

AN INTEGRATED METHODOLOGICAL APPROACH FOR SOURCE-CLAY DETERMINATION OF ANCIENT CERAMICS: THE CASE OF AEGINA ISLAND, GREECE

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Abstract—A new model is proposed for analysis of the source clays used to create ceramics, based on geographic, petrographic, mineralogical, mineral-chemistry, and geochemical criteria. The development of this model became feasible after the discovery of a Pliocene volcanic clay horizon on NW Aegina Island, Greece. The volcanic clay contains smectite, mixed-layer chlorite-smectite, biotite, and palygorskite and has greater feldspar content than the underlying Pliocene marls, which contain R0 mixed-layer illite-smectite, mica, dolomite, serpentine, talc and gypsum, and, in some places, palygorskite. The two units have distinct geochemical characteristics. In general the Pliocene volcanic clay is richer in SiO₂, Al₂O₃, and Fe₂O₃ and poorer in Na₂O, MgO, and P₂O₅ than the Pliocene marls. The Nb, Zr, Hf, Th, and rare earth element (*REE*) contents are also significantly greater in the Pliocene volcanic clay and comparable to those of the dacitic rocks of the island, reflecting the volcanic origin of the clay.

The proposed model was used to identify the source-clay materials that were used for the production of ceramics on the island of Aegina (Aeginetan Ware). All five criteria should be considered in any provenance study. The use of individual criteria on their own can lead to ambiguous conclusions. In the present study the geochemical criterion was particularly helpful. It provided robust evidence for the nature of the source clay. The Pliocene volcanic clay horizon and the underlying Pliocene marls are the candidate raw materials for Aeginetan Ware. Although the Pliocene marls have been invoked as raw materials for Greek Bronze Age (~3000–1100 BC) Aeginetan ceramics and are used as raw materials by modern Aeginetan ceramists, the geochemical characteristics of a large set of Bronze Age Greek Aeginetan sherds with fine and coarse fabrics coincide with those of the Pliocene volcanic clay. This comparative and cumulative evidence suggests that the Pliocene volcanic clay was the main source clay for ancient Aeginetan ceramics, regardless of the fabric (coarse or fine) and that admixture of different sources might not be necessary for fine-grained ceramics.

Key Words—Aegina Island, Archaeological Ceramics, Clay-material Multi-criteria Approach, Geochemistry, Greece, Mineralogy, Pliocene Volcanic Clay, Provenance Studies.

INTRODUCTION: RESEARCH APPROACH

Clay-rich materials have been used since ancient times in the fabrication of various types of ceramic articles (*e.g.* Freestone and Gaimster, 1997; Velde and Druc, 1999). The oldest pottery articles dated so far (12–14 ka) have been found in Japan and belong to the Jomon period (Kaner, 2003). Recognition of the source clays used as raw materials in ceramics involves a complex array of provenance studies. Examination of potential source clays has been included in provenance research designs of various cross-disciplinary ceramic studies (Jones, 1986, 1993; Douglass and Schaller, 1993; Shriner, 1999; Shriner and Dorais, 1999; Day and Kiriati, 1999; Whitbread, 2001; Whitbread *et al.*, 2002; Dorais and Shriner, 2002a, 2002b; Dorais *et al.*, 2004; Rathossi *et al.*, 2004; Ruby and Shriner, 2005; Prudencio *et al.*, 2006; Dias and Prudencio, 2008;

Marques *et al.*, 2010; Trindade *et al.*, 2010; Gauß and Kiriati, 2011; Braekmans *et al.*, 2011; Ma *et al.*, 2012). A major impediment to success in attempts to link specific ceramic samples with specific source clays has been the lack of an effective method of comparison and correlation between source-clay data and existing descriptions and characterizations of ceramic artifacts.

The recognition of clay horizons used for fabrication of clay ceramics in prehistoric and historic time periods can be paralleled with provenance studies of sedimentary rocks and industrial sedimentary clay deposits. Provenance studies that include mineralogical and/or geochemical fingerprinting are common in applied clay geology and sedimentary geology. These studies are useful in identifying the sources of constituent minerals, in understanding transport and deposition mechanisms, and in recognizing diagenetic or other alterations of argillaceous sediments (Cullers *et al.*, 1979; Wronkiewicz and Condie, 1990; Dombrowski, 1993; Slack and Stevens, 1994; Faupl *et al.*, 1998; Setti *et al.*, 2004; Gonzalez-Lopez *et al.*, 2005). The methods involved in provenance studies include analysis of textural features of characteristic minerals present in

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the rock (both clay minerals and heavy minerals), interpretation of the chemical trends in the sediments using trace elements, and radiometric dating (Marinoni *et al.*, 2008).

In the present contribution, an integrated approach for ceramic provenance analysis is proposed to identify clay-rich sediments used as raw materials for the fabrication of ceramics. The approach proposed is method-driven, relying on a set of verifications (Kingery, 1982). The weight-of-evidence approach recognizes that in attempting to identify the origin of source clays for ceramics there is generally no single fingerprint that is indisputable. Rather, the strength of the argument rests upon the successful combination of a variety of factors. Therefore, an attempt is made to introduce a set of geologic, mineralogical, and geochemical techniques as key tools for answering important questions. This approach, which combines field observations, petrographic analysis, mineralogy, mineral chemistry, and bulk-element analysis, focuses on the potential raw materials rather than the ceramic articles. The aim of this research is to show that the use of this interdisciplinary approach contributes to reliable ceramic source-clay provenance analysis and eventually, through experimental ceramic source-clay research, to a deeper understanding of ceramic technology changes.

As a reference study area, the island of Aegina, Greece was selected. Aegina was a major producer of ceramics for various purposes in Greece, from the Early Bronze Age (ca. 3000 to 2000 BC) through at least the Classical period, ca. 400 BC, (Gauß and Kiriati, 2011). Presumed Aeginetan ceramics of various ages have been found in many areas of the Aegean and the Greek mainland (*e.g.* Zerner, 1986, 1993; Nordquist, 1987; Rutter, 1989, 1990; Dietz, 1991; Forsén, 1996; Pullen, 2000, 2011; Lindblom, 2001; Rotroff, 2006). These ceramics suggest that exchange of ceramics between different locations was in progress from a very early time. Reliable provenancing of a source clay for ancient Aeginetan ceramics has been a specific problem. Two clay horizons on the island, the Pliocene volcanic clay unit and the underlying Pliocene marl, used by modern potters, are possible sources of the ceramics. A clayey horizon known as 'Plakakia clays' exposed along and near the NW coast of the island (Figure 1) was proposed by Hein *et al.* (2004) as a source of at least some Bronze Age Aeginetan ceramics. In their compilation, based on petrographic and chemical data, Gauß and Kiriati (2011) proposed that the two Aeginetan ceramic Fabric Groups (FG1 and FG2) had been produced from different sources: the coarser FG1 was derived from a volcanic sediment of Holocene age, whereas the finer FG2 was derived from a mixture of the Pliocene marls with material from a volcanic source, probably the same as that used for FG1, at a 80:20 ratio. Those authors considered the Plakakia clays to be Pliocene marls. No volcanic clayey horizon of substantial thickness which

would sustain the production of Aeginetan ceramics for ~2000 years was reported by Gauß and Kiriati (2011) on the island. The present study aimed to show that a substantial volcanic clay horizon is indeed present on the island and that use of the integrated approach employed here contributes to reliable archeological provenance analysis, which may resolve issues of possible mixing of raw materials for production of ancient ceramics.

GEOLOGIC FRAMEWORK

The volcanic island of Aegina is situated in the northwestern part of the Southern Aegean Volcanic Arc (SAVA) (Figure 1a), activity of which began during the Pliocene (Figure 1b). The island is composed of three units: (1) Alpine sediments; (2) Neogene pre-volcanic sediments; and (3) volcanic sequences (Dietrich *et al.*, 1991). The Alpine rocks span from Permian to Maastrichtian and include limestones (partly recrystallized in some horizons), cherts, and flysch. The Neogene (lower Pliocene) pre-volcanic sediments (namely Pliocene marls) consist of transgressive conglomerates at their base, followed by shallow marine limestones and marls (which are dolomitized in places); lacustrine sands and silts; breccias; and silty clays with intercalations of diatomites and fluviolacustrine silts and sands (Benda *et al.*, 1979; Stamatakis and Magganas, 1989).

The volcanic sequence includes some of the oldest rocks of the SAVA (Pe-Piper *et al.*, 1983) and comprises rocks that erupted in two episodes (Dietrich *et al.*, 1988; 1991). The first episode (4.4–3 Ma), known as the dacitic phase, began during the Early Pliocene, producing rhyodacitic tuffs and pumice, followed by andesitic dacite flows and plugs (Figure 2). The episode terminated with the eruption of dacitic pyroclastic and volcanoclastic flows. The first tuff (4.4 ± 0.2 Ma according to Müller *et al.*, 1979), associated with the Skotini volcano eruption (Figure 2), and the subsequent volcanoclastic flows, form the volcanic base of Aegina Island and were exposed throughout the rest of the Pliocene (Dietrich *et al.*, 1991). The second episode, known as the andesitic phase, was initiated during the Late Pliocene after a long period of quiescence. These rocks were erupted from two volcanic centers and produced minor amounts of pyroclastics and lavas of basaltic andesite composition. The basaltic andesite at Oros was dated to the Late Pliocene (2.1 ± 0.1 Ma) and the rhyodacite at Kakoperato, to a slightly earlier Late Pliocene age (2.2–2.45 Ma) (Morris, 2000) (Figure 2). Dietrich *et al.* (1991) designated as Pleistocene both fluviolacustrine and limnic deposits of clay, silt, and sand, often with intercalations of volcanoclastic volcanic material, followed by coastal calcareous sandstones and marly limestones, known as Poros.

Between the Pliocene marls and the Poros marly limestone, there is a 0.4–4 m thick, laterally extensive reddish brown clay-rich horizon, which is exposed along

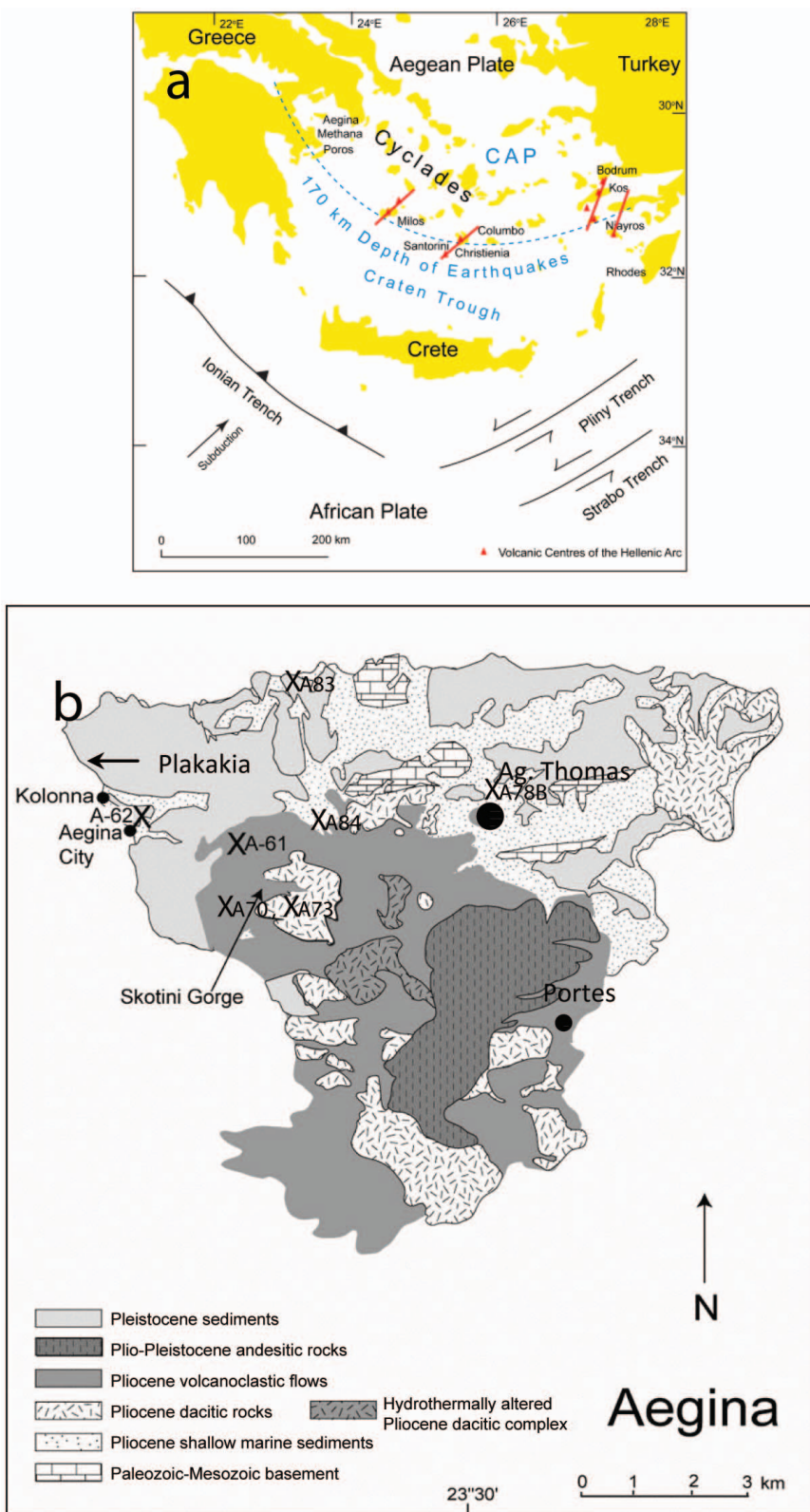


Figure 1. (a) The geographic location of the volcanic centers in the South Aegean Volcanic Arc (SAVA). (b) A simplified geologic map of Aegina Island. A61 and A62 are representative samples of the Aegina Pliocene volcanic clay. Samples A66, A58L and A58U were obtained 50 m upstream from A61.

