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U-Pb calcite geochronology, EPR, geochemistry, and C-O-Sr isotopes of Africano marbles in the Seferihisar (İzmir, Türkiye)

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Abstract: The Africano marbles (Africano Verde and Bigio Africano) extracted from the region of Sığacık (ancient Teos) region and its surroundings were widely used and even traded in construction and decorative items throughout the Roman period due to their brecciated and colourful appearance. There are two different types of Africano marble, the first consisting of marble breccias embedded in a dark matrix. In this type, the marble breccias show micritic, microsparitic, and sometimes sparitic textures formed by coarse-grained calcite, while the dark matrix consists of chlorite and/or serpentine minerals. The second type is Bigio Africano, which consists of grey-blue homogeneous limestones, composed mainly of microsparitic and sparitic calcite. The geochemical and isotopic characteristics of Africano marbles extracted from three different quarries indicate that these marbles generally originate from carbonates deposited in an open ocean environment. Africano marbles can be easily distinguished from other brecciated marbles (Marmor Sagarium, Marmo Docimeion) by their grain sizes, the textural differences in the marble breccias and their geochemical properties. The same distinction, however, does not apply to Bigio Africano. This grey marble is very similar to other grey marbles used in ancient times. The $^{87}Sr/^{86}Sr$ isotope ratios in the whole marble samples vary between 0.70723 (±0.0000059) and 0.70956 (±0.0000058). The $\delta^{13}C$ isotope values range from –4.96‰ (±0.08) to 3.36‰ (±0.08), while the $\delta^{18}O$ isotope values range from –11.17‰ (±0.10) to –5.41‰ (±0.10). For the first time in this study, the U-Pb calcite age of Africano marbles was determined to be 73.3 ± 11 Ma, and this age is compatible with the fossil ages of limestones from the Bornova flysch zone. All spectroscopic characterization studies and age analyses performed on the Africano marbles will be an important data source for researchers investigating the source of these marbles in the future.

Key words: Africano marble, geochemistry, Sr-C-O isotopes, U-Pb dating, provenance studies

1. Introduction

The ancient city of Teos, located in the Sığacık village (Figure 1) of the district of Seferihisar (İzmir city: ancient Ionia), was built on a peninsula extending in a north-south direction and has two natural harbours, one to the north and one to the south of the city. Strabo, in his work Geography of Ancient Anatolia, describes Teos as follows: "Teos is situated on a peninsula and has a harbour. To the north of the city, there is another harbour, which is thirty stadia from the city and is called Gerrhaiidai" (Strabo, Geography of Ancient Anatolia). The quarries of Teos produced both grey-blue marble (Bigio) and coloured marble (Africano), which were utilized as construction and decorative materials during the Roman period (Adak and Kadıoğlu, 2017). The marble known as Africano was used by the Romans from the middle of the 1st century BC (Corsi, 1845; Balance, 1966). In addition, this marble is also called "Marmor Luculleum" after the consul L. Licinus Lucullus, who sent several blocks and objects to Rome after the conquest of the Pontus region (Corsi, 1845; Dubois, 1908; Cantisani et al., 2014).

Africano marbles are characterized by their brecciated structure within a dark-coloured matrix and are typically shaded in black with varying hues of white, pink, red, or grey. Those with a dark green matrix are known as "Africano Verde", while those with a grey matrix speckled with red are known as "Bigio Africano" (Mielsch, 1985; Pensabene and Lazzarini, 1998). The first quarry of Africano marble, located identified near the ancient city of Teos was described by Ballance (1966). This area is now occupied by Lake Karagöl and is surrounded by piles of quarry blocks (Figure 2). Additionally, quarries near

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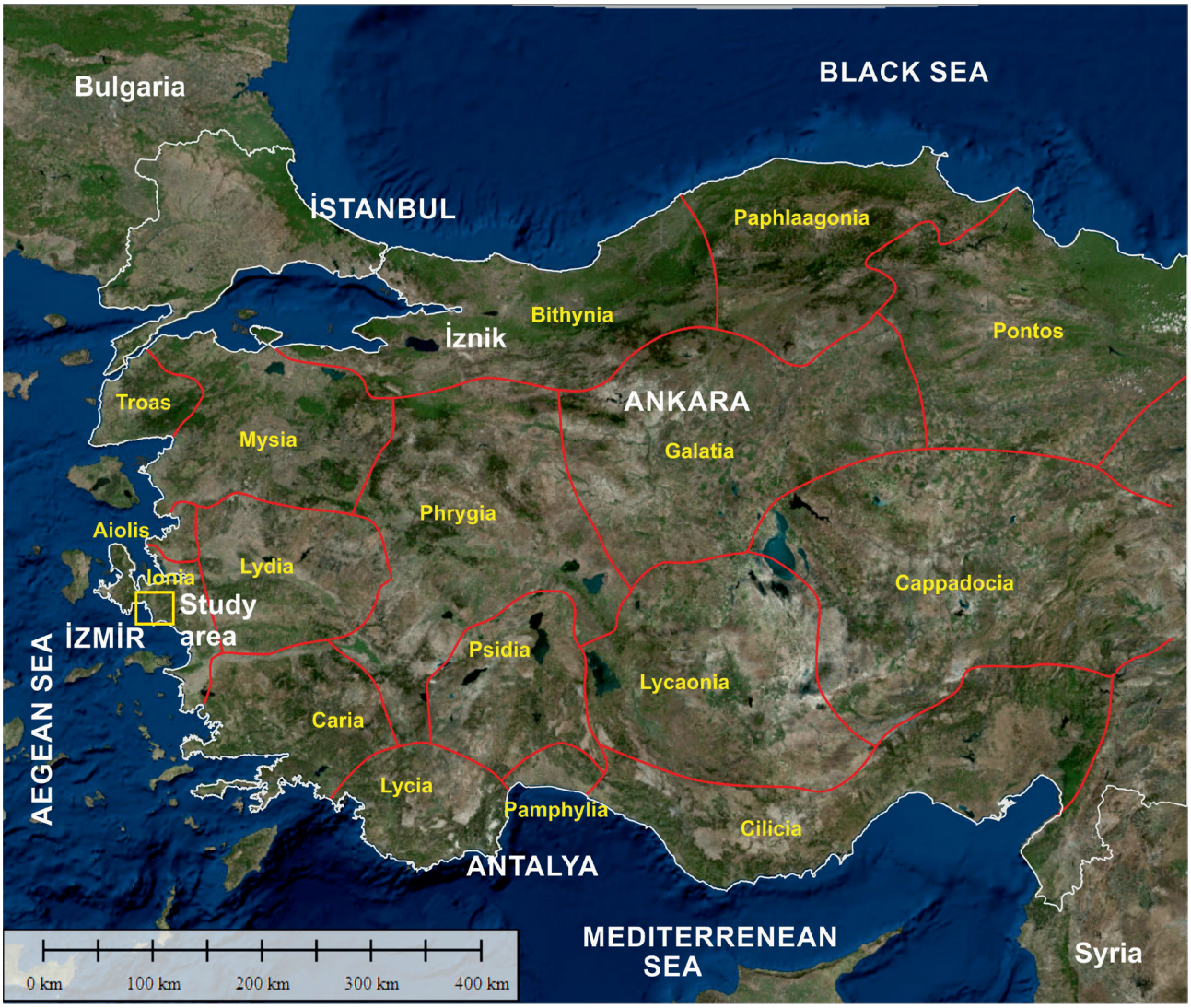


Figure 1. Location map of study area*
(*Anadolu Antik Bölgeler Haritası (Online). Web adress: https://mystichistory.blogspot.com/2008/06/antik-blgeler.html (visited 20.05.2024)).

Taşdibi Hill have yielded Bigio Africano marbles (Bruno et al., 2009). It has been observed that coloured Africano marbles are less common compared to other grey marbles. The quantity of coloured marbles decreased rapidly in the 2nd century AD, and by 166 AD, these types of marbles seem to have been exhausted. This situation is supported by archaeological evidence and inscriptions on marble blocks left in the quarries of Lake Karagöl and Turgut village (Adak and Kadıoğlu, 2017). Due to the high demand for coloured marble from Teos in Rome, a significant portion of the extracted marble was sent to Rome and Italy. In Teos itself, the small remnants of Africano marble indicate its use as a decorative material.

In this study, samples were collected from three different quarry sites near the ancient city of Teos and from the rubble piles within the ancient city. Petrographic descriptions were made on the collected samples, X-ray diffraction (XRD), electron paramagnetic resonance (EPR), geochemistry, and Sr-C-O isotope analyses were performed for the characterization of the marbles, and U-Pb calcite geochronology was carried out on one sample. A new data set is presented, which will be used to compare the data of this article with different marbles used in ancient times.

2. Geology

Africano marble, historically known as "Marmor Lucullaeum", "Marmo Luculleo", or "Africano", has been quarried from two sites near the village of Sığacık (ancient



Figure 2. Quarry locations in the Sığacık region: (a) Karagöl quarry (Quarry-1), (b) Bigio Africano marble quarry (Quarry-2), (c) The Africano quarry in the village of Turgut (Quarry-3), (d–e) Africano blocks inside the Karagöl quarry site, (f) Africano pieces in the ancient city of Teos, (g) Africano stones used in the base of a statue in Pompeii, which was destroyed by the eruption of Mount Vesuvius in 79 AD.

Teos) and from a quarry north of the village of Turgut (Figure 2). These marbles are extracted from limestone blocks within the units of the Bornova Flysch Zone (BFZ). The flysch sequence containing various blocks, first described in detail by Akartuna (1962) in western Türkiye, was named as the BFZ (Okay and Siyako, 1993; Okay, 1996; Moix et al., 2008). The BFZ is a regional olistostrome–mélange belt bounded by the İzmir-Ankara suture to the northwest and the Menderes Massif to the southeast (Okay and Konak, 2012). Solak et al. (2015) described the BFZ as a mélange of massive Mesozoic limestone and ophiolite blocks embedded into the Maastrichtian-Paleocene sheared siliciclastic sedimentary rocks. They considered the Late Triassic to Cretaceous age limestone blocks to be olistoliths or deformed and cut platform fragments. According to Okay and Konak (2012), the BFZ was mostly formed by tectonized mass flows and the blocks in the mélange are Mesozoic limestone and ophiolitic rock blocks surrounded by Cretaceous-Paleocene sheared sandstone and shale. They defined two types of limestone blocks in the mélange: (1) Late Triassic-Cretaceous shallow marine carbonates, and (2) Upper Triassic shallow marine section with Jurassic-Cretaceous pelagic limestones on top. They also emphasized that the ophiolitic blocks in the BFZ include Middle Triassic-Cretaceous ultramafic rocks, gabbro, basalt and radiolarian chert. Solak et al. (2015) suggested that the BFZ matrix consists of alternating sandstones and shales and is composed predominantly of flysch-type sedimentary rocks. They emphasized that these rocks contain planktonic foraminifera and micritic limestone lenses and calcareous shales thought to be locally Campanian-Paleocene (Konuk, 1977; Yağmurlu, 1980; Özer and İrtem, 1982; Erdoğan, 1990) and late Maastrichtian-late Paleocene ages (Sarı, 2013).

