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U-Pb calcite geochronology, EPR, geochemistry, and C-O-Sr isotopes of ancient marbles in the İznik Region (Bursa-Türkiye)

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Abstract: The İznik city (ancient Nicaea), located east of Lake İznik (known as -“Bithynia” in ancient times), has been an important political and cultural centre of Asia Minor since the Hellenistic period. Marbles produced in the quarries in the vicinity (Ömerli and İnikli villages, Deliktaş-Sarıtaş hills) were used both in the construction of the walls and in many ancient works in the city. Approximately eighteen ancient marble quarries producing grey and white marbles were investigated in the region. Petrography, EPR, XRD, C-O-Sr isotope and whole rock geochemistry analyses were performed for characterization of the samples collected from the quarries for the provenance studies. According to the new geochemistry and C-O-Sr isotope data, the limestones forming the marbles were deposited in open sea-ocean environments. U-Pb calcite dating determined that the white marbles were 93.06 ± 8.55 Ma, while the grey marbles were 94.84 ± 1.41 Ma and 88.03 ± 2.13 Ma (Upper Cretaceous: Cenomanian-Coniacian). These ages probably correspond to the crystallization/metamorphism ages of the marbles. The new data set obtained with this study will contribute to the understanding of the geological evolution of the region, and will help researchers to better understand the source region of some white and grey marbles used in ancient buildings.

Key words: Ancient marble, bigio antico, Nicaea, U-Pb calcite dating

1. Introduction

The city of İznik (ancient Nicaea), located south of the Sea of Marmara (Figure 1) and east of the İznik Lake (known as “Bithynia” in ancient times), has been an important political and cultural center in Asia Minor since the Hellenistic period (Benjelloun et al., 2018). İznik was founded in BC 316 named as “Antigonia” by Antigonius Monophthalmos, one of the commanders of Alexander the Great, King of Macedonia. Lysimachus, defeated Antigonius in BC. 301, took the city under his rule and gave the city the name of his wife “Nikaia”. City administration passed to the Kingdom of Bithynia in BC. 279. At the end of the long wars between the Bithynia Kingdom and the Romans, the city was captured by General Lucullus and its name was changed to “Nicaea”. After the Goths attack in A.D. 259, the walls of the city, which was built during the Bithynia Kingdom and severely damaged by the earthquake in A.D. 12, were rebuilt much stronger (Texier, 1882; Kılıçkaya, 1981; Demirkent, 2004). Nowadays the city is surrounded by a 4970 m long wall with 4 main and 12 secondary gates. Bricks and marbles brought from the surrounding quarries were used in the construction of the walls (Figure 2). One of the main gates (the Lefke Gate) of the city walls were built using both grey and white marbles (Figure 2a). There are numerous architectural elements made of grey marbles (Figure 2b). Marble was produced for monumental buildings from the quarries around the villages of Ömerli and İnikli, Deliktaş - Sarıtaş hills, which were opened and operated in the vicinity of İznik (recently eighteen ancient quarries have been identified in the region), especially during the Roman period (Figure 2). One of the well-known of these quarries is the Deliktaş quarry, which is famous for its Heracles relief, carved into the rock by the quarry workers 1800 years ago for protection and religious worship (Figure 2e). A significant part of these ancient quarries has been re-

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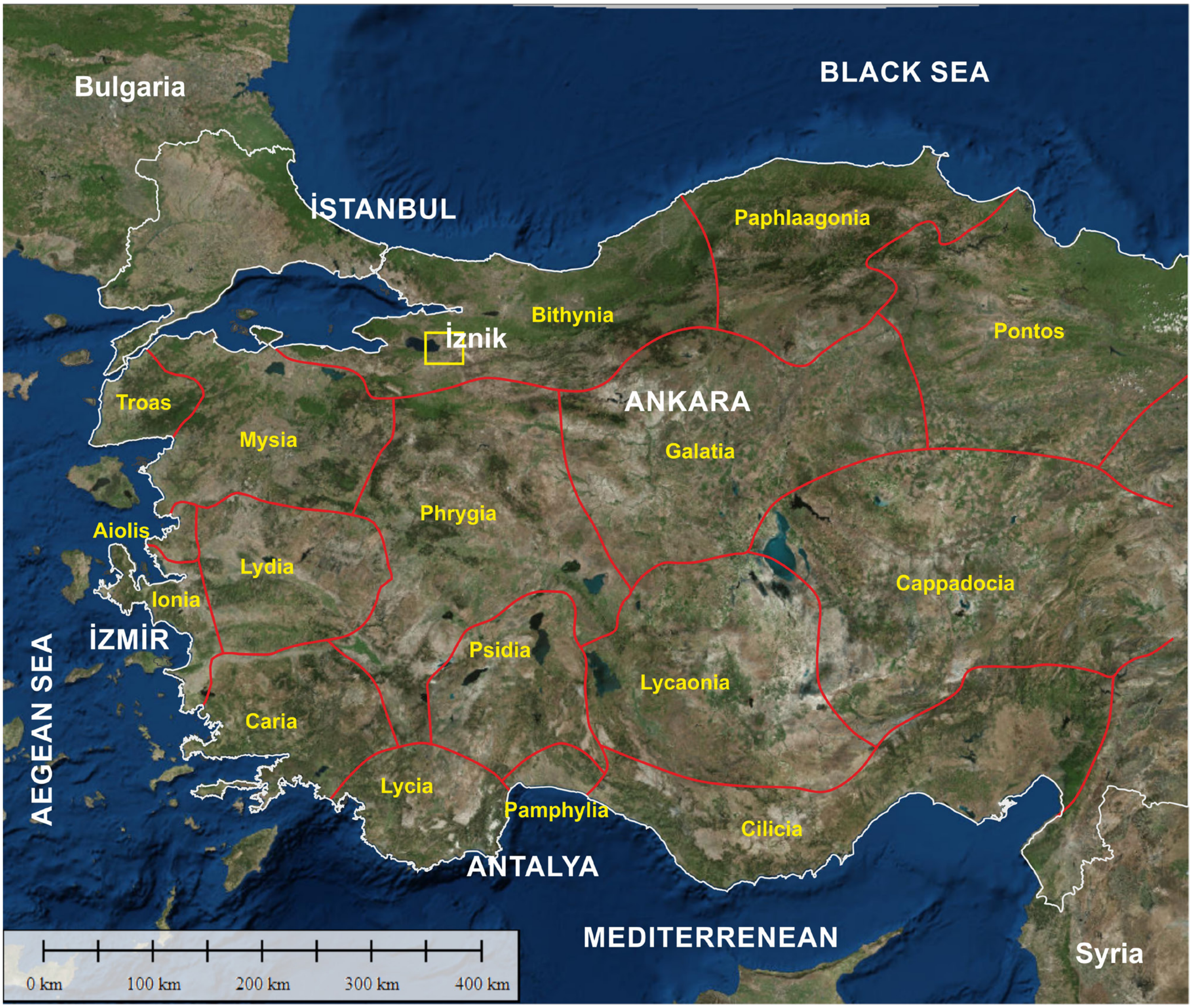

Figure 1. Location map of study area.[1]

[1] Tarih ve Arkeoloji (2008). Antik Bölgeler [online]. Website https://mystichistory.blogspot.com/2008/06/antik-blgeler.html [accessed 28 October 2024]

operated recently and therefore the ancient quarry sites have been partially destroyed (Yalman, 1993).

The characterization of ancient marbles and the determination of their source regions made significant contributions in the last quarter to the understanding of the origins of architectural elements and the determination of ancient trade routes. New analytical developments have been made in the characterization of ancient marbles by using different optical and spectroscopic methods such as petrography, cathodoluminescence (CL), whole-rock and isotope geochemistry, X-ray Diffraction (XRD), Electron Paramagnetic Resonance (EPR), Fourier Transform Infrared (FTIR), and RAMAN spectroscopies. Although petrography and XRD methods are useful tools for determining the mineralogical and textural properties of marbles, most of which are composed of calcite and some minor minerals, the use of several modern spectroscopic methods together gives good results in determining the source regions. Stable isotope analyses of carbon and oxygen in white marble are used as an important tool in investigating the origin of this marble (Craig and Craig, 1972). Another parameter as important as analytical data in the characterization of ancient marbles is the detailed geological study around the quarry areas.

This study characterizes two different types of marble (white and grey) originating from ancient quarries in the İznik region. A representative sample was taken from eighteen ancient marble quarries around İznik (Table

Figure 2. a) One of the main gates (the Lefke gate) of the city walls, built using grey-white marbles and brick, b) architectural elements (column headings and blocks) made of grey marbles, c) ancient grey marble quarry partially destroyed by modern marble quarry, d) Deliktaş quarry, e) Heracles relief, f) one of the big quarries where grey marble is produced, g-h) the white marble quarries near the village of Ömerli, and i) the mark engraved on the white marble surface by workers (from Öngen and Aysal, 2024).

1). We present a new dataset using petrography, EPR, XRD, C-O-Sr isotope analysis, geochemistry and U-Pb calcite LA-HR-ICP-MS dating methods to support future provenance studies. This study also provides important data for the geology of the region with new U-Pb calcite dating and geochemistry data obtained from marbles.