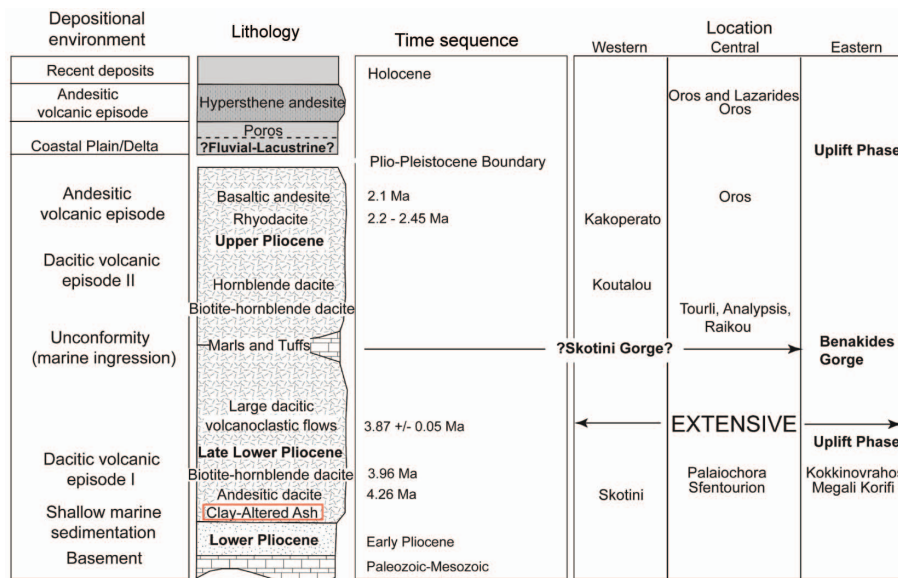


Figure 2. Composite framework visual for the time sequences of geologic activity on Aegina Island and the resultant depositional environment (modified after data from Dietrich *et al.*, 1991 and Morris, 2000). The time position of the clay-altered volcanic ash sediment is noted as Lower Pliocene.

nearly the entire northwestern coast of Aegina and along road cuts and ravine flanks, but does not crop out at the surface (Figure 3). The clay has not been recognized as a distinct unit in previous studies (*e.g.* Tsolis-Katagas, 1977; Dietrich *et al.*, 1991; Gauß and Kiriati, 2011) and was considered to be Pleistocene in age (Dietrich *et al.*, 1991). The clay-rich horizon consists of a fairly uniform mixture of clay and calcite nodules and contains abundant amphibole crystals embedded in the clay matrix. Internal stratification is largely absent, though some exposures display vertical changes in color. In many exposures, isolated pebbles or cobbles of older dacite are found suspended within the interior of the clay horizon. These characteristics clearly attest to an altered equivalent of a submarine airfall tuff deposit (Shriner *et al.*, 2007; Christidis *et al.*, in press). Shallow-marine microfossils are present. The microfossils present in the clay-altered ash unit suggest an Early Pliocene age for the original ash and suggest deposition on the adjacent submarine platform at depths ranging from shallow to deep (Figure 2). The depositional environment and the evolution of this bed will be the subject of future contribution to the literature.

MATERIALS AND METHODS

Samples were collected from the Pliocene volcanic clay underlying Poros calcareous sediments, from the Pliocene marls of the northwestern part of Aegina Island and the area of Agios Thomas, and from fresh outcrops of the dacitic volcanoclastic flows (Figure 1b). Sample N2 is a Pliocene marl from Ag. Thomas supplied by a local ceramist. Because the Pliocene volcanic clay was not

exposed on the surface, samples were obtained from ravine flanks, road cuts, and coastal cliffs. All samples were collected at a depth of 10–15 cm from the outcrop surface to minimize the effects of weathering and contamination. The volcanic clay samples contained abundant calcite nodules larger than 2 mm and small dacitic pebbles ~10 mm in size. These nodules and pebbles were removed by sieving; the material passing through the 2 mm sieve was used for further examination. The Pliocene marls selected were free of calcite nodules. The bulk mineralogy of the Pliocene volcanic clay and marl samples was determined by X-ray diffraction (XRD) (Siemens D500, CuK α radiation, graphite monochromator, 35 kV and 35 mA, 0.02° step size, and counting time of 1 s/step) on randomly oriented samples, initially crushed with a fly press and subsequently ground with pestle and mortar. The clay mineralogy was determined in materials dispersed in distilled water using an ultrasonic probe (20 s). The <2 μ m fractions were separated by settling, dried on glass slides at room temperature, and then solvated with ethylene-glycol (EG) vapor at 60°C overnight to ensure maximum saturation. The XRD traces of the clay fractions were obtained using a 0.02° step size and a counting time of 4 s/step. Mineral abundances were calculated from XRD data using *Autoquan*© software, which uses Rietveld refinement.

Major-element analysis of representative samples of Pliocene volcanic clays, Pliocene marls, and dacitic volcanoclastic flows cropping out on the island, was carried out by inductively coupled plasma-optical emission spectrometry (ICP-OES). Trace-element analysis of these samples was performed by ICP-mass spectrometry (ICP-MS). Both analyses were conducted

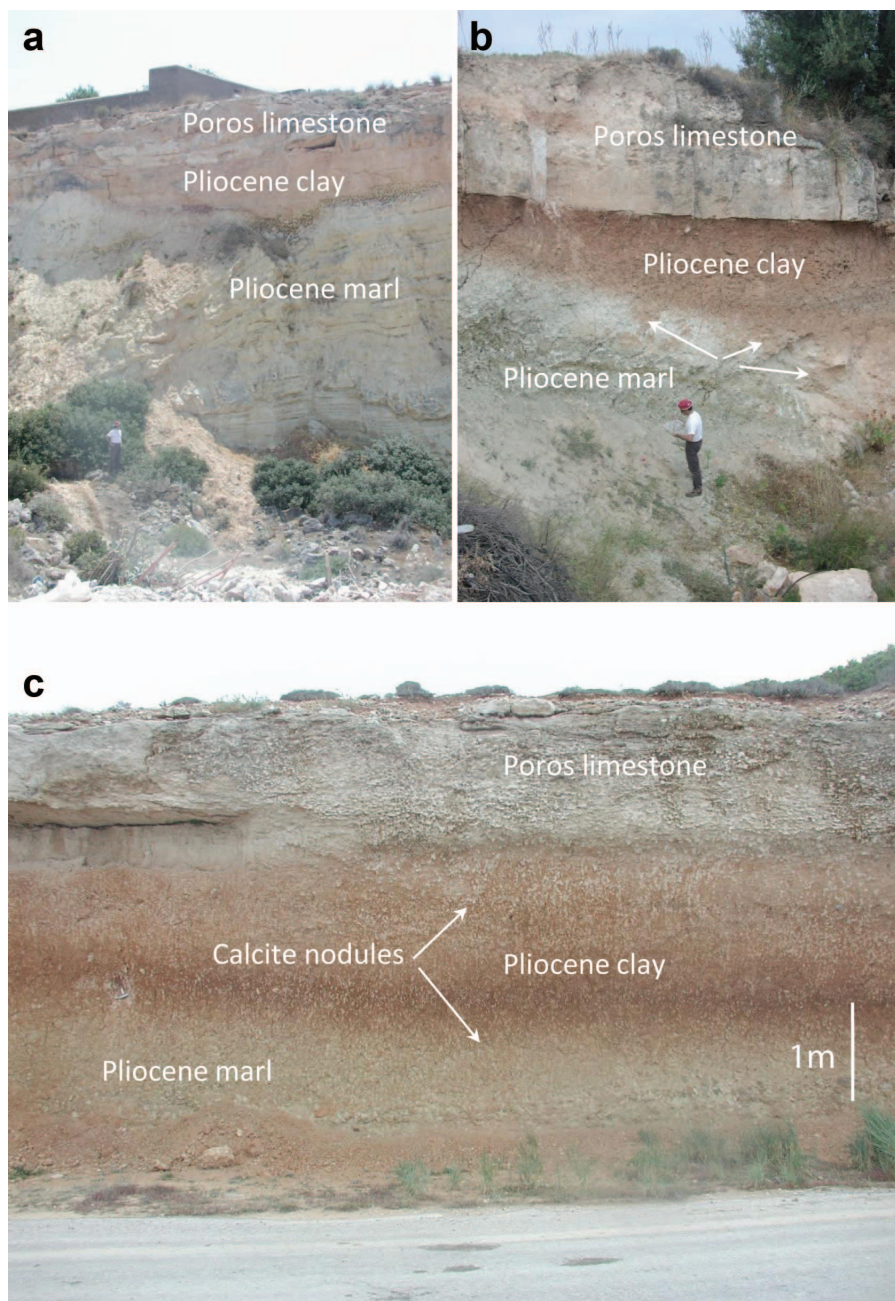


Figure 3. Typical exposures of the Pliocene volcanic clay between the Pliocene marl at the bottom and the Poros limestone. In outcrops free of debris from the overlying Pliocene clay, the boundary between the Pliocene volcanic clay and the Pliocene marl is sharp (3a). The arrows in 3b indicate debris from the overlying Pliocene volcanic clay. In 3c the boundary is obscured by the calcite nodules. See text for discussion.

at ACME Analytical Laboratories, Canada. Analysis involved fusion of 0.2 g samples with a lithium metaborate-lithium tetraborate mixture, followed by digestion in dilute nitric acid. Loss on ignition (LOI) was determined by mass difference after ignition at 1000°C. Data for trace elements, including rare earth elements (*REE*), in a large set of different types of ceramics from the archeological site of Kolonna were

obtained from Mommsen *et al.* (2001). The ceramics data used in the present study belong to the Mommsen *et al.* (2001) chemical groups A, E, F, and P, known to originate from Aegina. Furthermore, a sub-set of the Mommsen *et al.* (2001) original neutron activation analysis (NAA) sample set was supplied to the present authors by F. Felten, director of archeological excavations at Kolonna, University of Salzburg, Austria. This

sub-set was delivered as 83 highly polished thin sections. These thin sections were analyzed by electron microprobe analysis (EMPA). The ceramics data were compared with a databank of SAVA dacitic rock samples, including those from Aegina (Brophy *et al.*, in press; cf. <http://www.indiana.edu/~sava/>), in order to verify a local Aegina provenance for the chemical groups A, E, F, and P of Mommsen *et al.* (2001).

A second sample set of >80 sherds from Kolonna was supplied by Drs F. Felten and L. Berger (University of Salzburg, Austria) (see table under supplementary materials at the SAVA website, <http://www.indiana.edu/~sava/>), was assembled for further comparative study (Brophy *et al.*, in press; Christidis *et al.*, in press; Shriner *et al.*, in press), and was used in the present study for LOI determination. This second Kolonna sample set was comparable to the sub-set from Mommsen *et al.* (2001) in that the ceramics were predominantly of local provenance (L. Berger, pers. comm.). The sherds have been examined with optical microscopy, and analyzed by XRD and with comparative EMPA (Brophy *et al.*, in press). For 28 of the Aeginetan sherds, the LOI was determined by firing at 980°C for 2 h and was found to vary between 2.95 and 17.89% (average 7.97%), and is due mainly to the presence of calcite. In the present study, the Mommsen *et al.* (2001) chemical NAA data have been adjusted for LOI in order to be comparable with the LOI-adjusted potential source (Pliocene volcanic clay and the Pliocene marl) data. The LOI correction for the sherds is 7.97%. Note that statistical analysis was carried out on the dataset of Mommsen *et al.* (2001) by Hein *et al.* (2004).

