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Tracking the timing of Neotethyan oceanic slab break-off: Geochronology and geochemistry of the quartz diorite porphyries, NE Turkey

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geochemistry of the quartz diorite porphyries, NE Turkey

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The initiation of the break-off of the northern branch of the Neotethyan oceanic lithosphere is an important but poorly understood event in the geology of the Sakarya Zone (SZ) in northeastern Turkey. Although it is well-known that Latest Cretaceous intrusives (~ 70 Ma) and early Eocene adakitic magmatic rocks are present in the eastern SZ, early Eocene non-adakitic rocks are very limited, and their tectono-magmatic evolution has not been studied. We describe a small outcrop of non-adakitic quartz diorite porphyry in the Kov area of the Gümüşhane in northeastern Turkey. The genesis of these porphyries is significant in evaluating the syn- to post-collision-related magmatism. The LA-ICP-MS zircon U-Pb dating revealed that the Kov quartz diorite porphyries (KQDP) formed at ca. 50 Ma, coeval with adakitic rocks, and ~20 Myr later than the slab roll-back-related intrusive rocks. The KQDP are calc-alkaline in composition and enriched in large ion lithophile elements (LILEs) and light rare earth elements (LREEs) and depleted in high field strength elements (HFSEs; e.g., Nb, Ta, Ti), with significant negative anomalies of Nb, Ta, and Ti but positive anomalies of Th, U, and Pb. Isotopic compositions of the samples show limited range of variation and slight enrichment of $^{87}\text{Sr}/^{86}\text{Sr}(t)$ (0.70489 to 0.70555), $\varepsilon_{\text{Nd}}(t)$ (-1.4 to -1.2) with T_{DM} of 1.11 to 1.61 Ga. Pb isotopic ratios of the samples point to an enriched mantle source. They were likely crystallized from the melt that originated from an EMII-type spinel-facies subcontinental lithospheric mantle (SCLM), followed by the fractionation with insignificant crustal assimilation. The SCLM was metasomatically enriched, and the metasomatic agent was likely H₂O-rich fluids rather than sediments released from subducting oceanic crust during the Late Cretaceous closure of the Neotethyan oceanic lithosphere. In conjunction with the geological background and previous data, we propose that the generation of the KQDP resulted from a slab break-off event that caused ascending or infiltration of hot asthenosphere, triggering mantle melting. Such sporadic occurrences of the KQDP, with coeval adakitic rocks in the SZ, are likely associated with the onset of extensional tectonics due to the earlier stage of slab break-off along the region during the early Eocene period.

Sakarya Zone, NE Turkey

1. Introduction

The investigation of magmatic products in orogenic settings assists us to more accurately evaluate tectonic history and orogenic evolution (e.g., Mahéo et al., 2009; Wu et al., 2018; Liu et al., 2019). The SZ is one of the major tectono-magmatic belts in Anatolia and is commonly referred to as a well-preserved Late Cretaceous magmatic arc (e.g., Şengör and Yilmaz, 1981; Okay and Şahintürk, 1997; Yilmaz et al., 1997; Boztuğ et al., 2004, 2006; Kaygusuz et al., 2008; Karsli et al., 2010a, 2012a; Dokuz et al., 2019; Kandemir et al., 2019). However, initiation of arc-continent collision and post-collision extensional tectonics in the eastern part of the SZ during the Late Mesozoic to Early Cenozoic eras are poorly understood as there are very few exposed mantle-derived rocks in the entire region. Indeed, the lack of such rocks prevents an increased understanding of the subcontinental mantle processes and the geodynamic setting of the region. The post-collisional magmatism occurred approximately ~15 Myr in the eastern SZ during the Late Cretaceous-Paleocene (e.g., Topuz et al., 2005; Boztuğ et al., 2006; Karsli et al., 2007, 2010b, 2012b; Aydınçakır and Şen, 2013; Dokuz et al., 2013, 2019; Aydınçakır, 2014). The combination of early Eocene calc-alkaline quartz diorite porphyries (this study) and Early Eocene adakitic rocks are a manifestation of this magmatic activity. The petrogenesis of post-orogenic magmatism in the eastern SZ has not been adequately studied. The onset of syn- to post-collisional magmatism, with an adakite-like signature, were dated from 52 to 48 Ma, at which time, the Kov quartz diorite porphyries emplaced (Topuz et al., 2005, 2011; Dilek et al., 2010; Karsli et al., 2010b, 2011; Dokuz et al., 2013). This magmatic activity was followed by an extensive intra-continental extension-related pluton emplacement, and alkaline to calc-alkaline volcanism occurred between 45 to 40 Ma (Karsli et al., 2007, 2012b; Kaygusuz and Öztürk, 2015; Dokuz et al., 2019). The post-collisional magmatic activity tended towards the alkaline character and was widespread in the middle to late Eocene, but not ca. 50 Ma when the KQDP emplaced. Here, some controversy remains regarding

(1) mechanism that acted upon them. Also, it is still unclear when extensional forces commenced and what processes were responsible for the generation of magmatism. Little research has focused on separating the magmatic activities related to the slab break-off and intra-continental extensional events in the eastern SZ (Aydıncakır, 2014). Therefore, the early Eocene quartz diorite porphyries in the Kov area of Gümüşhane are the key petrological probes needed to reveal the geodynamic processes related to the onset of post-collisional extensional forces and lithospheric evolution beneath the SZ.

