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Key Points:

- We studied the geochemistry of fluid inclusions in travertine deposits from Pamukkale and Resadiye areas (Turkey).
- Concentrations of Ne-Ar and O2+N2 indicate that travertines from both areas precipitated from atmosphere-derived fluids
- The ³He/⁴He values indicate that Resadive travertines formed at shallow depth, while Pamukkale in an active system of lithospheric fractures

Supporting Information:

- Supporting Information S1
- Table S1
- Table S2

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Geochemistry of Fluid Inclusions in Travertines From Western and Northern Turkey: Inferences on the **Role of Active Faults in Fluids Circulation**

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Abstract The understanding of the relationship between the geochemistry of fluids circulating during travertine deposition and the presence of active faults is crucial for evaluating the seismogenetic potential of an area. Here we investigate travertines from Pamukkale and Resadiye (Turkey), sited in seismic regions and next to thermal springs. These travertines formed ~24,500-50,000 (Pamukkale) and ~240-14,600 years (Resadive) BP. We characterize fluid inclusions (FIs) and studied concentration of H_2O , CO_2 , $O_2 + N_2$, and ³He, ⁴He, ²⁰Ne, and ⁴⁰Ar, and bulk composition (trace elements and $\delta^{13}C-\delta^{18}O$). FIs from both localities are mainly primary with low salinity and homogenization temperature around 136-140 °C. H₂O is the major component followed by CO₂, with the highest gas content measured in Pamukkale travertines. Concentrations of Ne-Ar together with $O_2 + N_2$ indicate that travertines from both areas precipitated from atmosphere-derived fluids. The ³He/⁴He is 0.5–1.3 Ra in Pamukkale and 0.9–4.4 Ra in Reşadiye. Samples with R/Ra > 1 are modified by cosmogenic ³He addition during exposure to cosmic rays. Excluding these data, FIs of Resadiye are mostly atmosphere-derived. This implies a shallow formation where the circulation was dominated by meteoric waters, which is consistent with their young age. Instead, FIs of Pamukkale show mixing of mantle-, crustal-, and atmosphere-derived He, indicating that these travertines formed in lithospheric fractures. Based on the $\delta^{13}C_{CO2}$ and $\delta^{18}O$ of bulk rocks, we infer that travertines formed involving crustal- (mechanochemical rather than organic) and mantle-derived CO₂. Trace elements of Pamukkale and Resadiye show comparable rare earth element patterns. We conclude that travertines formed in response of seismogenetic activity.

1. Introduction

The tectonic setting of Turkey resulted in a prolonged seismic activity as testified by the occurrence of several catastrophic earthquakes lasting up to the present time (e.g., Barka, 1996, 1999; Koçyiğit et al., 1999; Güleç et al., 2002; Aydın et al., 2015). This high seismicity is related to the complex geodynamics governed by the collision between the Eurasian Plate and both the African and Arabian Plates (Sengör & Yılmaz, 1981). Most of the country lies on the Anatolian Plate, a small plate bounded by two major strike-slip faults: the North Anatolian Fault Zone (NAFZ) and East Anatolian Fault Zone (EAFZ). The western part of Turkey is also affected by the extensional tectonics in the Aegean Sea (Aegean Graben System) caused by the southward migration of the Hellenic volcanic arc.

Faults are important pathways for fluid circulation within the crust and upwelling of hydrothermal or mantle fluids (Alçiçek et al., 2013; Brogi, 2004; Brogi & Capezzuoli, 2009; Faccenna et al., 2008; Hilton, 2007; Smeraglia et al., 2018; Uysal et al., 2007); contrastingly, they can locally act as impermeable barriers (e.g., Person, 2007). Faults opening can be triggered by earthquakes, fluid overpressures, or localized dissolution (Gratier & Gueydan, 2007). Due to the fluids circulation and carbonate dissolution, the deposition of travertines may occur along faults and fissures that are seismically controlled rather than the near surface hydrologic regime (Faccenna et al., 2008; Özkul et al., 2013; Erol et al., 2015 and references therein; Smeraglia et al., 2018) or in hydrothermal conditions linked to primary sulfide ores (Slowakiewicz, 2003). Thus,

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Figure 1. (a) Simplified neotectonic map of Turkey showing Pamukkale and Reşadiye districts. (NAFZ: North Anatolian Fault Zone, EAFZ: East Anatolian Fault Zone, GG: Gediz Graben, BG: Büyük Menderes Graben). (b) Simplified geologic map of Çukurbağ Fissure Ridge (modified from Brogi et al., 2014, Altunel & Hancock, 1993).

travertine deposits have the potential to directly record information regarding fluid composition and the permeability of fracture networks during or after the seismic activity (Verhaert et al., 2003, 2004).

During the deposition processes, travertines often trap fluids as inclusions spread inside the solid matter. Investigation of chemical and isotopic compositions of fluids may yield significant information on their origin as well as on hydrodynamic conditions that controlled the deposition process (e.g., Pik & Marty, 2009, and references therein; Kele et al., 2011; Smeraglia et al., 2018). This type of survey becomes even more important when hydrothermal travertines (hereafter travertines) form in areas where tectonic activity is still active and may produce catastrophic earthquakes, such as in Turkey. In particular, fluid inclusions (FIs) may provide information on the presence of mantle-derived fluids that reached the surface making a proof of possible relationship between tectonics and circulating fluids over the faulted zones. In addition, they can add data on the existence of deep-rooted, lithospheric faults, which are able to drive mantle-derived fluids toward the surface (Batista Cruz et al., 2019; Caracausi et al., 2005; Hilton, 2007; Kennedy et al., 1997; Kulongoski et al., 2005; Marty et al., 1992; O'Nions & Oxburgh, 1988; Pik & Marty, 2009; Smeraglia et al., 2018).

This paper accounts for the studies carried out on selected travertine rocks from two key areas in western and northern Turkey: Çermik-Reşadiye (hereafter Reşadiye), located in the central part of NAFZ, and Çukurbağ-Pamukkale (hereafter Pamukkale), sited at the westernmost part of Turkey, close to the Aegean Graben System and next to Gediz graben and Büyük Menderes graben (Figure 1). The collected samples underwent multidisciplinary analyses on both the solid rock and FIs aimed to constrain the type of inclusions and their homogenization temperatures as well as the H₂O, CO₂, and O₂ + N₂ contents, and the elemental and isotope compositions of noble gas (He, ²⁰Ne, and ⁴⁰Ar) in FIs. Selected grains of bulk travertine were also analyzed for δ^{13} C and δ^{18} O of bulk calcite, which is the dominant component of these rocks. Our target is to establish the composition of fluids circulating at the time of travertine deposition, evaluate the relationship with fluids emitted in neighboring springs and local tectonic setting, and, finally, discuss the seismogenetic activity of faults where travertines formed.





Figure 2. (a) Relief map showing general extension of 1939 Erzincan earthquake-rupture (redline) and location of Reşadiye and (b) geologic map of the Reşadiye and surrounding region (modified from Usgu, 1997).

2. Geo-Tectonic Setting and Samples Location

The ongoing convergence between the Arabian and Anatolian plates exerts a major control on the recent tectonic activity in Turkey, which is marked by four major fault zones: Bitlis Suture Zone, NAFZ, EAFZ, and Aegean Graben System (Figure 1). The Bitlis Suture Zone was formed in the middle Miocene by the collision of the Eurasian plate with the Arabian plate that consumed the Neo-Tethyan oceanic crust (Şengör & Yılmaz, 1981). Because of this collision, the Anatolian plate underwent a nearly westward tectonic escape along two major strike-slip faults—right-lateral NAFZ and left-lateral EAFZ—that resulted in occurrence of numerous historical and recent earthquakes. A number of E-W trending graben systems (Dewey & Şengör, 1979) represent the western Anatolia where compressional tectonics changed to extensional regime.

The Pamukkale area is located in the northern section of Denizli basin, which is a part of the Aegean Graben System (Figure 1). The basin, bounded by NW-SE trending active normal faults in its north and south peripherals, is represented by a high extension rate up to about 25 mm/year (Reilinger et al., 2006). The pre-Oligocene metamorphic rocks of Menderes massif (e.g., gneiss, mica schist, and marble) comprise the basement in Denizli basin (Koçyiğit, 2005; Okay, 1989). They are unconformably overlain by the continental clastic rocks of Miocene to Plio-Quaternary age. Not only the historical to recent seismic events but also recently precipitating travertine deposits (Altunel & Hancock, 1993) manifest the active tectonism in the basin.

The Reşadiye area is located on the Kelkit segment of NAFZ in northern Turkey (Figure 2). The ophiolitic mélange of Upper Cretaceous age, so called the Sakarya Unit, consisting of serpentines and deep marine limestones interlayered with shale and lava is the major basement lithology in the area. Eocene sandstone-shale-conglomerate unit and Pliocene conglomerate-sandstone (Herece & Akay, 2003) represent the terrestrial clastics. In Reşadiye area, the fault zone attains a width of about 10 km and marks the bound-ary between the Sakarya Unit and the Eocene sandstone-shale (Uysal et al., 2006). The recent seismic activity of NAFZ at Reşadiye is shown by a fissure-ridge travertine of about 1-km long extending in NW-SE direction (Figure 3).



Figure 3. (a) General view of Reşadiye fissure-ridge travertine (looking to NW), (b) location of the samples collected along the travertine site, (c) southeastern part of fracture (looking to SE), and (d) central part of fracture (looking to NNW).

3. Samples and Methods

3.1. Samples Description and Location

The Pamukkale travertine is an E-W trending fissure-ridge travertine with length of 360 m and width of 30 m (Figure 1). Samples were collected along the main fracture from two separate banded travertine bodies that are close to each other (Figure 4). The band thickness varies from a few centimeters to 10 cm (Figures 4a–4g). Travertine samples were collected either by microdriller or by hammer (2 to 3-cm-long prisms; Figure 4d). The samples were generally taken from bottom and top (wall to vein) to gather subsamples (either in the form of powder or chip) to prevent or limit exposure to cosmic rays.

Reşadiye travertine occurs in the Kelkit segment of NAFZ (Figure 2). The NW-SE extending travertine having a length of about 1 km occurs in a well-developed fracture system that hosts carbonate veins recently precipitating from thermal waters (Figures 3 and 5). Samples from Reşadiye were taken only by hammer. A special attention was given to collect detritus-free, porous, moderately crystalline parts of travertines samples.



Figure 4. (a) General view of Çukurbağ fissure-ridge travertine (looking to NW). (b) Roman quarry showing the internal structure of travertine (looking to east), (c) general view of fracture (looking to east), (d) sampling with microdriller, (e) location of samples ÇB8-ÇB11, and (f, g) location of samples ÇB1-ÇB6 on the roman quarry wall and zoom of ÇB5 and ÇB6.

The 17 samples suite is composed of 11 samples from the Pamukkale region (Ç-marked samples: ÇB1, ÇB2, ÇB3, ÇB4, ÇB5, ÇB6, ÇB8, ÇB9, ÇB10, ÇB11, and ÇB12; Figures 1 and 4), and six samples from the Reşadiye region (R-marked samples: RS1A, RS1B, RS1C, RS2, RS3, and RS6; Figures 1–3 and 5).

3.2. Analytical Techniques

3.2.1. Petrographic and FIs Analysis

Polished thin sections of Pamukkale and Reşadiye travertine samples were prepared for mineralogical, petrographic, and FIs analyses at the laboratories of Earth Sciences Application and Research Centre of the Ankara University. FIs analysis was carried out using Linkam THMSG-600 model freezing-heating stage installed on a Leica DM 2500M polarizing microscope. The stage with a temperature range of -196 °C to 600 °C was calibrated with pure synthetic H₂O and H₂O-NaCl synthetic fluid inclusion standards. FIs assemblages were described using procedures given in Roedder (1984). Five doubly polished wafers were used for the determinations. During the measurement, all the inclusions were homogenized into liquid phase and no boiling was detected.

