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A PRELIMINARY PROVENANCE STUDY OF MARBLE ARTEFACTS FROM AIANI, ANCIENT UPPER MACEDONIA, GREECE

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ABSTRACT. Preliminary results on the provenance study of ancient marbles from Aiani, ancient Upper Macedonia, Northern Greece are presented in this work. Several samples (both archaeological and modern) were collected and analysed using thermoluminesence (TL) and Environmental Scanning Electron Microscopy coupled with Energy Dispersive System (ESEM/EDX). Chemical, morphological and mineralogical features revealed by ESEM/EDX, combined with TL spectra of natural and irradiated samples, allowed us to make some preliminary suggestions on the origin of ancient marble artefacts. According to ESEM/EDX results, Tranovalto marbles situated just Southwards of Aiani, where some modern white marble quarries occur, could be the most probable origin. TL spectra do not reveal any clear differences, except that of higher intensity of the fresh marbles comparing to the intensity of the ancient ones. Thus, a more detailed analytical work, employing more samples and analytical techniques is proposed in order to achieve satisfactory results.

Introduction

Provenance study of ancient marbles provides useful archaeological information, regarding contact, trade and other activities during ancient times. It could also help in detection of modern forgeries or ancient copies of original works (Polikreti, 2007). Several analytical methodologies were employed for the sourcing of ancient marble objects. Micro-petrography, mineralogy (X-ray diffraction), chemical analyses (AA, INAA, ICP etc.), thermoluminescence (TL), cathodoluminescence (CL), electron spin resonance (ESR), stable isotopes of carbon, oxygen and strontium, Environmental Scanning Electron Microscopy (ESEM/EDX) are those mostly used (Archambeault, 2004; Brilli et al., 2005; Liritzis, 2007; Rapp, Hill, 2006). Yet, discriminating ancient marble quarries proved to be a very difficult task and in many cases unsuccessful.

Aiani is located approximately 20 km to the South of the city of Kozani, Western Macedonia (Greece). Aiani was within the region of the ancient Kingdom of Elimeia which, together with the rest of the Greek Kingdoms (Tymphaia, Orestis, Lyncestis, Eordaia, Pelagonia) constituted the ancient Upper (i.e. mountainous) Macedonia. The systematic excavations which began in 1983, have revealed the architectural remains of both large and small buildings, rich in small finds; and groups of graves and organized cemeteries dating from the Prehistoric to the Late Hellenistic period. The ancient city of Aiani is located on the imposing hill called Megali Rachi (i.e. Big Hill). Three large public buildings together with several private houses, rich in finds, have been excavated. The clusters of graves and the extensive cemeteries, which have been discovered and partly excavated around the ancient city, date from the Late Bronze Age to the Late Hellenistic Period. The excavations in the Archaic and Classical necropolis revealed twelve chamber-tombs, smaller cist-graves and numerous pit-graves. The occurrence of public and private buildings composes a picture of a well-organized city from the Late Archaic to the Classical period (early V-IV c. BC; the VI c. is attested by pottery). The city had direct cultural relations and exchange with the rest of Greece. At the same time it had its own workshops for pottery, terracotta and metals (Karamitrou-Mentessidi, 1989; 1993; 1997; 1999a; 1999b; 2001).

An attempt to source the ancient marble artefacts from Aiani, ancient Upper Macedonia, Northern Greece, was made in the present study. For this reason, several samples from archaeological statues and from modern marble quarries were collected and analysed by thermoluminescence and Environmental Scanning Electron Microscopy coupled with Energy Dispersive System (ESEM/EDX).

Sampling and analytical methodology

Statues made of white marble were chosen for the present study (Fig. 2). Samples were collected from the site, called Livadia, within the archaeological site of Aiani. However, these samples were not collected during a single period of excavation.

Scraped off material from a fresh side of these statues were sampled. Details of the sampled archaeological material are shown in Table 1. Moreover, fresh marble samples collected from modern quarries or recent outcrops, situated in the vicinity of the Aiani archaeological area were collected for analysis. Sampling sites are shown in Figure 1 and characteristics of these recent marble samples are shown in Table 1. It should be noted that despite the presence of recent good quality marble quarries and carbonate deposits to the South and to the East of Aiani, there is lack of evidence of ancient quarries in this region. It is possible that modern, large-scale quarrying techniques have obliterated the marble deposits exploited in ancient times.

