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Crustal Contamination of Tertiary Volcanic Rocks: Evidence from K, U, Th and Radiogenic Heat Production Data in Eastern Pontides (NE Turkey)

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Abstract—Herein, we present new ^{238}U, ^{232}Th, and ^{40}K radionuclide concentrations, density and radiogenic heat production (RHP) data on the Tertiary volcanic rocks outcropping in Borçka, Gumushane and Trabzon regions within the Eastern Pontide Orogenic Belt (EPOB). The mean *K* values for Trabzon, Borçka and Gümüşhane regions were 2.19 ± 0.87%, 0.90 ± 0.70% and 0.59 ± 0.25%, respectively, the mean U values for Trabzon, Borçka and Gümüşhane regions were 2.12 ± 0.76 ppm and 1.29 ± 0.68 ppm and 0.90 ± 0.32 ppm, and the average Th values were calculated as 6.54 ± 2.32 ppm, 2.49 ± 1.93 ppm and 1.33 ± 0.60 ppm for Trabzon, Borçka and Gümüşhane regions, respectively. The average Th/U values are 3.38 ± 1.48 for the Trabzon region, 2.01 ± 1.22 for the Borçka region, and 1.69 ± 1.09 for the Gümüşhane region. Average U/Th values were calculated as 0.35 ± 0.14, 0.71 ± 0.52 and 0.89 ± 0.72 for the Trabzon, Borçka and Gümüşhane regions, respectively. The RHP values were determined as 1.16 ± 0.35 μWm^{-3}, 0.58 ± 0.33 μWm^{-3} and 0.37 ± 0.10 μWm^{-3} for Trabzon, Borçka and Gümüşhane regions, respectively. The Tertiary aged rocks in the EPOB that we have examined within this study scope have been derived from an enriched mantle, previously metasomatized by fluids derived from subducted slab. The parental magma of Eocene basaltic rocks was contaminated with crustal material during the ascension of the magma through the crust or in the shallow-level crustal magma chambers.

Keywords: Crustal contamination, radiogenic heat production, tertiary volcanics, Eastern Pontides.

1. Introduction

The gamma ray spectrometry has been widely employed in radioelemental concentrations of granitic plutons and volcanic rocks (Aydın et al. 2006; El-Arabi, 2007; Maden & Akaryalı, 2015a; Örgün et al. 2005) mineral exploration (El-Sadek, 2009; Maden & Akaryalı, 2015b), and environmental radiation monitoring (Maden et al. 2019, 2020). This method can identify the ^{238}U, ^{232}Th, and ^{40}K radionuclide concentrations directly at the measurement site within the study regions. Brai et al. (2002) and Arafa (2004) presented that these radioelemental amounts are generally high in granitic rocks within the continental crust. U–Th isotopes are fairly enriched in igneous rocks of granitic composition in comparison with the rocks of basaltic or ultramafic composition within the continental crust (Rudnick & Gao, 2003; Tzortzis & Tsertos, 2004).

Potassium generally occurs in silicates such as micas and feldspars, while Th and U are common in accessory minerals (apatite, monazite, zircon and allanite) within various metamorphic and magmatic rocks (Van Schmus, 1995). Potassium available in most of the granitic rocks is a major element in composition of K-feldspars (orthoclase, microcline, biotite) and muscovite. Th and U are found in comparatively high amounts in accessory minerals condensed in granitic rocks such as orthite or allanite, apatite, monazit, zircon and sphene (Bowie & Plant, 1983; Valković, 2019).

The U/Th, Th/U, K/Th and K/U ratios might allow us to figure out the enrichment or relative depletion of radioisotopes in island-arc volcanic suites (Omeje et al. 2013). The ratios of Th/U, Th/K and U/K are unlikely to change significantly during every stage of the magmatic evolution (Sato & Sato, 1977). The K/U values do not vary remarkably throughout the melting process (Hofmann, 2003; Hofmann et al. 1986; Jochum & Hofmann, 1997; Jochum et al. 1983, 1993; Sun et al. 2008). The worldwide mean planetary ratios of 1 × 10^4 for K/U and 3.7–4.0 for Th/U (Jaupart & Mareschal, 2003;

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McLennan, 2001; Rudnick et al. 1998). Rudnick and Gao (2003) represent the K/U ratio for the continental crust of 1.24×10^4. Arevalo et al. (2009) reported the highest K/U ratios for the back-arc basin basalts and depleted MORB mantle as 2.17×10^4 and 1.9×10^4, respectively. The estimated values for the Th/U ratio also has a significant range from 3.8 (McLennan, 2001) to 5.2–5.3 in the bulk continental crust (Wedepohl, 1995; Hacker et al. 2011). Karsli et al. (2011) and Kaygusuz et al. (2014) explained the genesis of igneous rocks based on the Th/U ratios as a lower crustal melt rather than the N-MORB-derived melts.

RHP owing to the abundance of radioelemental (^{238}U, ^{232}Th and ^{40}K) concentrations vary according to the geochemical and lithological characteristics of the rock formations (Kirti & Singh, 2006). Generally, granites generate higher RHP values than peridotites, basalts and sedimentary rocks (Fowler, 1990). RHP distribution in the continental lithosphere provides a significant information on the depletion of the mantle, and thermal evolution of the crust (Kumar et al. 2007; Perry et al. 2006). RHP values of the upper crustal rocks is higher than those of the lower crust and mantle-derived rocks (Moisio & Kaikkonen, 2006).

In the uppermost 10 km, crustal radioactivity is controlled by magmatic intrusion, metamorphism, tectonics, or U and Th redistribution processes by the presence of fluid circulation and micro-cracks (Čermák & Rybach, 1989). The RHP values for the metamorphic rocks in upper crust extend from 1.5 to 3.5 μWm^{-3}. Yet, majority of the values vary from 2 to 3 μWm^{-3} (Förster & Förster, 2000). Rimi (1999) recommended the RHP values for sedimentary rocks as 2.20 μWm^{-3}. Rudnick and Gao (2003) recommended to utilize of RHP values as 1.65, 1.00, 0.19 and 0.89 μWm^{-3} for upper, middle, lower and total crust, respectively. Verzhbitskii (2002) estimated RHP values as 0.85, 1.15 and 1.55 μWm^{-3}, for upper, middle, and lower crust, respectively, in the Eastern Black Sea basin. He (2009) calculated the RHP values for the upper, the middle, the lower crusts and the mantle as 1.10, 0.83, 0.37, and 0.24 μWm^{-3}, respectively. Additionally, Jokinen and Kukkonen (1999) utilized the RHP ratios as 1.8, 0.6, 0.2 and 0.002 μWm^{-3} for the upper, the middle, the lower crust and the lithospheric mantle, respectively. Vila et al. (2010) revealed that the lower continental crust is poorer in RHP than the upper crust.

The goal of our study is to determine the RHP content of volcanic rocks exposed in Artvin-Borcka, Gümüşhane and Trabzon within the EPOB. The uranium (U, ppm), thorium (Th, ppm), potassium (K, %) content and density values of the Tertiary aged volcanic rocks forming the arc region were determined. Thus, it has been demonstrated that the RHP values of the rocks vary depending on which parameters such as mineral content, density, and age. Our interest is on a relationship between heat production and parameters of mineral content, density, and age in Tertiary-aged volcanic rocks.