3.2.2. Chemistry and Noble Gas Isotopes of FIs

Travertine samples were prepared and analyzed for the chemical and noble gas isotope composition in the laboratories of Istituto Nazionale di Geofisica e Vulcanologia (INGV), Sezione di Palermo (Italy).

In detail, we determined the H₂O, CO₂, and atmospheric content (N₂ + O₂ + Ar) as well as the elemental and isotope composition of noble gas (He, Ne, and Ar) in FIs. Selected grains of bulk travertine were also analyzed for δ^{13} C and δ^{18} O on calcite, which is the dominant component of these rocks. All but two the solid



Figure 5. Field views of the sampling locations along the Reşadiye fissure-ridge travertine and representative photos of the investigated veins with sample labels. (For field locations see Figure 4.)

samples (Pamukkale, ÇB5 and ÇB6; Figure 4) show homogeneous characteristics at a visual analysis. The samples ÇB5 and ÇB6 were split into two portions (ÇB5-A, ÇB5-B, ÇB6-A, and ÇB6-B) and then prepared and analyzed in the same way as the others.

 H_2O and CO_2 in FIs were extracted by single-step crushing and quantified in terms of mol/g following the protocol described in Gennaro et al. (2017) and Rizzo et al. (2018). These major gas species retained in FIs provide an important contribution for the understanding of the type of circulating fluids during the rock formation, irrespective of the origin of minerals where FIs are trapped. Part of the travertine samples was gently broken and sieved by a >1-mm mesh. The portion of the selected sample material was weighed in an analytical balance and then loaded into a stainless steel tube (with internal diameter of about 1 and 10 cm in length). The amount of material loaded for each analysis varies from a minimum of 0.2 g to a maximum of 1 g, approximately.

In order to define the elemental and isotope composition of 3 He, 4 He, 20 Ne, and 40 Ar as well as the atmospheric content $(N_2 + O_2 + Ar)$ in the FIs hosted in the travertines, the samples were carefully fragmented in order to select the most homogeneous part, thus handpicked under a binocular microscope from the >1mm sieved fraction. The selected crystals were cleaned in an ultrasonic bath following internal protocol (e.g., Rizzo et al., 2015, 2018), and then each group of samples (0.2-5.2 g) was placed inside a stainless steel crusher capable of loading up to six samples simultaneously. FIs were released by in-vacuum single-step crushing at maximum 200 bars. This procedure is the most conservative in order to minimize possible contribution of cosmogenic ³He and radiogenic ⁴He grown/trapped in the crystal lattice (e.g., Hilton et al., 1993, 2002; Kurz, 1986). The atmospheric component was separated and quantified via a manometer at the time of crushing by the following steps: immediately after crushing, we read the total gas pressure $(N_2 + O_2 + O_2)$ $H_2O + CO_2 + noble gas$). Then, $N_2 + O_2 + noble gas were separated from the <math>H_2O + CO_2$ by using a cold finger immersed in liquid nitrogen (T = -196 °C) that allows to freeze H₂O and CO₂; after this step, we checked again the total pressure for quantifying the atmospheric component. Noble gas were separated from H_2O and CO_2 and were further cleaned in an ultrahigh vacuum ($10^{-9}-10^{-10}$ mbar) purification line. All the species of the gas mixture except noble gases were removed under Zr-Al getters and a cold finger filled with charcoal and put under liquid nitrogen. Helium (³He and ⁴He) and neon (²⁰Ne) isotopes were separated under a cryogenic trap initially cooled at ~8°K and then raised to ~41 and ~75°K to release He and Ne,

respectively. He and Ne were measured in two different split-flight-tube mass spectrometers (Helix SFT-Thermo). The values of ³He/⁴He ratio are expressed as R/Ra (where Ra is the ³He/⁴He ratio of air, which is equal to $1.39 \cdot 10^{-6}$; Mamyrin et al., 1970). The analytical uncertainty (1 σ) of the He isotopic ratio is between 1.5% and 15% and that of ²⁰Ne is <0.4%. ²⁰Ne was corrected for isobaric interference at *m*/*z* 20 (⁴⁰Ar²⁺) in accordance with INGV-Palermo analytical protocol (e.g., Rizzo et al., 2018). ⁴⁰Ar was analyzed by a multicollector mass spectrometer (GVI Argus), with an analytical uncertainty (1 σ) generally <0.4%. The uncertainty in the determinations of He, Ne, and Ar elemental contents was less than 1% excluding natural variability and the assumption on residual (not crushed) crystals. A prepurified air standard subdivided in tanks was used for He, Ne, and Ar elemental and isotopic recalculations. The analytical reproducibility of ⁴He, ³He/⁴He, ²⁰Ne, and ⁴⁰Ar of standards were < 2.4%, <2.6%, <1.4%, and < 2.4%, respectively. These values represent the standard deviation of measurements made during >1 year of analyses for He and Ne and 4 years for Ar, in the same setting conditions. Typical blanks for He, Ne, and Ar were < 10⁻¹⁵, <10⁻¹⁵, and <10⁻¹³ mol, respectively. Further details about the sample preparation and analytical procedures are available in Rizzo et al. (2015, 2018) and Correale et al. (2019).

3.2.3. Oxygen and Carbon Isotopes of Bulk Rocks

Oxygen and carbon isotope analyses of carbonate samples were carried out at INGV-Palermo and Environmental Isotope Laboratory of the University of Arizona. Briefly, about 0.1 mg of powder samples was put in a 12 mL screw cap Exetainer^(R) vial and then flushed with pure helium to remove the air in the headspace. Then, about 50 μ L of 100% H₃PO₄ was added to each sample for the conversion to carbon dioxide. The analyses were performed using a Thermo GB-II peripheral coupled with a Thermo Delta V Plus continuous flow isotope ratio mass spectrometer at INGV-Palermo and 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. The results are reported in delta per mil (‰) values relative to the Vienna Pee Dee Belemnite (V-PDB) international scale. The δ^{18} O values on the V-PDB scale are converted to the Vienna Standard Mean Ocean Water (V-SMOW) using the equation of Coplen et al. (1983): $\delta^{18}O_{VSMOW} = 1.03091^* \delta^{18}O_{VPDB} + 30.91$. The δ^{18} O is expressed in delta per mil (‰) relative to the VSMOW value. A Carrara Marble internal standard (MAB) and two international standards (NBS-18 and NBS-19) were used for calibration. Analytical reproducibility was better than 0.1‰ and 0.15‰ for δ^{13} C and δ^{18} O, respectively (1 σ).

3.2.4. Trace Element Analyses

Trace element analyses of travertine samples were carried out on a Thermo X-series II inductively coupled plasma mass spectrometry at the Radiogenic Isotope Laboratory of the University of Queensland with instrument conditions as described in detail in Saha et al. (2019). Briefly, carbonates were dissolved in a 2% nitric acid solution embedded with internal standards. The raw data were adjusted for the low, detectable blank, internal and external drift, and for oxides and doubly charged species. Instrument response was calibrated against two independent digests of the United States Geological Survey reference W-2 and confirmed by analysis of other reference materials. Corrections were applied for oxides using formation rates determined from pure single element rare earth element (REE) standards. The precision of the trace element measurements was evaluated by the relative standard deviation (RSD), which is the percentage of the standard deviation from the mean concentration of four measurements for each sample. The percent of RSD values are shown in Table 1. High RSD values (>15, except for Y) are due to very low REE concentration in the samples, and hence, the determination is performed close to the detection limit.

4. Results

4.1. Travertine Mineralogy

Pamukkale fissure-ridge travertines were sampled systematically from central fracture to banded vein parts (Figures 1 and 4). The collected samples were investigated by optical microscopy and X-ray diffraction analyses (17 samples). According to the collected results, veins consist of coarse-grained calcite and aragonite. In detail, four samples (ÇB-1, ÇB-2, ÇB-3, and ÇB-7) are only composed by calcite, whereas the remaining samples contain both calcite and aragonite. Aragonite is the dominant phase only in one sample (CB-4).

Reşadiye fissure-ridge travertines were sampled along the fracture in a way similar to the Pamukkale travertine (Figures 2 and 3). Therefore, porous, detrital, and organic-rich travertines were avoided focusing the



Table 1

Rare Earth Element + Y Contents (in ppb) of Pamukkale and Reşadiye Travertine Samples and Various Host Rocks (in ppm) in Pamukkale (Möller et al., 2004) and Fault Gouges (in ppm) in Reşadiye (Uysal et al., 2006)

Location	Sample No.	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Y	Er	Tm	Yb	Lu
Pamukkale	ÇB-1	1.72	1.95	0.23	0.62	0.05	0.32	-0.01	0.01	0.03	0.00	3.37	0.00	0.01	0.06	0.01
	ÇB-2	2.28	2.81	0.29	0.69	0.38	0.18	0.04	0.01	0.13	0.04	14.07	0.21	0.03	0.08	0.02
	ÇB-3	2.51	4.24	0.43	1.57	0.23	0.23	0.37	0.05	0.35	0.08	10.95	0.21	0.06	0.33	0.04
	ÇB-4	0.54	0.25	0.06	0.48	0.23	0.34	0.06	0.01	0.00	0.02	7.75	0.04	0.03	0.19	0.01
	ÇB-5	0.46	0.73	0.07	0.53	0.13	0.14	0.09	0.01	0.04	0.01	15.94	0.06	0.01	0.15	0.01
	ÇB-6	5.91	8.46	0.62	2.09	0.14	0.15	0.05	0.01	0.27	0.03	18.03	0.07	0.03	0.12	0.02
	ÇB-7	3.30	6.39	0.77	3.65	0.57	0.34	0.68	0.10	0.80	0.18	7.11	0.70	0.11	0.66	0.10
	ÇB-9	0.88	1.32	0.08	0.27	0.40	0.16	0.21	0.01	0.38	0.16	33.63	0.61	0.11	0.87	0.11
	ÇB-10	0.40	0.24	0.02	0.15	0.21	b.d.l.	0.14	0.04	0.45	0.10	37.80	0.77	0.13	0.97	0.21
	ÇB-11	0.82	0.78	0.07	0.48	0.51	0.38	1.77	0.42	6.12	2.24	243.07	8.71	1.51	10.68	1.36
	ÇB-12	2.27	4.32	0.59	1.78	0.25	0.18	0.57	0.03	0.44	0.10	23.62	0.25	0.05	0.35	0.07
	mean %RSD	16.3	18.4	35.4	34.3	62.4	14.2	71.4	84.4	73.4	53.3	4.1	48.1	49.8	47.3	55.0
	Gneiss	9.80	23.00	2.80	10.90	3.50	0.50	4.60	0.98	6.84	1.45	38.90	4.50	0.71	4.62	0.60
	Schist+marble	24.80	46.40	5.80	20.20	3.70	0.90	3.30	0.46	2.60	0.50	15.90	1.60	0.22	1.50	0.20
	Tertiary shale	71.70	146.60	17.40	62.90	12.40	2.41	11.00	1.60	8.80	1.60	43.20	4.50	0.60	4.00	0.60
Reşadiye	RS-1a	0.52	0.57	0.07	0.29	0.12	0.07	0.00	0.00	0.08	0.02	2.39	0.05	0.00	0.05	0.00
	RS-1b	0.55	0.58	0.01	0.26	0.28	0.36	0.00	0.00	0.04	0.00	2.82	0.17	0.00	b.d.l.	0.00
	RS-1c	1.18	1.50	0.21	0.95	0.21	0.23	0.04	0.01	0.31	0.01	3.07	0.09	0.03	0.03	0.02
	RS-2	0.35	0.61	0.05	0.30	b.d.l.	0.29	b.d.l.	0.00	0.01	0.00	2.06	0.08	0.00	0.03	0.01
	RS-3	0.60	0.33	0.07	0.27	0.11	0.36	b.d.l.	0.01	b.d.l.	0.01	2.23	0.03	0.02	0.00	0.01
	RS-4	3.20	5.30	0.58	2.23	0.29	0.55	0.58	0.06	0.38	0.06	6.88	0.19	0.02	0.10	0.02
	RS-6	0.59	0.41	0.06	0.03	0.24	0.06	b.d.l.	0.00	0.12	0.02	2.00	0.02	0.01	0.07	0.01
	RS-7	2.39	3.89	0.46	1.51	0.32	0.11	0.23	0.03	0.33	0.05	3.36	0.29	0.02	0.19	0.03
	mean %RSD	19.7	15.2	59.1	49.3	92.2	14.4	87.5	126.2	80.4	136.5	9.7	69.3	95.0	88.6	48.9
	Fault gouges (sar	ndstone ·	+ shale p	rotolith))											
	KSL 4–2 mµ	20.1	37.7	4.29	16	3.3	0.83	3.12	0.47	2.81	0.58	15.5	1.68	0.25	1.63	0.25
	KSLC 2–1 mµ	25.6	45.6	4.98	17.7	3.28	0.82	2.84	0.45	2.9	0.65	17	2.01	0.32	2.09	0.32
	KSL 1–0,5 mµ	23.6	40.7	4.34	15.2	2.88	0.76	2.73	0.45	3.05	0.72	18.7	2.25	0.35	2.38	0.37
	KSL 0,5–0,2 mµ	21.3	36.1	3.78	13.4	2.74	0.77	2.9	0.52	3.68	0.89	23.5	2.86	0.46	3.09	0.48
	KSL <0,2 mµ	6.89	11.5	1.23	4.57	1.13	0.36	1.44	0.29	2.25	0.57	15.2	1.9	0.31	2.08	0.32

