Cretaceous Subduction-Related Magmatism and Associated Porphyry-Type Cu-Mo Prospects in the Eastern Pontides, Turkey: New Constraints from Geochronology and Geochemistry

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Abstract

This study focuses on the Elbeyli-Ordu, Emeksen-Giresun, Güzelyayla-Trabzon and Ulutaş-Ispir porphyry-type prospects located in the Eastern Pontides, Turkey. Our new LA-ICP-MS U-Pb zircon age data reveal that the Elbeyli-Ordu Mo-Cu mineralization is hosted by a 77.0 ± 1.3 Ma-old monzonite/monzodiorite with a shoshonitic character. The Emeksen Mo mineralization, located ~40km southeast of the Elbeyli-Ordu prospect, consists of NW- and NE-striking quartz veins crosscutting a high-K calc-alkaline to shoshonitic granite dated at 78.5 ± 0.8 Ma, a granodiorite dated at 78.7 ± 0.5 Ma and porphyry granite dated at 77.7 ± 0.5 Ma. The Güzelyayla porphyry Cu-Mo prospect consists of a stockwork-type Cu-Mo mineralization crosscutting a calc-alkaline 81.4 ± 1.1 Ma-old dacite porphyry and Late Cretaceous calc-alkaline andesite. The Ispir-Ulutaş mineralization is hosted within a highly sericitized 131.1 ± 0.9 Ma-old quartz-porphyry that intruded into a 132.9 ± 0.6 Ma-old calc-alkaline granite porphyry. Our new U-Pb zircon ages, lithogeochemical and radiogenic isotopic data of the host rocks associated with the porphyry-type prospects in the Eastern Pontides indicate that they formed in an arc-related environment during Cretaceous subduction of the Neotethys Ocean, and the Ispir-Ulutaş prospect is attributed to the main stage of the northward subduction of the Neotethys during the Early Cretaceous. We conclude that the Güzelyayla and Emeksen hydrothermal systems were formed during a transitional compressional to extensional tectonic evolution, whereas the Late Cretaceous Elbeyli hydrothermal system was emplaced during an extensional arc magmatic event. Highly-oxidized, high-K calc-alkaline to shoshonitic magmas at Emeksen and Elbeyli were derived from a metasomatised, heterogeneous and enriched lithospheric mantle, with variable degrees of partial melting of the mantle wedge and variable crustal contamination. Mixing/mingling processes between mafic magmas derived from the lower crust and acidic magmas at upper crustal levels played an important role in the formation of Cu-Mo porphyry-type mineralization in the Eastern Pontides.

1. Introduction

The EW-trending Pontides of northern Turkey was formed as a consequence of northward subduction of the Neotethys Ocean along the Eurasia margin during the Mesozoic, and was followed by final collision with the Anatolides-Taurides platform during the Cenozoic (Akıncı, 1984; Okay and Şahintürk, 1997; Şengör and Yılmaz, 1981). These successive tectonic environments resulted in the formation of volcanogenic massive sulfide (VMS)-, porphyry- and epithermal-type deposits and prospects related to calc-alkaline and adakitic magmatism. This study focuses on porphyry-type mineralizations (**Fig. 1; Table 1**) in the Eastern Pontides, which are associated to Cretaceous subduction-related calc-alkaline magmatism.

Although a number of porphyry-type Cu-Mo±Au mineralizations (e.g. Emeksen-Giresun; Güzelyayla-Trabzon; Berta-Artvin; Ulutaş-Erzurum) have been documented in the Eastern Pontides since the 1970s (e.g. Giles, 1973; Soylu, 1999; Yalçınalp,

1995; Yavuz, 1992;), most of the scientific ore deposit studies in the region and exploration efforts concentrated on VMS deposits (e.g. Akıncı, 1980; Çağatay and Boyle, 1977; Eyüboğlu et al., 2014; Pejatović, 1979; Revan, 2010; Revan et al., 2014). By contrast, genetic aspects and the investigation of the geological settings of porphyry-type mineralization were neglected so far. Consequently, their relationship with respect to the magmatism and the geodynamic evolution of the Eastern Pontides remains poorly understood, due to the lack of geochemical and geochronological data.

Recent studies along the Eastern Pontides have provided abundant data and new interpretations for the geodynamic evolution, the regional geology, and the petrogenesis of volcanic and granitic rocks (e.g. Karlı et al., 2012a; Kaygusuz et al., 2013; Okay and Şahintürk, 1997; Okay and Tüysüz, 1999; Topuz et al., 2011). Nevertheless, the timing of the onset of subduction still remains open to question. Some authors suggested that subduction started during the Jurassic or earlier, (e.g. Adamia et al., 1977, 1981; Kazmin et al., 1986), whereas Okay and Şahintürk (1997) proposed that the volcanic arc developed later during the Turonian to Maastrichtian-Danian time interval. Therefore, dating the host rocks of porphyry-type mineralizations in the Eastern Pontides will allow us to place constraints on the geodynamic evolution of the belt. Thus, it is important to understand the timing and the nature of the magmatism associated with the various porphyry-type systems in order to constrain the exact relationships between ore-forming and geodynamic processes along the Eastern Pontides magmatic arc.

In this contribution, we report new U-Pb zircon age data of granitic rocks acquired by LA-ICP-MS for the Elbeyli-Ordu, Emeksen-Giresun, Trabzon-Güzelyayla and Ispir-Ulutaş-Erzurum porphyry-type prospects (**Fig. 1**) and new radiogenic isotope (Sr-Nd-Pb) and lithogeochemical data for the Elbeyli-Ordu and Emeksen-Giresun prospects to constrain the age of magmatism, the petrogenesis of the host rocks, and their relationship with the ore-forming events. In addition, we discuss our data within the frame of previously published geochronological, isotopic and lithogeochemical data of the Eastern Pontides, in order to offer a regional synthesis of the timing of magmatism and porphyry-type ore formation along the belt.

2. Regional Geology and Geodynamic Setting of the Eastern Pontides

Turkey comprises three main tectonic blocks with distinct stratigraphic and structural features, which are the Anatolide-Tauride block, Kırşehir Massif and the Sakarya block, which includes the Rhodope-Strandja zone, the Istanbul zone and the Eastern Pontides (**Fig. 1**; Ketin, 1966; Şengör and Yılmaz, 1981; Okay and Tüysüz, 1999). The three main tectonic blocks are bounded by major oceanic suture zones, including: the Izmir-Ankara-Erzincan Suture zone (IAEZ), the Intra-Pontide Suture zone, the Inner-Tauride Suture zone, and the Assyrian-Zagros Suture zone (Fig. 1). The amalgamation of these terranes and the creation of a single landmass occurred during closure of different branches of the Tethyan Oceans from the Late Mesozoic to the Early Cenozoic (e.g. Okay and Tüysüz, 1999; Rolland et al., 2009a; Topuz et al., 2013a; **Fig 1, Inset**).