The most important quarry for Africano marble was located under what is now Lake Karagöl (Quarry-1). Almost all the marbles were extracted, and the quarry was identified by the rust and residual blocks around the lake (Er, 2011). The marbles extracted from this quarry generally consist of grey and occasionally red-speckled limestone breccias (Africano or Africano Verde) with a matrix of green greywacke/shale. The second quarry (Quarry-2), located on the Sığacık - Seferihisar road, produced grey, medium to coarse crystalline marbles (Bigio Africano). These grey marbles were widely used in the ancient city of Teos. Another quarry (Quarry-1) producing marbles with similar textural characteristics to those found in Lake Karagöl is located north of the village of Turgut (Quarry-3). Grey marble breccias in green matrix were used throughout antiquity in many ancient buildings and objects in the Mediterranean basin (Figure 3). Today, the production of dark black-red marbles known as "Nero Africano" or "Fire Africano" and green marble known as "Teos green" continues.

3. Materials and analytical methods

3.1. Petrography and XRD analysis

A total of twelve samples were prepared for thin section analysis. Thin sections were prepared by cutting representative slabs from the marbles using a diamond-tipped rock saw and then thinning to the appropriate thickness using abrasive powders. This preparation process facilitated microscopic examination of the samples and allowed detailed determination of their petrographic characteristics. Petrographic analysis of the prepared thin sections revealed the mineralogical and structural characteristics of the samples, thus contributing to a better understanding of the relationships between stone quarries and ancient marbles. Petrographic thin sections were prepared from the samples collected from the ancient marble quarries of Seferihisar Ancient Marbles. The prepared thin sections were determined using a Leitz Ortoplan microscope and the Leica image analysis system. Representative marble samples were analysed for their mineralogical compositions by XRD. These analyses were carried out on powdered samples using a GNR APD-2000 Pro diffractometer in the X-ray Diffraction Laboratory of the İstanbul University–Cerrahpaşa, Department of Geological Engineering. The diffraction data were obtained by exposing the powdered samples to Cu-Kα X-ray radiation, which has a characteristic wavelength of 1.5418 Å. X-rays were generated from a copper (Cu) anode supplied with a voltage of 40 kV and a current of 30 mA. A goniometer speed of $2\theta=1^{o}$/min was set during the analyses. The data were collected between 5^{o} and 55^{o} for 2θ values with a step size of 0.02°, divergence and receiving slits were respectively set to 0.5 mm and 0.3 mm. Analysis of the X-ray patterns (phase identification) was done via Philips High Score Plus software package in conjunction with the JCPDS (Joint Committee on Powder Diffraction Standards) database.

3.2. Electron paramagnetic resonance (EPR)

X-band electron paramagnetic resonance (EPR) measurements were conducted using a Bruker EMX Nano benchtop spectrometer with an integrated referencing for g-factor calculation. During the EPR measurements a microwave frequency of 9.64 GHz was applied to the samples, and EPR spectra of all samples were measured using 25 cm long spin-free quartz tubes at room temperature with a modulation amplitude of 2 G for 5 scans at 1 mW power.

3.3. Geochemistry

The geochemical analyses were conducted at the Geochronology and Geochemistry Laboratory of the Department of Geological Engineering, at İstanbul University-Cerrahpaşa. The method described by Göçmengil et al. (2022) was used for whole rock analyses.

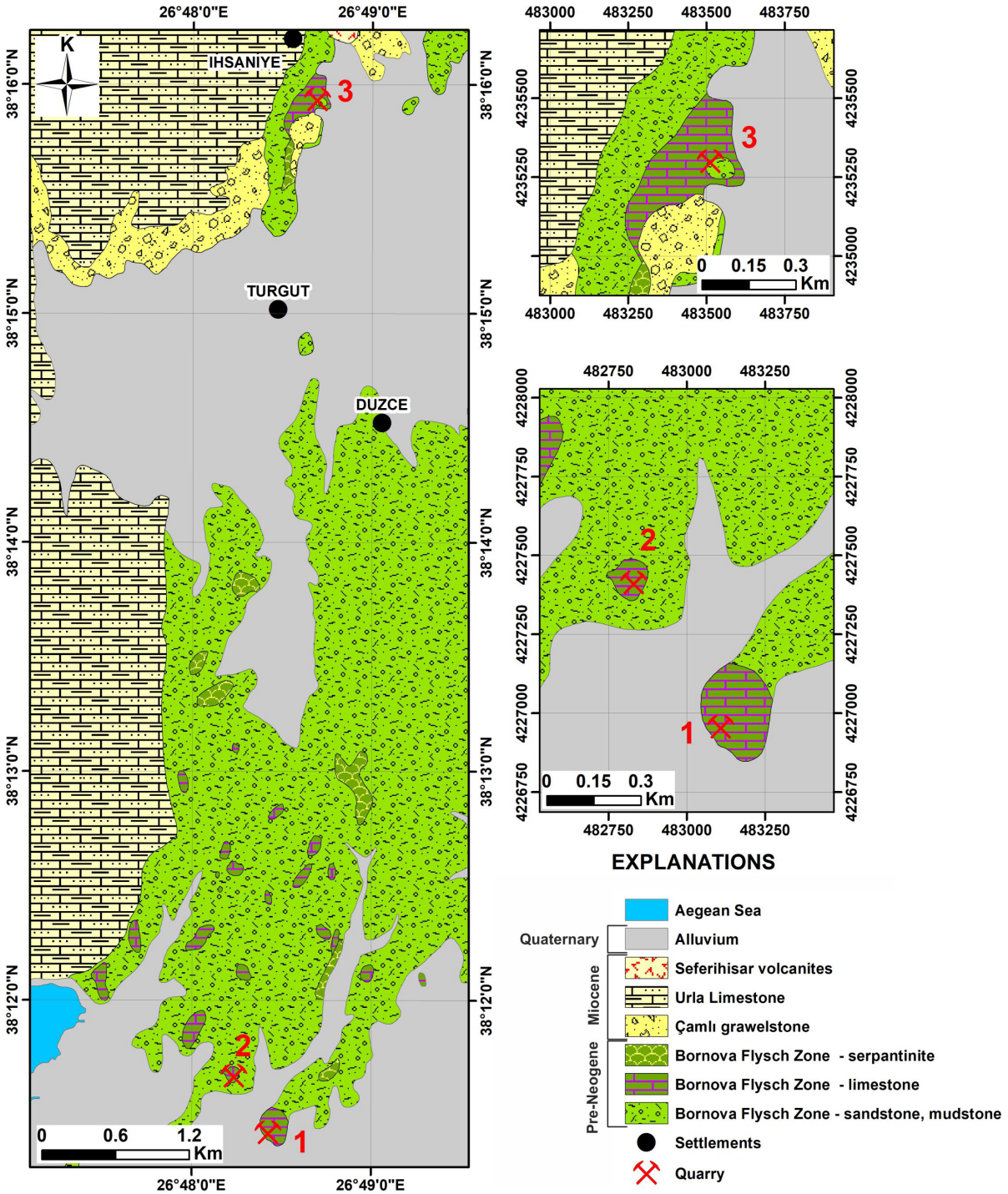


Figure 3. Geological map of the ancient Africano marble quarries of Sığacık region (taken from the MTA 1:100000 scaled Urla L-17 sheet; Coordinate system is WGS1984_UTM_Zone_35N).

In-situ analyses were performed using a Pekin Elmer NexION 2000 ICP-MS combined with an ESI NWR 213 nm solid-state laser ablation (LA) system. The laser spot size was 50 µm. External standards SRM612 and BCR-2g were used. A background signal of approximately 20 s was collected prior to ablation for each analysis. The ablation time was set to 30 s per sample with a laser repetition rate of 10 Hz. Helium was employed as the carrier gas (0.6 l/s).

Data evaluation was performed using the ICPMSDataCal software package (Liu et al., 2008). The results are given in Supplementary Table 1.

3.4. C-O-Sr isotopes

$\delta^{18}O$ and $\delta^{13}C$ values of marble samples were measured using an automated carbonate preparation device (KIEL-III) coupled to a gas-ratio mass spectrometer (Finnigan MAT 252) at the Environmental Isotope Laboratory of the University of Arizona (USA). Samples were reacted with dehydrated phosphoric acid (H_3PO_4) under vacuum at 70 °C. The isotope ratio measurement is calibrated based on repeated measurements of international standards NBS-19 and NBS-18, and analytical precision is ±0.1‰ for $\delta^{18}O$ and ±0.08‰ for $\delta^{13}C$ (1σ). Sr isotope compositions of marble samples were measured using the Nu Plasma High Resolution Multicollector Inductively Coupled Plasma Mass Spectrometer (HR-MC-ICP-MS) installed at the Radiogenic Isotope Laboratory of the University of Queensland, Australia. Sr isotope ratios were corrected for mass discrimination using the ratio of $^{86}Sr/^{88}Sr = 0.1194$. Replicate analyses of the international standard SRM 987 gave a mean $^{87}Sr/^{88}Sr$ value of 0.710249 ± 0.00002 (2σ).

