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RESEARCH ARTICLE
10.1029/2021TC006824

Key Points:

- U-Pb zircon ages in the Carboniferous to Triassic sandstones of the Istanbul Zone are mainly Carboniferous and Late Neoproterozoic–Cambrian
- The Istanbul Zone lacks Carboniferous igneous/metamorphic events, while they are characteristics of the Armorican Sakarya and Strandja zones
- The contact between the Avalonian Istanbul Zone and Armorican Sakarya Zone represents the eastward continuation of the Rheic Suture

Supporting Information:

Supporting Information may be found in the online version of this article.

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Citation:

Akdoğan, R., Hu, X., Okay, A. I., Topuz, G., & Xue, W. (2021). Provenance of the Paleozoic to Mesozoic siliciclastic rocks of the Istanbul Zone constrains the timing of the Rheic Ocean closure in the Eastern Mediterranean region. *Tectonics*, *40*, e2021TC006824. https://doi.org/10.1029/2021TC006824

Received 23 MAR 2021
Accepted 1 NOV 2021

Provenance of the Paleozoic to Mesozoic Siliciclastic Rocks of the Istanbul Zone Constrains the Timing of the Rheic Ocean Closure in the Eastern Mediterranean Region

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Abstract The Intra-Pontide Suture between the Istanbul and Sakarya zones was regarded debatably either as a Neotethyan Suture or a trace of the Rheic Suture in Turkey. Here, we present U-Pb ages and Lu-Hf isotopic compositions of detrital zircons from the Silurian to Triassic sandstones of the Istanbul Zone. Upper Silurian-Lower Devonian sandstone is dominated by Mesoproterozoic zircons (1950–900 Ma), with subordinate peaks at the latest Neoproterozoic to Silurian (750–420 Ma) and mid-Archean (2850–2750 Ma) confirming their Avalonian affinity. Detrital zircon ages from Carboniferous-Triassic sandstones show major peaks at Carboniferous-Early Permian (360–270 Ma) and Late Neoproterozoic–Cambrian (750–480 Ma) while Mesoproterozoic zircons are insignificant. The εHf(t) values of the detrital zircons exhibit a wide range from −21.3 to +11.7, and over 62% of zircon grains have negative values, largely coinciding with those of the Paleozoic igneous rocks in the Sakarya Zone. The Istanbul Zone is devoid of Carboniferous igneous and/or metamorphic rocks. Therefore, abundant Carboniferous zircons and the disappearance of the Mesoproterozoic zircons in the Carboniferous-Triassic sandstones of the Istanbul Zone require juxtaposition with a continental domain similar to the Sakarya and Strandja zones, which are characterized by widespread Carboniferous magmatism. We suggest that the Intra-Pontide Suture represents the trace of the Rheic Suture in Turkey, along which Avalonia and Armorica collided during the Early Carboniferous.

1. Introduction

The Paleozoic evolution of Europe and Eastern Mediterranean region involves successive rifting of the continental blocks such as Avalonia and Armorica from the northern margin of Gondwana-Land to the south, and their progressive accretion to the northerly continental domain is made of Laurentia and Baltica (e.g., Cocks & Torsvik, 2002; Meschede & Warr, 2019, pp. 37–40; Murphy et al., 2006; Nance et al., 2010, 2012; Okay & Topuz, 2017; Stampfli et al., 2002, 2013; Figure 1). The rifting of the Avalonia is thought to have occurred during Late Cambrian-Early Ordovician, and the amalgamation to Laurentia and Baltica during Late Ordovician-Silurian, leading to the formation of Laurussia (e.g., Cocks & Torsvik, 2002; Nance et al., 2010). On the other hand, Armorica has rifted from the northern margin of Gondwana during Late Ordovician to Silurian, and amalgamated to Laurussia by Early to Late Carboniferous (e.g., Nance et al., 2012, 2010; Meschede & Warr, 2019, pp. 37–40; Topuz et al., 2020). The oceanic domain, which opened as a result of detachment of Avalonia from Gondwana and closed due to collision of the Armorica with Laurussia, is called the Rheic Ocean. The closure of the Rheic Ocean and subsequent collision of Gondwana and Laurussia led to the Variscan Orogeny and resulted in the formation of Pangea.

The Rheic Suture between Armorica and Laurussia is well-documented in Europe. However, the easterly continuation of the Rheic Suture is still not well understood. This is due to the fact that parts of the Variscan orogenic belts underwent rifting and opening of the Neo-Tethyan Ocean during Permo-Triassic time (e.g., Şengör & Yılmaz, 1981; Stampfli & Borel, 2002; Stampfli & Kozur, 2006). These Neo-Tethyan oceanic domains were closed during the course of the Alpine orogeny (e.g., Schmid et al., 2020; Stampfli & Borel, 2002).

In the Eastern Mediterranean region, the Istanbul Zone, Moesian Platform, and Scythian Platform were regarded as eastern extension of Avalonia on the basis of its stratigraphic similarities and the detrital zircon pattern of the basement rocks (e.g., Okay et al., 2011; Ustaömer et al., 2011). On the other hand, due to similar pre-Mesozoic basement with widespread occurrence of Carboniferous crystalline rocks, the Sakarya and Rhodope-Strandja

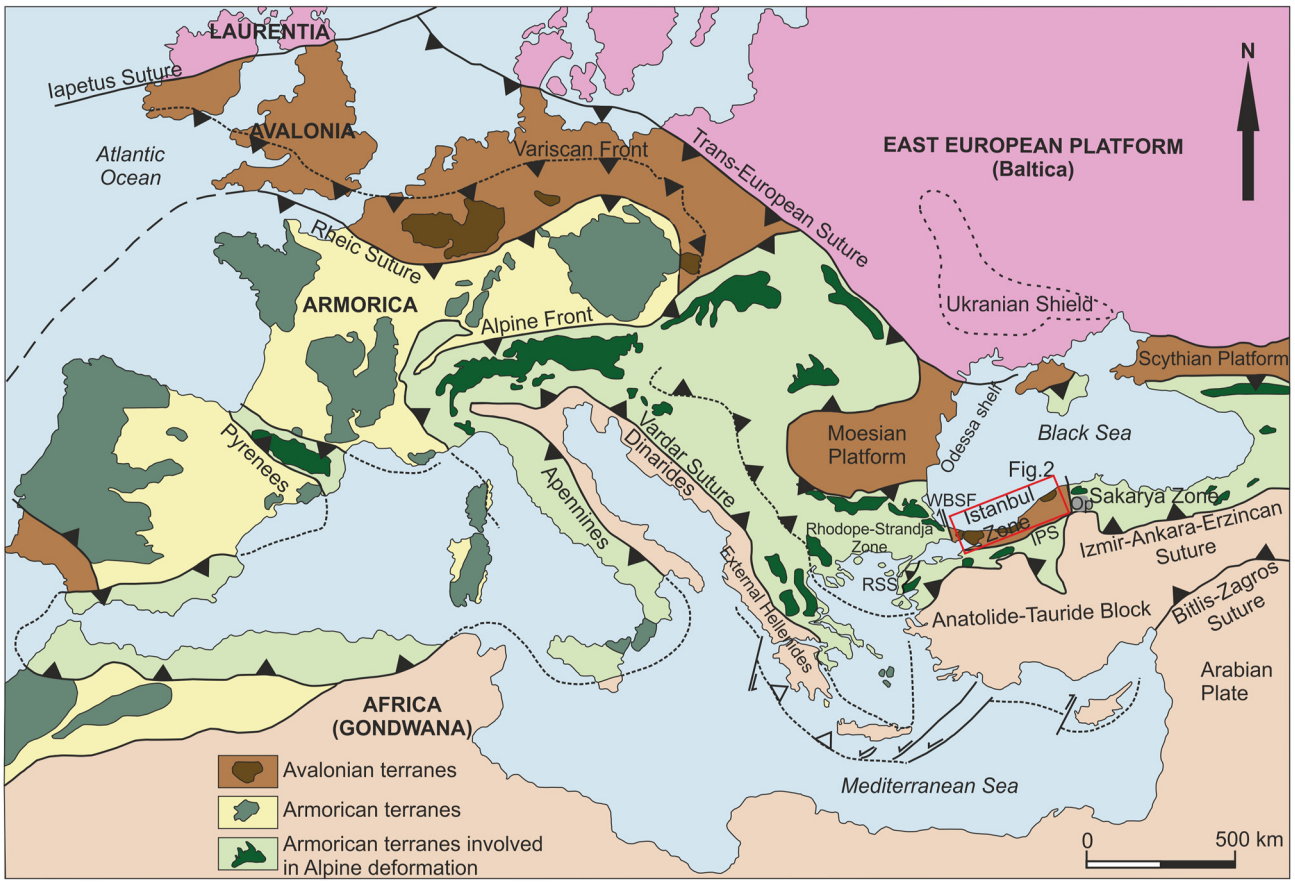

Figure 1. Simplified tectonic map of the Eastern Europe and Black Sea region, emphasizing Avalonian and Armorican terranes (modified after Topuz et al., 2020). WBSF, West Black Sea Fault; IPS, Intra-Pontide Suture; RSS, Rhodope-Strandja-Sakarya Suture; Op, Upper Cretaceous ophiolitic mélange.