In this contribution, we report new zircon U-Pb data, whole-rock geochemical, and Sr-Nd-Pb radiogenic isotope compositions for the early Eocene KQDP within the eastern SZ in northeastern Turkey. We combined our geochemical data with those from previous works to gather further insights into the magma evolution beneath the area. Therefore, the main objectives of this work are to (i) refine the possible source characteristics, and (ii) interpret the tectonic event responsible for the early Eocene magma generation in the SZ in northeastern Turkey.

2. Geological background of the eastern Sakarya Zone

The SZ (Fig. 1a), characterized by a complex geological history, is a well-preserved mountain belt containing a variety of rock types of varying ages. These rocks record traces of the closure of the Rheic, Paleotethys, and Neotethys oceans. The Paleozoic peridotitic blocks in the Gümüşhane and Bayburt areas indicate the presence of subduction-accretion complexes, attributed to the closure of the Rheic Ocean (Dokuz et al., 2011; 2015). The Variscan basement was composed of post-collisional Early to Middle Carboniferous granitoids (e.g., Okay and Leven, 1996; Topuz et al., 2010; Dokuz, 2011; Kaygusuz et al., 2012), volcanics (Dokuz et al., 2017), and metamorphic rocks (Çapkinoğlu, 2003; Okay et al., 2006; Topuz et al., 2007). Terrigenous clastics and shallow marine sedimentary successions, deposited in the Pular region in the eastern SZ, overlie the basement rocks along a nonconformity (Okay and Leven, 1996; Kandemir and Lerosey-Aubril,

the post-orogenic Middle Carboniferous Gümüşhane granitoids (Karsli et al., 2016).

Based on the geochemical characteristics of the intrusives, subduction-related events occurred in the Triassic period (e.g., Eyüboğlu et al., 2011; Karsli et al., 2014; Topuz et al., 2014). During the Early Triassic, a magmatic arc formed along the northern margin of Gondwana as a result of the southward subduction of the Paleotethyan oceanic lithosphere (Şengör and Yilmaz, 1981; Kocuyigit and Altiner, 2002; Dokuz et al., 2006, 2010; Ustaömer and Robertson, 2010; Karsli et al., 2017). The opening of the Neotethys Ocean as a back-arc basin in the SZ was due to southward subduction events (Şengör and Yilmaz, 1981). In contrast, the Cimmeride events, according to some researchers, are related to the result of the amalgamation of oceanic terranes (including oceanic plateaus, oceanic islands, and intra-oceanic arcs) to the active margin of Laurasia during the Late Triassic and Early Jurassic periods (e.g., Golonka, 2004; Okay et al., 2006; Meijers et al., 2010). The basement blocks are covered by Early Jurassic volcano-sedimentary units (Dokuz and Tanyolu, 2006; Şen, 2007; Kandemir and Yilmaz, 2009). The Early Jurassic volcanoclastic units of the Şenköy Formation are associated with the rifting due to the opening of the Neotethyan Ocean in the back-arc basin (Kandemir and Yilmaz 2009). The closure of the Paleotethys Ocean resulted in the formation of Middle to Late Jurassic granitoids and dacites associated with volcano-sedimentary rocks (Dokuz et al., 2006, 2010), then the SZ accreted to Laurasia in the north (Şengör et al., 1980; Şengör and Yilmaz, 1981; Dokuz et al., 2010, 2017). The Late Jurassic to Early Cretaceous Berdiga platform-type carbonates (e.g., Tüysüz, 1999) formed in a quiescent stage following rapid tectonic subsidence and arc-continent collision. The Jurassic volcanoclastics and the carbonates deposited in a south-facing passive continental margin of the northern Neotethys Ocean (Şengör and Yilmaz, 1981; Dokuz et al., 2017). Then, the SZ was subjected to compressional forces resulting from the northward subduction of the Neotethyan oceanic lithosphere during the Cretaceous period (Okay et al., 1994; Robinson et al., 1995; Şengör et al., 2003; Boztuğ et al., 2004; Kaygusuz et al., 2008; Karsli et al., 2010a, 2012a, 2018; Aydin, 2014). Such a subduction event caused the opening of the Black Sea in the northern Sakarya and

collision with the Tauride-Anatolide Block during the complete closure of the Neotethyan Ocean (Okay and Şahinturk, 1997; Boztuğ et al., 2004; Topuz et al., 2005; Hisarli, 2011; Karsli et al., 2010b, 2011; Rolland et al., 2012; Dokuz et al., 2013). The extensional forces started in the early Eocene, coinciding with the regional emplacement of adakitic rocks presumably derived from melting of thickened lower continental crust (Topuz et al., 2005, 2011; Dilek et al., 2010; Karsli et al., 2010b, 2011), or a detached oceanic slab (Dokuz et al., 2013). Middle Eocene submarine volcano-sedimentary rocks were intruded by high-K calc-alkaline I-type plutons (e.g., Boztuğ et al. 2004, 2006; Karsli et al. 2007, 2012b; Kaygusuz and Öztürk, 2015; Dokuz et al., 2019) and are covered by compositionally similar volcanic rocks (e.g., Aydınçakır and Şen, 2013). This Eocene magmatic activity may have been caused by orogenic collapse, slab break-off, or far-field extensional forces. Local late Miocene-Pliocene magmatic outcrops with subaerial, calc-alkaline, and alkaline character were interpreted in relation to the post-collision intra-continental extensional events in the eastern SZ (Aydin et al., 2008; Dokuz et al., 2013; Yücel et al., 2017; Karsli et al., 2019).