The Elbeyli Mo±Cu, Emeksen Mo, Güzelyayla Cu-Mo, and Ispir-Ulutaş Cu-Mo porphyry-type prospects are located at the Eastern Pontides, which is bounded in the south by the Izmir-Ankara-Erzincan Suture and in the north by the East Black Sea Basin (Fig. 1). To the east, the Eastern Pontides extends into the Lesser Caucasus (Adamia et al., 1977, 1981; Okay and Şahintürk, 1997). The geological evolution of the Eastern Pontides is the result of northward Cretaceous subduction of the Neotethys (e.g. Okay and Şahintürk, 1997; Şengör et al., 1980; Şengör and Yılmaz, 1981; Yılmaz et al., 1997), and Late Cretaceous to early Cenozoic collision to post-collision processes (e.g. Altherr, et al., 2008; Okay, 2008; Topuz et al., 2011). Ore deposits and prospects studied so far in the Eastern Pontides are Cretaceous to Eocene in age and are related to the evolution of the Tethyan Ocean (e.g. Eyüboğlu et al., 2014; Yiğit, 2009).

The basement of the Eastern Pontides comprises Carboniferous high-temperature and low-pressure metamorphic rocks, high-K, I-type granitic rocks, dacite, and Upper Carboniferous sedimentary rocks (Okay and Şahintürk, 1997; Topuz et al., 2007, 2010). Lower to Middle Jurassic volcanic and volcano-sedimentary units, which are crosscut by local gabbro, diorite and I-type granite intrusions, unconformably overlay the pre-Jurassic basement of the Eastern Pontides (Dokuz et al., 2006, 2010; Okay and Şahintürk, 1997; Şen, 2007; Ustaömer and Robertson, 2010). The Jurassic units volcano-sedimentary units are mainly interpreted as a rift-related sequence, which resulted in the opening of the southern branch of Neotethys along a rift zone in the south due to the southward subduction of the Paleotethys (Dokuz et al., 2010; Görür, 1988; Şengör et al., 1980; Şengör and Yılmaz, 1981; Yılmaz et al., 1997). However, this Jurassic magmatism in the Eastern Pontides and its eastern extension in the

Lesser Caucasus is interpreted also as back-arc magmatism during northward subduction of the Paleotethys (e.g. Rolland et al., 2009b, 2011; Topuz et al., 2013a; Ustaömer and Robertson, 2010; Ustaömer et al., 2012; **Fig 2**).

During the Late Cretaceous, intense calc-alkaline to tholeiitic, submarine magmatism in the Eastern Pontides was associated with northward subduction of the northern branch of the Neotethys beneath the Eurasian plate. (Akin, 1978; Akıncı, 1984; Eğin et al., 1979; Gedik et al., 1992; Gedikoğlu, 1978; Manetti et al., 1983; Peccerillo and Taylor, 1975). Magmatism began with basaltic and andesitic lava, grading upwards into dacitic and rhyolitic lava interbedded with limestone (Akıncı, 1984; Eğin et al., 1979) and was accompanied by abundant, mainly granitic to granodioritic Cretaceous intrusions (**Fig 1**).

Shortly after Late Cretaceous arc-related magmatism, closure of the Neotethys led to strong compressional deformation during the Cenozoic, characterized by crustal shortening, thickening and uplift (Okay and Şahintürk, 1997; Yılmaz et al., 1997) (**Fig 2**). The timing of the transition from subduction to collision has been interpreted to be Paleocene to Early Eocene (e.g. Okay and Şahintürk, 1997; Peccerillo and Taylor, 1975; Şengör and Yılmaz, 1981; Topuz et al., 2011). Middle to Late Eocene magmatic rocks are attributed to a switch of the tectonic regime from compression to extension caused by the opening of the eastern Black Sea Basin (Okay, 2008), although Nikishin et al. (2011) suggest that the eastern Black Sea Basin already opened during the Cenomanian to Coniacian. After a relatively short period of time of extension, the Eastern Pontides was uplifted above the sea level with minor

volcanism and terrigenous sedimentation at the end of the Eocene (Okay, 2008; Topuz et al., 2011).

3. Geological Settings of the Porphyry-Type Prospects

3.1. The Elbeyli-Ordu Mo±Cu prospect

The newly discovered Elbeyli Mo±Cu prospect lies within the Kabataş batholith, which is located in the westernmost part of the Eastern Pontides (**Fig 1**). Mineralization in the Elbeyli prospect is hosted by small monzonite/monzodiorite bodies (<2km²) and the surrounding Cretaceous volcanic and volcano-sedimentary rocks. The latter consist of andesitic and dacitic lava and pyroclastic rocks. Monzodiorite/monzonite has a pinkish color and a porphyritic texture. It consists of plagioclase, K-feldspar, pyroxene, amphibole, biotite and quartz. Plagioclase phenocrysts are subhedral and normally zoned (core: An_{51.9-44.3}, rim: An_{26.7-26.5}) and some plagioclase crystals are characterized by high albite contents in their rims (Ab_{70.5-69.6}) (**Appendix 1**).

The Elbeyli prospect consists of a quartz-pyrite±chalcopyrite stockwork, and NW-striking quartz-molybdenite-enargite±chalcopyrite veins. Stockwork quartz-pyrite±chalcopyrite mineralization dominates in the Cretaceous volcano-sedimentary rocks, whereas disseminated molybdenite mineralization can be observed around the vein systems crosscutting both volcanic and plutonic rocks. EW- and NE-trending faults cut the plutonic and volcano-sedimentary rocks, and control the quartz-pyrite veins (Delibaş et al., 2014). Late NW-trending faults, dipping 15-70° to the NE cut the former fault sets and control younger quartz-enargite-molybdenite±chalcopyrite veins

and zunyite-pyrophyllite-bearing alteration assemblages (Delibaş et al., 2015a). The NW-striking vein system at the Elbeyli prospect is characterized by an intermediate- to high-sulfidation mineral association including enargite, chalcopyrite, tennantite, tetrahedrite, molybdenite, galena, euhedral pyrite, and minor native bismuth. Enargite and euhedral pyrite are replaced by tennantite and tetrahedrite along rims and fractures. Molybdenite fills the abundant fractures of vein and disseminated pyrite.

3.2. The Emeksen-Giresun Mo Prospect

The Emeksen Mo prospect lies within the Emeksen batholith (Doğan, 1980), which is located in the Emeksen-Çakıldağ area within the Eastern Pontides (**Fig 1**). Reserve or resource data for the Emeksen prospect have not been defined so far, but available data show that average Mo contents of the veins vary between 0.08 % and 2.87 % (MTA, 1984).