In order to reduce the dilution effect of calcite, which is abundant in both sediment types, the geochemical comparisons for both the major and the trace elements, including the REE, were carried out on a volatile-free basis. This was achieved by recalculation of the elemental concentrations on a LOI-free basis for each sample. In this manner the geochemical compositions of the sediments were directly comparable to those of the sherds, after LOI correction of the latter (see above). In geochemical plots involving elemental ratios, normalization by LOI was not necessary.

Gold-coated broken surfaces of representative Pliocene volcanic clay samples were examined using a JEOL JSM-5400 scanning electron microscope (SEM) equipped with an Oxford Link energy dispersive spectrometer (EDS) for qualitative analyses, in order to determine the textural relationships between the various mineral phases of the clays and marls. In selected samples the clay fraction was separated, spread on glass slides, coated with carbon and examined by SEM to detect the presence of palygorskite. Particle-size distribution of the sand and coarse silt fraction of the Pliocene volcanic clay and Pliocene marls was obtained by wet sieving after removal of calcite nodules by hand picking (Christidis *et al.*, in press).

RESULTS

Geologic characteristics of the Pliocene volcanic clay and the volcanic marls

The Pliocene volcanic clay horizon is a horizontal bed that underlies the Poros marly limestones (Figure 3a,b). Where it is exposed, its thickness varies from 40 cm to almost 4 m depending on the paleo-surface of the underlying rocks, which consist of Pliocene marls (Figure 3). In general, the thickness and the D₅₀ particle size obtained from the particle-size distribution curves (data not shown) increase towards the volcanic centre of Skotini, from which the original volcanic ash is considered to have been derived (Figure 1b). The contact with the underlying Pliocene marls is, in general, discordant and sharp without gradual transitions, reflecting the hiatus between the two horizons (Figure 3a). This suggests a depositional setting controlled by water depth, as is expected in coastal environments. In places, debris from the overlying Pliocene volcanic clay may make the contact between the two horizons obscure (Figure 3b). The contact with the overlying Poros marly limestones is also sharp (Figure 3).

The Pliocene volcanic clay bed is light red to brownish-red in color, becoming darker brown in places, and contains abundant calcite nodules, which are either scattered in the clay bed or are aligned vertically (Figure 3c). These nodules, which are more abundant in the Pliocene volcanic clay compared to the Pliocene marls, may also obscure the boundary between the two horizons. Such nodular textures are typical of calcretes; they are associated with downward movement of groundwater in arid environments (Collinson and Thompson, 1988) and indicate post-depositional soil-formation processes. Nodule formation is more intense away from the volcanic edifice of the island and is evident along the northern coastline. The amphiboles present in the clay bed are identical in composition to those present in the Aeginetan volcanic rocks thus reflecting the volcanic component of the clay horizon (Brophy *et al.*, in press; website, <http://www.indiana.edu/~sava/>). Gauß and Kiriatzi (2011) described a similar ~30 cm thick reddish clayey horizon close to the Portes area in the E-SE coast of Aegina, free of microfossils and pedogenic carbonate nodules (Figure 1), which those authors attributed to weathering of volcanic rocks and which was assumed to be Holocene in age.

The underlying Pliocene marls are pale green to off-white or brownish in color. In the northwestern part of the island they are exposed only in road cuts and ravine flanks, as is the overlying Pliocene volcanic clay. According to Benda *et al.* (1979), their maximum thickness reaches 70 m in the area of Ag. Thomas (Figure 1b). In this area the Pliocene volcanic clay is missing and the marls are overlain directly by unaltered

tuff and tuffite followed by andesitic breccias (Benda *et al.*, 1979; Stamatakis and Magganas, 1989).

Mineralogy and mineral textures

Representative photomicrographs of Aeginetan sherds with coarse and fine fabric are shown in Figure 4. More photomicrographs with coarse and fine fabric are shown under the 'Petrographic Database' on the SAVA website. The fine fabric (Figure 4a) is characterized by a texture in which larger crystals of hornblende, biotite, and feldspar are embedded within a finer matrix, consisting of quartz, feldspar, oxyhydroxides, calcite, and Ca-silicates (diopside and gehlenite), the latter formed during firing. The presence of diopside and gehlenite was verified by XRD in the second Kolonna sample set (data not shown). Small porphyritic dacite rock fragments are present (data not shown). The coarse fabric is characterized by the presence of rock fragments of porphyritic dacite and crystals of hornblende, biotite, and feldspar minerals (Figure 4b). The

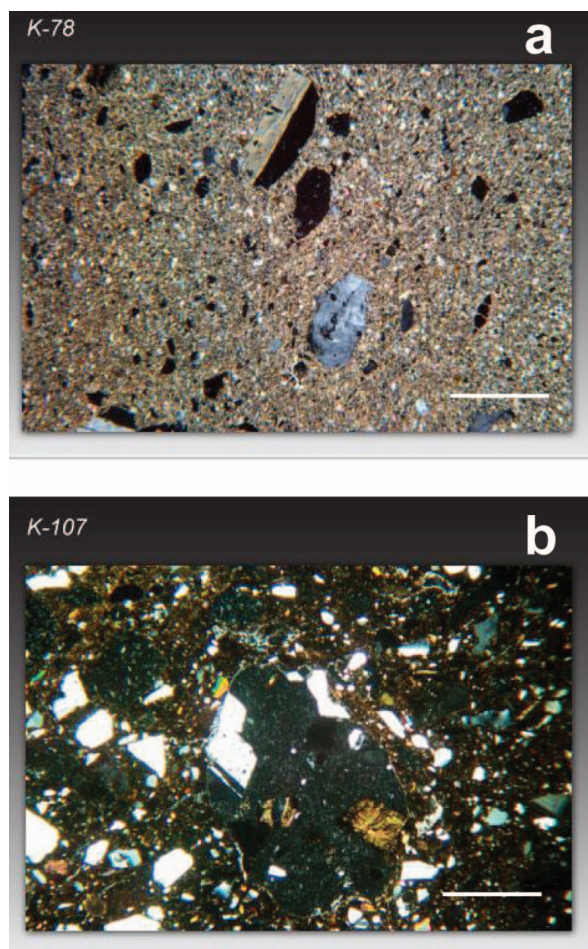


Figure 4. Representative photomicrographs of Aeginetan sherds with fine fabric (a) and coarse fabric (b). Crossed polars. Scale bars = 125 µm.

presence of calcite was verified by XRD. High-temperature Ca minerals have not been detected in the sherds with coarse fabric. The coarse fabric is considered to be equivalent to FG1 and the fine fabric is equivalent to FG2 of Gauß and Kiriatzi (2011).

Typically, the Pliocene volcanic clay consists of quartz, igneous plagioclase (mainly andesine), clay minerals, hornblende, K-feldspar, biotite, calcite, and Fe-oxyhydroxides (Figure 5a). The clay mineral content is, on average, ~25% of the total clay. The composition of the hornblende is comparable to that of the hornblendes from the volcanic rocks of Aegina and of the hornblendes in the volcanic sherds of chemical groups A, E, F, and P of Mommsen (Brophy *et al.*, in press). The Aegina hornblendes have chemical fingerprints (Dietrich *et al.*, 1988 and references therein) distinct from those of their counterparts in other volcanic centers of the SAVA, being richer in K₂O (Dorais *et al.*, 2004; Brophy *et al.*, in press; see Brophy's report on the SAVA website). The air-dried clay fraction consists of mica, chlorite, kaolinite, palygorskite, a phase with a diffraction maximum at 14–15 Å, quartz, calcite and feldspars. The 14–15 Å phase after EG solvation splits into two components, a smectitic one which swells to 17.5–17.8 Å and a second phase at 15 Å (Figure 5b). The presence of palygorskite was also suggested in the bulk samples (Figure 5a). The large *d* value of the swollen phase is attributed to the Lorenz polarization factor due to the small particle size of smectite. Smectite (confirmed by EDS analysis not shown) occurs in the form of wavy flakes (Figure 6a). Upon heating at 375°C, the low-angle peaks collapse to a large one at 10 Å and a minor one at 13.7 Å. This suggests that the second swelling phase corresponds to chlorite-rich, R0 mixed-layer chlorite-smectite (C-S). Fine-grained chlorite and mixed-layer C-S flakes have replaced biotite (Figure 6b), as was suggested by EDS analysis.

Pliocene marl samples from the northwestern part of Aegina Island consist of quartz, calcite, dolomite, albite, gypsum, mica, chlorite, kaolinite, R0 mixed-layer illite-smectite and in places, traces of amphibole, serpentine, and talc (Figure 5a,b). Minor palygorskite is also present in places (Figure 5b). The presence of serpentine and talc suggests that the source material was different from that of the Pliocene volcanic clay and included an ultrabasic component, possibly derived from ophiolite rocks. Ophiolite rocks are common components of the Sub-Pelagonian Unit to which most of the Aeginetan Alpine rocks belong (Dietrich *et al.*, 1991). The Pliocene marl samples differ in many ways, in terms of bulk mineralogy, from the overlying Pliocene volcanic clay: (1) they contain dolomite, serpentine, talc, and gypsum; palygorskite is scarce and they lack mixed-layer C-S and K-feldspar; (2) they contain only trace amphibole (the Pliocene volcanic clay is considerably richer in amphibole) and albite rather than andesine; and (3) feldspars are considerably less abundant than in the Pliocene

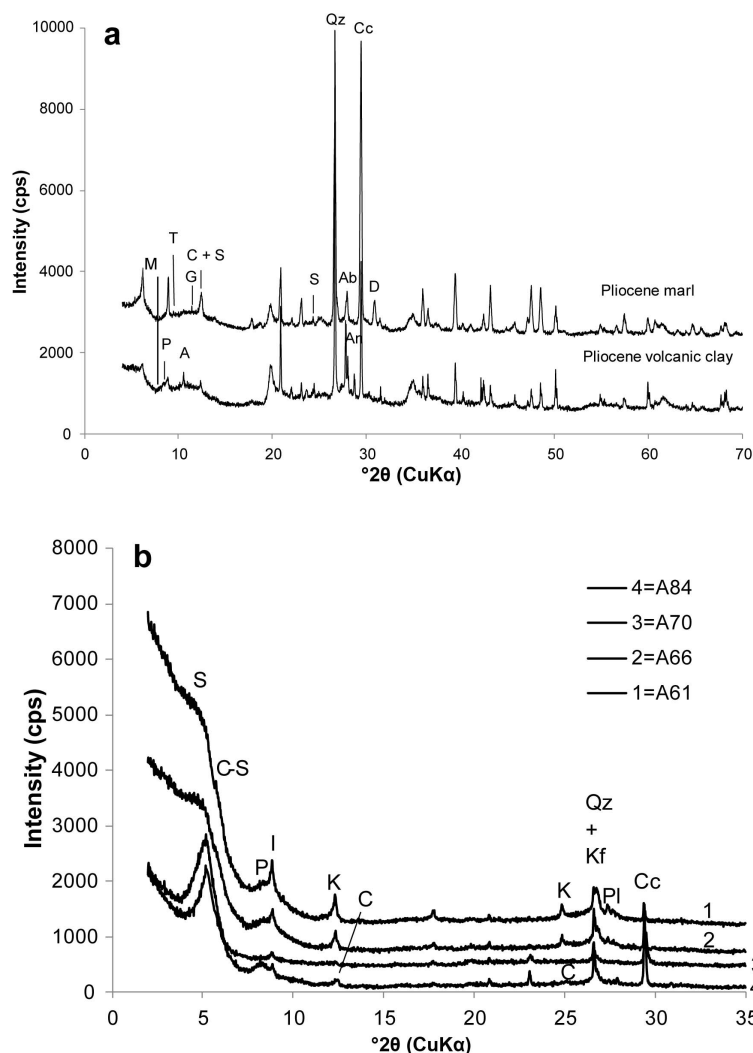


Figure 5. XRD traces of: (a) randomly oriented powdered samples. Symbols: A = amphibole, P = palygorskite, G = gypsum, C = chlorite, S = serpentine, D = dolomite, Ab = albite, An = anorthite, and; (b) of oriented clay fractions after EG solvation of the Pliocene volcanic clays (A61 and A66) and the Pliocene marls (A70, A84). The differences in mineralogy are indicated by symbols. S = smectite, I = illite, P = palygorskite, K = kaolinite, C = chlorite, C-S = mixed-layer chlorite-smectite, Qz = quartz, Kf = K-feldspar, Pl = plagioclase, Cc = calcite.