2. Geology

The study area is located in the east of the Armutlu Peninsula, within a belt called the Sakarya Zone and/or Sakarya Continent (Şengör and Yılmaz, 1981). Akartuna (1968) stated that the metamorphic rocks around İznik (Metamorphics) start with a metaclastic-carbonate sequence containing low-grade felsic volcanic and volcanosedimentary units and marble masses in the form of blocks, lenses, or interlayers. Bargu (1982) defined the metamorphic rocks around İznik as "Dereköy Metamorphics" and the marbles as "İznik marbles" and suggested that they may be pre-Permian in age. Bargu (1982) divided the Dereköy Metamorphics into three main groups: pelitic, carbonate, and basic rocks. He emphasized that the NE-trending İznik marbles consist of coarsely crystalline grey and grey-white marbles, their thickness reaches 500 m, and they overlie the Dereköy Metamorphics with a transitional and concordant contact. Although Göncüoğlu et al. (1987) named the low-grade metamorphic rocks in the study area as "İznik Metamorphics", Yılmaz et al. (1995) defined it as "İznik Metamorphic Assemblage". Göncüoğlu et al. (1987) claimed that the structural lower part of the İznik Metamorphics is composed of dolomite and basic-volcanic interlayered meta sandstones, conglomerate, siltstone, felsic tuff, and pyroclastic units. They also emphasized that the middle part of the sequence consists of felsic volcanic and volcanoclastic rocks, purple-red-pink coloured mudstones, and micritic limestones, while the upper part is a transition to the lower units and consists of massive limestones with chert interlayers (Figure 3). Göncüoğlu et al. (1987) reported that although the lower dolomites do not contain fossils, there are pelagic bivalvia in the micritic layers that are very similar to Daonellids, indicating a Triassic age. Yılmaz et al. (1997) claimed that the metamorphism of the İznik Metamorphics extends to the greenschist facies metamorphism, and they distinguished the rock units forming the metamorphic group in detail and revealed the pre-metamorphism stratigraphic sequence. According to Yılmaz et al. (1997), the sequence consists of thick Palaeozoic and Mesozoic sequences, including the Upper Cretaceous, and that the

Table 1. Coordinates of ancient marble quarries around İznik.

Quarry Name	**Latitude**	**Longitude**	**Sample**
OC-1	40°27'11.61"N	29°46'0.38"E	+
OC-2	40°27'2.84"N	29°45'38.99"E	+
OC-3	40°26'58.37"N	29°45'37.07"E	+
OC-4	40°27'6.99"N	29°45'19.91"E	+
OC-5	40°26'47.04"N	29°44'48.70"E	+
OC-6	40°26'47.72"N	29°44'39.42"E	+
OC-7	40°26'52.29"N	29°44'37.01"E	+
OC-8 (Deliktaş)	40°26'46.17"N	29°43'59.44"E	+
OC-9	40°26'49.56"N	29°44'11.71"E	+
OC-10	40°29'36.69"N	29°43'37.99"E	+
OC-11	40°29'35.81"N	29°44'17.09"E	+
OC-13	40°30'41.26"N	29°42'39.93"E	+
OC-14	40°30'44.23"N	29°42'39.92"E	+
OC-15	40°30'47.27"N	29°42'31.76"E	+
OC-16	40°30'45.56"N	29°42'34.04"E	+
OC-17	40°30'46.75"N	29°42'38.33"E	+
OC-18	40°30'44.93"N	29°42'41.75"E	+
OC-19	40°30'40.07"N	29°45'4.95"E	-
OC-20	40°30'41.29"N	29°45'23.22"E	-

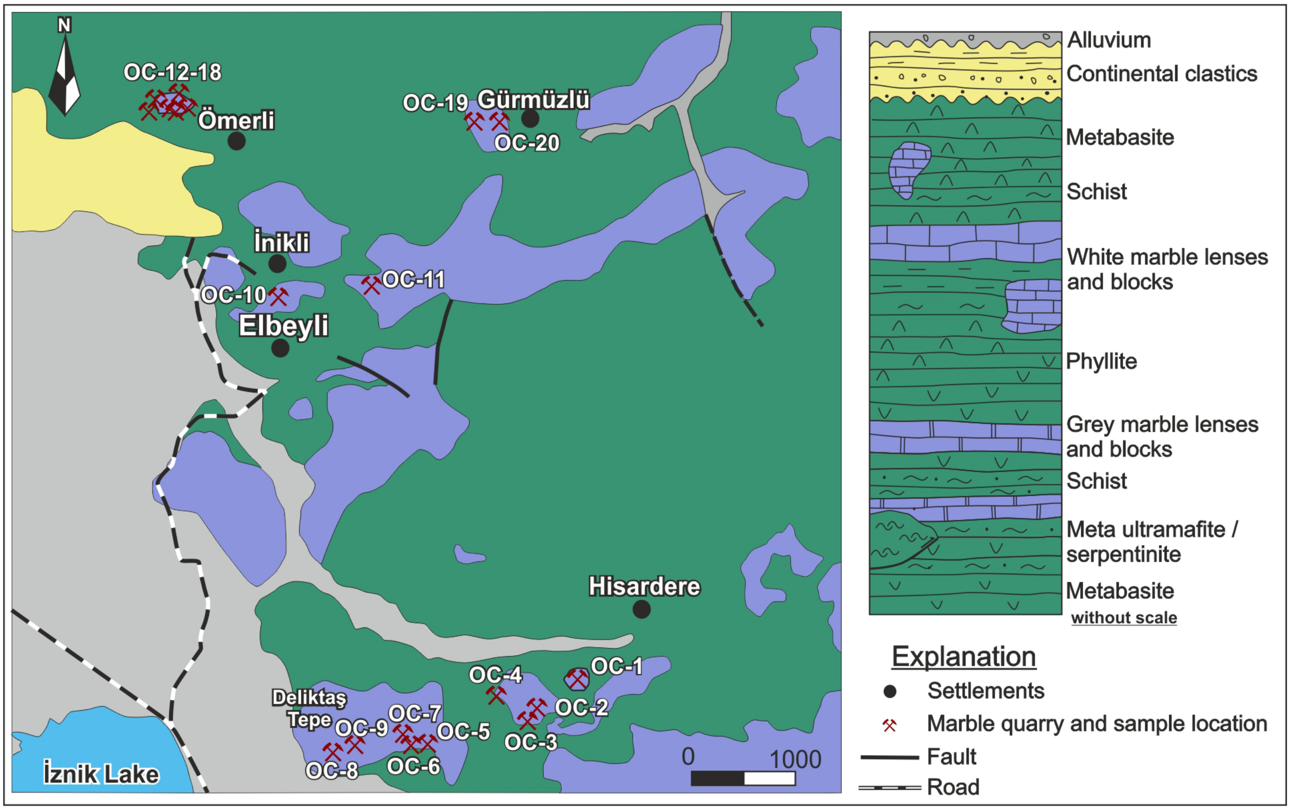

Figure 3. Simplified geologic map and stratigraphic section antic marble quarries of İznik Region (simplified from Kandemir et al., 2014).

degree of metamorphism generally decreases towards the top of the sequence, and as a result, almost the primary features of the upper units of the sequence are preserved. They also suggested that there is a great similarity between the İznik metamorphic series and the contemporaneous units in the southern zone, and that the İznik metamorphic group may represent a part of the Sakarya continent that has undergone metamorphism. Yılmaz et al. (1997) reported that the uppermost rocks of the İznik Metamorphics are composed of Late Cretaceous aged, slightly metamorphosed pelagic limestone-mudstone-radiolarites, intercalated with basaltic lavas and laterally passing into a slightly metamorphosed flysch sequence. Moreover, they emphasized that the flysch sequence contains abundant recrystallized limestone/marble and ophiolite blocks (such as gabbro, serpentinized ultramafic rocks and spilitic lavas), and that the blocks are found as long lenses in a well-foliated metasedimentary matrix. All these units are identical to the Cenomanian-Turonian pelagic rocks to the south. As a result, they pointed out that the İznik metamorphic assemblage is comprised of units up to and including Turonian (~93–88 Ma). Tetiker (2023) stated that the İznik Metamorphics consist of foliated metapsammite, metapelite, and metacarbonate levels and highly deformed green-grey-black colored thick metamagmatic rock levels (metavolcanite, metagabbro) intercalated with these rocks. Additionally, Tetiker (2023) stated that the unit underwent metamorphism in the lower greenschist facies, based on the petrographic and crystal chemistry data obtained in the İznik Metamorphics, and claimed that it was similar to the upper levels of the Lower Karakaya complex with these features. Özer (2018) stated that recrystallized limestones belonging to the İznik Metamorphics predominantly contain chert bands and chert nodules. He also determined that recrystallized limestones, which are exposed in the high topographic areas (plateaus) to the south of the İznik Metamorphics, are alternating with dolomitic and rudist-bearing recrystallized limestones indicating middle-late Turonian age where chert is minor.