3.5. U-Pb Calcite geochronology

U-Pb dating of calcite marble was performed using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at ETH Zurich. The equipment used included an ASI RESOlution S-155 excimer (ArF, 193 nm) laser ablation system paired with a Thermo Element XR sector-field ICP-MS. Samples were prepared as polished chips mounted in epoxy. Analytical and data reduction procedures followed those described by Roberts et al. (2017), using NIST SRM614 and WC-1 calcite as primary reference materials. Spot sizes of 110 μm and a pulse rate of 5 Hz with energy density of 2 J cm-2 were used, following the methods described by Guillong et al. (2020). U-Pb ages were determined using Tera-Wasserburg Concordia lower intercepts and the IsoplotR software package (Vermeesch, 2018). A long-term excess variance of 2% relative was added quadratically to the uncertainty of individual lower intercept dates, following Guillong et al. (2020). Validation of the results was carried out using secondary reference materials ASH-15 (Nuriel et al., 2020), JT (Guillong et al., 2020), B6 (Pagel et al., 2018), and an additional in-house standard, PDF-9B, as detailed in the supporting information. Corrections for calcite matrix effects were made using WC-1 with anchoring to an initial common-lead value of 0.85, while the samples and secondary reference materials were not anchored. No corrections for were made for disequilibrium. All uncertainties are reported at the 95% confidence level. All U-Pb raw and WC-1 corrected data are reported in Supplementary Table 2 and Tera-Wasserburg plots for each individual sample are presented in the corresponding section.

4. Results

4.1. Mineralogy and petrography

The primary mineral phase of the samples taken from the Africano marble quarries (indicated by the code TO) and the marbles used in the ancient city of Teos (indicated by the code TAK) is calcite. Quarries I and III, where Africano marble was extracted, have the typical characteristics of Africano Verde. They have a brecciated texture. Brecciated fragments are mostly composed of grey, red and white marbles. The red colour of the breccias is due to hematite staining (Figure 4). In addition to marble fragments, radiolarite, chert, mafic and ultramafic rock fragments are also found in the matrix. Additionally, these marble breccias contain minor amounts of basic volcanic fragments, quartz, and feldspar minerals (Figures 4a–4b). The breccias, which form the main lithology of these marbles are embedded in a dark green, black and brown matrix derived from mafic, ultramafic and pelitic rocks. XRD analyses confirm that the matrix of these marbles, which are characterised by their coloured binders, consists mainly of chlorite and/or serpentinite minerals. The marble breccias generally show microsparitic and micritic textures (Figures 4c–4d), although breccias with coarser sparitic calcite crystals are also occasionally found (Figure 4 a; Figures 4c–4d). Stylolitic fractures are visibly filled with brownish, fine insoluble minerals (Figures 4c–4d, 4g–4h). Some of the brecciated marbles from the same quarries have fractures and cracks stained with red iron oxides (Figure 4 m,t) such as hematite, making them easily identifiable. These particular marbles are known as Teos Fire. The Quarry-II consists of grey marble. These marbles are known as Bigio Africano. A common feature of the marbles produced from all three quarries is that they do not contain fossils. The marbles extracted from Quarry-II differ significantly from those obtained from Quarries-I and III. The grey marbles (Figures 4i–4j, 4k–4l) are more massive and homogeneous limestones. The grey marbles consist of medium to coarse crystalline calcite crystals and contain small amounts of dolomite (Figure 4e, 4u). According to XRD analysis, calcite is the dominant mineral in all marble groups. However, the marbles contain lesser amounts of dolomite, quartz, albite, hematite, chlorite and serpentinite minerals (Figure 5).

4.2. EPR results

EPR spectroscopy is a valuable tool for creating a database that can be used for provenance studies. The ions such as Manganese (Mn^{2+}), Cobalt (Co^{2+}), and Iron (Fe^{3+}) ions can be detectable using EPR Spectroscopy due to the paramagnetic nature (Poretti, 2016; Duliu et al., 2019). Hence leaving traces aids provenance studies by showing a clear resonance signal (Polikreti et al., 2002; Poretti, 2016; Duliu et al., 2019). Almost all natural carbonates have Mn and by conducting EPR spectroscopy analysis the Mn^{2+} can be observable with other impurities (Polikreti et al.,

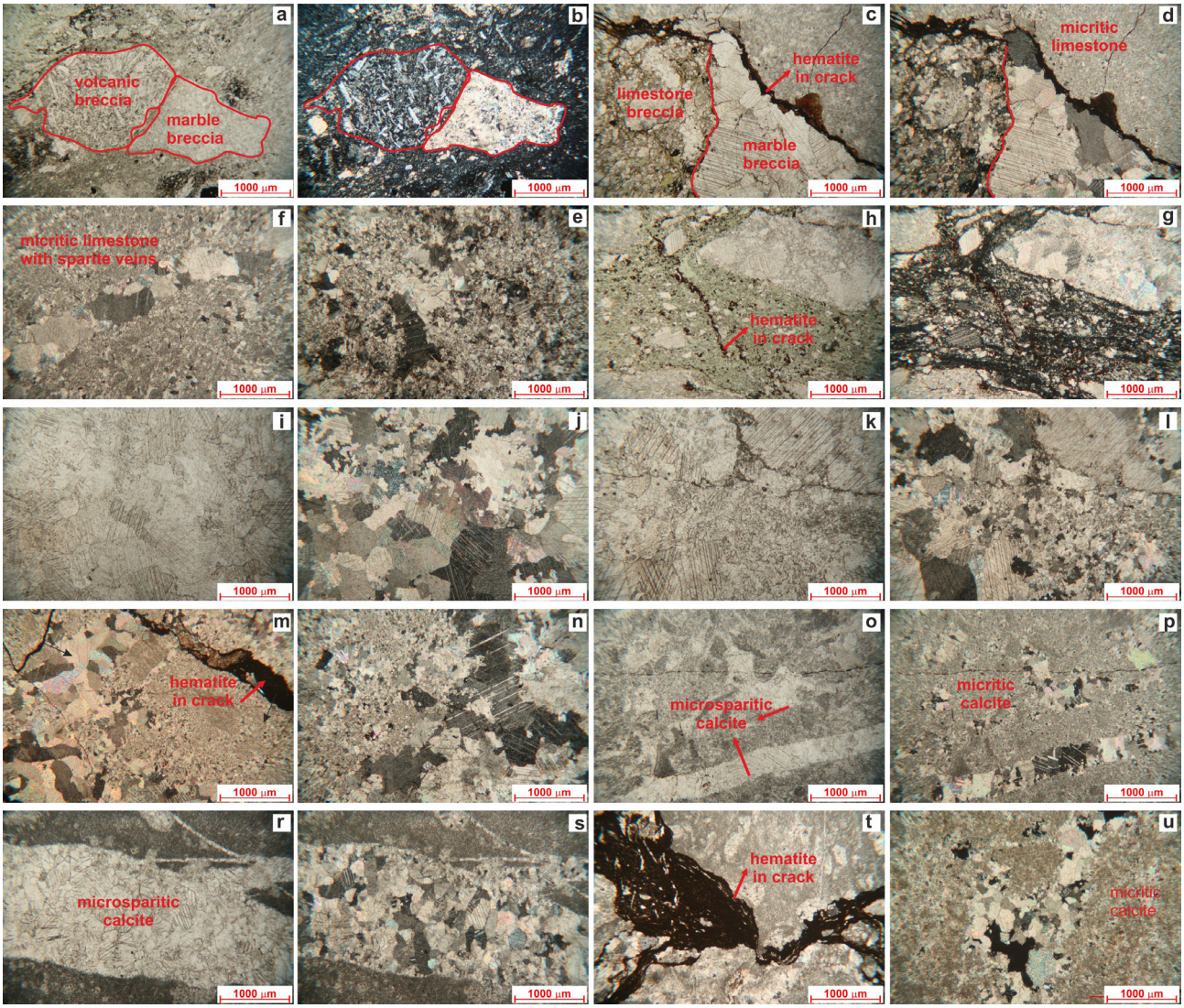


Figure 4. Micro photographs of the Quarry-1. (a–b): Africano marbles containing volcanic and sparitic limestone and/or marble breccias within a green-coloured matrix; (c–d): Brecciated marble containing microsparitic and sparitic limestone breccias, (e): Marble with microsparitic texture, (f): Marble exhibiting micritic and microsparitic texture, (g–h) Brecciated marble with microsparitic and sparitic breccias in a green matrix (a, c, e, f, g: Plain-polarized light (PPL); b, d, h: Cross-polarized light (CPL)). Micro photographs of the Quarry-2. (i–l): Grey coloured, medium- to coarse-grained marble (i, k: PPL; j, l: CPL). Micro photographs of the Quarry-3. (m): Brecciated marble containing microsparitic and sparitic breccias; (n): Marble containing microsparitic and sparitic breccias; (o–s): Marble with micritic and microsparitic vein; (t): Cracks of hematite-filled micritic limestone; (u): microsparitic and sparitic breccias (m, o, r, t: PPL; n, p, s, u: CPL).

2002; Poretti, 2016; Duliu et al., 2019). Figure 6 (a) shows the EPR spectra of samples TAK-2, TAK-3, and TAK-4. All three spectra show a characteristic hyperfine sextet signal of Mn^{2+}. This is mainly due to the electron and nuclear spin number of Mn^{2+} ion which is S = 5/2 and I = 5/2, respectively. Also, the forbidden ΔMI = 2 transitions were observed between each hyperfine signal (Sheng et al., 2005). Also, it should be noted only the Mn2+ paramagnetic defect center has been observed in the samples which indicates no other metal ions or paramagnetic impurities exist in the samples. The results indicate that Mn^{2+} ions have replaced Ca^{2+} ions in the lattice, which is expected due to their similar atomic radii and oxidation states. This substitution led to the successful incorporation of Mn^{2+} ions into the lattice without creating vacancies or interstitials. Consequently, no dipolar broadening was observed, suggesting that the Mn^{2+} ions are well-isolated within the lattice, resulting in a clear and strong EPR signal. The intensity and linewidth of the EPR spectra vary significantly between samples, which can be attributed

