Petrography and mineralogy of the white marble and black stone of Göktepe (Muğla, Turkey) used in antiquity: new data for provenance determination

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Abstract

The discovery near Göktepe (Muğla province, Western Turkey) of an ancient quarrying site of white marbles and black stones has recently been reported by some authors. Assigning the provenance of stone from ancient artifacts to Göktepe is currently possible mainly thanks to chemical, EPR and MGS data. Petrographic description, which many researchers use to characterize ancient marbles, is still incomplete. Several thin sections of both types of stone were thus examined in this study, and also used for cathodoluminescence analysis. As the rock is more than 99% calcite, trace minerals could only be detected in some samples by XRD analysis of insoluble residues after acetic acid attack. Data on strontium and manganese contents and carbon and oxygen isotopes were also recorded, for better understanding of some petrographic features.

A new method of grain size characterization was tentatively introduced to improve the description of grain size variability in the white marble. Microstructure and grain size measurements on thin sections of this marble identify two petrographic varieties: the first is extremely fine with signs of dynamic recrystallization, and the second exhibits texture and MGS similar to those of Carrara marble.

Statuary samples of white marble from Villa Adriana (Tivoli, Rome), preliminarily assigned in a previous study partly to Carrara and partly to Göktepe quarry, are reconsidered here.

A certain degree of variability was found in the structures and textures in the thin sections of the Göktepe black stone. It may have undergone transformations at an advanced stage of diagenesis. One important source of this variability seems to be a fluid alteration event, revealed by both isotopic and chemical data and trace mineral assemblages.

1. Introduction

An ancient quarry has recently been discovered near Göktepe (Muğla province) in south-western Turkey, approximately 30 km NE of Muğla and 40 km SW of Aphrodisias (Fig. 1). The area was first reported in 2006 (Yavuz et al., 2009) and later was both archeologically described and scientifically characterized by Attanasio et al. (2009, 2015), who classified both white and black stones as marbles. The site was initially considered to be a relatively small exploited area which, however, produced fine-grained, high-quality sculptural stone, black or white (with a less frequent gray variety), as well as a highly characteristic, two-toned black-and-white stone (Fig. 2). Bruno et al. (2015) estimated that the site could yield an overall gross marble production of 40,000 m^3, of which one-third to half consisted of definitely usable marble. If this estimate is valid, then the site cannot be considered small, but medium at least.

If exploitation was extensive, then also the artifacts produced with this material should be correspondingly abundant. After archeometric studies on the Göktepe stones, Bruno et al. (2015) demonstrated that its use and circulation within the Mediterranean basin, especially during the Roman Imperial Age, was huge, ranging far beyond its geographical region of origin. The above authors reported that they had identified some 160 sculptures made of Göktepe white marble out of 500 statues studied, dispersed over a wide range of locations from Roman Gaul to North Africa, Italy, Greece and Turkey. Both white and black stones seem to have been extensively used for statuary because of their peculiar working qualities, probably due

to their fine grain size and compactness. Until now, the white marble of Göktepe has been considered to be used exclusively for sculpture; the black type was certainly used for both statuary and architectural elements, especially column shafts. There are many unfinished columns lying near the quarry fronts (Fig. 2D). Another example appears in the *Odeion* of Aphrodisias, where fragmentary spiral black columns assigned to the Göktepe stone are placed on the *scenae frons* (Yavuz et al., 2009).

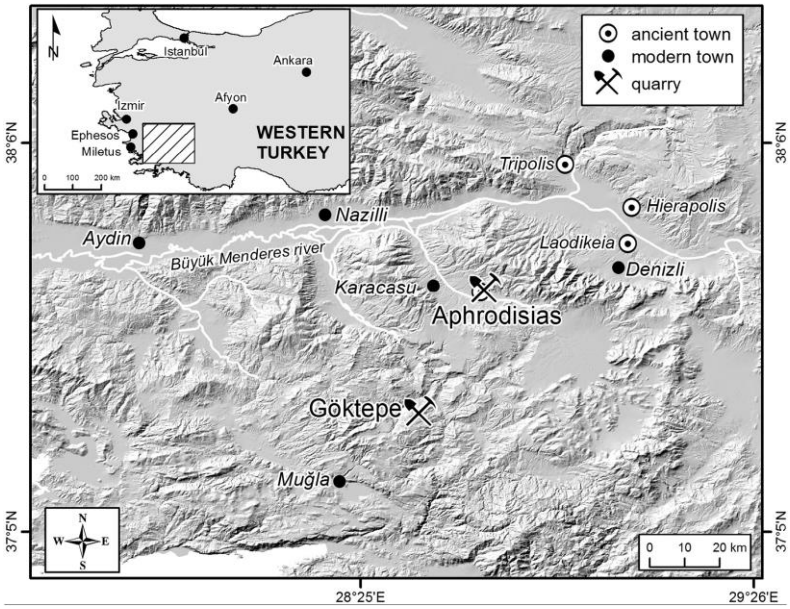

Fig. 1. Map of the location of the Göktepe quarry.

1.1. *The Göktepe black stone*

According to Bruno et al. (2015), the black stone of Göktepe can be identified with the typical, so-called *nero antico*, which Faustino Corsi (1845) identified with the black marble quarried in the Mani Peninsula near Cape Tenaros (south Peloponnese, Greece) and also called *marmor Taenarium* for that reason. Gnoli (1971) believed the black stone came from Djebel Aziz, a few kilometers south-west of the ancient Chartago (Tunisia), where a large quarry front reveals ancient activity. *Nero antico* probably pertains more to an appearance than to a provenance, and it may be more correct to think that the term refers to a certain number of different types of stone with the same uniform black aspect. Almost all the marble of sculptures and artifacts with the appearance of *nero antico,* with few exceptions, were attributed by Bruno et al. (2015) to the Göktepe quarries. The reasons for this are that, even without in-depth scientific proof, macroscopic identification is relatively easy, mainly because the authors contend that there are few alternatives and, in some cases, the Göktepe black stone is characterized by yellowish cross-shaped calcitic veins, which facilitate identification (Fig. 2F). Although the importance of Göktepe black stone may be viewed as predominating over the black stones used in antiquity, identification on this basis does not aid demonstration of its supremacy. Archeometric investigation is always advisable when a safe provenance attribution of black stone artifacts must be established (in addition, the above-mentioned calcitic veins indicating Göktepe origin are rarely present).

The black stones exploited in antiquity are not so scarce and the macroscopic differences are often very subtle, making the distinction among the various provenances impossible in several cases. In geological terms, real black marbles are not very abundant as far as we know, and in any case they have been exploited to a limited extent (not including the gray varieties, of which there are many). There are black marbles from Cape Tenaros, Mylasa, Halicarnassus (Lazzarini, 2007), Aphrodisias (Long, 2012), a black variety from the island of Lesbos (Lazzarini, 2007), and the very probable existence of an ancient black quarry near Laodikeia, supplying the many columns which have been found there. Black limestone used in antiquity was more abundantly exploited; some of the provenances are still unknown and, only including those of better quality, it is possible to identify limestones from Ain el Ksir and Djebel Aziz in Tunisia, the Greek island of Chios (Brilli et al., 2010) and Teos on the Sığacık peninsula in Turkey (Pensabene and

Lazzarini, 1998). Databases concerning black stones (Attanasio et al., 2009; 2012; 2015; 2017; Yavuz et al., 2009; Brilli et al., 2010; Lazzarini, 2013) have greatly contributed to the studies of provenance of the stone of black artifacts and they have also highlighted a number of problems concerning their nomenclature and geological nature. These difficulties are due to different points of approach and directly affect the study of black artifacts, especially when petrographic study is not addressed. The first concerns the use of the old nomenclature (*nero antico, bigio antico, bigio morato*). As already mentioned, this terminology was probably originally intended to describe the appearance of the archeological pieces carved in black, or in different gray scale stones with different surface finish, but not necessarily designed to relate each one directly to a single specific source. Moreover, earlier scholars may have made mistakes in the visual inspection of some emblematic statuary. However, as such terminology was commonly used in texts on archaeology and art history, the current scientific analytical approach aims at relating each old name with one or several stone sources, to define them precisely and relate the names to their geological properties, with the final aim of using them when analyses are not available. Within this framework, the recent contribution of Attanasio et al. (2017) on *bigio antico* offers an approach for the whole ancient 'black' decorative stones with the aim of resolving the problem. Their classification, based on the use of stones (sculptural or architectural) makes sense for a first approximation. However, this basic scheme also tries to relate them with the old names (*nero antico* and *bigio morato*) and with their respective petrographic features, but logically this relationship does not always match well. Consequently, our position in this study is to elude classical terminology and use the general name of Göktepe black.

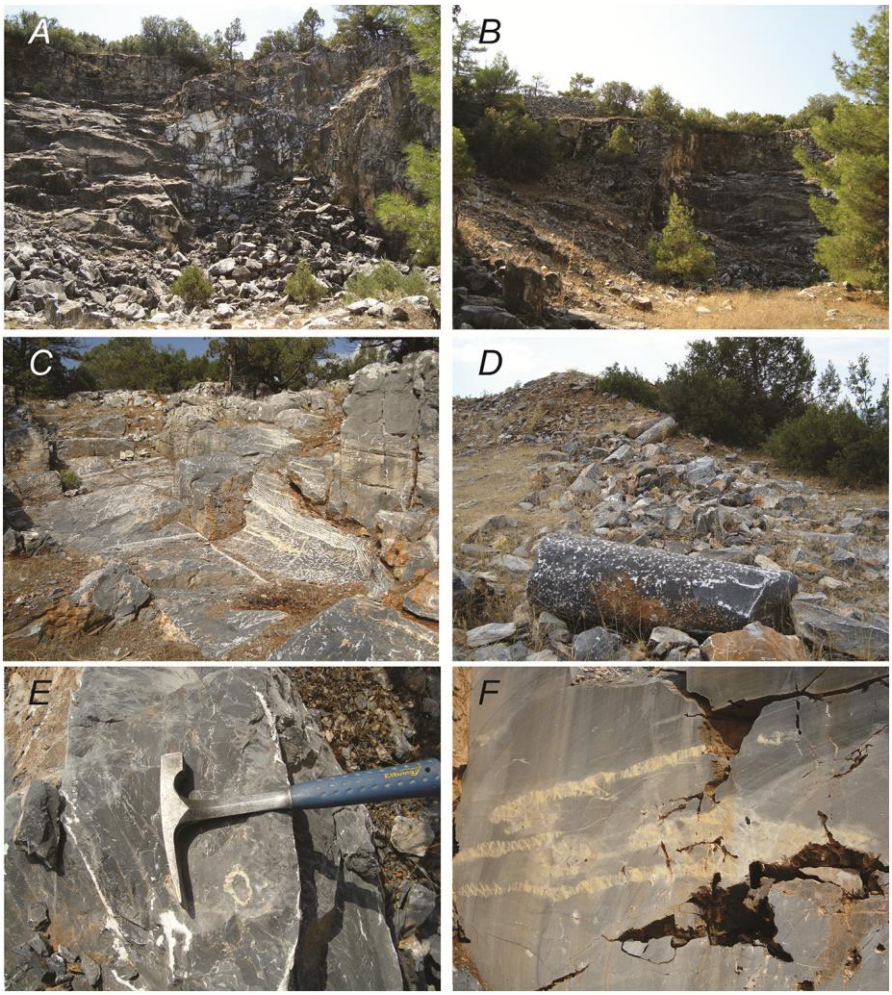

Fig. 2. Panoramic views of the Göktepe quarry fronts and details of the stone. A) and B) Panoramic views of quarry fronts of the Göktepe white marble; C) view of a quarry front of the Göktepe black stone; D) debris of Göktepe black stone, some unfinished column shafts are clearly visible; E) detail of a recrystallized bivalve shell; F) typical yellowish cross-shaped calcite veins. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The second problem concerns the identification of the geological nature of certain black stones in order to describe and name them correctly. In particular, as we shall see below, Göktepe black is a carbonate rock which shows different degrees of recrystallization at the boundary between advanced diagenesis and very low metamorphism. The identification of this particular geological domain has been controversial for a long time in many lithologies, and carbonate rock is no less problematic. Being in this transition, selecting the proper name requires specific analytical methods to guarantee the possible presence of certain diagnostic metamorphic components in comparison with the sediment, a method which is unusual in archeometric studies. Examination of the whole set of the thin sections and specific XRD analyses carried out on the Göktepe black allowed us better understanding of the evolution of the prograde process. The degree of calcite recrystallization, the impure composition (clays and organic matter) of the black carbonate protolith, together with the presence of thick shelled-walls of large prismatic calcite and the proper shape of the bioclasts are all keys to our petrographic understanding of the aggradation process of recrystallization.

1.2. *The Göktepe white marble*

It is even more difficult to obtain evidence on the use of the white statuary variety, owing to the obvious macroscopic similarities with other fine-grained white marbles. Archeometric investigation is needed when reliable attributions to this type of marble are required, especially because during the last few years, several contributions have revealed that many sculptures thought to be from Carrara are in fact of Asiatic origin. The erroneous attribution of Carrara made in the past is comprehensible because the Göktepe quarries have only recently been discovered and also because some parameters usually used in provenance studies do not discriminate them.

This observation was previously noted after the archeometric study of a selection of 62 fragmented sculptures from the collections stored in the reserves of Villa Adriana (Lapuente et al., 2012a). It should be noted that petrographic study of the Göktepe marble was not available at that time, except for average grain sizes (0,291 ± 0,1 mm) and maximum grain size (average MGS ≤ 0,66 mm) after Attanasio et al. (2009). In spite of this difficulty, several groups of pieces were identified by means of petrography, optical cathodoluminescence (CL), C and O stable isotopes, and two complementary techniques (EPR and quantitative CL+SEM). Their marble sources were positively distinguished in seven of the eight groups of samples. From the fine-grained marbles, 18 pieces were clearly assigned to Göktepe (group G), six were identified as Carrara (group C1); a third group of 15 samples were difficult to identify with certainty, since they shared the characteristics of both Carrara and Göktepe marbles. The latter group was provisionally assigned to another possible Carrara origin (group C2) due to its similar petrographic features. However, other parameters such as EPR and CL (microfacies and quantitative) pointed to an origin at Göktepe. Both groups G and C2 of statuary from Villa Adriana are re-examined here, taking into account additional data about white Göktepe, in particular trace elements (Attanasio et al., 2015; Poretti et al., 2017), the holotype microphotograph (Antonelli and Lazzarini, 2015) and petrographic comparison with quarry samples reported here. The homogeneous nature of samples in each statuary group is remarkable, enhancing their respective archeometric parameters (see Table 3 in the Supplementary materials).

1.3. *Archeometric approach for definition of white and black Göktepe stones*

The almost invariable identification of *nero antico* with Göktepe black stone and the new assignation of white marble sculptures to Göktepe white marble, previously often believed to pertain to Carrara, are considerations which require more than macroscopic identification based on subjective eye evaluations. In-depth archeometric analyses of the stones quarried at Göktepe are essential in order to study the artifacts properly. Attanasio et al. (2015) tried to achieve this by using a large number of samples, which were analyzed for stable isotopes, some petrographic characteristics, EPR, and strontium and manganese trace elements. In their work, the above authors demonstrated that isotopes show very modest or no capacity to distinguish Göktepe white from the most frequently exploited fine-grained marbles used in antiquity, especially from that from Carrara, with which it is frequently confused. Similarly, isotopes fail to characterize the Göktepe black properly. Both types have a very wide range of carbon and oxygen isotopic compositions. In particular, the trace elements, strontium and manganese, seem to be the most promising indicators to identify the Göktepe white marble which, on average, has very high strontium with respect to other white fine-grained marbles and very low manganese. As the EPR of a marble is related to the spectral

features of the manganese occurring in the defects of the calcite crystal lattice and CL is related to manganese due to its luminescence behavior, they are other good indicators of Göktepe origin in a given white marble.
The Göktepe black stone may also be characterized thanks to these chemical constituents, although they are less evident. This characteristic is attributed to the presumed aragonitic nature of the Göktepe protolith, which makes the rock richer in strontium and more depleted in manganese than any marble which had a calcitic protolith. In any case, diagenesis and metamorphism tend to transform metastable aragonite into calcite, with consequent chemical adaptation, and this may have given rise to the great variability of this stone - particularly in the case of strontium, which shows distribution with a long tail toward low contents. This means that relying solely on strontium or manganese contents to establish the provenance of an unknown marble artifact is not always effective. There is also the possibility that marbles from different provenances have trace element values similar to those of the average Göktepe marble.
This reveals the importance of relying on more than one or two variables when studying the provenance of marble artifacts, as widely recognized in past studies, together with sufficiently large databases in relation to each variable. In this respect, the present study aims at improving the available data on the Göktepe marbles, in order to characterize them better. In particular, while geochemical characterization has been abundantly investigated, there are few descriptions of the petrographic features of the Göktepe carbonate rock in the relative literature.
Petrography was the first method used in marble provenancing (Lepsius, 1890; Washington, 1898) and is still one of the most frequently adopted. We examined these aspects in more depth by observations of thin sections, XRD, and CL analysis, providing improved petrographic descriptions and showing that initial petrographic analysis can be crucial in determining the carbonate nature and provenance of this rock. The samples of this study were also analyzed for isotopes, strontium and manganese, for better understanding of the relations between petrography and chemical and isotopic characteristics.