Kandemir et al. (2014) correlated the İznik Metamorphics with the units in the Biga Peninsula with their revision studies in the region; They divided the İznik Metamorphics into Kalabak group and Karakaya complex. The Kalabak group (Duru et al., 2012), cropping out in very large areas throughout the Sakarya Zone, is represented by the Torasan and Sazak formations (Duru et al., 2007) consisting of phyllite, metabasite, schist, serpentinite slices and marble layers. Within this formations, there are white marble bands with thicknesses of up to 100–150 m at different levels (quarries to the north of Elbeyli). These marble bands are composed of medium-grained calcite minerals in granoblastic texture and locally with boudinage structure. The age of the unit is accepted as Devonian-Carboniferous based on correlation (Kandemir et al, 2014). The Kalabak group is tectonically overlain by a rock assemblage consisting mainly of metabasites and alternated phyllites and marbles in the greenschist facies to the northeast of Lake İznik (quarries to the west of Ömerli). The marbles, which occur partly as olistoliths and partly as regular bedded successions, show densely boudinage structure. These rocks, which belong to the İznik Metamorphics, are also accepted by some authors as the equivalent of the Triassic sub-series of the Karakaya Complex (Lower Karakaya Complex), which consists of Permo-Triassic clastic and volcanic series and spreads widely from east to west in Türkiye (Göncüoğlu et al., 1986; Okay and Göncüoğlu, 2004, Kandemir et al., 2014). Middle Triassic conodont age was obtained from the marbles of this complex around Bursa (Kozur et al., 2000). The youngest unit in the region, consists of sedimentary rocks that unconformably overlay the İznik Metamorphics, in the northwest of the study area.

3. Materials and analytical methods

3.1. Petrography and XRD analysis

Thin sections for petrographic analysis were prepared from the samples collected from the ancient marble quarries of İznik. The prepared thin sections were investigated using the Leitz ortoplan microscope and the Leica image analysis system. In addition, 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 Istanbul University–Cerrahpasa (IUC), Department of Geological Engineering. Diffraction data were acquired by exposing the powdered samples to Cu-K_α 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

X-band electron paramagnetic resonance (EPR) measurements were conducted using Bruker EMX Nano Benchtop spectrometer with an integrated referencing for g-factor calculation. During the EPR measurements a 9.64 GHz microwave frequency 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

Chemical composition of marble samples was determined at the Geochronology and Geochemistry laboratory established at the IUC by using a Perkin Elmer Avio 200 ICP-OES system (Supplementary Table 1). Analysis package in this step included all major oxides (SiO_2, Al_2O_3, TiO_2, Fe_2O_3, MgO, MnO, CaO, K_2O, Na_2O, and P_2O_5) after $LiBO_2$ fusion. The loss on ignition was given as the weight difference after ignition at 1050 °C. Trace and rare earth element analysis were conducted by using a Pekin Elmer NexION 2000 ICP-MS combined with an ESI NWR 213 nm solid-state Laser Ablation (LA) system. Laser spot size was 80 µm in our measurements. NIST SRM610, SRM612 and SRM1412 were used as external standards. For each analysis, approximately 30 s of background signal was collected before ablating the sample. The ablation time was 50 s with a laser repetition rate of 10 Hz for each sample. Helium was used as the carrier gas (0.6 l/s). Data reduction was performed using the SILLS software package (Guillong et al., 2008).

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 $^{86}Sr/^{88}Sr = 0.1194$. The repeated analyses of the SRM 987 international standard yielded 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. The analytical and data reduction procedures followed those described by Roberts et al.

(2017), employing NIST SRM614 and WC-1 calcite as primary reference materials. Spot sizes of 110 µm and a pulse rate of 5 Hz with an energy density of 2 J cm^{-2} were used, adhering to the methodologies outlined 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, as per 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, whereas the samples and secondary reference materials were not anchored. No corrections for disequilibrium were applied. 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 related section.

4. Results

4.1. Mineralogy and petrography

There are two different types of marble in the İznik region, white and grey, which were exploited in ancient times. Grey marbles consist of almost 90%–95% medium- to coarse-grained calcite, and have granoblastic and/or heteroblastic textures (Figures 4a, 4b). A small amount of organic matter converted into graphite in the rock is noticeable in thin sections. Graphite is mostly concentrated along fracture and crack planes and its proportion is about 1%–2% in the rock. The white marbles are fine to medium grained, and the granoblastic and heteroblastic texture is characteristic. Although the white marbles are composed mainly of calcite, locally hematite-limonite (~2%–3%) staining is observed (Figures 4c, 4d). These marbles are also known as yellow-spotted marbles, as the hematite-limonite content in them gives the rock a yellowish-brown colour in hand samples. The maximum grain size of grey marbles varies between 0.3–3.1 mm, and the grain size of white marbles varies between 0.5–2.5 mm. Although mainly composed

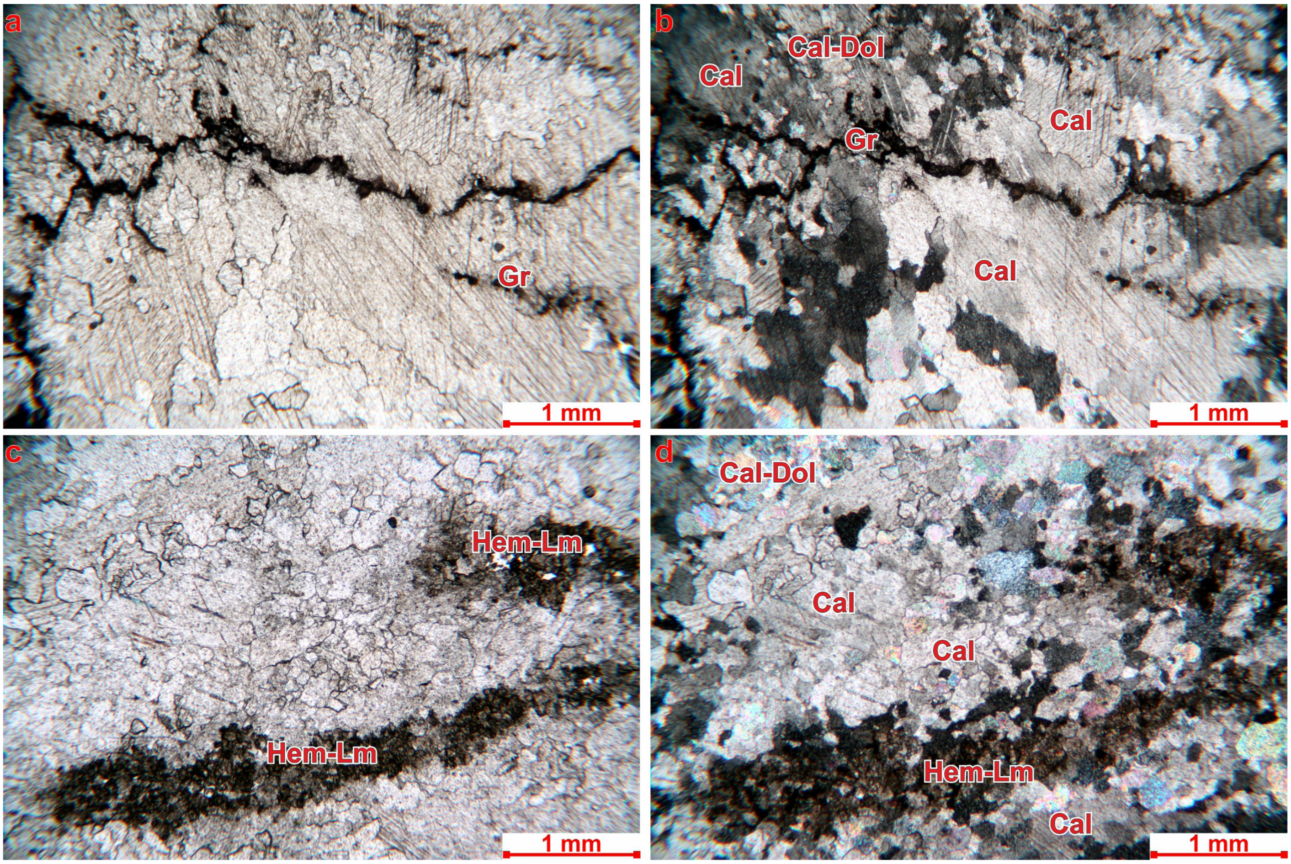

Figure 4. a–b) Heteroblastic texture and organic matter residues transformed into graphite in the grey marbles of the İznik region (a: plain polarized (PPL), b: crossed polarized light (CPL)). c–d) Hematite-limonite minerals that give the rock a yellowish colour in marbles with a granoblastic and/or heteroblastic texture (c: PPL, d: CPL). Abbreviations: Cal: calcite; Dol: dolomite; Hem: hematite; Gr: graphite; Lm: limonite (Whitney and Evans, 2010).

Table 2. $^{87}Sr/^{86}Sr$, $\delta^{13}C$ and $\delta^{18}O$ isotope values of İznik white and grey marbles.