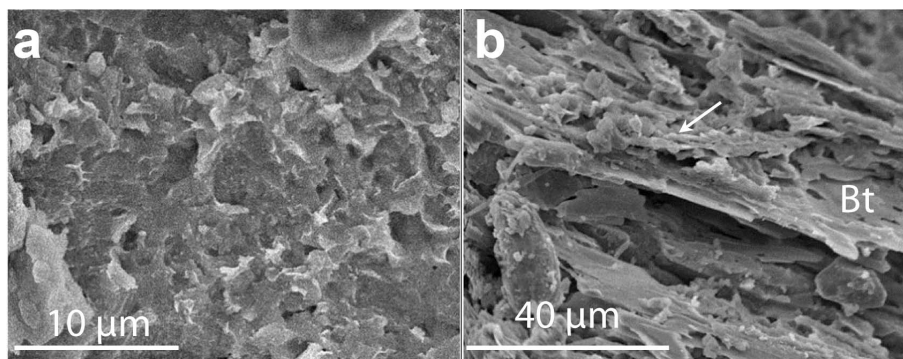


Figure 6. SEM images of the Pliocene volcanic clay: (a) smectite flakes with subhedral morphology; (b) mixed-layer chlorite-smectite and chlorite (shown by arrows), replacing biotite (Bt).

volcanic clay. The absence of opal-A and/or opal-CT suggests that the marl may correspond to the lower zone of the Ag. Thomas section, which is also free of opal-A and/or opal-CT (Stamatakis and Magganas, 1989). The presence of gypsum and dolomite suggests deposition in a shallow-marine depositional environment characterized by intense evaporation in an arid climate. The clay mineralogy of the marl samples is also different from that of the Pliocene volcanic clay: the clay fraction of the Pliocene marl is dominated by R0 mixed-layer illite-smectite with subordinate mica and chlorite and contains abundant calcite, and palygorskite is present in places (Figure 5b). In general the Pliocene marls are richer in clay minerals than the Pliocene volcanic clay. The different mineralogy suggests different sources for the two sediments.

Geochemistry

Mass fractions of major-element oxides, trace elements, and *REE* determined by chemical analysis of the Pliocene volcanic clay and the Pliocene marls are listed in Table 1. The chemical composition of the Plakakia samples used by Hein *et al.* (2004) and the A, E, F, and P groups of Mommsen *et al.* (2001) are listed in Table 2. The two sediment types have distinct chemical compositions, which reflect sediment supply from different sources. In general, the Pliocene volcanic clay has larger SiO_2 , Al_2O_3 , Fe_2O_3 , and TiO_2 contents and smaller MgO , Na_2O , and P_2O_5 contents than the marls (Table 1). The two types also have comparable concentrations of K_2O (Table 1). The large MgO content in the Pliocene marl samples reflects the contribution of dolomite and the ultrabasic component represented by serpentine and talc. The CaO content of the two materials mainly reflects the presence of carbonates and to a lesser degree of plagioclase feldspar in the Pliocene volcanic clay. In general, the Pliocene marl samples are richer in CaO than the Pliocene volcanic clay. However, samples from the Pliocene volcanic clay with abundant calcite nodules which are <2 mm are also rich in CaO . In addition, the

two sediment types display significant differences in trace-element chemistry. In general, the Pliocene marls are richer in Ni and Cr than the Pliocene volcanic clay in accordance with the presence of serpentine and talc, due to the ultrabasic input. The Pliocene volcanic clay is richer in high field strength elements (Zr, Nb, Y, Th, and Hf) and poorer in U than the Pliocene marls (Table 1). Moreover, the volcanic clays display heterogeneity which is not explained by calcite dilution; sample A83, which was collected from the north coast of the island, away from the Skotini volcanic center (Figure 1), has a fine grain size and is geochemically different from the remaining volcanic clay samples, being poorer in Ba, Th, Sr, the light *REE* (*LREE*), and Y, but not in the heavy *REE* (*HREE*) and Sc, and richer in Ni and Co.

The differences in geochemical composition were used to separate the two sediment types with geochemical plots. In the present study the concentration ratios were used instead of elemental concentrations to avoid possible problems with concentration dilution by calcite. Based on the geochemical data, MgO and P_2O_5 are important discriminating elements, which separate the two sediment types according to their chemical composition. The different geochemical signatures of the two sediment types are evident from geochemical plots of the $\text{Al}_2\text{O}_3/\text{MgO}$ vs. SiO_2/MgO (Figure 7a) and $\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5$ vs. $\text{SiO}_2/\text{P}_2\text{O}_5$ elemental ratios (Figure 7b).

Concentration ratios of certain trace elements are also useful for separation of the two sediment types (Figure 8). These diagrams also include the Plakakia clays (Hein *et al.*, 2004) and the sherd groups A, E, F, and P of Mommsen *et al.* (2001). The average compositions of the different horizons were also plotted. Note that Gauß and Kiriati (2011) considered the Plakakia clays to be Pliocene marls. The concentration ratios of trace elements have often been used in diagrams for analysis of sedimentary processes and provenance analysis of sedimentary rock units at a large scale (*e.g.* McLennan and Taylor, 1991; McLennan *et al.*, 1993). The Th/Sc and Th/Co ratios are indicative of differences

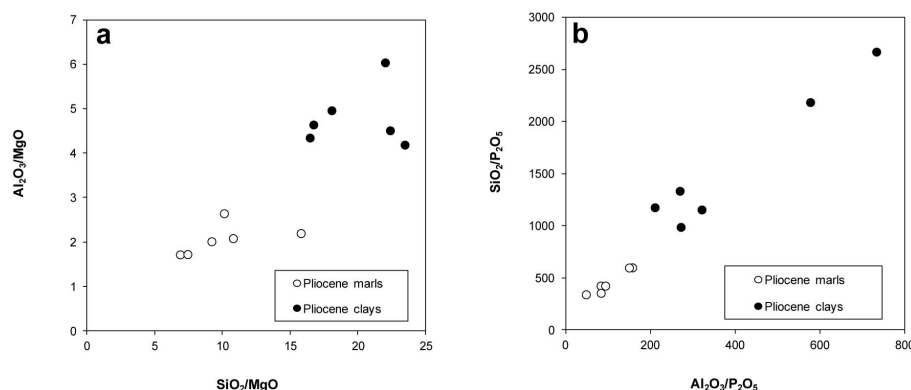


Figure 7. Geochemical plots for discrimination of the Pliocene marl and Pliocene volcanic clay: (a) SiO_2/MgO vs. $\text{Al}_2\text{O}_3/\text{MgO}$; (b) $\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5$ vs. $\text{SiO}_2/\text{P}_2\text{O}_5$.

Table 1. Chemical composition (wt.%) of the Pliocene volcanic clay and the Pliocene marl samples from Aegina Island.

	Pliocene clays						Pliocene marls					
	A61	A62	A66	A58L	A58U	A83	A70	A73	A78B	A84	C8	N2
SiO ₂	46.31	47.15	43.77	53.45	29.71	53.48	34.18	36.13	38.45	37.74	36.03	39.35
TiO ₂	0.64	0.5	0.6	0.73	0.39	0.65	0.39	0.38	0.49	0.33	0.52	0.52
Al ₂ O ₃	12.83	8.4	11.54	14.66	8.14	10.76	6.58	9.41	8.38	5.23	8.96	9.1
Fe ₂ O ₃	5.64	4.28	5.33	6.51	3.23	5.89	3.63	4.28	5.11	3.27	4.46	4.88
MnO	0.08	0.07	0.07	0.09	0.05	0.08	0.03	0.05	0.07	0.02	0.05	0.06
MgO	2.77	2.01	2.66	2.96	1.35	2.39	3.17	3.57	4.18	2.39	5.24	5.3
CaO	11.26	16.59	12.42	4.54	27.95	7.63	21.94	18.82	18.67	24.35	18.13	16.11
Na ₂ O	0.58	0.5	0.62	0.67	0.46	0.54	0.7	1.04	0.8	0.56	0.83	0.77
K ₂ O	1.82	1.41	1.7	2.19	1.21	1.63	0.91	0.55	1.64	0.84	1.65	2
P ₂ O ₅	0.04	0.04	0.02	0.02	0.03	0.04	0.08	0.06	0.09	0.11	0.06	0.11
Cr ₂ O ₃	0.033	0.107	0.041	0.041	0.023	0.08	0.039	0.019	0.052	0.042	0.048	0.05
LOI	17.7	18.8	21	13.9	27.3	16.7	28.2	25.4	21.9	24.9	23.7	21.6
Total	99.7	99.86	99.77	99.76	99.84	99.87	99.85	99.71	99.83	99.78	99.68	99.85
Concentrations (ppm)												
Ba	283	154	241	327.3	187.2	184	162	288	154	211	193	167
Ni	135	181	148	175	81	253	165	80	325	172	228	249
Sc	14	10	13	17	8	15	9	11	13	9	13	14
Mo	0.9	0.5	0.7	0.8	0.5	0.6	0.1	0.2	1.5	4.1	29.5	3
Cu	21.7	16.5	21.6	29.1	20.9	26.2	17	15.8	28.4	25	26.4	30.8
Pb	14.4	9.8	12.3	16.7	8.8	9.3	6.2	7.2	10.7	4.7	14.5	15.4
Zn	52	33	52	70	30	47	30	22	61	33	73	70
As	6.2	16.5	6.5	7.7	13.1	13.8	2.1	2.4	7.2	8.3	5.1	5.7
Cd	0.2	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.6	0.1	0.2
Sb	0.2	0.1	0.2	0.2	0.2	0.1	0.1	0.1	0.3	0.1	0.2	0.3
Ag	0	0	0	0	0	0	0	0	0	0	0.1	0.1
Au*	14	6.7	3.4	12	17.4	3.8	4.2	11.7	7.1	4.4	1.6	2.5
Hg	0	0.01	0.01	0.01	0.01	0	0.01	0.02	0.01	0.01	0.02	0.04
Tl	0.3	0.2	0.3	0.3	0.2	0.2	0.1	0.1	0.2	0.1	0.2	0.2
Se	0	0	0.5	0	0.5	0	0.5	0	0.5	0	0	0
Be	0	0	0	1	0	0	0	0	0	0	0	0
Co	20.3	18.5	17.5	21.5	10.4	22.5	12.1	14	28.1	11.9	18.6	26.1
Cs	6.5	5.6	5.9	8	3.9	6.9	5.9	1.9	6.8	5.8	7.6	8.4
Ga	15.2	10.5	14	19.2	10.6	13	8.4	9.7	10.6	7.1	11.1	12.2
Hf	3.9	4.5	3.9	4.8	3.1	4.3	1.9	1.9	2.3	2.1	2.3	2.5
Nb	11.5	8	10.2	14.4	8.7	10.9	5.4	4.5	6.5	4.9	7.5	7.7
Rb	74.4	59.4	66.4	96.8	52.5	75.5	40	20.2	64.1	41.9	71.3	75
Sn	2	1	2	3	2	2	1	0	1	1	0	0
Sr	323.8	515.4	355.6	273.2	719.8	237.6	335.1	707.9	350.9	506.4	435.3	308.5
Ta	0.8	0.7	0.8	1	0.5	0.7	0.4	0.4	0.5	0.4	0.5	0.6
Th	9.5	7.6	8.2	11	7.9	6.8	4.5	6	5.7	3.9	5.4	5.1
U	1.4	1.9	1.4	1.7	1.2	1.5	1.7	1.8	2.4	3.2	6.3	3.5
V	92	79	85	118	69	108	64	74	77	83	78	87
W	1.4	0.7	1.3	1.3	0.8	1.5	0.5	0.5	0.8	1	0	0
Zr	127.2	138.7	132.5	164.2	109	148.3	69.6	65.7	77.6	81.4	82.9	83.1
Y	23.6	17.8	18.8	18.7	18.5	17.4	13.3	11.4	17.5	16	18.2	20.9
La	28.7	21.6	22	22.6	20.1	19.2	13.3	13.3	15.8	12.7	18	18.8
Ce	57.2	45.9	49.7	65.4	42.1	46.2	24.8	27.3	30.5	25.5	33.4	34.3
Pr	6.65	4.7	5.2	5.58	4.67	4.56	3.14	3.02	3.67	3.04	4.12	4.3
Nd	24.6	19.5	19.6	22.9	20	17.5	12.4	12.9	13.6	12.7	17.4	17.9
Sm	5.1	3.5	4.1	4	3.6	3.5	2.5	2.5	3.5	2.5	3.6	3.9
Eu	1.05	0.76	0.83	0.83	0.75	0.73	0.61	0.62	0.68	0.57	0.8	0.84
Gd	4.1	3.01	3.3	3.07	3.22	2.86	2.23	2	2.8	2.17	3.02	3.55
Tb	0.77	0.57	0.63	0.55	0.49	0.6	0.39	0.41	0.5	0.47	0.49	0.53
Dy	3.85	2.96	3.1	3.2	2.91	2.83	2	1.92	3	2.44	3.03	3.29
Ho	0.8	0.57	0.63	0.63	0.56	0.64	0.44	0.41	0.57	0.56	0.61	0.64
Er	2.33	1.63	1.81	1.84	1.59	1.74	1.22	1.12	1.55	1.38	1.7	1.8
Tm	0.36	0.26	0.32	0.3	0.27	0.3	0.21	0.16	0.26	0.27	0.26	0.28
Yb	2.36	1.64	2.15	2.11	1.59	1.84	1.21	1.23	1.8	1.43	1.6	1.88
Lu	0.38	0.26	0.36	0.32	0.25	0.33	0.19	0.18	0.25	0.25	0.26	0.29

* Concentration in ppb.