2. *Geological Settings*

Anatolia consists of four major tectonic units or terranes that are divided by the suture zones (Okay & Tüysüz, 1999). The EPOB is one of the major tectonic elements of Turkey, which is a branch of the Sakarya zone (Fig. 1a). The EPOB qualified by three volcanic phases improved throughout the Liassic, Late Cretaceous, and Eocene periods (Arslan et al. 1997; Çamur et al. 1996; Kandemir & Yılmaz, 2009) characterize a well-preserved island arc suite (Okay & Sahinturk, 1997; Şengör & Yilmaz, 1981; Yilmaz et al. 1998). Eyüboğlu et al. (2006) subdivided this belt into three distinct tectonic domains with regard to tectonic and lithological characteristics as northern, southern and axial zones. The northern zone is generally composed of Late Cretaceous to Tertiary volcanics, granitic and gabbroic rocks (Aydınçakır, 2014; Aydınçakır & Şen, 2013; Eyüboğlu et al. 2006; Kaygusuz & Aydınçakır, 2009, 2011; Eyüboğlu et al. 2016). The southern zone includes mainly Mesozoic and Tertiary aged sedimentary rocks, Pulur, Ağvanis and Tokat metamorphic massifs, Late Carboniferous aged Gümüşhane and Köse Granitoids (Dokuz, 2011; Topuz et al. 2010). Late Cretaceous aged shoshonitic and ultrapotassic volcanics, Early Eocene aged adakitic intrusions (Aydınçakır, 2016; Eyüboğlu et al. 2011; Karsli et al. 2010; Topuz et al. 2005) are also located within this zone. The axis zone is characterized by large ultramafic masses and Middle-Late Cretaceous ophiolitic sedimentary melange

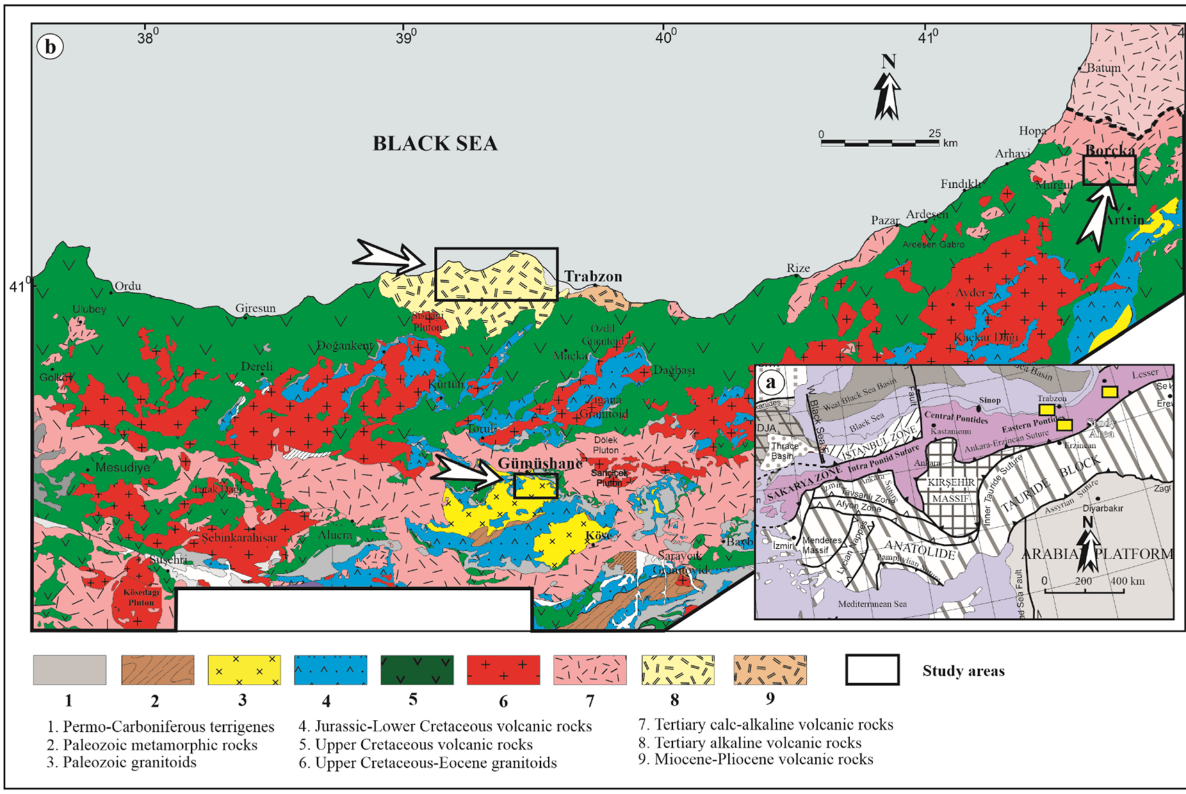

Figure 1

a Tectonic units of Turkey and the study regions (Okay & Tüysüz, 1999), **b** Geological map showing the spread of Tertiary volcanics and intrusions in the Eastern Pontides (modified from Aydınçakır & Şen, 2013; Güven, 1993; Yücel et al. 2017)

(Eyüboğlu, 2015). The Artvin-Borçka and Trabzon regions situated within the northern zone and the Gümüşhane region located within the southern zone of EPOB are composed of the three study regions (Fig. 1b).

The main lithostratigraphic units in the Eocene-aged Borçka region are differentiated from oldest to youngest as Kızılkaya Formation, Çağlayan Formation, Bakırköy Formation and Borcka Volcanics. The Borçka volcanic rocks studied showing tholeiitic-calc-alkaline affinities and having low-to-medium K content mainly consist of Borçka basalt (pillow and basaltic lavas), Civanköy suite (tuff and basaltic–andesitic breccia), and basaltic dyke. The Eocene aged volcanic rocks, which outcropped between Borcka-Artvin, obtained 39.9 ± 05 Ma and 46.1 ± 0.6 Ma Middle Eocene (Lutetian) ages by ^{40}Ar-^{39}Ar aging method by Aydınçakır and Şen (2013) (Table 1). The main solidification processes included in the evolution of the volcanics contain of fractional crystallization, with little crustal contamination. All the evidence verifies the conclusion that the parental magma of the rocks possibly originated

Table 1

Geochronology data previously made in the study regions

Region	Age [Ma]	Period
Trabzon	43.86–45.31[a]	Middle Eocene
	41.32–44.87[a]	
Gümüşhane	45.8[b]	Eocene
	33.45–43.99[c]	Middle-Upper Eocene
	37.7–44.5[d]	Eocene
	44.68–48.71[e]	Eocene
Borçka	39.9–46.9[f]	Middle Eocene (Lutetian)

[a]Yücel et al. (2017)

[b]Aslan (2010)

[c]Kaygusuz et al. (2011)

[d]Arslan et al. (2013)

[e]Eyüboğlu et al. (2013)

[f]Aydınçakır and Şen (2013)

from an enriched mantle, previously metasomatized by fluids attained from subducted slab, in a post-collisional, extension-related geodynamic setting (Aydınçakır & Şen, 2013).

The Tertiary volcanics narrowly spread to the Trabzon and Giresun areas in the northern part of the EPOB. These volcanics divided into Tonya and Trabzon groups (Arslan et al. 1997) composed of three volcanic suites: Miocene aged (1) basanite-tephrite suites, Eocene (2) trachyte-trachyandesite and (3) basalt-trachybasalt-basaltic trachyandesite. Eocene volcanic rocks settled between Tonya and Giresun areas (Yücel et al. 2017) are delineated by dike-sill-domes (basaltic dikes-sills, andesitic dikes-domes, and trachytic dikes), lavas (pillow lavas and basaltic lavas) and volcaniclastics (breccias and tuffs). Miocene volcanic rocks located in Trabzon area (Aydın et al. 2008; Yücel et al. 2017) are represented by dikes, sills, tuffs, breccias and brecciated lavas. The studied Tertiary volcanic rocks are overlain unconformably by Miocene-Pliocene sedimentary rocks, saprolitic clay occurrences (Arslan et al. 2006), and Quaternary marine alluvium (Keskin et al. 2011). The age of the volcanites was determined as 43.86–45.31 Ma and 41.32–44.87 Ma (Middle Eocene-Lutetian), respectively, with the ^{40}Ar–^{39}Ar aging method in the Trabzon region located in the northern zone of the EPOB (Yücel et al. 2017) (Table 1). Yücel et al. (2014, 2017) stated that Tertiary alkaline volcanics in the northern Zone of Eastern Pontide developed temporally and spatially as a result of the lower continental crust interaction of the enriched lithospheric mantle source associated with subduction. In addition, these volcanics are associated with the formation of regional extension and thinning of the lithosphere because of lithospheric slice rupture and subsequent delamination.