$^{87}Sr/^{86}Sr$ isotope ratios					
Sample ID	**Sr^{88}(v)**	**Rb^{85}**	**$^{87}Sr/^{86}Sr$**	**2σ**	
Deliktaş	40.19	±0.0000491	0.70839	±0.0000081	İznik grey
OC-1	37.93	±0.0000061	0.70874	±0.0000067	İznik grey
OC-6	39.02	±0.0000052	0.70830	±0.0000059	İznik grey
OC-10	37.83	±0.0000218	0.70805	±0.0000062	İznik white
OC-12	33.87	±0.0000030	0.70756	±0.0000058	İznik white
C-O isotope ratios					
Sample ID	**$\delta^{13}C$ VPDB**	**1σ**	**$\delta^{18}O$ VPDB**	**1σ**	
Deliktaş	2.93	±0.08	–4.85	±0.10	İznik grey
OC-12	1.94	±0.08	–7.53	±0.10	İznik white

of calcite, it has been found in the XRD patterns of gray marbles to contain a small amount of dolomite (~1%–2%) and quartz (~1%–2%) (Figure 5).

4.2. EPR results

The EPR data allows people to create a database to use in the provenance studies for detecting the traces of paramagnetic ions such as Manganese (Mn^{2+}), Cobalt (Co^{2+}), and Iron (Fe^{3+}) ions (Poretti, 2016). Due to the paramagnetic nature of the transient metal ions, a clear resonance signal can be recognized and used for the characterization of the marble samples (Duliu et al., 2019). Nearly all natural carbonates include Mn, via EPR spectroscopy the Mn^{2+} can be observable with other impurities (Poretti, 2016; Duliu et al., 2019). Figure 6 shows the EPR spectra of the marble samples labelled as Deliktaş, OC-1, OC-6, OC-10, and OC-12.

4.3. Whole-rock geochemistry

Whole-rock major oxide, trace element, and REE data of twenty-five samples from İznik grey and white marbles are listed in Supplementary Table 1. CaO content is generally

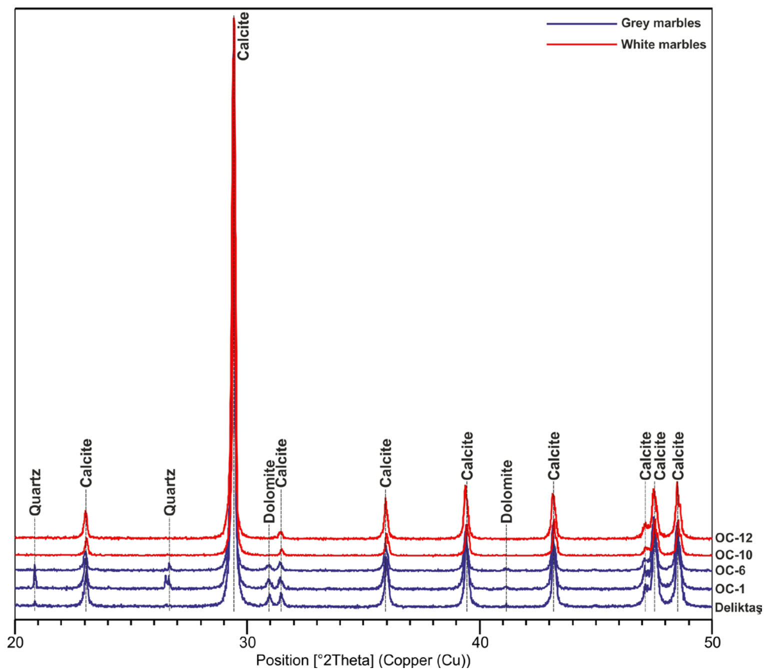

Figure 5. XRD diffraction pattern of İznik marbles and the defined mineral paragenesis.

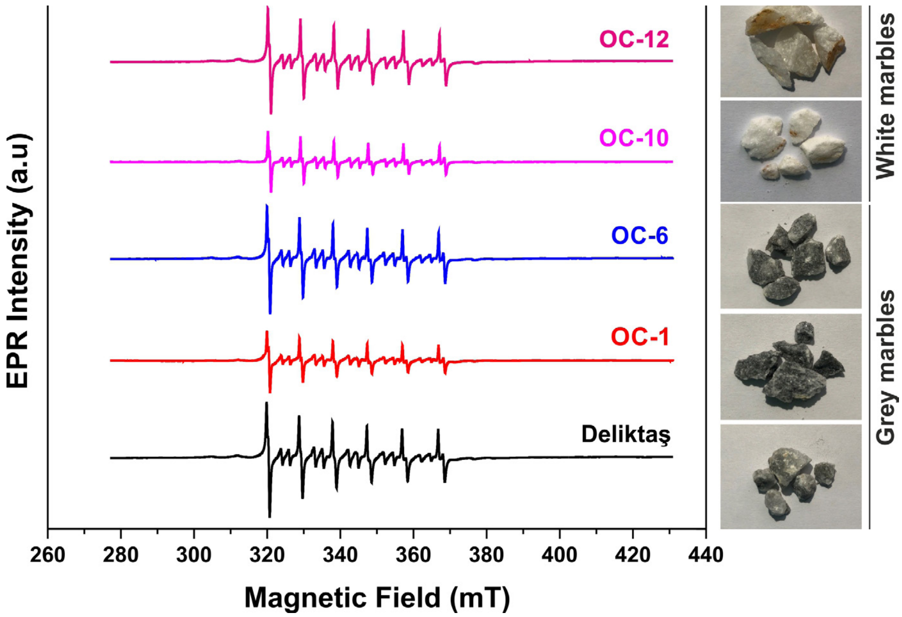

Figure 6. The EPR spectra of the Deliktaş, OC-1, OC-6, OC-10, and OC-12 samples recorded at room temperature.

above 50 wt.% (52.13–55.99 wt.%) in both groups of marble (Figure 7). In only two samples of grey marble these values were measured as 26.40 and 33.28 wt.%. While SiO_2 contents are generally in the range of 0.03–0.3 wt.%, it is above 1 wt.% (1.310–3.46 wt.%) in only five samples of grey marbles. TiO_2 values of both groups of marbles were below the detection limit. In only two samples of grey marble, this value could be measured as 0.01 wt.%. Al_2O_3 contents are generally between 0.01–0.37 wt.%. In two samples of grey marble, this value was measured above 1 wt.% (1.42–2.35 wt.%). Fe_2O_3 contents are generally in the range of 0.03–0.08 wt.% for the two groups. A group of samples, mostly consisting of grey marbles, has relatively higher values, between 0.13% and 0.68 wt.%. Like TiO_2, MnO, Na_2O, K_2O, and P_2O_5 values are mostly below the detection limits in both groups of marble. A limited number of measurements could be made for both major element oxides (0.005–0.12 wt.% MnO; 0.023–0.04 wt.% Na_2O; 0.01–0.68 wt.% K_2O; 0.01–0.253 wt.% P_2O_5). Trace element values for both grey & white marble groups (Figure 7) are as follows: Sc 0.02–2.37 ppm & 0.01–4.32 ppm, V 0.01–40.91 ppm & 0.01–13.30 ppm, Co 0.06–0.58 ppm & 0.06–3.00 ppm, Ni 0.01–3.74 ppm & 0.17–2.54 ppm, Cs 0.01–1.57 ppm & 0.01–0.17 ppm, Rb 0.007–26.86 ppm & 0.004–0.36 ppm, Ba 3.60–287.69 ppm & 0.65–116.55 ppm, Sr 120.87–917.31 ppm & 86.02–176.613 ppm, Y 1.22–4.287 ppm & 3.008–18.90 ppm, Zr 0.07–10.52 ppm & 0.02–16.66 ppm and ΣREE 4.74–11.17 ppm & 19.37–44.20 ppm.

4.4. C-O-Sr isotope geochemistry

The $^{87}Sr/^{86}Sr$ isotope ratios of grey marble whole-rock samples are between 0.70830 (± 0.0000081) and 0.70874 (±0.0000059) while white marble samples values are between 0.70756 (±0.000058) and 0.70805 (±0.0000062). $\delta^{13}C$ and $\delta^{18}O$ isotopes were also measured in İznik marbles. The $\delta^{13}C$ isotopes were determined between 1.94 (± 0.08) and 2.93 (±0.08) ‰ (VPDB-Vienna Peedee Belemnite). The $\delta^{18}O$ isotopes also were determined between –4.85 (±0.10) and –7.53 (±0.10) ‰ (VPDB). All isotope geochemistry results are given in Table 2.

4.5. U-Pb calcite geochronology

U-Pb calcite dating was performed on two samples of grey marble (Deliktaş and OC-6 samples) and one sample of white marble (sample OC-10) in the İznik region. Measurements were made at a total of 43 points on the grey marble sample taken from the Deliktaş ancient marble quarry. When we plotted 39 of the 43 measured points on the Tera-Wasserburg diagram, a lower intercept age of 94.84 ± 1.41 Ma (MSWD: 4.9) was obtained from Deliktaş grey marble (Figure 8a). Measurements were made at a total of 53 points on the grey marble sample taken from the OC-6 ancient marble quarry. As a result of the measurements, lower intercept age of 88.03 ± 2.13 Ma (MSWD: 3.7) was obtained from the OC-6 sample (Figure 8b). In the white marble sample from the OC-10 ancient marble quarry, measurements were taken at a total of 35 points. Among these measurements, those from 28 points yielded a lower intercept age of 93.06 ± 8.55 Ma (MSWD: 1.6; Figure 8c).