2. Materials and analytical methods

During a sampling campaign in 2014, 62 samples were randomly collected from various fronts of the Göktepe quarry area. Of these, 46 samples came from outcrops of Göktepe white in District 3, as described by Attanasio et al. (2009). Sixteen samples came from Göktepe black in Districts 1 and 2; five of these were collected from unfinished column shafts dispersed in ancient and modern mounds of rubble found almost everywhere in the quarry area (Fig. 2).
The fresh surfaces of all samples were macroscopically examined to select nine of uniform white, one gray (which will be included in the results from the white stone) and ten of black, and were cut into thin sections for petrographic and mineralogical study under a polarizing microscope. Of the black stones, three samples were unfinished column shafts scattered among the quarry debris. In addition, 34 thin sections from archeological statuary samples of Villa Adriana (Lapuente et al., 2012a,b) were re-examined. They correspond to one sample in black statuary assigned to Göktepe (TI-VA_46) and the previously mentioned groups of white samples: 18 thin sections of Göktepe (group G) and 15 thin sections of group C2, provisionally assigned to Carrara. Additional elemental analyses were carried out to verify the previous identification.

Petrography. Textures, crystal boundary shapes and MGS were determined, since they are well-known to be diagnostic for marble discrimination (Weiss, 1954; Herz, 1955; Moens et al., 1988; Lazzarini, 2004; Lapuente 2014; Antonelli and Lazzarini, 2015).
A new method for graphic visualization of the grain size distribution of Göktepe white marble was tentatively introduced in this study to test its effectiveness in marble provenance investigations and, in particular, to be applied to cases of apparent visual similarity. As the operative technique is in its early stages and is time-consuming, it was only adopted in five representative thin sections: two from quarry samples with different texture, two from statuary samples (one each from G and C2 groups) and one from a thin section of Carrara. Nis-Elements D software for image capture, supplied by Nikon, was used to acquire measurements. These were drawn by the operator along the largest dimension of each calcite grain (Fig. 3A) on the computer screen, under convenient magnification and crossed polarized light. A screen section

of 12 mm^2, the same area as the microphotographs (4 x 3 mm) usually published in the relative literature as representative views, was used for acquisitions. Varying numbers of measurements (200-300) were made on each thin section, depending on the grain size of each sample. Data were organized in decimal ranges between ≤ 0,1 and ≥ 1 mm and then reconverted to percentages for graphic representation. This grain size distribution (Fig. 3B) allowed the definition of a new parameter, the Most Frequent Size (MFS), which provides additional indications of the degree of homogeneity in texture and grain size (homeoblastic/heteroblastic), especially useful in comparing fine-grained marbles. This parameter represents the grain size (or range of grain sizes) with the highest frequency in the frequency histogram, expressed in millimeters (or microns) per percentage of measurements. The data of each sample were also organized in columns as the accumulative summation of each size range. In this case, for better comparison among samples, the percentage of grains > 0,4 mm is marked in each column in Fig. 3C.

On one hand, the aim of using this parameter was not to replace MGS, which has been successfully used in many cases (e.g., Lapuente et al., 2014; Antonelli and Lazzarini, 2015), but for this particular case of similarity in fine-grained marbles. On the other hand, the MGS of Göktepe white is recognized as a parameter with low discriminating power against other fine-grained marbles, due to the sporadic presence of coarser calcite crystals (Attanasio et al. 2015). In fact, a wide range of values (from 0,35 to 1,60 mm) was measured in 25 unpublished samples (Antonelli and Lazzarini, 2015).

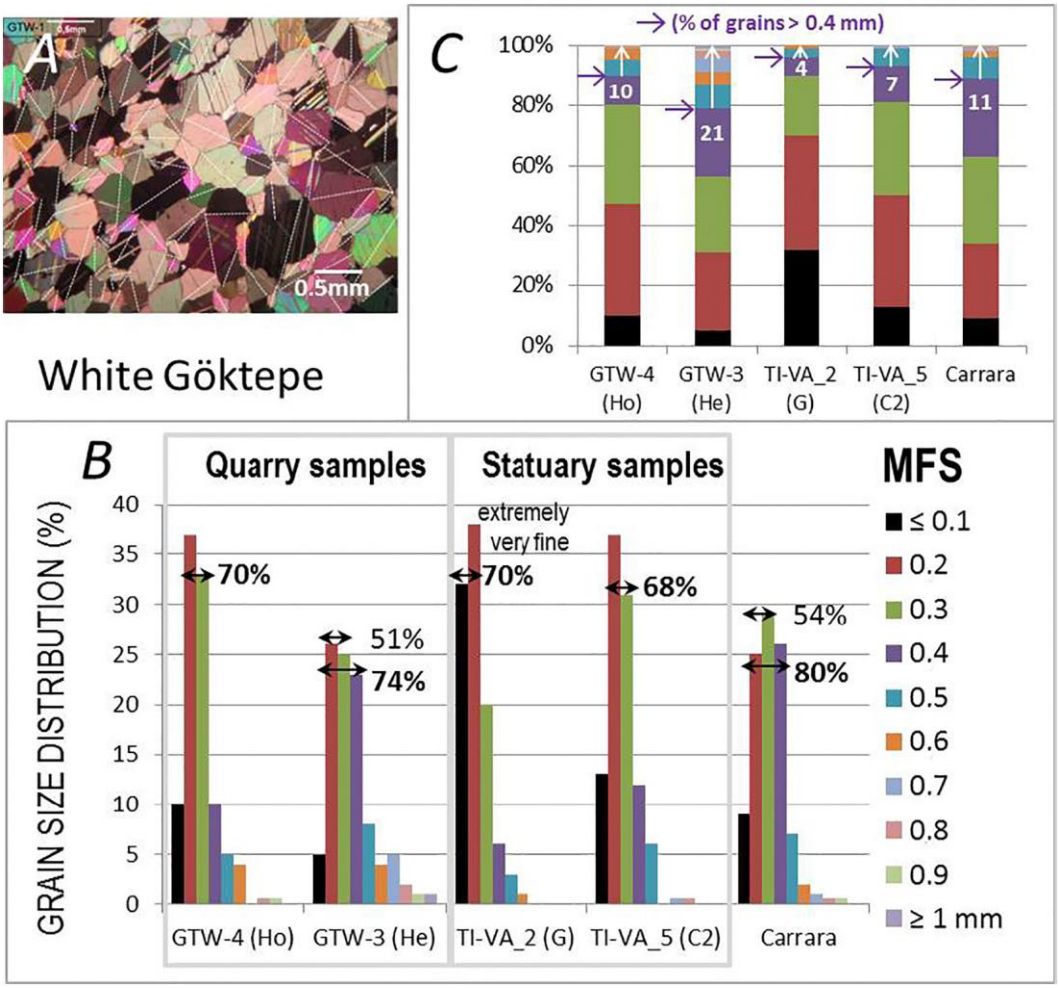

Fig. 3. (A) Example of measurements of grain size dimension (Göktepe white marble). Each line represents largest dimension in each crystal; lines were drawn under the proper magnification of the microscope and measured by the software. (B) and (C) grain size distribution obtained from two representative quarry samples, two statuary samples of white marble (G and C2 groups) and one sample of typical Carrara marble. Histograms of the grain size distribution in decimal range of sizes are expressed in percentage. The parameter Most Frequently Size (MFS) is defined by the set of bars that reach highest values in the graph, obtained by the indicated percentage of measurements (in bold). (C) Data of each sample are organized in one column as the accumulative summation of each decimal size range. For better comparison among samples, the percentage of grains>0.4mm is marked in each column.

Cathodoluminescence. The thin sections from both quarry and statuary pieces were used for CL analysis on CL8200 Mk5–1 cold equipment coupled to a NIKON Eclipse 50iPOL OM. Electron energy was 15–20 kV and beam current was operated at 250–300 mA. The observed luminescent colors, intensity and distribution of each sample were recorded with an automatic digital NIKON COOLPIX5400 camera. CL images were automatically checked (29 mm focal length, f/4.6 aperture, 1 s exposure, ISO-200) to obtain comparative images of their CL intensity (brightness). The CL characteristics of carbonates are well-known to be related to chemical impurities such as Mn^{2+} and REE ($Sm^{3+,}$ Tb^{3+}, Dy^{3+}, Eu^{2+}/Eu^{3+}) and quenching ions (Machel, 1985, 2000; Machel et al., 1991; Habermann et al., 1996, 1998; Casenave et al., 2003; Richter et al., 2003). CL can produce slightly different results according to the instrumentation used and the relative settings (Lapuente and Royo, 2016). For comparisons, with a certain degree of approximation, we used the CL image of one white Carrara marble as the standard reference pattern, since it exhibits what we consider to be medium orange intensity (Fig. 5A).

***Stable isotopes and elemental analyses*.** All white and black quarry samples were analyzed for carbon and oxygen stable isotopes and strontium and manganese, which are the trace elements which generally substitute calcium (or magnesium) in calcite minerals. Stable isotopes of the statuary samples previously analyzed from Villa Adriana (Lapuente et al., 2012a,b) were also re-evaluated (TI-VA, samples). From these, eight white samples of group (G), six white samples of group (C2) and the sample in statuary black (TI-VA_46) were also included in trace element analyses.

Oxygen and carbon isotopes were determined on calcium carbonate samples by isotope ratio mass spectrometry (IRMS). A Thermo Gasbench II automatic preparation device was used for phosphoric acid digestion at 72°C and CO_2 purification; a Finnigan Delta Plus mass spectrometer measured the carbon and oxygen isotope ratios of carbon dioxide expressed in the usual delta notation, which represents the relative deviation in parts per thousand of the heavy/light isotope ratio of the samples from that of a reference standard. The international standard used was PDB for both oxygen and carbon isotopes, and analytical precision was better than 0.1‰ for both.

Varian Vista-PRO was used for trace element determination by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) on solutions of HCl (3%) in which suitable sample aliquots were dissolved. All solvents and reagents were of the highest purity grade commercially available. Deionized water (resistivity 18 MΩ cm^{-1}) obtained from a Milli-Q purification system was used to prepare all standard and sample solutions. Emission lines for ICP-AES analysis were chosen according to previous interference studies. Internal standards were added to compensate for any effects from acid or instrument drift. The accuracy of all measurements was assessed according to the Certified Reference Material from National Institute of Standards and Technology (Gaithersburg, MD, USA). The precision of the method, defined as the closeness of agreement between mutually independent test results, was determined in terms of the percentage of the variation coefficient. The limits of detection (LOD) and quantification (LOQ) of each analyte were calculated as the analyte concentration corresponding to three and ten times, respectively, the standard deviation of ten independent measurements of the blank, divided by the slope of the calibration curve. Analytical precision was calculated as the percentual relative standard deviation of a set of ten readings of the same sample of calcite standard performed in a single run. Results indicated precision values always under 5%. Accuracy was less than 10% for the two elements.

XRD analyses and CHN contents. Aliquots of the samples were powdered for determination of X-ray diffraction (XRD) spectra (PHILIPS PW 1840 diffractometer; CuKa/Ni: 40 KV and 20 mA) to detect dolomite, calcite, and any accessory minerals. Two selected samples of black marble variety were analyzed by XRD after dissolution in a 0.8N solution of acetic acid, a practice already tested for determining accessory minerals in carbonate rocks (Jurik, 1964). The residues of these samples were also analyzed for CHN contents and carbon isotopes by Elemental Analyzer (EA) and EA-IRMS, respectively, to determine the origin of the carbonaceous matter which presumably gives this carbonate rock its black color. A Flash 1112 Thermo EA was used for CHN determination; EA was also on line with the mass spectrometer through a ConFlo II interface. The samples, combusted to produce the elementary gases (CO_2, N_2, H_2O), were separated by gas chromatography. Only CO_2 gas after purification was introduced to the source of the mass spectrometer for carbon isotope analysis.

3. Results. Göktepe white marble

3.1. *Petrography and CL*

3.1.1. *White quarry samples*

Representative microphotographs of each thin section of quarry white marbles are shown in figure 5. Table 1 summarizes their petrographic and CL features. All of them are pure calcitic marbles with isotropic fabric and Grain Boundary Shapes (GBS) from straight to curved, in a polygonal granoblastic texture (mosaic), with evident triple points due to almost stable conditions reached over long periods of metamorphism. However, observed in detail, they also have calcite grains with slightly indented boundaries, without signs of extensive intracrystalline deformation, except rare undulatory extinction in isolated calcite. They are fine-grained marbles with MGS from 0,9 to 1,1 mm and have homeoblastic texture (samples GTW-1, 4, 7,11, 15). Some samples (GTW-2, 3, 5, 10) show individual crystals or patchy small areas of recrystallization with larger calcite grains developing a partly heteroblastic texture. Accessory minerals were absent at the optical microscope observation scale.

Taking into account the petrographic homogeneity of the white quarry samples and for better observation of their microstructure, two samples (GTW-4 and GTW-3) were selected for magnified views (Figs. 4B, C). Their grain size measurements were taken as illustrative of both textures (homeoblastic and slightly heteroblastic) and are labeled GTW-4(Ho) and GTW-3(He), respectively. Data obtained (in percentages) are shown in figures 3B and C. Certain differences characterize both textures: in GTW-4(Ho), the Most Frequent Size (MFS) ranges between > 0,1 and 0,3 mm (measured in 70 % of grains), whereas in GTW-3(He) this range of sizes was obtained in 51 % of measurements: in fact, GTW-3(He) has a wider MFS range between >0,1 and 0,4 mm (in 74% of measurements). In figure 3C, GTW-3(He) does show that 79% of grains are ≤0,4 mm, whereas in GTW-4(Ho), the same size is measured in 90% of grains. This difference, obviously, highlights the existence of coarser crystals in the slightly heteroblastic texture, which contribute to reach higher MGS.

These diagrams also show data from two representative statuary samples from Villa Adriana (explained in the next section) and from one typical Carrara marble. The Carrara example shows an MFS between 0,2 and 0,4 mm in 80% of measurements.

The CL of the white Göktepe quarry samples is homogeneous and reddish, with very low intensity. The margins of the grains and the polysynthetic gemination traces show no luminescence (Figs. 4B and 4C).

The Göktepe white marbles have a gray variety, which has similar characteristics to the white marble of Göktepe. The thin section of gray sample GTB-5 (Table 1 and Figs. 5J, K) shows a very fine-grained calcite marble with occasional anisotropic fabric due to calcite layering. It also displays a slightly foliated microstructure with grain size variations in irregular bimodal bands. In each millimeter band, the texture is homeoblastic, with alternating fine-grained aggregates (≤ 0,2 mm), and others ranging from > 0,2 to 0.8 mm. Very fine grains of an opaque accessory - presumably graphite, as detected by XRD - are scattered between the carbonate crystals, thus producing differences in gray tones in hand specimens. Its CL-pattern is of very low intensity similar to the white marble samples.