Gümüşhane pluton, which is third region of this study, is in the southern zone of EPOB. This pluton consisting of quartz monzodiorite, granodiorite and granite, is bounded by the pre-Jurassic rhyolitic pyroclastics to the south. Kurtoğlu Metamorphic complex, including of gneisses, mica schists and phyllites, cut by metagranitic dikes, is the oldest unit of the region (Eyüboğlu et al. 2013; Topuz et al. 2007). This metamorphic complex cutting by the late Carboniferous Gümüşhane and Köse intrusive complexes are unconformably overlain by the early-middle Jurassic rift-related Şenköy Formation (Kandemir & Yılmaz, 2009), which is covered by the late Jurassic-lower Cretaceous Berdiga Formation. The late Cretaceous period is symbolized by a thick turbiditic sequence with some interlayered felsic tuffs. All exposed rock units are cut by early Eocene adakitic porphyries (Eyüboğlu et al. 2011, 2013; Karsli et al. 2010) and are uncomformably covered by the middle Eocene Alibaba Formation composing of basaltic-andesitic volcanic rocks and their pyroclastics. All these lithological suites are cut by unknown aged basaltic dikes.

Aslan (2010) stated that the tuff belonging to the Eocene rocks in the vicinity of Gümüşhane has a U–Pb zircon age of 45.8 My and the main magma of the volcanics derives from the enriched upper mantle source. Kaygusuz et al. (2011) stated that Torul volcanics of Eocene age are in the range of 33.45 to 43.99 My (Middle-Upper Eocene) of K / Ar ages, and the origin magma is probably a source of enriched upper mantle, which has been subjected to metasomatism by previous loss fluids. According to the Arslan et al. (2013), Eocene volcanic rocks located in the Gümüşhane, Bayburt areas ranged from 37.7 ± 0.2 to 44.5 ± 0.2 Ma (Middle Eocene) ages of ^{40}Ar-^{39}Ar. Geochronological (U–Pb) studies conducted by Eyüboğlu et al. (2013) stated that the age data of the adacitic rocks is 48.71 Ma and the age data of the nonadactic rocks is 44.68 Ma (Table 1).

3. Data and Methodology

Gamma ray spectrometry is based on the principle of separating the potassium, uranium and thorium elements found naturally in the earth's crust according to gamma ray energy emitted from the earth ranging from 0 to 3 meV. A three-window, 512-channel Gamma Surveyor instrument with a NaI(Tl) scintillation detector was employed to detect the concentrations of heat-producing elements of ^{238}U, ^{232}Th, and ^{40}K. For determining the activity concentrations, suitable photopeaks at several energy levels were considered and the appropriate regions were selected for each peak. The activity concentrations of ^{40}K were determined directly from the 1460.8 keV gamma emissions. ^{238}U concentration was estimated by measuring the 1764.5 keV gamma rays from ^{214}Bi. Similarly, 2614.5 keV gamma rays from ^{208}Tl were employed to demonstrate the activity concentration of ^{232}Th (IAEA, 2003).

The bismuth germanium oxide (BGO) detector of the instrument has a volume of 21.2 in^3. The NaI(Tl) detector including a sensor was settled over the unweathered compact outcrops with smooth areas. The 2π geometry was secured for in situ measurements during the survey. Throughout the measurements, it was kept away from the environmental factors that could cause erroneous readings as presented by Loevborg et al. (1971) and Ray et al. (2008).

The measurement duration is adjusted based on the amplitude of radiation and required measurement precision. An ideal measurement time at specific conditions is decided experimentally to ensure accurate results. If a 2 × 2″ NaI(Tl) detector is operated and the measuring time is fixed to 3 min, the result will have guarantee degree of 1 ppm for U and Th and of 0.1% for K quantity. In the case of a 2 × 2″ BGO detector, similar features are achieved at around 1-min time. Deficient measurement time yields inadequate stability of achieved results (IAEA, 2003; Maden & Akaryalı, 2015a, b; Maden et al. 2019).

The RHP value (A in μWm^{-3}) depending on radioelement concentrations of ^{238}U, ^{232}Th, and ^{40}K has been derived using the equation of Rybach (1976):

$$A = \rho(0.0957C_U + 0.0256\mathrm{C_{Th}} + 0.0348C_K), \quad (1)$$

where ρ is the density in gcm^{-3}, $\mathrm{C_{Th}}$ and $\mathrm{C_U}$ are the thorium and uranium concentration in ppm, respectively, and $\mathrm{C_K}$ is the potassium concentration in %. The density of a rock sample used in this equation could be computed as the ratio of the rock mass (*gr*) to volume (cm^{-3}) of the same rock sample.

In the present study, in situ measurements of radioelemental concentrations of ^{238}U, ^{232}Th and ^{40}K were performed in three different regions, Trabzon, Borcka and Gümüşhane, with gamma ray spectrometry at 311, 301 and 304 stations, respectively. The distances between the survey locations are variable and irregular due to the topographical condition of the region. In order to determine the density of the rocks (basaltic-andesitic and their pyroclastics), 100 samples were taken from fresh rocks within the study regions. A total of 916 gamma ray spectrometry measurements were taken. When four different variables are considered in each measurement, the total number of data points is 3672. The total data set in this study is 7444 by counting the ratio values of K, U and Th elements, 100 density values and RHP values (Table 2).

4. Results

Numerical results obtained from the gamma ray spectrometer measurements and density estimation of rocks are provided to determine the RHP potential of the volcanic rocks located in three different regions such as Artvin-Borcka, Gümüşhane and Trabzon within the EPOB. A total of 916 ^{238}U, ^{232}Th and ^{40}K concentration measurements taken on Tertiary rocks in Trabzon ($N = 311$), Gümüşhane ($N = 304$) and Borçka ($N = 301$) regions are reported in Appendixes A, B and C. The locations of the measurement points are given in Fig. 2.

The plot of ^{238}U, ^{232}Th and ^{40}K versus latitude taken in three different regions is given in Fig. 3. The frequency of ^{238}U, ^{232}Th and ^{40}K concentration are presented in Table 2 and plotted in Fig. 4. The Trabzon region is characterized by very high levels of ^{232}Th (2.38–16.50 ppm) and ^{40}K (0.72–8.92%) with a mean value of 6.54 ± 2.32 ppm and 2.19 ± 0.87%, respectively. The activity concentrations of ^{238}U in the Trabzon region ranged from 0.64 to 5.17 ppm with an average of 2.12 ± 0.76 ppm. The ^{40} K values vary between 0.17 and 3.58%, ^{238}U values vary from 0.23 to 5.17 ppm and ^{232}Th values vary between 0.33 and 10.17 ppm in the andesite samples of Borçka region. The average concentrations of ^{238}U, ^{232}Th and ^{40} K in the Borçka area are 1.29 ± 0.68 ppm, 2.49 ± 1.93 ppm and 0.90 ± 0.70%, respectively. In the Gümüşhane region, the activity concentrations of ^{238}U, ^{232}Th and ^{40}K ranged from 0.27 to 2.32 ppm with an average of 0.90 ± 0.32 ppm, 0.12 to 3.22 ppm with an average of 1.33 ± 0.60 ppm and 0.09 to 1.61% with an average value of 0.56 ± 0.25%, respectively.