The basement of the Emeksen-Çakıldağ area consists of early Mesozoic metamorphic sequences, which are unconformably overlain by Lower to Upper Cretaceous volcanic and volcano-sedimentary rocks (Kamitani et al., 1977). The Late Cretaceous plutonic rocks, which host Mo mineralizations, intrude into the volcanic and volcano-sedimentary sequences of the region. On the basis of geological, mineralogical, and textural characteristics, we have subdivided the plutonic rocks into four main phases, including granodiorite, granite, porphyritic granite and gabbro-diorite. Granodiorite, granite and porphyritic granite have gradational contacts with each other, whereas the gabbro-diorite stocks and dykes of the northern zone have sharp intrusive contacts with granite and older volcanic sequences. In many places,

granitic rocks contain microgranular, roughly oval dioritic enclaves, which are fine-grained, medium to dark grey, and have sharp contacts with their hosts.

The porphyritic granite is the predominant intrusive unit of the region and it consists of euhedral to subhedral normally zoned plagioclase (core: An_{38.06-35.82}, rim: An_{28.49-20.27}), quartz, subhedral K-feldspar (core: Or_{84.8}, rim Or_{90.2}) (**Appendix 2**), subhedral amphibole and biotite. Apatite, zircon, titanite and rutile are the most common accessory minerals and epidote, chlorite and sericite are alteration products of the main mineral association. The other major plutonic phase of the Emeksen area is an epi-granular, coarse-grained granite. The granite is exposed in the western part of the area and it is mineralogically very similar to that of the porphyritic granite, except that the latter has a more pronounced porphyritic texture. Furthermore, plagioclase phenocrysts display both normal (core: An_{76.6-65.5}, rim: An_{31.7-13.7}) and slight reverse zoning, with low An cores (An_{51.4-50.3}) surrounded by relatively high An rims (An_{67.5-53.6}) (**Appendix 2**).

The granodiorite is medium-grained and grey to dark grey in color. It has predominantly an epi-granular texture, and amphibole, biotite, plagioclase, quartz and K-feldspar are the main mineral phases. The secondary minerals consisting of sericite, chlorite, calcite and as well as muscovite are very common within the granodiorite because of the intense sericitic alteration. Plagioclase crystals display normal (core: An_{52.3-48.0}, rim: An_{33.4-31.5}) and reverse zoning (core: An_{48.18-38.75}, inner rim: An_{49.5-43.6}, outer rim: An_{34.1-32.5}) (**Appendix 2**).

Mo mineralization in the Emeksen area is related to stockwork and NW-, and NS-striking vertical/sub-vertical quartz veins crosscutting the granodiorite, the granite and the porphyritic granite (Delibaş et al., 2014; 2015b). Sericitic alteration consists of muscovite and biotite is the dominant alteration around veins.

3.3. The Güzelyayla-Trabzon Cu-Mo prospect

The Güzelyayla Cu-Mo prospect is located about 50km south of the city center of Trabzon (**Fig 1**). Exploration campaigns allowed to define 186.2 Mt at 0.3 % Cu equivalent and 0.002-0.021% Mo of total proven and probable reserves according to Er et al. (1992) and Güner and Güç (1990).

The known stratigraphy in the Güzelyayla prospect is entirely composed of Upper Cretaceous volcanic rocks with intercalations of siltstone-mudstone and limestone, and all volcanic- and volcano-sedimentary units are crosscut by a porphyritic granite, a dacite porphyry, and quartz porphyry dykes (Çınar and Yazıcı, 1985; Nebioğlu, 1983).

A porphyritic granite is the largest intrusive body in the mapped area of the Güzelyayla prospect and is exposed in the southern part of the area. It is pinkish to grey in color and it has a dominantly porphyritic texture. Plagioclase and quartz are the common phenocrysts within the medium-grained and epi-granular groundmass. The porphyritic granite is crosscut by the dacite porphyry, which hosts the Cu-Mo mineralization. It is mostly composed of quartz, plagioclase, K-feldspar, biotite and minor amphibole. Magnetite, hematite and rutile are present in nearly every sample. Apatite and zircon are common accessory minerals of the dacite porphyry.

The Güzelyayla Cu-Mo prospect consists of two types of mineralization known as stockwork-type and dissemination. Stockwork-type quartz veins crosscutting the dacite porphyry and Cretaceous volcanic rocks are typically rich in chalcopyrite, pyrite, pyrrhotite, rutile and minor molybdenite, whereas disseminated mineralization in dacite porphyry is characterized by chalcopyrite, magnetite and pyrite. On the other hand, molybdenite is mainly enriched in the late stage, 0.1 to 4cm thick quartz veins cutting dacite porphyry and Cretaceous volcanic rocks (Delibaş et al., 2014).

4.4. The Ispir-Ulutaş-Erzurum Cu-Mo prospect

The Ulutaş Cu-Mo prospect lies within the Ispir batholith (**Fig 1**). Based on drill-hole data, the total reserves were estimated at 73.6Mt at a grade of 0.31% Cu and 0.022% Mo (Giles, 1973; Soylu, 1999; Yiğit, 2009).

Porphyry type Cu-Mo mineralization at the Ulutaş prospect is hosted by granite porphyry and quartz porphyry of the Ispir batholith, which is a calc-alkaline multi-phase plutonic complex varying from granite through quartz diorite to syeno-diorite. A granodiorite phase of the batholith exposed 1 km east of the prospect yielded a K-Ar age of 132 ± 5 Ma (Giles, 1973).

The oldest units exposed in the northwestern part of the Ulutaş area are Paleozoic-Lower Mesozoic metamorphic rocks. The metamorphic basement is covered by strongly folded, weakly metamorphosed Cretaceous lava flows of dacitic to rhyolitic composition and pyroclastic rocks with intercalations of laminated mudstone, and shale (Giles, 1973; Taylor and Fryer, 1980). The basement units and volcano-sedimentary sequence are intruded by Ulutaş intrusions that form an erosion window

in the Eocene volcanic- volcano-sedimentary rocks, comprising andesitic to basaltic lava, tuff and agglomerate with marl, conglomerate, sandstone and limestone intercalations (Giles, 1973; Taylor and Frey, 1980).

A granite porphyry hosting Cu-Mo mineralization exposed in the northern part of the area represents the largest intrusive unit in the region. It is characterized by a pronounced porphyritic texture at the outcrop scale. Central parts of the granite porphyry are characterized by intrusions of NE-trending, steeply dipping quartz porphyry dykes or stocks, with a porphyritic texture with phenocrysts of embayed quartz and a fine-grained groundmass of quartz and highly sericitized plagioclase. Both granite porphyry and quartz porphyry are crosscut by dioritic, andesitic dykes hosting pyrite-chalcopyrite veinlets (1 to 2mm), The granite porphyry contains micro-granular, roughly oval medium to dark grey dioritic enclaves, which have sharp contacts with their host. All units are overlain by Pleistocene to recent glacial debris and alluvial sediments (Giles, 1973).