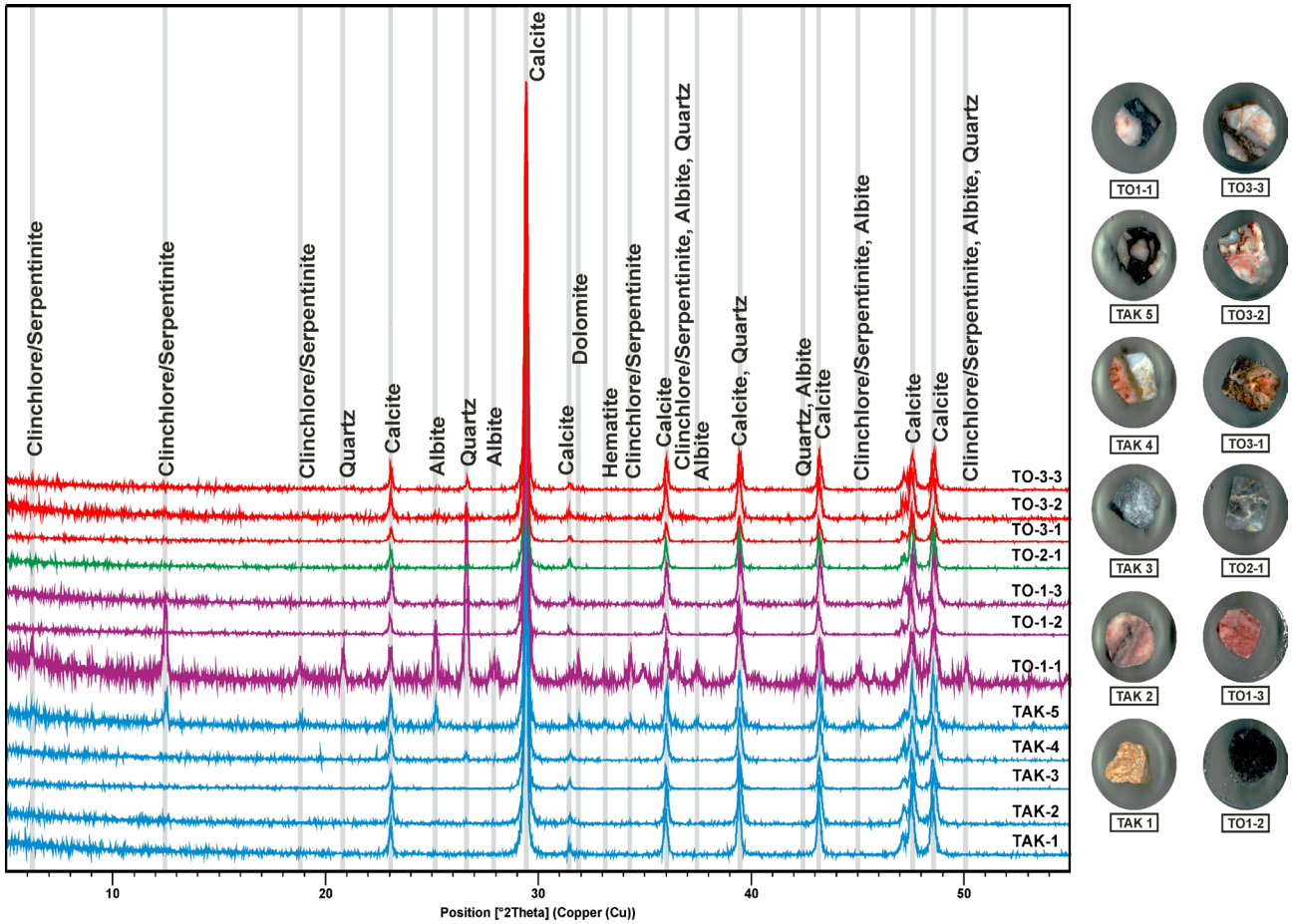


Figure 5. XRD diffraction pattern of Africano marbles and the mineral compositions described.

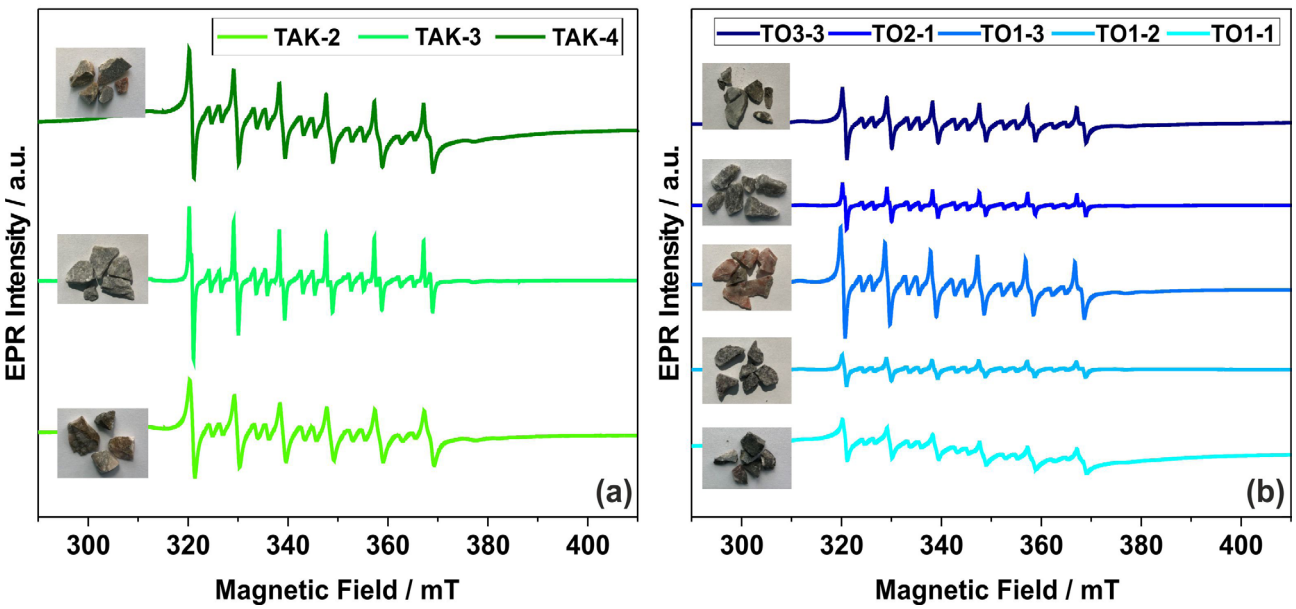


Figure 6. a) The EPR spectra of TAK-1, TAK-2 and TAK-3 samples collected from the vicinity of the around the ancient city of Teos, and b) TO1-1, TO1-2, TO1-3, TO2-1, and TO3-3 samples collected from the Africano marble quarries.

to differences in the concentration and local positioning of Mn^{2+} ions within the lattice. These variations suggest that the geological history of each sample influences the distribution and behaviour of Mn^{2+} ions. In Figure 6 (b), the EPR spectra of samples collected from the Africano marble quarries (TO3-3, TO2-1, TO1-3, TO1-2, and TO1-1) exhibit the characteristic sextet signal of Mn^{2+} ions, as observed in Figure 6(a). However, notable changes in both the signal intensity and linewidth are evident, indicating that the incorporation of Mn^{2+} ions is accompanied by differences in their localization within the lattice and substantial changes in local strain. These factors contribute to broadening in some spectra, as increased lattice strain or Mn^{2+} clustering leads to enhanced dipolar interactions, while isolated Mn^{2+} ions yield sharper linewidths. This suggests that strain and Mn^{2+} distribution are key factors affecting the magnetic environment and EPR response.

4.3. Whole-rock geochemistry

This study is based on the analysis of a total of 13 marble samples collected from different quarries and the immediate vicinity of the ancient city of Teos. In addition to bulk-rock and in-situ point analyses were carried out on marble samples from different coloured zones. This comprehensive approach provides a detailed understanding of the chemical composition and elemental distribution within the marbles, covering both the overall characteristics and the variability between different coloured zones. The results are shown in Supplementary Table 1.

Africano marble samples from different quarries show significant variations in chemical composition. The CaO contents of the samples taken from Quarry-1 vary between 38.88 wt.% and 43.93 wt.%, with lower contents of SiO_2 (0.01–1.92 wt.%) and other major oxides. However, a whole rock sample from Quarry-1 shows a significantly different composition with higher SiO_2 (28.79 wt.%) and MnO (10.3 wt.%). Trace element analysis of Quarry-1 samples shows concentrations of Sc (0.20–1.36 ppm), Cr (2.49–28.10 ppm) and Sr (45.48–388.28 ppm) (Figures 7a–7b).

Quarry-2 samples, particularly grey marble, have higher CaO contents (53.54–55.99 wt.%) but lower levels of SiO_2 (0.08–1.48 wt.%) and trace elements such as Cr (2.15–25.60 ppm) and Sr (89.71–281.47 ppm) (Figures 7c–7d).

Quarry 3 samples show a wider range of CaO content (44.27–55.74 wt.%), with significant amounts of SiO_2 (up to 7.32 wt.%) and MgO (up to 4.86 wt.%). Trace elements such as Ni and Zr also show greater variation in Quarry 3 samples, ranging from 0.02 to 112.83 ppm and 0.01 to 98.95 ppm respectively (Figure 7e–7f).

Samples from the immediate vicinity of the ancient city of Teos show a diverse composition with CaO ranging from 32.52 to 55.98 wt.% and SiO_2 up to 11.98 wt.%. Fe_2O_3 concentrations can also be quite high, reaching 18.42 wt.%. Hematite formations in the cracks of the marble samples (Figure 4) are responsible for the high Fe_2O_3 values. Trace elements such as V (0.01–106.37 ppm), Cr (0.34–55.96 ppm) and Sr (2.14–441.36 ppm) show significant variability in these samples (Figures 7g–7h).

4.4. C-O-Sr Isotope geochemistry

The $^{87}Sr/^{86}Sr$ isotope ratios in marble whole rock samples range from 0.70723 (± 0.0000059) to 0.70956 (±0.0000058). The $\delta^{13}C$ isotope values are between −4.96‰ (±0.08) and 3.36‰ (±0.08), while the $\delta^{18}O$ isotope values range from −11.17‰ (± 0.10) to −5.41‰ (±0.10) (Table).

4.5. U-Pb calcite geochronology

U-Pb calcite dating was performed on a sample of Africano marble from Quarry-1 near Karagöl Lake in the Seferihisar region. Measurements were made at a total of 27 points on the grey marble sample taken from the ancient marble quarry. When the 27 measured points were plotted on the Tera-Wasserburg diagram, a lower intercept age of 73.3 ± 11 Ma (MSWD: 0.2) was obtained for the Africano marble from Quarry-1 (Figure 8).

