Middle Eocene high-K acidic volcanism in the Princes’ Islands (İstanbul) and its geodynamic implications

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Abstract: The rock assemblages of the Princes’ Islands, which are located to the south of mainland Istanbul, are regarded as parts of the Lower Paleozoic quartz sandstones, although they were initially considered as volcanic rocks by Swan in 1868. They differ from quartz sandstones by their vesicular texture and are devoid of any stratigraphic layering. Their mineral constituents are plagioclase (30%–35%), feldspar (35%–40%), and quartz (20%–25%), corresponding to rhyolite. The crystallization age of the rhyolites is 45.66 ± 0.84 Ma on the basis of the U-Pb zircon data. They show high-K calc-alkaline affinity. On primitive-normalized spider diagrams, negative anomalies of Ba, Nb, Sr, P, and Ti and positive anomalies of Pb are noteworthy. Their chondrite-normalized REE patterns are characterized by strongly fractionated patterns with demonstrative negative Eu anomaly, whereby middle REE are not fractionated relative to the heavy REE. These geochemical features suggest a fractionating mineral assemblage of feldspar, apatite, and biotite without significant involvement of garnet. The Lutetian rhyolites of the Princes’ Islands are a part of the Middle Eocene magmatic associations of the West Pontides, related to collision of the Menderes-Taurus block with the Pontides.

Key words: İstanbul, quartz sandstone, rhyolite, Middle Eocene, West Pontides

1. Introduction

The Tethys Ocean, which began to subduct under Laurasia during the late Paleozoic-early Mesozoic (Topuz et al., 2018), was completely consumed during the Eocene along the İzmir-Ankara-Erzincan suture (IAES) (Şengör and Yılmaz, 1981). Destruction of the Tethys Ocean is associated with collision of the Pontides with the Kırşehir block (KB) and the Menderes-Taurus block (MTB) along the IAES (e.g., Okay and Tüysüz, 1999; Espurt et al., 2014).

The models explaining the Eocene tectonic setting of the Pontides are a matter of debate. The suggested models include: (a) an arc-related environment (Yılmaz et al., 1981, 2001; Erçan et al., 1995; Robinson et al., 1995; Delaloye and Bingöl, 2000; Köprübaşi et al., 2000; Okay and Satır, 2006; Ustaömer et al., 2009; Eyüboğlu et al., 2010, 2011), (b) a postcollisional environment (Harris et al., 1994; Genç and Yılmaz, 1997; Arslan et al., 2006; Kaygusuğ and Öztürk (2015), (c) a postcollisional setting comprising slab break-off (Altunkaynak, 2007; Keskin et al., 2008; Gülmez et al., 2013), (d) postcollisional extension (Topuz et al., 2005, 2011; Kürkçüoğlu et al., 2008; Kaygusuğ et al., 2011; Temizel et al., 2012; Arslan et al., 2013; Aslan et al., 2014; Yücel et al., 2014), and (e) lithospheric delamination (Köprübaşi and Aldanmaz, 2004; Karslı et al., 2010; Kaygusuğ et al., 2011; Arslan et al., 2013).

It is stated that Eocene magmatism is not present in the western section of the İstanbul-Zonguldak Tectonic Unit (İZTU), except for the Armutlu-Almacık zone (e.g., Gülmez et al., 2013). In this study, I present new U-Pb zircon age and geochemical data for volcanic rocks from the Princes’ Islands, located in western section of the İZTU, with the aim of shedding light on the Eocene geodynamic evolution.

2. Geological setting

The study area is located in the İZTU, forming the western part of the Pontides, to the east of the Rhodope-Strandja zone and to the north of the Sakarya zone (Figure 1). The İZTU includes Ordovician to Carboniferous sedimentary rocks, which unconformably overlie metamorphic rocks of Proterozoic age (e.g., Yiğitbaş et al., 1999). In the western section of the İZTU, these sequences are locally intruded by a Late Permian magmatic body (e.g., Yılmaz, 1977). All these rocks are unconformably overlain by Permo-Triassic siliciclastic and carbonate rocks (Türkecan and Yurtsever, 2002; Özgül, 2012). The western part of the İZTU was probably above sea level during Jurassic and early...
Cretaceous times. Upper Cretaceous-Paleocene sequences sit on the older rock units with major unconformity (e.g., Tüysüz et al., 2004). Additionally, there are local granodiorite intrusions of Late Cretaceous age (Öztunali and Satr, 1975). The Paleozoic sedimentary rocks are thrust over the Upper Cretaceous volcanosedimentary rocks and Paleocene sedimentary rocks to the north of İstanbul from south to north (Türkecan and Yurtsever, 2002).