For the ESEM/EDX analysis, a Philips QUANTA 200 Environmental Scanning Electron Microscope (ESEM), coupled with an Oxford INCA Energy 200 Energy Dispersive System (EDS) was used. Images were taken mostly in back-scattered electron (BSE) mode and, where appropriate, were supplemented with secondary electron (SE) mode.

The thermoluminescence (TL) measurements of powdered aliquots of the marble samples were performed using an automated Risø TL system model TL DA-12. This reader is provided with an EMI 9635 QA photomultiplier, and the emission was observed through a blue filter (a FIB002 of the Melles-Griot Company) where the wavelength is peaked at 320-480 nm. Full-width at half-maximum (FWHM) value is 80716 nm, and peak transmittance (minimum) is 60%. It is also provided with a ^{90}Sr/^{90}Y source, with a dose rate of 0.020Gy s^{-1} calibrated against a ^{60}Co photon source in a secondary standards laboratory. All the TL measurements were performed using a linear heating rate of 5º Cs^{-1} from room temperature up to 550ºC, in a N_2 atmosphere. Several aliquots of 5 mg of marble sample were used for each measurement. The incandescent background was subtracted from the TL data.

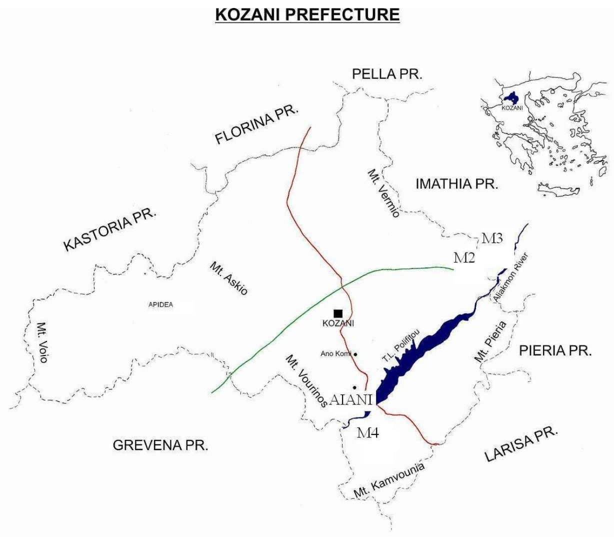

Fig. 1. Map showing Aiani's archaeological site (where samples 7474, 10519, 10537 and 10545 from ancient marble statues were taken), along with sampling locations of material from recent marble quarries (M2-Zoodochos Pigi, M3-Veria, M4-Tranovalto)

Fig. 2. Characteristic statue of a bearded man, dated to the V c. BC; sample 10545 was scraped off from a clear surface of this statue

Table 1
Characteristics of the seven marble samples (four ancient and three recent) analysed in this study

Sample	Description
10519	Scraped off material from a plinth of a statue (V c. BC)
10537	Scraped off material from the upper or lower limbs of a statue (V c. BC)
10545	Scraped off material from the head of a bearded male statue (V c. BC)
7474	Scraped off material from the head of a female statue (V c. BC)
M2	Fresh fragments from an outcrop near Zoodochos Pigi, on the national road Kozani-Veria
M3	Fresh fragments from Veria, recent marble quarry
M4	Fresh fragments from Tranovalto, recent marble quarry

Results and discussion

ESEM/EDX analysis

ESEM/EDX provides information for the morphological, mineralogical and chemical characteristics of the marble samples. Characteristic images of the marble texture and the morphology of calcite crystals are shown on Figure 3. Table 2 contains the chemical composition (EDX) of the major elements of representative calcite crystals from all marble samples analysed in our study. Although these values coincide well with those demonstrated for marbles collected from the same geographical area (Dagounaki et al., 2004), a differentiation in their chemical composition is observed, even within ancient marbles, a fact that inhibits any possible correlation.

Parameters like maximum grain size or grain boundary shape have been used for the provenance study of archaeological marbles (Capedri, Ventuselli, 2004). Nevertheless, the small amount of samples, along with the small number of ESEM images and EDX spectra acquired in our study restrain any possible interpretation.