3. Methodology

We selected the fourteen quartz diorite porphyrie samples from the intrusion in the Kov area, Gümüşhane (NE Turkey) (Fig. 1b,c). LA-ICP-MS zircon U-Pb datings, major and trace element analyses, and whole-rock Sr-Nd and Pb isotope analyses were performed to interpret the genesis of the quartz diorite porphyries in the SZ and the geodynamic setting of the intrusion. Technique details are given in Appendix A.

4. Results

4.1. $^{40}\text{Ar}/^{39}\text{Ar}$ incremental heating and LA-ICP-MS zircon U-Pb dating

A quartz diorite porphyrie sample was dated by the $^{40}\text{Ar}/^{39}\text{Ar}$ incremental heating method. The results are given in Table S1 and depicted in Figure 2a. The $^{40}\text{Ar}/^{39}\text{Ar}$ dating of a hornblende

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plateau is restricted by 14 steps during the incremental heating. The hornblende separation of KKL1 yielded a predictable result, and it seems a best accord between the plateau and isochron ages (Table S1). Additionally, we applied a zircon separation process to the sample KKL24. Zircon domains are usually colorless and display mostly prismatic morphologies, with pyramidal termination. The fractured domains show oscillatory zoning patterns with a length of 100-180 μm , which is consistent with magmatic origin. Cathodoluminescence (CL) images show that the zircon domains chosen for U-Pb dating analyses are free of visible inclusions. The results of dating analyses are provided in Table S2 and the concordia diagram depicted in Figures 2b, c. A total of five spots from each of the eight zircons were measured. As shown in Table S2 and Figure 2a, concordant analyses yield weighted mean ages of 50.1 ± 1.5 Ma (MSWD=0.034). The plateau age of 45.08 ± 0.55 Ma of the hornblende separation and the weighted mean age of 50.1 ± 1.5 Ma (MSWD=0.034) of the zircon from the Kov intrusion is thought to be the crystallization age of the porphyries, coinciding with the early phases of the post-collisional events in the eastern SZ.

4.2. Mineralogy and Petrography

The KQDP, observed as small subvolcanic stocks in the field (Figs. 1c and 3a), are dark gray to green in color with microgranular porphyritic texture (Fig. 3b). The stock is more or less homogeneous in petrographical characteristics and does not contain any enclaves. They generally contain phenocrysts (up to ~ 2 mm in size) of plagioclase (andesine to labradorite), amphibole (hornblende), and clinopyroxene (augite) with lesser biotite and quartz microphenocrysts set in the microcrystalline matrix of feldspar and quartz (Fig. 3c-f). Microscopically, the porphyries demonstrated phenocryst clots of plagioclase+amphibole+quartz (Fig. 3c, d). Clinopyroxene (10-15%) and amphibole (5-10%) phenocrysts are the most common mafic minerals in the samples. Some clinopyroxene phenocrysts have amphibole rims (Fig. 3e), produced during the late magmatic stage. Amphibole occurs as euhedral to subhedral crystals with prismatic habit and

crystals and partly altered to chlorite. Plagioclase phenocrysts are normally zoned (Fig. 3c) and show lamellar twinning (Fig. 3d). They are weakly altered to sericite and clay minerals. Quartz occasionally forms subhedral microphenocrysts (Fig. 3c) but usually occupies the interstices between other minerals. Fe-Ti oxide (titanomagnetite), zircon, and apatite occur as accessory minerals. According to the normative mineralogy, all the samples are defined as silica-oversaturated rocks and have high plagioclase (~62–67%), moderate quartz (~11–19%), and low orthoclase (4.5–9.0%) and hypersthene (6.3–8.6%) abundances. Thus, normative hypersthene imparts the subalkaline character to the KQDP.

4.3. Whole-rock geochemical composition

Based on the geochemical composition results (Table S3), all the samples fall within the gabbroic diorite field in the total alkali versus silica diagram (Fig. 4a) designed by Middlemost (1994). The samples show moderate SiO_2 concentration, ranging from 54.51 to 56.42 wt.% (Table S3). All the samples have high concentrations of Al_2O_3 (18.30–18.73 wt.%), $\text{Fe}_2\text{O}_3^{\text{tot}}$ (7.21–7.75 wt.%), and CaO (6.98–8.34 wt.%). Their Mg# [$(100 \times \text{MgO}) / (\text{MgO} + 0.9 \text{Fe}_2\text{O}_3^{\text{tot}})$] varies from 46 to 51. Co and Ni concentrations are low, ranging between 17.9–28.9 ppm and 3.3–4.1 ppm, respectively. The samples are of I-type geochemical character with ASI [=molar $\text{Al}_2\text{O}_3 / (\text{CaO} + \text{K}_2\text{O} + \text{Na}_2\text{O})$] ranging from 0.91 to 0.97 and exhibit metaluminous features, whereas the early Eocene adakitic porphyries show metaluminous to peraluminous signatures (Fig. 4b). They demonstrate a calc-alkaline geochemical nature (Fig. 4c).