The Middle Eocene magmatic and volcanic rocks in the Armutlu-Almacık zone are represented by basic to granitic volcanic rocks, dykes-sills, and coeval granites. The volcanic rocks exhibit a continuous trend from basalt to dacite. The Middle Eocene magmatic-volcanic assemblages show subduction components and display tholeiitic to low-K subalkaline affinities (e.g., Kürkçüoğlu et al., 2008; Gülmez et al., 2013).

3. Geology of the Princes' Islands
The geology of the Princes' Islands is represented by Ordovician to Carboniferous sedimentary rocks (Ketin, 1953; Çılgın, 2006; Özgül, 2012) (Figure 2). The Ordovician quartz sandstones are the dominant lithology on the islands (Figure 2). To the southwest of Büyük Ada, there is a roughly N-S directed thrust zone along which the Ordovician sandstones are thrust over the Devonian carbonate rocks. This thrust is regarded as the southerly extension of the Maltepe-Beykoz nappe on the mainland of İstanbul (Seymen, 1995; Çılgın, 2006). To the north of Heybeli Ada and northeast of Büyük Ada, Carboniferous clastic rocks, which comprise sandstone, mudstone, and minor limestone, are juxtaposed with Ordovician quartz sandstones by large normal faults (Çılgın, 2006; Özgül, 2012) (Figure 2).

Felsic volcanic rocks, the topic of this study, extend roughly in the NW-SE direction and cover approximately 4 km² (Çılgın, 2006) (Figure 2). They mostly crosscut the Ordovician quartz sandstones (Swan, 1868). The felsic volcanic rocks, which show strong alteration on the Princes' Islands, are distinguished from the Paleozoic quartz sandstones by their vesicular texture and massive appearance (Figure 3).

The discussion about these volcanics has a history of 150 years. The first person who dealt with these rocks was Swan (1868). His observations from Prinkipo to Antigoni, the initial names for Büyük Ada and Burgaz Ada, respectively, were as follows: (a) The units are similar to the quartz sandstones observed on all of the islands; however, feldspar and quartz minerals in the rocks show euhedral crystal forms unlike those in sedimentary rocks. (b) The
unstratified rocks are different from the quartz sandstones described as Paleozoic based on their vesicular textures. (c) The joint systems observed in these two rock groups are distinct. Swan (1868) stated that they are volcanic rocks and described them as trachyte according to their mineral composition. The rocks were also determined as felsic volcanics by von Hochstetter (1870) and Önalan (1981). In contrast, the rocks were described as altered quartz sandstones belonging to the Paleozoic sequence by Ketin (1953), Kaya (1973), and Özgül (2012).

4. Petrography
The felsic volcanic rocks have aphanitic and porphyritic textures. Plagioclase-oligoclase (30%–35%), alkali
feldspar-sanidine (35%–40%), and quartz (20%–25%) are the main phenocrysts (Figure 4). Amphibole, biotite, zircon, and apatite are conspicuous accessory minerals. Plagioclase forms euhedral to subhedral crystal forms and rarely displays polysynthetic twinning. Sanidine crystals also exhibit euhedral to subhedral forms. The felsitic groundmass displays sericitization, saussuritization, chloritization, kaolinization, and oxidation. The volcanic rocks of the Princes’ Islands are rhyolite according to their mineral assemblage.

5. Analytical methods

Zircon grains were separated from host minerals by heavy liquids after crushing, grinding, sieving, and cleaning at the Mineral Extraction Laboratory of Istanbul University for radiometric age dating. Zircons were extracted from ~1 kg of the freshest rhyolite and large zircon grains of ~63–200 µm were taken for analysis after being handpicked under a binocular microscope. The U-Pb zircon ages were determined by LA-ICP-MS at the Geological Institute of the Bulgarian Academy of Sciences in Sofia. Details of the analysis technique were given by Peytcheva et al. (2015).

Special care was taken in the selection of the samples for geochemical analysis. Ten samples were selected and prepared for geochemical analyses at the Sample Preparation Laboratory of Istanbul University. The altered surfaces of each sample were cleaned and the sample was prepared for geochemical analysis by crushing in a jaw crusher and grounding in an agate ball mill.