Note. b.d.l. = below detection limit.

attention on samples made of coarse-grained calcite and aragonite. Travertine mass (each band) was sampled laterally from central axis or fracture. Both microscopy and XRD (semiquantitative) analyses provided that Reşadiye samples are composed by pure calcite.

The studied travertines are represented by a typical banded texture (Figure S1a), and banding is wider for the Pamukkale samples (up to 0.5 mm). Calcites in both travertine deposits comprise fine to moderately crystalline, radial, needle-shaped elongated crystals with length of about 0.5 to 1 mm for Pamukkale and 1 to 2 mm for the Reşadiye area. As more pronounced for the Pamukkale travertines, the bands are filled with organic material (Figure S1b in the supporting information).

Regarding the size of calcite crystals, the Pamukkale fissure-ridge travertine might be formed under stagnant flow conditions with rapid crystallization rate, whereas the Reşadiye travertine must have been precipitated under a dynamic flow regime accompanied by a slow crystallization rate.

4.2. Trace Element Compositions

REE and yttrium (Y) concentrations of travertine samples from Reşadiye and Pamukkale areas are given in Table 1. Total REE contents of Pamukkale travertines vary in a wide range from 2.3 to 35.8 ppb (mean 10.9 ppb), and those of Reşadiye site, except for one sample with extremely high total concentration (RS-5: 1,376 ppb), are from 1.6 to 13.6 (mean 4.7 ppb). As shown in the Post Archean Australian Shale (PAAS)-normalized (Taylor & McLennan, 1985) diagram (Figure 6), except for sample RS-5 from Reşadiye and sample ÇB-11 from Pamukkale, REE concentrations of travertines are significantly lower (up to 5 orders of magnitude) than the PAAS. Despite being close to the detection limit of the analytical method, REE and Y in most samples are still measurable and show light REE (LREE) depletions on PAAS-normalized patterns, with heavy





Figure 6. Post-Archean Australian Shale (PAAS)-normalized (Taylor & McLennan, 1985) diagram for the travertine samples host rocks (red shaded) from Pamukkale (Möller et al., 2004) and fault clays (blue shaded) from Reşadiye area (Uysal et al., 2006). Note that light gray shaded area is for the vein travertines from Central Australia (Uysal, unpublished data, cf., Ring et al., 2016), and pink area and pattern are for the vein travertines from SW USA (Priewisch, 2014), which are shown for comparison purposes.

REE (HREE) contents being about tenfold greater than LREE. The majority of samples display notable positive Eu and Y and slight negative Ce anomalies. The large positive Eu anomaly reflects plagioclase accumulation in the source rock. The elevated Y/Ho ratios are typical of hydrogenous fluids.

REE + Y contents of travertines in both fields are compared to the host rocks and fault gouges with concentrations given in Table 1. Element concentrations of schist, marble, and shale (Möller et al., 2004) exposing at Pamukkale are (red-shaded pattern) represented by a perfect flat-like trend and are about 2 orders of magnitude higher than those measured on travertines in the same area. On the other hand, REE + Y contents of illitic fault clays (blue shaded pattern, Uysal et al., 2006) at Reşadiye (data only available for this area) with a smooth pattern are nearly 1000-fold greater than travertine samples (Figure 6).

4.3. Carbon and Oxygen Isotope Composition of Bulk Rocks

Carbon and oxygen isotope composition of bulk rocks are reported in Table 2. Carbon and oxygen isotope ratios of Pamukkale travertines fall in the range of $5.02\% < \delta^{13}C < 7.22\%$ (V-PDB) and $-16.84\% < \delta^{18}O < -11.47\%$ (V-PDB), while those from Reşadiye are in the range of $5.18\% < \delta^{13}C < 7.85\%$ (V-PDB) and $-17.84\% < \delta^{18}O < -12.05\%$ (V-PDB), respectively (Figure 7). These data include measurements carried out in two different laboratories (see section 3.2.3), whose data are quite congruent with each other (Table 2), and represent a comprehensive and detailed data set that includes some measures of different portions of the same sample in a few selected travertines (i.e., ÇB5A and ÇB5B, ÇB6A and ÇB6B; Table 2). In the plot of $\delta^{18}O$ versus $\delta^{13}C$ (Figure 7), travertines from Reşadiye and Pamukkale display a positive correlation ($R^2 = 0.96$ and 0.83, respectively) and a general overlapping, with the exception of two samples showing the lowest $\delta^{18}O$ (RS4) and the highest $\delta^{13}C$ (RS5) values. However, these two samples were not analyzed for the geochemistry of FIs and will not be discussed further. More in detail, travertines from Reşadiye show a steeper increasing trend toward higher $\delta^{13}C$ values compared to those from Pamukkale that instead reach higher $\delta^{18}O$ values (Figure 7).

4.4. Fluid Inclusions

4.4.1. Description

Since the studied FIs are very small (3.2 to 5.3 μ m for Pamukkale and 5.2 to 19 μ m for Reşadiye travertines) and scarce, microthermometric measurements were taken on a limited number of primary inclusions (n = 15). Primary inclusions hosted in calcite and aragonite are irregularly shaped, cubic, or rectangular (Figure S2) but represent the dominance of inclusions. The secondary inclusions are rounded or oval and rarely show necking-down structure. All the inclusions were homogenized into the liquid



Table 2

Data of Carbon and Oxygen Isotope Composition of Pamukkale and Reşadiye Travertine Samples

		δ ¹³ C ‰	δ^{18} O ‰	δ^{18} O ‰	
Location	Sample No.	V-PDB	V-PDB	V-SMOW	Laboratory
Çukurbağ-Pamukkale	ÇB-1	6.88	-11.47	19.09	University of Arizona
	ÇB-2	6.37	-12.82	17.69	
	ÇB-3	7.22	-12.49	18.03	
	ÇB-4	6.2	-13.32	17.18	
	ÇB-5	5.91	-14.79	15.66	
	ÇB-6	5.41	-15.96	14.46	
	ÇB-7	6.91	-12.5	18.02	
	ÇB-8	5.57	-16.26	14.15	
	ÇB-9	5.84	-15.87	14.55	
	ÇB-10	5.85	-15.43	15.00	
	ÇB-11 CP 12	50	-15.30	15.08	
	ÇB-12 CB-1	6.38	-12.83	17.68	INCV Palermo
	ÇB-1 CB-2	6.27	-12.83	17.08	
	ÇB-2 CB-3	6.07	-12.81	17.70	
	ÇB-3 CB-4	5.87	-13.44	17.52	
	CB-5A	5.71	-15.01	15.44	
	CB-5B	5.84	-14.69	15.77	
	CB-6A	5.02	-16.84	13.55	
	CB-6B	5.32	-16.03	14.38	
	ÇB-8	5.36	-16.68	13.71	
	ÇB-9	5.53	-16.14	14.27	
	ÇB-10	5.56	-15.92	14.50	
	ÇB-11	6.06	-15.71	14.71	
	ÇB-12	5.67	-15.56	14.87	
	PK-4	11.3	-9.3	21.32	Özkul et al., 2013
	PK-5	6.1	-10.7	19.88	
	PK-6	5.9	-10.2	20.39	
	PK-7	5.9	-10.6	19.98	
	PK-8	5.8	-11.1	19.47	
	PK-9	7.1	-10.3	20.29	
	PK-10	8.2	-10.5	20.09	
	PK-11	9.7	-9.7	20.91	
	PK-12	11.5	-9	21.63	
	PK-13 CP 6	11.7	-9.1	21.53	
	ÇB-0 CB-7	4.5	-13.0	14.65	
	ÇB-7 CB-8	5.5	-14	17.20	
	ÇВ-8 СВ-9	43	-15.2	15.24	
	CB-10	4.7	-4.8	25.96	
	CB-11	5.2	-15.8	14.62	
	CB-12	5.3	-16.6	13.80	
	ÇB-13	5.1	-11.1	19.47	
	Pamukkale samples of 2009	5.2	-11.2	19.36	Kele et al. (2011)
	-	5.1	-11.1	19.47	
		6.2	-10.8	19.78	
		6.6	-10.1	20.50	
Termal-Reşadiye	RS-1a	5.48	-15.92	14.50	University of Arizona
	RS-1b	5.23	-16.49	13.91	
	RS-1c	5.25	-16.53	13.87	
	RS-2	6.52	-14.25	16.22	
	RS-3	6.69	-13.3	17.20	
	RS-4	5.27	-17.84	12.52	
	RS-5	7.85	-12.05	18.49	
	RS-6	5.3	-16.03	14.38	
	RS-7	5.5	-15.39	15.04	DIGUE
	RS-1a	5.72	-15.84	14.58	INGV-Palermo
	KS-1b	5.18	-16.67	13.72	
	RS-1c	5.19	-16.69	13.70	



Table 2 ((continued)
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Location	Sample No.	δ ¹³ C ‰ V-PDB	δ ¹⁸ O ‰ V-PDB	δ ¹⁸ O ‰ V-SMOW	Laboratory
	RS-2 RS-3 RS-6	6.35 6.87 5.24	-14.97 -13.43 -16.25	15.48 17.06 14.16	

Note. Carbon and oxygen isotope ratios are expressed as δ^{13} C and δ^{18} O in per mil and referred to the standard V-PDB. V-PDB = Vienna Pee Dee Belemnite; V-SMOW = Vienna Standard Mean Ocean Water.

phase upon heating. The ice melting temperatures (Tm-ice) were converted to salinity using data for the H_2O -NaCl system (Bodnar, 1993).