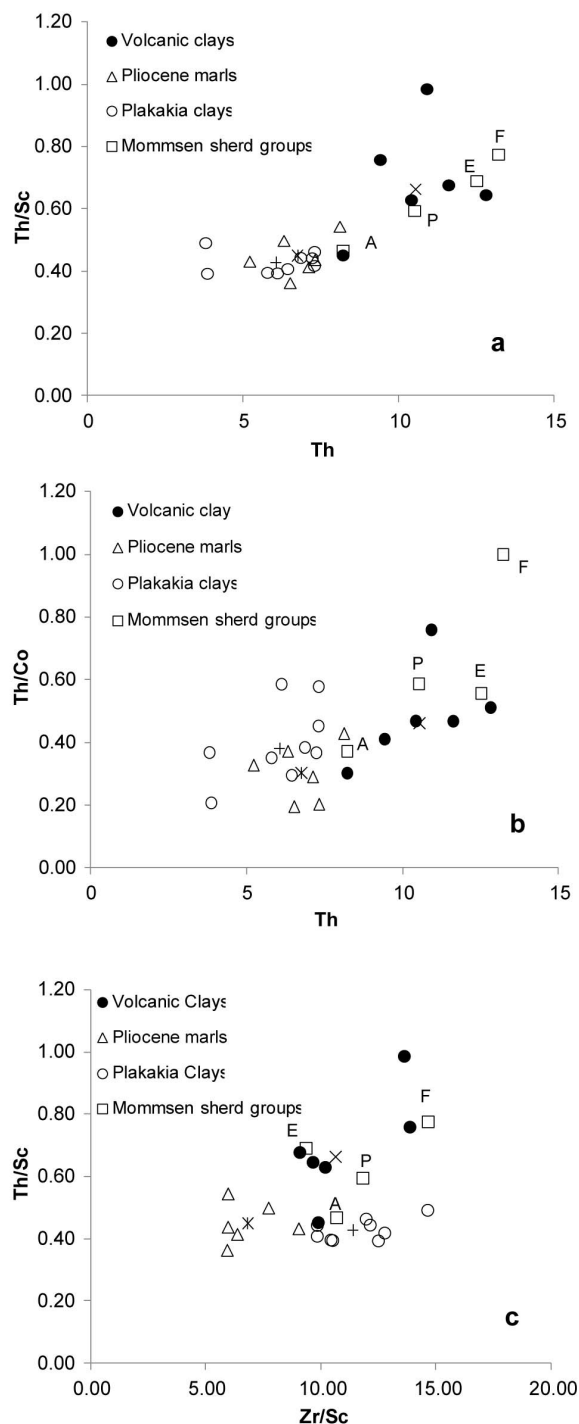


Figure 8. Trace-element concentration ratios of the Pliocene volcanic clay, the Pliocene marl, and the Plakakia clays (Hein *et al.*, 2004). (a) Th/Sc vs. Th; (b) Th/Co vs. Th; (c) Zr/Sc vs. Th/Sc. The trace-element composition from the A, E, F, and P groups of the Aeginetan sherds (Mommsen *et al.*, 2001) are plotted as solid squares with the Pliocene volcanic clay. + = mean composition of the Plakakia clays, x = mean composition of the Pliocene volcanic clay and * = mean composition of the Neogene marls. See text for discussion.

in bulk composition between rocks, because Th is an incompatible element in igneous processes, whereas Sc, Co, and Ni are compatible elements and are transported in terrigenous sediments during sedimentary processes (McLennan *et al.*, 1993). The Zr/Sc ratio is also indicative of zircon enrichment, with Zr being present in zircon and Sc, while not hosted in zircon, is indicative of provenance. The Pliocene volcanic clays are separated from the Pliocene marls by having greater Th/Sc and Zr/Sc ratios. The Plakakia clays in general have similar Th/Sc and Th/Co ratios to the Pliocene marls suggesting a common provenance (Figure 8a,b). The Zr/Sc ratio is greater, however, indicating a larger zircon content in the Plakakia clays (Figure 8c), in accordance with the reported heterogeneity of the Pliocene marls (Benda *et al.*, 1979). The Mommsen sherd groups plot in the same area as the Pliocene volcanic clay, with sherd group A plotting at the boundary with the plotted areas of the Plakakia clays and the Pliocene marls. The volcanic clay sample, A83, has smaller Th/Sc and Th/Co ratios than the remaining volcanic clay samples and plots very close to sherd group A, confirming that the volcanic clay is also geochemically heterogeneous.

The Pliocene volcanic clay is significantly enriched in REE compared to the Pliocene marl samples, as indicated in the chondrite-normalized plot (Figure 9). The Pliocene volcanic clay has a greater Ce/Yb ratio

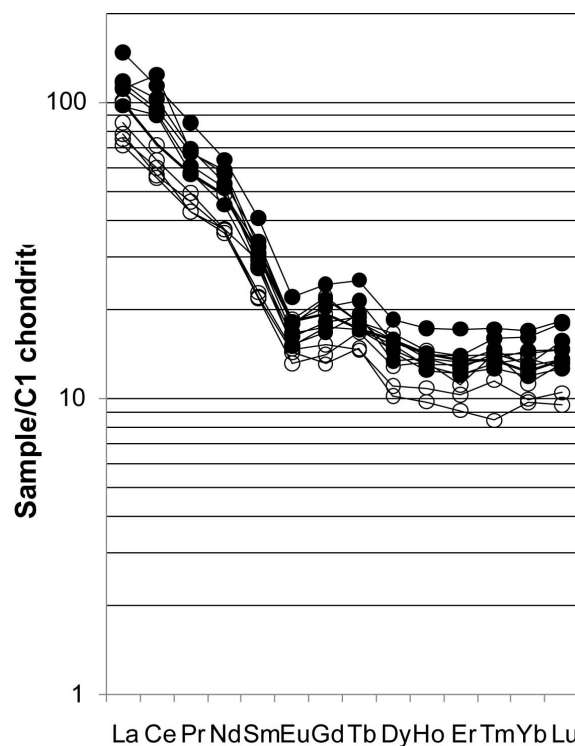


Figure 9. Chondrite-normalized REE plots of the Pliocene volcanic clay (black circles) and the Pliocene marl (open circles). See text for discussion.

Table 2. Chemical compositions of the A, E, F, and P chemical groups of Mommsen *et al.* (2001), and the Pliocene marls from the Plakakia area (Hein *et al.*, 2004).

	Mommsen Aeginetan sherd Groups				Marls from the Plakakia area					
	A	E	F	P	Plaka1	Plaka2	Plaka3	Plaka7	Plaka8	Plaka9
Concentrations (%)										
Ti	0.39	0.41	0.35	0.40	0.23	0.26	0.18	0.17	0.22	0.28
Fe	4.15	3.61	4.09	5.03	2.96	1.70	3.26	1.43	3.16	3.62
Ca	11.00	8.50	3.20	3.70	10.40	22.60	9.80	25.20	10.30	8.00
Na	1.04	1.28	1.90	1.70	1.08	0.49	0.69	0.45	1.23	1.58
K	1.98	2.37	1.89	2.04	0.98	0.65	1.29	0.58	1.35	1.26
Concentrations (ppm)										
Ba	306	387	540	630	114	110	128	30	98	114
Ni	332	255	58	89	284	187	354	149	288	347
Cr	402	322	71	126	401	215	407	175	397	470
Sc	16.1	14	14.8	20.3	11.4	7.2	13.7	5.6	12.7	12.6
Zn	90	86	73	84	62	35	74	33	73	76
As	9.3	8.4	7.5	4.7	4.2	1.7	5.2	1.3	10.8	2.2
Sb	0.77	0.64	0.36	0.50	0.54	0.29	0.75	0.27	0.79	0.65
Co	20.3	17.4	11.5	20.6	12.9	13.7	12.7	7.5	10.2	14.6
Cs	5.69	5.79	4.77	5.54	4.15	2.69	5.4	2.43	6.14	5.91
Hf	4.06	4.18	5.35	5.39	2.98	1.80	3.34	1.64	3.25	3.28
Rb	74	84	83	97	47	32	63	27	68	61
Ta	0.65	0.66	0.80	0.87	0.43	0.27	0.56	0.23	0.55	0.48
Th	7.55	9.69	11.50	12.10	4.53	2.84	5.75	2.76	5.90	5.61
U	2.14	2.15	1.67	1.93	1.20	0.83	1.51	0.59	1.51	3.67
W	n.a.	n.a.	n.a.	n.a.	1.13	0.78	1.07	0.66	1.39	1.40
Zr	172	131	217	240	119	90	175	82	152	153
La	22.2	24.1	26.7	28.6	16	12.5	15.9	13	17.3	17.5
Ce	46.1	48.6	60.8	63.5	31.2	22.8	36.1	24.4	33	35.1
Nd	20	19.6	21.5	25	7.9	9.3	12.8	8	14.3	19.2
Sm	3.8	3.62	4.43	4.55	2.69	1.76	2.73	1.59	2.82	2.93
Eu	0.94	0.96	1.12	1.16	0.73	0.53	0.75	0.49	0.76	0.74
Tb	0.57	0.57	0.64	0.66	0.52	0.41	0.47	0.35	0.51	0.53
Yb	2.3	2.23	2.58	2.67	1.94	1.55	1.78	1.35	1.79	0.26
Lu	0.35	0.35	0.39	0.43	0.29	0.22	0.28	0.18	1.89	0.28

n.a. = not available.

than the Pliocene marl (Table 1). The Plakakia samples have *REE* concentrations similar to the Pliocene marl samples, in agreement with the common provenance of the two sediments (Tables 1, 2). The enrichment of *REE* in the volcanic clay is due partially to dilution from calcite, but it also reflects differences in the non-carbonate sources. This is because the Pliocene volcanic clay samples A62 and A58U, which are rich in CaO, have greater abundances of *REE* (especially of the *LREE*) than the Pliocene marls with comparable CaO contents (Table 1). As mentioned previously, the *REE* data have been recalculated on a volatile-free basis. Hence, the lower abundance of *REE*, especially the light *REE* of the Pliocene marl samples, is partly attributed to the contribution of the ultrabasic component, as indicated by the presence of serpentine and talc. The *REE* concentrations of the Pliocene volcanic clay samples, after correction for dilution by calcite, are comparable to those of the volcanoclastic dacitic volcanic rocks of the island (Tables 1, 3).

Table 3. *REE* concentrations (ppm) of the Aeginetan dacitic volcanoclastic flows.

	Aeginetan dacitic epiclastic flows and altered dacites			
	A76	A81A	A81B	C5
La	20.7	30.4	25.1	27
Ce	46.5	75.3	59.4	48.9
Pr	4.42	7.2	5.66	5.65
Nd	17.2	28.1	22	22.9
Sm	3.3	5.7	4.5	4.3
Eu	0.81	1.06	1.04	0.98
Gd	3.23	4.5	3.72	3.56
Tb	0.55	0.86	0.66	0.52
Dy	3.18	4.45	3.61	3.16
Ho	0.65	0.83	0.7	0.66
Er	2	2.53	2.1	1.85
Tm	0.29	0.41	0.36	0.29
Yb	1.97	2.76	2.08	2.04
Lu	0.34	0.47	0.37	0.34

DISCUSSION

The Pliocene volcanic clay as a possible source of the Aeginetan ceramics

The two clay-rich sedimentary horizons present in the northwestern part of Aegina display distinct mineralogical and geochemical characteristics which reflect different sources and depositional environments. The Plakakia clays (Hein *et al.*, 2004) are actually Pliocene marls as shown in the previous section (*cf.* Tables 1, 2), in agreement with the suggestion of Gauß and Kiriatzi (2011) and this is reflected in the mineralogical and geochemical signatures of the sediments, which display different patterns (Figures 7–9). This evidence does not address the issue of which of these sediments was the source for ancient Aeginetan Ware, however. That question requires a comparison of the geochemistry and mineralogy of selected Aeginetan Ware sherds with the source-clay data.