zones were thought to be parts of Armorica in Europe (e.g., Okay & Topuz, 2017; Okay et al., 2008; Ustaömer, Robertson, Ustaömer, et al., 2012; Ustaömer, Ustaömer, & Robertson, 2012). However, the suture zone between the Avalonian Istanbul Zone and the Armorican Sakarya Zone in the south, called as the Intra-Pontide Suture, has long been regarded as a Neo-Tethyan suture (e.g., Marroni et al., 2020; Şengör et al., 2019; Şengör & Yılmaz, 1981), and there is no consensus on the timing of the opening and closing of the intervening ocean (e.g., Akbayram, Okay, & Satır, 2013; Akbayram, Şengör, & Özcan, 2016; Elmas & Yiğitbaş, 2001, 2005; Okay & Topuz, 2017; Okay et al., 2011; Robertson & Ustaömer, 2004; Şengör & Yılmaz, 1981). In this study, we examine the provenance of the Paleozoic to Lower Mesozoic sedimentary rocks of the Istanbul Zone integrating U-Pb detrital zircon ages, Th/U values, and Lu-Hf isotope analysis of the dated zircon grains. Our new dataset combined with previous geochronological data from Paleozoic-Mesozoic sedimentary rocks indicates that the Istanbul Zone was amalgamated with an Armorican type terrane, such as the Sakarya and Rhodope-Strandja zones during Early Carboniferous, and the Intra-Pontide Suture probably represents the eastward continuation of the Rheic Suture, which was reworked by the Alpine Orogeny.

2. Geological Background

The Pontide mountain belt, the northernmost tectonic unit of Turkey, is made of three continental blocks called the Istanbul Zone, Sakarya Zone, and Rhodope-Strandja Zone (Okay & Tüysüz, 1999).

2.1. The Istanbul Zone

Istanbul Zone is a 400 km long and 75 km wide continental fragment located between Rhodope-Strandja Zone in the west, the Sakarya Zone in the south and east, and Black Sea in the north (Figure 1). The boundary between

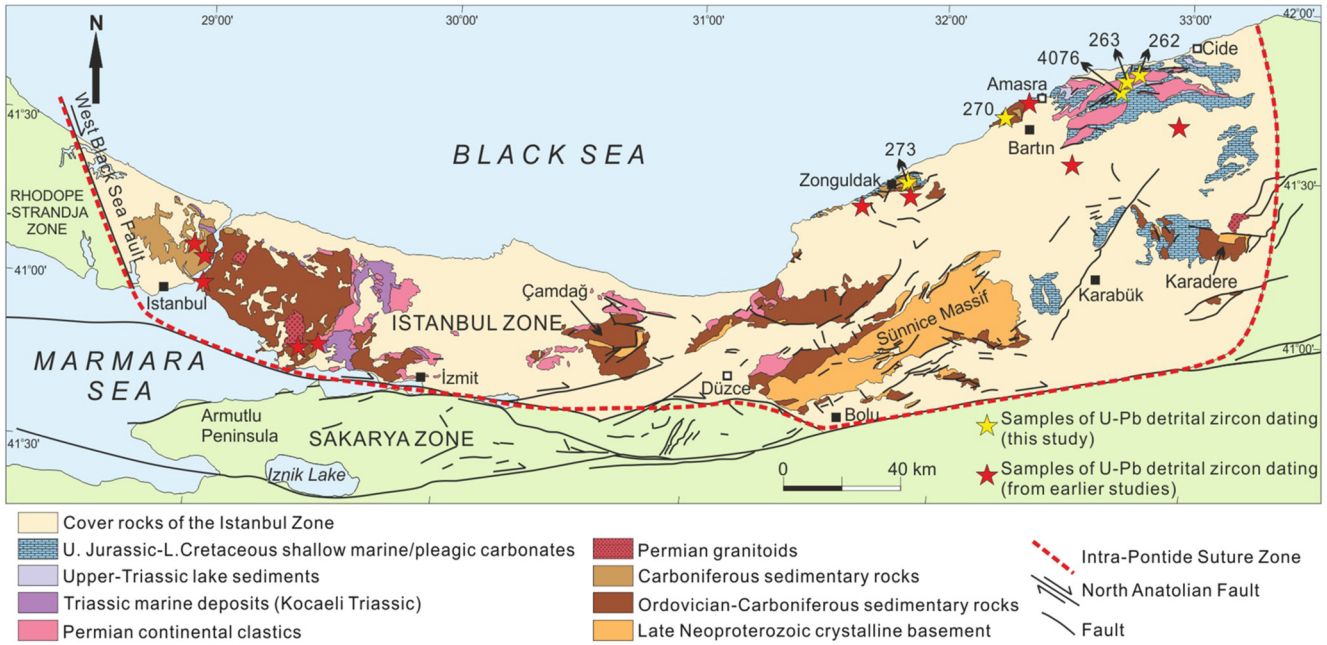

Figure 2. Geological map of the Istanbul Zone showing the pre-Cretaceous rocks (modified after Okay et al., 2013; Türkecan & Yurtsever, 2002). Samples used for U-Pb detrital zircon dating in earlier studies are also shown (Akdoğan et al., 2017; Okay & Topuz, 2017; Okay et al., 2011; Ustaömer et al., 2011).

the Rhodope-Strandja Zone and Istanbul Zone is represented by right lateral strike slip fault passing through a wide valley filled up by Eocene-Oligocene sedimentary rocks, called Western Black Sea Fault, which offsets the Upper Cretaceous volcanic arc north of Istanbul (Okay et al., 1994, 2017, Figure 2). Recently, Ülgen et al. (2018) argued that the boundary is a thrust fault. However, the Triassic sequences north of Istanbul attributed by Ülgen et al. (2018) to the Strandja Massif, form part of the Triassic sequence of the Istanbul Zone (e.g., Kaya & Lys, 1980), and the thrust fault is a well-known Eocene structure, which extends for more than 60 km east of the Bosphorus (Akartuna, 1963; Baykal, 1942). The Istanbul Zone is bounded in the south at present by the active dextral North Anatolian Fault (NAF). The pre-NAF nature of boundary between the Istanbul Zone and the Sakarya Zone is debated (e.g., Akbayram, Okay, & Satır, 2013; Akbayram, Şengör, & Özcan, 2016; Bozkurt et al., 2012; Elmas & Yiğitbaş, 2001, 2005; Göncüoğlu & Erendil, 1990; Göncüoğlu et al., 2008; Görür & Okay, 1996; Robertson & Ustaömer, 2004; Okay & Topuz, 2017; Okay, et al., 1994; Özcan et al., 2012; Şengör & Yılmaz, 1981; Tüysüz, 1999; Yılmaz et al., 1995). Before the opening of the Black Sea, the Istanbul Zone was located on the southern margin of Odessa Shelf north of the Black Sea and was contiguous with the Moesian Platform; it moved to the present position during Late Cretaceous opening of the Western Black Sea basin (Okay et al., 1994; Figure 1).

The Istanbul Zone has a Late Neoproterozoic granitic and metamorphic basement (Chen et al., 2002; Ustaömer et al., 2005). The basement comprises (i) medium-to high-grade metamorphic rocks consisting of quartzofeldspathic gneiss and amphibolite, (ii) disrupted metaophiolite consisting of amphibolite/metagabbro and metaperidotite, and (iii) meta-andesite to -rhyolite intercalated with metasedimentary rocks. These metamorphic rocks are intruded by voluminous granites with U-Pb zircon ages of 565–576 Ma (Chen et al., 2002; Okay et al., 2008; Ustaömer & Rogers, 1999; Ustaömer et al., 2005; Yiğitbaş et al., 2004) (Figures 2 and 3). A continuous, > 5 km thick sedimentary succession of Ordovician to Carboniferous age unconformably overlies the crystalline basement (Dean et al., 2000; Özgül, 2012).