Table 2

Statistical information of K, U, Th concentrations, density and RHP values for Trabzon, Gümüşhane and Artvin regions

Region	N	K [%]		U [ppm]		Th [ppm]		RHP [μWm^{-3}]		N	Density [g cm^{-3}]	
		Range	Mean ± sd	Range	Mean ± sd	Range	Mean ± sd	Range	Mean ± sd		Range	Mean ± sd
Trabzon	311	0.72–8.92	2.19 ± 0.87	0.64–5.17	2.12 ± 0.76	2.38–16.50	6.54 ± 2.32	0.55–3.02	1.16 ± 0.35	30	2.30–3.00	2.64 ± 0.19
Gümüşhane	304	0.09–1.61	0.56 ± 0.25	0.27–2.32	0.90 ± 0.32	0.12–3.22	1.33 ± 0.60	0.14–0.76	0.37 ± 0.10	40	2.34–2.84	2.62 ± 0.13
Borçka	301	0.17–3.58	0.90 ± 0.70	0.23–5.17	1.29 ± 0.68	0.33–10.17	2.49 ± 1.93	0.21–2.14	0.58 ± 0.33	30	2.28–2.97	2.64 ± 0.18

The density of volcanic rocks such as basalt and andesite were estimated to calculate the RHP values in the study region (Table 2). The density versus latitude and frequency of density values are plotted in Fig. 5. Whole density data range from 2.28 gcm^{-3} to 3.00 gcm^{-3} for three different regions. The density values for Trabzon, Borçka and Gümüşhane region change from 2.30 gcm^{-3} to 3.00 gcm^{-3}, 2.28 gcm^{-3} to 2.97 gcm^{-3} and 2.34 gcm^{-3} to 2.84 gcm^{-3}, respectively. The mean density values were estimated as 2.64 ± 0.19 gcm^{-3}, 2.64 ± 0.18 gcm^{-3} and 2.62 ± 0.13 gcm^{-3} for Trabzon, Borçka and Gümüşhane regions, respectevily, remain virtually constant for three different regions (Table 2).

The RHP values of Trabzon ranges from 0.55 to 3.02 μWm^{-3}, from 0.21 to 2.14 μWm^{-3} for Borçka, and from 0.14 to 0.76 μWm^{-3} for Gümüşhane in the Tertiary volcanic rocks. The computed RHP values from measured concentrations of U, Th and K yield mean values in order of 1.16 ± 0.35 μWm^{-3} for Trabzon, 0.58 ± 0.33 μWm^{-3} for Borçka and 0.37 ± 0.10 μWm^{-3} for Gümüşhane (Table 2, Fig. 6a, b).

5. *Discussion*

The naturally occurring, long-lived radioactive decay schemes of K, Rb, Sr, Th and U are highly important to establish the chronology of magmatic process (Wilson, 1989). In general, radioelemental (^{238}U, ^{232}Th and ^{40}K) measurements from the Trabzon region are on the level of 1–2 amplitude, which is bigger than those of Gümüşhane and Borçka regions.

K, U and Th elements on the ternary diagram shows the dominance of Th with respect to U and K, exhibiting the relative decrease of K and U in the Trabzon region (Fig. 7). Most measurements are located close to the Th and U apex, indicating a large Th and U enrichment and relative K loss for Gümüşhane and Borçka regions. While the highest contribution to RHP values in Trabzon is Th, U and Th make the biggest contribution in Gümüşhane. While the mean ^{232}Th value is close to the lower crustal value, the ^{40}K value is near the continental crust value of Wedepohl (1995). An increase in U and

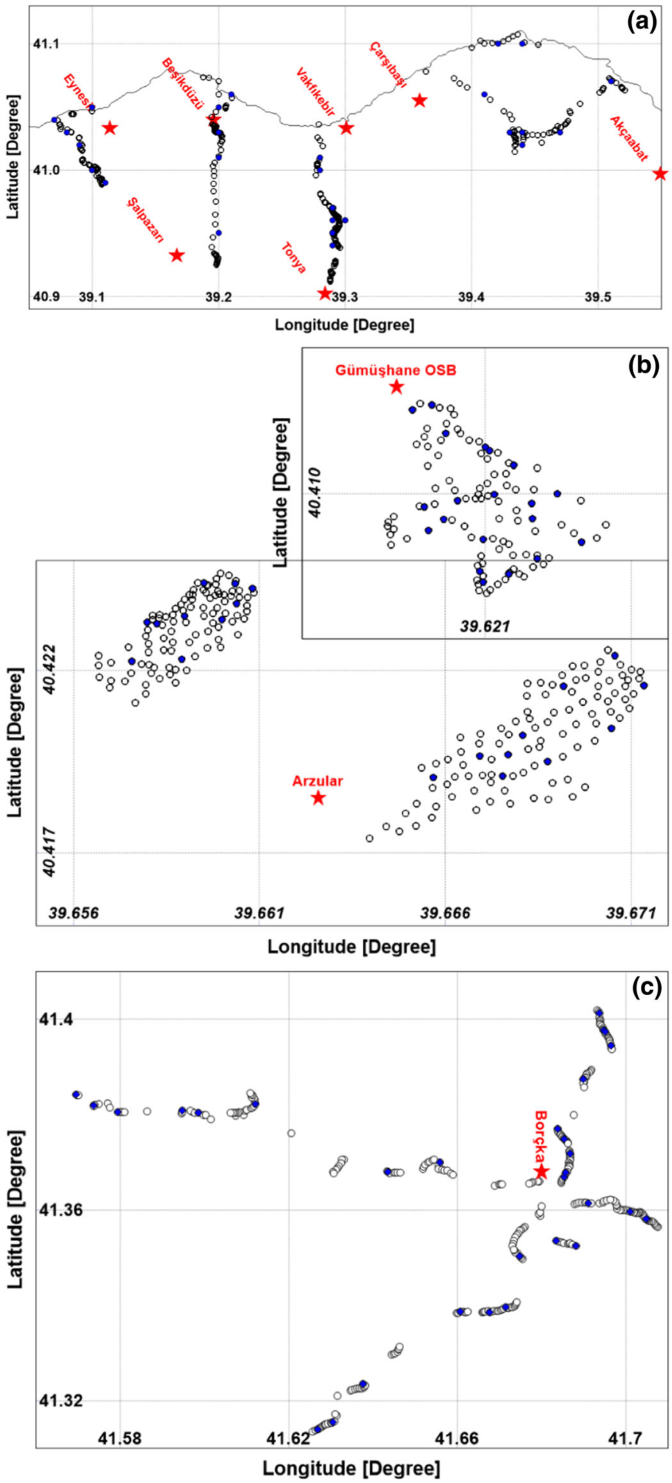

Figure 2

Gamma ray spectrometer measurement points and rock samples for density calculations in the Trabzon (**a**), Gümüşhane (**b**) and Borçka (**c**) regions. Blue filled squares show the locations of rock samples taken for density calculation