5. Discussion

5.1. Description of ancient brecciated marbles

Brecciated marbles were popular decorative stones in ancient times. Brecciated marbles exploited from various quarries were used in many ancient structures in the Mediterranean region. The Seferihisar (Teos) region was one of the three most important marble production areas of the Roman Empire in Anatolia, along with the marble quarries of the Prokonnesos (Marmara Island) and Dokimeion (İscehisar-Afyonkarahisar, and Altıntaş-Kütahya) (Albustanlıoğlu, 2006, 2007). Like the Africano marble, which is the subject of this study, one of the most widely used brecciated marbles is "Pavonazetto". This marble now called "Afyon Violet Marble" and also known as "Marmor Docimium", "Marmor Synnadicum", "Marmor Phrygium", "Marmo Frigio", consists of white marble breccias embedded in a purple matrix. While the white marble breccias consist mainly of calcite minerals, the purple matrix consists of calcite, quartz, muscovite and clinochlore minerals. The purple matrix is also rich in iron and manganese elements. The calcites that form the white marble breccias are medium- to coarse-grained and have distinct lamellar twins. In marbles with purple matrix, mica minerals are dense in dark-coloured levels, and calcite minerals are quite prominent in light-coloured levels (Bağcı, 2020). Another marble with a brecciated structure and red matrix is the marbles of the Bilecik-Vezirhan region, also known by different names such as "Marmor Sagarium", "Marmor Corallina", "Breccia Corallina" , and "Breccia Nouvalata". It is generally composed of micritic and biomicritic limestones, consisting of white, beige and

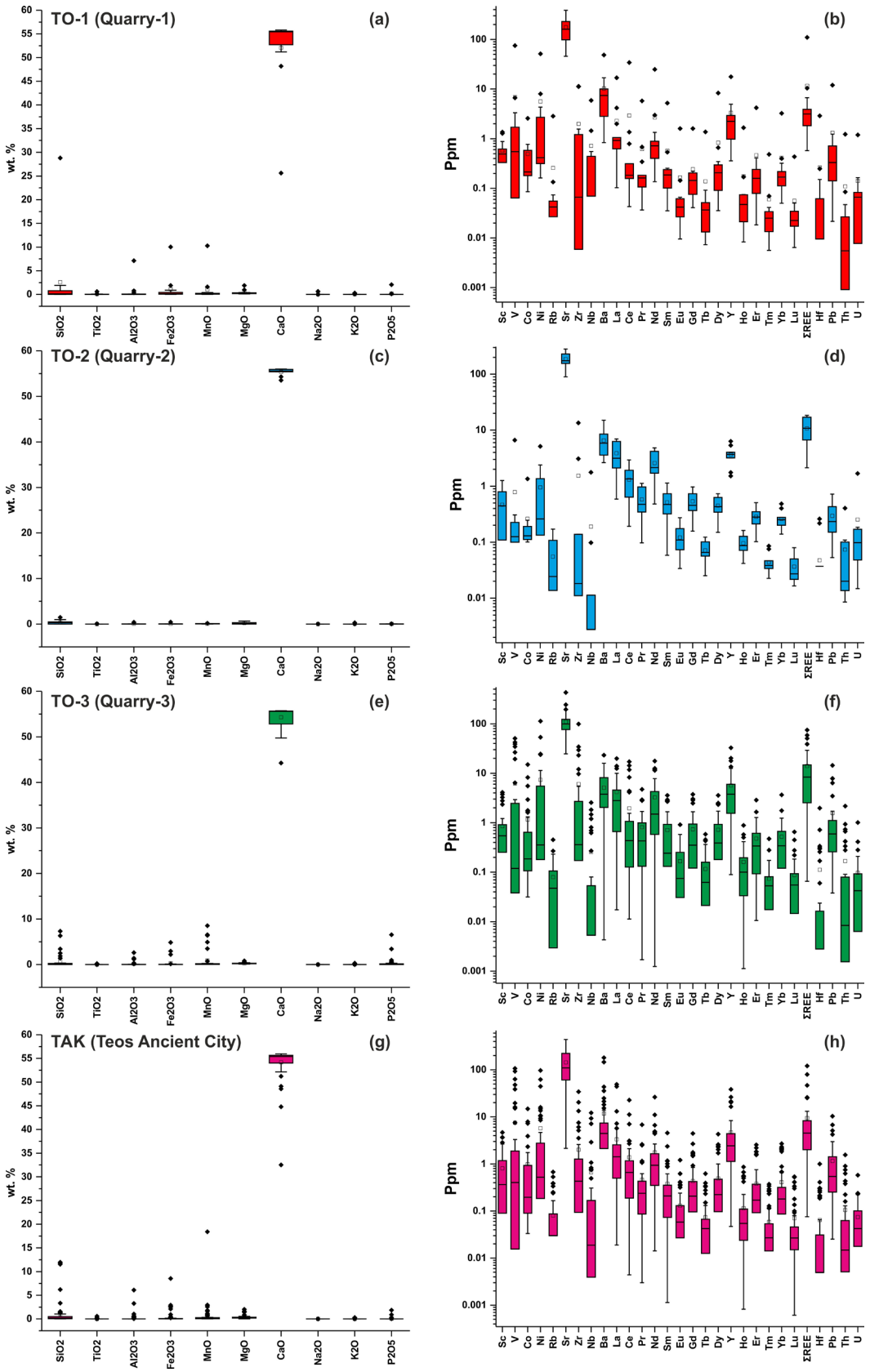


Figure 7. Box and whiskers plot for major oxides (a, c, e, g) and trace elements (b, d, e, h) of Africano marbles.

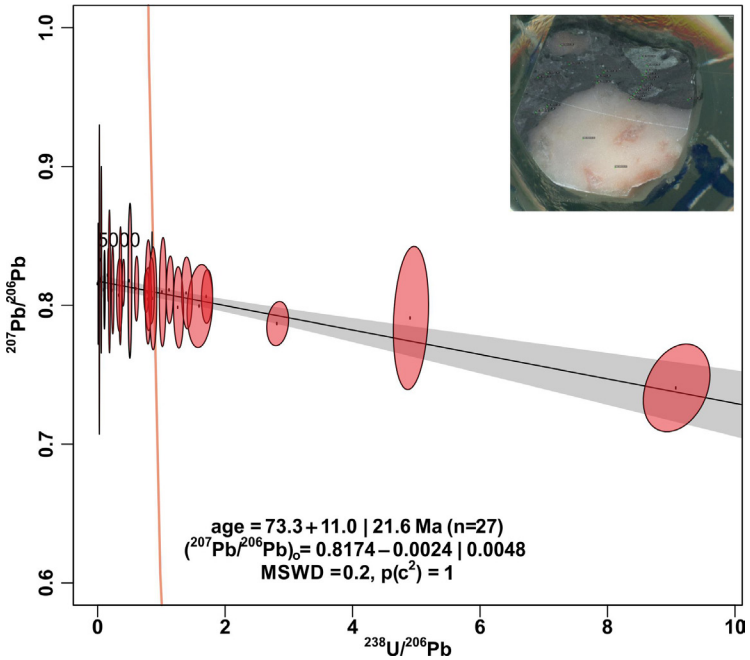


Figure 8. Tera-Wasserburg diagram for the Africano marble extracted from Quarry-1.

cream coloured, angular limestone breccias of different sizes embedded in a red (coral) coloured matrix, and is named "Breccia Corallina" in Italian due to its coral-coloured matrix. Another marble in the brecciated marble class was produced in the Karaburun peninsula. This marble, known as "Broccatellone" and "Breccia Corallina", is similar in texture to the marbles of the Bilecik-Vezirhan region, but differs from other marbles by the differences in the pieces of marble that form the brecciated texture. Another brecciated marble is "Portasanta" from the Greek island of Chios. The matrix of Portasanta is dark red, the clasts are lighter in colour than the matrix, and locally, the matrix appears much more red (Castisani et al., 2014). Another marble that is quite characteristic with its brecciated structure consisting of black and white colours is the marble called "Marmor Celticum". It has a very distinct contrasting structure formed by very black limestone and pure white calcite and dolomite veins (Öngen and Aysal, 2024). Among all these brecciated marbles, the Africano marble has many distinctive features. The brecciated clasts of Africano marble mostly composed of grey and white marbles. However, basic volcanic rock, radiolarite and chert clasts are also observed. The clasts often contain hematite flecks which give the stone a reddish colour. The matrix is distinctly black and dark green. Important parameters that can help characterize Africano marbles will be discussed in detail in the next section.

5.2. Characterization for provenance analysis

The ancient city of Teos was famous for its coloured marbles known as Africano or Marmor Luculleum (Lucullus Marble). Grey marbles known as Bigio Teos or Bigio Africano were also produced and used locally. Africano and Bigio Africano marbles were extracted from the Karagöl, Taşdibi, Turgut-Kesikkaya, Yelki-Küçükkaya and Beyler-Sarıkayalar marble quarries located near Seferihisar (Ancient Teos) (Kun and Türkmen, 2001; Kadıoğlu, 2016; Adak and Kadıoğlu, 2017).

As explained in the previous section, the brecciated types of Africano marbles (Quarry-1 and 3) are different from other brecciated marbles and can therefore be easily distinguished from other brecciated marbles. However, it is difficult to distinguish the Bigio Africano marbles produced from Taşdibi quarries (Quarry-2) from other grey marbles, such as the İznik grey marbles. The maximum grain size measurements (MGS) values of Africano and Bigio Africano marbles are very close to each other. The MGS values for marbles produced from Quarry-1 is 0.13–0.6 mm, for Quarry-2 is 0.2–0.6 mm, for Quarry-3 is 0.3–1.2 mm, and for samples taken from the Ancient City is 0.2–2.6 mm. Comparing these values with the MGS values of other marbles from around the Mediterranean by Antonelli and Lazzarini (2015), it can be seen that they have grain sizes similar to those of Docimeion, Carrara, Pentelli, and Hymettos marbles (Figure 9). The MGS values of other marbles are generally larger than those of the Africano marbles.