3.1.2. *Statuary white samples (groups G and C2)*

The petrographic and CL images of the white statuary samples (groups G and C2) from Villa Adriana (Lapuente et al., 2012a) are shown in the Supplementary Materials (Figs. $S1_1$, $S2_1$, $S1_2$ and $S2_2$). Due to their petrographic homogeneity, clearly shown in the microphotographs of each group, one representative sample of each (TI-VA_2 and TI-VA_5) was selected to be measured for grain size distribution The statuary sample of group G (TI-VA_2) shows an MFS ≤ 0,2 mm in 70% of measurements, indicating that its grain size is mostly very fine, whereas the sample of group C2 (TI-VA_5) shows a grain size distribution similar to that of the homeoblastic quarry samples. Magnified microphotographs are shown in Figs. 5D and E. Petrographic and CL features are listed in Table 1.

Samples of Group G were assigned to white Göktepe according to MGS, stable isotopes, EPR and CL (quantitative and microfacies) by Lapuente et al. (2012a). According to their petrography (Table 1), they are all extremely fine-grained calcitic marbles with MGS ≤ 0,6 mm and MFS ≤ 0,2 mm in 70% of grains. This distinctive feature is clearly visible in the grain size distribution diagram of Fig. 3B. In addition, only 4% of

grains were > 0,4 mm (Fig. 3C). They show clearly anisotropic to apparent isotropic[1] microstructures according to the thin-section orientation (Fig. $S1_1$). Calcite exhibits slightly oriented grains to the clearly foliated fabric, as indicated by either grain shape or preferred crystallographic orientation. GBS ranges from curved to indented or embayed, typical of a diffusive mass transfer mechanism. Those sutured contacts together with very small subgrains reveal intracrystalline plasticity as a result of a deformation mechanism. As a consequence, straight boundary grains, or triple points, are moderately to rarely observed in this group. All these petrographic characteristics are so peculiar as to make this marble significantly different from any other classical white statuary marble.
The samples generally exhibit low CL intensity. Brighter luminescence is concentrated along the grain borders or within crystals in tiny spots; this particular CL-microfacies may help to identify this variety of white Göktepe marble.
The samples of Group C2 are petrographically quite uniform (Figs. $S2_1$) with very low CL intensity (Fig. $S2_2$). They consist of polygonal mosaic of predominantly homeoblastic fine-grained calcite grains with isotropic fabric. MGS and MFS are 0.8 mm and > 0,1 and 0,3 mm respectively in 68 % of grains (Fig. 3B). Instead, only 7% of grains are > 0,4 mm (Fig. 3C). Petrographic and CL characteristics are very similar to those described for the Göktepe quarry samples of homeoblastic texture. This indicates that the provisional assignment of these marbles to Carrara by Lapuente et al. (2012a) may be erroneous and a revised attribution to Göktepe may be advisable.

3.2. *Trace elements*

Strontium and manganese were identified by Attanasio et al. (2015) as the best parameters to discriminate the white Göktepe marbles from others used in antiquity. Poretti et al. (2017) confirmed these results and also emphasized the fact that the Göktepe white marble presents an overall peculiar trace element composition. As already explained by Attanasio et al. (2015), Göktepe marble had an aragonitic protolith. In aragonite minerals, Sr can easily substitute Ca in the crystal lattice, whereas Mn rarely does so; consequently, the Göktepe marble contains more Sr and less Mn in comparison with other marbles with calcitic precursors.
The samples of the present study were also analyzed for Sr and Mn, and approximately confirmed the data of Attanasio et al. (2015) and Poretti et al. (2017) (Fig. 6a). The range of these two elements, especially that of Sr, is in any case quite large, mainly due to two factors: a) recrystallization from aragonite to calcite, which favored the expulsion of Sr from the mineral structure; b) fluid rock alteration, already recorded by the isotopic compositional trend, which positively correlates with the Sr data.
The statuary samples from Villa Adriana (TI-VA) analyzed here have high levels of Sr, in the middle of the range defined by the quarry samples, confirming their Göktepe provenance for both G and C2 groups. Their very low Mn contents match the CL intensity observed (microfacies and quantitative) and the EPR data reported by Lapuente et al. (2012a).

3.3. *Isotopes*

The isotopic behavior of the Göktepe samples, both white and black, have already been described by previous authors (e.g., Yavuz et al., 2009; Attanasio et al., 2009, 2015). The new data reported here do not show substantial differences with respect to above studies; in fact, most of them cluster in a narrow area approximately between -3 and -2‰ of $\delta^{18}O$ and +2 and +3.5‰ of $\delta^{13}C$ (Fig. 6b). These values are not very different from those exhibited by most of the marbles quarried in classical times. They are the typical values of the marine carbonates from which all these marbles derived before diagenesis or metamorphism. Differences with respect to these compositions can be observed in those rocks which were isotopically altered by circulating aqueous fluids during their geological history. These differences may be observed in some of the Göktepe black and white stones, since the data distribution is evidently tailed toward more negative values for both carbon and oxygen.
The isotopic data of the samples from Villa Adriana fall within the main cluster of the Göktepe data. This does not disprove a Göktepe origin for both groups (G and C2) of white statuary.

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[1] Note that the representative sample (TI-VA_2) is not apparently anisotropic (due to the random thin-section orientation) but was deliberately selected for better comparison with the others in the same figure 3, all isotropic.

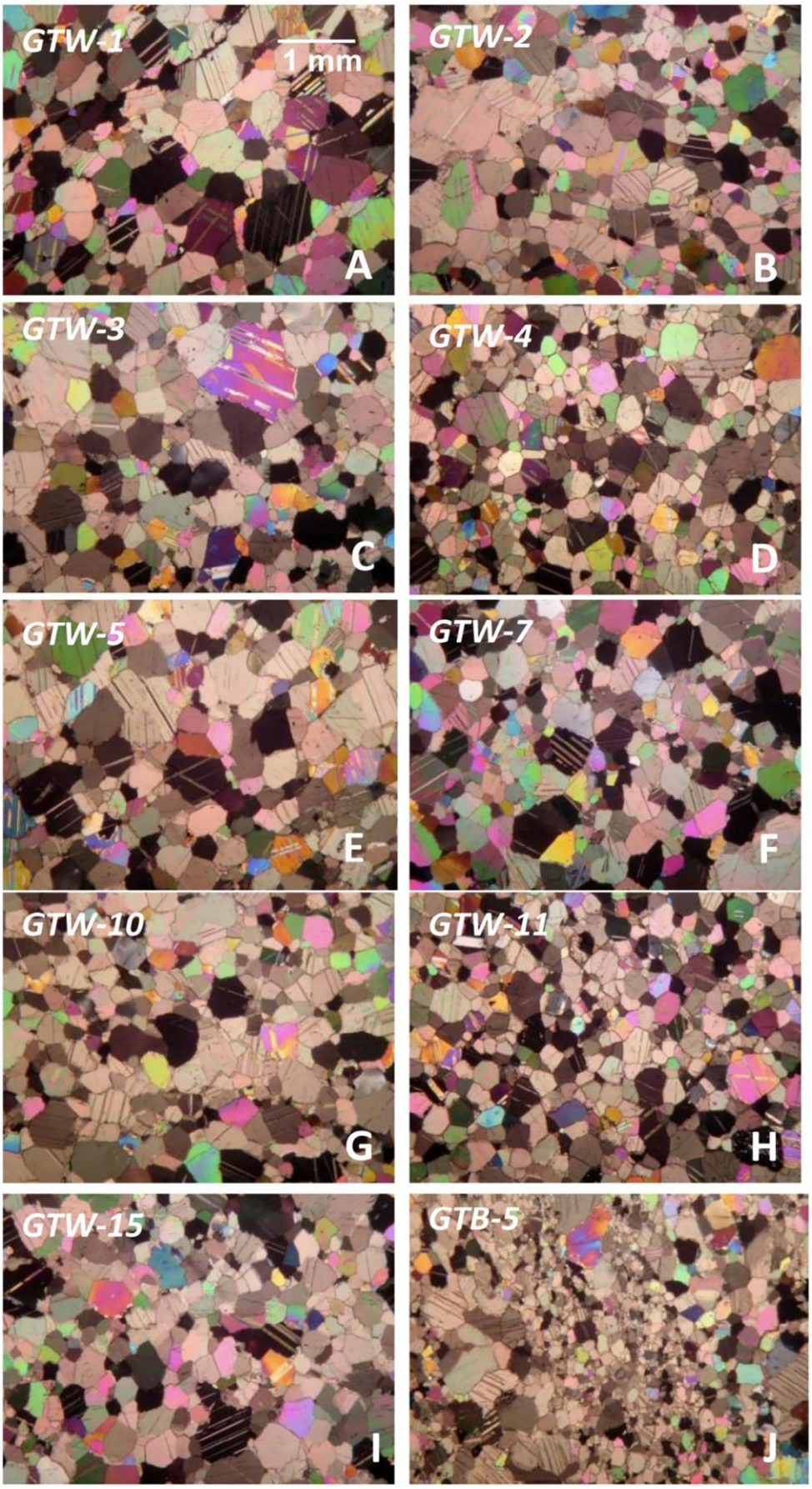

Fig. 4. Microphotographs in analyzed polarized light of quarry samples of Göktepe white.

Table 1
Petrographic and cathodoluminescence features of Göktepe marbles (white and light gray) in quarry and statuary samples. The parameter MFS (in bold characters) is defined after the graphic representation of the grain size distribution in % (see Fig. 3, and Section 2 in the text).

Göktepe marbles		Samples	Fabric texture	Grain Boundary Shape (GBS) Intracrystal strain	Minerals	MGS mm	Most Frequent Size (MFS) Grain size distribution (%) Fig. 3B	CL intensity
White	**Quarry samples** Quarry District 3 (Attanasio et al., 2009)	**GTW-4** (Fig. 4B) similar to GTW-1, 7, 11, 15 (Fig. 5)	Isotropic, homeoblastic, granoblastic, polygonal	Straight, curved, (indented)	Calcite	0.9	**70% (> 0.1–0.3 mm)** 90% ≤ 0.4 mm 10% (> 0.4–0.9 mm)	Very low
		GTW-3 (Fig. 4C) similar to GTW-2, 5, 10 (Fig. 5)	Isotropic, homeo-(hetero) blastic, granoblastic, polygonal	Straight, curved, indented (undulatory extinction)	Calcite	1.1	51% (> 0.1–0.3 mm) **74% (> 0.1–0.4 mm)** 79% ≤ 0.4 mm 21% (> 0.4–1.1 mm)	Very low
	Statuary samples Villa Adriana (Lapuente et al., 2012a) Figs. $S1_1$, $S1_2$, $S2_1$, $S2_2$	TI-VA_2 Group G (Fig. 4D)	Anisotropic, Isotropic, homeo-(hetero) blastic, granoblastic (Polygonal)	Curved, indented, embayed, (straight) (Subgrains; deformed shape, crystallogr. preferred orientation) (Undulatory extinction)	Calcite	0.6	**Extremely fine 70% ≤ 0.2 mm** 96% ≤ 0.4 mm 4% (> 0.4–0.6 mm)	Low
		TI-VA_5 Group C2 (Fig. 4E)	Isotropic, homeoblastic, granoblastic, polygonal	Straight, curved (undulatory extinction)	Calcite	0.8	68% (> **0.1–0.3 mm**) 93% ≤ 0.4 mm 7% (> 0.4–0.8 mm)	Very low
Light gray	**Quarry sample**	**GTB-5** (Fig. 5J–L)	Anisotropic, isotropic, slightly foliated	Straight, curved, indented	Calcite Fine opaques	0.8	Bimodal 50% ≤ 0.2 mm 50% (> 0.2–0.8 mm) by visual estimation	Very low

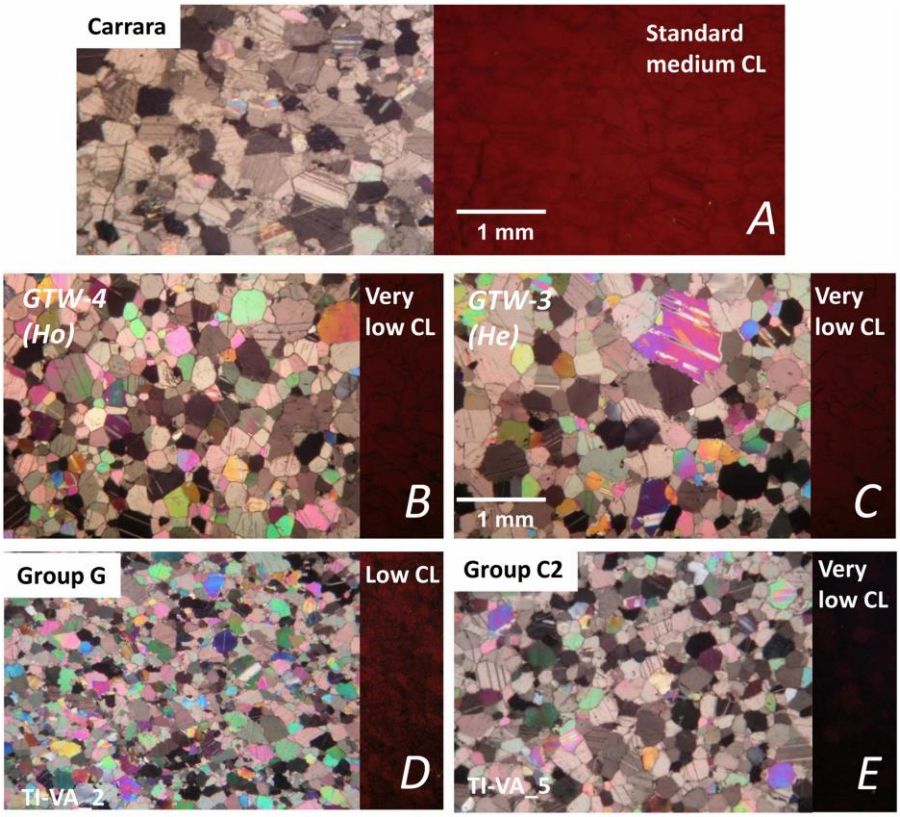

Fig. 5. Microphotographs in analyzed polarized light and CL-patterns. (A) Carrara marble shows a medium CL intensity. (B) and (C) Göktepe quarry samples with homeoblastic (B) and homeoblastic to slightly heteroblastic (C) textures (CL is very low). (D) and (E) white statuary samples from Villa Adriana from Lapuente et al. (2012a), (group G, sample TI-VA_2 and group C2, sample TI-VA_5); extremely fine texture with low CL intensity in (D), texture similar to Carrara with very low CL intensity in (E).

4. Results. Göktepe black stone

4.1. Petrography and CL

Table 2 lists the petrographic and CL features of black Göktepe stones. A selection of microphotographs is shown in Figs. 7a and b.

Macroscopically, Göktepe black is very fine-grained, with great compactness and smoothness, favored by the presence of carbonaceous matter. This type is sometimes characterized by decimetric cross-shaped yellowish calcite veins which can often facilitate identification of its provenance in artifacts (Fig. 2f).). It also

has small white patches and veins, mostly due to carbonate recrystallization of bioclasts (Fig. 2e). Although the Göktepe black stone can definitely be classified as carbonate rock, it must be examined on a microscopic scale (Fig. 7) in order to refine the classification and identify its geological nature. Petrographic observations of thin sections revealed the gradual transition between a partially recrystallized limestone and an almost totally recrystallized carbonate rock. For this reason, we subdivided the Göktepe black stone into two groups, Lithotype 1 and Lithotype 2 (Fig. 7a and 7b, respectively; Table 2). The pristine depositional nature and texture of the rock were totally or partially obliterated by recrystallization; the rock ranges from dismicrite to sparstone, according to the classification of Wright (1992), either in scattered micropatches of sparitic calcite (> 0,01 mm) with mosaic texture developing in the mud matrix, or associated with fragmented bioclasts (with larger calcite crystals). The existence of an argillaceous matrix enriched in organic matter gave a particular diagenetic lamination in the compaction of sediment, which seems to prevail during the aggrading process of recrystallization.