Table 2
Chemical composition of representative calcite crystals from the marble matrix of each sample, as determined by EDX analysis (semi-quantitative data)

Sample	Major elements oxides (%)				
	CaO	MgO	CO_2	SiO_2	Al_2O_3
10519	75	-	25	-	-
10537	76	-	23	0.4	0.3
10545	85	0.3	14	-	-
7474	75	0.4	24	-	-
M2	81	-	19	-	-
M3	78	-	22	-	-
M4	76	0.4	23	-	-

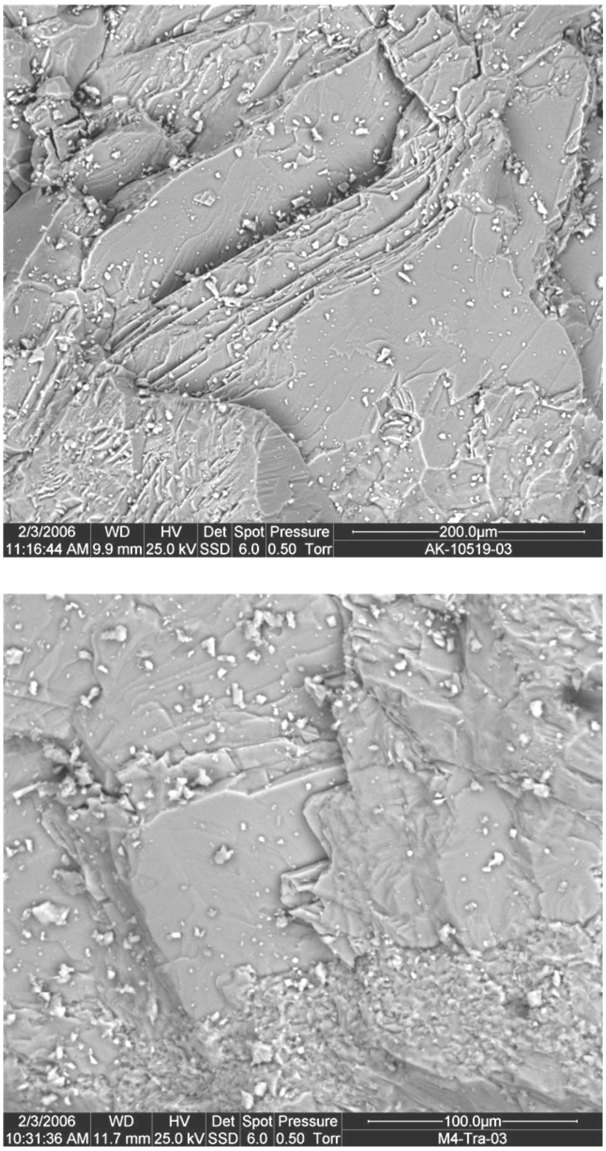

Fig. 3. Characteristic ESEM microphotographs of the marble fabric of an archaeological N-10519 (upper photo) and a recent N-M4 (lower photo) marble sample

