–Turonian and Eocene cherts.

The cherts are mostly composed of micro- and mega-quartz and also chalcedony. The burial depth and time seem to be the principal factors facilitating silica diagenesis. Dissolution/precipitation and recrystallization are the prevailing mechanisms for silica transformations.

The patina of the artifacts is usually white or multi-coloured, and has an increased calcite/quartz ratio greater than the unaffected and silica-enriched core. It is commonly formed naturally through incomplete silica diagenesis, while its development is favoured when the artifact has originated from nodular cherts. Late chemical weathering and oxidation may contribute to form some red-brownish-type patinas.

7. References

- Bornovas, J., 1964. Geological Study of Leukada Island. *Technical Report IGSR X(1)*, 142 (in Greek).
- Cady, S. L., H.-R. Wenk, and K. H. Downing., 1996. HRTEM of Microcrystalline Opal in Chert and Porcelanite from the Monterey Formation, California. *American Mineralogist*, 81, 1380–95.
- Chatzimpaloglou, P., 2014. Cherts and Siliceous Pre-historic Artifacts from Meganisi Island, Lefkas. MSc Thesis, University of Athens, 205.
- Chatzimpaloglou, P., A. Magganas, N. Galanidou, M. Kati, and G. Iliopoulos. (in prep.). Sourcing the Lithic Raw Materials of Prehistoric Artifacts from Meganisi. In *The Long-term History of the Inner Ionian Sea Archipelago*, edited by N. Galanidou, M. Gatsi, and O. Vikatou.
- Danelian, T., H. Tsikos, S. Gardin, F. Baudin, J. P. Bellier, and L. Emmanuel., 2004. Global and Regional Palaeoceanographic Changes as Recorded in the Mid-Cretaceous (Aptian-Albian) Sequence of the Ionian Zone (NW Greece). *Journal of the Geological Society*, 161, (4), 703–709.
- Flemming, N. C., M. N. Çağatay, F. L. Chiocci, N. Galanidou, G. Lericolais, T. Missiaen, F. Moore, A. Rosentau, D. Sakellariou, B. Skar, A. Stevenson, and H. Weerts., 2014. *Land Beneath the Waves: Submerged Landscapes and Sea Level Change. A Joint Geosciences-Humanities Strategy for European Continental Shelf Prehistoric Research*, edited by N. C. Chu, and N. McDonough. Ostend: Position Paper 21 of the European Marine Board.
- Galanidou, N., 2014. Archaeological Survey on the Inner Ionian Sea Archipelago. In C. Smith (ed.) *Encyclopaedia of Global Archaeology*, 3882–3888. New York: Springer.
- Galanidou, N., 2015. Seascape Survey on the Inner Ionian Sea Archipelago. In *Field Archaeology from Around the World. Ideas and Approaches*, edited by M. Carver, B. Gaydarska, and S. Mondon-Subias, 101–106. New York: Springer.
- Galanidou, N., 2018. Parting the waters. Middle Palaeolithic archaeology in the central Ionian Sea. *Journal of Greek Archaeology*, 3, 1–22.

Galanidou N., O. Vikatou, M. Gatsi-Stavropoulou, A. Vasilakis, G. Iliopoulos, V. Staikou, M. Veikou, J. Forsén, C. Morgan, J. Vroom, C. Papoulia, P. Zervoudakis, K. Prassas., 2018. The archaeological survey in the Inner Ionian Sea Archipelago. In *Archaeological work in Aetoloakarnania and Lefkas from prehistory to the roman period, Proceedings of the 2nd International Archaeological and Historical Conference, I.P. Mesolonghiou, 6-8 December 2013*, edited by O. Vikatou, V. Staikou, and F. Saranti. 445–473 (in Greek). Mesolonghi.

He, J., Y. Zhou, H. Li, and X. Wang., 2011. Study on Geochemical Characteristics and Depositional Environment of Pengcuolin Chert, Southern Tibet. *Journal of Geography and Geology*, 3, 178–188.

Hesse, R., and U. Schacht., 2011. Early Diagenesis of Deep-sea Sediments. In *Deep-Sea Sediment*, edited by H. Hüneke, and T. Mulder, 557–713. Amsterdam: Elsevier.

Iliopoulos, G. and I. Kousis. (in prep.). The Geology and Stratigraphy of Meganisi Island. In *The Long-term History of the Inner Ionian Sea Archipelago*, edited by N. Galanidou, M. Gatsi, and O. Vikatou.