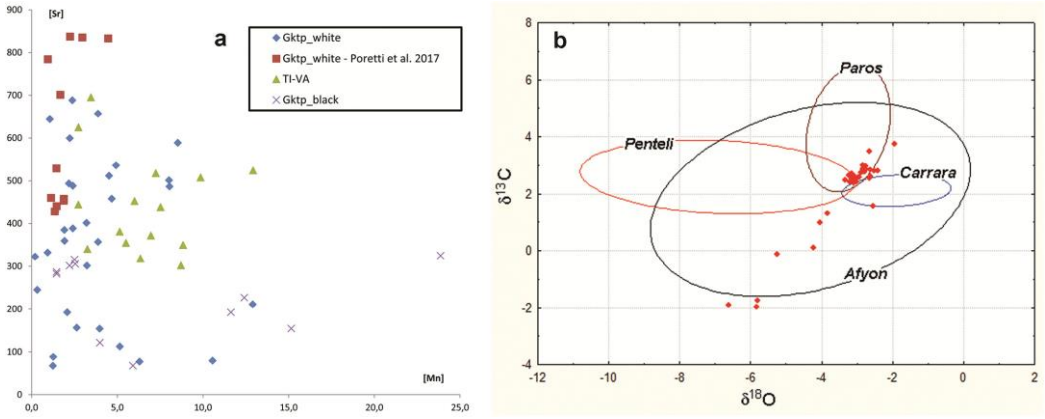

Fig. 6. a) Scatterplot of the concentration of strontium and manganese (units in ppm) of the Göktepe white and black for the samples of this study and that of Poretti et al. (2017); b) scatterplot of the carbon and oxygen isotope compositions of the Göktepe white marble, ellipses represent the probability distribution (99%) of isotope data of the most important fine-grained white marbles exploited in classical times. Data, represented by the ellipses, are from the database of Attanasio et al.,2006. Delta units are versus V-PDB international standard.

4.1.1 Lithotype 1 (GTB-1, GTV_1b, GTB-3, GTBC-3)

Lithotype 1 was defined as a partially recrystallized limestone; microscopic examination showed the highly heterogeneous fabric of this carbonate rock (even in the same thin section) due to irregular distribution of components and variable aggradation in the size of calcite (e.g., Fig. 7a A,B,C,D). Instead, the partial state of recrystallization allows us to identify the composition and microstructure of the carbonate protolith. The original sediments were mud-supported bioclasts (from less than 10% and, in some cases, reaching 25%) in various states of fragmentation, mudstone-wackestone (Dunham, 1962), or fossiliferous micrite -sparse biomicrite (Folk, 1962). The fossils are thick-shelled marine bivalves (mostly rudists), gastropods and unidentified microfauna. The identified skeletal grains showed that rudists are the most significant thanks to two aspects, their shape and the microstructure of their shelled walls. The typical arrangements of large prismatic calcite together with the roughly sub-parallel alignment of crystals, sometimes disjointed and broken away from the shells, are perfectly identified in this lithotype. Different views are shown for sample GTBC-3 (Fig. 7a G,H), with various sectioned microstructures, also in transverse section, in which they exhibit a lenticular shape (Fig. 7a E,H). Individual crystals, segmented and separated from the rest of the microstructure, occasionally appear as monocrystals isolated in the matrix (Fig. 7a E,F).

As regards the original impure sediment, the presence of organic matter and argillaceous mud in various quantities and irregularly distributed (from disperse [Fig.7a D] to flattened in dark planar laminations [Fig.7a H]) revealed a remarkable feature in the rock proper of diagenetic origin (Flügel, 2010). Before thermal transformation into well-crystallized graphite, proper to metamorphic conditions, the process of maturation of organic matter led to the formation of layered oriented polyaromatic components (graphitized carbon particles) during diagenetic carbonization (Buseck and Beyssac, 2014). The dark planar lamination (Fig. 7a G) (sometimes crinkled or stylo-laminated by pressure solution) may be misinterpreted as metamorphic pervasive foliation. This distinctive feature is only visible microscopically (e.g., Fig. 7a H), since the stone shows a high degree of compactness when freshly cut.

Table 2
Petrographic, mineralogical and cathodoluminescence features of Göktepe black stone in quarry and archeological samples. Minerals and components have been identified by Optical Microscopy (OM) and by X ray diffraction (XRD), (whole rock samples and residues after acid attack).

Black Göktepe		Location	Sample	Fabric texture	Minerals OM	XRD + (acid attack)	Original sediment % recrystallized matrix/(MGS mm)	Lithotype	Cl. Int.
Quarry samples Quarry District 3 (Attanasio et al., 2009)		Quarry District 3 (Attanasio et al., 2009)	GTB-1 GTV 1b (Fig. 6A to D)	Heterogeneous, massive micrite partially recrystallized Recrystallized bioclasts: radiaxs (thick-walls prismatic microstructure); gastropods	Calcite, clays, organic mat (disperse)	Calcite	Bituminous biomicrite (mudstone-packstone) Mud-supported bioclasts (< 25%) ≤25% mosaic micropatches with individual crystals (MGS ≤ 0.05 mm) Calcite shelled-walls (MGS > 1 mm)	(1) Partially recrystallized limestone	Very low/ low
			GTB-2 (Fig. 7C)	Heterogeneous, very scarce micrite, almost totally recrystallized Recrystallized disjointed shelled-walls Calcite microveins (MGS ≤ 0,4 mm) Laminated? scarce impure micrite	Calcite, clays?, opaques (graphite?)	Calcite	Obliterated bituminous limestone? (deduced) ≥95% mosaic groundmass with individual crystals (MGS ≤ 0.15 mm) MGS ≤ 0.6 mm (in isolated prismatic crystals from wall microstructure)	(2) Almost totally recrystallized limestone sparstone (Ultra-fine marble quality)	
			GTB-3 (Fig. 6E, F)	Heterogeneous, massive micrite partially recrystallized Recrystallized disjointed shelled-walls Calcite microveins (MGS ≤ 0.25 mm)	Calcite, clays, organic mat (disperse)	Calcite	Bituminous biomicrite (mudstone) Mud-supported fragmented bioclasts (< 10%) ≤10% mosaic micropatches with individual crystals (MGS ≤ 0.05 mm) MGS ≤ 0.6 mm (in isolated prismatic)	(1) Partially recrystallized limestone	
Archeological samples	COLUMN SHAFTS		GTB-4 GTBC-5 GTBC-6 (Fig. 7D)	Heterogeneous, massive/laminated micrite totally recrystallized Recrystallized: disjointed shelled-walls, "ghosts" (lenticular-shape, replaced by mosaic calcite, but clearly recognized some lamellar shelled-walls inside) Lamination non pervasive, preserved in recrystallized microbands	Calcite, clays?, opaques (graphite?)	Calcite + (quartz, chlorite illite/kaolinite, feldsp., graphite chabazite) Calcite	Obliterated bituminous limestone? (deduced) ≥95% mosaic groundmass with individual crystals (MGS ≤ 0.15 mm) "ghosts" in mosaic (MGS ≤ 0.8 mm)	(2) Almost totally recrystallized limestone sparstone (ultra-fine marble quality)	
		Quarry District 3 (Attanasio et al., 2009)	GTBC-1 (Fig. 7E to H						
			GTBC-2 (Fig. 7A, B)	Heterogeneous, micrite mostly recrystallized Recrystallized: bioclasts (lenticular-shape), disjointed shelled-walls Lamination non pervasive	Calcite, clays, laminated carbonized organic matter	Calcite	Partially obliterated bituminous limestone ≤50% mosaic patches with individual crystals of MGS ≤ 0.15 mm MGS (≤0.6 mm, in mosaic lenticular-shape, or in isolated prismatic monocrystals)	(1 to 2) Partially recrystallized/ limestone to sparstone	
			GTBC-3 (Fig. 6G, H)	Heterogeneous, massive/laminated micrite partially recrystallized Recrystallized: bioclasts (lenticular-shape), disjointed shelled-walls Lamination non pervasive		Calcite + (quartz, chlorite illite/kaolinite, feldsp., graphite, chabazite) Calcite	Bituminous biomicrite (mudstone-packstone) Mud-supported fragmented bioclasts (< 10%) ≤15% mosaic micropatches laminated with individual crystals MGS ≤ 0.05 mm MGS > 1 mm (in isolated prismatic crystals from wall microstructure)	(1) Partially recrystallized limestone	
	STATUARY	Villa Adriana (Lapuente et al., 2012b)	TI-VA_46						

The grain size of the calcite, being partially patchy, is quite heterogeneous, which meant that it was not suitable for systematic MGS or MFS measurements. In any case, the differing MGS observed in each thin section and in various microstructures are listed in Table 2. The finer calcite (0,02 mm) constitutes most of the recrystallized matrix. Calcite is quite uniform in size (0,05 and 0,25 mm respectively) in mosaic patches and microveins, and is the largest in the prismatic microstructure of shelled-walls, ranging from 0,6 mm to more than 1mm.

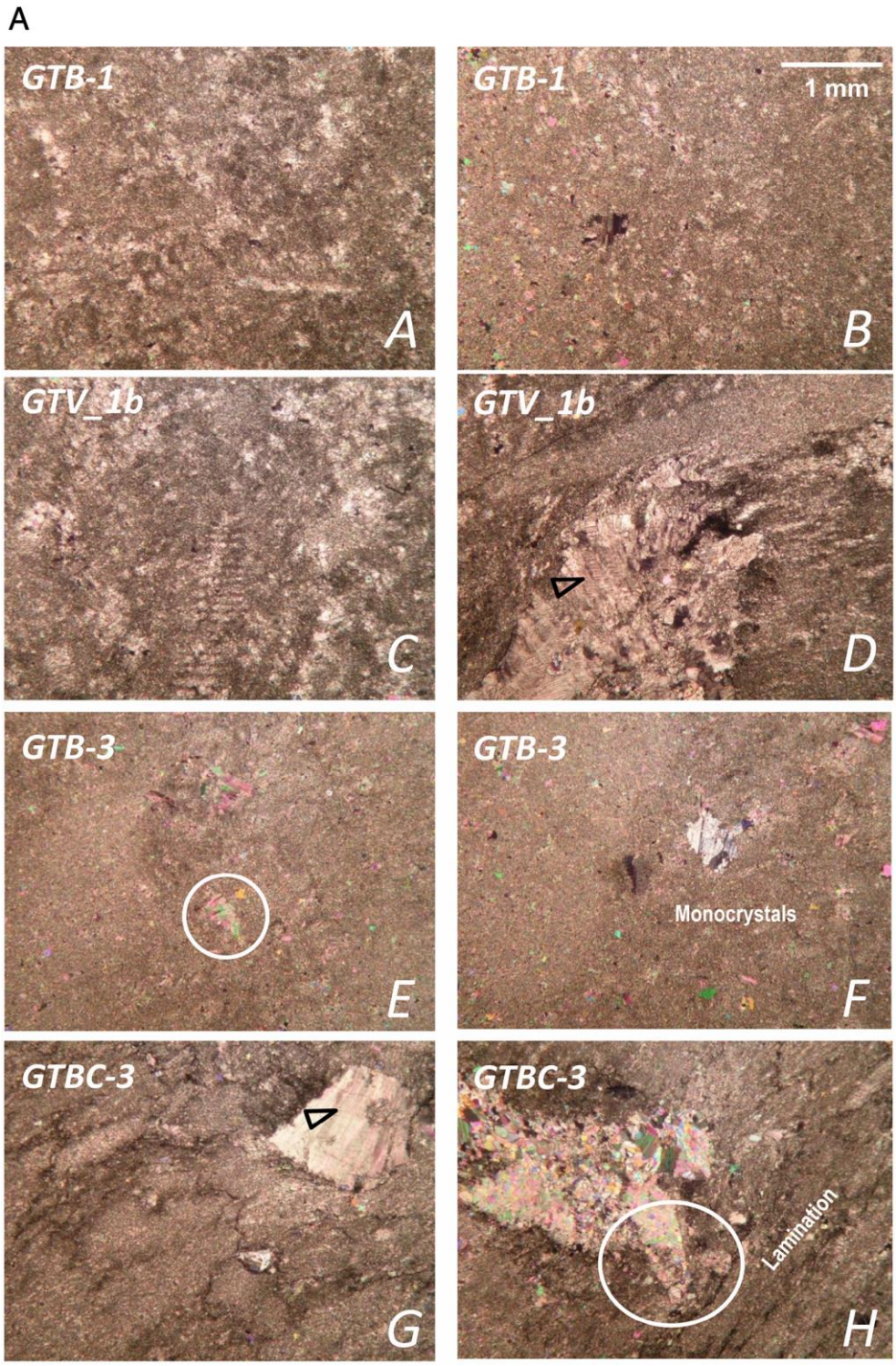

Fig. 7. a – Microphotographs in analyzed polarized light of quarry samples of Black Göktepe Lithotype 1. (A) to (D) Different views of the same partially recrystallized limestone (sample GTB-1 and GTV_1b); (E) and (F) sample GTB-3 shows the presence of fragments of bioclasts, in lenticular shape with arrangements of large prismatic calcite in side (E) and isolated monocrystals derived from bioclasts (F); (G) and (H) sample GTBC-3 shows different views of sectioned shells, typical arrangements of large prismatic calcite (G) and transverse section with lenticular shape are visible in (H), organic matter and argillaceous mud, flattened in dark planar laminations, is marked.
b – Microphotographs in analyzed polarized light of quarry samples of Black Göktepe. (A) and (B) transition from Lithotype 1 and Lithotype 2 (GTBC-2 sample); micritic matrix is more abundantly recrystallized (≤50%) than in Lithotype 1, but the flattened impure mud lamination of micrite is still visible. Lenticular-shape forms with mosaic calcite and some prismatic arrangements (proper to the shelled-walls) are interpreted as recrystallized bioclasts. Local signs of pressure solution (common in low grade deformation), can be recognized along the contact of some rigid lenses of bioclasts with the fine impure matrix. (C) to (H) Recrystallized carbonate rock (Lithotype 2); ultrafine grained groundmass of calcite (≤0,15 mm) with some isolated larger monocrystals and lenticular-shape patches interpreted as “ghosts” of bioclasts. Some lamellar shelled-walls with prismatic arrangement microstructure are still visible in (E) and (F), in crossed and plane polarizers respectively. Signs of pressure solution and preserved lamination are marked.