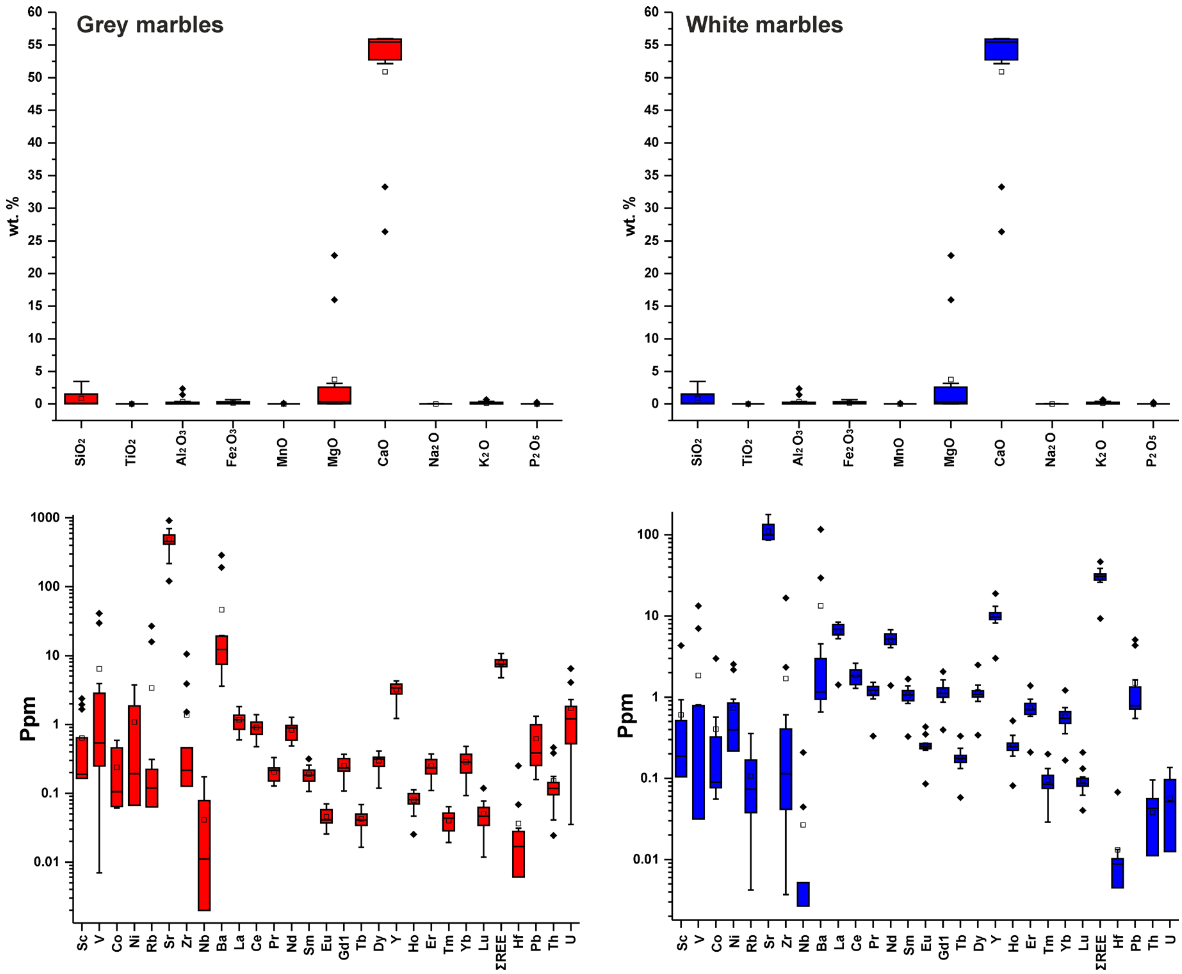

Figure 7. Box and whiskers plot for major oxides and trace elements of İznik marbles.

5. Discussion

5.1. Description of ancient white and grey marbles

Many white, white-grey and grey marbles around the Mediterranean provinces were exploited during ancient times, traded in wide areas, and has been used in many historical buildings and artefacts. Determining the sources of these marbles, which predominantly contain calcite and dolomite, and have similar lithological and petrographic features is more problematic than coloured marbles. Some of the white marbles commonly used in the Mediterranean province are; Proconesos, Docimium, Aphrodisias, Göktepe, Hasançavuşlar (Türkiye-Asia Minor), Carrara (Italy), Naxos, Paros, Thasos, Pentelicon, Hymettus (Greece). While most of the white marbles were used as columns, column capitals, covering and paving stones, some were used in the production of sculptures and other artefacts. Proconnesian marble was one of the most famous and widely used marbles of the ancient world. The quarries, which cover a very large area on the Marmara Island, are mostly located in the northern part of the island, proceeding from east to west, in Altıntaş, Saraylar Village, Çamlık and Mandıra localities and in the Silinte Harmantaş region (Asgari, 1973; Poretti, 2016). Another important source of marble in Türkiye is the quarries around Afyonkarahisar city. Marble quarries were exploited from the quarries near the İscehisar district (ancient Dokimeion or Docimium) and are still operated today (Yavuz Çelik and Sabah, 2008; Bağcı, 2020). Due to these features, they are similar to the white marbles of the İznik region. Other important white marble sources are Aphrodisian and Göktepe marbles. The city of Aphrodisias was close to marble quarries and workshops that produced low-cost sculptural and architectural marble elements (Monna and Pensabene, 1977). Both white and dark grey-black marbles are found in the Göktepe quarries. Göktepe white marble is a fine-grained white marble. It is located in Muğla Province, approximately 40 km southwest of Aphrodisias, and contains traces of ancient mining activities (incomplete works, inscriptions, buildings, ...) (Yavuz et al. (2009; Attanasio et al., 2015a; Brilli et al.,

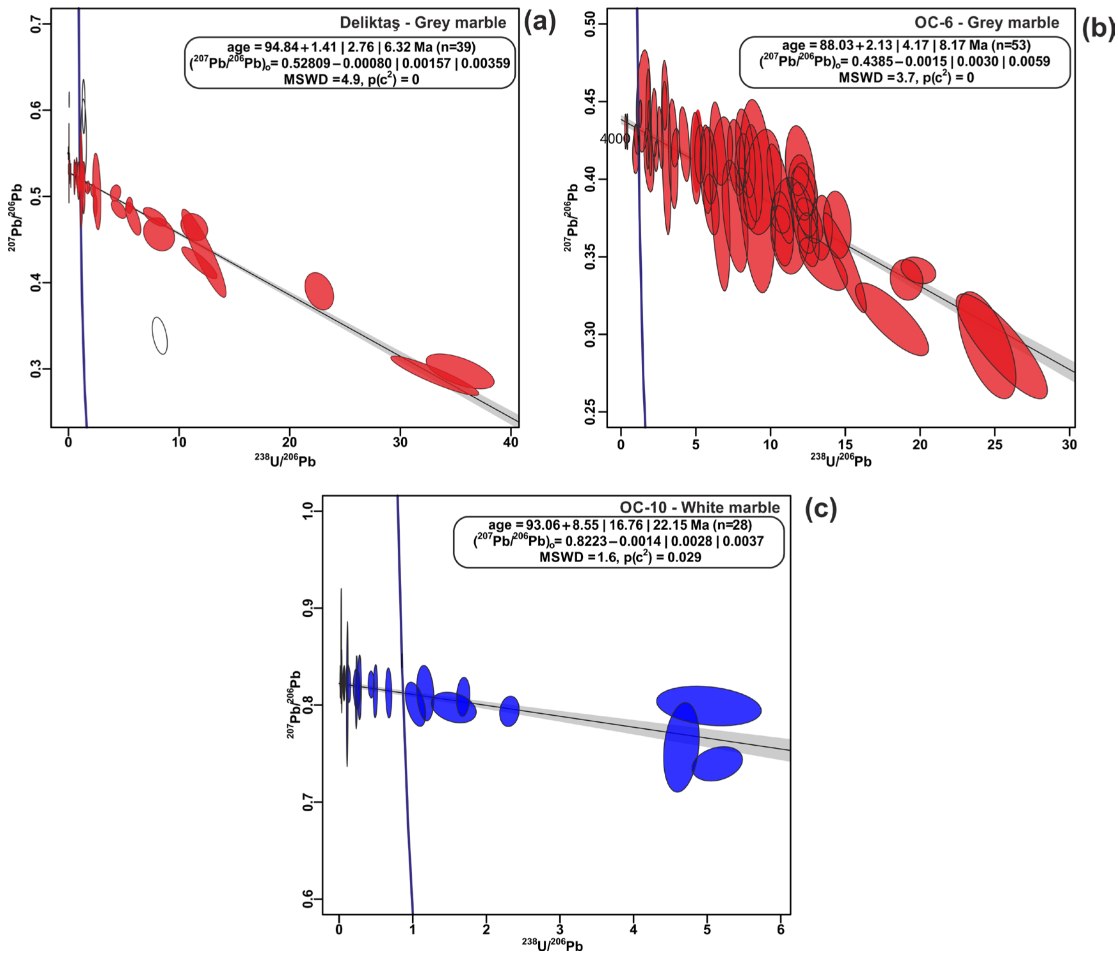

Figure 8. Tera-Wasserburg diagrams for the İznik marbles: a) Deliktaş grey marble, b) OC-6 grey marble, c) OC-10 white marble.