In the Istanbul region, the Paleozoic sequence forms a transgressive series starting with Ordovician lacustrine shales, siltstones, fluviatile sandstone, and conglomerates overlain by shallow marine Ordovician quartzites. The quartzites pass up into a clastic sequence of siltstone, sandstone and shale of late Ordovician to Early Silurian age, which are overlain by Silurian-Lower Devonian shallow marine limestones (Haas, 1968; Özgül, 2012; Sayar & Cocks, 2013; Sayar, 1979, 1984, and references therein). The limestones are overlain by Lower to Middle Devonian siltstones and shales rich in brachiopods, trilobites, and corals. This is followed by Middle Devonian to

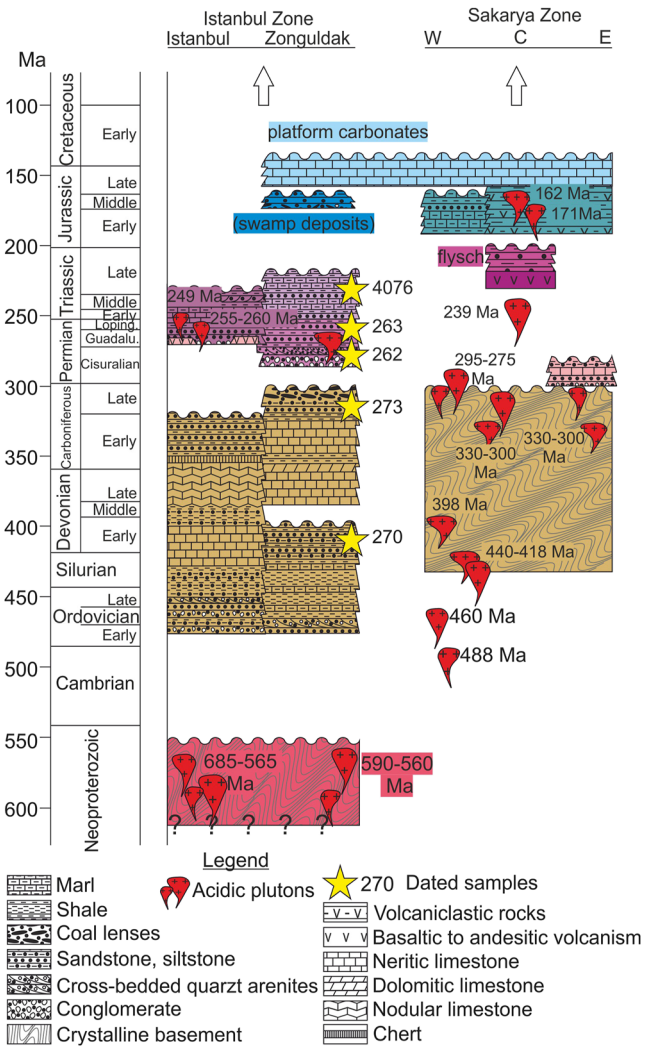

Figure 3. Generalized chrono-stratigraphic chart of the Istanbul and Sakarya zones. The time scale is after Gradstein et al. (2012). Isotopic ages are from Aysal et al. (2012, 2018), Ballato et al. (2018), Bozkurt et al. (2012), Chen et al. (2002), Dokuz (2011), Dokuz et al. (2010), Kaygusuz et al. (2012, 2016), Nzegge (2008), Nzegge et al. (2006), Okay et al. (2008, 2013, 2015), Sunal (2012), Topuz et al. (2010, 2020), Ustaömer et al. (2005), Ustaömer, Robertson, Ustaömer et al. (2012), and Ustaömer, Ustaömer and Robertson (2012).

lowest Carboniferous (Tournaisian) deep marine limestones and shales (Çapkınoğlu, 2001, 2005; Göncüoğlu et al., 2004; Okay et al., 2020). The pelagic limestones are overlain by a characteristic thin horizon of black radiolarian cherts of Early Carboniferous (Tournasian) age (Noble et al., 2008). In the Istanbul region, the Paleozoic sequence ends with a thick sequence of Lower Carboniferous siliciclastic turbidites. The Paleozoic sequence in the eastern part of the Istanbul Zone shows some differences from the western part: it starts with Ordovician to Silurian sandstones, graptolite-bearing shales and limestones, which are overlain by Devonian to Lower Carboniferous shallow marine carbonates. The carbonates are overlain by a thick sequence of coal-bearing sandstone and shale of Late Carboniferous age. The Ordovician to Carboniferous sequence of the Istanbul Zone was deformed during the Late Carboniferous by folding and thrusting and are intruded by middle-upper Permian granitoids (Aysal et al., 2018; Okay et al., 2013).

The Paleozoic series are unconformably overlain by thick (>3000 m) Permian continental red beds (Çakraz Formation; Gand et al., 2011; Okuyucu et al., 2017; Stolle, 2016; Figures 2 and 3). There are no Permian marine deposits in the Istanbul Zone. Permian continental deposits and Paleozoic succession in the western part of the Istanbul Zone are overlain by an angular unconformity by the Triassic shallow to deep marine siliciclastic rocks and carbonates, known as Kocaeli Triassic units (Tüysüz et al., 2004 and references there in). The red continental deposits of the Çakraz Formation are overlain by the lacustrine sediments of the Upper Triassic Çakrazboz Formation in the Zonguldak region (Alişan & Derman, 1995), which are in turn unconformably overlain by coal-bearing Middle Jurassic paralic deposits (Himmetpaşa Formation; Derman et al., 1995).

The Upper Jurassic–Lower Cretaceous (Kimmeridgian–Berriasian) shallow-marine platform carbonates (İnaltı Formation), locally with a basal continental clastic horizon, lie unconformably over the Permo–Triassic series of the Istanbul Zone, and extend east to the Sakarya Zone; the Upper Jurassic limestones are the first common cover rocks over the Istanbul and Sakarya zones (e.g., Okay et al., 2018; Tüysüz, 1999). The deposition of the Upper Jurassic–lowermost Cretaceous shallow-marine carbonates was followed by uplift and erosion during Valanginian–Hauterivian. The limestones are in turn unconformably covered by the Lower Cretaceous (Barremian-Aptian) clastic–carbonate shelf deposits near Zonguldak and Amasra regions and siliciclastic turbiditic sequence in the south-southeastern parts of Bartın region.

2.2. The Sakarya Zone

The Sakarya Zone is the main tectonic unit of the Pontides, extending 1500 km north of the İzmir-Ankara-Erzincan Suture (Figures 1 and 2). Pre-Jurassic basement of the Sakarya Zone is represented by three main components: (i) Carboniferous high temperature-low pressure (HT-LT) metamorphic rocks (e.g., Okay, 1996; Topuz et al., 2004, 2007), (ii) voluminous Carboniferous granitoids (e.g., Dokuz, 2011; Nzegge et al., 2006; Okay et al., 1996; Topuz et al., 2010; Ustaömer, Robertson, Ustaömer, et al., 2012; Ustaömer, Ustaömer, & Robertson 2012) are covered by unmetamorphosed Permo-Carboniferous sedimentary rocks (e.g., Çapkınoğlu, 2003; Kandemir & Lerosey-Aubril, 2011; Okay & Leven, 1996), (iii) Permo-Triassic accretionary complex (Okay & Göncüoğlu, 2004; Okay & Monié, 1997; Okay et al., 2002; Topuz et al., 2014, 2018; Ustaömer & Robertson, 1994, Figure 3). There are also small stocks of the Mid to Upper Ordovician (ca. 460 Ma) and Devonian (ca. 390–400 Ma) metagranites intruding undated low-grade metamorphic rocks in the western part of the Sakarya Zone (Aysal et al., 2012; Okay et al., 1996, 2008; Sunal, 2012). On the basis of the presence of Carboniferous eclogites at the Fore Range Zone of the Greater Caucasus (Perchuk & Philippot, 1997; Somin, 2011), the HT-LP metamorphism is thought to have occurred during

Table 1
Sample Information Used for U-Pb Detrital Zircon Geochronology and Lu-Hf Isotope Analysis

			Coordinates UTM (36T)		Description			Zircon		
	Sample ID	Location	Easting	Northing	Formation	Lithology	Stratigraphic age	Number of analysis	Number of concordant analysis (90%–110%)	Number of Lu-Hf isotope analysis
1	270	Amasra (Bartın)	0,435,819	4,613,298	Fındıklı	Sandstone	Upper Silurian-Lower Devonian	119	100	89
2	273	Kozlu (Zonguldak)	0,402,302	4,586,159	Kozlu	Sandstone	Upper Carboniferous	120	84	-
3	262	Kurucaşile (Bartın)	0,478,506	4,629,574	Çakraz	Sandstone	Permian	120	102	98
4	263	Kurucaşile (Bartın)	0,477,486	4,626,916	Çakraz	Sandstone	Permian	150	120	–
5	4076	Kurucaşile (Bartın)	0,475,619	4,623,708	Çakrazboz	Sandstone	Upper Triassic	180	80	76

early Carboniferous at the mid-lower crustal part of a magmatic arc (Okay & Topuz, 2017). All these basement units were unconformably overlain by Jurassic volcanic and volcaniclastic rocks (Akdoğan et al., 2018; Altıner et al., 1991; Genç & Tüysüz, 2010; Kandemir & Yılmaz, 2009; Şen, 2007). Upper Jurassic-Lower Cretaceous shallow marine carbonates lie over the volcaniclastic rocks of the Sakarya Zone and also pre-Jurassic basement of the Istanbul Zone (Altıner et al., 1991; Okay et al., 2018; Tüysüz, 1999; Vincent et al., 2018, Figures 2 and 3).