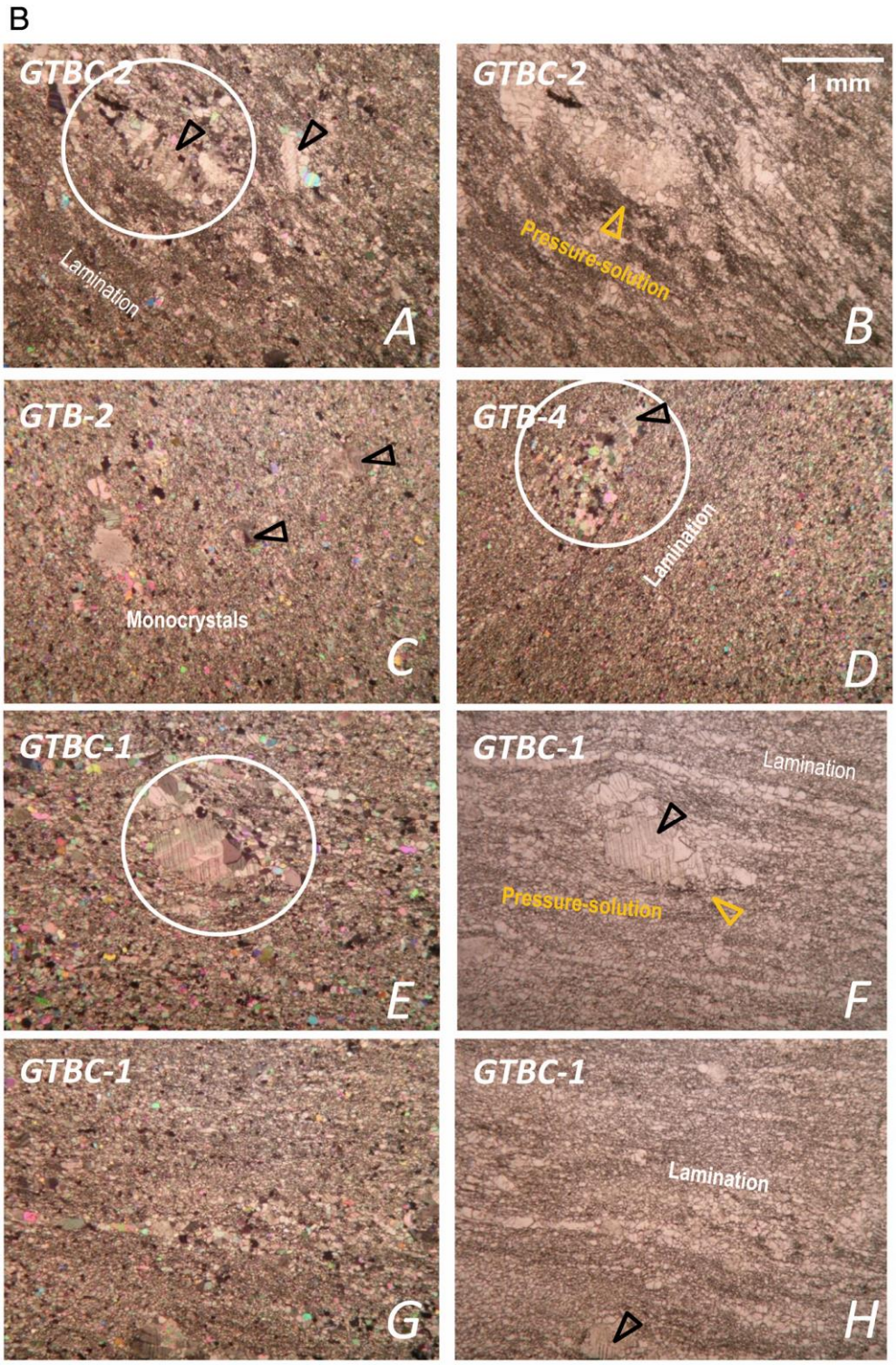

Fig. 7. (continued)

The black statuary artifact from Villa Adriana (TI-VA_46 in Lapuente et al. 2012b) is similar to this lithotype. The transition from Lithotype 1 to Lithotype 2 is shown in sample GTBC-2 (Fig. 7b A,B), in which the micritic matrix is more abundantly recrystallized (≤ 50%) than in Lithotype 1, although the flattened impure mud lamination of micrite is still visible. Indeed, the recrystallized micropatches deriving from the matrix are elongated following the same lamination, probably imposed by the presence of carbonized particles during compaction. Another important feature is the existence of lenticular-shaped forms with mosaic calcite, but also some prismatic arrangements (proper to shelled-walls) which can be interpreted as recrystallized bioclasts. Outside the geological context, these lensed forms may be erroneously interpreted as porphyroclasts (large relict grains of pre-existing polymineral grains embedded in a new finer-grained

groundmass of recrystallized material associated with shear deformation and ductile flow). However, diagenetic compaction with local signs of pressure solution (common in low-grade deformation) is found along the contact of some of these rigid lenses of bioclasts with the fine impure matrix. Indeed, isolated monocrystals (fragmented shelled-walls) are embedded in the laminated matrix (see details in Fig. 7b A,B). Microscopic observation of this thin section, with adequate magnification, is a key to our interpretation that this lamination and the lenticular shapes must not be misunderstood as features of mylonitic structures. It is important to note that the mylonitic texture considered to be an important feature of the Göktepe black according to Attanasio et al. (2015) was not found in our samples, although obviously it may have developed locally, associated with specific shear zones.

4.1.2 Lithotype 2 (GTB-2, GTB-4, GTBC-1, GTBC-5, GTBC-6)

In Lithotype 2 (Fig.7b), the carbonate rock shows almost total recrystallization (≥ 95 %) involving an ultrafine grained groundmass of calcite with some larger isolated monocrystals and lenticular-shaped patches of a mosaic of larger calcite (MGS ≤ 0,6mm), interpreted as "ghosts" of bioclasts. Some lamellar shelled-walls with prismatic arrangement microstructure are still visible (Fig. 7b C,D,E,F,H). Samples GTB-4, GTBC-1, GTBC-5 and GTBC-6 are petrographically similar despite recrystallization, and have preserved their laminated character lying over the previous lamination and recognizable by the heterogeneous size reached in each alternating sub-parallel micro-layer (Figs. 7b F,H). All the samples in this group show small dispersed opaque crystals, presumed to be graphite. No signs of dynamic recrystallization were seen, but signs of pressure solution are associated with the presence of a black matrix at the bottom of some rigid lenses of recrystallized bioclasts (Fig. 7F). The MGS of calcite in the groundmass is in fact slightly larger (≤ 0,15 mm) than that of Lithotype 1 (≤ 0,05 mm), confirming the prograding process of recrystallization. Small microveins filled with coarse calcite (MGS ≤ 0,4 mm) are also present.

The CL of the Göktepe black samples is not uniform. The patterns present a generally black background which reflects the color of the stone; the coarser calcite crystals show very low red luminescence. High luminescence characterizes a large number of minute spots, probably associated with dispersed impurities. However, cathodoluminescence has never been proposed or considered useful as a technique for identifying the provenance of ancient black stones.

***4.2** Mineralogy*

On the whole, X-ray diffraction of samples did not reveal no-carbonate accessory minerals, with the exception of the minor presence of the most intense peak of quartz. Carbonate minerals are composed almost exclusively of calcite, and the occasional finding of dolomite is always less than 1%, evaluated by comparison of the most intense peaks of calcite and dolomite. The results of XRD calcite versus dolomite are listed in the supplementary Table 4 of de Supplementary materials.

For Lithotypes 1 and 2, large powdered samples of about 10 grams of the black stone were selected, respectively GTBC-3 and GTB-4, and acidified with acetic acid (0.8N) for complete carbonate digestion. This acid attack should prevent clay minerals and various oxides from dissolving. The solution was then filtered and the resulting product dried. The insoluble residues were fine black powders, constituting 0.6% and 0.4% in weight of the original samples for Lithotype 1 and 2, respectively (Table 3). XRD analysis of the residue showed that the mineralogical phases in both samples were dominantly composed of quartz, chlorite, chabazite (Ca-zeolite) and illite/kaolinite, with subordinate graphite and a feldspar mineral (plagioclase). Table 4 (presented as a supplementary file) lists the mineralogy of the insoluble residues of black Göktepe, the diffractograms of which are shown in figure 8a,b. In any case, the two lithotypes showed clear differences in the quantitative proportions of their mineral phases. The main differences appear in the contents of chabazite, which dominates the XR diagram of Lithotype 2, and graphite, which is much more intense in Lithotype 2.

***4.3** Characterization of carbonaceous matter*

The residues were also elemental analyzed for CHN percentages (for results, see Table 4, supplementary materials). Five repetitions were performed in both cases, and carbon contents turned out to be 6% and 15% of the residues of Lithotypes 1 and 2, respectively; the analysis did not discriminate between graphite

and organic carbon. Nitrogen and hydrogen were detected in small quantities and were definitely organic in origin. The C/H atomic ratio varied from 0.5 to 1.5 in the most common kerogen material, and Lithotype 1 had a C/H ratio of 0.8 which, if we assume that the graphite in this lithotype is negligible, should indicate a certain degree of carbonization. Carbonaceous matter showed an isotopic composition (-12.7‰), confirming progressive maturation, during which volatilization of gas species (e.g., CH4) fractionated the carbonaceous residue. Fractionation produced an isotopic composition heavier than that of the pristine organic matter, which generally shows much more negative $\delta^{13}C$ values (average -25‰). The carbon of Lithotype 2, which had more than twice the percentage of the carbon of Lithotype 1, should be of different origin and/or nature, since it certainly constituted most of the graphite, as shown by XRD. In addition, the difference in $\delta^{13}C$ (about 3‰) confirms the difference in carbonaceous matter between the lithotypes.

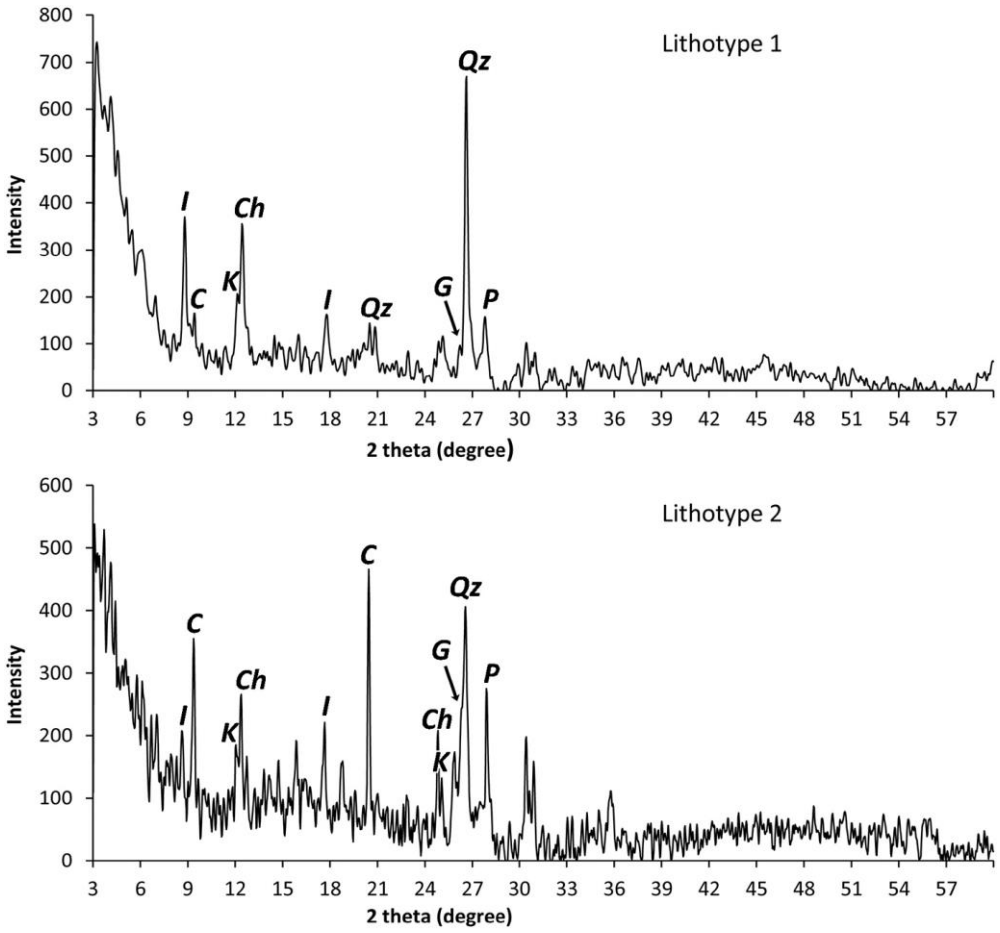

Fig. 8. XR diffractograms of the Lithotype 1 and 2 from Göktepe black samples. C=chabazite, Ch=chlorite, G=graphite, I=illite, K=kaolinite, P=plagioclase, Qz=quartz.

4.4 *Trace elements and isotopes*

Trace element and isotopic data are presented in a supplementary file (Tab.Supp. 3) and are shown in figures 6a, b. The Göktepe black samples show similar trace element and isotopic behavior to the white ones, although Sr on average has a slightly lower concentration. Similarly, the decrease in Sr concentrations is accompanied by decreases in the compositions of oxygen and carbon isotopes, confirming that this rock too was partially involved in the alteration process which reset the isotopes and chemistry to new environmental conditions. Black Göktepe (Lithotype 1) is confirmed in the statuary TI-VA_46 of Villa Adriana by high Sr contents (318 ppm) and very low Mn (6 ppm).

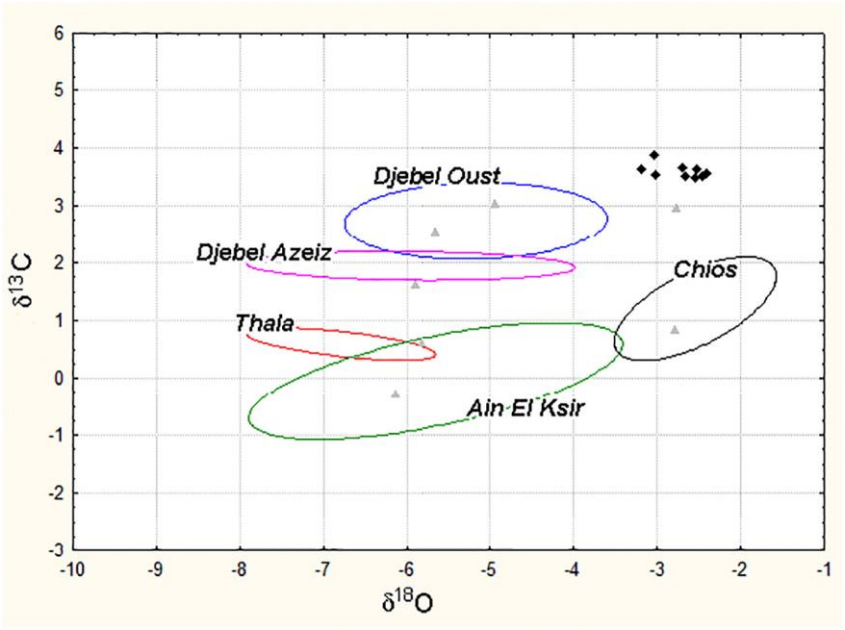

Fig. 9. Scatterplot of carbon and oxygen isotope compositions of black limestones exploited in classical times represented by ellipses. Data are from Brilli et al. (2010). Black and gray dots represent Göktepe data presumably belonging to Lithotype 1 and Lithotype 2, respectively.

5. Discussion

5.1. *Göktepe White*

5.1.1. Göktepe and Carrara comparison

Göktepe white is a pure calcitic marble, as shown by its almost mono-mineral character; no accessory minerals were detected by optical microscopy. The presence of minimum amount of quartz was revealed by XRD of the whole rock. Both homeoblastic and slightly heteroblastic textures (in larger individual crystals or in patches) were very common, so that larger crystals, which move the MGS parameter toward higher values, were often found, leading to a deceptive grain-size picture of the marble. The case of the comparison between marbles from Göktepe and Carrara, to which white marble artifacts were (or may have been) often erroneously attributed in the past, is emblematic. The grain size of Carrara marble seems on average coarser than that of Göktepe marble, although MGS estimations of Göktepe white marble are often similar to those for Carrara (see Attanasio et al., 2000; Gorgoni et al., 2002; and Antonelli and Lazzarini, 2015 for Carrara, and Attanasio et al., 2015; and the present work for Göktepe). Examination of the grain size distribution may be another good method for describing and comparing this marble with others, especially from Carrara. The distribution in decimal categories of grain size facilitates comparisons of very fine to fine-grained marbles. In particular, MFS is a parameter which should faithfully reflect the similarity (or otherwise) in size of each microstructure (homeo- or heteroblastic), as shown in the Results (see 3.1.1 and Figs. 3B, 3C).

As regards grain size distribution, our preliminary results obtained from the single sample of Carrara (Figs. 3B, 3C) reveal very subtle differences when compared with the respective samples from the Göktepe quarry. At first view, the histograms of Fig. 3B show that the distribution of this Carrara is comparable to that obtained from the heteroblastic sample GTW-3(He). In fact, MFS (ranging between > 0,1 and 0,4 mm) is quite similar in both samples, and corresponds to 80% of grains in Carrara and 74% in Göktepe. The similarity is even more evident when observed over a more restricted range of sizes (between > 0,1 and 0,3 mm), being 54% of grains in Carrara and 51% in Göktepe. However, in figure 3C, the grain size distribution of Carrara seems to be intermediate between both quarry samples of Göktepe, since only 11% of grains were > 0,4 mm in Carrara, a value very close to that obtained for the homeoblastic sample GTW-4(Ho), which was 10%.

In conclusion, this method seems to be sufficiently sensitive to reveal differences in texture and points to the great similarity between this Carrara and the quarry samples studied here. In this sense, other methods are required to discriminate Carrara and Göktepe marbles unambiguously.