2018; Al-Bashaireh, 2021). Göktepe white marble is very similar to Carrara marbles in Italy in terms of crystal size and colour, and is a marble composed almost entirely of calcite minerals (Brilli et al., 2018; Wielgosz-Rondolino et al., 2020). Another marble that is not as white as the Göktepe white marbles but attracts attention with its grey spotted structure comes from the Hasançavuşlar (Muğla province) region. This marble, called Greco scritto, was produced from the quarries in and around Hasançavuşlar village near the ancient city of Ephesus (Attanasio et al., 2012).

One of the important white marbles is Carrara marble. Due to its white colour and high quality, it was used especially in sculpture from the 5th century BC onwards; later, in the middle of the 1st century BC, it was exploited by the Romans for use in sculpture and architectural elements, and reached the peak of its production, replacing the Greek marbles used in Rome during the reign of Trajan (Dolci and Nistri, 1980; Herz and Dean, 1986; Dolci, 1988; Attanasio et al., 2006; Al-Bashaireh, 2021). Many of the white marbles found within the borders of Greece today were used extensively throughout ancient times. Naxos marble is one of the oldest used of these marbles. Parian (Paros) marble is the most famous crystal white marble of classical times. It is extracted from different parts of Paros island. Snow-white pure dolomitic marbles of the Thassos region were one of the most important marble sources in ancient times. Bruno et al. (2002) divided Thasos marbles into two main groups: calcitic and dolomitic marbles. Poretti (2016) pointed out that both marble groups, in his studies on calcitic and dolomitic marbles, have heteroblastic and mosaic texture, and generally exhibit an isotropic structure characterized by a lineated and stressed microstructure. He also implied that the maximum grain size of calcitic marbles is 5 mm, while the grain size of dolomitic marbles varies between 0.9 mm and 1.5 mm. Since classical antiquity, the quarries at Mount Hymettus and Mount Pentelicon have been the primary source of Greece's white marble (Pike, 2009; Poretti, 2016). Poretti (2016) suggested that calcite crystals show saturated to embayed shapes, and that the polygonal texture representing equilibrium conditions has almost completely disappeared and the calcite mineral boundaries are very irregular. Hymetian marbles (quarries are located on Mount Hymettus, southeast of Athens) are bluish-grey, grey in colour, fine-grained and emit a sulphur odour when ground (Goette et al., 1999; Attanasio et al., 2006). The sulphur odour easily distinguishes these marbles from many other similar marble groups. Although İznik white marbles are similar to many white marbles used in ancient times in terms of mineralogical and textural properties, they are more similar to Docimium (Afyon honey) marble, one of the ancient marble groups mentioned above. Both marbles have a yellowish colour due to the hematite/limonite minerals, and have yellow spots and/or veins. With these features, they differ from other white marbles.

In ancient times, the use of grey marble was more limited than white marble. Although Proconessos-like white-grey banded marbles are common, the use of homogeneous grey marble is relatively less. The most famous grey marble of the ancient period is the marble known as "Bigio antico". According to Borghini (1997), the term "Bigio antico" is defined for medium- to coarse-grained grey marbles with different colour tones from light grey to almost black and mostly with mottled effects and fossil fragments. However, this definition also fits many varieties of bigio; Among these, "bigio antico", quarried near Moria on Lesbos Island, is thought to be the most important grey coloured marble used in ancient times, according to its macroscopic and archaeometric characteristics (Leka and Zachos 2015). This important marble on the island of Lesbos is a grey coloured fossiliferous limestone known as "Marmor Lesbium", "Bigio antico", "Marmor Batthium", "Battio" and Bigio lumachellato scuro". The term "Marmor Lesbium" appears quite frequently in archaeological literature. It generally includes Megalodon fossils (6 to 12 cm in diameter) and other microfossils (Crinoidea and Biomikrite, Bivalves and Corals) (Leka and Zachos, 2015). In their study, Attanasio et al. (2015b) investigated the problem of the origin of grey marble, and found that the grey marble used in most sculptures and architectural elements comes from Lesbos, Rhodos, Jebel Aziz, Jebel Oust, Göktepe, Mountanistika, Teos, Belevi and İznik. Yavuz et al. (2009) stated that most of the grey marble produced as a result of their work in the ancient buildings and ancient marble quarries around İznik may have been used in the region, but a significant amount of marble must have been exported.

As conclusion, it is difficult to say the origins of all these marbles without detailed archaeometric studies. Therefore, such studies have been carried out for the grey marbles of the İznik region, which are the main subject of this study, and a series of suggestions that may help distinguish them from other grey-coloured marbles are presented below.

5.2. Characterization for provenance analysis

There are many large and small ancient marble quarries in the İznik region. Both white and grey marbles were extracted from these marble quarries in ancient times (Yavuz et al., 2009). The largest marble quarries were generally set up for grey marble. The quarries developed from white marble were limited to smaller sizes compared to grey marble, as the marble is very fractured and cracked. There have been attempts to reoperate some ancient marble quarries today, but most of the quarries were abandoned after small excavations. Yavuz et al. (2009) announced the İznik region as a new Bigio antico marble area with their study. They described the quarries in the region in detail for the first time, considering that the solid grey marbles that formed the main structure of İznik's Roman Theater (ancient Nicea) might have been brought from a nearby area and in the light of the local information's. Maximum grain size measurements (MGS) values of İznik grey and white marbles are very close to each other. According to the maximum grain size measurements made on thin sections, grey marbles have maximum grain sizes between 0.3–3.1 mm, and white marbles have maximum grain sizes between 0.5–2.5 mm. When these values are compared with the MGS values of the marbles analysed by Antonelli and Lazzarini (2015), it is seen that they are similar to other ancient marbles around the Mediterranean (Figure 9), except for the coarse-grained Naxos marbles. But, it seems quite difficult to distinguish both grey and white marbles from other marbles using grain size values. According to Yavuz et al. (2009), İznik grey marble is a granoblastic textured, coarse-grained marble in colours ranging from grey to dark grey, heavily sprinkled with whitish spots and veins. They claimed that although it is texturally very similar to the Bigio Antico (Lesbos marble), which was widely used in ancient times, the most obvious difference is that there are no fossils in this marble. Although this feature distinguishes İznik grey marble only from Lesbos marbles, it is not valid for other bigio types.

EPR spectra of all five samples show six hyperfine structure lines that are characteristic of Mn^{2+}. Since Mn has an atomic number of 25, Mn^{2+} has an electronic configuration that ends up with 3d5 (Bulka et al., 1991; Weihe et al., 2009; Duliu et al., 2019). The five unpaired electrons of Mn^{2+} at its last orbital lead to a nuclear spin number of $I = 5/2$ and an electronic spin number of $S = 5/2$ (Bulka et al., 1991; Weihe et al., 2009; Duliu et al., 2019). When an external magnetic field is applied, six hyperfine transitions, which are $5/2 \leftrightarrow 3/2$, $3/2 \leftrightarrow 1/2$, $1/2 \leftrightarrow -1/2$, $-1/2 \leftrightarrow -3/2$, and $-3/2 \leftrightarrow -5/2$ will occur due to the Zeeman effect (Wildeman, 1970; Bulka et al., 1991; Weihe et al., 2009; Duliu et al., 2019). The EPR spectra of all these marbles present dominant as well as sharp Mn^{2+} peaks and it can be concluded that the concentration of the Mn^{2+} is lower than 1% (Fujiwara, 1964). This situation is also compatible with geochemical analyses. Mn contents in both grey marbles and white marbles are <1 wt.%. The EPR spectra of all these marbles present dominant as well as sharp Mn^{2+} peaks. Although the XRD results indicate that the grey marbles, which are Deliktaş, OC-1, and OC-6, have a small amount of dolomites and quartz, there is no clear signal showing the existence of dolomites as given in other works (Weihe et al., 2009; Covaci and Duliu, 2013).

Geochemical analyses and isotope geochemistry data also make an important contribution to determining the source areas of marbles. However, today there is no marble geochemistry analysis database that will allow comparison of all marble types. Using the limited geochemistry data in the literature, we made a comparison between the Fe, Mg, Mn, and Sr values of İznik, Göktepe, and Carrara marbles (Figure 10). Although the Fe contents of İznik grey and white marbles are in similar ranges to Carrara marbles, the Fe contents of Göktepe marbles, which consist of very pure calcite crystals, are quite low. While Mg and Mn contents are in a wide range in İznik grey marbles, they are in a narrower range in white marbles. However, in Göktepe marbles, both Mg and Mn are in an almost very narrow range. The relatively more abundant Mn and Mg content in Carrara marbles is noteworthy. İznik grey marbles have the highest Sr content compared to the other four marbles (İznik white, Carrara and Göktepe 2&3–4). İznik white and Carrara marbles have low Sr values. Göktepe marbles are represented by an Sr value, which is the average of two marble groups.