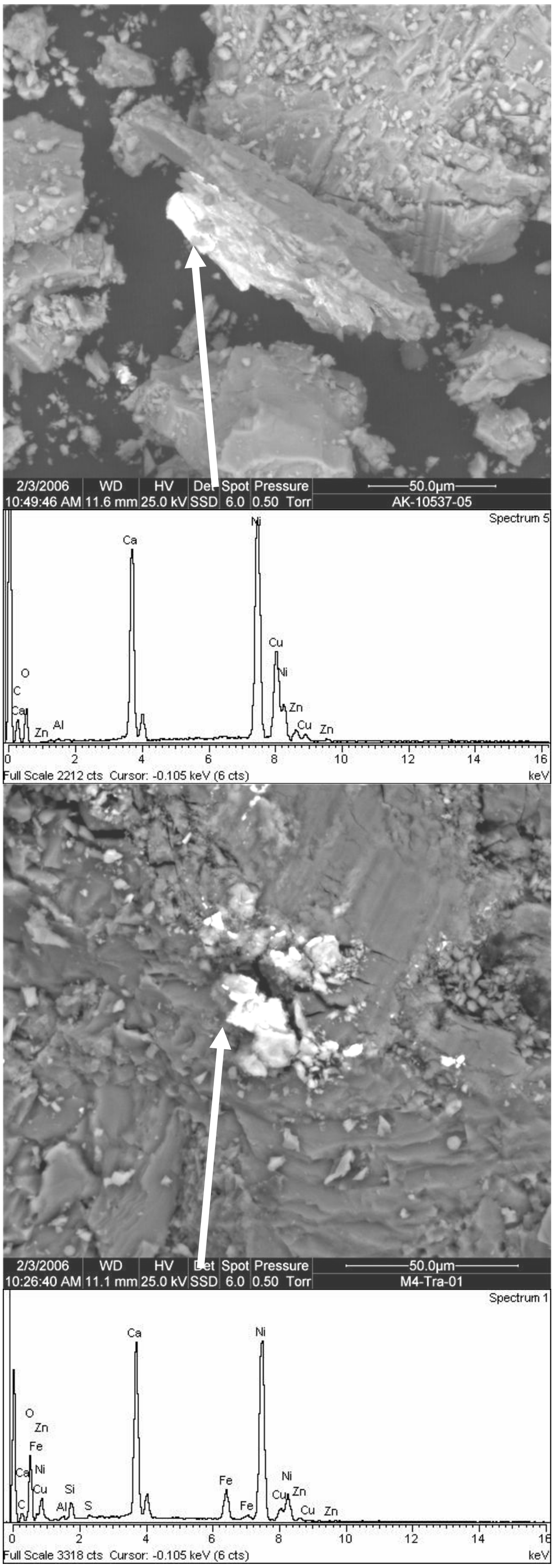

Fig. 4. Characteristic ESEM microphotographs and EDX spectra of a Ni-rich impurity within marble matrix of an archaeological N-10537 (upper photo) and a recent N-M4 (lower photo) marble sample

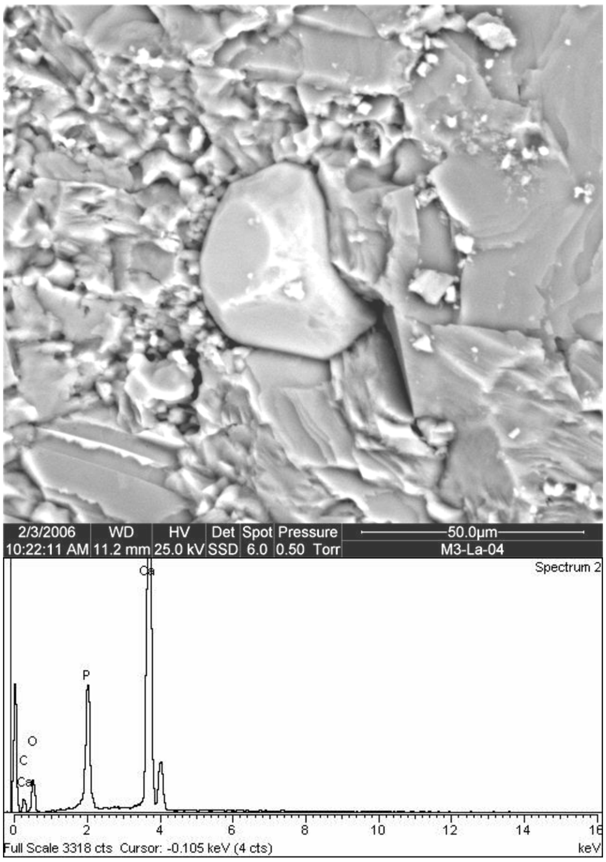

Fig. 5. Characteristic ESEM microphotograph and EDX spectrum of an apatite (?) impurity within the matrix of Veria (M3) recent marble sample

Accessory minerals and impurities in marbles have also been used as discriminating factors (Capedri, Ventuselli, 2004; Shackley, 2008). Ni-rich particles are clearly shown (Fig. 4) both in archaeological sample 10537 and in the recent one from the Tranovalto area (M4). This could be an indication for a possible relation between these two samples. Nickeliferous rocks predominate in the ophiolite complex of the Vourinos Mountain (Apostolikas et al., 2000; Rassios, 2000; Skarpelis, 2000; Skarpelis, 2006) nearby Aiani's region and were regarded as a good source indicator for ceramic artefacts and iron slags in previous studies (Iordanidis et al., 2007a; 2007b). Another impurity, probably an apatite crystal (Fig. 5) refers to the fresh sample M3 from the Veria's area. This mineral has not been detected in the other samples and may exclude this quarry as a possible origin of the ancient samples analysed in this study.

Overall, it should be noted that ESEM/EDX seems to be capable of providing important information for a provenance study of ancient marbles. However, in our case, a much larger number of samples and ESEM images and EDX spectra are required in order to have sound results.