Porphyry-type mineralization in the Ulutaş area consists of stockwork veins and NW-striking quartz veins, with disseminated chalcopyrite along the vein systems, and molybdenite within the 1-2cm thick quartz veins (Soylu, 1999).

4. Results

4.1. Whole-rock geochemistry of intrusive rocks

The analytical techniques used in the present study are summarized in **Appendix 3** and the major and trace element data of the Elbeyli and Emeksen intrusive rocks are presented in **Appendix 4 and 5**. Geochemical data for the Güzelyayla and Ulutaş

intrusions were taken from Yalçınalp (1992) and Taylor and Frey (1980), respectively. The Zr/TiO_2 vs. Nb/Y diagram (Winchester and Floyd, 1977) is used to classify intrusive rocks from Elbeyli and Emeksen (**Fig 3a**), because of the effects of hydrothermal alteration, and the classification terminology of the plutonic rocks are taken from Middlemost (1985).

Plutonic rocks from Elbeyli range in composition from monzonite to diorite with SiO_2 contents varying from 58 to 63.5 wt.%, and the Emeksen plutonic rocks range in composition from granodiorite to monzonite with SiO_2 contents varying from 63.5 to 75 wt.%, whereas the Güzelyayla samples are granodioritic and the Ispir-Ulutaş samples are granitic in composition. Dioritic rocks crosscutting the granitic rocks at Emeksen are dioritic/gabbroic in composition (**Fig 3a**). The Elbeyli samples have higher Al_2O_3 (average: 16 wt.%), FeO_t (6.5 wt.%), MgO (average: 2.2 wt.%) and CaO (average: 4 wt.%) contents when compared to the Emeksen granitic and granodioritic samples (average: 15 wt.%, 4 wt.%, 1.2 wt.% and 2.3 wt. %, respectively) and the K_2O/Na_2O ratio for the Elbeyli and Emeksen samples vary between 1.5 to 2.5 and 1 to 2, respectively. Diorite samples of the Emeksen prospect, on the other hand, have high FeO_t (average: 11.5 wt.%), MgO (average: 5.3 wt.%) and CaO (average: 9.5 wt.%) and low contents of SiO_2 (average: 53.2 wt.%), Na_2O (average: 2.5 wt.%) and K_2O (average: 0.3 wt.%). Güzelyayla and Ispir- Ulutaş samples and also granodioritic and granitic rocks from the Emeksen prospect are all sub-alkaline in nature, whereas the Elbeyli monzonitic samples straddle the boundary between alkaline to sub-alkaline series in the total alkali (Na_2O+K_2O) vs. SiO_2 diagram (**Fig 3b**). In the AFM diagram (**Fig. 3c**), Elbeyli and Emeksen granitic and granodioritic rocks and also the Güzelyayla and Ispir-Ulutaş samples plot in the calc-alkaline field, whereas diorite

samples from Elbeyli have a tholeiitic character. However, there is a clear transition from calc-alkaline to tholeiitic compositions for all rock series (**Fig 3c**). Samples from Elbeyli exhibit a shoshonitic compositional trend, while Emeksen granitic and granodioritic samples mainly belong to the high-K calc-alkaline to shoshonitic series. On the other hand, Güzelyayla and Ispir-Ulutaş samples range in composition from calc-alkaline to high-K calc-alkaline (**Fig 3d**).

Binary plots of Elbeyli and Emeksen samples for most of the major elements show a good correlation with SiO_2 (**Fig 4**). TiO_2 , Al_2O_3 , MgO , CaO and FeO_t contents decrease with increasing SiO_2 , and K_2O and Na_2O concentrations slightly increase with increasing SiO_2 (**Fig 4**). Although trace element variations of the Elbeyli and Emeksen samples show some scattering, Ni and V contents decrease with increasing SiO_2 . La and Ba display a slight positive correlation with increasing SiO_2 for the Emeksen samples (**Fig 4**). The Elbeyli rocks have higher Ni and V contents ranging from 9 to 16 ppm (average 8.5 ppm) and 106 to 174 ppm (average 122 ppm), respectively, whereas the Emeksen granite and granodiorite samples have variable and lower Ni (ranging from 3 to 17 ppm; average: 5 ppm) and V (ranging from 18 to 150 ppm, average: 61) contents. In addition, both Elbeyli and Emeksen samples have low to moderate Sr contents (for Elbeyli average: 363 ppm; for Emeksen granodioritic and granitic sample average: 233 ppm), compared to adakitic rocks. However, they have relatively high Y (Elbeyli average: 21 ppm; Emeksen average: 20 ppm) and Yb concentrations (Elbeyli average: 1.8 ppm; Emeksen average: 2 ppm) and explain low to moderate Sr/Y and La/Yb ratios for both Elbeyli and Emeksen samples. Therefore, in the Sr/Y vs. Y diagram (**Fig 5a**), the Elbeyli and Emeksen granite and granodiorite samples plot within the normal volcanic-arc field,

whereas the Emeksen porphyritic granite and Güzelyayla dacite porphyry samples straddle the boundary between the adakitic and volcanic-arc fields. Similarly some samples of the Güzelyayla prospect plot in both adakitic and calc-alkaline fields on the Sr/Y vs. SiO₂ diagram (**Fig 5b**). Furthermore, La/Yb ratios remain constant for variable SiO₂ contents of the Emeksen (granitic and granodioritic) and Elbeyli samples (**Fig 5c**).

The Elbeyli, Emeksen, Güzelyayla and Ispir-Ulutaş samples have nearly similar mantle-normalized spider patterns and they display subduction-related features (**Figs 6a-d**), including high concentrations of large-ion lithophile elements (LILE), low contents of high field strength elements (HFSE), and negative Nb and Ti and positive Pb, K and U anomalies. The Emeksen granodioritic and granitic samples show moderate negative Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.5\text{-}0.9$) and variable light rare earth element (LREE) enrichments ($(\text{La}/\text{Yb})_N = 7\text{-}13.5$) and more pronounced depleted medium rare earth element (MREE) patterns in chondrite-normalized REE diagrams (**Fig 7**), whereas the Elbeyli samples are characterized by weak negative Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.7\text{-}0.9$) with $(\text{La}/\text{Yb})_N$ of 8.0-10, when compared to the Emeksen granodioritic and granitic samples (**Fig 7**). Diorite samples from Emeksen have highly variable LREE enrichments with $(\text{La}/\text{Yb})_N$ of 0.8-2 and have either positive or negative Eu anomalies with (Eu/Eu^*) values ranging from 0.7 to 1.2 (**Fig 7c**).