2.3. The Rhodope-Strandja Zone

The Rhodope-Strandja Zone is located between the Moesian Platform to the north and the Sakarya Zone to the south (Okay & Tüysüz, 1999, Figures 1 and 2). It is delimited by the dextral strike-slip West Black Sea Fault in the east (Okay et al., 1994). The Rhodope-Strandja Zone has a polymetamorphic crystalline basement. An earlier episode of metamorphism and deformation is thought to have taken place during Carboniferous (Okay et al., 2001). The rock types involved in Carboniferous metamorphism range between Upper Neoproterozoic metagranites and Paleozoic metasedimentary rocks, which are intruded by voluminous Upper Carboniferous and Permian granites (Okay et al., 2001; Sunal et al., 2006, 2008; Şahin et al., 2014). Triassic to Middle Jurassic continental to shallow marine sedimentary rocks were deposited over this basement. The whole sequence was metamorphosed and deformed at Late Jurassic-Early Cretaceous mainly in greenschist facies (Okay et al., 2001; Sunal et al., 2011). The metamorphic rocks are unconformably overlain by earliest Upper Cretaceous (Cenomanian) shallow marine sandstones that pass up into a thick sequence of volcanic and volcanogenic rocks of Late Cretaceous age.

The Paleozoic basement rocks of the Rhodope-Strandja Zone resemble those of the Sakarya Zone. Therefore, they are regarded as a single continental block during the Paleozoic (e.g., Okay & Topuz, 2017; Okay et al., 2001). However, their post-Triassic sequences and Late Jurassic-Early Cretaceous metamorphism are unknown in the Sakarya Zone, suggesting that both zones underwent different geodynamic evolutions. This is testified by the presence of the Late Cretaceous high-pressure metamorphic rocks and ophiolitic mélanges (Aygül et al., 2012; Beccaletto & Jenny, 2004; Okay & Satır, 2001; Okay et al., 2001; Topuz et al., 2008). The exact timing of the rifting of the Sakarya and Rhodope-Strandja zones are unconstrained. The suture separating the Sakarya Zone and Rhodope-Strandja zones were regarded as westward elongation of the Intra-Pontide suture, which separates the Sakarya and Istanbul zones (e.g., Marroni et al., 2020; Şengör & Yılmaz, 1981, Figure 1). However, no Late Cretaceous high-pressure rocks have been documented from the Intra-Pontide Suture between the Istanbul and Sakarya Zones.

3. Analytical Methods

In order to constrain the source areas of the Paleozoic to Mesozoic clastic rocks of the Istanbul Zone, we performed petrographic observations, U-Pb detrital zircon dating, and Lu-Hf isotope analysis on five sandstone samples. Internal structure and the Th/U values of the dated zircons are also used to discriminate their origin. The UTM coordinates of the investigated samples and short summary of the analytical data are given in Table 1, and

the sample locations are shown in the geological map in Figure 2. The petrographic descriptions of the samples are given in Text S1.

Detrital zircon grains were separated using conventional separation techniques including crushing, sieving, washing, and magnetic and heavy liquid separation at Mineral Separation Laboratories of Eurasian Institute of Earth Science Istanbul Technical University (see Text S2). Zircons were randomly hand-picked under binocular microscope from heavy mineral separates. Hand-picked zircons were placed over a double-sided band and embedded into an epoxy resin. The epoxy mounts were ground and polished in order to reveal the internal structure of zircons. Cathode-luminescence (CL) images were taken from the polished mounts by an electron-scanning microscope with an attached cathode-luminescence detector in State Key Laboratory for Mineral Deposits Research of the Nanjing University. A laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS, ThermoFisher Scientific iCAP QR ICP-MS coupled to a Geolas 193 nm laser system) at the State Key Laboratory for Mineral Deposits Research of the Nanjing University was used for U-Pb zircon dating of the zircons. Analytical procedure for U–Pb dating is given in Text S3, and all analytical results are listed in Table S1.

Zircon Hf isotopic analyses were carried out at the State Key Laboratory for Mineral Deposits Research, Nanjing University, using a Neptune plus MC-ICP-MS with the ESI NWR193HE laser ablation system. Hf isotopic measurements were performed on the same spots or the same age domains of the zircon grains with concordant U-Pb age (discordance <10%). Analytical procedure for Hf measurements is given in Text S4, and the results are given in Table S2.

4. Analytical Results

4.1. Zircon Morphology, Internal Structure and Origin

The CL images of the dated zircon grains mostly exhibit a clear oscillatory zonation and sector zoning (Figure S2 in Supporting Information S1). Shapes of zircons range from nearly euhedral to rounded. The rounded grains make >70% (visual estimation) of the detrital zircons.

U and Th concentrations of the dated zircons form the Upper Silurian-Lower Devonian sandstone (sample 270, Fındıklı Formation) range 12–571 and 5–397 ppm, respectively, while those from the Upper Carboniferous sandstone (sample 273) are 51–1096 and 13–735 ppm, respectively (Table S1). Zircons from these two samples generally have quite similar Th/U ratios ranging from 0.13 to 2.78 and from 0.13 to 2.40, respectively. Only one grain from both samples has Th/U ratio less than 0.1. Generally, zircons with Th/U values below 0.1 are attributed to metamorphic origin, and those with Th/U values above 0.1 to igneous origin (e.g., Belousova et al., 2002; Hoskin & Ireland, 2000; Hoskin & Schaltegger, 2003; Rubatto, 2002). Permian continental sandstone samples from the Çakraz Formation (samples 263 and 262) have U and Th concentrations ranging from 26 to 1282 ppm and from 5 to 1661 ppm, respectively (Table S1). Th/U ratios of the zircons from sample 263 span 0.01 to 5.5 and those from the sample 262 range from 0.22 to 1.52. Detrital zircons from these samples have predominantly Th/U ratios >0.1. There are only five grains with Th/U ratio <0.1 from sample 263. U and Th values from of the detrital zircons from Upper Triassic sandstone sample of Çakrazboz Formation (sample 4076) are 19–897 ppm and 10–549 ppm, respectively. The Th/U ratios are 0.11–2.59. Based on Th/U ratios, we can conclude that the dated zircons were overwhelmingly derived from igneous rocks, and those of metamorphic origin are minimal. This is in line with the internal structures of the zircons, which commonly exhibit oscillatory and sector zoning (Figure S2 in Supporting Information S1).

4.2. U-Pb Detrital Zircon Ages

A total of 645 spot analyses were performed on detrital zircons from five sandstone samples of Paleozoic to Mesozoic rocks of the Istanbul Zone. 486 zircon grains (75% of the total population) yielded concordant U–Pb ages at 90%–110% level and are used in this study (Tables 1 and S1).