The calc-alkaline quartz diorite porphyries show enrichment in large ion lithophile elements (LILEs; e.g., Ba, Rb, Th, and K) relative to the high field strength elements (HFSEs; e.g., Nb and Ti), and show negative Nb, Ta and Ti anomalies in the multi-element diagrams (Fig. 5a). Samples exhibit slightly fractionated chondrite-normalized rare earth element (REE) patterns, and thus, they are represented by relatively flat heavy rare earth elements (HREE) and are enriched in light rare

(La/Yb)_N ratios are moderate, between 3 and 5, and mostly <4 (Table S3).

4.4. Radiogenic isotopes

Whole-rock Sr-Nd-Pb isotope data are in Table S4. The initial ⁸⁷Sr/⁸⁶Sr(t) isotopic ratio and ε_{Nd}(t) were calculated as representing an origin of 50 Ma. The samples exhibit relatively uniform and relatively high initial ⁸⁷Sr/⁸⁶Sr(t) isotopic ratios of 0.70531 to 0.70583 and a narrow range of ε_{Nd}(t) of -2.4 to 0.2, with depleted mantle Nd model ages (*T*_{DM}) of 0.98–1.69 Ga (Table S4). The samples belong in the right quadrants of the Sr-Nd isotope diagram (Fig. 6a). When compared to the reference fields, the samples plot close to the early Eocene lower crust-derived adakitic volcanics (Karsli et al., 2010) and granitoid porphyries (Karsli et al., 2011), the late Miocene crust-derived adakitic rocks (Dokuz et al., 2013; Karsli et al., 2019), the early Eocene Yoncalik adakitic samples (Dokuz et al., 2013), the early Eocene non-adakitic volcanics (Aydınçakır, 2014) in the eastern SZ and the early Eocene Ekmekçi granodiorite porphyries in the western SZ (Sunal et al., 2019). The KQDP plot a considerable distance away from the middle Eocene shoshonitic Sıldağı pluton in the eastern SZ (Karsli et al., 2012b) and mid-ocean ridge basalt (MORB; Hofmann, 2003).

The samples have relatively constant lead isotopic ratios of ²⁰⁶Pb/²⁰⁴Pb (18.633–18.709), ²⁰⁷Pb/²⁰⁴Pb (15.592–15.587), and ²⁰⁸Pb/²⁰⁴Pb (38.867–38.718) (Table S3), which plot above the North Hemisphere Reference Line (NHRL) restricted by Pb-Pb values of MORB and ocean island basalt (OIB) from the northern hemisphere (Hart, 1984) (Fig. 6b,c). Their Pb isotopic compositions are not far from EM2 end-member (Zindler and Hart, 1986), the middle Eocene shoshonitic Sıldağı pluton (Karsli et al., 2012b), and the marine sediments (Plank and Langmuir, 1998) rather than EM1 end-member (Zindler and Hart, 1986).

5. Discussion

5.1. Timing of the calc-alkaline Kov quartz diorite porphyries formation

of possible thermal effects at low temperatures. Alterations along the margins and cleavage planes of hornblende crystals result in argon loss, potentially underestimating sample age in the low-temperature heating steps. The flat plateau ages in the sample KKL1 (Fig. 2a) decrease the possibility of significant argon loss related to hydrothermal alteration. The agreement between the plateau age (45.08 ± 0.55 Ma) and the isochron age (43.09 ± 3.56 Ma) indicates minimal extraneous argon and negligible hydrothermal thermal effects. However, the alignment of points in the isochron plots suggests that there is an extraneous (perhaps inherited or excess) ^{40}Ar in the system. Therefore, we also dated the zircons separated from sample KKL24, as zircon has the highest closure temperature and shows high resistance during overprinting geological processes. Also, it is sensitive to crystallization records saved during the growth of zircon domains. The measured zircons are of magmatic origin, mirrored by their oscillatory zone textures. The majority of measured spots are close to the concordant curve, suggesting that the zircon U-Pb isotope system remained largely closed after zircon crystallization. The analyses yielded weighted mean $^{206}\text{Pb}/^{238}\text{U}$ ages of 50.1 ± 1.5 Ma with an MSWD of 0.034, indicating the emplacement age of the KQDP (Fig. 2b,c). However, the porphyries were formerly dated as Jurassic in age (ca. 171 Ma; Eyüboğlu et al., 2016). The stratigraphic relationships in the field show that the subvolcanic stock intruded into the volcano-sedimentary rocks of the Early Jurassic Şenköy Formation (Kandemir and Yilmaz, 2009). As a result, our new weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age data invalidates the previous Middle Jurassic age of the intrusion, which was possibly obtained from the inherited zircon domains. Therefore, we conclude that the Kov quartz diorite porphyries emplaced at ~50 Ma in the eastern SZ. The intrusion is coeval with adakitic rocks (Karsli et al., 2010b) exposed in the eastern SZ, and the granitoid porphyries emplaced in the western SZ (Sunal et al., 2019) and the eastern SZ (Karsli et al., 2011).