Karakitsios, V., 2003. Evolution and Petroleum Potential of the Ionian Basin (Northwest Greece). *AAPG International Conference & Exhibition, September 21–24, 2003, Barcelona, Spain, Official Program: 47* (full paper in CD-ROM, 12 pages).

Karakitsios, V., N. Kafousia, and H. Tsikos., 2010. Oceanic Anoxic Events as Recorded in the Mesozoic Sedimentary Record of Mainland Greece. *Hellenic Journal of Geosciences*, 45, 123–131.

Magganas, A., M. Stamatakis, K. Kyriakopoulos, and M. Dermitzakis., 1993. Biogenic Siliceous Sediments as a Source Material for the Authigenesis of Silica Polymorphs, Zeolites and Barite: A Study Case from Tertiary Porcellanitic Rocks of Greece. *4th Panhellenic Symposium of Oceanography and Fisheries, Rhodes, 26–29 April 1993*, 1–4. Rhodes: National Centre of Marine Research.

Magganas, A., M. Stamatakis, K. Kyriakopoulos, and M. Dermitzakis., 1996–1997. Authigenic Minerals and Geochemical Features of Tertiary Porcelanites

and Cherts from Greece. *Annales Géologiques des Pays Helléniques*, 37, 981–97.

Manakos, K., 1985. *Geological Map of Greece, 1:50000. Kalamos Sheet*. Athens: IGME.

Murray, R. W., 1994. Chemical Criteria to Identify the Depositional Environment of Chert: General Principles and Application. *Sedimentary Geology*, 90, 213–232.

Piper, D., and M. Bau., 2013. Normalized Rare Earth Elements in Water, Sediments, and Wine: Identifying Sources and Environmental Redox Conditions. *American Journal of Analytical Chemistry*, 4, 69–83.

Riech, V., and U. von Rad., 1979. Silica Diagenesis in the Atlantic Ocean: Diagenetic Potential and Transformations. In *Deep Drilling in the Atlantic Ocean: Continental Margins and Paleoenvironment*, edited by M. Talwani, W. Hay, and W. B. F. Ryan, 315–340. Washington D.C.: American Geophysical Union. doi: 10.1029/ME003p0315.

Sakellariou D., and N. Galanidou., 2016. Pleistocene submerged landscapes and Palaeolithic archaeology in the tectonically active Aegean region. In *Geology and Archaeology: Submerged Landscapes of the Continental Shelf*, edited by J. Harff, G.N. Bailey, and F. Luth, 145–178. London: Geological Society, Special Publications 411.

Sakellariou D. and N. Galanidou., 2017. Aegean Pleistocene Landscapes Above and Below Sea-Level: Palaeogeographic Reconstruction and Hominin Dispersals. In *Under the Sea: Archaeology and Palaeolandscapes of the Continental Shelf*, edited by G.N. Bailey, J. Harff, and D. Sakellariou, 335–359. Cham: Coastal Research Library, Springer. doi: 10.1007/978-3-319-53160-1.

Skourtsis-Coroneou, V., N. Solakious, and I. Constantinidis., 1995. Cretaceous Stratigraphy of the Ionian Zone, Hellenides, Western Greece. *Cretaceous Research*, 16, 539–558.

Stamatakis, M., M. Dermitzakis, A. Economou-Amilli, and A. Magganas., 1988. Petrology and Diagenetic Changes in Miocene Marine Diatomaceous Deposits from Zakynthos Island, Greece. In *Siliceous Deposits of the Tethys*

and Pacific Regions, edited by J. R. Hein, and J. Obradovic, 129–139. New York: Springer-Verlag.

Stamatakis, M., M. Dermitzakis, A. Magganas, and M. Vlachou., 1989. Petrology and Silica Minerals Neof ormation in the Miocene Sediments of Ionian Islands, Greece. *Giornale di Geologia* 51(1), 61–70.

Taylor, S. R., and S. M. McLennan., 1985. *The Continental Crust: Its Composition and Evolution*. Oxford: Blackwell.

Zavitsanou, A., D. Sakellariou, G. Rousakis, P. Georgiou, and N. Galanidou., 2015. Paleogeographic Reconstruction of the Inner Ionian Sea during Late Pleistocene Low Sealevel Stands: Preliminary Results. Paper presented in the *11th Panhellenic Symposium on Oceanography and Fisheries, Mytilene, Lesvos Island, Greece*, 997–1000.