The Upper Silurian-Lower Devonian sandstone (sample 270) yielded 100 concordant U-Pb zircon ages (Tables 1 and S1). The obtained ages range between 2954 and 434 Ma (Figure 4). Late Paleoproterozoic-early Neoproterozoic zircons (2184–919 Ma; 79% of the concordant zircon population) dominate the zircon population with less pronounced late Neoproterozoic-early Cambrian (628–487 Ma; 7%) zircons. There are also tiny clusters

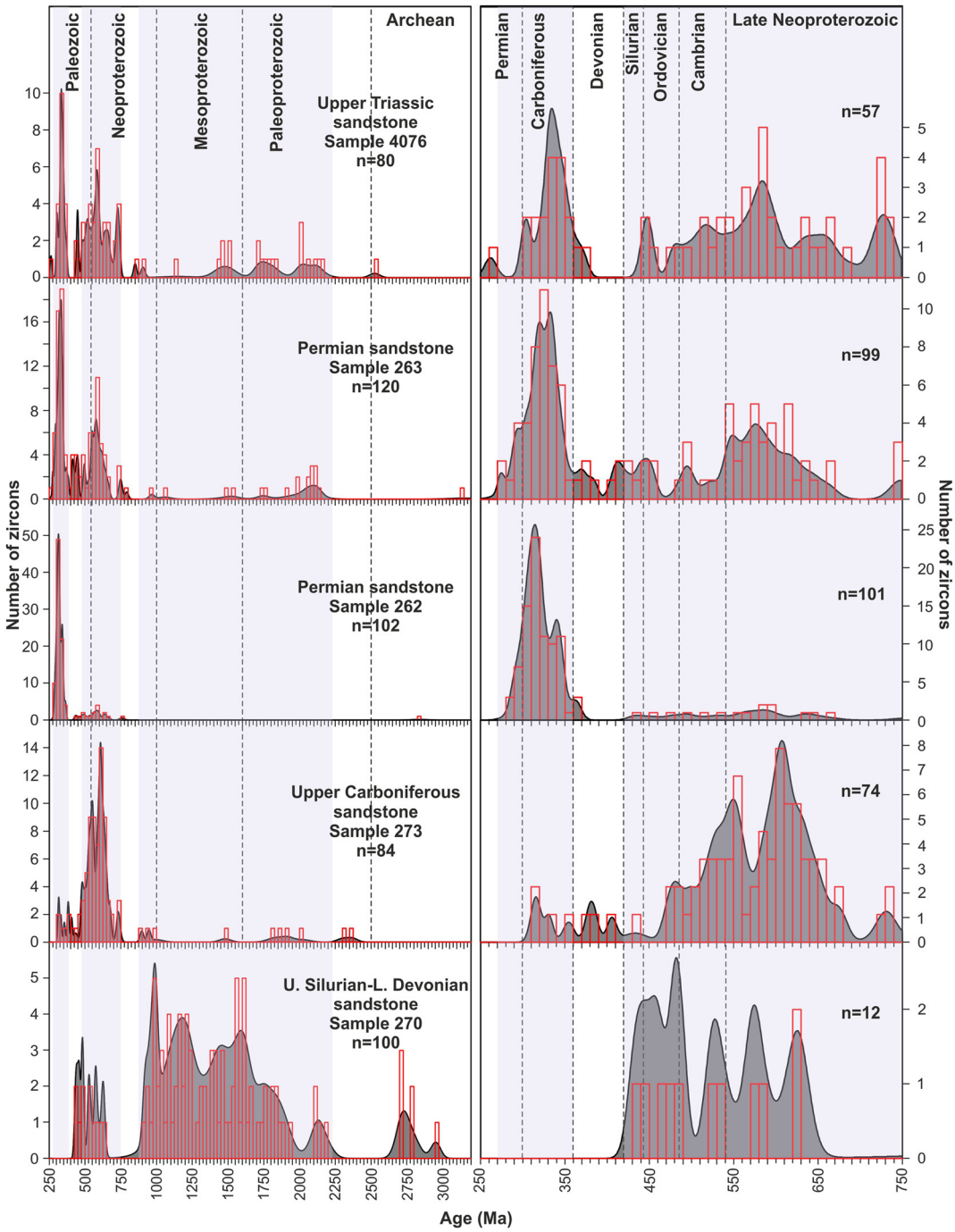

Figure 4. Age histogram with probability density curves of five sandstone samples from the Paleozoic to Mesozoic successions of the Istanbul Zone. Histograms on the right show the late Neoproterozoic and Phanerozoic zircons from of the same sample.

of Ordovician-early Silurian (539–434 Ma; 4%), middle Paleoproterozoic (2185–2110 Ma; 4%), and Archean (2955–2709 Ma; 6%) zircons.

Out of 120 analyzed zircons from the Upper Carboniferous sandstone (sample 273), 84 grains yielded concordant U-Pb zircon ages (Tables 1 and S1). The obtained ages range between 2371 and 315 Ma (Figure 4). Late Neoproterozoic-early Cambrian zircons (740–495 Ma; 74% of the concordant zircon population) dominate the

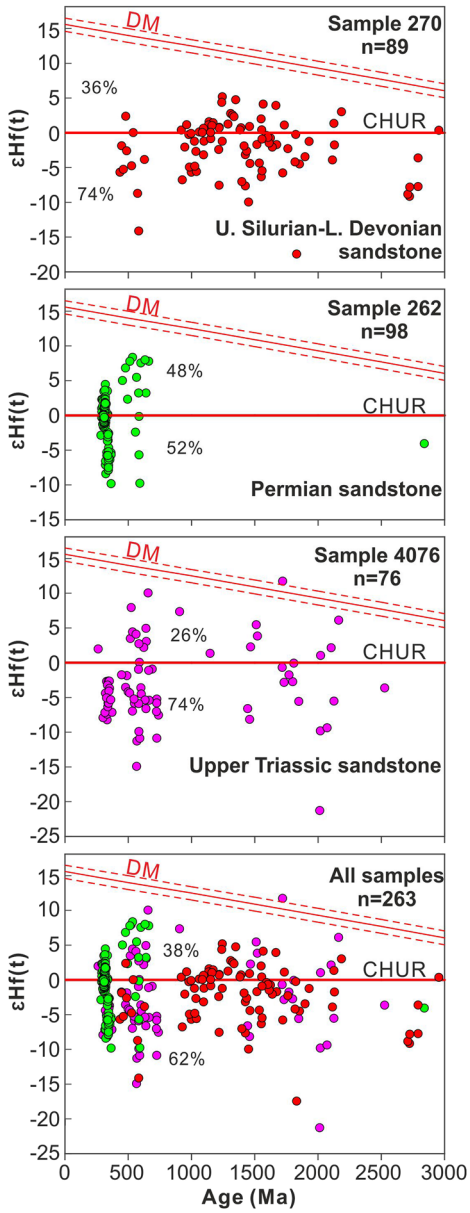

Figure 5. Detrital zircon age versus εHf(t) values of the Paleozoic to Mesozoic sandstones of the Istanbul Zone. DM, depleted mantle; CHUR, chondritic uniform reservoir plotted using HafniumPlotter (Sundell et al., 2019).

zircon population. There is a less pronounced cluster of Ordovician-Carboniferous zircons (485–315 Ma; 12%). There are also Paleoproterozoic zircons (2371–1818 Ma; 7%) with widely separated ages without a significant peak.

Permian continental sandstones (samples 262 and 263) yielded 102 and 120 concordant U-Pb detrital zircon ages respectively (Tables 1 and S1). They show a similar age pattern (Figure 4). In both samples Carboniferous-earliest Permian zircons (355–274 Ma; 57% of the concordant zircons) dominate the zircon population. Likewise, both samples display a significant peak at late Neoproterozoic–Cambrian (758–489 Ma; 25%; Figure 6). There are also widely spaced Ordovician to Devonian (478–362 Ma; 9%) and Archean–Mesoproterozoic zircons (3149–1057 Ma; 9%) without significant peak.

Only 80 concordant ages were obtained out of 180 detrital grains from the Upper Triassic sandstone (sample 4076) (Tables 1 and S1). The ages range from 2526 to 262 Ma (Figure 4). Similar to those samples 262 and 263, this samples also yielded major zircon population at Late Neoproterozoic–Cambrian (740-489 Ma; 43%) and Carboniferous (20%). There are also minor peaks at Ordovician (5%), early Mesoproterozoic (1520–1440 Ma; 6%), and Middle and Late Paleoproterozoic (2170–2010 Ma; 9% and 1850–1710 Ma; 9% respectively).

4.3. Lu-Hf Isotope Values

The εHf(t) values of the zircon grains from the Upper Silurian-Lower Devonian sandstone (sample 270) range between −17.4 and + 5.2, whereby the negative εHf(t) values make 64% (Table S2, Figure 5). Positive εHf(t) values indicate mantle derived melts whereas negative values are indicative of recycled, old crust-derived melts from which zircons were originated. Late Neoproterozoic–early Paleozoic (628–434 Ma) and Archean (2954–2709 Ma) zircons show mostly negative εHf(t) values. Detrital zircons from the Permian continental sandstone (sample 262) display εHf(t) values ranging between −9.8 and + 8.4. The negative εHf(t) values are found in the 52% of the zircons. The εHf(t) values of the zircon grains from the Upper Triassic sandstone (sample 4076) vary between −21.3 and 11.7. The negative εHf(t) values make 74% of the data.