5.2. Petrogenesis of the Kov quartz diorite porphyries

fingerprint and feature a significant depletion in Nb content (Fig. 5a). Such a geochemical signature implies that a continental material has contributed to their origin as Nb is depleted in the continental crust (e.g., Rudnick and Gao, 2003). Furthermore, the depletion of Nb and Ti argues against a normal MORB or OIB source. Silica with isotopic and element ratios illustrated in Figure 7 tend to indicate fractional crystallization rather than crustal contamination for the evolution of the magma. Nb depletion relative to N-MORB and lower $\epsilon_{\text{Nd}}(t)$ (-2.4 to 0.2) values compared to MORB (Fig. 6a) suggest that an enriched lithospheric mantle participated in the generation of the KQDP. In addition, their calc-alkaline geochemistry and moderate silica contents are consistent with those of evolved mantle-derived melts. The samples exhibit more radiogenic isotopic ratios ($^{87}\text{Sr}/^{86}\text{Sr}(t)$ of 0.70531 to 0.70583 and $\epsilon_{\text{Nd}}(t)$ of -2.4 to 0.2) than that of asthenospheric melt ($\epsilon_{\text{Nd}}(t)=+5$; Basu et al., 1991). This suggests a source of enriched subcontinental lithospheric mantle rather than an asthenospheric melt.

The Pb isotope ratios are identical to those of an EM2-type end-member (Fig. 6b,c). The enrichment in LILEs and LREEs suggests a source of metasomatized lithospheric mantle. The HREE fractionation of mafic lavas generally results from the melting of a mantle source, including garnet or mantle enrichment by fluids/melts released from garnet-bearing subducting sediments (e.g., O'Neill, 1981; Avanzinelli et al., 2008). Since the quartz diorite porphyries exhibit a nearly flat HREE pattern, such features suggest that garnet was not included in the mantle source of the rocks, and the partial melting occurred at shallower depths, indicating a source region of spinel-bearing peridotite facies.

The KQDP have high La/Ta ratios (45 to 90) and low La/Ba ratios (0.03 to 0.04), which are identical to those of an enriched lithospheric mantle. These results are consistent with the lead isotope ratios of the samples (EM2; Fig. 6b,c). There is a consensus regarding the earlier northward subduction of the Neotethyan oceanic slab during the Late Cretaceous to Early Paleocene periods (e.g., Okay and Şahintürk, 1997; Boztuğ et al., 2004, 2006; Kaygusuz et al., 2008; Karsli et al., 2010a, 2012a; Aydin, 2014; Dokuz et al., 2019). This subduction event might

possess radiogenic ^{208}Pb ($^{208}\text{Pb}/^{204}\text{Pb} > 38$), implying that the metasomatic event was relatively old, with adequate time to accumulate radiogenic ^{208}Pb .

The relative enrichment in LILEs and depletion in HFSEs of the samples are evidenced by a melt, fluid, or sediment metasomatism prior to partial melting during ancient subduction events. The relative enrichment in LILEs and depletion in HFSEs are expected when slab-derived fluids cause metasomatism in the mantle wedge. In contrast, subducted oceanic slab-derived melts elevate LREEs and Th (e.g., Woodhead et al., 2001). In this case, the binary variation of incompatible trace elements versus isotope ratios reflects the origin traces of metasomatic processes (Hawkesworth et al., 1997; Turner et al., 1997; Guo et al., 2006). The subducting sediments are enriched in Th and LREEs, whereas fluid-mobile elements such as U and Pb are carried by fluid components into the mantle wedge (Hawkesworth et al., 1997; Turner et al., 1997; Kessel et al., 2005). As Th is fluid immobile, the addition of subducting sediments, rather than fluids from subducting oceanic slab, should be responsible for the transfer of Th to mantle (e.g., Elliott et al., 1997; Kessel et al., 2005; Plank, 2005). The KQDP feature depletion in HFSEs and exhibit a large range of U/Th and narrow range of Th/Nb ratios (Fig. 8a). They show low Ba/Th ratios and do not plot near the field of Global Subducting Sediments (GLOSS; Plank and Langmuir, 1998) (Fig. 8b). Such geochemical trends suggest that the metasomatic process is likely controlled by slab-derived hydrous fluids rather than the addition of subduction-related sediments. Th and LREE mostly partition into sediment melt or supercritical liquid at higher temperature, and pressure conditions (e.g., Stalder et al., 1998; Kessel et al., 2005) and Ba is known as a highly fluid mobile element (e.g., Class et al., 2000; Hochstaedter et al., 2001). The KQDP have low Ba/Th (95-128) and high La/Sm (4-5) ratios, suggesting that mantle enrichment involved a greater proportion of sediments than fluids.

The formation of hydrous mineral phases (i.e., phlogopite or amphibole) in the mantle wedge is controlled by the subduction-related mantle enrichment processes (Beccaluva et al., 2004). Therefore, to affirm these processes, we assessed the element compatibility of phlogopite and

and Graham, 1999; Yang et al., 2004). The most primitive sample KKL2 of the KQDP has relatively low Ba/Rb (9.5) and Nb/Th (1.17), and high Rb/Sr (0.12) ratios. These ratios imply that the source contains phlogopite, but not amphibole, as is depicted in the diagram of Rb/Sr versus Ba/Rb (Fig. 8c). The positive correlation between Ba/Zr and Ba/Nb ratios of the samples supports the presence of phlogopite to the mantle source region (Fig. 8d). There is a large variation in the Ce/Pb ratio between samples. Such a variation can be controlled by the inset of Ce-rich phases (like phlogopite) into the mantle wedge prior to partial fusion. Another way to achieve such a variation is through the contribution of altered oceanic crust (Kelley et al., 2005). However, this was ruled out due to the relatively high radiogenic isotopic composition of the samples. The phlogopite abundance in the mantle source could argue against a significant reduction in their Ce/Pb ratios relative to those of MORB and OIB, as the Ce and Pb partition coefficients for phlogopite are 0.0007 and 0.019, respectively, and residual phlogopite in the mantle source may increase the Ce/Pb ratio in the melt (e.g., Williams et al., 2004; Guo et al., 2006). Therefore, the higher Ce/Pb ratios (11 to 17) argue against the asthenospheric melt as the source of contamination.