All EPR spectra recorded at room temperature clearly show clear six lines which are traces characteristic of Mn^{2+}. Mn has an atomic number of 25 and its electronic configuration ends up with $3d^5$, and these five unpaired

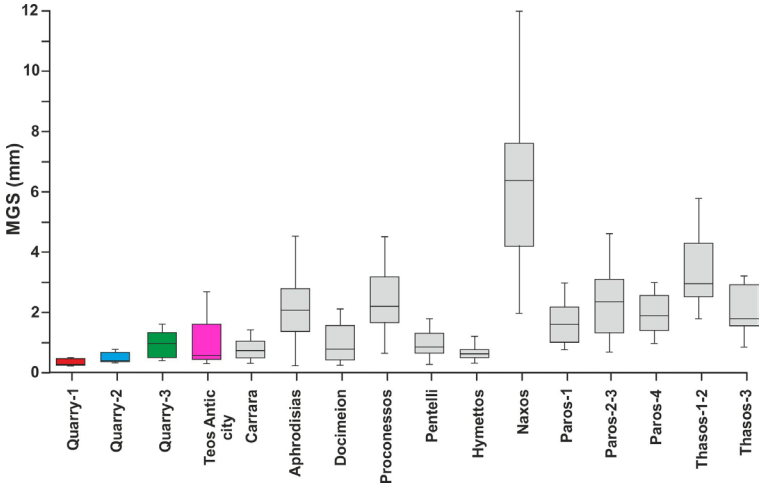


Figure 9. Comparison of MGS values for Africano marbles with Mediterranean marbles (values taken from Poretti, 2016).

electrons of Mn^{2+} are in the last orbital. Hence, it has a nuclear spin number of I = 5/2 and an electronic spin number of S = 5/2 (Bulka et al., 1991; Polikreti et al., 2002; Weihe et al., 2009; Duliu et al., 2019). By applying an external magnetic field these six hyperfine transitions belonging to 5/2 ↔ 3/2, 3/2 ↔ 1/2, 1/2 ↔ −1/2, −1/2 ↔ −3/2, and −3/2 ↔ −5/2 will occur due to the Zeeman effect (Wildeman, 1970; Bulka et al., 1991; Polikreti et al., 2002; Weihe et al., 2009; Duliu et al., 2019). The EPR spectra of all these samples have sharp and dominant Mn^{2+} peaks and thus the concentration of the Mn^{2+} is less than 1% (Fujiwara, 1964; Polikreti et al., 2002). Although the Mn values of the brecciated parts consisting of marble clasts are low, the Mn values are high, especially in red-colored spotted marbles and in the matrix.

Geochemical analyses were carried out on the brecciated and Bigio types of Africano marbles collected from different quarries, and from the wastes around the ancient city of Teos. Analyses carried out on various representative rock fragments, including whole-rock, breccias and matrix. The data obtained suggested that while the breccias forming the Africano marbles and the Bigio Africano samples exhibited similar behaviour, whole-rock and matrix analyses were quite variable (Figure 10). Marbles and marble breccias composed of calcite minerals have high CaO contents and low MgO contents. This is confirmed by the determination of very little dolomite content in XRD analyses. However, the Fe_2O_3 and MnO values of the samples with red patches and having a red matrix are significantly higher than the others. Similarly, the Sr, Ba, and ΣREE values also reflect this change quite well.

A good way to distinguish limestones deposited in different geological environments is to use REY (Rare Earths and Yttrium) spider plots normalized to chondrite and Post-Archean Australian Shale (PAAS) (Figure 11). The normalized REY patterns of carbonate rocks are similar to the REY patterns of seawater, providing important information about the environments in which the carbonate rocks formed (Figures 11 11a, 11c, 11e, 11g). The PAAS-normalized REY plot shows (Figures 11 b, 11d, 11f, 11h), it is seen that the samples collected from both the quarries and the vicinity of the ancient city of Teos have a pattern similar to modern seawater and are located between the modern seawater and the North American Shale Composite (NASC) values (Gromet et al., 1984). However, the REY patterns of Bigio Africano marbles are seen to be concentrated in a narrower range than those of brecciated Africano marbles. The fact that the patterns of the brecciated Africano marbles are spread over such a wide range must be a result of the effect of the different breccias and the different matrix. In these diagrams, the REY patterns of the marbles show significant Ce depletion and HREE and La enrichment. This similarity to the seawater REE patterns indicates that the primary limestones forming the marbles were deposited in an open ocean environment (De Baar et al., 1991; Bau and Dulski, 1996; Zhang et al., 2017). According to Shields and Webb (2004), the slight MREE enrichment observed in red-mottled and red-matrix marbles can be attributed to the preferential adsorption of LREEs and HREEs on Mn- and Fe-oxyhydroxides. A significant positive Y anomaly is also observed, which is due to the effect of the clastic material and/or the different matrix. Furthermore, the REY values are compatible with the Indian Basement, Pacific Basement, and Walvis Ridge (Atlantic). The Rb - Sr - Ba triangle diagram (Figure 12) proposed by Zhang et al. (2017) is a useful tool to distinguish between inland freshwater limestones, continental margin limestones, and

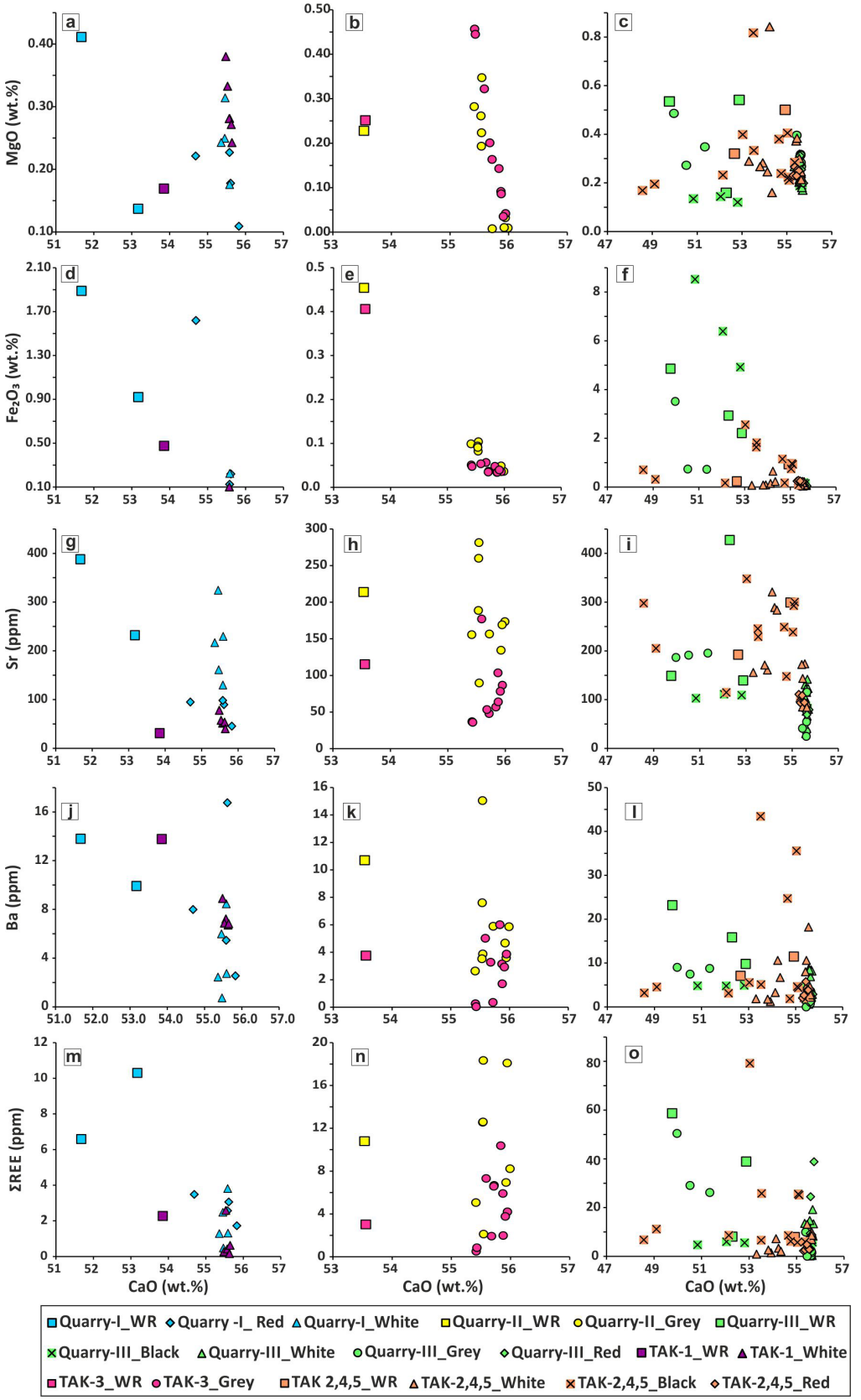


Figure 10. Harker diagrams for the Africano marbles.