5. Discussion

In order to assess the provenance of Paleozoic-Mesozoic clastic sedimentary rocks, we also compiled a total of 853 concordant detrital zircon ages from Ordovician, Lower Carboniferous, Triassic, and Lower Cretaceous sandstones of the Istanbul Zone (in total 12 samples) from previous studies (Akdoğan et al., 2017; Okay & Topuz, 2017; Okay et al., 2011; Ustaömer et al., 2011; Ülgen et al., 2018, Figure 6). The initial εHf values reported in this study are also compared with initial εHf values in literature (Figure 7). εNd(t) values of the whole rock samples are also compared when the εHf(t) values are not available, because initial εHf values are mostly coupled with initial εNd values.

5.1. Provenance of the Upper Silurian-Lower Devonian Sandstone–Avalonian Affinity of the Istanbul Zone

Among the detrital zircon ages obtained from Upper Silurian-Lower Devonian sandstone collected from Amasra region (Figure 2), Late Paleoproterozoic to earliest Neoproterozoic zircons form the most significant age population (83%) with main cluster at the Mesoproterozoic period (51%; Figure 4). Similar zircon age distribution was

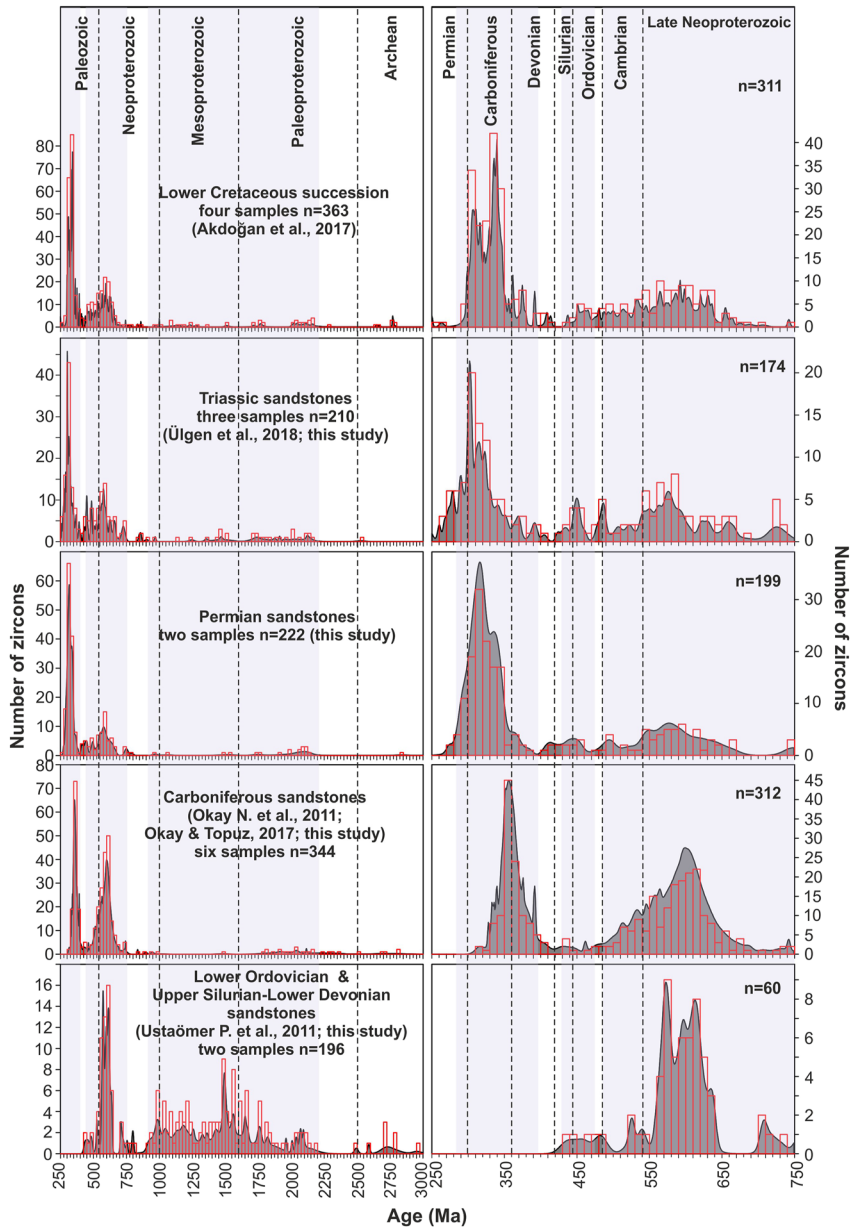

Figure 6. U-Pb detrital zircon age histograms with probability density curves of Lower Ordovician quartzites (Ustaömer et al., 2011), Upper Carboniferous turbidites (Okay et al., 2011), Lower Carboniferous coal measures (Okay & Topuz, 2017), Triassic clastic rocks (Ülgen et al., 2018), and Lower Cretaceous shelf to turbiditic sequences of the Istanbul Zone (Akdoğan et al., 2017) and samples from this study. Histograms on the right show the late Neoproterozoic and Phanerozoic zircons from of the same samples. Sample locations are shown in Figure 2.

reported from Lower Ordovician arkosic sandstone of the Istanbul Zone (Ustaömer, 2011; Figure 6). The Avalonian type terranes are characterized by the presence of Mesoproterozoic ages and the nearly absence of detrital zircons with ages between 2450 and 2050 Ma in their source area (Nance & Murphy, 1994; Samson et al., 2005; Winchester et al., 2006). Abundant Mesoproterozoic detrital zircons (51%) from the Upper Silurian-Lower Devonian sandstone sample of the Istanbul Zone together with the gap observed between 2700 and 1950 Ma (very few detrital zircon grains observed in this range; Figure 4), indicate that the Istanbul Zone forms part of the Avalonian as suggested by Ustaömer et al. (2011) and Okay et al. (2011). Avalonia rifted from Gondwana during Early Ordovician (Arenig, 475 Ma) and collided with the Baltica during the latest Ordovician-Early Silurian (Ashgill, 445 Ma, Cocks & Torsvik, 2002, Figure 8a). However, the timing of the rifting of the Istanbul Zone

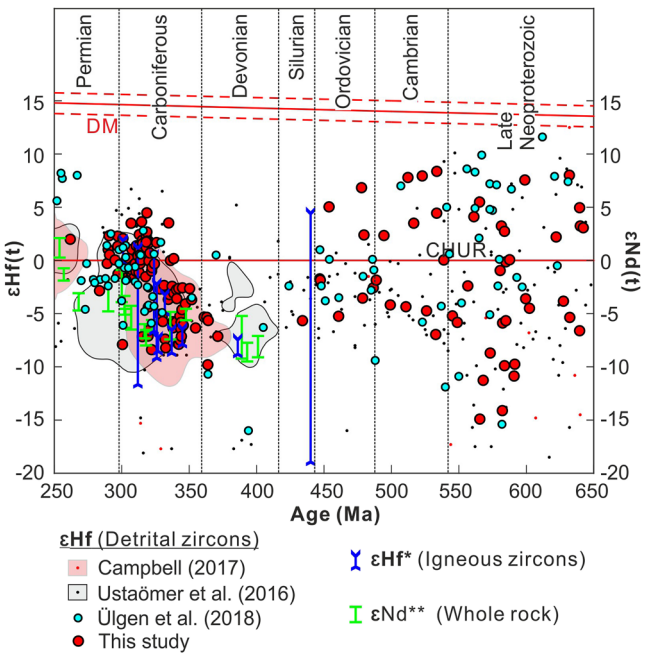

Figure 7. Initial εHf values versus age histogram comparing the data in this study with those from literature. The line for depleted mantle (DM) is taken from Sundell et al. (2019). The literature zircon initial εHf values are from Campbell (2017), Karslı et al. (2016, 2020), Liu et al. (2018), Şengün et al., (2020), Topuz et al. (2020), Ustaömer et al. (2016), and Ülgen et al. (2018). The initial whole rock εNd values are also shown from literature (e.g., Aysal et al., 2012, 2018; Dokuz, 2011; Karslı et al., 2016; Kaygusuz et al., 2012, 2016; Nzegge et al., 2006; Sunal, 2012; Topuz et al., 2010).

from northern margin of Gondwana and accretion to the southern margin of Baltica-Laurentina in the north are not well constrained.