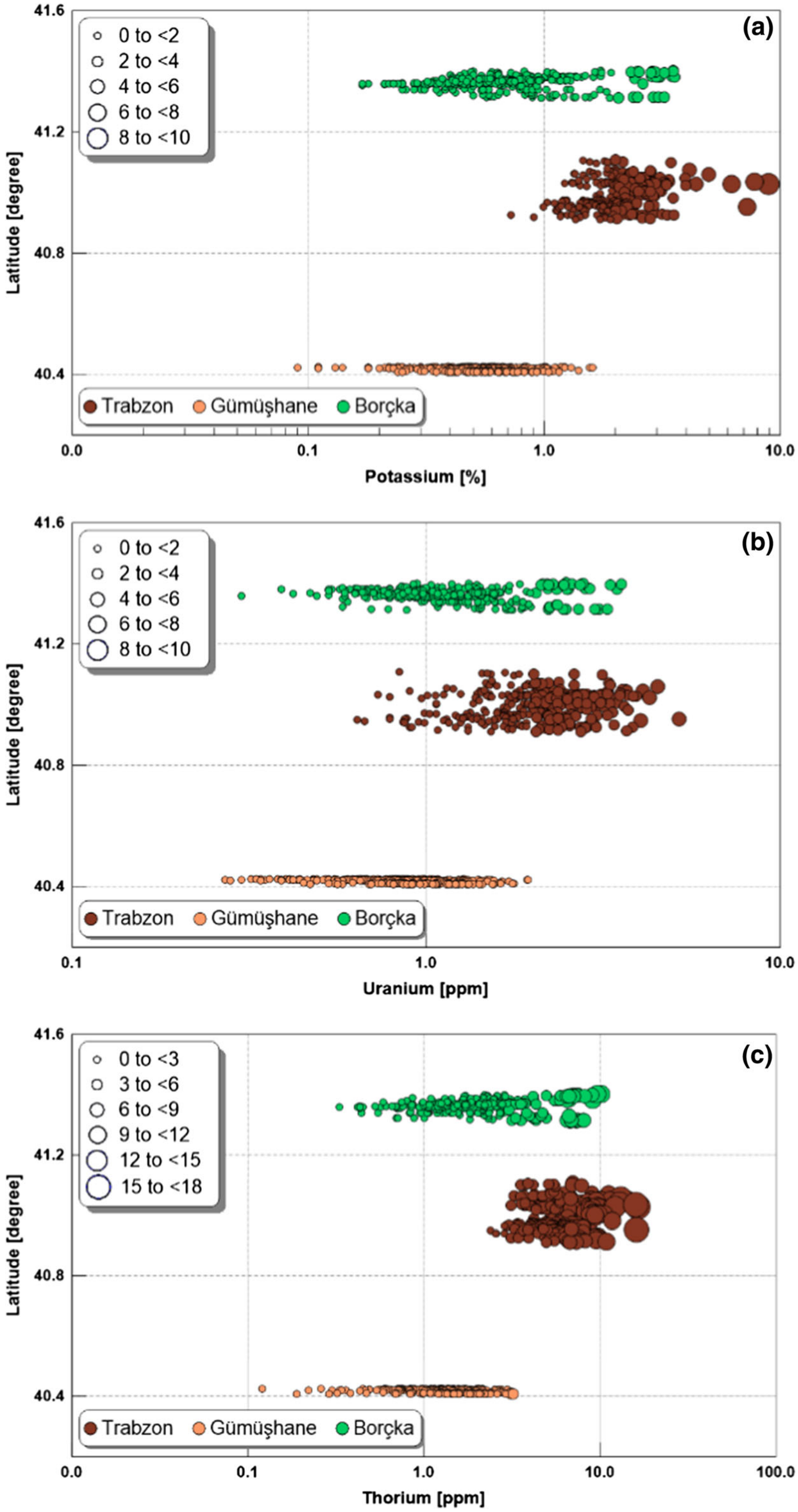

Figure 3
Plot of K, U and Th versus latitude for Trabzon, Gümüşhane and Artvin-Borcka regions

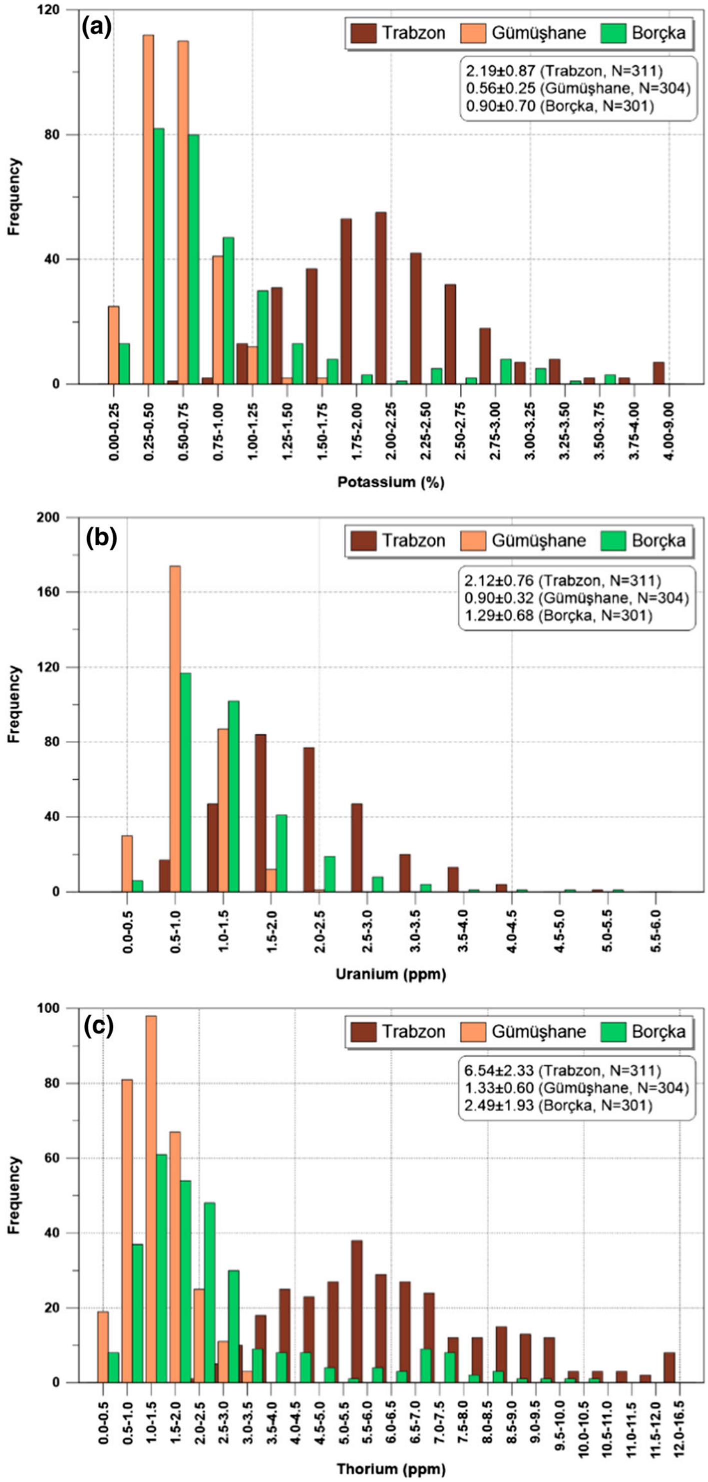

Figure 4
Histogram plots of K, U and Th measurements made in Trabzon (**a**), Gümüşhane (**b**) and Artvin-Borcka (**c**) regions