The different *REE* patterns and the concentration ratios of the two sediment types studied have been utilized as part of the compelling evidence that shows that the Pliocene volcanic clay was the main raw material used for the fabrication of Aeginetan ceramics in the Bronze Age represented by the A, E, F, and P groups of Mommsen *et al.* (2001) (Figures 8, 10). The *REE* of the sherds derived from different types of ceramics plot in the same field as the samples from the Pliocene volcanic clay (Figure 10a). The *REE* geochemical characteristics of the Neogene marls (Figure 10b) do not match those of the ceramic articles for groups A, E, F, and P in the database of Mommsen *et al.* (2001). According to their trace-element composition, the Aeginetan sherds of groups E, F, and P (Mommsen *et al.*, 2001) have comparable affinities with the Pliocene volcanic clay and are distinctively different from the Pliocene marls, including the Plakakia clays of Hein *et al.* (2004). The comparison with the existing data of Mommsen *et al.* (2001) for Aeginetan sherd material demonstrates that, at least from a geochemical point of view, the main source material for Aeginetan Ware might have been the Pliocene volcanic clay. The *REE* data suggest that the Pliocene volcanic clays might have been the raw materials used for the manufacture both of the fine- and the coarse-grained Aeginetan ceramics (Figure 10a).

The Aeginetan sherds of group A (Mommsen *et al.*, 2001) plot separately from the other three groups, in the margin of the plotting area of the volcanic clay samples and in contact with the Pliocene marls and the Plakakia clays (Figure 8). Moreover, the Th/Sc and Th/Co ratios of group A sherds are comparable to those of the Plakakia clays and sample A83 of the volcanic clays. This indicates that the source materials of this sherd group might either be a mixture of the volcanic clay and Pliocene marl at a ratio of ~0.3:0.7 to ~1:1, considering the average compositions of the sediment types (Figure 8), or it could be a volcanic clay with composi-

tion similar to that of sample A83. The suggestion of mixing between the Pliocene marls and a small amount (up to 20%) of volcanic clay was invoked by Gauß and Kiriatzi (2011) for FG2 sherds in that study, which were considered to be equivalent to Mommsen's sherd groups A and E. Although the mixed-sources scenario may be valid, however, it has three shortcomings. First, the sherd group E of Mommsen *et al.* (2001), included in the FG2 sherds (Gauß and Kiriatzi, 2011), clearly has

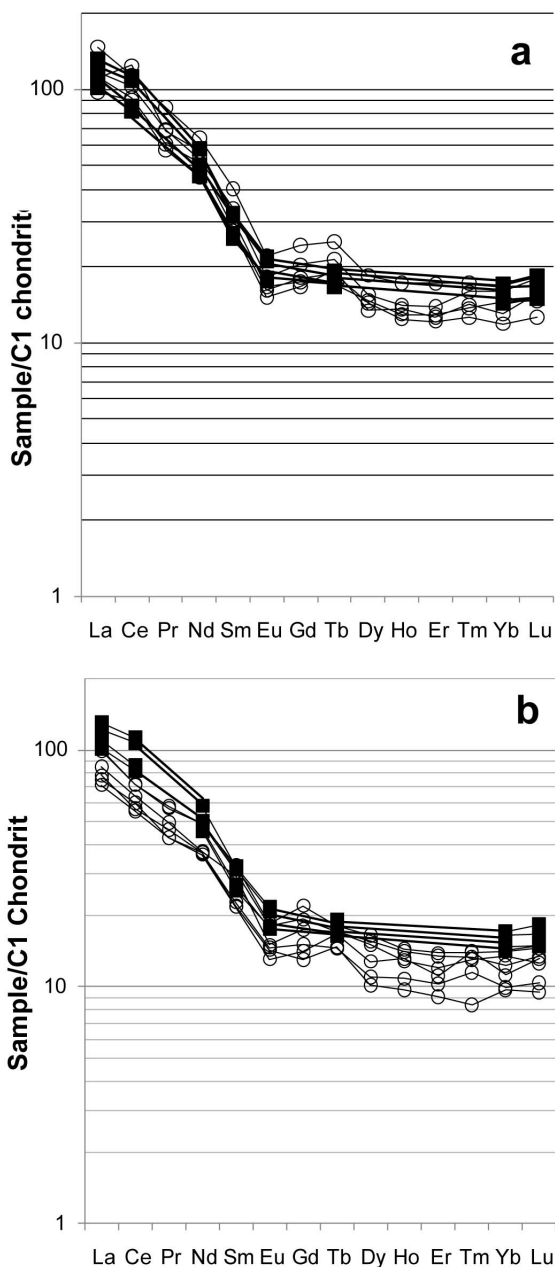


Figure 10. Chondrite-normalized *REE* plots of the Aeginetan sherd groups A, E, F, and P of Mommsen *et al.* (2001) (solid squares) and (a) the Pliocene volcanic clay and (b) the Pliocene marl. See text for discussion.

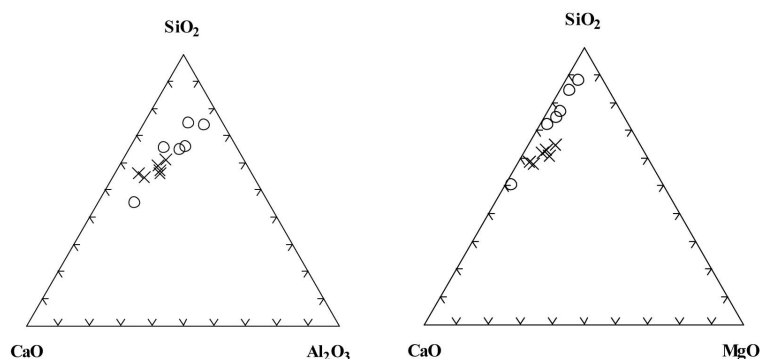


Figure 11. SiO_2 -CaO- Al_2O_3 and SiO_2 -CaO-MgO plots for the Pliocene volcanic clay (\circ) and the Pliocene marl (\times). See text for discussion.

geochemical affinities typical of the Pliocene volcanic clays (Figure 8, 10). Second, volcanic clay samples are found with geochemical characteristics similar to sherds of group A (e.g. sample A83). Third, if there had been mixing then the group A sherds would have had coarse volcanic fragments, which is not the case. This suggests that the volcanic clay would have been processed possibly by levigation prior to mixing. Hence, use of the Pliocene marls, or their equivalent Plakakia clays, might not have been necessary, at least as main components of the ceramic mass, and also for the sherds of group A.

Mineralogy is a less sensitive tool for discrimination purposes, because in most sedimentary basins clastic sediments are supplied from common precursor rock types. The role of mineralogy may become more significant if volcanic or chemical sediments are important components of the sediments. In such cases, the sources of non-clastic sediments should be recognized. However, the mineralogical composition of the raw materials affects the firing characteristics and the

properties of the ceramics, with the presence or lack of calcite being a significant controlling parameter (Peters and Iberg, 1978; Cultrone *et al.*, 2001; Traoré *et al.*, 2003; Trindade *et al.*, 2010). The Pliocene volcanic clay yielded end products without a significant degree of melting and abundant high-temperature phases after firing up to 1050°C (Shriner *et al.*, in press). Firing of the Pliocene marls produced significant amounts of melt and deformation of the ceramics after prolonged firing at $\sim 1000^\circ\text{C}$ (C. Shriner, unpublished data).

The two sediment types plot in the same areas in the SiO_2 -CaO- Al_2O_3 and the SiO_2 -CaO-MgO ternary diagrams, with the Pliocene marl samples plotting closer to the CaO corner due to their greater CaO contents (Figure 11). At firing temperatures of $>800^\circ\text{C}$ the Pliocene marl samples yield end products with similar Ca-silicates to the Pliocene volcanic clay (diopside and gehlenite). However, at lower temperatures, calcite disappears at 700°C after 3 h of firing in the Pliocene marls (Figure 12), whereas, in the Pliocene volcanic clay it persists up to 900°C (Shriner *et al.*, in press). The

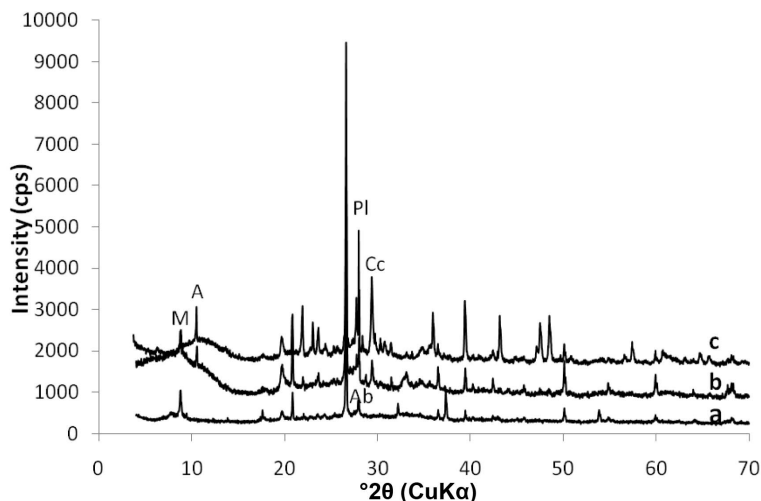


Figure 12. XRD traces of (a) Pliocene marl fired at 700°C for 3 h; (b) Pliocene volcanic clay fired at 700°C for 3 h; and (c) Aeginetan sherd from Felten/Berger collection fired at low temperature. Note the striking similarity between traces b and c. See text for discussion. A = amphibole, M = mica, PI = plagioclase, Ab = albite, Cc = calcite.

mineralogical composition of the Bronze Age Aeginetan ceramics fired at low temperatures is comparable with the Pliocene volcanic clay, not the Pliocene marl, both fired at 700°C (Figure 12). It seems that the Aeginetan ceramists were using the Pliocene volcanic clay for its special firing properties, and were targeting special temperature-time ranges, which were different for the coarse- and fine-grained ceramics (Shriner *et al.*, in press).

Comparison of the geochemical correlation with existing statistical methods

The geochemical correlation of the Pliocene volcanic clay and the Pliocene marls involved a correction for dilution of calcite by recalculation of the major and trace-element concentrations for LOI, so that the geochemical features of the different sediment types could be comparable. Correction is only partial, for two reasons, however. First, it accounts only for the CO₂ but not for the CaO of the calcite and dolomite, the latter being present in the Pliocene marls. Second, LOI includes the weight loss due to dehydroxylation of phyllosilicates including the clay minerals. The Pliocene marls are richer in clay minerals than the Pliocene volcanic clay. Therefore, part of the greater LOI is due to the greater H₂O loss during dehydroxylation, which partly counterbalances the greater CaO content of the marls due to carbonates. With the existing data it is not possible to estimate the relative contribution of the dehydroxylation of phyllosilicates to the LOI.

The methods used so far for correction of calcite dilution for grouping of pottery sherds use the concentration ratios instead of elemental concentrations (Buxeda i Garrigos, 1999) and the “best relative fit factor” (Beier and Mommsen, 1994; Mommsen, 2004). Although concentration ratios overcome the problem of calcite dilution, they reduce the available degrees of freedom in the system and hence reduce the significance of the geochemical information available for discrimination/correlation purposes, in the same manner as two lines having the same slope may be parallel and may not coincide. Moreover, the ratios may lead to erroneous assumptions when applied to distinguish geologic formations in a sedimentary unit. Indeed, different abundances of two hypothetical elements A and B in two distinct rock types may yield comparable elemental ratios and, hence, misleading results. Careful selection of concentration ratios is necessary, therefore, which in the case of sedimentary formations should have geochemical/geologic significance, such as those frequently used in diagrams for analysis of sedimentary processes and provenance analysis of sedimentary rock units at a large scale (*e.g.* McLennan and Taylor, 1991; McLennan *et al.*, 1993). In the present study the use of carefully selected concentration ratios helpful in understanding geologic processes (Th/Sc, Th/Co, Zr/Sc) provided indications of the use of the Pliocene volcanic clay as

the main source of Aeginetan ceramics. The results are meaningful because the two main sediment types in Aegina have different origins and geotectonic affinities (volcanic *vs.* clastic). Scandium has been used to normalize geochemical data prior to multivariate analysis in archeometric pottery studies (Dias and Prudencio, 2008), although the observed trends and deviations from these trends were not addressed in detail. As quartz and calcite are essential components of the source rocks in Aegina, corrections during provenance analysis are necessary only if there is evidence that they are present as tempers in the sherds, which is not the case. Detailed petrographic analysis has shown that the calcite nodules in FG1 Aeginetan ceramics are pedogenic (Gauß and Kiriatzi, 2011), *i.e.* mineralogical constituents of the sediments, in accordance with the present study (Figure 3).