However, the graphic grain size of the statuary samples from Villa Adriana reveals two important aspects (Fig. 3B and C). One is the distinctive and extremely fine-grained marble of group G which, in petrographic terms, is completely different from that of Carrara. The other aspect concerns the almost similar distribution of the grain size measured for the statuary sample of group C2 and those of Carrara and Göktepe quarry GTW-4(Ho). Both conclusive aspects will be discussed separately.
However, the intensity of CL (according to microfacies or quantitative CL) is certainly another method for separating white Göktepe stone from that of Carrara (Lapuente and Royo, 2016), according to their low Mn values. The difference in both CL intensities is shown in figure 4, in which the standard medium CL of Carrara is compared with the low to very low CL in the Göktepe samples. These differences may also be clearly observed in other cases, since many Carrara samples have higher CL intensities.
The white marble of Göktepe does not show peculiar carbon or oxygen isotope compositions. Most of the isotope data are similar to those of most classic white marbles, and are thus of very little help in identifying Göktepe in the artifacts carved from unknown marble. Nevertheless, their distribution shows a tail toward lower values which, in specific cases, may be of some help in discriminating this marble, especially from fine grain-size marble provenances (Carrara, Paros or Penteli), the data from which never approach such regions as those shown in the $\delta^{18}O/\delta^{13}C$ diagram. These lower values are similar to the isotopic data of Afyon marble (Antonelli and Lazzarini, 2015). Fortunately the CL patterns of Afyon and Pentelic marbles are very distinctive (Lapuente and Royo, 2016).
Sr and Mn trace elements effectively differentiate Göktepe marble. Mn contents may be extremely low and Sr remarkably high, with values of up to 800 ppm, rarely verified in other classic marbles. Poretti et al. (2017) demonstrated that other elements such as REE and Y are very effective in discriminating Göktepe white marble; the elements in question are technically more difficult to be determined in marble than Sr and Mn, which can be reliably determined by many analytical methods. Nevertheless, the range distribution of marble from the Göktepe quarries, especially that of Sr, is quite large, with values which may be as low as a few tens of ppm or as high as 800 ppm. Attanasio et al. (2015) attributed the low content of Sr to a particular area in the Göktepe quarries, labelled as district 4D. As the sampling for white marble of the present study was performed at random in district 3D and did not include district 4D of Attanasio et al. (2015), this means that low Sr contents may also be recorded in some quarry fronts of district 3D. The large variation in Sr may be partly due to a water-rock alteration process which also influenced isotopic compositions: if this were so, the distributions of Sr and isotopes may be functions of the sample locations. Our sampling strategy did not aim at spatial distribution of data and no relationships can be demonstrated.

5.1.2 Revised attribution of archeological samples

The archeometric study of 62 statuary pieces from Villa Adriana published by Lapuente et al. (2012a) had the advantage of working with a large number of samples, which were separated into several groups according to their homogeneous petrographic characters. Following a sequential multi-technique approach, with petrography and CL-microfacies as a first step, combined with stable isotopes, the samples of groups G and C2 were assigned to Göktepe and possibly Carrara marble, respectively. Complementary techniques, EPR and quantitative CL were used to refine these identifications, on the basis of the only available comparative data at that time (Attanasio et al., 2009). They are reconsidered here with updated reference data (Attanasio et al., 2015; Antonelli and Lazzarini, 2015; Poretti et al., 2017) and with the petrographic comparisons with quarry samples reported here. The homogeneous nature of samples in G and C2 groups is remarkable, enhancing the value of their respective archeometric parameters (Supp.Tab. 3).
The *Statuary G samples* have very small grain; EPR and CL features (microfacies and quantitative intensity at 620 nm) were significant in discriminating this group. Lapuente et al. (2012) reported average MGS < 0,5 mm, estimated from 18 thin sections (Fig. $S1_1$), which matched the data from Göktepe reported by Attanasio et al. (2009). However isotope values overlap those of Göktepe and Carrara (Fig. 6b). On the whole, with the exception of one sample, they reveal strongly overlapping data for $\delta^{18}O$ (from -2,74 to -2,5) and $\delta^{13}C$ (from 2,77 to 2,98). Low EPR intensity values (from 0,0116 to 0,1655) matched the low EPR values of the Göktepe quarries and also served to reject Carrara as their origin (they are completely outside the range of Carrara, with a mean value of 0,685) or any other known fine-grained marble.
Concerning the new data reported here on Sr and Mn contents, high Sr (from 302 to 524 ppm) and low Mn (8 ppm, on average) strongly confirm their Göktepe origin. In the petrographic study of quarry samples

performed here, there are no comparable varieties to this type. As figure 3B shows, this extremely fine marble was significantly different from the rest of the white marbles analyzed. Compared with the limited petrographic data reported by other authors, this type may be similar to the very fine-grained Göktepe specimens reported by Attanasio et al. (2015), and especially to that shown in the photomicrograph by Antonelli and Lazzarini (2015).

In conclusion, although this extremely fine marble was not detected in the quarry samples studied here, it must be admitted that the white Göktepe marble is identifiable by its grain size distribution. This petrographic type of high statuary quality should be defined by its own MGS if it is to be properly discriminated from other fine classic marbles. Otherwise, the larger MGS measured in other white Göktepe marbles unnecessarily expands the statistics, hindering identification.

The *Statuary C2 samples* were provisionally assigned to a possible Carrara origin (C2 group) by Lapuente et al. (2012). The lack of petrographic study of the Göktepe quarries affected the provenance assignment , as the specimens showed intermediate analytical characteristics between the two locations. In fact, the assignment was based on the MGS (higher than that of Group G) and texture similar to that typical of Carrara (Fig. $S2_1$), whereas CL and EPR pointed to a possible Göktepe origin. Isotope values did not aid discrimination (Fig. 6b), as their $\delta^{18}O$ ranges from -2.93 to -2.16 and $\delta^{13}C$ from 2.58 to 2.86. Quantitative CL revealed the lower intensities in the spectrum at 620 nm (from 1,72 to 3,6) from all analyzed samples. These values matched their very weak CL intensity observed by optical-CL (Fig $S2_2$) and also the extremely low intensities obtained in EPR analyses (0,0111 to 0,0276); these data are completely outside the range of Carrara or any other known fine-grained marble. In this case, C2 group, totally different from the extremely fine group G samples, was thought to be of possible Carrara origin, on the basis of two factors: first, because this was not the first time that anomalously low intensities in EPR did not rule out origin from Carrara (Attanasio et al. 2005) and second, because otherwise many previous provenance studies based on petrography would require further examination. In fact, over the past six years, several contributions have revealed some erroneous attributions of Carrara in the past. This is one of the reasons why it was deemed important to include this revision here.

Regarding the new data, petrographic comparisons between quarry and C2 statuary samples show great similarities in microstructure and grain size distribution (Tab. 1). In particular, the graphs obtained with the method adopted in this paper reveal the similarity between the homeoblastic GTW-4 quarry sample and the representative sample of group C2 (Fig. 3B). In both, MFS falls in the range > 0,1-0,3 (in 70% and 68% of measurements, respectively) and MGS ranges between 0,9 and 0,8 mm. The homeoblastic texture, common to both samples, can also be deduced from the values shown in figure 3C. In both, the percentage of grains > 0,4 mm are respectively 10% and 7%, i.e., quite different from the 21% of grains measured in the slightly heteroblastic texture of sample GTW-3(He). This should be sufficient to acknowledge that group C2 is, in fact, another Göktepe petrographic group different from the extremely fine Group G. However, as previously mentioned, Carrara marbles also have similar petrographic features. Fortunately, as the concentrations of Sr and Mn have been proved to be quite effective for discriminating Göktepe , these trace elements were tested on six available samples of group C2 (see section 3.2): their very low Mn contents (4 ppm on average) matches their very low CL intensity; Sr ranges from 340 to 695 ppm - values which strongly confirm their Göktepe origin and definitely rule out an Italian source for this marble.

5.2 Göktepe Black

Although the Göktepe black stone is chemically and isotopically similar to the Göktepe white marble, it is petrographically quite different and more variable. Previous archeometric studies have geologically defined this stone as a marble which underwent low-grade metamorphism. Macroscopically, it is more similar to some well-known ancient limestones than to black marbles. Microscopically, according to the results presented here, it is an impure limestone, partially or almost totally recrystallized, without signs of ductile deformation or dynamic recrystallization. Its petrographic features can be set within at least two main lithotypes, regardless of samples locally affected by shear zones and due to fault rocks.

Minerals and microstructure transformations indicate that the first type (Lithotype 1) is a highly diagenized carbonate rock; the second (Lithotype 2) is a crystalline carbonate rock in which the original pristine depositional nature and texture were almost totally obliterated by recrystallization. Although in terms of quality they are similar to ultrafine grained marbles, several petrographic aspects support the hypothesis of

a prevailing sedimentary nature. Some considerations must be taken into account to define its geological nature better. The degree of calcite recrystallization is generally used to evaluate the aggrading process of recrystallization in sedimentary-diagenetic contexts. Some authors (e.g., Arkai and Kovács, 1986) facing the problem of defining rocks which underwent temperatures and pressures between diagenesis and metamorphism, coined the term 'meta-sparite' (> 0,03 mm) to describe very fine mosaic groundmass in which, however, calcite exhibits some indications of metamorphism, such as the presence of complex twinning. In our samples, this size was reached, but traces of twins were not detected. Although this reference size may aid the identification of black Göktepe, specific circumstances must be taken into account, all due to the nature (texture and composition) of the black protolith, a bituminous argillaceous bioclastic limestone, which inevitably affected the recrystallization of limestone in two opposite ways, inhibiting and releasing the aggrading size process.

On one hand, the presence of certain components such as clays and organic matter inhibits the earlier process of crystal coarsening from micrite mud. According to Bausch (1968), the existence of more than 2% of clay in sediments prevents the aggrading process in limestone. In addition, as already noted, during diagenesis but before thermal transformation into well-crystallized graphite (proper to metamorphic conditions), mature layers of oriented poly-aromatic organic matter were enhanced by graphitized carbon particles (Buseck and Beyssac, 2014). These components constitute dark microstructures with flattened to planar lamination, which may also hinder early calcite growth. When these laminated microstructures are not pervasive, they may be misinterpreted out of their correct context as metamorphic foliations.

On the other hand, the presence in the sediment of previous large calcite crystals in bioclasts (whether original shells or transformed from aragonite) aided better growth of these calcites during the aggrading process, allowing them to reach a coarser size in comparison with the groundmass. In these circumstances, the final size achieved by the crystals and their heterogeneous distribution are directly inherited from the original fabric.

Lastly, depending on the degree of recrystallization, the original depositional fabric may have been totally obliterated; conversely, some shelled relicts may have been preserved and identified by their shape or a particular calcite microstructure (arrangements in the original shells). This prevailing sedimentary nature of the studied samples points to a poor degree of recrystallization, which did not reach the true gradient of metamorphism. In fact, the definitive term adopted is 'sparstone'.

The ultrafine mosaic calcite texture observed in Lithotype 2 may be related to diagenetic recrystallization or very low metamorphism (as indicated by the joint presence of this black stone and the white marble), during which blastesis was inhibited by the characteristics of the original protolith. Since Göktepe black stone does not show any signs allowing it to be definitively attributed to low-grade metamorphism, the Subcommission on the Systematics of Metamorphic Rocks (SCRM) (Schmid et al. 2007) recommends that: 'those rocks which do not show any sign of very low-grade metamorphism should be given the appropriate non-metamorphic rock name, regardless of their close spatial and genetic relationship to the metamorphic rocks. This implies that metamorphic rock names may alternate with sedimentary ones in the same geologic profile or map.

Trace mineral investigations corroborated the differences observed in thin sections. Lithotype 1, the petrographic description of which approaches that of a diagenized limestone, also has an assemblage of trace minerals which may confirm this interpretation. Lithotype 1 is mainly composed of chlorite and illite/kaolinite minerals, together with detrital quartz and feldspars. Graphite makes a minor contribution in mineral traces, and the black matter observed in it must mainly be ascribed to organic matter, matching the microscopically observed diagenetic structures. Lithotype 2, almost totally recrystallized, coarser in grain size and petrographically similar to an ultrafine marble, shows a similar assemblage of minerals, with the exception of the more abundant presence of graphite and, in particular, chabazite.

Maximum temperature is difficult to assess on the basis of the mineralogical assemblages. The chlorite mentioned in previous studies to sustain the metamorphic nature of the Göktepe black stone cannot be safely used for this purpose, since it may be of detrital origin. Graphite represents minor contributions in mineral traces. The presence in Lithotype 2 of chabazite, which belongs to a calcic zeolite group, is the most outstanding mineralogical element. It generally forms in circulating fluids of mafic rocks during the early stage of a thermal history of the rock (Liou et al., 1991; Frey and Robinson, 1999). This zeolite was probably introduced into the rock body from external fluids rising from layers of the local sequence, in which mafic

meta-volcanite interbedded schists occur (Attanasio et al. 2015). This was probably the same event which was responsible for the isotopic alteration which involved both white and black stones; the sample of Lithotype 2, which was studied for mineralogy, does show isotopic composition in the alteration tail (see isotopic diagram ($\delta^{18}O$ = -6,14‰ and $\delta^{13}C$ = -0,29‰; Fig. 7a). As graphite may result from the transformation of organic matter during metamorphism or by precipitation from carbon–bearing fluids (Luque et al., 2012), the graphite in Lithotype 2 may have originated by precipitation from this alteration fluid, as its greater quantity and different isotopic composition with respect to Lithotype 1 may confirm. These aspects are concomitant in Lithotype 2 sample with enrichment of Mn and depletion of Sr. All these indications show that the Göktepe carbonate rock underwent interactions with thermal fluids which caused isotopic and chemical resetting to new temperatures and/or composition of fluids, until the fluids themselves preserved their alteration potential. This resetting event, which may have occurred at any time during the thermal history of this rock, probably contributed to greater calcite crystal growth. Its geochemical and petrographic effects are visible in the graphitic sparstone of Lithotype 2.
Further investigations are required to determine the temperatures reached by this rock, although this information is not crucial for the purpose of this paper, which aims at better petrographic and mineralogical characterization to identify the rock.

6. Conclusions

This study aimed at providing an improved description of the petrography and mineralogy of the white and black stones of Göktepe, exploited in ancient times in the Caria region of Turkey and probably mainly used by the aphrodisiensis sculptors and stonemasons. Some authors consider the white variety to have been the most frequently used marble in classical times for portraits. Attanasio et al. (2015) archeometrically studied this marble, to discriminate it from other classical marbles according to differing techniques. Of these, petrography has received less in-depth study. The petrographic study of thin sections of classical marbles is crucial for an understanding of their provenance, and is widely adopted in marble provenance studies.
Microscopically, white Göktepe marble shows at least two different petrographic types of pure calcite statuary quality. Image analysis software has been tentatively used to clarify the linear dimensions of each grain in an area representative of each thin section of Göktepe white. For a better description of the differences of both types, grain-size distributions were represented in figures, for clear-cut characterization and definition of a new parameter, the Most Frequent Size (MFS), to be used together with Maximum Grain Size (MGS). Grain-size distribution data and MSF applied to some samples in this study seem to characterize well both types of Göktepe white marble.
In terms of microstructure, texture and grain size, one type is similar to Carrara marble. It was identified not only in quarry samples, but also in statuary pieces from Villa Adriana (group C2) after the critical revision made in this paper, rejecting the possible Carrara origin wrongly interpreted in the past. In the studied samples, MGS ranges from 0,8 to 1,1 mm in isotropic granoblastic textures, mostly homeoblastic, with MFS (> 0,1-0,3 mm) in about 70% of grains. Being petrographically and isotopically very similar to Carrara marble, additional methods such as the intensity of CL and the high Sr content had to be used to discriminate the Göktepe type from Carrara marble.
The second petrographic type is extremely fine, the finest white marble ever exploited in antiquity. Although it was not identified in the quarry samples of this study, all techniques applied to statuary group G of Villa Adriana indicate a Göktepe origin, which is confirmed here with chemical data. It probably represents the very distinctive marble and the best statuary quality of all white Göktepe. It has a mosaic texture of fine calcite with MFS ≤ 0,2 mm in 70% of grains, and MGS of 0,6 mm, although only about 4% is > 0,4 mm. Unlike the other type, this extremely fine marble shows clear signs of dynamic recrystallization.
As regards the black Göktepe stone, thin sections show that the carbonate rock has very fine but heterogeneous grain size and variable structures. Petrographically, the stone can be identified as a diagenized carbonate rock, with highly heterogeneous recrystallization, mainly due to the heterogeneities of the protolith and the effects of compaction. The heterogeneity of the rock allows us to distinguish at least two main general lithotypes with different grain sizes and microstructures. Study of trace mineral contents, performed by dissolution in acetic acid of the whole rock and XRD of the residue, showed that

alteration produced by infiltration through the rock of a fluid at low temperature probably involved a portion of that rock and contributed to the differences between the lithotypes. A calcic-zeolite phase and graphite were probably precipitated from this fluid. This process, which chemically and isotopically altered the rock, probably also enhanced recrystallization.