Homogenization temperatures of the inclusions vary in a narrow range from 114 to 148 °C (with average of 136 °C) for Reşadiye travertines and 132 to 145 °C (with average of 140 °C) for Pamukkale travertines. The last ice melting temperatures of the Reşadiye travertines are within the range of -0.8 to 0 °C corresponding to salinities of 0 to 1.5 wt % NaCl equivalent. Concerning the Pamukkale travertines, last ice melting temperatures vary from -3.6 to -0.2 °C that estimate salinities of 0.4 to 7.0 wt % NaCl equivalent.

4.4.2. Chemistry

The chemistry of FIs is given in Table 3. Travertine from Pamukkale (ÇB1, ÇB2, ÇB3, ÇB4, ÇB5, ÇB6, ÇB8, ÇB9, ÇB10, ÇB11, and ÇB12) have variable H_2O and CO_2 contents in the range from $5.6 \cdot 10^{-10}$ to $5.1 \cdot 10^{-4}$ mol/g and from $6.3 \cdot 10^{-9}$ to $3.8 \cdot 10^{-7}$ mol/g, respectively (Figure 8). Those from Reşadiye (RS-1A, RS-1B, RS-1C, RS2, RS3, and RS6) have H_2O and CO_2 ranging from $5.6 \cdot 10^{-9}$ to $1.8 \cdot 10^{-6}$ mol/g and from $2.6 \cdot 10^{-9}$ to $3.3 \cdot 10^{-8}$ mol/g (see Table 3), respectively (Figure 8). The samples ÇB2 and ÇB3 show the greatest H_2O and CO_2 concentrations, $5.1 \cdot 10^{-4}$ and $3.8 \cdot 10^{-7}$ mol/g, respectively, while the samples ÇB10 and RS2 have the lowest H_2O and CO_2 contents, $5.6 \cdot 10^{-10}$ mol/g and $2.6 \cdot 10^{-9}$ mol/g, respectively. In general, H_2O is the major component of FIs, followed by CO_2 . During their formation, travertines from Pamukkale area trapped more gas than those from Reşadiye (Figures 8 and 9).

Helium concentrations vary from $4.2 \cdot 10^{-14}$ to $1.6 \cdot 10^{-12}$ mol/g in Pamukkale, while from $3.6 \cdot 10^{-15}$ to $4.4 \cdot 10^{-14}$ mol/g in Reşadiye (Table 4 and Figure 9). All other noble gas, including nitrogen content, are consistent with a significant atmospheric component. Indeed, the composition of N₂, ²⁰Ne, and ⁴⁰Ar, suggests that the atmospheric component is present in bulk FIs from both areas. Nitrogen content in Pamukkale varies from $5.3 \cdot 10^{-10}$ to $1.3 \cdot 10^{-7}$ mol/g, while in Reşadiye from $1.1 \cdot 10^{-10}$ to $3.1 \cdot 10^{-9}$ mol/g. ²⁰Ne and ⁴⁰Ar vary from $3.0 \cdot 10^{-14}$ to $4.7 \cdot 10^{-12}$ mol/g and from $6.3 \cdot 10^{-12}$ to $1.5 \cdot 10^{-9}$ mol/g in Pamukkale, respectively, and from $4.6 \cdot 10^{-15}$ to $2.1 \cdot 10^{-13}$ mol/g and from $1.4 \cdot 10^{-12}$ to $3.8 \cdot 10^{-11}$ mol/g in Reşadiye, respectively



Figure 7. Diagram of δ^{18} O versus δ^{13} C (V-PDB). Literature data are from Kele et al. (2011) and Özkul et al. (2013). V-PDB = Vienna Pee Dee Belemnite.

(Figure 9). Mean noble gas and nitrogen concentrations are systematically higher in Pamukkale than in Reşadiye, as observed for major components. Figure 9 shows the concentration of N_2 versus He-Ar and Ar versus Ne-He, where it is possible to notice that their relative ratios are close to air, with all the samples showing an excess of He with respect to air content. **4.4.3.** Noble Gas Isotope Composition

The isotope composition of FIs is given in Table 4. The ³He/⁴He ratio not corrected for air contamination varies from 0.91 to 4.37 Ra in travertine belonging to Reşadiye, while from 0.49 to 1.28 Ra in samples from Pamukkale (Figure 10). Samples from Reşadiye have ³He/⁴He ratios close to air except for sample RS6, which shows a higher range of ratios (2.76 < R/Ra < 4.37). Different from Reşadiye, samples from Pamukkale display ratios lower than air (0.49 < R/Ra < 0.94), with the exception of ÇB2 sample that displays a slightly greater ratio than the air value (1.22 < R/Ra < 1.40, Figure 10). Typical atmospheric, crustal, and mid-ocean ridge basalt ³He/⁴He ratios are 1, 0.01–0.05, and 7–9 Ra, respectively (Graham, 2002; Ozima & Podosek, 1983). Travertines of Pamukkale display the highest He content and lowest ³He/⁴He ratio than those from Reşadiye



Table 3

Concentration of Major Gaseous Components of Fluid Inclusions Expressed as mol/g, and Information of Weight and Size of Crushed Travertines

Location	Sample	Analysis	Loaded	Residual	Crystal	CO_2	H_2O
Location	Sample	uate	(g)	(g)	Size (IIIII)	mor/g	mor/g
Termal-Reşadiye	RS-1A 1	24/11/16	0.27	0.13	>1	4.5E-09	1.8E-08
	RS-1A 2	24/11/16	0.56	0.16	>1	4.7E-09	1.0E-07
	RS-1A 3	24/11/16	1.02	0.17	>1	4.4E-09	1.4E-07
	RS-1A 4	25/11/16	0.96	0.01	>1	3.9E-09	2.4E-07
					mean	4.4E-09	1.2E-07
		/ /			std dev	3.5E-10	9.1E-08
	RS-1B 1	25/11/16	0.27	0.004	>1	1.6E-08	2.1E-06
	RS-1B 2	25/11/16	0.27	0.001	>1	1.8E-08	1.6E-06
	RS-1B 3	25/11/16	0.27	0.0003	>1	2.5E-08	1.9E-06
					mean	2.0E-08	1.9E-06
	DC 1C 1	29/11/16	0.20	0.00		4./E-09	2.8E-07
	RS-IC I	28/11/10	0.29	0.00	>1	0.4E-09	0.4E-09
	RS-1C 2	28/11/10	0.51	0.00	>1	2.4E-09	2.4E-08
	K3-1C 5	20/11/10	0.32	0.00	>1	4.7E-09	0.2E = 0.08
					std dov	4.3E-09	3.1E-08
	RS-21	28/11/16	0.24	0.00		2.0E-09	2.6E-00
	RS-2 1 RS-2 2	28/11/10	0.24	0.00	>1	2.0E-09	2.0E-09
	RS-2.2 RS-2.3	28/11/16	0.05	0.00	>1	2.9E-09	1.1E-08
	R5-2-5	20/11/10	0.55	0.00	mean	2.5E-09	1.5E-08
					std dev	3.3E-10	1.5E 00
	RS-3 1	29/11/16	0.35	0.00	>1	1.4F-08	5.2E-09
	RS-3 2	29/11/16	0.55	0.00	>1	4.2E-08	6.6E-09
	RS-3 3	29/11/16	0.50	0.00	>1	1.4E-08	4.9E-09
	10000	27/11/10	0100	0100	mean	2.3E-08	5.6E-09
					std dev	1.6E-08	8.9E-10
	RS-6 1	29/11/16	0.31	0.00	>1	4.0E-08	1.2E - 08
	RS-6 2	30/11/16	0.56	0.07	>1	3.2E-08	1.4E-06
	RS-6 3	30/11/16	0.53	0.05	>1	2.7E-08	8.0E-08
					mean	3.3E-08	5.0E-07
					std dev	6.6E-09	7.9E-07
Çukurbağ-Pamukkale	ÇB-1 1	21/02/17	0.36	0.07	>1	2.7E-08	9.4E-05
	ÇB-1 2	01/03/17	0.34	0.05	>1	8.2E-08	5.9E-04
	ÇB-1 3	02/03/17	0.33	0.03	>1	2.5E-07	3.5E-04
					mean	1.2E-07	3.4E-04
					std dev	1.2E-07	2.5E-04
	ÇB-2 1	21/02/17	0.33	0.01	>1	4.7E-08	1.3E-03
	ÇB-2 2	22/02/17	0.22	0.04	>1	3.8E-08	1.4E-04
	ÇB-2 3	01/03/17	0.23	0.01	>1	8.0E-08	7.8E-05
					mean	5.5E-08	5.1E-04
					std dev	2.2E-08	7.1E-04
	ÇB-3 1	21/02/17	0.33	0.06	>1	8.7E-08	1.5E-04
	ÇB-3 2	28/02/17	0.23	0.03	>1	2.2E-07	7.0E-05
	ÇB-3 3	03/03/17	0.35	0.10	>1	7.8E-07	8.0E-05
	ÇB-3 4	03/03/17	0.31	0.11	>1	4.5E-07	5.4E-05
					mean	3.9E-07	8.9E-05
					std dev	3.0E-07	4.3E-05
	ÇB-4 1	21/11/16	1.03	0.38	>1	3.4E-08	-
	ÇB-4 2	21/11/16	0.54	0.21	>1	2.8E-08	1.9E-04
	ÇВ-4 3	22/11/16	0.24	0.10	>1	1.1E-06	8.4E-05
	ÇВ-4 4	22/11/16	0.23	0.10	>1	1.9E-08	4.3E-05
	ÇB-4 5	22/11/16	0.24	0.01	>1	1.4E-07	1.7E-05
	ÇВ-4 б	22/11/16	0.27	0.08	>1	8.1E-08	3.3E-05
					mean	2.3E-07	7.3E-05
		24/02/17	0.24	0.01	std dev	4.2E-07	6.8E-05
	ÇB-5 (A) 1	24/02/17	0.34	0.01	>1	1.2E-07	2.7E-07
	$\zeta B-5(A) 2$	28/02/17	0.34	0.04	>1	9.0E-08	4.9E-07
	ÇВ-5 (A) З	02/03/17	0.32	0.01	>1	1.6E-08	5.8E-07



 Table 3 (continued)