Similarly the best relative fit factor may not yield reliable conclusions if a significant proportion of the calcite or quartz present in the sherds is not temper. Hein *et al.* (2004) applied a best relative fit factor to the elemental composition of sherd groups A, E, F, and P of Mommsen *et al.* (2001) and concluded that the Plakakia clays have geochemical similarity with the group A sherds, but not with sherds from groups E, F, and P. After application of the same statistical approach to the Pliocene volcanic clay the concentrations of all elements other than Na and Sb showed differences of <2σ. The Na and Sb showed differences slightly greater than 2σ (Figure 13a). Likewise, in the Pliocene marls, all elements other than Hf showed differences of <2σ. Following the reasoning of Hein *et al.* (2004), all three sediments could be considered as the raw materials for group A sherds. The Pliocene volcanic clay displays very good geochemical similarity with sherd groups E, F, and P, suggesting that the Pliocene volcanic clay could well be the source of all the Aeginetan sherds. Indeed in the case of group E the concentrations of all elements except for Na and Sb showed differences of <2σ (Figure 13b). In the case of the P group the concentrations of all elements except for Na and Sb showed differences of <2σ (Figure 13c). Finally, in the F-group sherds the concentrations of all elements except for Na showed differences of <2σ (Figure 13d). The difference observed for Na and Sb was also valid for the Pliocene marls, which are equivalent to the Plakakia clay, and is attributed to analytical constraints, *i.e.* the analytical method used probably underestimated the Na and Sb contents of the rocks.

Application of the 2-tailed t-test to the Pliocene volcanic clay data and the fitted group A, E, P, and F data as hypothetical means showed a 5% level of significance for most elements. A 1% level of significance was observed for K, Ni, U, and Zn in the A group, for U and Zn in the E group, for As, Ni, and Cs in the P group and for Cs in the F group. For Na and Sb the test showed significant differences in all groups due to the

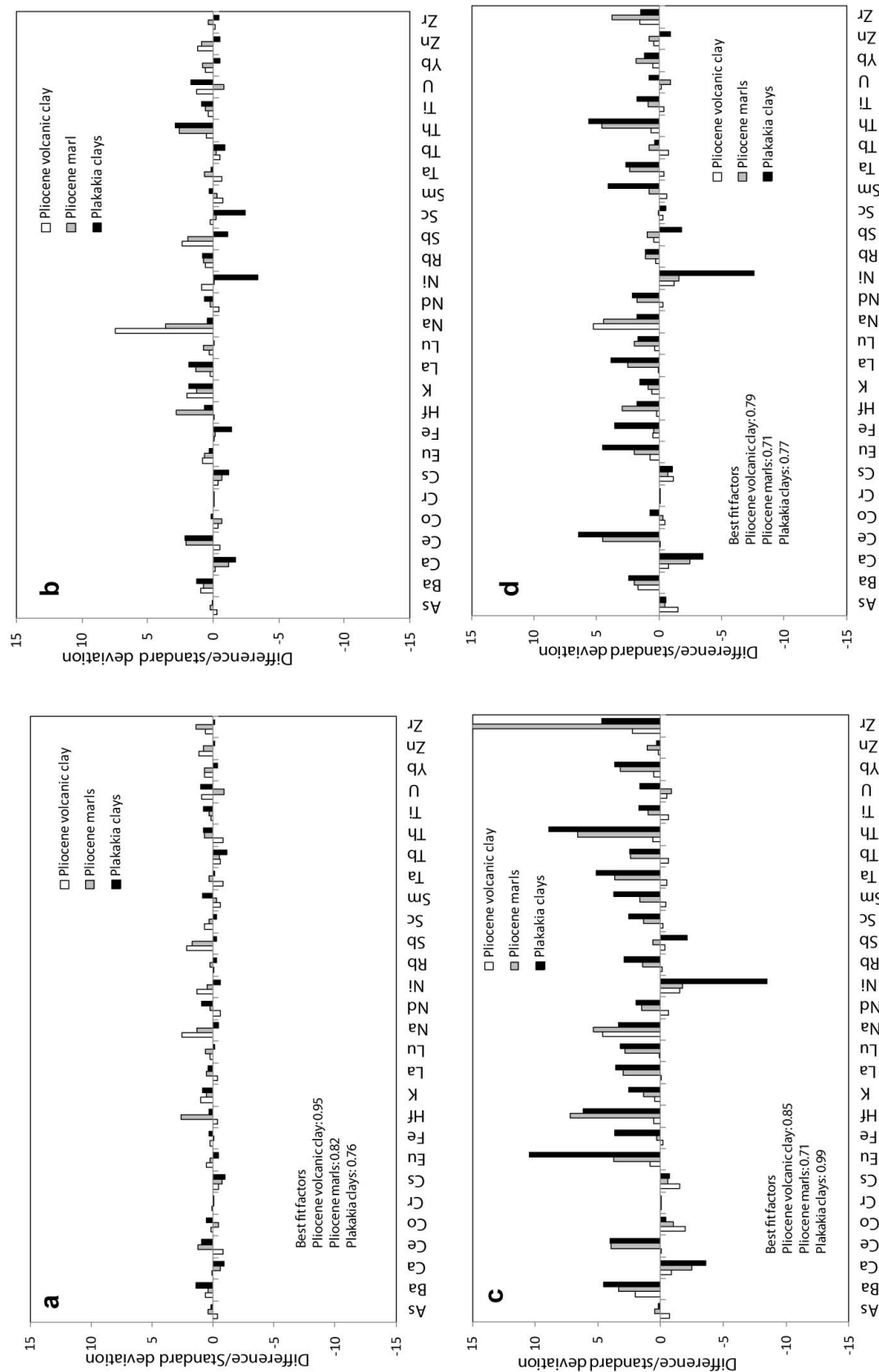


Figure 13. Comparison of chemical compositions of the Aeginetan sherds: (a) group A; (b) group E; (c) group P; and (d) group F (Mommssen *et al.*, 2001) and the chemical composition of the Pliocene volcanic clay, the Pliocene marls, and the Plakakia clay (Hein *et al.*, 2004). The diagrams display the differences between the elemental concentrations ($x_{\text{sherds}} - x_{\text{clay}}$) normalized over the total standard deviation ($(\sigma_{\text{sherds}}^2 + \sigma_{\text{clay}}^2)^{1/2}$). The best-fit factors were applied to correct the shifts of the trace-element compositions due to firing of the raw materials. The best-fit factors for the Plakakia clays are from Hein *et al.* (2004).

analytical constraints noted previously. Finally, the test showed significant differences between the sherds and the Pliocene volcanic clay for Ba, Ni, and Zr in groups P and F. The different Ba, Ni, and Zr contents of the F and P groups of Mommsen *et al.* (2001) relative to the Pliocene volcanic clay are attributed to the presence of a slightly different volcanic component, the possible product of a different volcanic eruption from the same volcanic centre. Hence, application of the best relative fit factor (Beier and Mommsen, 1994) yielded satisfactory results for sherd groups E, F, and P as it excluded the Plakakia clays as a possible source of these sherds (Hein *et al.*, 2004). Nevertheless, it did not yield an unequivocal conclusion about the source of group-A sherds because, apart from the Pliocene volcanic clay, both the Plakakia clays and their equivalent Pliocene marls could also be considered as source materials.

As an independent test of evidence, canonical discriminant analysis and principal component analysis (PCA) were applied to identify any possible relationships between the three sedimentary horizons under consideration, *i.e.* the Pliocene volcanic clay, the Pliocene marls and the Plakakia clays, with the A, E, F, and P sherd groups of Mommsen *et al.* (2001). Both analyses were performed with the *SYSTAT* version 8.0 code. Geochemical fingerprinting with multivariate statistical methods has been used to distinguish between or to correlate clay horizons such as bentonites, which may extend over large areas (Huff *et al.*, 1991) and can be used in exploration for economic clay deposits (Christidis, 2001).

Nineteen trace elements (As, Ba, Ce, Co, Cr, Cs, Hf, La, Lu, Nd, Ni, Rb, Sc, Sm, Ta, Th, U, Zn, and Zr) and one minor element (Ti) were selected for the analysis (variables), based on the availability of data in Mommsen *et al.* (2001) and Hein *et al.* (2004) and their geochemical affinity (compatible *vs.* incompatible during igneous processes). The plot of the discriminant scores, using the first two discriminant functions, is shown in Figure 14a. The boundaries of the different fields of the horizons correspond to the lines of equidistance between group means. The first two discriminant functions explain 94.9% of the total variance among the samples. The three different sedimentary horizons are clearly separated and the A, E, F, and P sherd groups of Mommsen *et al.* (2001) plot very close to the Pliocene volcanic clays (data not shown). Separation of the sherd discriminant scores and the scores of the Neogene marls and the Plakakia clays occurs along both discriminant functions (Figure 14a). Similar results were obtained from the plot of the scores for the first two principal components obtained from the PCA (Figure 14b). In this analysis the first principal component accounts for 64% of the variance of the data and the second component for 18% of the

variance. The Pliocene marls and the Pliocene volcanic clays clearly plot in the same area, separately from the Pliocene volcanic clays. The A, E, F, and P sherd groups of Mommsen *et al.* (2001) plot with (groups A and E) or close to (groups P and F) the Pliocene volcanic clays.

Nevertheless, although the canonical discriminant analysis clearly indicates that the Pliocene volcanic clays might be the only source for the A, E, F, and P sherd groups of Mommsen *et al.* (2001), the Plakakia clays plot as a clearly different horizon from the Pliocene marls, which should not be the case. Moreover, in the PCA, the P and F sherd groups of Mommsen *et al.* (2001) plot at the margins of the Pliocene volcanic clays plotting area, although detailed petrographic analysis has shown that they have typical Aeginetan volcanic fabric (Gauß and Kiriati, 2011 and the present study). These remarks indicate that statistical analysis of the chemical data alone may not be sufficient for similar studies, because they do not take into account compositional variations within geologic formations, and underline the necessity for thorough geologic-

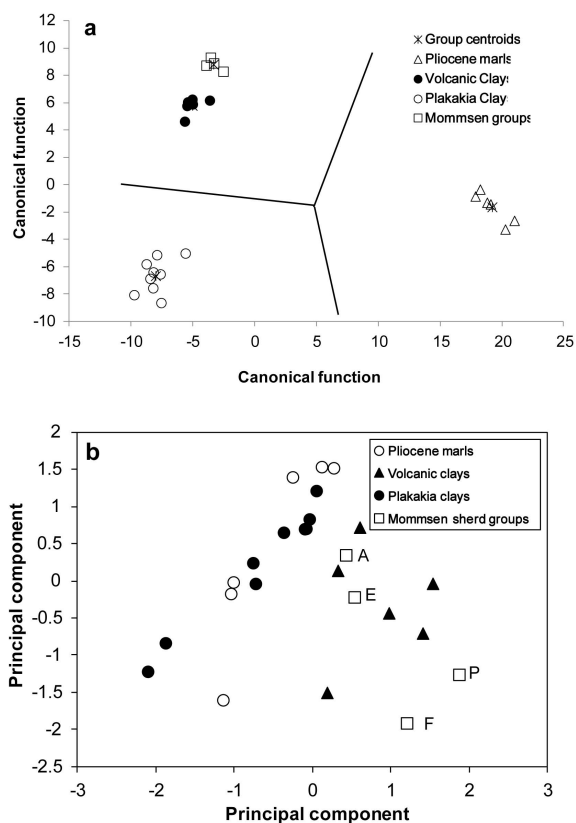


Figure 14. (a) Canonical discriminant plots of the samples using the first two discriminant functions. The plot clearly separates the three sediment types. See text for discussion. (b) Principal component analysis plots of the scores for the first two principal components. The plot separates the Plakakia clays and the Pliocene marls from the Pliocene volcanic clay. See text for discussion.

mineralogical-geochemical investigation of the potential source rocks of ancient ceramics during provenance analysis, which is discussed below.