TL analysis

Figure 6 presents the TL glow curves of (a) the received aliquots of powdered marbles and (b) the pre-heated aliquots up to 500ºC and further irradiated. Samples M2, M3 and M4 taken from modern quarries exhibits TL glow curves with larger intensity in comparison with their possible archaeological deteriorated counterparts. This general overview, only on total intensities using broad spectra of filters, arises as a simple excellent methodology to authenticate disputable marble objects. All studied marble aliquot types (i.e. natural and preheated-irradiated) match in this analytical routine. As a general observation all the TL curves displays emission peaks circa 250ºC as a shoulder encircled in maxima peak circa 350ºC (Baietto et al., 2000; Galloway, 2003; Polikreti et al., 2003). It is noticeable that a fresh powdered marble sample reach up to 70000 a.u., while the same preheated-irradiated aliquot only recover up to 2000 a.u.. This could be interpreted as a strong irreversible destruction of the TL emission centres. Probably, additional luminescence analyses could help us to discriminate among the emissions from different regions of the spectra.

A simple genetic typology of the samples taken from modern open quarries (M2, M3 and M4) and the other four ancient specimens (10419, 10537, 10545 and 7474) collected during archaeological excavations is clearly detected by the TL technique. TL spectra discriminate well the fresh marbles with high crystallinity parameters characteristic of perfect crystallographic lattices (assuming that the external weathered rock layers were removed, allowing us to collect fresh marble sample with high crystallinity). Conversely, grounded archaeological fragments, for many years suffered weathering, hydration and loss of coherence between interfaces, producing finally, hydrous, amorphous components and specimens with low crystallinity. It is well known that TL glow curves intensities are linked with the structural state of the sample and those amorphous samples do not display TL emission.

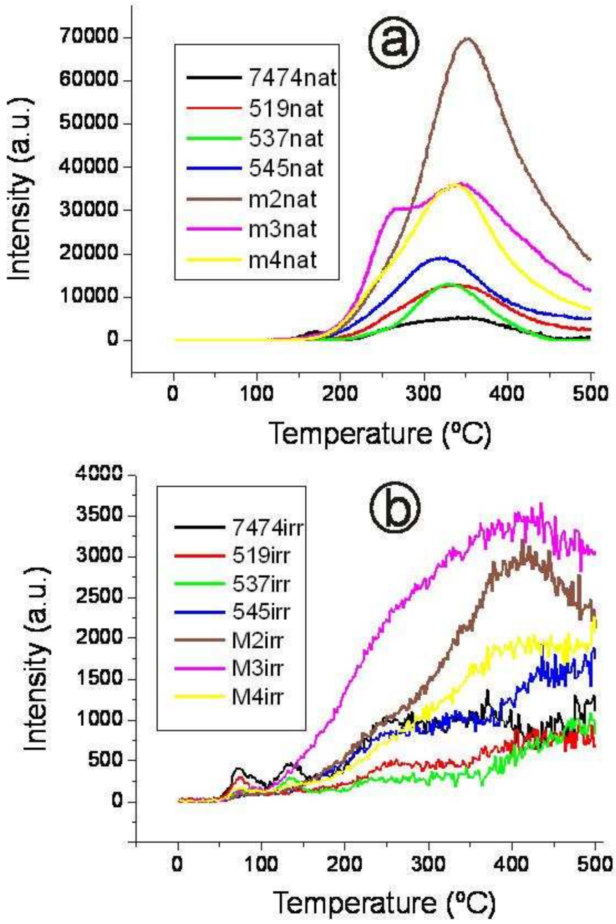

Fig. 6. Natural (a) and irradiated (b) TL glow curves of the powdered marble samples of this study (see Table 1 for sample ID)

Conclusions

ESEM/EDX and TL analyses were employed for the provenance study of ancient marble artefacts from Aiani, ancient Upper Macedonia, Greece. Fresh marbles were also collected from the broader Kozani area, analysed and correlated with the ancient ones. ESEM/EDX study may provide an indication for Tranovalto marble quarry as the origin of most ancient marbles, based on the calcite composition and the presence or absence of accessory minerals (nickeliferous impurities or apatite crystals). However, TL spectra could not provide clear differentiation, notwithstanding the difference in the intensity of TL spectra (higher in modern versus ancient marble samples). More analytical work, preferably applying supplementary techniques on more marble samples is proposed so as to achieve better results.

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