To date, there are no well-documented Ordovician-Silurian igneous rocks in the Istanbul Zone. On the other hand, Ordovician–Silurian igneous rocks were reported from the Sakarya Zone (Figure 3; Okay et al., 2008; Topuz et al., 2020; Please note that Okay et al. (2008) incorporated the Armutlu Peninsula into the Istanbul Zone where he reported an Ordovician metagranite. However, recent unpublished data by Okay suggest that the Armutlu Peninsula is part of the Sakarya Zone. Likewise, the metaclastic rocks in the Strandja Zone contain detrital zircons with Ordovician to Silurian igneous crystallization ages (Natal'in et al., 2012). Early Ordovician epoch in the Istanbul Zone is represented by transgressive clastic sequences resting unconformably on the Late Neoproterozoic basement. The source of Ordovician-Silurian detrital zircons in Upper Silurian–Lower Devonian sandstone (sample 270) remains as an open question, since no magmatic rocks of Ordovician–Silurian age are known from the Istanbul Zone so far. However, the Istanbul Zone should have been added to the southern margin of Baltica-Laurentina before Devonian, as the Devonian and Carboniferous foraminiferal assemblages in the Istanbul Zone display typical Laurussian affinity (e.g., Kalvoda et al., 2003). Thus, the Istanbul Zone to the north formed the passive margin of Laurussia facing to the Rheic Ocean in the south (Figure 8a).

5.2. Provenance of the Carboniferous to Upper Triassic Siliciclastic Rocks of the Istanbul Zone

Gondwana derived terranes are characterized by generation of voluminous arc-related Upper Neoproterozoic igneous rocks beginning at ca. 760 Ma and peaking at ca. 635–570 Ma (e.g., Murphy et al., 2000; Nance et al., 2002). Almost all detrital zircon ages (86%) from the Upper Carboniferous, Permian, and Upper Triassic sandstones range from the Late Neoproterozoic (750 Ma) to Permian (274 Ma) with a major peak at Carboniferous (34%; Table S1, Figure 4). The contribution of the Mesoproterozoic zircons is minimal (<3%). Similar detrital zircon distributions with a prominent peak of Carboniferous zircons were obtained from Lower Carboniferous (Visean) flysch (Okay et al., 2011) and Upper Carboniferous (Westphalian) coal measures (Okay & Topuz, 2017) of the Istanbul Zone (Figure 6). Similarly, Carboniferous zircons also constitute the main detrital zircon population in the Triassic clastic sequence near Kocaeli and Istanbul, and in the Lower Cretaceous clastic sequence of the Istanbul Zone (Akdoğan et al., 2017; Ustaömer et al., 2016; Ülgen et al., 2018, Figure 6). Furthermore, the abundance of Mesoproterozoic detrital zircons decreases from Ordovician-Silurian to Carboniferous-Triassic siliciclastic rocks (Figures 4 and 6).

The obtained Late Neoproterozoic–early Cambrian (689–487 Ma) detrital zircon ages from this study match well with the age of the Late Neoproterozoic crystalline basement (ca. 590–560 Ma, Chen et al., 2002; Okay et al., 2008; Ustaömer et al., 2005) and Permian detrital zircons with the ages of the Permian acidic intrusions of the Istanbul Zone (ca. 262–257 Ma; Aysal et al., 2018; Okay et al., 2013; Ustaömer et al., 2005). However, there are no records of Devonian and Carboniferous magmatic and metamorphic events in the Istanbul Zone (Figures 2 and 3), which can potentially provide numerous Carboniferous and Devonian zircons to Carboniferous and younger clastic rocks. Abundant Carboniferous and sparse Devonian zircons require a continental domain with Carboniferous crystalline rocks similar to the Sakarya and Rhodope-Strandja zones (Figure 4). As described above, both the Sakarya and Rhodope-Strandja zones are characterized by widespread metamorphic and igneous rocks of Carboniferous age (Dokuz, 2011; Kaygusuz et al., 2012, 2016; Nzegge, 2008; Nzegge et al., 2006; Okay et al., 2001; Sunal et al., 2011; Topuz et al., 2004, 2007, 2010; Ustaömer, Ustaömer, & Robertson, 2012; Figure 3). They are regarded as eastward extension of the Armorica in Europe (Okay & Topuz, 2017; Okay et al., 2008; Ustaömer, Robertson, Ustaömer, et al., 2012; Ustaömer, Ustaömer, & Robertson, et al., 2012; Winchester J.A. and the PACE TMR Network Team, 2002, Figure 1). We therefore suggest that the Istanbul Zone collided with the Sakarya/Rhodope-Strandja Zone during the Early to Late Carboniferous following southward

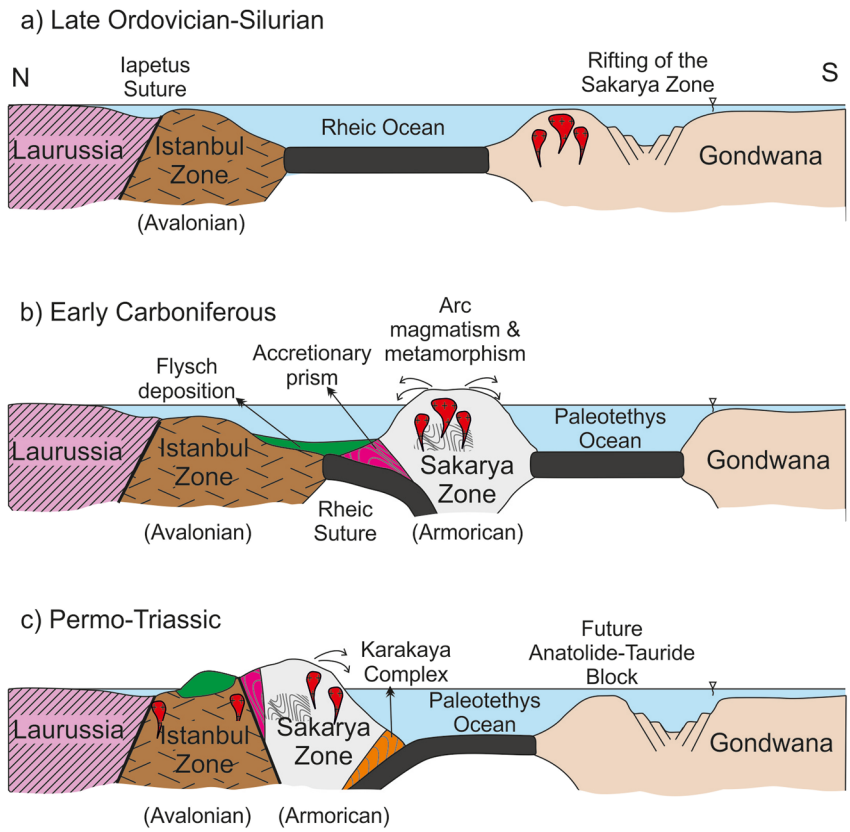

Figure 8. Tectonic model illustrating the evolution of the Rheic Ocean in the Eastern Mediterranean region.

subduction of the Rheic Ocean beneath the Sakarya Zone (Figure 8b) as previously postulated by Okay and Topuz (2017) on the basis of regional geological constraints such as (i) coeval nature of Early Carboniferous HT-LP metamorphism and voluminous acidic magmatism similar to those in Central Europe, (ii) presence of sporadic Carboniferous HP metamorphic rocks close to the northern margin of Greater Caucasus and Strandja-Rhodope zones, and (iii) deposition of Middle Permian red beds with a pronounced unconformity over Silurian to Early Carboniferous sedimentary rocks. Thus, this provenance study on the Paleozoic to Lower Mesozoic clastic rocks of the Istanbul Zone verifies the validity of Okay and Topuz (2017)'s suggestion.

As stated above, our study documents a major provenance change using the U-Pb detrital zircon ages and defines the timing of the collision of the two continental domains; the Istanbul and Sakarya zones, as the Early to Late Carboniferous. There are also other proxies, which can be used to constrain the timing of this collisional event as described by Hu et al. (2016) in detail. The Early to Late Carboniferous collision between the Sakarya and Istanbul zones is further supported by the following observations in the Istanbul Zone (i) deepening character of the sedimentation from Late Devonian to Early Carboniferous, (ii) cessation of the marine sedimentation during Late Carboniferous, (iii) Carboniferous contractional deformation and (iv) the presence of major middle Permian unconformity (see Figure 3 and Section 2.1.). On the other hand, in the Sakarya Zone, Devonian and Carboniferous periods are represented by metamorphic rocks and gabbroic to granitic intrusions (Figure 3). Upper crustal rocks of Late Devonian and Carboniferous ages apart from a minor exposure of uppermost Carboniferous to lowermost Permian sedimentary rocks (e.g., Okay & Leven, 1996) are mostly absent, implying that the Sakarya Zone was undergoing erosion, and was supplying sediment to the Istanbul Zone. This state lasted up to Early Jurassic time when there was a large-scale marine transgression in the Sakarya Zone (see Figures 3, 8b and 8c). Reworking of the pre-Carboniferous clastic rocks of the Istanbul Zone was minimal. This can also explain the nearly absence of 2050–2400 Ma and 1000–1500 Ma zircons in Carboniferous and post-Carboniferous clastic rocks of the Istanbul Zone. High pressure metamorphic rocks related to the Carboniferous accretion are not known along the Intra-Pontide suture and are only documented along the fore-range in the Greater Caucasus (Okay & Topuz, 2017, and references therein).