Clearly, mineralogical investigation of acid attack residues on archeological samples is impossible, because many grams of material would be required, as it is 0.6% at best; this is why mineralogical investigation cannot be applied usefully in marble provenance studies. In any case, this study does explain some features observable in thin sections and allows us to evaluate their degree of reliability when used to define provenance.

The origin of black stones used in antiquity has recently aroused growing interest, especially after the discovery of the Göktepe quarries. Recent data (Lazzarini, 1997; Attanasio et al., 2009, 2015; Yavuz et al., 2009; Brilli et al., 2010) have been of enormous help in locating the provenance of black stones. Macroscopically, most of them do not show great differences. At present, identification of Göktepe stone should not cause great difficulties as regards scientific bases, because petrographic investigations can identify it. The true (geologically speaking) black marbles, originally identified as *neri* or *bigi antichi*, are petrographically very different from the Göktepe stone, in that they clearly have larger grain size (Lazzarini et al. 1999; Lazzarini, 2007). Most of the black stones used in antiquity are limestones (Agus et al., 2006; Pensabene and Lazzarini, 1998; Brilli et al. 2010, 2011; Lazzarini, 2013). The Göktepe black stone which is most similar to these ancient black limestones is Lithotype 1: it generally has isotopic composition which is clearly different from the ancient limestones. Figure 9 shows the black limestones described by Brilli et al. (2010) in a $\delta^{18}O/\delta^{13}C$ diagram, together with the Göktepe data which may be attributed to Lithotype 1. Their field mainly falls outside those of some well-known black limestones quarried in antiquity.

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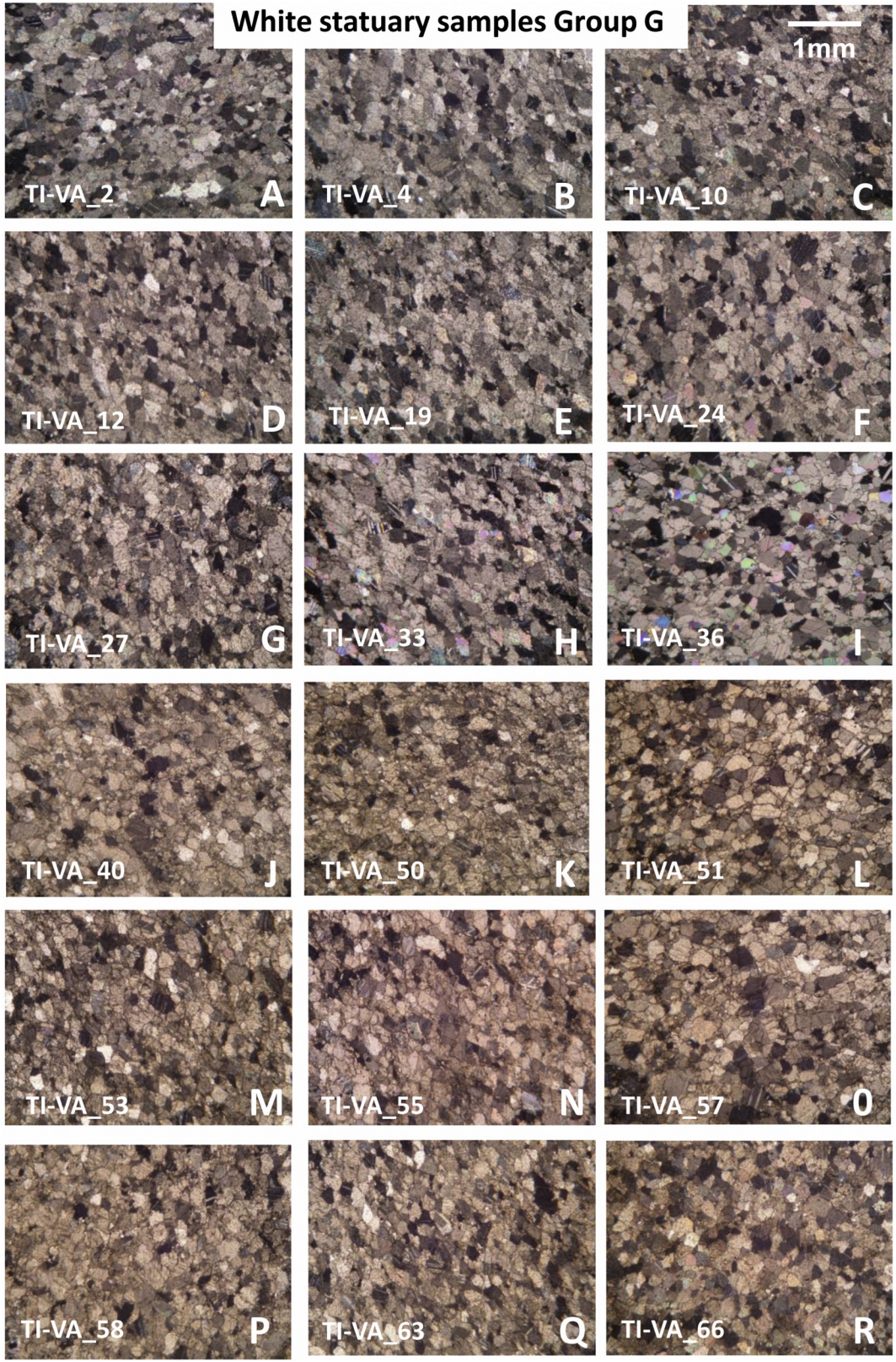
White statuary samples Group G
1mm
TI-VA_2
A
TI-VA_4
B
TI-VA_10
C
TI-VA_12
D
TI-VA_19
E
TI-VA_24
F
TI-VA_27
G
TI-VA_33
H
TI-VA_36
I
TI-VA_40
J
TI-VA_50
K
TI-VA_51
L
TI-VA_53
M
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N
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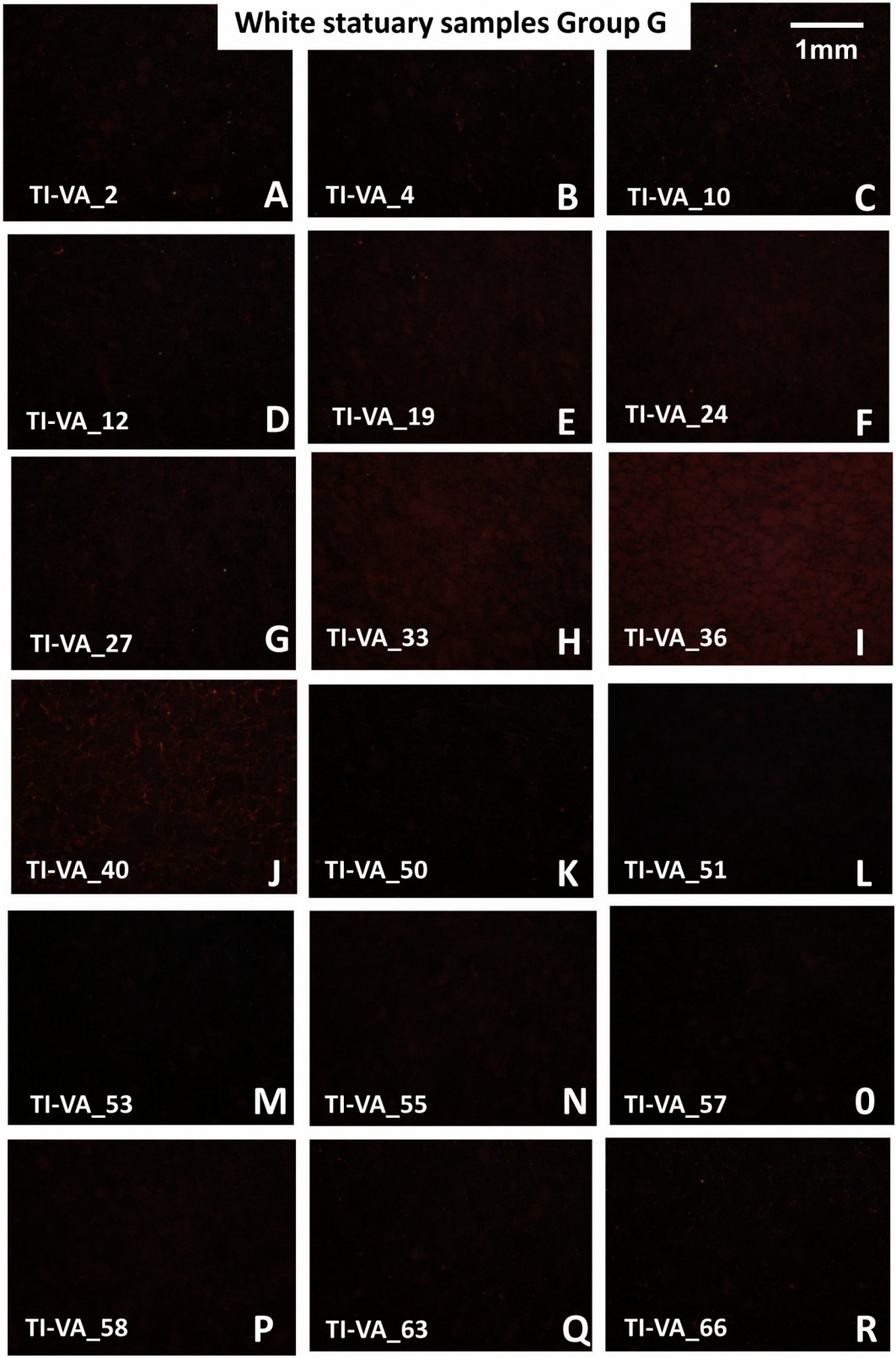
TI-VA_58
P
TI-VA_63
Q
TI-VA_66
R


White statuary samples Group G
1mm
TI-VA_2
A
TI-VA_4
B
TI-VA_10
C
TI-VA_12
D
TI-VA_19
E
TI-VA_24
F
TI-VA_27
G
TI-VA_33
H
TI-VA_36
I
TI-VA_40
J
TI-VA_50
K
TI-VA_51
L
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P
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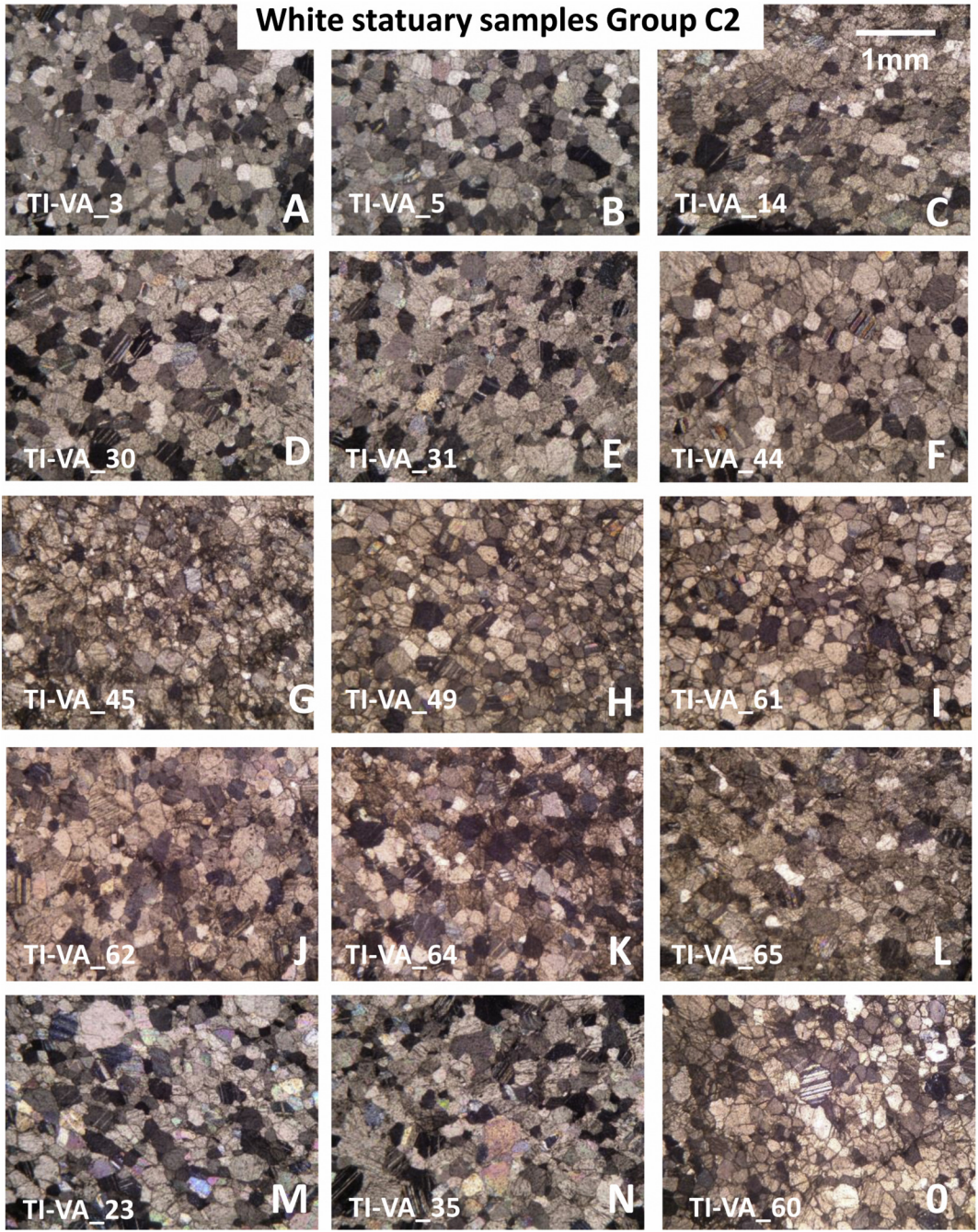
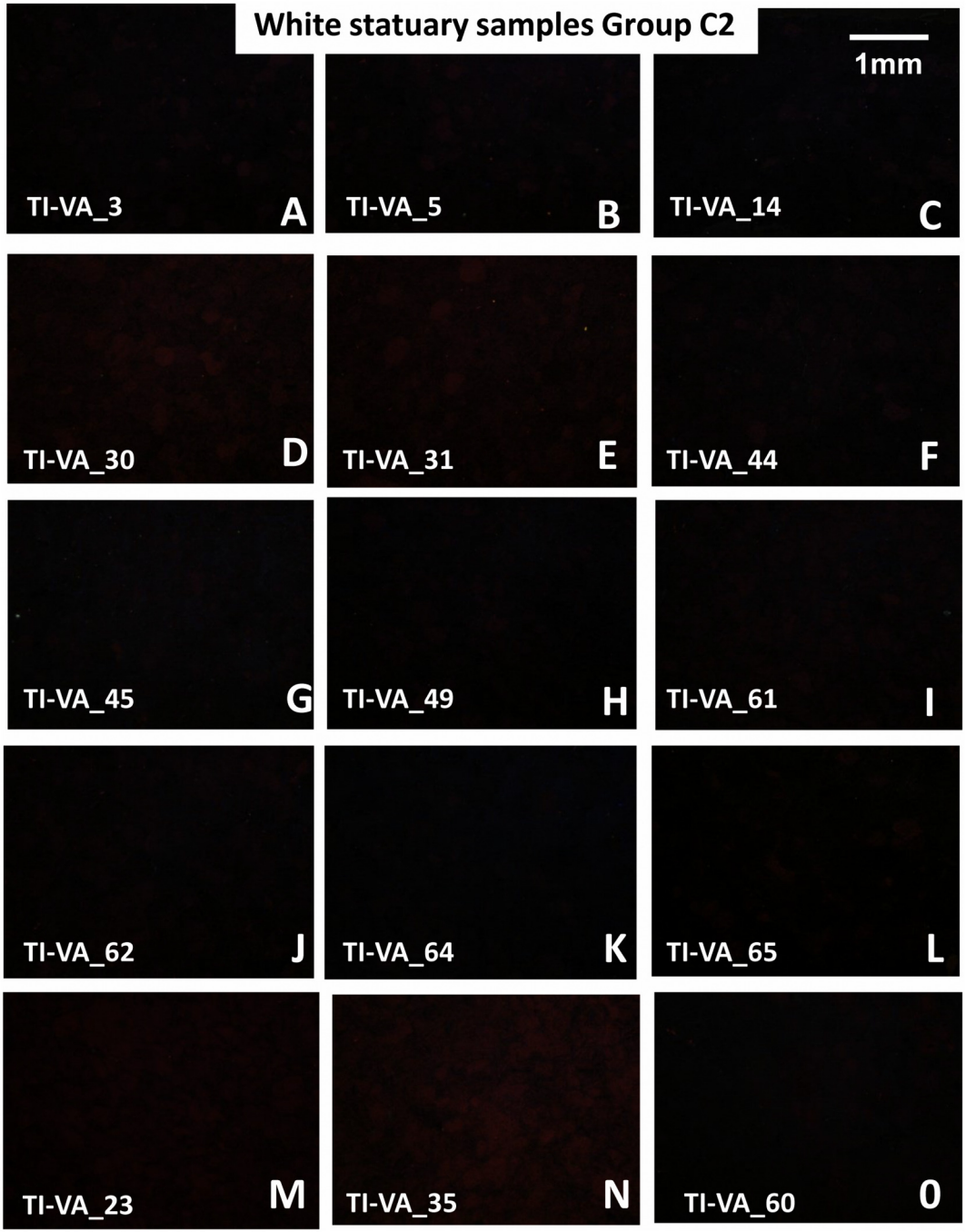
TI-VA_66
R