REE+Y spider plots (Figures 11a, 11b) normalized to chondrite and Post-Archaean Australian Shale (PAAS: Taylor and McLennan 1985). provide important clues in

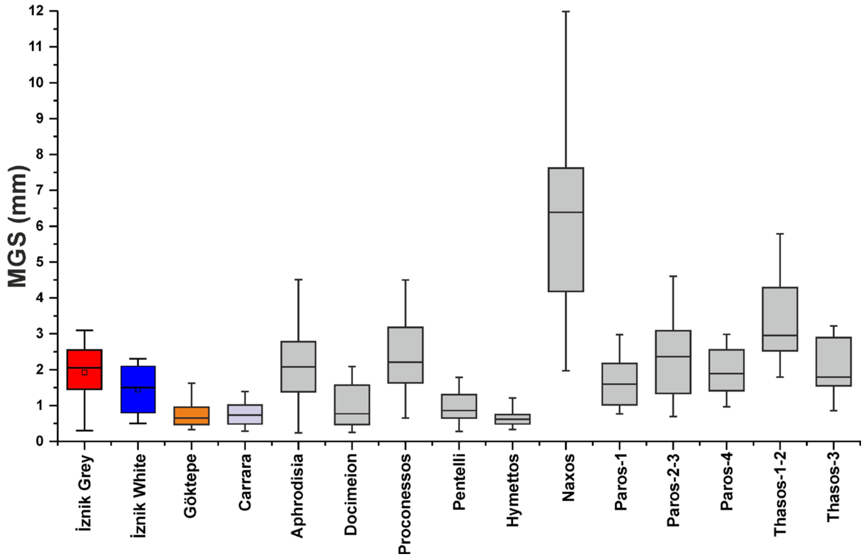

Figure 9. Comparison of MGS values recommended by Antonelli and Lazzarini (2015) for İznik marbles (this study) with Mediterranean marbles (values taken from Poretti, 2016).

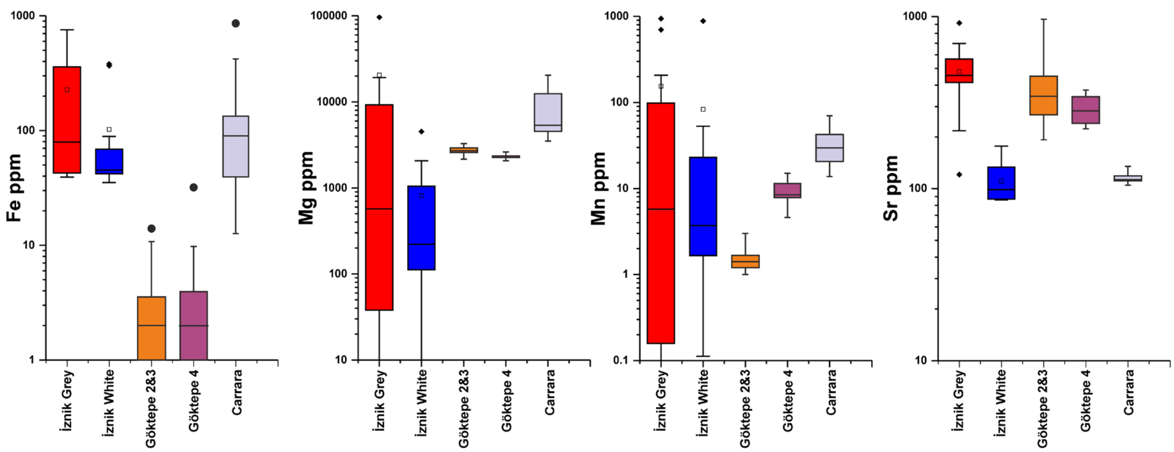

Figure 10. Box and whisker diagrams showing the comparison of Fe, Mg, Mn and Sr contents of İznik marbles with Göktepe and Carrara marbles (Göktepe and Carrara data are from Wielgosz-Rondolino et al., 2020).

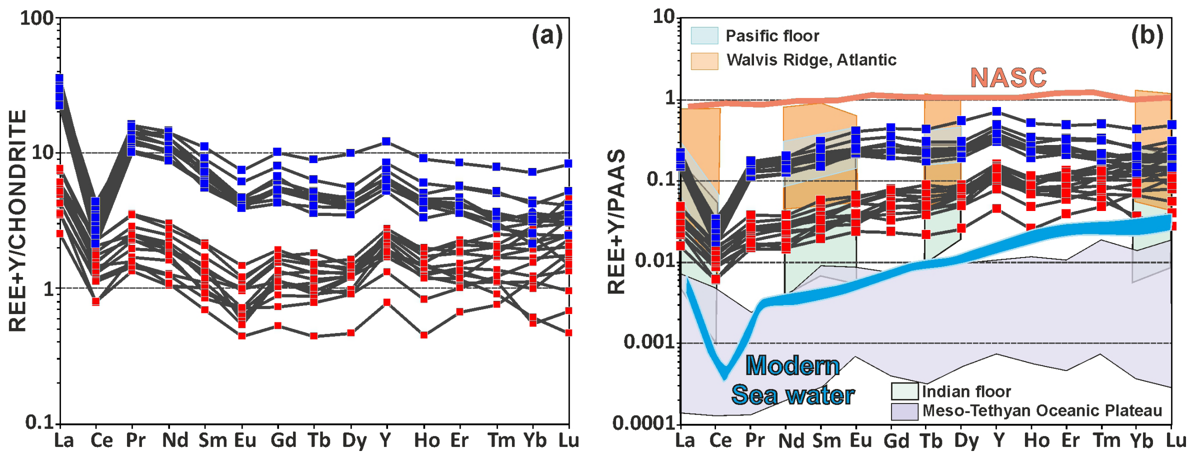

Figure 11. a) REE+Y concentrations of İznik marbles normalized to chondrite (Sun and McDonough, 1989). b) REE+Y diagrams for İznik marbles normalized to PAAS (Taylor and McLennan,1985). Other data sources: Pacific Ocean floor–Liu et al., 1988; Indian Ocean floor–Liu and Schmitt, 1990; Walvis Ridge–Liu and Schmitt, 1984; Meso-Tethyan ocean plateau-Zhang et al., 2017; Modern Sea water- Zhang and Nozaki,1996; NASC- Gromet et al., 1984.

distinguishing between limestones deposited in different geological environments. REE+Y patterns are a widely used technique to understand the environments in which carbonate rocks were deposited. Because the REE+Y counter pattern of modern seawater is similar to the pattern of carbonates. In the PAAS-normalized REE+Y diagram, it is seen that both grey and white marbles present a similar pattern to the modern sea and are located between modern sea water and North American Shale Composite (NASC) values (Gromet et al., 1984). Moreover, it is seen that the REE+Y contents of grey marbles are almost ten times richer than white marbles. In these diagrams, HREE enrichment and positive La and negative Ce anomalies are clearly observed. This type of REE pattern typically resembles the seawater REE pattern (e.g., De Baar et al., 1991; Bau and Dulski, 1996). This suggests that scavenging from seawater is a dominant mechanism in the recovery of limestone REE from open ocean environments (Zhang et al., 2017). According to Shields and Webb (2004), a small fraction of these have slight MREE enrichment, which can be attributed to the preferential adsorption of LREEs and HREEs to Mn- and Fe-oxyhydroxides. However, a distinct Y positive anomaly is observed, which is a result of the clastic material coming into the environment. It is also clear that REE+Y values are compatible with Indian floor, Pacific floor and Walvis ridge (Atlantic). The Rb - Sr -Ba triangular diagram (Figure 12) is a useful tool to distinguish inland freshwater limestones, continental margin limestones, and open ocean limestones (Zhang et al., 2017). In this diagram, it can be seen that İznik marbles are mostly traced to the open ocean environment, and very few examples are located in the inner environment and marginal areas.

The Sr isotope values of İznik marbles are between 0.70830 (±0.0000081) and 0.70874 (±0.0000059), and the values of white marble samples are between 0.70756 (±0.000058) and 0.70805 (±0.0000062). A comparison of the Sr isotope values of İznik marbles (Figure 13) with other marbles known in the Mediterranean region (Barbin et al., 1992; Brilli et al., 2005; Wielgosz-Rondolino et al., 2020) shows that grey marbles have a higher $^{87}Sr/^{86}Sr$ isotope ratio than all other marbles. On the other hand, white marbles have $^{87}Sr/^{86}Sr$ values in similar ranges as Carrara, Thasos, Naxos, Aphrodisias, and Proconessos marbles. This difference between the white and grey marbles of the İznik region is probably due to the detrital materials in the grey marbles.