There are a few petrological and provenance studies reporting initial εHf values of the igneous zircons from both the Istanbul and Sakarya zones. As pointed out above, the Carboniferous igneous and metamorphic events are confined to the Sakarya Zone. The initial εHf values of the granitic to gabbroic rocks in the Sakarya Zone range from +1.7 to −15 (Karslı et al., 2016; Liu et al., 2018; Şengün et al., 2020; Ustaömer et al., 2016). Likewise, initial εNd values of gabbroic to granitic rocks are characterized by negative values ranging from −1 to −8.4 (Dokuz, 2011; Karslı et al., 2016; Kaygusuz et al., 2012, 2016; Nzegge et al., 2006; Topuz et al., 2010, 2020). Despite the continental crust-like εHf and εNd isotopy, inherited zircons are non-existent to minimal among the dated zircons from the igneous rocks of Carboniferous age. This situation implies that the Sakarya Zone during the Carboniferous was underlain to a large extent by a lithospheric mantle with continental-crust like isotopic compositions, as discussed by Topuz et al. (submitted). The initial εHf values of the Carboniferous detrital zircons from the Permian and Upper Triassic sandstones from the Istanbul Zone are characterized by 65% negative values. Similar εHf(t) distribution has been reported from the detrital zircons from the Triassic sandstones of the Istanbul Zone by Ülgen et al. (2018) (Figure 7). The source of the detrital Carboniferous zircons with positive εHf(t) values is unclear. The εHf(t) values show a isotopic pull-up (εHf(t) increase in over time) from 360 to 290 Ma (Figure 7). Detrital Carboniferous zircons from the Upper Triassic Karakaya Complex of the Sakarya Zone are also characterized by predominantly negative εHf(t) zircon values (Campbell, 2017; Ustaömer et al., 2016) (Figure 7). A pull-up from 360 to 300 Ma is recognizable in the dataset of Campbell (2017). The reason of this isotopic pull-up in the zircon initial εHf values is unclear. All the detrital zircons with Silurian and Devonian crystallization ages from the clastic rocks of the Istanbul Zone are characterized by negative εHf(t) values (Figures 5 and 7). This is also consistent with the detrital zircon data in Ustaömer et al. (2016). Devonian (meta-)granitic rocks in the Sakarya Zone demonstrate negative initial εNd (−5.3 to −9.4) and εHf zircon values (−7.1 to −8.5), suggesting derivation from crustal melts (Aysal et al., 2012; Sunal, 2012; Ustaömer et al., 2016). In case of the Silurian magmatism, the documented granitic rocks display negative initial εHf values, and basic/gabbroic rocks, on the other hand, display positive initial εHf values, indicating the presence of both crustal and mantle-derived melts (Karslı et al., 2020; Topuz et al., 2020).

5.3. The Nature of the Contact Between the Istanbul and Sakarya Zones, the Intra-Pontide Suture

The tectonic boundary between the Istanbul and the Sakarya zones is represented by the Intra-Pontide Suture (Figures 1 and 2). Existence of an oceanic domain between the Istanbul and Sakarya zones has been suggested due to striking stratigraphical differences. There are Upper Cretaceous ophiolitic mélanges cropping out at the eastern part of the Intra-Pontide suture (Figure 1). In terms of rock types and ages of the tectonic blocks involved in mélange, these ophiolitic mélanges hardly differ from the ophiolitic mélanges along the Izmir-Ankara-Erzincan suture (e.g., Göncüoğlu et al., 2012, 2014; Marroni et al., 2014, 2020). Toward the eastern end of the Intra-Pontide-Suture, the width of the Sakarya Zone becomes narrow, and the Intra-Pontide and Izmir-Ankara-Erzincan suture approaches each other (Figure 1). The currently active right-lateral North Anatolian Fault locally runs along the Intra-Pontide suture (Figure 2). The North Anatolian Fault is thought to be active since Middle Miocene and has a total offset of 60–85 km (Akbayram, Sorlien, & Okay, 2016; Armijo et al., 1999; Şengör et al., 2005). All these features complicate the deduction of the primary geological relationships among the different rock associations along the suture.

The evolution of the Intra Pontide Suture is highly contentious. Suggested times for the closure range from Triassic to Early Eocene (e.g., Akbayram, Okay, & Satır, 2013; Akbayram, Şengör, & Özcan, 2016; Bozkurt et al., 2012; Elmas & Yiğitbaş, 2001, 2005; Göncüoğlu et al., 2008; Görür & Okay, 1996; Okay et al., 1994; Robertson & Ustaömer, 2004; Şengör & Yılmaz, 1981; Şengör et al., 2019; Tüysüz, 1999; Yılmaz et al., 1995). Researches who suggest Late Mesozoic-Early Cenozoic closure proposed that the Intra-Pontide oceanic domain first opened during the Triassic (e.g., Marroni et al., 2020). To summarize, there are highly divergent ideas on the evolution of the Intra-Pontide Ocean. The detrital zircon record of Paleozoic to Mesozoic rocks in the Istanbul Zone (this study, Akdoğan et al., 2017; Okay & Topuz, 2017; Okay et al., 2011; Ustaömer et al., 2016; Ülgen et al., 2018) clearly demonstrate that the provenance of the sedimentary rocks abruptly changes during the Early Carboniferous. The pre-Carboniferous sedimentary rocks display an Avalonian-type affinity, while detrital zircon record of the Carboniferous and post-Carboniferous sedimentary rocks display an Armorican-type signature similar to those of the Sakarya and Rhodope-Strandja zones. This situation can be best explained by the juxtaposition of the Istanbul and Sakarya zones during Early Carboniferous, thus closure of the Intra-Pontide suture (Figure 8). In turn, Intra-Pontide suture can be considered as the eastward extension of the Rheic Suture in Turkey. There

was no other adjacent continental domain, which could have provided the Carboniferous detrital zircons into the sedimentary rocks of the Istanbul Zone. Northerly areas, such as Ukrainian shield, is made up of Archean and Paleoproterozoic crystalline rocks (Bogdanova et al., 2008; 2010; Claesson et al., 2006). The second important implication of the detrital zircon record is that there is no significant change during Late Paleozoic and Mesozoic time. Detailed geological, petrological, and geochronological studies are necessary along the Intra-Pontide Suture to understand whether the Intra-Pontide Suture was reworked during Mesozoic and Early Cenozoic time.

6. Conclusion

Detrital zircon age pattern from the Paleozoic clastic rocks of the Istanbul Zone displays a drastic change in the Carboniferous, and this new age pattern continues up to the Late Mesozoic. The detrital zircons in the pre-Carboniferous clastic rocks are characterized by major populations of Mesoproterozoic and Late Neoproterozoic–Cambrian zircons, which is common in the Avalonian-type terranes. However, the Carboniferous and post-Carboniferous clastic rocks have major population of Carboniferous detrital zircons in addition to Late Neoproterozoic–Cambrian zircons, while the Mesoproterozoic zircons drastically diminish. This has important implications, because the Istanbul Zone is devoid of any Carboniferous igneous and metamorphic events. This can be best accounted by the accretion with an Armorican-type continental block, which lacks Mesoproterozoic igneous and metamorphic rocks, and where Carboniferous igneous and metamorphic events are dominant. The only candidate for such terranes is the neighboring Sakarya and Rhodope-Strandja zones. Therefore, we suggest that the source for the Carboniferous detrital zircons in the Istanbul Zone lies in the Sakarya-the Rhodope-Strandja zones. The suture between these continental blocks represents a Carboniferous suture, probably the eastward extension of the Rheic Suture in Turkey. Later reworking of this suture during the Alpine Orogeny did not influence the detrital zircon age pattern.

Data Availability Statement

All new data presented in this article are available in Supporting Information File (SI, Tables S1 and S2). The data can also be found at Akdoğan et al., 2021 (doi: 10.17632/zhycjy7p5p.1).

Acknowledgments
Xiumian Hu and Remziye Akdoğan gratefully acknowledge financial supports by the National Science Foundation of China-Tethyan Major Project (No. 91755209). We thank Mehmet Ali Oral for preparation of the thin sections. Helps of Wei Li during U-Pb dating and of Juan Li during cathodoluminescence imaging are gratefully acknowledged. Careful and constructive reviews by Matthew Campbell and two anonymous reviewers considerably improved the manuscript.

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