All samples were analyzed by ICP-ES and ICP-MS at ACME Labs (Vancouver, Canada). ICP-ES was used for major oxides, Ba and Sc, and Cu, Zn, and Ni. Other trace elements and rare earth elements (REEs) were analyzed by ICP-MS. Major elements have a detection limit of 0.01%. Trace elements have a detection limit between 0.01 and 1 ppm. Major and trace elements were measured from
aliquots samples of 0.2 g following LiBO$_2$ fusion and HNO$_3$ acid digestion. One gram of sample split was ignited for 2 h at 1000 °C and then cooled in a desiccator and weighed with the difference in weight represented as percent loss on ignition (% LOI). Calibration, verification standards, and reagent blanks were added to the sample sequence. The elemental concentrations of the samples were acquired using the CANMET standards (i.e. SY-4, STD SO-17) at ACME Labs, and USGS standards (i.e. W-2, AGV-1, G-2, GSP-2, BCR-2) were applied as known external standards. The analytical accuracy was better than ±3%.

6. Geochronology of rhyolites in Princes’ Islands
One sample (FS-Brg-2) was selected for LA-ICP-MS U-Pb zircon dating. The results of the analysis are given in Table 1. Selected zircon grains are transparent and light-brown under binocular microscope. Representative cathodoluminescence (CL) images of the zircon grains selected from the rhyolites are given in Figure 5. The zircon grains have oscillatory zoning and sector zoning, and are transparent, dark brown, stumpy, and euhedral to prismatic, ranging in size from 100 to 200 µm (Figure 5). The CL images of zircon grains support a magmatic origin. U and Th concentrations of sample FS-Brg-2 range from 166.5 to 431.8 and 83.8 to 369.6, and Th/U ratios are scattered from 0.45 to 0.86 (Table 1).

Sixteen zircon grains define a concordia age of 45.66 ± 0.84 Ma (2σ, MSWD = 2) (Figure 6). Based on the morphological and geochemical features of the zircons, the age is interpreted as the age of igneous crystallization for rhyolites of the Princes’ Islands.

7. Geochemistry
SiO$_2$ and Al$_2$O$_3$ contents of rhyolites range from 70.06% to 73.04% and from 12.69% to 15.74%, respectively. K$_2$O/Na$_2$O ratios are in the range of 0.33 to 0.38 (Table 2). LOI values are consistent with advanced alteration, as observed petrographically, and range from 3.6 to 8.1. They have moderate Sr values, ranging from 129 to 139 ppm. Ba values are in the range of 124–142 ppm. Zr abundances are relatively high, varying from 213 to 234 ppm. The ASI value ranges from 1.31 to 1.99 (Table 2), similar to that of S-type granite. Due to the small outcrop area of the rhyolites (~4 km$^2$) and restricted SiO$_2$ values, there is no significant trend in major-trace element fractionation diagrams.

The analyzed samples fall into the rhyolite field in the Nb/Y–Zr/Ti diagram of Pearce (1986) (Figure 7a) and the high-K calc-alkaline field of the classification diagram of Hastie et al. (2007) (Figure 7b).

On the primitive mantle-normalized element concentration diagram (Figure 8a), the rhyolites of the Princes’ Islands display negative anomalies in Ba, Nb, Ce, P, and Ti and positive anomalies in K, Nd, Zr, and Y. They show depletion in Nb relative to Ce. This means that all samples of rhyolites contain subduction components.

The rhyolites have similar REE patterns and show a prominent enrichment in LREEs (those from La to Nd), MREEs (from Sm to Ho), and HREEs (from Er to Lu) with respect to the chondrite values of Boynton (1984) (Figure 8b). Negative Eu anomalies (Eu/Eu* = 0.67–0.90) in the rhyolites are related to negative Ba, Nb, Sr, P, and Ti anomalies, suggesting crystallization of plagioclase, apatite, and biotite without significant involvement of garnet and alkali feldspar. In addition, chondrite-normalized La/Yb and Gd/Yb ratios of rhyolites range from 3.56 to 5.04 and from 1.23 to 1.51, respectively.

8. Discussion
The rocks defined as Paleozoic quartz sandstones (e.g., Özgül, 2012) are, in fact, volcanic rocks as initially
The temporal and spatial equivalences of the rocks, which are associated with the consumption process of the Tethys Ocean, are confined to a narrow belt along the İAES (Keskin et al., 2008; Gülmez et al., 2013). The Lutetian rhyolites were not formed during a lithospheric delamination process, because the mentioned rocks should be observed along the N-S directional line in a wide geography, covering the İAES and the KB with the MTB.

In the West Pontides, the final phase of the collision is described as Chattian (Elmas et al., 2016). The Kazdağ core complex, accepted as the beginning of the extensional tectonic regime in Western Anatolia, started during the latest Oligocene (c. 22–19 Ma; Okay and Satır, 2000). The collision related to the destruction of the Tethys Ocean lasted ~25 million years. Therefore, the Lutetian rhyolites of the Princes’ Islands formed in a syncollisional instead of postcollisional setting.