Location	Sample	Analysis date	Loaded (g)	Residual (g)	Crystal size (mm)	CO ₂ mol/g	H ₂ O mol/g
			.0/	.0,		7 (E 00	4.5E 07
					mean	7.6E-08	4.5E-07
	CR 5 (R) 1	24/02/17	0.28	0.03		5.5E = 08 3.1E = 07	1.0E-07 7.3E-06
	CB - 5 (B) 2	24/02/17	0.20	0.03	>1	3.1E = 07 1.1E = 08	7.5E-00 3.6E-07
	ÇB-3 (B) 2 CB-5 (B) 3	27/02/17	0.33	0.01	>1	1.1E = 0.08	5.0E-07
	ÇD-3 (D) 3	02/03/17	0.55	0.04	mean	2.4E-03	0.1L-00
					std dev	1.2E-07	4.0E-00
	CB-6(A) 1	24/02/17	0.32	0.05		2.5E_08	1.4E-06
	CB-6(A) 2	27/02/17	0.32	0.05	>1	1.9E-08	1.4E = 00 1.9E = 07
	CB-6(A) 3	02/03/17	0.30	0.01	>1	2.7E_08	2.0E_06
	ÇD-0 (A) 5	02/03/17	0.50	0.09	mean	2.7E-08	1.2E-06
					std dev	2.4E-00 4.0E-09	9.3E-07
	CB-6 (B) 1	22/02/17	0.26	0.02		4.0E-09	7.2E-06
	ÇB-6 (B) 2	22/02/17	0.20	0.02	>1	3.9E_08	1.2E-00
	ÇB-6 (B) 3	02/03/17	0.30	0.05	>1	3.7E-08	1.3E - 0.5 1.3E - 0.5
	ÇD 0 (D) 5	02/03/17	0.50	0.07	mean	4.1E-08	1.3E 05
					std dev	5.8E-09	5.5E-06
	CB-8 1	30/11/16	0.43	0.01	>1	1.9E-08	7.3E-07
	ÇB-8-2	30/11/16	0.43	0.01	>1	4.0F-08	2.8E-06
	ÇB 0 2 CB-8 3	30/11/16	0.52	0.00	>1	6.2E-00	5.0E-08
	ÇD 0 5	50/11/10	0.52	0.02	mean	2.2E-08	1.2E-06
					std dev	1.7E-08	1.2E 00
	CB-91	22/11/16	0.26	0.06	>1	3.1E-09	-
	CB-9 2	22/11/16	0.27	0.09	>1	2.1E-08	4.2E-08
	CB-9 3	23/11/16	0.27	0.10	>1	1.1E-08	7.3E-09
	CB-94	23/11/16	0.28	0.05	>1	2.7E-09	2.7E-09
	3	,,			mean	9.5E-09	1.7E-08
					std dev	8.6E-09	2.2E-08
	CB-101	01/12/16	0.28	0.02	>1	7.1E-09	
	CB-10 2	01/12/16	0.60	0.05	>1	5.6E-09	1.1E-09
	3				mean	6.4E-09	5.6E-10
					std dev	1.0E-09	7.9E-10
	CB-11 1	23/11/16	0.25	0.08	>1	2.8E-07	2.9E-07
	ČB-11 2	23/11/16	0.26	0.07	>1	1.9E-07	6.4E-07
	св-11 3	23/11/16	0.27	0.07	>1	9.5E-08	1.4E-05
	CB-11 4	23/11/16	0.26	0.13	>1	1.8E-07	1.4E-06
	3				mean	1.8E-07	4.1E-06
					std dev	7.5E-08	6.8E-06
	ÇB-12 1	24/11/16	0.26	0.08	>1	9.3E-08	5.5E-08
	ÇB-12 2	24/11/16	0.28	0.02	>1	9.5E-09	8.1E-08
	CB-12 3	24/11/16	0.54	0.09	>1	1.5E-08	6.9E-08
	, -				mean	3.9E-08	6.8E-08
					std dev	4.7E-08	1.3E-08

(Figure 10). In general, there is no clear trend between 3 He/ 4 He ratio and He content, except for sample RS6 that has the lowest He content and shows 3 He/ 4 He values greater than 1 Ra. This behavior suggests the occurrence of secondary addition of cosmogenic 3 He, due to the exposure of these rocks to cosmic rays (see section 5.2.1). Secondary addition of 3 He is not evident in RS2 and RS3 samples, even these have the same He content of RS6 (Figure 10). Figure 11 shows 3 He/ 4 He versus the 4 He/ 20 Ne, where it is possible to distinguish which samples are subject to greater atmospheric component. The 4 He/ 20 Ne ratio ranges between 0.1 and 3.1 in Pamukkale, and from 0.2 to 1.2 in Reşadiye deposit. Samples showing 4 He/ 20 Ne < 0.318 (or 0.285 in case of Air Saturated Water, ASW) probably suffered a diffusive loss of He, which induced a fractionation on this ratio. Therefore, samples ÇB8, ÇB11, ÇB12, RS-1B, RS-6, and RS-1C will not be further discussed in terms of 3 He/ 4 He. In general, Pamukkale samples show a lower atmospheric component than those from Reşadiye (Figure 11). Since travertines from Pamukkale trapped more gas than Reşadiye samples, this could indicate that fluids in excess cannot belong to air or ASW circulating at shallow levels.



Figure 8. CO₂ and H₂O concentration in travertines FI from Reşadiye and Pamukkale areas, expressed in mol/g.

5. Discussion

5.1. Origin of Travertine Deposits

5.1.1. Age, Tectonics, and Chemistry of Travertines

Carbonate veins in the Pamukkale area that formed in a time span from ~24,500 to 50,000 years BP are regarded as the products of seismically driven fluid injections into basement rocks propagated to the surface across preexisting horizontally bedded travertines (i.e., Uysal et al., 2009). Upward migration of CO₂-rich fluids from which the carbonate veins precipitated took place simultaneously with the fracture generation and its propagation to the Earth's surface. Since the generation of fissure-ridge banded travertine is attributed to active faulting (Hancock et al., 1999; Uysal et al., 2007; Brogi et al., 2014), seismicity is likely to be associated with the hydrothermal degassing of CO₂ (Uysal et al., 2009) and the noble gas that were trapped in calcite veins investigated in this study. This is consistent with previous studies suggesting that mantle (CO₂ and ³He) degassing occurs currently along active fault systems in Turkey (Güleç et al., 2002; Mutlu et al., 2008; Pfanz et al., 2014). However, even the cold groundwater discharges and associated travertines might bear the signals of deep-rooted fluid migration, which could be possible only through the active tectonic zones. An interesting example is the Antalya travertine plateau in the southwestern Turkey (the largest in the world, ~650 km²) formed by Kirkgöz group of karst springs (T = 18 °C, mean Q = 18 m³/s). Earthquakes with magnitudes of 4 to 6 and focal depths of 80 to 100 km occur in this area. Helium isotopic composition of Kırkgöz springs (³He/⁴He up to 2.60 Ra; Özyurt & Bayarı, 2014) suggests an apparent fluid migration from local mantle. Furthermore, noble gas signals in groundwater in the Konya Closed Basin of central Anatolia, which is marked by low recent seismic activity but extensive late Pliocene-early Holocene volcanism, suggest fluid migration from mantle and crustal sources (³He/⁴He up to 2.13; e.g., Özyurt & Bayarı, 2014, Bayarı et al., 2017).

Reşadiye samples are also from the fissure-filling banded travertines similar to those from Pamukkale. However, they are from a fracture system along the 360-km 1939 Erzincan earthquake ($M_s = 7.8$)-rupture segment in the plate boundary hosted by the NAFZ (Karabacak et al., 2019, Figure 2). Reşadiye samples yield much younger Holocene ages (245–14,678 years) of which statistical evaluations indicate that the crustal deformation intensified at least eight different periods during the last 7,000 years along this part of the NAFZ (Karabacak et al., 2019). Although Pamukkale vein samples can be expected to be emplaced as subsurface (but near surface) deposits having been eroded for the last ~24 ka (Uysal et al., 2019), the Reşadiye veins can be regarded as surface deposits due to very young U-Th ages up to few hundreds of years (Karabacak et al., 2019). Indeed, as we discuss below, there are some differences in noble gas compositions in FIs between the Pamukkale and Resadiye samples.

PAAS-normalized REE patterns of vein travertines from Reşadiye along the NAFZ and Pamukkale in the western Anatolian extensional region are displayed in Figure 6. For comparison, REE patterns of



Figure 9. Diagrams of elemental concentrations measured in travertine FI after single-step crushing of Ar versus (a) N_2 and (b) Ne, (c) He versus N2 and (d) Ar.

previously reported fault gouges near Resadiye (Uysal et al., 2006) and the Pliocene limestone hosting the travertine veins in Pamukkale (Uysal et al., 2007), as well as vein travertines from central Australia (Uysal, unpublished data, cf., Ring et al., 2016) and southwestern United States (Priewisch, 2014), are also shown. Samples from Reşadiye and Cukurbag areas apparently show a similar REE pattern, with an enrichment in HREE relative to middle REE and LREE (average La/Lu values for Pamukkale and Resadiye samples are 84.9 and ~69.7, respectively), negative Ce (except for two samples), and positive Eu anomalies (for Pamukkale samples, Figure 6). However, this is due to extremely high Ba/Eu ratio causing BaO+ interferences on Eu (Uysal et al., 2007) and Y anomalies. In addition, Resadiye and Pamukkale vein travertines are considerably depleted in REE in comparison to the host limestone in Pamukkale and to the vein travertines from Australia and United States (Figure 6). As previously discussed by Uysal et al. (2007), the REE pattern of the fissure travertines from Pamukkale (and Resadiye vein travertines are like them) does not show any similarities to the REE pattern of the host limestone. The lower REE abundance in vein travertines from Pamukkale has been interpreted as being a result of transient nature of the water-rock interaction during seismically controlled groundwater movements, and the HREE enrichment was related to carbonate complexation processes in shallow groundwater source for these carbonates (Uysal et al., 2007, and references therein). The Australian and U.S. travertine veins have higher REE abundance (up to 2 orders of magnitude) when compared to Pamukkale and Resadive travertines (Figure 6). The higher REE content for Australian travertines can be explained by the longer residence time of groundwater of the Great Artesian Basin, which is circulating at depths >3 km and interacting with Neoproterozoic/Cambrian basement (Ring et al., 2016). Instead, the Pamukkale (and evidently Reşadiye) fissure travertines were interpreted to have deposited from a less mature and younger water in a close proximity to the recharge area (Uysal et al., 2007). 5.1.2. Carbon and Oxygen Isotope Systematics of Travertines

Figure 7 shows a plot of δ^{18} O versus δ^{13} C where the data of present work are compared to those of previous studies (Kele et al., 2011; Özkul et al., 2013). Carbon and oxygen isotopic compositions of travertine from Pamukkale are consistent with our results with the exception of some samples (ÇB10, ÇB9, and ÇB6). However, samples from other travertine deposits in the Pamukkale area have variable isotope values (more pronounced for the δ^{13} C).

 δ^{13} C and δ^{18} O values of studied travertine samples are higher than organic and marine sources, and indeed, decarbonation reactions that cause CO₂ degassing seem to be the sole mechanism behind the observed isotope compositions (e.g., Karabacak et al., 2017). During CO₂ removal from the travertine-precipitating waters, lighter isotopes (¹⁶O and ¹²C) are preferentially released, which results in residual fluid enriched in δ^{13} C values (Uysal et al., 2007). δ^{13} C values of dissolved gases from the water phase at Reşadiye are



Table 4

The Noble Gas (He, Ne, and Ar) Isotope Composition and N2 concentration of Fluid Inclusions in Travertines