White statuary samples Group C2
1mm
TI-VA_3
A
TI-VA_5
B
TI-VA_14
C
TI-VA_30
D
TI-VA_31
E
TI-VA_44
F
TI-VA_45
G
TI-VA_49
H
TI-VA_61
I
TI-VA_62
J
TI-VA_64
K
TI-VA_65
L
TI-VA_23
M
TI-VA_35
N
TI-VA_60
O


White statuary samples Group C2
1mm
TI-VA_3
A
TI-VA_5
B
TI-VA_14
C
TI-VA_30
D
TI-VA_31
E
TI-VA_44
F
TI-VA_45
G
TI-VA_49
H
TI-VA_61
I
TI-VA_62
J
TI-VA_64
K
TI-VA_65
L
TI-VA_23
M
TI-VA_35
N
TI-VA_60
0

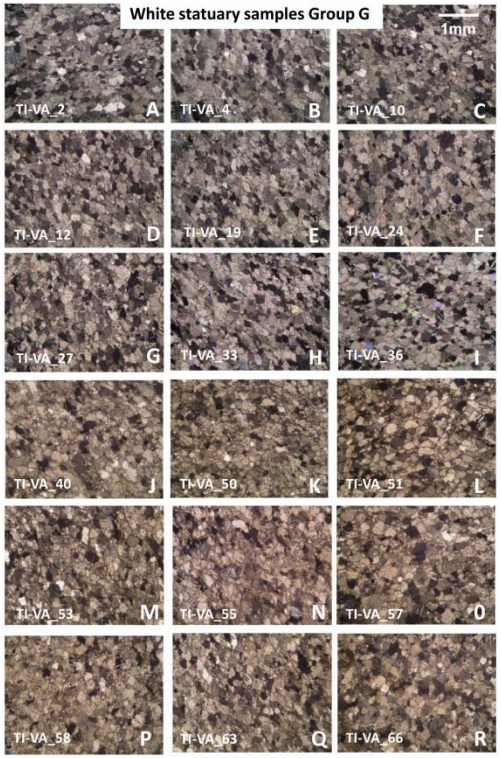


Fig. S1.1. (A) to (R): Petrography (crossed polarizers) of white statuary samples from Villa Adriana (Group G) in Lapuente et al. (2012a).

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Journal of Archaeological Science: Reports, Volume 19, 2018, 625–642

http://dx.doi.org/10.1016/j.jasrep.2018.03.037

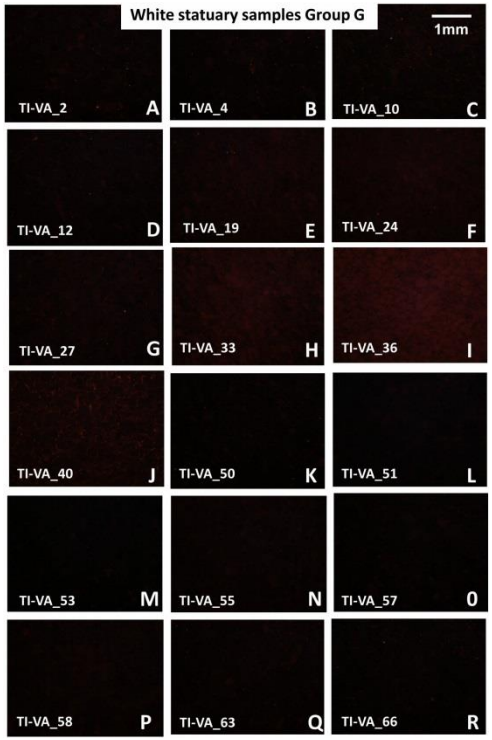

Fig. S1.2. (A) to (R): CL-patterns of white statuary samples from Villa Adriana (Group G) in Lapuente et al. (2012a).
Note that is visually non-luminescent, but with low intensity in the quantitative CL.
CL of sample TI-VA-2 is shown in Fig. 5D after polishing with diamond grains, exhibiting a low intensity in reddish.

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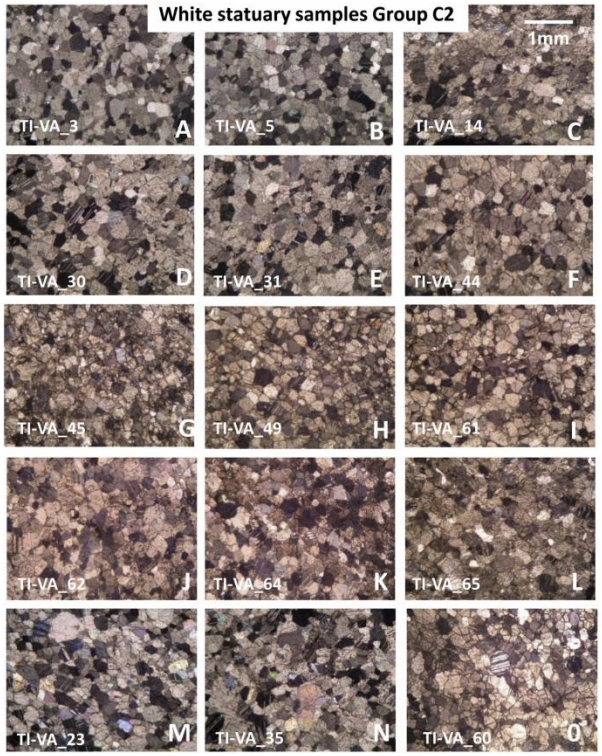

Fig. S2.1. (A) to (O): Petrography (crossed polarizers) of white statuary samples from Villa Adriana (Group C2) in Lapuente et al. (2012a).

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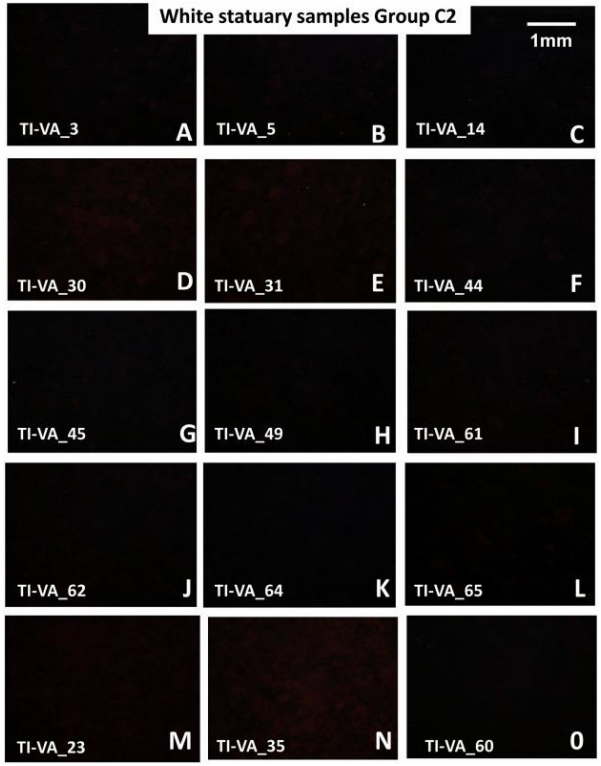

Fig. S22. (A) to (O): CL-patterns of white statuary samples from Villa Adriana (Group C2) in Lapuente et al. (2012a).
Note that is visually non-luminescent, but with very low intensity in the quantitative CL.
CL of sample TI-VA-5 is shown in Fig. 5E after polishing with diamond grains, exhibiting a very low intensity in reddish.

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Table 3 – Data of white archaeological samples.

	Group	Sample TI-VA	$\delta^{18}O$ ‰ vs. PDB	$\delta^{13}C$ ‰ vs. PDB	CL QUANTITATIVE 620nm	CL QUANTITATIVE 375nm	EPR Int	EPR W	Sr (ppm)	Mn (ppm)
White Statuary samples Villa Adriana (Lapuente et al. 2012a)	G	2	-2.61	2.81					302	9
		4	-2.54	2.89					707	10
		10	-2.58	2.88			0.0730	0.4156		
		12	-2.65	2.84	20	4.2	0.0736	0.4492	438	8
		19	-2.56	2.91	8.6	4.4				
		24	-2.61	2.82			0.0415	0.4612		
		27	-2.74	2.87						
		33	-2.72	3.55	9.1	4.8	0.0620	0.4976		
		36	-2.56	2.85						
		40	-2.54	2.91	44.2	4.6	0.1655	0.4049	524	13
		50	-2.59	2.82						
		51	-2.51	2.98			0.0236	0.4158		
		53	-2.60	2.83			0.0491	0.5431		
		55	-2.58	2.83	13.2	5.8			452	6
		57	-2.53	2.91						
		58	-2.58	2.80	11.2	3.7			381	5
		63	-2.50	2.77	27.8	5.3			350	9
		66	-2.51	2.85	13.4	5.4	0.0116	0.5164		
	C2	3	-2.31	2.69					371	7
		5	-2.91	2.58	2	5.9			695	3
		14	-2.61	2.86	3.6	2.7				
		23	-2.22	2.58						
		30	-2.93	2.62						
		31	-2.57	2.60						
		35	-2.19	2.72	2.2	5.3	0.0111	0.5108		
		44	-2.89	2.59						
		45	-2.50	2.77						
		49	-2.92	2.61	2.2	4.6	0.0123	0.49	625	3
		60	-2.21	2.72	1.7	5.2			354	6
		61	-2.89	2.57						
		62	-2.16	2.75	2.6	4.9	0.0223	0.58	340	3
		64	-2.46	2.73	2.9	5.9	0.0276	0.54	444	3
		65	-2.88	2.58						

Table 4 – Isotopes and Sr-Mn data. Dolomite (dol) vs. calcite(cc) detection by XRD.

sample	color	XRD	$\delta^{13}C$ ‰vs.PDB	$\delta^{18}O$ ‰vs.PDB	Sr (ppm)	Mn (ppm)
GTW_1	white	cc	2.84	-2.62	385	1.9
GTW_2	white	cc	2.88	-2.76	322	0.2
GTW_3	white	cc	2.87	-2.82	494	2.2
GTW_4	white	cc	2.81	-2.42	332	0.9
GTW_5	white		2.79	-2.51	536	4.9

GTW_6	white		-1.98	-5.83	77	6.3
GTW_7	white		2.60	-2.61	427	1.4
GTW_8	white		-4.63	-5.62	67	1.2
GTW_9	white		0.97	-4.05	154	4.0
GTW_10	white		2.56	-2.95	501	8.0
GTW_11	white		2.54	-3.02	458	4.7
GTW_12	white		-1.75	-5.79	79	10.6
GTW_13	white		0.09	-4.22	192	2.1
GTW_14	white		-1.93	-6.61	88	1.3
GTW_15	white		2.41	-3.19	512	4.5
GTW_16	white		2.56	-2.96	301	3.2
GTW_17	white		2.37	-3.09	486	8.1
GTW_18	white		3.00	-2.82	657	3.9
GTW_19	white		0.09	-4.22	156	2.6
GTW_20	white		2.60	-3.08	359	1.9
GTW_21	white		2.42	-3.02	401	3.2
GTW_22	white		2.51	-3.06	599	2.2
GTW_23	white		2.51	-3.12	589	8.5
GTW_24	white		1.30	-3.83	245	0.3
GTW_25	white		2.50	-3.15	644	1.1
GTW_26	white		-0.13	-5.24	113	5.2
GTW_27	white		2.38	-3.10	688	2.4
GTV_1	white	cc, dol<1%	3.75	-1.93	488	2.4
GTV_2	white	cc, dol<1%	1.57	-2.55	211	13
GTB_5	grey	cc	3.00	-2.82	357	3.9
GTV_1	white		3.75	-1.93	388	2.4
GTV_2	white		1.57	-2.55	211	13
GT1	white		2.72	-2.89	701.0	1.7
GT2	white		2.49	-3.05	460.0	1.1
GT4	white		2.46	-3.33	528.6	1.4
GT5	white		2.62	-3.18	440.6	1.5
GT6	white		2.70	-3.14	457.8	1.9
GT7	white		2.62	-3.22	453.3	1.9
GT8	white		2.78	-2.84	427.8	1.3
GT9	white		2.77	-2.77	784.3	0.9
GT10	white		2.96	-2.76	837.0	2.2
GT11	white		3.50	-2.65	834.8	3.0
GT12	white		2.54	-2.64	832.5	4.5
GTB_1	black	cc	3.51	-2.45	226	12
GTB_2	black	cc	1.62	-5.90	121	4.0

GTB_3	black	cc	0.60	-5.81	67	5.9
GTB_4	black		-0.29	-6.14	154	15
GTBC_1	black		3.53	-3.00	316	2.5
GTBC_2	black		3.63	-2.52	282	1.5
GTBC_3	black		3.63	-3.17	305	2.6
GTBC_4	black		3.02	-4.93	192	12
GTBC_5	black		3.54	-2.40	301	2.2
GTBC_6	black	cc	3.49	-2.54	286	1.5
GTV_1b	black	cc, dol<1%	3.65	-2.69	325	24
D_153B	black	cc	0.83	-2.77		
D_165B	black		2.96	-2.76		
D_164B	black		3.50	-2.65		
D_162B	black		2.54	-5.64		
D_163B	black		3.88	-3.03		

Table 5. Elemental and isotopic analysis of the insoluble residues of the two samples representative of lithotype 1 and 2.

	Lithotype 1	***Lithotype 2***
Mineralogy (XRD)	Quartz, chlorite, illite, kaolinite, graphite, feldspars	Quartz, chabazite, chlorite, illite, kaolinite, graphite, feldspars
% insoluble residue	0.6	0.4
%C weight % of the residue	5.53 (0.03 RSD)	22.5 (0.08 RSD)
%N	0.19 (0.14 RSD)	0.12 (0.20 RSD)
%H	0.66 (0.20 RSD)	0.74 (0.36 RSD)
$\delta^{13}C$ ‰	-12.7	-9.8