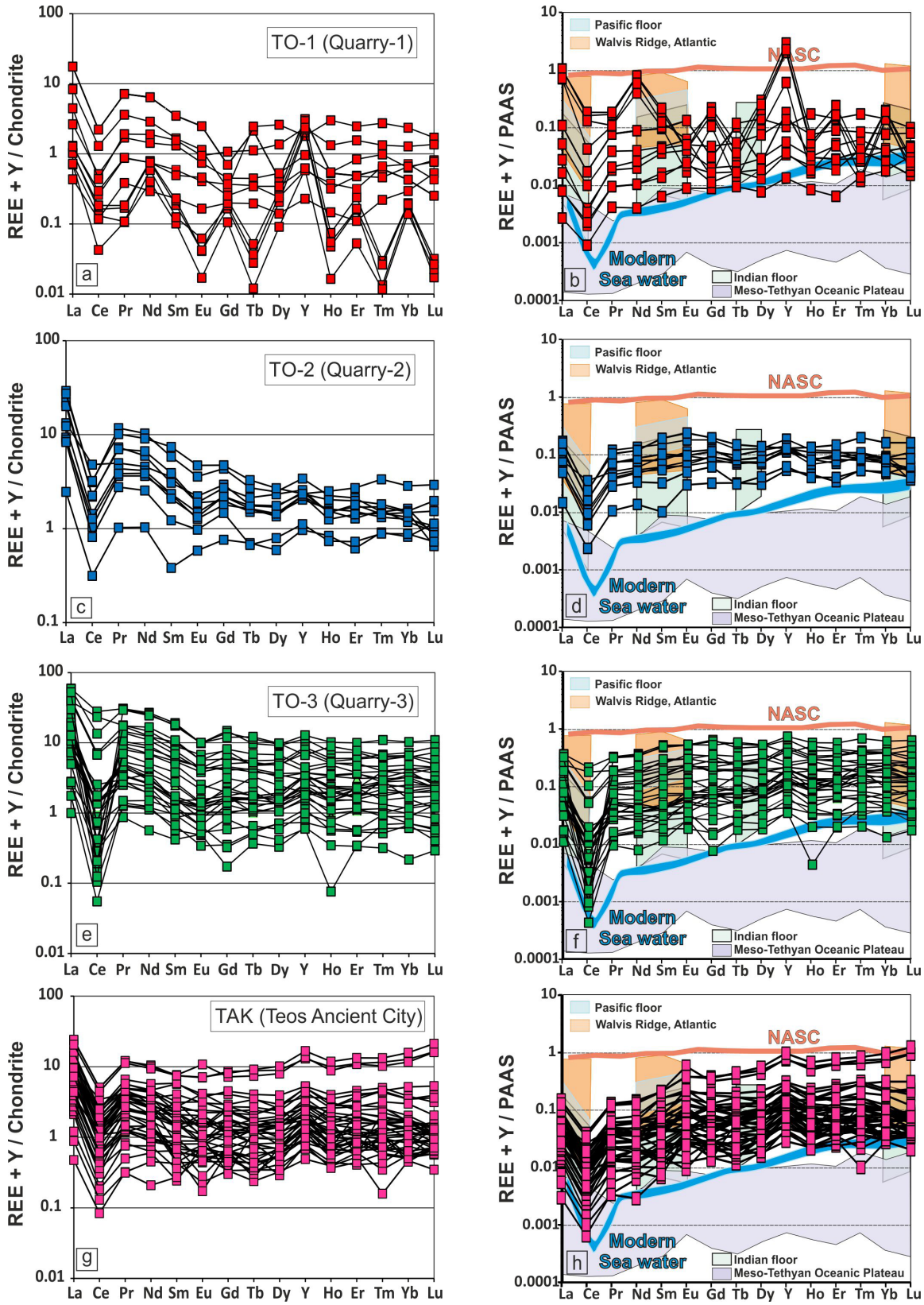


Figure 11. (a–c–e–g) Chondrite-normalized and (b–d–f–h) PAAS-normalized REY diagrams for Africano marbles (Chondrite value from Sun and McDonough,1989; PAAS value from McLennan,1989).

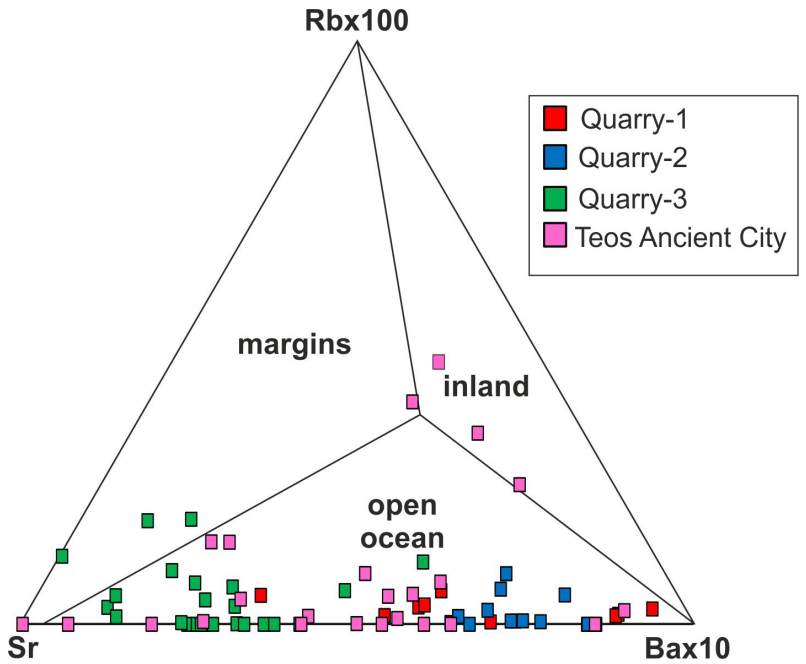


Figure 12. Rb–Sr–Ba triangular diagram of limestones deposited in various depositional environments (Zhang et al., 2017).

open ocean limestones. In this diagram, it can be seen that the Africano marbles are mostly traced to the open ocean environment, and very few examples are located in the inland and margin environments.

Trace element data and various geochemical ratios are commonly used to constrain the paleo-redox conditions of sedimentary processes. Researchers such as Jones and Manning (1994) and Nath et al. (1997) have used trace element ratios including Ni/Co, V/Cr, V/(V + Ni), and U/Th to assess the palaeo-redox conditions of ancient sediments (Figure 13).

A reducing depositional environment is indicated by a V/(V + Ni) ratio greater than 1, whereas a ratio less than 1 indicates oxidising conditions (Lewan, 1984). The calculated V/(V + Ni) ratios for the three ancient quarries and their associated samples range from 0.1–0.71, 0.2–0.80, and 0.1–110.65, respectively, with most samples indicating an oxic environment. According to Hu et al. (2015), Ni/Co ratios below 5 indicate oxic conditions, values between 5 and 7 indicate dysoxic conditions, and ratios above 7 indicate suboxic to anoxic conditions. In the present study, Ni/Co ratios ranged from 1.42–22.49, 0.1–0.28, and 0.2–24.21 respectively, reinforcing the conclusion that deposition occurred predominantly in an oxic environment. Only a few samples from Quarry-I and Quarry-III exhibited Ni/Co ratios greater than 5, placing these samples outside the oxic environment. V/Cr ratios ranged from 0.01–1.23, 0.01–8.85 and 0.01–6.46 respectively, further supporting a generally oxic depositional environment. Suttner and Dutta (1986) highlighted that the binary plot of Ni/Co vs. V/Cr can serve as a useful tool for delineating redox conditions. The cross plots of vanadium and nickel for the samples analysed (Figures 13a, 13d, 13g) indicate that the limestones are of mixed marine and terrestrial origin, with Quarry-III and associated samples specifically deposited in environments ranging from marine anoxic to marine terrestrial conditions (Figure 13g). Rimmer (2004) suggested that the Ni/Co vs. V/(V + Ni) plot indicates that the majority of the samples studied were deposited under oxic conditions, although certain samples with higher Ni/Co ratios correspond to dysoxic and suboxic to anoxic conditions (Figures 13b, 13e, 13h). Similarly, the Ni/Co vs. V/Cr plot revealed the presence of dysoxic to suboxic/anoxic conditions (Figures 13c, 13f, 13h), with samples clustering in these plots according to their environmental characteristics. The $^{87}Sr/^{86}Sr$ isotope ratios of Africano marbles are between 0.70723 (±0.0000059) and 0.70956 (±0.0000058). A comparison of the Sr isotope values of the Africano marbles (Figure 14) with other well-known marbles in the Mediterranean region (Barbin et al., 1992; Brilli et al., 2005; Wielgosz-Rondolino et al., 2020) shows that the Africano marbles have a higher $^{87}Sr/^{86}Sr$ isotope ratio than all other marbles. On the other hand, the Africano marbles have $^{87}Sr/^{86}Sr$ values in a similar range to Carrara, Naxos, Pentellikon, and Dokimeion marbles. Such a wide range of $^{87}Sr/^{86}Sr$ isotope ratios is probably an effect of the different matrices.

The $\delta^{13}C$ and $\delta^{18}O$ isotope values of the Africano marbles vary between –4.96 (±0.08) and 3.36 (±0.08), respectively, and the $\delta^{18}O$ isotope values vary between

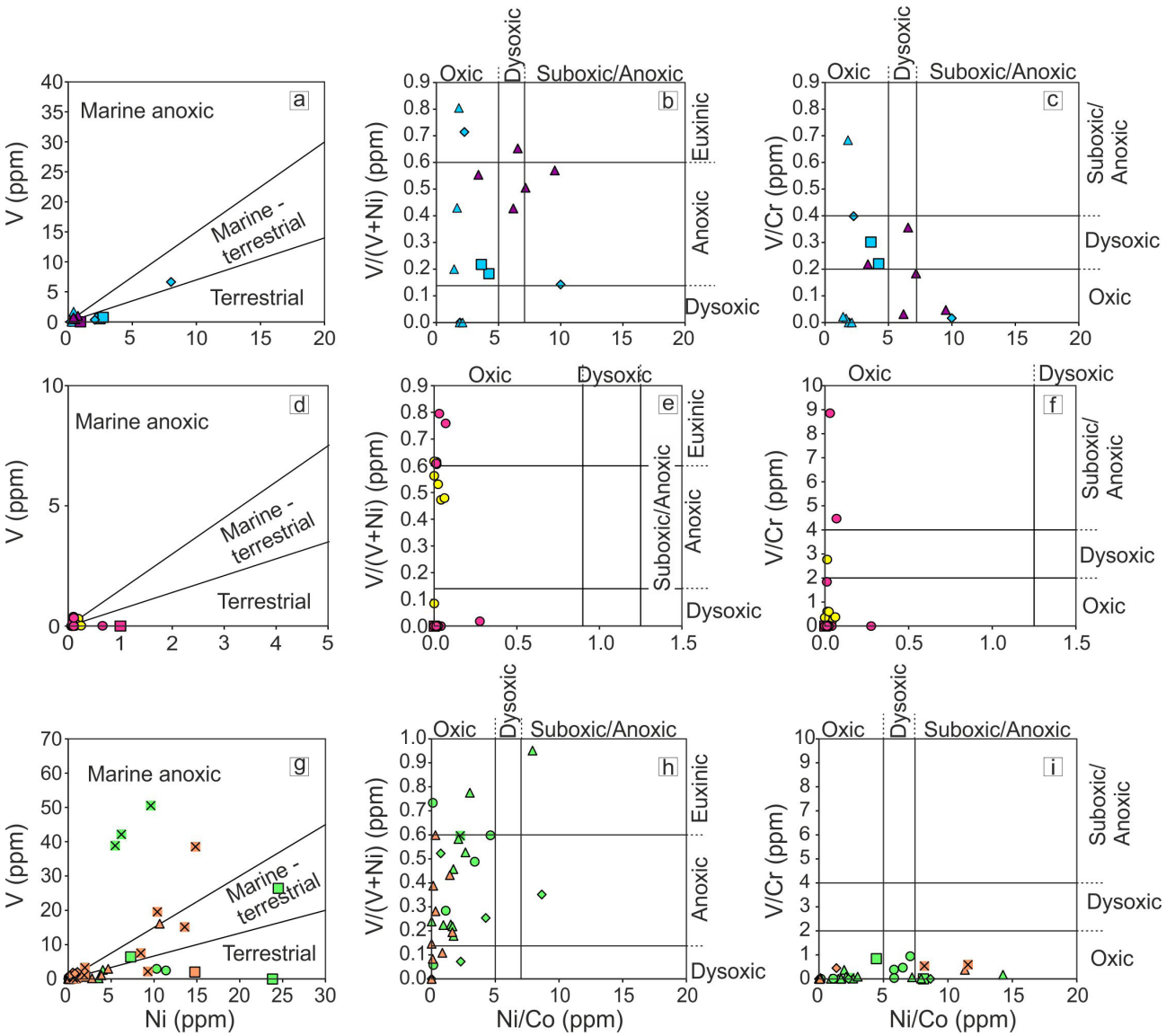


Figure 13. Plot of redox sensitive trace element ratios (a,d,g) V versus Ni. (b,e,h) V/(V + Ni) versus Ni/Co. (c,f,I) V/Cr versus Ni/Co for the Africano marbles (Range values taken from Rimmer, S.M., 2003 and Tangwa et al., 2023. Symbols are explained in Figure 10).