Location	Sample	⁴ He mol/g	³ He mol/g	²⁰ Ne mol/g	N ₂ mol/g	⁴⁰ Ar mol/g	⁴ He/ ²⁰ Ne	R/Ra	Err tot \pm
Cukurbağ-Pamukkale	ÇB 10 (4)	8.7E-14	8.2E-20	5.8E-14	1.9E-09	2.3E-11	1.5	0.68	0.032
	ÇB 2 (2)	4.8E-14	8.2E-20	9.2E-14	2.0E-09	2.4E-11	0.5	1.22	0.078
	ÇB 9 (4)	7.9E-14	6.8E-20	3.7E-14	8.9E-10	1.1E-11	2.1	0.62	0.031
	ÇB-1	2.3E-13	2.4E-19	2.7E-13	6.8E-09	8.2E-11	0.8	0.75	0.033
	ÇB-10 (2)	4.8E-14	8.5E-20	1.3E-13	9.3E-09	1.1E-10	0.4	1.28	0.064
	ÇB-10 (3)	1.0E-13	9.5E-20	5.6E-14	9.4E-09	1.1E-10	1.8	0.67	0.035
	ÇB-11	1.6E-12	-	4.7E-12	-	-	0.3	-	-
	ÇB-11 (2)	9.2E-13	1.3E-18	2.9E-12	1.3E-07	1.5E-09	0.3	1.05	0.042
	ÇB-12 (2)	4.9E-13	4.9E-19	1.3E-12	-	-	0.4	0.72	0.012
	ÇB-12 (3)	2.0E-13	2.9E-19	2.5E-12	4.3E-08	3.7E-10	0.1	1.04	0.019
	ÇB-2	5.6E-14	-	9.8E-14	6.1E-09	7.0E-11	0.6	-	0.000
	ÇB-3	1.3E-13	1.6E-19	1.6E-13	3.3E-09	3.9E-11	0.8	0.86	0.040
	ÇB-4	1.3E-13	-	2.2E-13	4.2E-09	5.0E-11	0.6	-	-
	ÇB-4 (2)	1.3E-13	2.0E-19	1.9E-13	8.4E-09	1.1E-10	0.7	1.13	0.049
	ÇB-5 (A)	7.0E-14	8.8E-20	1.3E-13	3.8E-09	4.5E-11	0.5	0.91	0.051
	ÇB-5 (B)	6.7E-14	9.8E-20	1.1E-13	2.4E-09	2.9E-11	0.6	1.05	0.069
	ÇB-6 (A)	4.2E-14	5.6E-20	5.1E-14	2.1E-09	2.5E-11	0.8	0.94	0.095
	ÇB-6 (B)	1.1E-13	8.8E-20	8.5E-14	2.2E-09	2.7E-11	1.3	0.58	0.054
	ÇB-8	1.4E-13	-	5.1E-13	2.4E-08	2.9E-10	0.3	-	-
	ÇB-8 (2)	5.2E-13	5.9E-19	1.4E - 12	-	-	0.4	0.81	0.022
	ÇB-8 (3)	5.2E-13	3.5E-19	1.5E-12	3.5E-08	4.3E-10	0.3	0.49	0.018
	ÇB-9	5.3E-14	8.8E-20	3.5E-14	5.2E-10	6.3E-12	1.5	1.20	0.103
	ÇB-9 (2)	6.9E-14	9.7E-20	6.1E-14	2.7E-09	3.3E-11	1.1	1.02	0.044
	ÇB-9 (3)	9.4E-14	7.2E-20	3.0E-14	8.3E-10	1.0E-11	3.1	0.55	0.032
Termal-Reşadiye	RS-1A	1.5E-14	-	2.6E-14	7.5E-10	9.0E-12	0.6	-	-
	RS-1A (2)	2.3E-14	3.7E-20	4.1E-14	1.5E-09	1.9E-11	0.6	1.14	0.046
	RS-1A (3)	1.9E - 14	2.6E-20	5.4E-14	6.9E-10	8.3E-12	0.3	1.01	0.044
	RS-1B	3.2E-14	-	5.7E-14	2.3E-09	2.7E-11	0.6	-	-
	RS-1B (2)	3.6E-14	5.9E-20	6.6E-14	2.9E-09	3.5E-11	0.5	1.19	0.054
	RS-1B (3)	4.5E-14	7.1E-20	2.1E-13	3.1E-09	3.8E-11	0.2	1.15	0.043
	RS-1C	2.0E-14	4.4E-20	3.4E-14	-	-	0.6	1.54	0.230
	RS-1C (2)	2.3E-14	3.0E-20	4.5E-14	1.7E-09	2.1E-11	0.5	0.93	0.039
	RS-1C (3)	2.7E-14	3.5E-20	9.4E-14	1.3E-09	1.5E-11	0.3	0.91	0.042
	RS-2	3.7E-15	-	6.6E-15	1.5E - 10	1.8E-12	0.6	-	-
	RS-2 (2)	8.0E-15	1.2E-20	2.1E-14	8.3E-10	1.0E-11	0.4	1.04	0.039
	RS-3	8.0E-15	-	$1.4E{-}14$	1.5E - 10	1.8E-12	0.6	-	-
	RS-3 (2)	7.2E-15	1.0E-20	1.2E-14	4.2E-10	5.1E-12	0.6	1.05	0.083
	RS-6	4.8E-15	-	6.9E-15	3.0E-10	3.6E-12	0.7	-	-
	RS-6 (2)	4.0E-15	2.4E-20	4.6E-15	2.2E-10	2.6E-12	0.9	4.37	0.183
	RS-6 (3)	7.1E-15	2.7E-20	2.4E-14	3.4E-10	4.1E-12	0.3	2.77	0.154
	RS-6 (4)	7.1E-15	2.7E-20	6.1E-15	3.3E-10	4.1E-12	1.2	2.76	0.136
	RS-6 (5)	6.2E-15	2.7E-20	7.4E-15	-	-	0.8	3.09	0.143
	RS-6 (6)	3.6E-15	1.6E-20	5.5E-15	1.0E-10	1.4E-12	0.6	3.16	0.249

reported in the range of -2.28 to -1.76 (% V-PDB, De Leeuw et al., 2010). Likewise, carbon isotope values of dissolved inorganic carbonate in spring water in the Pamukkale area was measured -1.0 to +2.52 (% V-PDB, Kele et al., 2011). These values are lower than in travertine samples of this study (5.02% to 7.85% V-PDB, Figure 7), which might be attributed to the volatile (CO₂) loss from the Reşadiye and Pamukkale geothermal waters.

Oxygen isotope composition of thermal waters in the Reşadiye and Pamukkale geothermal sites was studied in detail by previous works. δ^{18} O values of Reşadiye waters vary from -12.7% to -11.6% VSMOW (Süer et al., 2008), and those of issuing near Pamukkale travertines are in the range of -8.3% to -7.6%VSMOW (Kele et al., 2011, Figure 7). Assuming mineral water equilibrium and using the oxygen isotopic fractionation factors from water into calcite ($\Delta^{18}O_{calcite-water}$. Friedman & O'Neil, 1977), we estimated the δ^{18} O values of waters that precipitated the travertine samples. Taking discharge temperatures of 41.3 °C for Reşadiye (Süer et al., 2008) and 56.1 °C for the Pamukkale (Kele et al., 2011) waters, δ^{18} O of paleo-





Figure 10. Concentrations of He (mol/g) versus ³He/⁴He not corrected for air contamination (R/Ra values). Errors are 1σ values. The plot at the bottom is a zoom of that at the top in a narrower scale of R/Ra. The solid and dotted blue lines indicate the change of ${}^{3}\text{He}/{}^{4}\text{He}$ ratios at different extents of mixing assuming that only production of cosmogenic ³He in 250 and 50 years, respectively, is influencing the samples. They were calculated starting from an average production rate of ³He in limestone of ~103 atoms $g^{-1}/year^{-1}$, after scaling at the latitude and altitude of our sampling locations (Kurz, 1986; Lal, 1991; Yokoyama et al., 1977). See text for further details. The dotted green line indicates the change of ${}^{3}\text{He}/{}^{4}\text{He}$ ratios at different extents of mixing assuming that only production of radiogenic ⁴He in 50,000 years is influencing the sample. It was calculated following the equations proposed by Graham et al. (1987) and Ballentine and Burnard (2002), and based on the U and Th concentration measured in our samples, assuming the time span corresponding to the highest estimated age of travertines (i.e., 50,000 years). The dotted horizontal red line indicates ${}^{3}\text{He}/{}^{4}\text{He}$ in AIR (1 Ra).

waters are computed to be -12.8% to -6.8% VSMOW for Reşadiye and -8.3% to -3.2% VSMOW for Pamukkale, indicating a meteoric origin. Supposing that the water temperatures of those areas remained unchanged over the investigated time intervals, the mean of calculated $\delta^{18}O_{water}$ values is about 1% to 2% higher than the actual values. Another attempt was made here to estimate $\delta^{18}O$ of fluids using the homogenization temperatures measured on travertines. Taking average temperature of 136 °C for Reşadiye travertines and 140 °C for the Pamukkale travertines, oxygen isotope compositions of fluids is found -0.9% to +5.1% (VSMOW) and +0.2% to +5.7% (VSMOW) for the respective fields. These high values might be due to continuous prograde reactions between water and country rocks during seismically controlled groundwater movements, as inferred from REE depletion observed in both areas (Figure 6; see also section 5.1.1).

Travertine stable isotope geochemistry is controlled by the regional fluid flow, active tectonics, and climate variations (Capezzuoli et al., 2018; Kele et al., 2011; Özkul et al., 2013). Literature data show some variations in the stable isotopic compositions of recent and fossil travertines within the Denizli basin (Özkul et al., 2013). Kele et al. (2011) showed that δ^{13} C values of travertines are more positive in the Pamukkale area with respect to other sites in the same basin, arguing for a contribution of CO₂ released by thermo-metamorphic processes associated with magmatic activity. This is in agreement with evidences from the geochemistry of FIs (see sections 5.2 and 5.3).

5.2. Geochemistry of FIs 5.2.1. Characterization of FIs

A detailed observation of single FI within Reşadiye and Pamukkale travertines revealed the presence of primary and secondary inclusions. The presence of primary inclusions indicates that fluids trapped within travertines are representative of the time of formation of the rocks from both localities. Homogenization temperatures measured on Pamukkale (132–145 °C) and Reşadiye (114–148 °C) calcites reflect the minimum trapping temperature of FIs. These are notably higher than discharge temperatures of hot springs (56.1 °C and 41.3 °C, respectively) that recently precipitate travertines.

The Pamukkale geothermal field is located at the intersection of the Büyük Menderes graben and the Gediz graben (Figure 1a). Since this field is a protected area due to magnificent travertine terraces, drilling of thermal water wells is not allowed and therefore we cannot verify the existence high-temperature fluids as revealed by the results of FI analysis. However, the bottom-hole temperatures of wells (at depths between 600 and 3,100 m) drilled in the Kızıldere geothermal field, nearly 25 km northwest Pamukkale, are up to 240 °C (Şimşek et al., 2000). Furthermore, reservoir temperatures estimated by various chemical geothermometers for the Pamukkale springs are in the range of 110 to 175 °C (Gökgöz & Filiz, 1994; Mutlu & Güleç, 1998). All these findings provide the evidence of the presence of high-temperature fluids in the system, which were seismically (rapidly) injected and then entrapped in FIs. However, we cannot test this hypothesis for the Reşadiye field because no well data are available. In fact, reservoir temperatures calculated for the Reşadiye spring are from 76 to 106 °C (Mutlu & Güleç, 1998), which are slightly lower than homogenization temperatures measured in FIs (114–148 °C). In some other studies, the temperature difference between thermal springs and fluids trapped in FIs in fissure-ridge type travertines is attributed to progressive cooling of fluids in time (e.g., Gasparrini et al., 2013; Rimondi et al., 2016).

This suggests that the temperature of fluids circulating at the time of travertine deposition has cooled down in time probably due to meteoric water infiltration. However, in this eventuality we should expect an increase of atmospheric contribution to the deep fluids, which is not the case. Another alternative is that





Figure 11. Diagram of ⁴He/²⁰Ne versus ³He/⁴He not corrected for air contamination (R/Ra), in which we can evaluate the atmospheric component. The dotted red lines indicate binary mixing between AIR (³He/⁴He = 1 Ra and ⁴He/²⁰Ne = 0.318) and three natural end-members not contaminated by air having ⁴He/²⁰Ne = 1,000 and ³He/⁴He = 8 Ra (local mantle with MORB-like features), ³He/⁴He = 1 Ra(a mixed magmatic-crustal term), and ³He/⁴He = 0.05 Ra (typical crustal end-member). MORB = mid-ocean ridge basalt.

during the seismic events deeply circulating hot waters were rapidly involved in travertine precipitation but did not reach the surface.

Salinities of FIs of Pamukkale and Reşadiye calcites are of 0.4 to 7.0 wt % and 0 to 1.5 wt % NaCl equivalent, respectively. These values are too low to propose long residence time for interaction with the source rocks, as instead observed for hydrothermal brines related to ore deposits (Slowakiewicz, 2003). However, this hypothesis does not agree with the findings of Uysal et al. (2007) who suggested that Pamukkale fissure travertine did not precipitate from high-temperature fluids.