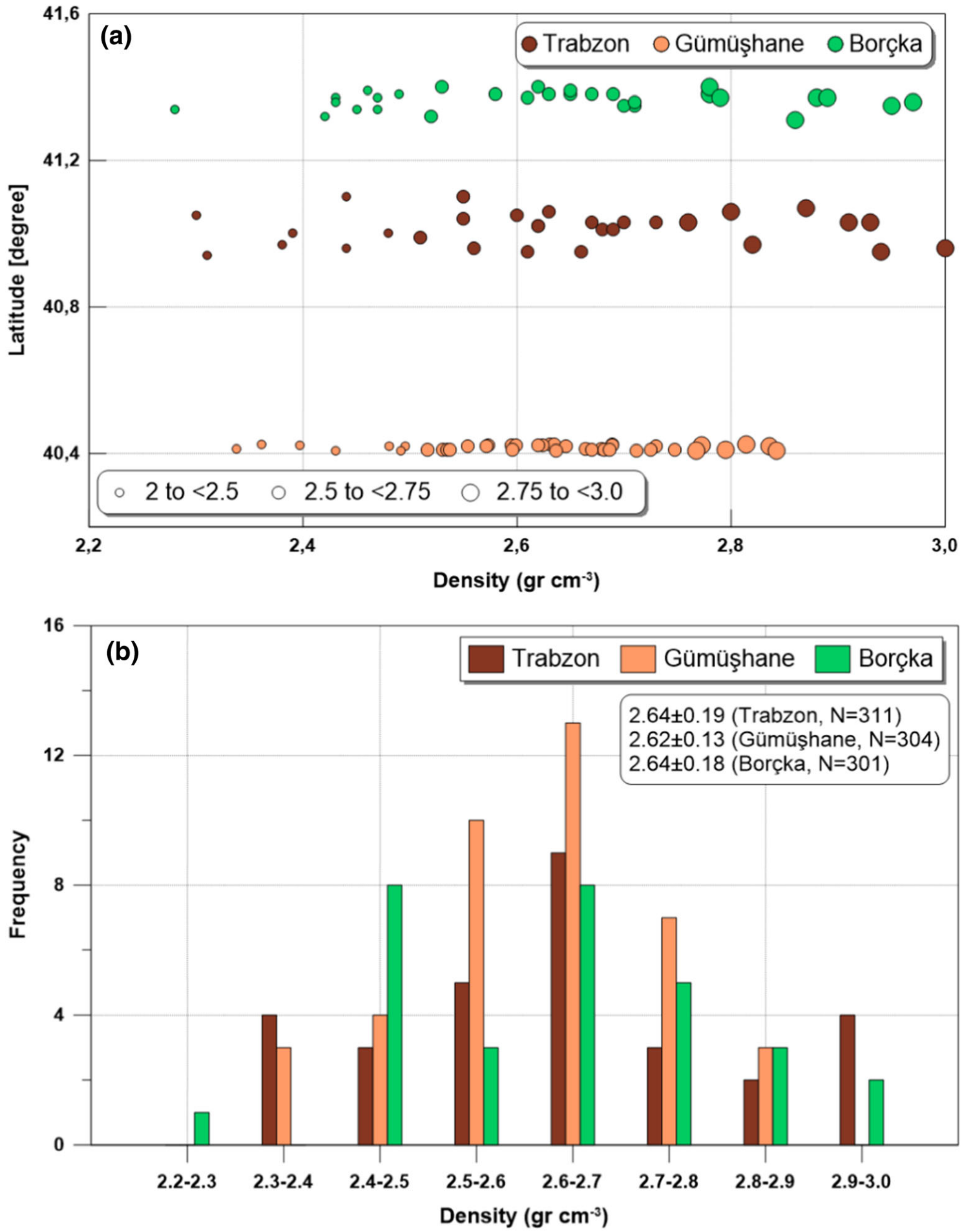

Figure 5
a Density versus latitude and **b** frequency plot of density values calculated from rock samples taken from Trabzon, Gümüşhane, and Artvin-Borçka regions

Th values indicates the presence of resistate minerals such as brannerite, monazite, and zircon.

The density range of rocks with an andesite-basalt composition, being almost stable throughout the upper crust, are strongly affected by their geochemical composition, especially the SiO_2 content (Tassara, 2006). An inverse relationship was observed between RHP and age values, and RHP seems to decrease with increasing geological age. RHP values give the highest value for Trabzon, while

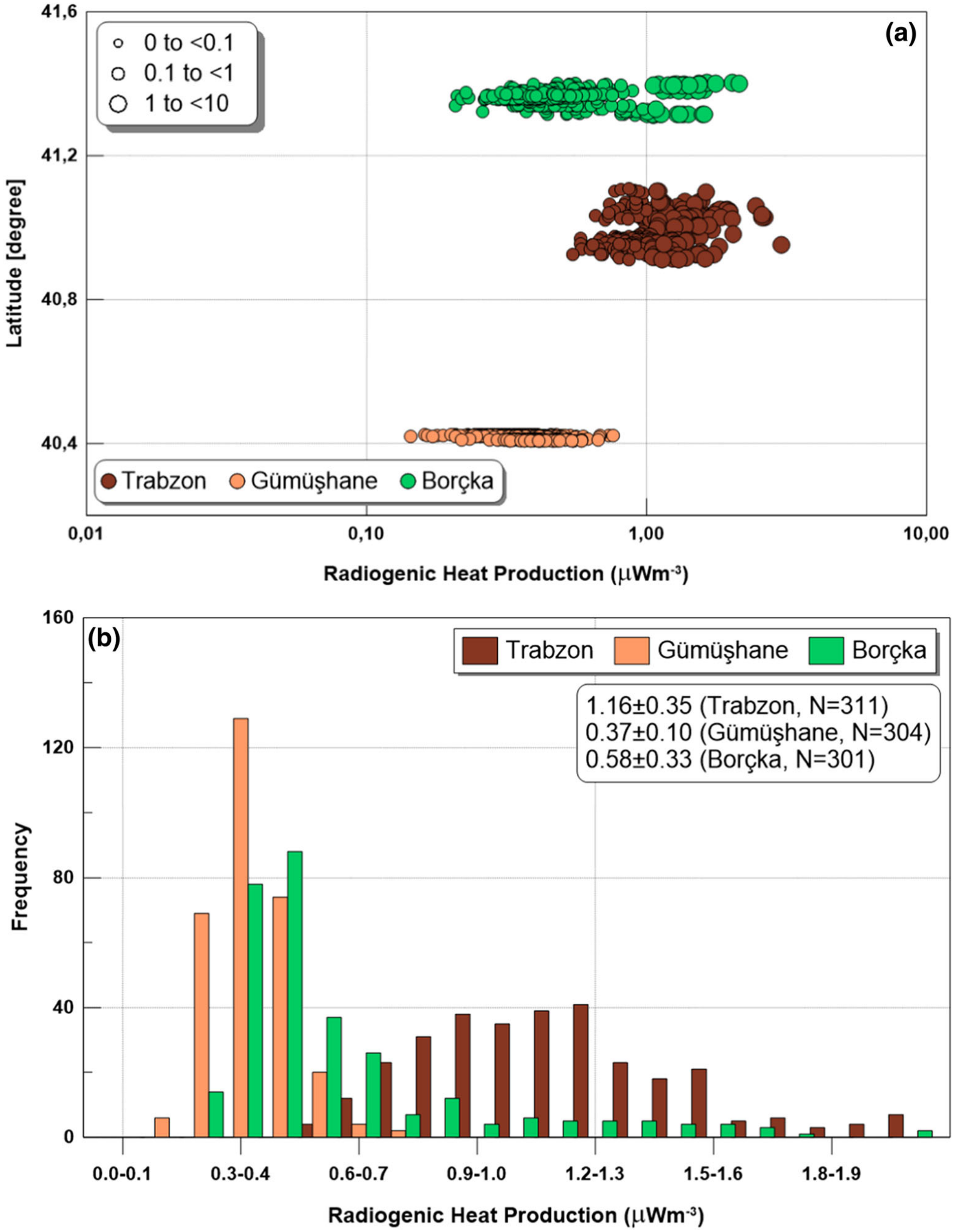

Figure 6
a RHP versus latitude and **b** Histogram plots for Trabzon, Gümüşhane and Artvin-Borcka regions

other regions have lower RHP values. Low radiogenic heat production values (0.37 μWm^{-3}) representing a possible presence of hot mantle material. The parental magmas of the Eocene volcanic rocks might be related to partial melting of the lithospheric mantle caused by upwelling of asthenosphere as stated by Maden (2012a) and Yücel et al. (2017). When the K, U and Th values of three different regions are considered, Th gives the substantial contribution to the RHP content. This might be

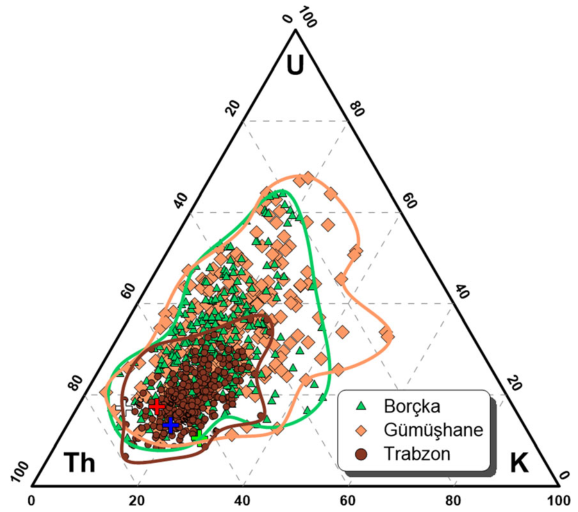

Figure 7
Ternary plot prepared for K, U, Th values in Trabzon, Gümüşhane and Artvin-Borcka regions. The red, blue, green, and white plus stands for the upper, middle, lower, and continental crust values

related to the presence of minerals that contain Th as a trace element in their chemical content.