Amphibole should be stable in the source if a relative depletion in MREEs is observed in the chondrite-normalized REE patterns of the samples (Ge et al., 2002). The KQDP are not depleted in MREEs in the chondrite-normalized REE patterns (Fig. 5b). The mantle wedge beneath the region could have been modified by a carbonatitic or an adakititic oceanic slab melt. Zr and Hf depletions relative to Sm and Eu in the multi-element diagram (Fig. 5a, b) are expected if a carbonatitic melt metasomatizes the overlying mantle wedge (e.g., Guo et al., 2009). The absence of Zr-Hf depletion relative to Sm and Eu in the multi-element diagram of the samples rule out carbonatite metasomatism as a significant agent. The samples also plot within the field of fluid-related subduction metasomatism in the diagram of $(\text{Ta/La})_N$ versus $(\text{Hf/Sm})_N$ proposed by La Flèche et al. (1998) (Fig. 8e). This reveals that the mantle source underwent a metasomatic event resulting from subducting slab-derived fluids. Furthermore, the variations on the $(\text{Ta/La})_N$ versus

(Fig. 8e). The second pathway for metasomatism is the addition of slab melt in equilibrium with the rutile-bearing eclogitic residue to the mantle wedge prior to partial fusion. The slab melt is mostly characterized by enrichment of LILE and LREE and depletion of HFSE, HREE, and Y (e.g., Ge et al., 2002). Although the trace element variations in the multi-element diagram (Fig. 5a, b) mimic an enrichment by slab melt, the variations on the Nb/Zr versus Th/Zr diagram of the samples point to fluid-related metasomatism rather than melt-related enrichment (Fig. 8f).

6. Geodynamic framework

The Early Cenozoic tectono-magmatic events of the eastern SZ remain unclear. The early Eocene KQDP exposed in the eastern SZ are one of the best examples explaining the nature and evolution of the collision to post-collisional dynamics in the region. As mentioned in the above sections, they were likely formed by the melting of a phlogopite-bearing spinel peridotite source and coeval with the adakitic magmatism exposed during the early Eocene period. As previously documented, the emplacement of adakitic magmatism has been attributed to the post-collision extensional forces (Topuz et al., 2005, 2011; Dilek et al., 2010; Karsli et al., 2010b, 2011; Dokuz et al., 2013). However, the onset of extensional deformation after the arc-continent collision is still a matter of debate, and there remains a lack of a suitable tectonic model for the emplacement of the KQDP.

There are a few geodynamic mechanisms that need to be considered before clarifying the genesis of early Eocene magmatism: (1) ocean-ridge subduction (e.g., Sun et al., 2009; Zhang et al., 2014), (2) slab roll-back (e.g., Hawkins et al., 1990; Yan et al., 2016), (3) lithospheric delamination (e.g., Kay and Kay, 1993; Meissner and Mooney, 1998), and (4) slab break-off (e.g., Davies and von Blanckenburg, 1995). Ocean-ridge subduction results in voluminous magmatic activity and HT/LP metamorphism and provides infiltration of a hot asthenospheric mantle. This event triggers the formation of MORB-like adakitic and boninitic magmas (Sisson et al., 2003; Windley et al., 2007). The lack of adakites with MORB-like composition and boninites in the

eastern SZ. This body of evidence prompted us to rule out the possibility of ridge subduction during the early Eocene period. Although the other potential mechanism is the slab roll-back process, it cannot play a key role in the generation of the KQDP, as the subduction does not continue into the early Eocene period (e.g., Şengör and Yılmaz, 1981; Okay and Şahintürk, 1997; Topuz et al., 2005; Dokuz et al., 2013). Moreover, it is inferred that the terminal closure of the northern branch of Neotethyan Ocean was formed during the Latest Cretaceous to early Paleocene (e.g., Şengör and Yılmaz, 1981; Okay and Şahintürk, 1997). A magmatic pause during the Paleocene is likely consistent with the cessation of Late Cretaceous subduction in the region. During a roll-back process, an extension of the arc lithosphere induces an essential driving force for the generation of the back-arc basin. Partial melting beneath the region triggers the formation of back-arc basin basalts, most of which show arc-like and MORB-like compositional characteristics (e.g., Hawkins et al., 1990; Xu et al., 2003). This is not the case for the studied area during the early Eocene period, clearly excluding the slab roll-back model for the generation of the KQDP in the eastern SZ.