–11.17 (±0.10) and –5.41 (±0.10). The $\delta^{13}C$ VPDB values of the marble samples from the ancient quarries and the ancient city are generally in the positive range, although one sample from the ancient city had a negative value (Table). Positive $\delta^{13}C$ values have been associated with increased algal populations and photosynthetic activity in shallow marginal marine environments (Milliman and Muller, 1977). On the other hand, negative values of $\delta^{13}C$ reflect diagenetic modification of carbonates (Bellanca et al., 1995) as well as the effects of stormy water conditions (Allan and Matthews, 1982). Negative values of $\delta^{18}O$ VPDB in limestone sediments indicate postdepositional modification by meteoric water and/or diagenetic processes. High precipitation and wet seasonal climatic conditions were associated with the most negative $\delta^{18}O$ VPDB values (Nagarayan et al., 2008). High negative $\delta^{18}O$ PDB values indicate a limited influence of precipitation and temperature, while low negative values indicate more humid palaeoclimatic conditions (Tangwa et al., 2023). Furthermore, the C-O isotope values of Africano marbles are quite close to those typical of marine limestones and do not differ significantly from other known marble types from the Mediterranean region (Figure 15). In fact, Africano marbles do not show a clear distinction in terms of Sr and C-O isotopes when compared to other carbonate marbles.

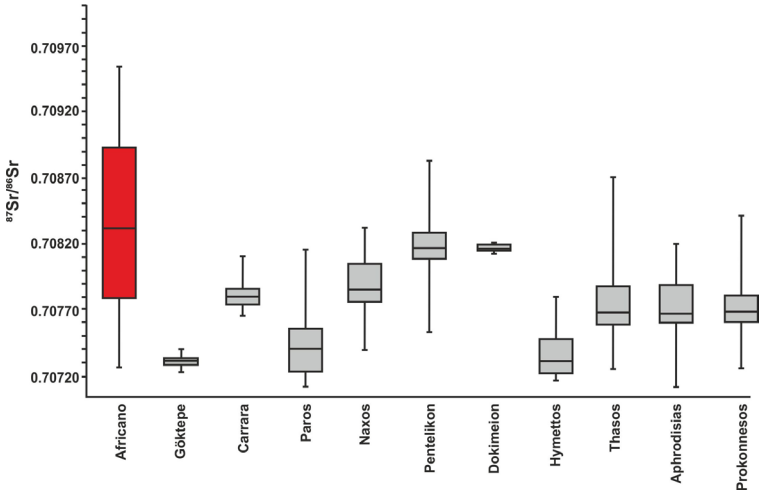


Figure 14. $^{87}Sr/^{86}Sr$ isotope diagrams for Africano marbles (this study), and other well-known marbles from the Mediterranean region (Brilli et al., 2005; Barbin et al., 1992; Wielgosz-Rondolino et al., 2020).

Table. $^{87}Sr/^{86}Sr$, $\delta^{13}C$ and $\delta^{18}O$ isotope values of Africano marbles.

$^{87}Sr/^{86}Sr$ isotope ratios					
Sample ID	**Sr88(v)**	**Rb85**	**$^{87}Sr/^{86}Sr$**	**±2σ**	
TO-1-1	35.96	0.0000117	0.70956	0.0000058	Africano
TO-2-1	37.95	0.0000454	0.70831	0.0000075	Grey marble
TO-3-1	38.09	–0.0000169	0.70723	0.0000059	Africano
C-O isotope ratios					
Sample ID	**$d^{13}C$ VPDB**	**1 s**	**$d^{18}O$ VPDB**	**1s**	
TO1-2	2.85	±0.08	–11.17	±0.10	Africano
TO1-3	2.24	±0.08	–9.73	±0.10	Africano
TO3-2	2.48	±0.08	–8.50	±0.10	Africano
TO3-3	3.02	±0.08	–8.87	±0.10	Africano
TAK-1	–4.96	±0.08	–8.51	±0.10	Africano
TAK-2	2.88	±0.08	–10.02	±0.10	Africano
TAK-3	3.36	±0.08	–5.41	±0.10	Africano
TAK-4	2.85	±0.08	–9.16	±0.10	Africano
TAK-5	2.51	±0.08	–8.69	±0.10	Africano

In this study, a U-Pb calcite age was obtained from for the first time from Africano marbles. A U-Pb calcite age of 73.3 ± 11 Ma (MSWD: 0.2) was obtained from Africano marbles of from the Lake Karagöl quarry. This age represents the recrystallization age of calcite minerals and probably correspond to the depositional ages of marbles. This age corresponds to the Upper Cretaceous (Campanian- Maastrichtian) period.

Solak et al. (2015) mentioned the presence of huge Mesozoic limestone and ophiolite blocks embedded in Maastrichtian-Paleocene sheared siliciclastic sedimentary rocks within the BFZ. They suggested that the limestone blocks, which range in age from Late Triassic to Cretaceous, may be olistoliths or deformed and cut platform fragments. Sarı (2018) emphasized that planktonic foraminiferal assemblages such as *Abathomphalus mayaroensis, Contusotruncana contusa, Globotruncanita conica* and *Racemiguembelina fructicosa* were found in the pelagic, laminated micritic limestone stack in the Gökdere area near the city of İzmir and that these rocks were all late

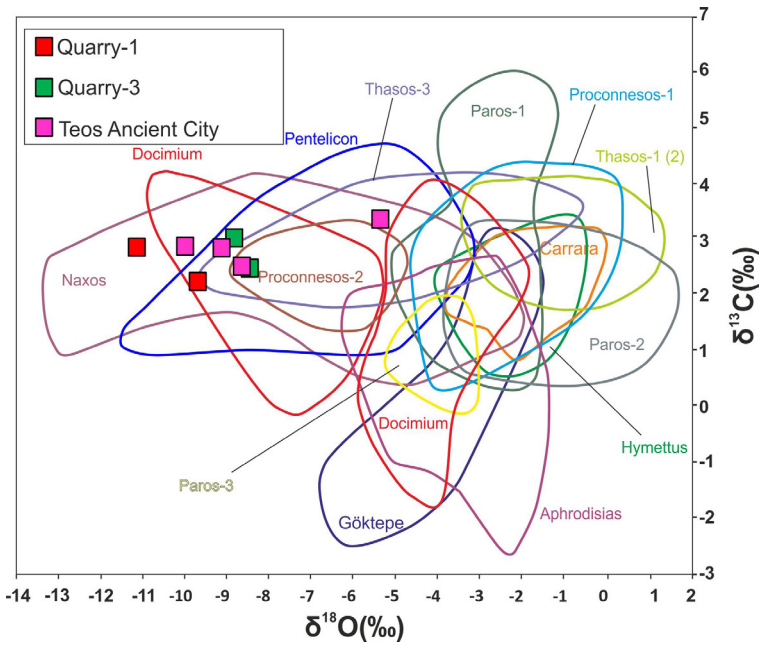


Figure 15. Stable C and O isotope diagrams for Africano marbles (this study) and comparison with well-known marbles of the Mediterranean region (after Antonelli and Lazzarini, 2015; modified by Al-Bashaireh, 2021).

Maastrichtian in age. He also suggested that the flysch-type sediments below and above these pelagic limestones could also be of late Maastrichtian age, and based on the presence of *Globotruncana linneiana* Sp. in the uppermost parts of the sequence, he implied that the age of these sequences did not extend into the late Maastrichtian. The fact that both fossil and U-Pb calcite ages (taking into account analytical uncertainties) show the same period has allowed a clearer understanding of the formation ages of the marbles. Future age data will be an important guide for provenance studies.

6. Conclusions

The marbles of Teos, known as Africano marbles, were widely used in construction and decoration throughout the Roman period. These marbles were extracted and processed from three ancient quarries (Quarry-1, Quarry-2, Quarry-3) located near the village of Sığacık. These marble deposits are derived from limestones from limestone blocks within the BFZ. Africano marbles generally exhibit a brecciated texture within a dark coloured matrix, particularly in Quarry-1 and Quarry-3. In addition, these marbles have white, pink, red and dark coloured veins. The primary mineral phase in these marbles is calcite, while the red colouring is due to hematite inclusions. The characteristic breccia texture of Africano marbles are embedded in a dark matrix composed of chlorite and/or serpentinite minerals. The marble breccias typically show microsparitic and micritic textures; however, brecciated calcites from Quarry-3 often show sparitic textures. Besides, another variety of Africano marble, known as Bigio Africano, consists of grey, massive and homogeneous limestones from Quarry-2. The maximum grain size (MGS) for each group is as follows Quarry-1; 13–0.6 mm, Quarry-2; 0.2–0.6 mm, Quarry-3; 0.3–1.2 mm and Teos Ancient City; 0.2–2.6 mm. The CaO content for each group of Africano marbles is as follows Quarry-1; 38.88–43.93 wt.%, Quarry-2; 53.54–55.99 wt.%, Quarry-3; 44.27–55.74 wt.%, Ancient City of Teos; 32.52–55.98 wt.%. The SiO_2 content is remarkably low in all groups. The $^{87}Sr/^{86}Sr$ isotope ratios measured in whole rock samples range from 0.70723 (±0.0000059) to 0.70956 (±0.0000058). The $\delta^{13}C$ isotope values range from –4.96 (±0.08) to 3.36 (±0.08), while the $\delta^{18}O$ isotope values range from –11.17 (±0.10) to –5.41 (±0.10). In the REY and Rb-Sr-Ba triangular diagrams, Africano marbles are predominantly plotted within the open ocean field, with a few samples positioned in inner and marginal basin environments. Considering all available data, it is evident that the brecciated types of Africano marbles (Quarry-1 and Quarry-3) are distinct from other brecciated marbles. However, it is difficult to distinguish the Bigio Africano marbles from Quarry-2 from other grey marbles such as the İznik grey marbles.

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Supplementary materials
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