The Middle Eocene magmatic and volcanic rocks in the Armutlu-Almacık zone, ranging in age from Ypresian to Priabonian (c. 50–36 Ma; Kürkçüoğlu et al., 2008;
Figure 5. Representative CL images of dated zircon grains from sample FS-Brg-2. The red circles mark the analyzed domains.

Figure 6. U-Pb concordia diagram for the dated zircons from sample FS-Brg-2. The ‘n’ symbol represents the number of spots.
Table 2. The results of whole-rock major (wt.%), trace (ppm), and rare earth elements (REE) (ppm) geochemical analysis of rhyolites of the Princes’ Islands, including coordinates of all samples. The dated sample is represented in bold font.

| Sample     | Rhyolites f Burgaz Ada | Rhyolites of Heybeli Ada | Rhyolites of Büyük Ada |
|------------|------------------------|--------------------------|------------------------|
|            | FS-Brg-1               | FS-Brg-2                 | FS-Brg-3               | FS-Brg-4               | FS-Hyb-1 | FS-Hyb-2 | FS-Hyb-3 | FS-Hyb-4 | FS-Ba-1 | FS-Ba-2  |
| Coordinates| 0673404 / 4528110      | 0673799 / 4527561        | 0673901 / 4527048      | 0673098 / 4527352      | 0673908 / 4527352      | 0673908 / 4527352      |
| SiO₂       | 0.29                   | 0.29                     | 0.29                   | 0.29                   | 0.29                   | 0.29                   |
| TiO₂       | 0.38                   | 0.37                     | 0.34                   | 0.31                   | 0.36                   | 0.38                   |
| Al₂O₃      | 15.32                  | 14.68                    | 14.03                  | 13.09                  | 12.69                  | 14.56                  |
| Fe₂O₃      | 2.03                   | 2.66                     | 3.45                   | 3.39                   | 3.74                   | 3.05                   |
| MnO        | 0.06                   | 0.03                     | 0.05                   | 0.08                   | 0.01                   | 0.06                   |
| MgO        | 1.21                   | 1.27                     | 1.18                   | 1.14                   | 1.16                   | 1.19                   |
| CaO        | 1.64                   | 1.72                     | 1.51                   | 1.34                   | 1.96                   | 1.87                   |
| Na₂O       | 3.81                   | 3.93                     | 3.62                   | 3.64                   | 3.45                   | 3.63                   |
| K₂O        | 1.23                   | 1.15                     | 1.33                   | 1.44                   | 1.51                   | 1.63                   |
| P₂O₅       | 0.13                   | 0.11                     | 0.11                   | 0.12                   | 0.14                   | 0.13                   |
| Cr₂O₃      | 0.001                  | 0.002                    | 0.002                  | 0.003                  | 0.001                  | 0.003                  |
| LOI        | 5.2                    | 5.2                      | 6.3                    | 6.1                    | 5.6                    | 5.3                    |
| Sum        | 97.85                  | 97.15                    | 95.68                  | 95.11                  | 97.34                  | 97.58                  |
| Sc         | 8.00                   | 7.00                     | 8.00                   | 6.00                   | 6.00                   | 6.00                   |
| V          | 16.00                  | 14.00                    | 17.00                  | 15.00                  | 16.00                  | 16.00                  |
| Cr         | 5.80                   | 5.20                     | 6.40                   | 7.20                   | 4.10                   | 5.60                   |
| Co         | 3.00                   | 4.00                     | 2.00                   | 1.00                   | 5.00                   | 1.00                   |
| Ni         | 62.00                  | 64.00                    | 61.00                  | 60.00                  | 65.00                  | 74.00                  |
| Zn         | 17.10                  | 17.30                    | 17.60                  | 18.20                  | 17.10                  | 16.60                  |
| Ga         | 37.00                  | 35.00                    | 39.00                  | 41.00                  | 35.00                  | 38.00                  |
| Sr         | 135.00                 | 129.00                   | 134.00                 | 132.00                 | 131.00                 | 134.00                 |
| Y          | 44.00                  | 43.00                    | 42.00                  | 45.00                  | 41.00                  | 43.00                  |
| Zr         | 218.00                 | 215.00                   | 225.00                 | 213.00                 | 220.00                 | 229.00                 |
| Nb         | 9.00                   | 7.00                     | 8.00                   | 10.00                  | 7.00                   | 9.00                   |
| Th         | 5.10                   | 5.30                     | 5.20                   | 5.10                   | 5.30                   | 5.20                   |
| Cs         | 0.90                   | 0.70                     | 0.80                   | 0.80                   | 0.90                   | 0.70                   |
| Ba         | 135.00                 | 132.00                   | 128.00                 | 124.00                 | 142.00                 | 130.00                 |
| Pb         | 8.20                   | 8.60                     | 8.20                   | 8.60                   | 8.10                   | 8.30                   |
| Ta         | 0.57                   | 0.51                     | 0.57                   | 0.53                   | 0.53                   | 0.54                   |
| Hf         | 5.20                   | 5.40                     | 5.30                   | 5.30                   | 5.50                   | 5.50                   |
| U          | 1.50                   | 1.60                     | 1.70                   | 1.60                   | 1.60                   | 1.60                   |
| La         | 24.00                  | 26.00                    | 24.00                  | 23.00                  | 27.00                  | 23.00                  |
| Ce         | 36.00                  | 42.00                    | 45.00                  | 38.00                  | 39.00                  | 36.00                  |
| Pr         | 4.55                   | 4.68                     | 4.75                   | 4.58                   | 4.69                   | 4.57                   |
| Nd         | 23.40                  | 25.60                    | 27.10                  | 22.30                  | 27.60                  | 24.60                  |
| Sm         | 5.30                   | 5.90                     | 7.50                   | 6.30                   | 6.90                   | 5.40                   |
| Eu         | 1.40                   | 1.40                     | 1.50                   | 1.60                   | 1.50                   | 1.40                   |
Table 2. (Continued).