Development of an integrated geoarcheological provenance model and approach

The characterization of ceramic articles with petrographic techniques and chemical analysis of major and especially trace elements are important tasks in modern archeological science (Middleton and Freestone, 1991; Mommsen *et al.*, 1994; Day and Kiriatzi, 1999; Demirci *et al.*, 2004; Riederer, 2004; Josephs, 2005; Alden *et al.*, 2006; Stoltman, 2006; Abbott *et al.*, 2008; Mommsen and Japp, 2009; Braekmans *et al.*, 2011; Gauß and Kiriatzi, 2011). The subdiscipline which is responsible for provenance studies of ceramic artifacts is termed geoarcheology. The field of geoarcheology has evolved into a scientific discipline that utilizes a variety of elaborate analytical techniques (Brothwell and Pollard, 2001 and references therein).

Usually, a geoarcheological approach focuses on the characterization and study of ancient pottery production, distribution, and consumption rather than the importance of the raw materials used. Chemical analysis by itself is widely accepted as being adequate for provenancing pottery articles (*e.g.* Mommsen, 2004). However, the more sophisticated “integrated methodology” (Tite, 1999), which proposes a combination of petrographic examination and chemical analysis of ceramic sherds with conventional archeological methods, has also been considered. The latter approach suggests determination of the ceramic production center, investigation of the regional geology where the pottery originated, and collection of representative raw materials (Tite, 1999). Although the aforementioned studies assist in reconstructing the technology used in pottery production and in understanding the social relationships and changes in prehistoric and historic periods, provenancing of raw materials used to fabricate the ceramics is based mainly on petrographic observations and to a lesser degree on grain-size analysis of quartz temper or analysis of heavy minerals present in the sherds. In this sense they are ‘end-product oriented’ rather than ‘raw-material oriented’. This difference in approach affects the interpretation of technological changes and social implications (Tite, 1999 and references therein).

Provenance studies in geoarcheology are based on the assumption that the chemical and physical characteristics of ceramics must reflect the physical and chemical characteristics of the clay from which they were fabricated. It is important, therefore, to establish safe criteria that will enable direct comparison of the possible raw materials with ceramics data. In most cases thus far, these criteria are geochemical (Dias and Prudencio, 2008; Ma *et al.*, 2012) or a combination of geochemical and petrographic criteria (Gauß and Kiriatzi, 2011). Reliable criteria for provenance of raw materials used in

the fabrication of ceramics have not been proposed to date, however. Several of the existing approaches, integrated or not, focus on the provenance of the ceramic articles rather than on the raw materials employed (Tite, 1999 and references therein; Mommsen, 2004; Li *et al.*, 2005; Braekmans *et al.*, 2011; Dias *et al.*, 2013, among many others). In studies where provenance analysis is considered, either the results which used *REE* are qualitative (Ma *et al.*, 2012) or the geochemical differences between the ceramics and the raw materials are simply attributed to the inhomogeneity of the latter (Prudencio *et al.*, 2006), or they do not refer directly to ancient ceramics but record geochemical differences between sediments (Marques *et al.*, 2010) and/or their fired products (Trindade *et al.*, 2010) and consider their possible use as raw materials in ancient ceramics. The proposed integrated model, which is valid for clay raw materials used in the production of ceramics, comprises five criteria, which all should be considered, namely: geographic/geologic, petrographic, mineralogical, mineral-chemical, and geochemical criteria. These criteria are complementary and interrelated.

The geographic/geologic criterion requires that the raw material should have been close to the main ceramics production center. From an archeological perspective the ancient production sites should have been built close to the clay sources so that the craftsmen had access to a constant supply of raw materials in order to make proper blends if necessary. Ceramic articles were used in everyday life. Hence, continual production was necessary. In contrast, raw materials that played different roles, such as precious metals or metals used for production of weapons (*i.e.* ‘strategic’ raw materials), could be transported from greater distances or imported. On Aegina, the main production and exporting center for ceramics was the archeological site of Kolonna (Figure 1b). Therefore, the source of the clay raw materials is expected to have been in the vicinity of the site. Both the Pliocene volcanic clay and the marls crop out within a few km of Kolonna, fulfilling the geographic criterion. Moreover, the location of the Pliocene volcanic clay provides reliable answers to the questions about the thickness of the volcanic clay (Gauß and Kiriatzi, 2011): the mechanism of eruption allowed transportation and deposition of the volcanic ejecta mainly toward the north in seawater, leading to 0.4–4 m-thick pyroclastic deposits, which would sustain the production of ceramics for 2000 years. The thickness of these pyroclastic deposits is not extensive in the E-SE part of the island, either due to the mechanism of the eruption or/and due to the depositional environment in that area, which was terrestrial. This is indicated by the lack of Poros marly limestones in the Portes area (Figure 1). Finally, the presence of Poros marly limestone is associated with the formation of pedogenic calcite nodules and palygorskite. The existence of pedogenic calcite is ubiquitous in the Aeginetan ceramics (Gauß and Kiriatzi, 2011).

The textural variations, which were mentioned in the results, and by default, the chemical variations among coarse- and fine-grained Aeginetan Ware sherds, may reflect differences in the particle size and the transport mechanisms of the original volcanic ash (Christidis *et al.* in press). Thus, coarser materials were deposited closer to the volcanic center of Skotini and finer were transported further away from the volcanic vent. This is important geographic evidence for the archeological community. The sorting of the volcanic material during transport may explain the geochemical differences among the volcanic clay samples (*e.g.* sample A83). The presumed archeological theory (Lindblom, 2001 and references therein) has been that the Aeginetans placed a coarse ‘temper’ (presumably a local andesite) in a fine-grained clay (presumably a marl, adjoining the settlement of Kolonna). An alternative scenario for mixture of two sources has also been proposed at least for some ceramic groups (Gauß and Kiriati, 2011). The possibility of an alternative source or that the ‘temper’ might have been a natural component of the clay deposit has not been considered. The existence of reference materials renders the issue less clear. If this was not a mixture with a generic marl, the use of a clay source other than that presumed needs to be suggested. It is completely different social behavior for a group of potters to (1) intentionally add a temper to a pre-existing clay, than (2) to look for a natural clay deposit that fulfills their functions as potters and the demands of a changing market and environment.

The petrographic criterion can assist in distinguishing potential source materials according to their fabric, as volcanic, sedimentary or metamorphic (Tite, 1999; Braekmans *et al.*, 2011; Gauß and Kiriati, 2011) (Figure 4a,b). Betancourt and Myer (in Zerner, 1986) reported the original petrographic sample for “Aeginetan Ware” and named the fabric the “Volcanic Ash Group”, but they did not differentiate between coarse and fine ceramic samples. Their sherd samples of both the coarse- and fine-grained ‘Aeginetan Ware’ had a comparable volcanic matrix or groundmass and attested to a single source. Petrographic analysis in this study confirms that fine- and coarse-fabric groups of Aeginetan Ware consist of a fine-grained volcanic ash-like matrix that contains dispersed fragments of various igneous minerals (*e.g.* quartz, feldspar, and hornblende), as well as fragments of volcanic rock. However, use of the petrographic criterion as a single test of evidence for provenance has two main shortcomings. First, it does not prove that the raw material originated from Aegina. Textures similar to those of the Aeginetan rocks are observed in volcanic rocks from other volcanic centers of the SAVA, such as Methana and Poros which are close to Aegina. Second, if a volcanic rock was used as a non-plastic temper in clayey or marly sediment, as is often the case in ancient ceramics, then it might be difficult to distinguish the nature of the raw material, as

was also suggested for the fine-grained Aeginetan Ware (*e.g.* Gauß and Kiriati, 2011). Hence the petrographic criterion should be used cautiously and always in combination with other criteria.

Mineralogical and mineral-chemistry criteria are important tools for provenance analysis because they can assist in identification of the clay source and allow prediction of the high-temperature phases after firing. Microanalytical data of amphiboles in ceramic sherds from Aegina have been used to suggest a single source for Aeginetan pottery and to propose the establishment of trade routes in the area (Dorais and Shriner, 2002a, 2002b; Dorais *et al.*, 2004). The main difficulty in applying this criterion is the selection of suitable tracer minerals and the necessity for a large database with analytical data from the broader area for this mineral, in order to provide a reliable compositional range typical for the particular source rocks. For Aegina, amphiboles have proven to be reliable tracers, because they are chemically distinct from their counterparts in other volcanic centers of the SAVA (Dietrich *et al.*, 1988; Dorais and Shriner, 2002a; Brophy *et al.*, in press; <http://www.indiana.edu/~sava/>). The sherds contain hornblende with Na₂O and K₂O contents which are identical to their counterparts in the Aeginetan dacites and the Pliocene volcanic clay. Nevertheless, there is a partial overlap with the composition of the amphiboles from the volcanoes of Methana and Milos (Brophy *et al.*, in press; <http://www.indiana.edu/~sava/>), suggesting that the use of mineral chemistry alone as a provenance tool sometimes may not be conclusive. Feldspars can also be used as mineralogical tracers in the present study. The presence of different feldspars in the two sediment types (andesine and K-feldspar in the Pliocene clay *vs.* albite in the Pliocene marl) and the persistence of feldspar in fired products formed under low firing conditions (Figure 13) provide a significant mineral-chemical criterion for provenancing in Aegina. However, such a criterion would not be useful in other areas if the different sediments contain similar types of feldspars.

The geochemical criterion is relatively reliable and has been used and tested for stratigraphic correlation purposes (Huff *et al.*, 1991). Moreover, it has been used by Hein *et al.* (2004) to assign a clay source to the group-A sherds of Mommsen *et al.* (2001). The present authors consider that the geochemical criterion is a strong component of the model because it relies on the information provided by a large number of chemical elements, not on a single parameter. However, it must be used cautiously when there is indication of addition of tempers or mixing of raw materials from different sources. There are two ways to use the geochemical criterion: either (1) by direct comparison of the chemical composition of the materials or rocks in question using binary or ternary plots (Figures 7–11); or (2) by applying statistical methods, including multivariate

methods. The former approach is straightforward and may provide useful information if mixing of materials has not taken place, the number of rock units examined is limited, and the units have distinct chemical compositions. In both approaches the geochemical criterion must be used after correction for dilution by carbonates and quartz temper. In the present study the elemental concentrations were normalized on a volatile-free basis. The use of concentration ratios instead of simple element concentrations might assist in this regard (Dias and Prudencio, 2008), provided that suitable ratios with geochemical/geologic significance are selected (McLennan and Taylor, 1991; McLennan *et al.*, 1993). The statistical methods should be applied as a means of verification of the conventional geochemical approach (Figures 13–14). The selection of suitable chemical elements as tracers can assist in the recognition of the correct source. In the case of Aegina, the Pliocene volcanic clay is geochemically distinct from the Pliocene marls in terms of both major and trace elements, including the REE (Figures 7–11). In the present study, the geochemical criterion was conclusive for the source of the Aeginetan sherds.

Application of statistical methods may assist in a better separation of the possible clay source rocks, especially if several rock types are present (Figure 14). Alternatively, they may compare the average elemental concentrations between different populations (Figure 13, Hein *et al.*, 2004). Nevertheless, as statistical approaches are not always conclusive (*e.g.* Hein *et al.*, 2004), they may provide misleading results if analysis is not associated with detailed mineralogical study and geologic fieldwork, which will allow recognition of possible alternative clay sources. It may be useful to apply conventional binary or ternary geochemical plots for a rough estimation before applying statistical tools.

The aforementioned discussion clearly demonstrates that there is not a single criterion that may yield reliable results in ceramic provenance studies aiming at determination of the clay sources. Our approach is based on the combination of different criteria that complement each other and are interrelated.

CONCLUSIONS

A late Lower Pliocene volcanic clay unit, which was originally an ash deposit, was identified on Aegina Island, Greece. That volcanic unit has been differentiated from the underlying Lower Pliocene marl previously considered as the main source for Aeginetan Ware (Hein *et al.*, 2004), and has been shown to be the main raw material for Aeginetan Ware. In addition, an integrated approach that may contribute to reliable ceramic provenancing and processing analysis was proposed. The approach uses geographic, petrographic, mineralogical, mineral-chemical and geochemical criteria. All five criteria should be used together in any

successful provenance study, because each individual criterion, on its own, could lead to ambiguous conclusions. This approach showed that it is not necessary to assume admixture of different sources for the fabrication of fine-grained Aeginetan ceramics, suggesting that the role of Pliocene marls was probably limited, contrary to previous studies. Thus, the different textures in Aeginetan ceramics may well be explained either by selection of different sections of the same horizon having different particle-size distribution for fabrication of different ceramic styles or/and by use of approaches such as levigation to remove the coarse-grained fractions. The next step is to evaluate effectively the source clays to provide an estimate of the firing temperature of the ancient ceramics – this will be the subject of a future publication.

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