The $\delta^{13}C$ and the $\delta^{18}O$ isotope values of İznik marbles are 1.94 (±0.08) –2.93 (± 0.08), and – –4.85 (±0.10)– –7.53 (±0.10) ‰ (VPDB), respectively. These values are close to the typical values of marine limestones. When we compare the C-O isotope values of İznik marbles with other well-known marble types from the Mediterranean region, we see that there is no significant difference (Figure 14). When İznik marbles are compared to other carbonate marbles, both Sr and C-O isotopes do not present a very clear distinction. In this study, U-Pb calcite ages were obtained from İznik marbles for the first time. U-Pb calcite ages of 94.84 ± 1.41 Ma (MSWD: 4.9) and 88.03 ± 2.13 Ma (MSWD: 3.7) were obtained from grey marbles, and 93.06 ± 8.55 Ma (MSWD: 1.6) from white marbles. These ages represent the crystallization ages of calcite minerals and probably correspond to the metamorphism that formed marbles. These ages are between 94.84 ± 1.41 Ma and 88.03 ± 2.13 Ma, and correspond to the Upper Cretaceous (Cenomanian-Coniacian) period. Özer (2018)

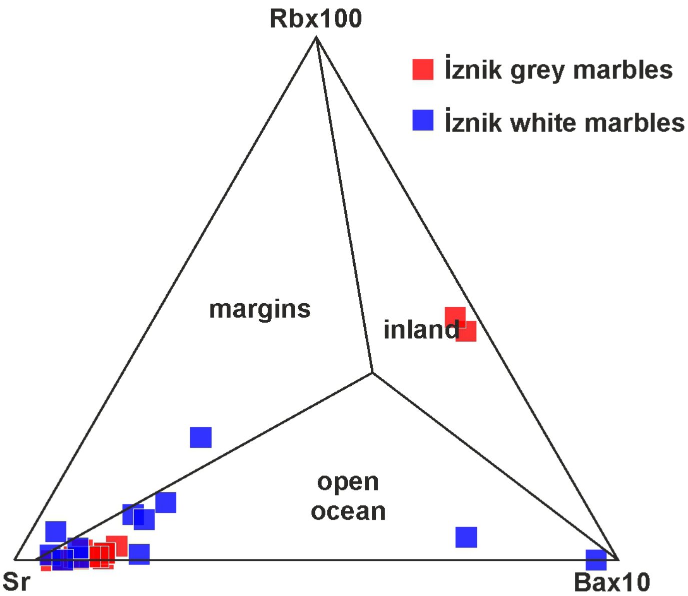

Figure 12. Rb–Sr–Ba triangular diagram of limestones deposited in various depositional environments (Zhang et al., 2017).

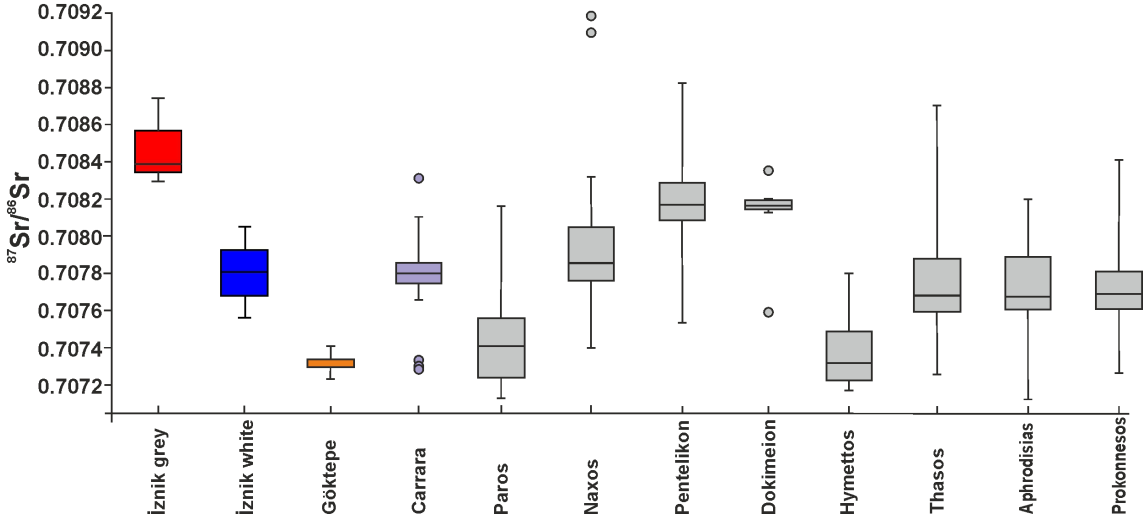

Figure 13. $^{87}Sr/^{86}Sr$ isotope diagrams for İznik grey and white marbles (this study), and other well-known marbles from the Mediterranean region (Brilli et al., 2005; Barbin et al., 1992; Wielgosz-Rondolino et al., 2020).

detected recrystallized limestones containing rudist fossils alternating three or four times in the upper parts of the 900 m thick dolomitic and recrystallized limestones that unconformably overlie the Late Triassic metasediments in Aluç Plateau (Elmalı village), northeast of İznik. He said that the rudists were in their original living position and formed a biostrome with a thickness of 3–5 m. Moreover, in the Rudist fauna, *auvagesia sharpei, Sauvagesia sp., Bournonia africana, Durania arnaudi, Radiolites aff. trigeri, Radiolites sp. ve Hippurites aff. nabresinensis* species indicating the middle-late Turonian, and emphasized that these levels contained very poorly preserved foraminifera. The fact that both fossil and U-Pb calcite ages indicate the same period will allow a clearer understanding of the formation ages of marbles, which are thought to be older.

6. Conclusion

In the ancient buildings of İznik, marble extracted from the surrounding marble quarries was used in the construction of the walls and gates. In the east of İznik, around the

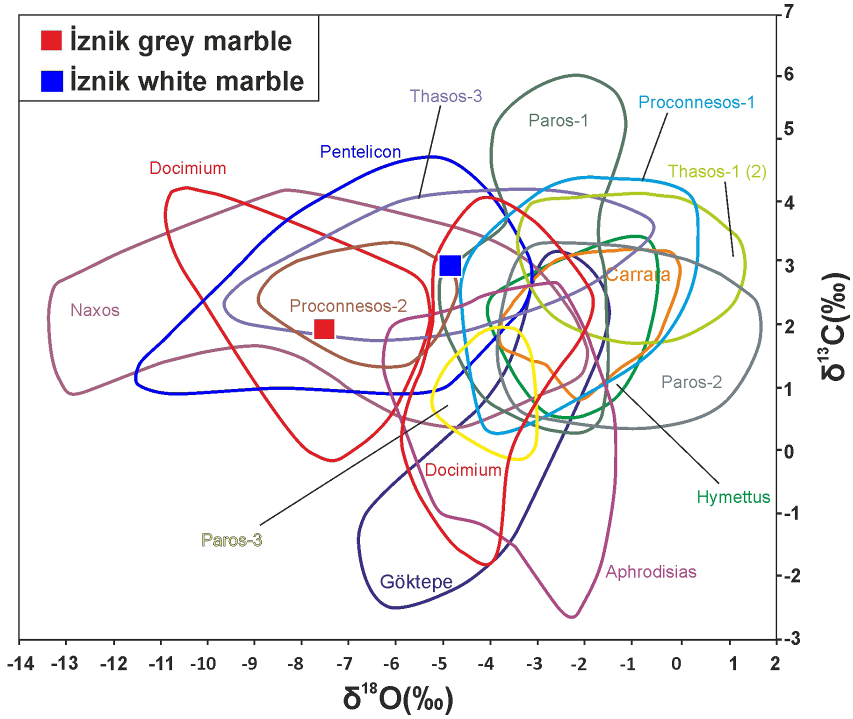

Figure 14. Stable C and O isotope diagrams for İznik marbles and comparison with well-known marbles of the Mediterranean region (after Antonelli and Lazzarini, 2015; modified by Al-Bashaireh, 2021).

Ömerli and İnikli villages, and the Deliktas and Saritas hills, approximately twenty marble quarries have been identified where grey and white marbles were produced.

The main mineral is calcite for both marble groups. White marbles also contain hematite-limonite staining locally while grey marbles have a small amount of dolomite and quartz according to XRD patterns. Both groups have granoblastic and heteroblastic textures. Maximum grain size values (MGS) of İznik white and grey marbles are very close to each other (between 0.5–2.5 mm and 0.3–3.1 mm respectively).

CaO content is generally above 50 wt.% (52.13–55–99 wt.%) in both groups of marble, while SiO_2 contents are generally in the range of 0.03–0.3 wt.%. The Fe contents of İznik grey and white marbles in the range of 0.02–0.47 wt.%. While Mg and Mn contents are in a wide range in İznik grey marbles (0.02–13.72; 0.01–0.09 ppm respectively), they are in a narrower range in white marbles (0.01–0.45; 0.01–0.09 ppm respectively). The EPR spectra of all these marbles present dominant as well as sharp Mn^{2+} peaks.

REE pattern of the two group of İznik marbles suggests that scavenging from seawater is a dominant mechanism in the recovery of limestone from open ocean environments. The other geochemical characteristics of the marbles of İznik are also mostly indicated to the open ocean environment.

While grey marbles have high $^{87}Sr/^{86}Sr$ isotope ratios between 0.70830 and 0.70874, white marbles have $^{87}Sr/^{86}Sr$ isotope ratios between 0.70756 ± 0.70805.

The $\delta^{13}C$ isotopes were determined between 1.94 and 2.93, while the $\delta^{18}O$ isotopes also were determined between –4.85 and –7.53.

U-Pb calcite ages of 94.84 ± 1.41 Ma (MSWD: 4.9) and 88.03 ± 2.13 Ma (MSWD: 3.7) were obtained from grey marbles, and 93.06 ± 8.55 Ma (MSWD: 1.6) from white marbles. These ages correspond to the Upper Cretaceous (Cenomanian-Coniacian) period.

All geochemical, petrographic, and geochronological data obtained during this study aimed to correlate the data which is collected from different marbles from Mediterranean provinces (both cities and quarries). However, it still needs to be conducted, especially on geochemistry from different localities, to compare the present data.

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Supplementary material

Supplementary material is available at the following link: https://aperta.ulakbim.gov.tr/record/286095