4.2. U-Pb Zircon Geochronology

Abundant geochronological data have been obtained in recent years for Upper Cretaceous to Paleocene granitoids related to Neotethys subduction and collision in the Eastern Pontides (e.g. Boztuğ et al., 2004; Boztuğ and Harlavan, 2008; Karslı et

al., 2010; Kaygusuz et al., 2008, 2009, 2013, 2014). However, no reliable geochronological data have been produced so far for granitic rocks, which host porphyry type prospects in the region. Therefore, seven plutonic rock samples were chosen from the Elbeyli (OFA-1), Emeksen (GE-1, GE-2, and GE-4), Güzelyayla (TMG-1) and Ispir-Ulutaş areas (Ei-1 and Ei-3) for U-Pb dating by LA-ICP-MS. The analytical techniques used in the present study are summarized in **Appendix 1**, the results are listed in **Appendix 6 to 12**, and $^{206}\text{Pb}/^{238}\text{U}$ Concordia plots are shown in **Figures 8 and 9**.

Sixteen spots were analyzed on zircon grains separated from a monzonite/monzodiorite from the Elbeyli prospect (sample OFA 1, **Appendix 6**), eight of these were excluded from age calculation due to their strong discordance and eight concordant analyses yielded a weighted mean age of 77.0 ± 1.3 Ma with a MSDW of 2.2 (**Fig 8a**). Three rock samples were collected at the Emeksen prospect, including a porphyry granite (sample GE-1), a granodiorite (sample GE-2), a granite (sample GE-4). Fifteen spots from magmatic zircons of the porphyry granite (GE-1, **Appendix 7**) and from the granodiorite (GE-2, **Appendix 8**) yielded weighted mean ages, respectively, of 77.7 ± 0.5 Ma with a MSWD of 2.7 (**Fig 8b**) and 78.7 ± 0.5 Ma with a MSWD of 2.5 (**Fig 8c**). Analyses of ten spots in zircons from the granite sample (GE-4, **Appendix 9**) from the Emeksen prospect yielded a weighted mean age of 78.5 ± 0.8 Ma with a MSWD of 1.6 (**Fig 8d**). For sample TMG-1 from the Güzelyayla prospect, sixteen spot were analyzed on zircon grains (**Appendix 10**). Five of these were excluded because they were interpreted as xenocrystic cores yielding a weighted mean age of 287 ± 7 Ma (**Fig 9a, inset**). Eleven concordant analyses gave a weighted mean age of 81.4 ± 1.1 Ma with a MSWD of 4.4 (**Fig 9a**). At

the Ispir-Ulutaş prospect, eleven spots on zircons from quartz porphyry (sample Ei-1, **Appendix 11**) gave a weighted mean age of 131.1 ± 0.9 Ma with a MSWD of 0.92 (**Fig 9b**), and twenty spots on magmatic zircons from the granitic wall rock of the mineralization (sample Ei-3, **Appendix 12**) yielded a weighted mean age of 132.9 ± 0.6 Ma with a MSWD of 1.5 (**Fig 9c**).

4.3. Whole-rock Sr, Nd and Pb isotopic compositions

The age-corrected (80 Ma) initial Sr, Nd and Pb isotope data for whole-rock samples from Elbeyli and Emeksen are presented in **Appendix 13 and 14**, and the analytical techniques used in the present study are summarized in **Appendix 3**.

Initial $\epsilon\text{Nd}(\text{T})$ values of the Elbeyli monzonitic samples range from 0.7 to 1.3 and $^{87}\text{Sr}/^{86}\text{Sr}_i$ isotope ratios vary from 0.70478 to 0.70482. The initial Nd and Sr isotopic compositions of the granitic and granodioritic host rocks from the Emeksen prospect are characterized by a wide range of $\epsilon\text{Nd}(\text{T})$ values from -4.7 to -2.0 and $^{87}\text{Sr}/^{86}\text{Sr}_i$ ratios from 0.70567 to 0.70780, whereas diorite samples from Emeksen have higher $\epsilon\text{Nd}(\text{T})$ values of 3.3 to 4.8 and a very narrow range of $^{87}\text{Sr}/^{86}\text{Sr}_i$ ratios between 0.70466 and 0.70500. $^{143}\text{Nd}/^{144}\text{Nd}_i$ and $^{87}\text{Sr}/^{86}\text{Sr}_i$ of the Emeksen granitic and granodioritic samples display a slight negative correlation, and overlap with the composition of Upper Cretaceous arc-related granitoids of the Eastern Pontides (**Fig 10a**). The Elbeyli monzonite and Emeksen diorite yielded higher $^{143}\text{Nd}/^{144}\text{Nd}_i$ ratios and lower $^{87}\text{Sr}/^{86}\text{Sr}_i$ ratios when compared to the Emeksen granite and granodiorite, and Upper Cretaceous arc-related granitoids of the Eastern Pontides (**Fig 10a**). The $^{87}\text{Sr}/^{86}\text{Sr}_i$ ratios of the granite and the granodiorite from Emeksen are inversely correlated with SiO_2 contents (**Fig. 10b**), whereas the $^{143}\text{Nd}/^{144}\text{Nd}_i$ ratios display a

slight positive correlation with SiO₂ contents (**Fig 10c**). The ⁸⁷Sr/⁸⁶Sr_i and ¹⁴³Nd/¹⁴⁴Nd_i ratios of the Elbeyli monzonite and the Emeksen diorite remain nearly constant regardless of the SiO₂ content (**Figs 10b-c**).

Except diorite, the Emeksen samples have highly variable and the most radiogenic ²⁰⁶Pb/²⁰⁴Pb_i (18.681-18.831), ²⁰⁷Pb/²⁰⁴Pb_i (15.662-15.671) and ²⁰⁸Pb/²⁰⁴Pb_i (38.691-38.789) ratios. By contrast, diorite from the Emeksen prospect has lower lead isotope ratios (²⁰⁶Pb/²⁰⁴Pb_i = 18.338-18.686, ²⁰⁷Pb/²⁰⁴Pb_i = 15.628-15.661, ²⁰⁸Pb/²⁰⁴Pb_i = 38.618-38.774), as well as two rock samples from Elbeyli (²⁰⁶Pb/²⁰⁴Pb_i of 18.598 and 18.623, ²⁰⁷Pb/²⁰⁴Pb_i of 15.653 and 15.657, ²⁰⁸Pb/²⁰⁴Pb_i of 38.619 and 38.649) (see **Appendix 14**). In the ²⁰⁶Pb/²⁰⁴Pb_i vs ²⁰⁷Pb/²⁰⁴Pb_i space (**Figure 10d**), all samples show a slight positive correlation and plot between the Zartman and Doe (1981) upper crust and orogen evolution lines.