Lithospheric delamination is an alternative process commonly invoked for the explanation of magma generation in the post-collisional setting. In this model, negative buoyancy of the lower continental lithosphere due to eclogitization is thought to be the most important driving force as it causes gravitational instability in the lower lithosphere (e.g., Krystopowicz and Currie, 2013). Replacement of lithosphere by asthenosphere, having relatively lower density, induces crustal uplift (Kay and Kay, 1993; Garzzone et al., 2008; Bartol and Govers, 2014; Göğüş et al., 2017). Collisional delamination is an unlikely mechanism as it requires a significant vertical seismic gap, which is not the case beneath this region. By this mechanism, hot asthenosphere approaches close to the lower part of the crust after removal of the lithosphere (e.g., Krystopowicz and Currie, 2013; Hobbs and Ord, 2015). This causes a large volume of crustal-derived melt by partial melting of the lower crust, which does not appear in the region. Finally, recent studies have shown that

the ... (e.g., Okay et al., 2004; Okay et al., 2010; Albino et al., 2014; Dokuz et al., 2019).

A slab break-off event, which is associated with the detachment of an oceanic slab, has been proposed as an explanation for the magmatism during the early stages of continent-continent or continent-arc collision (e.g., Davies and von Blanckenburg, 1995). The presence of a magmatic silence from Maastrichtian (~70 Ma) to late Paleocene (~56 Ma) periods is attributed to the cessation of subduction of the northern branch of Neotethys and initial collision of the SZ with the Anatolide-Tauride Block (e.g., Okay et al., 1994; Okay and Şahintürk, 1997; Şengör et al., 2003; Boztuğ et al., 2004; Topuz et al., 2005, 2011; Karsli et al., 2011; Dokuz et al., 2013, 2019; Aydınçakır, 2014; Kandemir et al., 2019). Furthermore, it is well-known that the subduction most likely lasted until the end of the Cretaceous period in this area (Okay et al., 1994; Okay and Şahintürk, 1997; Boztuğ et al., 2004, 2006; Kaygusuz et al., 2008; Karsli et al., 2010a, 2012a, 2018; Aydın, 2014; Dokuz et al., 2019; Kandemir et al., 2019). In this case, the slab break-off model can satisfactorily explain the origin of the early Eocene KQDP in the eastern SZ. Davies and von Blanckenburg (1995) suggested that a period of at least ~15-20 Myr after the initial collision is required to commence a slab break-off event. Also, a long period is required for the lithospheric thinning to result in widespread magmatic activity; hence the lithospheric thinning is likely not the trigger for the generation of the KQDP. These magmatic events were delayed by ~20 Myr after the onset of collision. The early Eocene adakitic magmatism was followed by intensive calc-alkaline to alkaline magmatism during the middle to late Eocene (~45-40 Ma) in an extensionally thinned continental crust (e.g., Dokuz et al., 2019). Two such types of magma generation may be interpreted as a change in thermal dynamics. The lithospheric delamination and subsequent upwelling of the asthenosphere could have changed the thermal dynamics and onset melting of much of the subcontinental lithospheric mantle, in turn triggering the orogenic collapse and transtensional deformation. Recently, Dokuz et al. (2019) has suggested that the generation of middle to late Eocene magmatism might be controlled by both extensional forces applied during the late stage of slab break-off and far-field extensional effects induced by the north-dipping

magmatism was regionally widespread in the middle to late Eocene period, but not ~50 Ma when the KQDP and adakitic emplaced. In the region, It is thought that the slab break-off process of the northern Neotethyan Ocean could be responsible for the generation of the early Eocene adakitic magmatism (e.g., Topuz et al., 2005, 2011; Dilek et al., 2010; Karsli et al., 2011, Dokuz et al., 2013) All of these interpretations indicate that the initial stage of the slab break-off event might have prevailed at ~50 Ma in the SZ and it was responsible for the magma generation of the early Eocene KQDP.

The early Eocene KQDP and adakitic rocks in the SZ exhibit a convergent plate setting in Figure 9. They plot in the area of active continental margin and away from MORB (Fig. 9a, c). However, the middle to late Eocene calc-alkaline to alkaline rocks outcropped in the region fall within the field of the post-collisional setting (Fig. 9b). These observations strongly support the early Eocene KQDP sharing a systematic convergent setting compositional signature and that they were most probably formed in a slab break-off stage of a collisional environment, apparently consistent with the slab break-off process. The break-off of the subducted oceanic lithosphere would cause a compensating upwelling and infiltration of hot asthenosphere, melting the metasomatized and hydrated lithosphere by earlier oceanic subduction. The initial age of slab detachment should be ~50 Ma when the KQDP and coeval adakitic rocks emplaced. The essential relationships between the petrogenesis of the early Eocene KQDP and the early Eocene geodynamic evolution of the eastern SZ may be summarized: we infer that the early Eocene KQDP and coeval adakitic formed in an extensional environment of an earlier stage of a slab break-off event. Continental extension due to slab break-off resulted in the infiltration of hot asthenosphere, triggering partial melting of previously enriched phlogopite- and spinel-bearing peridotite beneath the eastern SZ at ~50 Ma (Fig. 10a, b). As a result of the partial melting, the early Eocene KQDP and coeval adakitic rocks likely formed during the extension stage of the continent at ~50 Ma in the eastern SZ.

7. Conclusions

Petrographic, geochemical and Sr-Nd–Pb isotope studies on the early Eocene KQDP have led us to the following main conclusions.