5.2.2. Entrapment of Cosmogenic, Nucleogenic, and Radiogenic Helium

The wide variability of ³He/⁴He observed in travertines especially from Reşadiye (Figure 10) suggests the occurrence of secondary processes involving FIs. We thus evaluate the possible addition of nucleogenic and cosmogenic ³He as well as radiogenic ⁴He to FIs trapped in travertine. We highlight that the addition of secondary He occurs in the crystal matrix as observed in FI study. In addition, reticular helium is normally released via rock/mineral melting or multistep crushing, while we used single-step crushing, which is a conservative method in order to minimize the release of helium from the crystal matrix (e.g., Correale et al., 2016; Kurz, 1986; Rizzo et al., 2018). However, other studies that used our

approach found that in a sufficient time span a certain percentage of helium might diffuse from the crystal matrix into the FIs (Barry et al., 2015; Day et al., 2015).

Nucleogenic ³He originates from the reaction of ⁶Li $(n, \alpha) \rightarrow {}^{3}H(\beta) + {}^{3}He produced by thermalized neutrons from <math>(\alpha, n)$ reactions within the rocks (e.g., Andrews & Kay, 1982; Lal, 1987). Thus, the production of nucleogenic ³He is a function of Li concentration in the rock, although Lal (1987) found that even in Li-rich rocks this contribution is insignificant compared to cosmic ray spallogenic ³He. To verify this condition in our samples, we calculated the amount of nucleogenic ³He theoretically accumulated in a time span corresponding to the age estimated for each of the travertines (see section 5.1). In the computation, we considered the Li content measured in our samples (Dirik et al., 2018), a nucleogenic ³He production rate of 6.13×10^{-6} atoms g⁻¹·year⁻¹·ppm⁻¹ Li for a neutron flux of 1 neutron cm⁻²/year and a neutron absorption mean free path of 73.5 cm for sandstone rocks (Lal, 1987). We also took into account a neutron production rate of approximately 2 neutrons g⁻¹·ppm⁻¹ U·year⁻¹ per gram of rock and 0.7 neutrons g⁻¹·ppm⁻¹ Th·year⁻¹ per gram of rock (Dunai et al., 2007). The results of calculation indicate that the nucleogenic ³He produced in travertines from Reşadiye and Pamukkale is from 4 to 6 orders of magnitude lower than ³He measured in our samples (Tables 4 and S2). This confirms that nucleogenic ³He has a negligible effect on our data, even assuming 100% diffusion of reticular helium into FIs, and thus, it cannot explain the observed variability of ³He/⁴He.

Cosmogenic ³He is produced from thermal neutrons of cosmic ray and depends on geomagnetic latitude and altitude as well as on exposure time to cosmic ray and involved lithology (Dunai & Wijbrans, 2000; Lal, 1991; Lal & Peters, 1967). Starting from an average ³He production rate in limestone of ~103 atoms g⁻¹/year, we scaled this rate at the latitude and altitude of our sampling locations (Kurz, 1986; Lal, 1991; Yokoyama et al., 1977). Considering the estimated age for each of the travertines (see Table S1 and section 5.1), we calculated the amount of ³He theoretically accumulated in our samples (Table S2). Because the ³He measured in our samples is from ~2- to 85-fold lower than the corresponding cosmogenic ³He, it is unrealistic that the latter (i.e., 100%) diffused completely from the crystal matrix into the FIs (Tables 4 and S2). In fact, this assumption would lead to measure ³He/⁴He enormously higher than what we recorded. More reasonably, diffusion of ³He occurred at a lower extent and only partially involved the investigated samples (i.e., RS6 and RS1C) or travertines were exposed over a shorter time than their estimated age, as those exhumed in quarries. We cannot rule out the possibility that travertine outcrops were eroded and thus exposed for a limited time with respect to their estimated age. However, we do not have constraint to support this hypothesis but as shown below it does not have any implication on the outcome of this approach. In support of a shorter exposure time of travertines, in Figure 10 we report two possible mixing curves showing ³He accumulation in





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Figure 12. Diagram of age of Reşadiye and Pamukkale travertines (Karabacak et al., 2019; Uysal et al., 2019) versus He concentration (mol/g) and ${}^{3}\text{He}/{}^{4}\text{He}$ not corrected for air contamination (R/Ra values).

case of exposure of 50 or 250 years. This effect is more pronounced in sample RS6, which is characterized by one of the lowest He concentrations and the highest ${}^{3}\text{He}/{}^{4}\text{He}$ ratios (between 2.76 and 4.37 Ra) of the whole data set (Figure 10). We argue that travertines only with ${}^{3}\text{He}/{}^{4}\text{He} > 1$ Ra were modified by the addition of cosmogenic ${}^{3}\text{He}$ into the FIs and will not be further discussed in the text for constraining the origin of FIs.

We now discuss the effect of radiogenic ⁴He ingrowth from U and Th decay, because it could increase the He content and decrease the ³He/ ⁴He. The production of ⁴He is due to α -decay of ²³⁵U, ²³⁸U, and ²³²Th decay chains and is thus directly proportional to the concentration of these radioelements in the rock samples. Following the equations proposed by Graham et al. (1987) and Ballentine and Burnard (2002), and considering the measured U and Th concentrations, we calculated the radiogenic ⁴He produced over the time span corresponding to the estimated travertines age. The results reported in Table S2 and Figure 10 show how ⁴He measured in FIs is from ~2.5 to 87 times higher than radiogenic ⁴He ingrowth from U and Th decay. Assuming 100% diffusion of radiogenic ⁴He into FIs, the ³He/⁴He of our samples would decrease slightly or negligibly. The only exception is for the Pamukkale samples CB2, CB4, CB5, CB6, CB9, and CB10 whose ratio would be decreased from 0.8 to 0.2 Ra. Travertines from Resadiye would never be modified because of their lower U and Th concentrations and their younger age (245-14,678 years BP) compared to Pamukkale (24,542-49,629 years BP).

A further evidence for the negligible influence of the radiogenic ⁴He ingrowth can be evaluated by plotting He concentration in FIs and ³He/ ⁴He versus time (Figure 12). He concentration does not show any increase

with increasing travertine age, as instead expected in case of radiogenic 4 He ingrowth. Similarly, 3 He/ 4 He does not vary with increasing age of travertines, with the exception of sample RS6 from Reşadiye.

5.2.3. Helium Excess as Evidence of the Lack of Diffusive Fractionation

The geochemistry of FIs highlights how all the samples have a large contribution of atmospheric component. In fact, the relative N2, Ne, and Ar ratios are close to the theoretical values in atmosphere, indicating that this component was already present at the time of precipitation of travertines (Figure 9). The fact that we record ratios more similar to AIR rather than to ASW (at standard temperature and pressure) implies that travertine formation occurred in an air-dominated environment that is close to the surface, in agreement with indications by mineralogy of the samples. Instead, helium is normally in excess with respect to theoretical He/Ar, He/Ne, and He/N2 values in air, with higher concentrations in Pamukkale than in Reşadiye, as observed for major gaseous components (Figures 8 and 9). This leads to two important considerations: (1) helium did not diffuse from FIs and it was preserved from travertine formation, and (2) helium in excess could have a different origin than the atmosphere. In support of the first consideration, we take into account the results of an experimental study by Copeland et al. (2007, and references therein), who suggested that helium diffusion in carbonates is similar to that in apatite and the closure temperature is in the range of 60-80 °C. This could imply that travertine precipitated at temperature < 60 °C, as indicated by Süer et al. (2008) and Kele et al. (2011), excluding any diffusive loss. In a more recent study, Cherniak et al. (2015) highlighted that modeling the helium diffusion in calcite is complex due to multidomain diffusion, which differs among the samples that formed in different environments. However, these considerations are valid when helium is retained in the crystal matrix and not in the FIs. It is important to recall that we extracted helium hosted in FIs and not the bulk content including that eventually hosted in the crystal lattice, which is extracted by in-vacuo rock melting (decarbonation at $T \sim 1000$ °C). The single-step crushing method we used is conservative allowing minimizing possible mixing of helium from the FIs and from the crystal lattice (see section 5.2.1).



Further evidence of the lack of helium diffusion is from the comparison of He concentration with 3 He/ 4 He in our data set (Figure 10). In fact, in case of helium loss, we should expect an isotope fractionation according to the faster diffusivity of 3 He with respect to 4 He (Cherniak et al., 2015). In our data, we do not observe any obvious correlation between concentration and isotope ratio. The lowest 3 He/ 4 He values are measured in Pamukkale travertines in which helium concentrations, although variable, are found systematically higher than in Reşadiye. Therefore, in the following sections, we will examine the hypothesis that helium in excess could have a different origin than the atmosphere.

5.2.4. Helium Isotopic Composition of Paleo-Fluids Trapped in Travertine

After evaluating the effect of secondary processes on He concentration and ${}^{3}\text{He}/{}^{4}\text{He}$ of FIs, we can now discuss the origin of paleo-fluids trapped in travertine at the time of their formation. For this purpose, to assess the atmospheric component of samples we plot ${}^{4}\text{He}/{}^{20}\text{Ne}$ versus ${}^{3}\text{He}/{}^{4}\text{He}$ not corrected for air contamination (Figure 11).

Samples from Reşadiye have ${}^{3}\text{He}/{}^{4}\text{He} \sim 1$ Ra and ${}^{4}\text{He}/{}^{20}\text{Ne}$ between 0.2 and 0.6 that are close to theoretical values in the atmosphere and ASW (${}^{3}\text{He}/{}^{4}\text{He} = 1$ Ra, ${}^{4}\text{He}/{}^{20}\text{Ne} = 0.318$ [AIR], and ${}^{4}\text{He}/{}^{20}\text{Ne} = 0.285$ [ASW at standard temperature and pressure]). This indicates that shallow waters that were circulating during the travertine deposition or studied travertine samples represent a very shallow portion of the fracture along which they precipitated. We argue that ${}^{4}\text{He}/{}^{20}\text{Ne}$ ratios slightly exceeding AIR and ASW values result from a low extent of fractionation of air component during the FI entrapment. Helium in the hot springs sampled over the Reşadiye area has ${}^{3}\text{He}/{}^{4}\text{He}$ of 0.36 Ra (Figure 11), indicating that helium content of modern fluids circulating in local fault systems likely implies mixture between crust and mantle reservoirs (Güleç et al., 2002). Reşadiye is located on the central NAFZ segment, where Tatar et al. (1996) reported the presence of Pliocene-Quaternary volcanics associated to the Niksar pull-apart basin formation explaining the ${}^{3}\text{He}$ excess recorded in fluids circulating in this NAFZ segment (De Leeuw et al., 2010; Güleç et al., 2002).

 3 He/ 4 He ratios in FIs trapped in Pamukkale travertines range between 0.5 and 1.0 Ra with 4 He/ 20 Ne between 0.3 and 3.1 (Figure 11). Most samples have appreciably different ratios from theoretical values in AIR and ASW, indicating the entrapment of fluids originating from distinct sources. A further sign in this direction comes from the amount of gas (H₂O, CO₂, N₂, and noble gas) trapped in FIs from Pamukkale, which is systematically higher than that extracted from the Reşadiye samples (Figures 8 and 9). Although crystallization conditions of travertines could play a role in the entrapment of FIs, as indicated by the size of calcite crystals, we argue that the difference in 3 He/ 4 He ratios further indicates that fluids circulating at the time of precipitation were also different.