5. Discussion

5.1. Fractional Crystallization with Crustal Contamination and Magma Mixing/Mingling

The geochemical analyses indicate that the Elbeyli, Emeksen, Güzelyayla and Ispir-Ulutaş granitic and monzonitic rocks share many features, such as LILE enrichment, negative Nb and Ti anomalies, and LREE enrichment over HREE, and the ages of the host rocks of both prospects agree well with the age of other arc-related granitoids of the Eastern Pontides (e.g. Karslı et al., 2010; Kaygusuz and Şen, 2011; Kaygusuz et al., 2014). However, the Elbeyli and Emeksen host rocks have distinct trace element and isotopic compositions, which imply different petrogenetic

processes during their evolution, including crustal contamination, partial melting and magma mixing/mingling.

Decreasing MgO, FeO_t, TiO₂, CaO, P₂O₅, Ni and V concentrations correlating with increasing SiO₂ contents in each rock groups are consistent with fractional crystallization (**Fig 4**), which is supported by phenocryst assemblages of plagioclase, amphibole, clinopyroxene and accessory apatite and Fe-Ti oxides in both the Elbeyli and Emeksen samples. The main differences are the absence of correlation of K₂O and Ba with SiO₂ in the Elbeyli samples, in contrast to the Emeksen samples, which reveal a positive correlation among these elements (**Fig 4**). This suggests that K-feldspar fractionation was negligible during the early stages of the petrogenesis at Emeksen. The strong enrichment in Ba (see **Appendix 5**) at Emeksen cannot be explained by fractional crystallization only.

REE ratios can help in revealing fractionation of garnet and/or amphibole during fractional crystallization (Davidson et al., 2007; Macpherson et al., 2006). Low to moderate, and nearly constant La/Yb ratios of 13.2 at Elbeyli and 14.6 at Emeksen (**Fig 5c**), and decreasing Dy/Yb ratios with increasing SiO₂ (**Fig 11a**) are inconsistent with garnet fractionation and only reveal amphibole fractionation. This conclusion is also supported by the concave-shaped trend of MREEs to HREEs in the chondrite-normalized plots (**Figs 7a-b**), and decreasing Gd/Yb ratios with increasing SiO₂ contents for both groups (not shown). In addition, the Elbeyli monzonite samples display a more marked increase in Zr/Sm with increasing SiO₂ (**Fig 11b**), which reflects a dominant amphibole fractionation during their magmatic evolution (e.g. Davidson et al., 2007; Hora et al., 2009; Macpherson et al., 2006). Decreasing CaO,

and Al_2O_3 concentrations (**Fig 4**), and Sr/Y ratios (**Fig 5b**) with increasing SiO_2 contents, and negative Eu anomalies (**Figs 7a-b**) are consistent with plagioclase fractionation at relatively shallow crustal levels in the absence of high-pressure amphibole fractionation, therefore leading to a normal arc trend with low Sr/Y ratios (average 17.2 for Elbeyli and 12 for Emeksen samples) (e.g. Castillo et al., 1999; Chiaradia, 2009a; Davidson et al., 2007; Hora et al., 2009; Macpherson et al., 2006; Rodriguez et al., 2007). Additionally, the Elbeyli samples display a sharp decrease in Na_2O and Sr (not shown) at constant SiO_2 concentrations of ~56 %. This pattern can be explained by sudden Na-rich plagioclase crystallization, which may have taken place after the pyroxene-Ca-plagioclase-amphibole fractionation during the emplacement of the monzonitic/granitic body.

Marked depletions of Nb and Ti, and enrichments in U, Th, K and Pb are not only indicative of arc-related magmatism, but can also be related to crustal contamination/assimilation processes (Whalen et al., 1996). DePaolo (1981) pointed out that crustal contamination or assimilation affects the isotopic composition of magmas and may explain negative $\epsilon\text{Nd}(\text{T})$ values as well as increasing $^{87}\text{Sr}/^{86}\text{Sr}_i$ ratios with increasing SiO_2 contents. In this study, high $\text{K}_2\text{O}/\text{TiO}_2$ and $\text{K}_2\text{O}/\text{P}_2\text{O}_5$ ratios (average 15 and 49, respectively) in the Emeksen granitic rocks and higher Th/Yb (average 12) and lower Nb/Th (average 0.4) ratios with marked Th enrichment in comparison to Elbeyli monzonitic rocks in primitive mantle-normalized plots (**Fig. 6**) indicate that crustal contamination could have played a role during their evolution. Also, negative $\epsilon\text{Nd}(\text{T})$ values, highly variable $^{87}\text{Sr}/^{86}\text{Sr}_i$ ratios between 0.70567 to 0.70780 (**Fig 10a**), and high radiogenic Pb isotopic compositions (**Appendix 14**) of the Emeksen rocks support a significant role of crustal contamination.

Conversely, both granitic and granodioritic samples from Emeksen are characterized by decreasing $^{87}\text{Sr}/^{86}\text{Sr}_i$ and increasing $^{143}\text{Nd}/^{144}\text{Nd}_i$ ratios with magmatic evolution, which support mixing with high $\epsilon\text{Nd(T)}$ and low $^{87}\text{Sr}/^{86}\text{Sr}_i$ magmas. Such features can be explained by magma mixing/mingling processes (**Figs 10b-c**). Furthermore, decreasing $\epsilon\text{Nd(T)}$ values with increasing LREEs/MREEs (La/Gd) ratios, and increasing $\epsilon\text{Nd(T)}$ values with increasing MREEs/HREEs (Gd/Yb) ratios suggest that amphibole fractionation was accompanied by assimilation or mixing with low $\epsilon\text{Nd(T)}$ material/magma (DePaolo, 1981; Chiaradia et al. 2009b). However, increasing $\epsilon\text{Nd(T)}$ with decreasing Gd/Yb in the Emeksen samples also suggests mixing with a high $\epsilon\text{Nd(T)}$ magma (**Fig 11c**). Moreover, evidence for mixing/mingling processes include the presence of abundant mafic micro-granular enclaves (MMEs), disequilibrium textures, such as amphibole and biotite inclusions arranged along the crystallographic directions of the host plagioclase, as well as normal (e.g. core: $\text{An}_{76.6-65.5}$, rim: $\text{An}_{31.7-13.7}$) and reverse zoned plagioclase crystals (e.g. core: $\text{An}_{51.4-50.3}$, rim: $\text{An}_{67.5-53.6}$) in the Emeksen granitic samples (see **Appendix 2**). Xenocrystic cores (287.1 ± 7 Ma) of zircon grains of the Güzelyayla dacite porphyry (**Fig 9a, Inset**) and common microgranular enclaves in the granite porphyry of the Ispir-Ulutaş prospect also support crustal contamination and magma mixing/mingling processes. All of these characteristics, therefore, indicate the involvement of crustal components and magma mixing/mingling process during ascent of magmas to the surface.

The Elbeyli samples, on the other hand, have relatively lower Th/Yb (average 9.8) and higher Nb/Th (average 0.7) ratios, and they have nearly constant trends of $^{87}\text{Sr}/^{86}\text{Sr}_i$ and $^{143}\text{Nd}/^{144}\text{Nd}_i$ ratios with increasing SiO_2 contents (**Figs 10b-c**), documenting limited crustal contamination.