The RHP value of Trabzon region is significantly lower than the estimates (1.65–1.80 μWm^{-3}) of Rudnick and Gao (2003) and Jokinen and Kukkonen (1999) but close to that (1.15- 1.10 μWm^{-3}) of Verzhbitskii (2002) and He et al. (2009) as suggested for middle and upper crust, respectively. The obtained average RHP value for the Gümüşhane region is equal to the value of the lower crust recommended by He et al. (2009). In the Borçka region, the estimated RHP value is close to the value of middle crust determined by Jokinen and Kukkonen (1999). Therefore, it is possible to say that there is a crustal effect on the tertiary aged volcanic rocks in the study regions.

In EPOB, the K/U values extend from 0.26 $\times$ 10^4 to 3.27 $\times$ 10^4 for Trabzon, from 0.13 $\times$ 10^4 to 3.21 $\times$ 10^4 for Gümüşhane and from 0.15 $\times$ 10^4 to 2.72 $\times$ 10^4 for Borçka regions (Table 3, Fig. 8a). The average K/U ratio of 1.14 $\pm$ 0.42 $\times$ 10^4 determined from Trabzon region is very close to the average K/U value of 1 $\times$ 10^4 for upper crust estimated by Taylor and McLennan (1985), but lower than the estimates (1.27 $\times$ 10^4 and 1.3 $\times$ 10^4) of Jochum et al. (1983) and Rudnick and Gao (2003) for N-MORB and continental arc values, respectively. The mean K/U ratio of 0.74 $\pm$ 0.47 $\times$ 10^4 in Borcka and 0.70 $\pm$ 0.42 $\times$ 10^4 in Gümüşhane regions are smaller than that assumed for the upper crustal layer of 1 $\times$ 10^4 (Taylor & McLennan, 1985), and might prove some potassium loss due to weathering. On the other hand, the mean K/U values for Borçka and Gümüşhane regions are very close to the K/U values of 7000–9000, 6000–7000 for the silicate earth as suggested by Lassiter (2004), Albarède (1998) and Davies (1999).

The Th/U values calculated for Trabzon region varying between 1.01 and 12.00 with a mean value of 3.38 $\pm$ 1.48 are quite close to the value of Taylor and McLennan (1985) for the upper crust. The average of Th/U values ranging from 0.32 to 8.36 was calculated as 2.01 $\pm$ 1.22 in the Borçka region. In the Gümüşhane area, Th/U values ranged between 0.17 and 7.59, and the mean value was calculated as 1.69 $\pm$ 1.09 (Fig. 8b). The study areas give very high Th/U values. Higher Th/U values calculated in three different regions are associated with mantle-derived volcanic rocks such as MORB and continental tholeiites contaminated with crustal material (Wedepohl, 1969).

Table 3
Statistical information for Th/U, U/Th and K/U values for all regions

Region	N	Th/U		U/Th		K/U (10^4)	
		Range	Mean $\pm$ sd	Range	Mean $\pm$ sd	Range	Mean $\pm$ sd
Trabzon	311	1.01–12.00	3.38 $\pm$ 1.48	0.08–0.99	0.35 $\pm$ 0.14	0.26–3.27	1.14 $\pm$ 0.42
Gümüşhane	304	0.17–7.59	1.69 $\pm$ 1.09	0.13–5.74	0.89 $\pm$ 0.72	0.13–3.21	0.70 $\pm$ 0.42
Borçka	301	0.32–8.36	2.01 $\pm$ 1.22	0.12–3.14	0.71 $\pm$ 0.52	0.15–2.72	0.74 $\pm$ 0.47

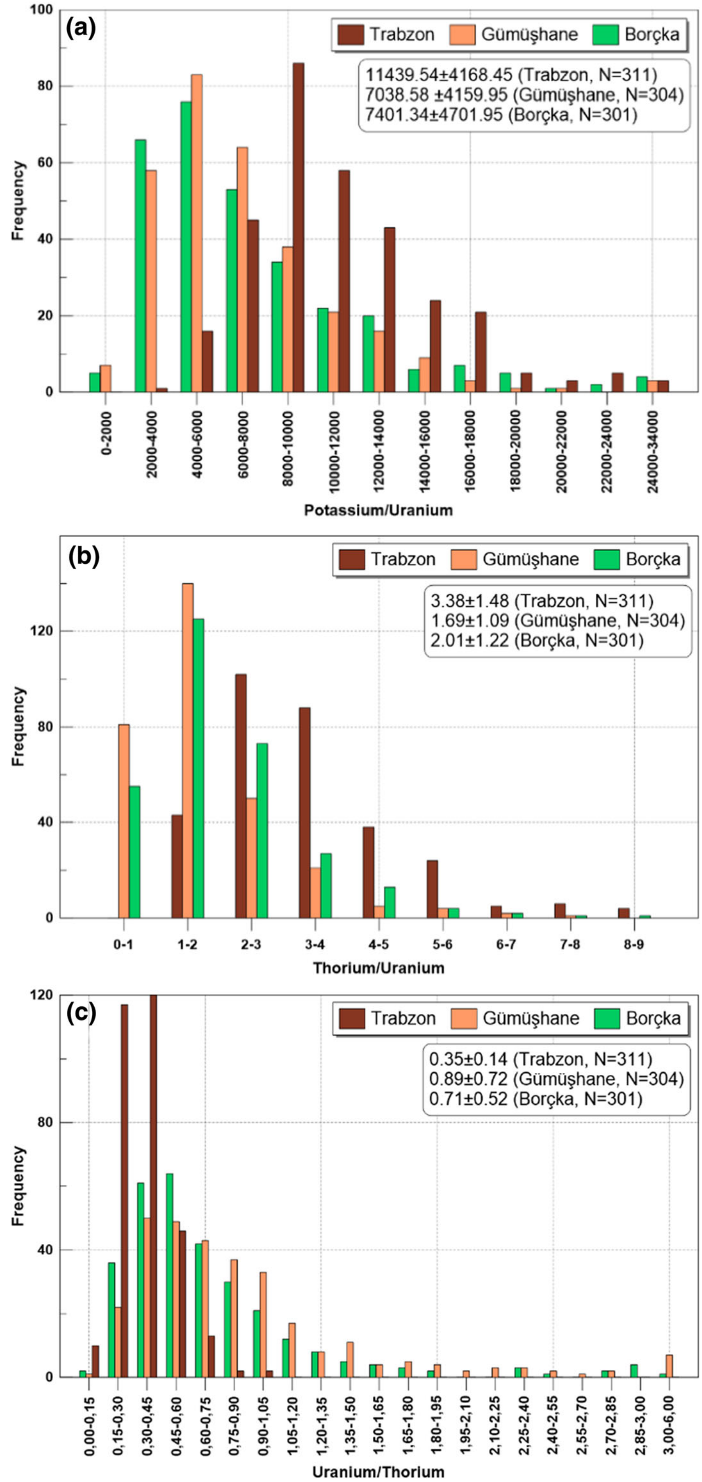

Figure 8
Histogram plots for **a** K/U, **b** Th/U and **c** U/Th ratio values of Trabzon, Gümüşhane and Artvin-Borcka regions