In fact, the fluids trapped in Pamukkale travertines originated from the atmosphere-mantle-crust ternary mixing of the gases dissolved in the circulating waters. Four major thermal springs (T = 35.5 °C; Şimşek et al., 2000) emerging at the edge of Pamukkale travertine area discharge CO₂-dominated gases with ³He/⁴He up to 3.7 Ra (Ercan et al., 1995; Güleç et al., 2002; Mutlu et al., 2008; Karakuş & Şimşek, 2013; Güleç & Hilton, 2016; Pfanz et al., 2018, Figure 10). Those magmatic-like values are the highest recorded within the Büyük Menderes graben (Karakuş & Şimşek, 2013; Şimşek, 1990), suggesting that this area is characterized by a network of joints, fractures, and lithospheric faults that permit the rise of deep fluids, although evidences of magmatism were found in the neighboring area. For the Pamukkale area, Güleç and Hilton (2006) suggested that the transfer mechanism of heat and helium is accomplished by volcanic or by plutonic activity with no surface equivalent.

5.3. Origin of CO₂

 CO_2 plays the major role in travertine deposition. It is well known how CO_2 -rich waters enhance Ca dissolution and any change in the physical-chemical conditions (e.g., temperature drop or degassing) dramatically decreases the Ca solubility inducing its precipitation. As the Ca dissolution is a function of pH, the higher the dissolved CO_2 content, the higher the amount of dissolved Ca is and even up to the saturation. The CO_2 degassing occurs contemporary to Ca precipitation forming travertine deposits; thus, this process allows the solid deposits to trap microbubbles from the degassed gas phase.

Deposition of such huge size of travertine deposits requires vast amount of CO_2 . Considering that an organic CO_2 source is excluded based on the range of $\delta^{13}C_{CO2}$, the released CO_2 may have a crustal or mantle-

derived origin. Mantle-derived CO_2 can only be degassed from the melted portion of the mantle, for example, magma bodies intruded into shallow crustal layers as already observed along the southern Apennines (e.g., Italiano et al., 2001) or in Colorado Plateau region (Crossey et al., 2009), or in Baja California Peninsula (Batista Cruz et al., 2019). Recent experimental results, aimed to sketch different origin for terrestrial CO₂ and then degassing of mantle or mantle products, provided models on CO₂ generation as a result of hydrolysis (e.g., Kissin & Pakhomov, 1969) or metamorphic decarbonation processes (e.g., Gianelli, 1985; Kerrick & Connolly, 2001). Laboratory experiments combined with field observations (Italiano et al., 2008) pointed the attention on possible effective mechanochemical production of CO₂ in cold, seismic areas due to mechanical stress on carbonate rocks (Italiano, 2011). These experiments carried out by a ring mill demonstrated that stress application on calcite and calcite/clay mixture produces CO2 and CH4. Although the experimental approach cannot be compared to a natural system, the experiments show a way to model the processes occurring on a fault plane where mineralogical phases are involved and modified with the total reorganization of the crystalline lattice and the contemporary production of a gas phase. Such a model does not necessarily require thermal energy to break down the carbonate. As this energy is available only if a mantle contribution exists, the ${}^{3}\text{He}/{}^{4}\text{He}$ mixed with the CO₂-dominated gas phase should have a mantle signature (Batista Cruz et al., 2019; Italiano, 2011; Italiano et al., 2008).

In continental settings, similar to the NAFZ, the EAFZ or the Apennine chain, it was long established that the presence of mantle-He correlates well with tectonic and magmatic activity (Polyak & Tolstikhin, 1985). As such, ${}^{3}\text{He}/{}^{4}\text{He}$ was used in several tectonically active regions to identify mantle-derived products intruded at shallow levels in the crust (e.g., Italiano et al., 2001; Batista Cruz et al., 2019) or, contrastingly, to exclude the contribution of mantle-derived products in CO₂-rich fluids (Italiano et al., 2008). We suggest that the large amount of CO₂ dissolved in the groundwaters that originated the Pamukkale and Reşadiye travertines may also have and had a mainly crustal, metamorphic (i.e., stress-derived) origin.

5.4. Relations Between Tectonics and Fluid Circulation for Travertines Formation

The evidences from the geochemical features of paleo-fluids trapped in travertines from Reşadiye and Pamukkale areas and those from the local hot springs highlight a complex circulation system through faults and fractures within the upper crust. In both areas, we observe a difference between fluids circulating at the time of travertine precipitation and those currently feeding the local hot springs. This difference seems not systematic and reveals that travertines from Reşadiye and Pamukkale formed in different paleo-environmental and geo-tectonics conditions that are separately discussed.

In the case of Reşadiye travertines, FIs are mostly of atmospheric origin and related to the circulation of shallow meteoric waters besides local hot springs show a crustal-derived signature with a slight addition of mantle-derived He (3 He/ 4 He = 0.82–1.09 Ra; de Leeuw et al., 2010, Figure 11). To explain this difference, we propose three hypotheses.

- 1. Our samples represent a very shallow portion of the fracture along which travertines precipitated.
- 2. The fracture system through which Reşadiye travertines formed was different from that feeding present hot springs.
- 3. The CO₂ output and intensity of fluids circulation over the Reşadiye area changed in time.

In the first hypothesis, our samples represent a very shallow portion of the fracture systems responsible for the formation of travertines, where the circulation of meteoric water was dominant with respect to CO_2 -rich mantle-derived fluids. In support of this, we recall the young age of these travertines (245–14,678 years). If this is the case, then fluids circulating within the fracture systems are supposed to be isotopically identical to those feeding the hot springs.

The second hypothesis implies different fracture systems responsible for the travertine formation and hot springs circulation. If we assume that seismic activity enhances fracturing and increases permeability (e.g., Sturrock et al., 2017, and references therein), the first hypothesis would imply that fractures in which travertines formed were not active during the precipitation or the fracture formation was associated to low-magnitude and shallow seismicity with little effect on the permeability changes. However, there are no evidences in the area of a spatial and/or temporal variability in fluid composition of the hot springs, which

could lead to argue for the presence of different fracture systems. In fact, hot springs have a homogeneous composition and are likely fed by more interconnected faults that enable the circulation of nonatmospheric fluids.

The third hypothesis correlates the formation of travertines to the total CO_2 output over the Reşadiye area. This implies variable balance of mixing between deep and shallow fluids, which might change the kinetics of travertine precipitation. Fluids feeding the hot springs were originally circulating within the same fracture system along which travertines formed. There are several evidences that vein mineralization in fractures occurs over short timescales after the seismic activity (Moore et al., 2000; Uysal et al., 2007; Smeraglia et al., 2018, and references therein) because of variable amounts of dissolved CO_2 in the circulating fluids. The dissolved CO_2 content affects the precipitation kinetics of travertine. CO_2 contents above the equilibrium allow fast $CaCO_3$ precipitation during fluid uprising inducing the fracture self-sealing and progressive decrease of fluid circulation. This process may lead to a near-complete degassing of ³He, and the resultant FIs would have a noble gas composition identical to ASW.

In the case of Pamukkale, FIs show a significant addition of mantle-derived ³He and atmosphere-derived He (${}^{3}\text{He}/{}^{4}\text{He}$ down to 0.5 Ra, corresponding to a minimum of ~6% of mantle contribution, Figure 11. For this calculation we assumed 8 Ra for the local mantle; Aral et al., 2015; Italiano et al., 2017). We argue that these travertines formed in a system of lithospheric-type fractures that able to enhance the circulation of mantle fluids. Different from travertines, recent hot springs display a clear magmatic signature (${}^{3}\text{He}/{}^{4}\text{He} = 3.7$ Ra), confirming the rise of deep fluids. In addition, the Pamukkale FIs systematically show higher gas content in comparison to Reşadiye, suggesting an additional CO₂ input, possibly originated from a mechanochemical process. This implies that fault reactivation in coincidence of energetic seismogenetic activity provided the necessary mechanical energy for devolatilization of carbonate rocks. This fits with the evidence that the Çürüksu graben, the eastern segment of the Büyük Menderes graben, is one of the most seismically active regions in Turkey (e.g., Altunel & Hancock, 1993; Altunel & Karabacak, 2005; Karakuş & Şimşek, 2013). We can now evaluate the aforementioned three hypotheses proposed for Reşadiye to explain the compositional difference of fluids that precipitated the travertines and fed the local hot springs.

In favor of the first hypothesis, we highlight the enormous ${}^{3}\text{He}/{}^{4}\text{He}$ variability recorded in hot springs moving westward in respect to Pamukkale area, where the ratios drop down to 0.16 Ra (west of Germencik) due to a progressive dilution of mantle volatiles resulting from the systematic addition of ${}^{3}\text{He}$ -depleted crustal gas contribution (Karakuş & Şimşek, 2013). Wiersberg et al. (2011) suggested that the regional trend of ${}^{3}\text{He}/{}^{4}\text{He}$ within the Büyük Menderes graben correlates with the rates of active crustal deformation as the highest helium isotopic ratios are recorded in coincidence of the largest extension and shear strain rates. Another support to this hypothesis is the older formation time of the travertines (24,542–49,629 years) with respect to Reşadiye, which could record a different tectonic setting with respect to present. Thus, the formation of travertines could have been preseismic, sin-seismic, or postseismic.

However, we cannot rule out hypotheses 2 and 3. In case of hypothesis 3, the formation of travertines postponed the occurrence of energetic seismic events that would have modified the permeability of faults interconnecting the zones between deep and shallow crust (e.g., Caine et al., 1996; Frima et al., 2005; Olierook et al., 2014; Ran et al., 2014), as well as fluids circulation, reducing the ascent of mantle-derived fluids. This hypothesis is supported by the ongoing seismic unrest in this part of Turkey (Karakuş & Şimşek, 2013; Uysal et al., 2007, 2009).

The study of fluids geochemistry trapped in travertines at the time of their formation is somehow pioneering in trying to reconstruct the seismic history and evaluating the potential hazardousness of active seismogenetic areas. At the best of our knowledge, only a few studies (Pik & Marty, 2009; Pili et al., 2011; Smeraglia et al., 2018) already used a similar approach for analogous applications, revealing successful and promising results for this important and actual topic. The travertine formation is also closely related to CO_2 degassing and dissolution in groundwaters, which implies the CO_2 origin, mixings, and degassing processes. Nevertheless, further investigations are still necessary to improve the potential outcomes from this approach, which requires a multidisciplinary study.

6. Conclusions

We investigated the mineralogy and geochemistry of FIs of travertine deposits from Pamukkale and Reşadiye (western and northern Turkey, respectively), which are located in proximity to thermal springs in regions of high seismicity. The studied travertines formed \sim 24,500–50,000 years (Pamukkale) and \sim 240–14,600 years BP (Reşadiye). This study leads to the following evidences.

- 1. The REE patterns of the fissure travertines from Pamukkale and Reşadiye vein travertines are comparable and do not show any similarities to those of the host limestone due to transient nature of the water-rock interaction during seismically controlled groundwater movements.
- 2. δ^{13} C and δ^{18} O values of bulk travertines suggest that the temperature of travertine formation was <60 °C, and that CO₂ involved in the deposition originated from the crust (mechanochemical rather than organic) and the mantle.
- 3. FIs are mainly primary type and showed homogenization temperatures from 114 to 148 °C for Reşadiye travertines and from 132 to 145 °C for Pamukkale travertines. This implies that during the seismic events deeply circulating hot waters were rapidly involved in travertine precipitation but did not reach the surface.
- 4. H₂O is the major component of FIs followed by CO₂, with an important contribution by atmospherederived fluids. The highest gas content was found in Pamukkale travertines, which reasonably formed at higher depths than those from Reşadiye.
- 5. The ³He/⁴He values filtered for cosmogenic ³He addition (due to exposure of travertines to cosmic rays) suggest a shallow formation of Reşadiye travertines, in accordance with evidences from the mineralogy and geochemistry of FIs. Instead, travertines from Pamukkale formed along lithospheric faults that enhanced the mixing of crustal-, mantle-, and atmosphere-derived fluids.

This work opens new perspectives for better understanding the origin of fluids during travertine formation and the role of their circulation in response to seismogenetic activity.

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