5.2. Nature of Magmatism in the Elbeyli and Emeksen prospects

The Upper Cretaceous high-K calc-alkaline to shoshonitic host rocks of the Elbeyli and Emeksen prospects display geochemical characteristics of arc magmas with marked depletions in Nb and Ti, and enrichments in U, Th, K and Pb, with steep REE patterns (**Figs 6 and 7**). As discussed in the previous section, fractional crystallization with weak crustal contamination has played an important role in the case of the Elbeyli magmas, whereas the Emeksen magmatism was dominated by fractional crystallization with significant crustal contamination and magma mingling/mixing processes.

The shoshonitic nature of the Elbeyli samples, together with positive $\epsilon\text{Nd(T)}$ values of +0.7 to +1.3, low $^{87}\text{Sr}/^{86}\text{Sr}_i$ ratios of 0.70478-0.70482, and high Rb (average 189 ppm), Ba (average 440 ppm) and U (average 7.6 ppm) contents speak against crustal contamination and fractional crystallization processes. These geochemical features are tightly linked to the source region rather than to fractional crystallization or crustal contamination processes. On the contrary, highly variable $^{87}\text{Sr}/^{86}\text{Sr}_i$ ratios between 0.70567 to 0.70780, $\epsilon\text{Nd(T)}$ values of -2.0 to -4.7, and high radiogenic Pb isotopic signatures of the Emeksen samples (**Fig 10d, Appendix 13-14**), accompanied by high and variable K_2O and Ba contents reflect crustal contamination and magma mixing processes rather than the source region.

Subduction-related fluids are enriched in Ba, Rb, U and Pb, and depleted in Th, Nb, Ta and Ti (Pearce, 1983). Furthermore, shoshonitic rocks forming in an arc setting display LILE and LREE enrichments with Ta, Ti, and Nb depletion (e.g. Muller and Groves, 1995). Although, Roberts and Clemens (1993) indicated that high-K, I-type

magmas can be produced by partial melting of meta-igneous rocks in the crust, some studies have shown that shoshonitic and K-rich mafic rocks in continental arcs could also be derived from K-rich metasomatised lithospheric mantle, and shoshonitic magmas are sourced from more strongly metasomatised magma reservoirs than those producing arc tholeiites and calc-alkaline magmas (e.g. Doglioni et al., 1999; Meen and Eggler, 1987; Wallace and Carmichael, 1992). Additionally, Conticelli et al. (2002) stated that the heterogeneity of metasomatised mantle sourcing arc magmas can explain variable degrees of K-enrichment in subduction zones. According to Foley (1992), interaction between metasomatic fluids with a lithospheric mantle source can produce vein networks of clinopyroxene/amphibole/phlogopite within the lithospheric mantle. In addition, mantle metasomatism can lead to the formation of hydrous phlogopite and/or amphibole (Beccaluva et al., 2004), and melts in equilibrium with phlogopite have relatively high Rb/Sr (>0.1) and low Ba/Rb (<20) ratios (Furham and Graham, 1999).

We use the Th/Yb vs. Ta/Yb plot of Pearce (1983) to constrain the source region of the magmas, which produced the host rocks of the Elbeyli and Emeksen prospects (**Fig 11d**). The monzonitic and granitic samples from the Elbeyli and Emeksen areas form trends that are parallel to the enriched mantle source, whereas gabbroic rocks of the Emeksen area are distributed along the depleted mantle array in the Th/Yb vs. Ta/Yb plot. As discussed in the previous section, high Th/Yb ratios of the Emeksen samples indicate crustal inputs, whereas Th-enrichments (high Th/Yb) of the Elbeyli samples can be attributed to upwelling of a hot asthenospheric mantle, rather than to crustal contamination, since $\epsilon\text{Nd(T)}$ values of +0.7 to +1.3 of the Elbeyli samples are inconsistent with significant contamination from crustal material. Additionally, the

Elbeyli and Emeksen samples have relatively high Rb/Sr (average of 0.5 and 0.7, respectively) and relatively low Ba/Rb (average of 2.4 and 5.5, respectively) ratios, suggesting the presence of phlogopite in equilibrium with a metasomatised mantle source.

The lower crust is mafic in composition and is strongly depleted in K and other highly incompatible elements relative to shallower levels of the crust (Rudnick and Gao, 2003). Therefore, the lower content of K₂O (average 0.3 wt.%) and of other incompatible (e.g. Sr, Ba) elements of the Emeksen gabbroic rocks is also consistent with a mafic lower crust, rather than a lithospheric mantle source.

The high-K calc-alkaline rocks of Emeksen and the shoshonitic rocks of Elbeyli fall along the partial melting line and fractional crystallization line, respectively, in the Nb vs. Ba/Nb plot (**Fig 12a**), which indicates that they were produced by different magmatic evolution trends. Additionally, the most evolved samples from Elbeyli, with a SiO₂ content of 63.6 wt.%, and the high-K calc-alkaline Emeksen rocks fall along the fluid-related enrichment array in the Rb/Y vs. Nb/Y plot (**Fig 12b**), whereas the more primitive samples from Elbeyli, with a SiO₂ content of 57.6 wt.%, lie along the melt enrichment trend (**Fig 12b**), with an inflection at a Nb/Y ratio of around 0.6, which may indicate that the magmas of the Elbeyli monzonitic rocks experienced a more intense/longer exchange with an enriched lithospheric mantle than the magmas related to the Emeksen rocks. Their relatively high Ni and V contents, with relatively high Mg# (33-44) and positive $\epsilon\text{Nd(T)}$ values also support this interpretation (see **Appendix 13**). In addition, the depth of the mantle source and the degree of partial melting can be revealed by the La/Sm vs. Sm/Yb plot (Ernst and Buchan, 2003), with

increasing Sm/Yb ratios reflecting the pressure-dependent changes from clinopyroxene to garnet in the mineral residue (Kay and Kay, 1991) (**Fig 12c**). In the Elbeyli and Emeksen samples, La/Sm ratio decrease progressively with increasing Sm/Yb ratios, and increasing La/Sm ratios with increasing SiO₂ (**Figs 12c-d**), which indicate that Elbeyli and Emeksen magmas come from nearly the same depth. However, higher La/Sm ratios, more distinct decreasing La/Sm ratios with increasing Sm/Yb ratios, and increasing La/Sm ratios with increasing SiO₂ contents in the Emeksen samples can be explained by crustal contamination. Partial melting of the lower continental crust can result in LREE enrichments (e.g. Lassiter and DePaolo, 1997), therefore the later trends of the granodiorite to granite at Emeksen (**Figs 12c-d**) reveal that the related magmas were transferred more rapidly to upper crustal levels and interacted more intensively with upper crustal materials.