| Element | 6.10 | 6.20 | 6.10 | 6.10 | 6.50 | 6.40 | 6.20 | 6.30 | 6.20 | 6.40 |
|---------|------|------|------|------|------|------|------|------|------|------|
| Gd      |      |      |      |      |      |      |      |      |      |      |
| Tb      | 1.10 | 1.30 | 1.20 | 1.00 | 1.10 | 1.30 | 1.20 | 1.00 | 1.30 | 1.10 |
| Dy      | 6.45 | 7.52 | 7.50 | 6.30 | 6.24 | 6.52 | 6.30 | 6.47 | 6.41 | 5.49 |
| Ho      | 1.39 | 1.34 | 1.54 | 1.36 | 1.57 | 1.63 | 1.32 | 1.37 | 1.61 | 1.54 |
| Er      | 4.25 | 4.12 | 4.38 | 4.21 | 4.68 | 4.34 | 4.38 | 4.69 | 4.21 | 4.19 |
| Tm      | 0.64 | 0.63 | 0.74 | 0.57 | 0.78 | 0.53 | 0.57 | 0.65 | 0.52 | 0.61 |
| Yb      | 3.68 | 3.92 | 3.97 | 3.75 | 3.92 | 3.97 | 3.21 | 3.31 | 3.69 |      |
| Lu      | 0.65 | 0.63 | 0.69 | 0.78 | 0.71 | 0.63 | 0.64 | 0.69 | 0.64 | 0.75 |
| ASI     | 1.44 | 1.35 | 1.38 | 1.31 | 1.16 | 1.30 | 1.41 | 1.19 | 1.36 | 1.53 |
| Eu/Eu*  | 0.75 | 0.70 | 0.67 | 0.78 | 0.68 | 0.72 | 0.91 | 0.75 | 0.70 | 0.75 |

Figure 7. Classification diagrams of the rhyolites from the Princes’ Islands. a) Nb/Y–Zr/Ti diagram after Pearce (1986); b) Co–Th diagram after Hastie et al. (2007). B: Basalt; BA/A: basaltic andesite and andesite; D/R: dacite and rhyolite; IAT: island-arc tholeiite; CA: calc-alkaline; H-K: high-K series.

Figure 8. a) Primitive mantle-normalized multi-element diagrams, b) chondrite-normalized REE diagrams for the rhyolites in the Princes’ Islands.
9. Conclusions

Based on my field observations and analytical data, the main conclusions are as follows: (a) The studied rocks defined as Paleozoic quartz sandstones are, in fact, rhyolites. (b) The crystallization age of these rhyolites is Lutetian based on the U-Pb age data. (c) The Lutetian rhyolites of the Princes’ Islands in the İZTU formed in a syncollisional setting based on the data of regional geological correlation. (d) Lutetian rhyolites of the Princes’ Islands form a part of the Middle Eocene magmatic volcanic province in the Armutlu-Almacık zone.

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