- 1- LA-ICP-MS U-Pb dating of zircon separations from the KQDP outcropped in the eastern SZ show that the studied KQDP were emplaced during the early Eocene period (~50 Ma).
- 2- The KQDP were generated from the partial melting of phlogopite-bearing subcontinental spinel peridotite. The mantle wedge from which they originated was metasomatized by fluids released from the previously subducted slab. Mafic parental magma of the KQDP emerged into its final magma chamber in the crust and underwent crystal fractionation and limited crustal assimilation.
- 3- The slab break-off scenario provides a satisfactory explanation of how the early Eocene KQDP and coeval adakitic rocks were formed in the eastern SZ (NE Turkey), as the compressional events due to the arc-continent collision in the region might have lasted until ~50 Ma when initial extensional events commenced. The extensional events caused the infiltration of hot asthenosphere, providing conditions for the partial melting of an enriched lithospheric mantle syn to thereafter break-off of the Neotethyan oceanic lithosphere.

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Figure captions

Figure 1. (a) Regional tectonic setting of Anatolia in relation to the Afro-Arabian and Eurasian plates [modified from Okay and Topuz (2017)]. **(b)** Simplified geological map of the Gümüşhane region and **(c)** Detail geological map of the Kov area in the Gümüşhane region (NE-Turkey), where the calc-alkaline KQDP emplaced.

Figure 2. (a) In situ zircon LA-ICP-MS U-Pb age concordia diagram of the KQDP. **(b)** the representative CL images of zircons from the sample KKL24.

Figure 3. (a-b) Macroscopic views showing the stratigraphic relationships and petrographical features of the porphyries. **(c-h)** microscobic views displaying textural relationships of the quartz diorite porphyries. The features are amphibole (Amp), plagioclase (Plg), clinopyroxene (Cpx), quartz (Q) and iron-titanium oxide (Fe-Ti).

Figure 4. (a) Rock classification diagram (Middlemost, 1994) for the KQDP. σ is a Rittmann index, defined as $(K_2O+Na_2O)^2/(SiO_2-43)$. **(b)** ASI versus SiO_2 [after Maniar and Piccoli (1989)] and **(c)** K_2O versus SiO_2 [after Peccerillo and Taylor (1976)] for the samples from the KQDP.

Fi (a) Nd-Sr isotope diagram of the KQDP from the Gümüşhane region. (b) Chondrite normalized (to values given in Sun and McDonough 1989) for the KQDP. (b) Chondrite normalized (to values given in Boynton 1984) rare earth element abundance patterns for the KQDP.

Figure 6. (a) Nd-Sr isotope diagram of the KQDP from the Gümüşhane region. (b) Plots of (a) $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ and (c) $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ for the selected samples from the KQDP. EM1 and EM2 were taken after Zindler and Hart (1986). The Northern Hemisphere Reference Line (NHRL) and Geochron (4.55 Ga) are also shown for comparison.

Figure 7. Plots of (a) Nb/La ratio versus SiO_2 ; (b) U/Nb ratio versus SiO_2 ; (c) Th/La versus SiO_2 ; (d) La/Yb ratio versus $\epsilon_{\text{Nd}}(t)$; (e) $^{87}\text{Sr}/^{86}\text{Sr}(t)$ versus SiO_2 and (f) $\epsilon_{\text{Nd}}(t)$ versus SiO_2 for the KQDP, indicating fractional crystallization.

Figure 8. The plots of (a) U/Th ratio versus Th/Nb ratio; (b) Ba/Th ratios versus $^{87}\text{Sr}/^{86}\text{Sr}(t)$ ratio; (c) Rb/Sr ratio versus Ba/Rb ratio; (d) Ba/Zr ratio versus Ba/Nb ratio; (e) (Hf/Sm)_N ratio versus (Ta/La)_N ratio (after La Flèche et al., 1998) and (f) Nb/Zr ratio versus Th/Zr ratio versus for the KQDP. Average N-type MORB and OIB are taken from Saunders and Tarney (1984). Data for GLOSS average are after Plank and Langmuir (1998).

Figure 9. Discrimination diagrams deciphering the tectonic setting of; (a) (Th)_n versus (Nb)_n (after Saccani, 2015), (b) R1– R2 plot of Batchelor and Bowden (1985) and (c) Th/Yb ratio versus Ta/Yb ratio (after Pearce, 1982) for the KQDP.

Figure 10. (a-b) A Schematic illustration for the geodynamic environments of the eastern Sakarya Zone during the Late Cretaceous to early Eocene. In the early Eocene period, post-collisional extension possibly related to slab break-off induced upwelling of asthenospheric mantle, which is responsible mechanism for the partial melting of an enriched mantle domain.

Table contents

Supplementary Table 1. $^{40}\text{Ar}/^{39}\text{Ar}$ incremental heating age data of the KQDP from the Gümüşhane region in the eastern Sakarya Zone, NE Turkey

Supplementary Table 2. LA-ICP-MS zircon U-Pb data of representative zircon crystals from the KQDP in the eastern Sakarya Zone.

Supplementary Table 3. Whole-rock analyses for major (wt.%) and trace element (ppm) of the KQDP in the eastern Sakarya Zone.

Supplementary Table 4. Whole-rock Sr, Nd and Pb isotopic compositions of the KQDP in the eastern Sakarya Zone.

- The Early Eocene porphyries are I-type metaluminous in composition
- These porphyries were derived from an enriched mantle domain
- Infiltration of asthenosphere due to slab break-off event triggered partial melting
- The porphyries represent an early stage of extensional tectonic in the Sakarya Zone

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