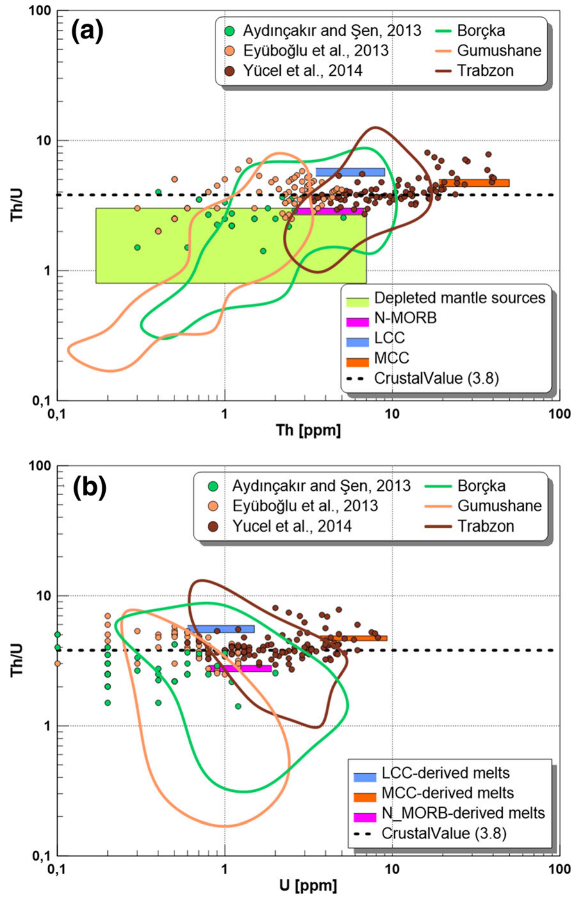

Figure 9
The plots of **a** Th/U versus Th and **b** Th/U versus U for the Trabzon, Gümüşhane and Artvin-Borcka regions. The composition of lower and middle continental crusts was taken from Rudnick and Gao (2003). Those of MORB and depleted mantle sources are from Sun et al. (2008) and McLennan et al. (1993). The dashed lines show the crustal value estimated by Taylor and McLennan (1985). LCC, lower continental crust; MCC, middle continental crust

The U/Th ratio in the Trabzon, Borçka and Gümüşhane regions ranged from 0.08 to 0.99, from 0.12 to 3.14 and from 0.13 to 5.74, respectively. The average U/Th values were calculated as 0.35 ± 0.14 for Trabzon, 0.71 ± 0.52 for Borcka and 0.89 ± 0.72 for Gümüşhane regions (Fig. 8c). High U/Th values are associated with water derived from subducted material in the arc region (Elliott, 1997). While the continental crust gives low U/Th values (0.25), the rocks originated from the depleted upper mantle give higher U/Th values (0.39) (Rudnick & Fountain, 1995; Sun & McDonough, 1989). Extremely high U/Th values (0.44) refer to island arc magmas related to subduction with low sediment contribution (Hawkesworth et al. 1997). The mean U/Th value obtained for Trabzon region is quite close to the values suggested by Rudnick and Fountain (1995) and Sun and McDonough (1989) for the rocks with depleted upper mantle origin. The average U/Th values calculated for Borcka and Gumushane are quite high and were considered to correspond to the subduction related low sediment contribution magmatism. While linear correlation was observed between Th/U values and age, an inverse relation was found between U/Th values and age. Higher U/Th and lower Th/U values comply with low age values (Table 3).

The Th/U versus Th and Th/U versus U plots for three different regions given in Fig. 9a, b showed that the magma originated from the mantle was contaminated by the lower continental crust materials in the Trabzon, Gümüşhane, Artvin-Borcka region (Fig. 9a, b). Magma originating from mafic mantle is exposed to crustal contamination during ascension or shallow-level crustal magma chambers (5–7 km) above the moho depth, which is consistent with the melting of the lithospheric mantle caused by rising of the asthenosphere (Maden, 2012a; Yücel et al. 2017). Crustal thickness is a key parameter in restricting ascending magmas fractionated at low pressures (Leeman, 1983). Maden (2012b) determined Moho temperature of 590 ± 60 °C at a depth of 35 km proving the existence of a brittle-ductile transition zone in the EPOB. The U and Th values obtained from geochemical analysis of the volcanic rocks in Trabzon (Yücel et al. 2014), Gümüşhane (Eyüboğlu et al. 2013), and Borçka (Aydınçakır & Şen, 2013) are not differ from the U and Th values obtained in this study (Fig. 9a, b). On the other hand, low RHP values reveal that the magmas did not expose to a considerable crustal contamination treatment during magma rising. The lower crust in island arcs might contain residue continental material ruptured from the continental substance by back-arc extension (Arculus & Johnson, 1981). Plot of K, U, Th and RHP values versus distance shows an inverse ralation for Trabzon, Gümüşhane and Borçka regions. The average K, U, Th and RHP values decreases with increasing distance from north to south, reflecting the decrease in RHP abundance with increasing geological age (Fig. 10).

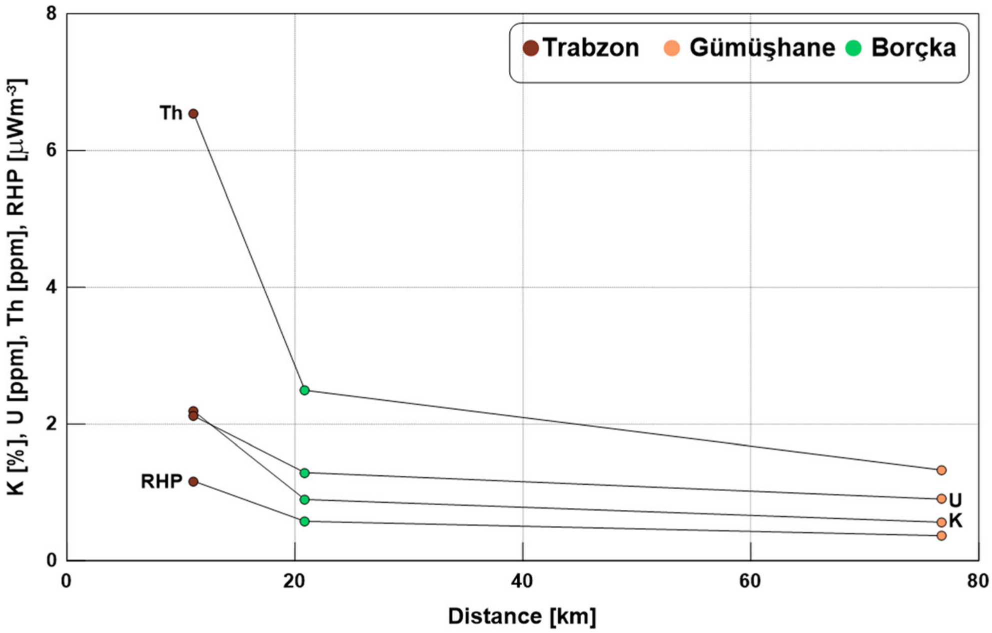

Figure 10
Average K, U, Th and RHP values versus distance for Trabzon, Gümüşhane and Borçka regions. Base point is assigned to the seashore for each region

6. Conclusions

Based on gamma ray spectrometry measurements, density and RHP estimations on the Tertiary aged volcanic rocks outcropping in Borçka, Gumushane and Trabzon regions from the EPOB (NE TURKEY), the following conclusions are drawn.

1. The average K, U, Th and RHP values decreases with increasing distance from trench (north) to arc (south), stating the decrease in RHP abundance with increasing geological age.
2. High Th/U values are associated with mantle-derived volcanic rocks such as MORB and continental tholeiite and are associated with water derived from subducting material in the arc region.
3. The higher U/Th value is related to the rocks derived from depleted upper mantle for Trabzon region and associated with subduction-related low sediment participation arc magmatism for the Borçka and Gümüşhane regions.
4. Average K/U values are compatible with a silicate earth model for Borcka and Gumushane regions and N-MORB model for Trabzon region.
5. Low radiogenic heat production values suggest a possible presence of relatively hot mantle material at shallow depth. Th makes the biggest contribution to RHP values, which is associated with the presence of minerals that contain Th as a trace element in their chemical content.
6. Mafic mantle derived magma is contaminated with crustal materials during ascension or shallow-level crustal magma chambers above the moho depth, which is convenient for melting of the lithospheric mantle.
7. It is concluded that Tertiary aged rocks in the EPOB are derived from the enriched upper mantle related to metasomatized by fluids derived from subducted slab.

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