Average Zr/Y, Nb/Y and Ce/Y ratios of the Elbeyli (7, 0.5 and 2.6, respectively) and the Emeksen (6, 0.5 and 2.7, respectively) samples are roughly similar to those of the upper crust (Zr/Y=9; Nb/Y=0.6; Ce/Y=3, Rudnick and Gao 2003). The Emeksen and Elbeyli samples plot mostly in the partial amphibolite melt field, and the Nb/Ta vs. Zr/Sm plot indicates that the Elbeyli and Emeksen samples are consistent with magmas produced by amphibolite/hornblende eclogite melting (**Fig 13**).

Based on these data, we can conclude that the high-K calc-alkaline Emeksen and shoshonitic Elbeyli magmas were derived from a metasomatised and heterogeneous lithospheric mantle source within the mantle wedge overlying the subducted plate. However, the Elbeyli monzonitic magma interacted more intensively and/or for a longer time with an enriched lithospheric mantle than the Emeksen magmas. Magma

influx from the metasomatised lithospheric mantle into lower-middle crust most probably resulted in crustal partial melting of amphibolitic mid-low crustal materials. However, while the Elbeyli magma was evolving at mid-crustal levels (~10-20km) involving low-pressure clinopyroxene-amphibole-plagioclase fractionation, the Emeksen magma evolved at upper crustal levels (~0-10km), including differentiation through fractional crystallization and crustal contamination/assimilation. In addition, it is possible that more primitive magmas from the lithospheric mantle and/or the lower crust may have reached upper crustal levels, possibly during stress relaxation of the crust as a result of slab roll-back during northward subduction. This is likely the case of the magmas at the origin of the Elbeyli shoshonitic rocks, and some of them may have mixed or mingled with high-K calc-alkaline to calc-alkaline magmas emplaced at upper crustal levels.

5.3. Geodynamic setting and mineralizations

The Upper Cretaceous ages of the host rocks of the Elbeyli (77.0 ± 1.3 Ma), Emeksen (77.7 ± 0.5 Ma, 78.5 ± 0.8 Ma, and 78.7 ± 0.5 Ma) and Güzelyayla prospects (81.4 ± 1.1 Ma) agree well with the age of other subduction-related granitoids of the Eastern Pontides (**Fig 2**). Therefore, our new geochronological and geochemical data indicate that the Elbeyli, Emeksen and Güzelyayla intrusions are the product of arc magmas linked to northward subduction of the Neotethys beneath the Eurasian plate.

One of the on-going debates about the geodynamic evolution of the Eastern Pontides is the onset age of subduction, as the ages proposed range from the Late Cretaceous (e.g. Okay and Şahintürk, 1997, Okay, 2008) to Jurassic or earlier (e.g. Adamia et al., 1977, 1981; Kazmin et al., 1986). According to Okay and Şahintürk

(1997), the volcanic arc developed during the Turonian to Maastrichtian-Danian (**Fig 2**). However, the Early Cretaceous ages (131.1 ± 0.9 Ma and 132.9 ± 0.6 Ma) of the calc-alkaline magmatic rocks from the Ispir-Ulutaş prospect and the presence of Early Cretaceous calc-alkaline granitoids in the eastern part of the Eastern Pontides (e.g. 142 Ma-old Rize pluton, Taner, 1977; 138.5 ± 2.2 Ma-old Çamlıkaya granitoid, Boztuğ and Harlavan, 2008; 132 ± 5 Ma-old Ispir batholith, Giles, 1973) indicate that subduction was already on-going during the Early Cretaceous. In addition, geochronological data from the metamorphosed oceanic accretionary and/or ophiolite complexes in the Eastern Pontides and the Lesser Caucasus support northward subduction of the northern branch of the Neotethys (Izmir-Ankara-Erzincan-Sevan-Akera oceanic basin) from the Late Paleozoic to the Late Mesozoic – Early Cenozoic (e.g. Boztuğ and Harlavan, 2008; Galoyan et al., 2009; Hässig et al., 2013; Nikishin et al., 2011; Rolland et al., 2010, 2011; Topuz et al., 2013b, 2014; Ustaömer et al., 2012). Therefore, the Lower Cretaceous ore-bearing granitoids in the Eastern Pontides agree well with the long-lasting subduction model proposed for the Eastern Pontides and the adjacent Lesser Caucasus from Late Paleozoic to the end of the Mesozoic (e.g. Adamia et al., 1981; Galoyan et al., 2009; Hässig et al., 2013; Rolland et al., 2010, 2011; Topuz et al., 2013b; Ustaömer et al., 2012). Furthermore, gradual lateral changes of the age and the nature of magmatism from Lower Cretaceous calc-alkaline in the east to Upper Cretaceous high-K calc-alkaline in the central part of the belt, and to Upper Cretaceous mantle-dominated shoshonitic composition in the west (**Figs 1 and 3d**), together with the absence of the Lower Cretaceous granitoids in the west of the belt, indicate that subduction may have started earlier in the eastern part of the belt.

Geochronological data by Karslı et al. (2012a) and Kaygusuz et al. (2014) and our data indicate that the high-K, calc-alkaline, shoshonitic to A-type granitoids were emplaced within a ca. 81 to 74 Ma time interval in the Eastern Pontides. Karslı et al. (2010, 2012a) concluded that the A-type and shoshonitic granitic magmas were emplaced in an extensional environment during subduction, reflecting transition from a compressional to an extensional arc setting attributed to slab roll-back, which started at ca. 79-81 Ma in the Eastern Pontides. VMS deposits in the Eastern Pontides hosted by Turonian (91.1 ± 1.3 Ma) and Upper Santonian to Lower Campanian (86.6 ± 0.8 Ma to 82.6 ± 1.0 Ma) felsic rocks are also attributed to an extensional environment (Eyüboğlu et al., 2014). The Turonian ages of the VMS host rocks are consistent with the age of high- K calc-alkaline to shoshonitic rocks from the Eastern Pontides, supporting the existence of a back-arc environment at the beginning of the Late Cretaceous along the belt. This agrees with Nikishin et al. (2011), who suggest back-arc basin opening during the Cenomanian to Coniacian. Therefore, our new geochronological and geochemical data allow us to conclude that the emplacement of magmatic rocks and mineralization at the Ispir-Ulutaş prospect may have been related to the main stage of the Early Cretaceous northward subduction of the Neotethys. While the Güzelyayla and Emeksen hydrothermal systems can be attributed to a transitional evolution from compression to extension, Upper Cretaceous shoshonitic magmatism, sourced by an enriched lithospheric mantle, and the associated hydrothermal system at Elbeyli could be the products of arc magmatism during an extensional stage, as a result of slab roll-back, rather than to the onset of subduction. This Late Cretaceous setting may also be responsible for the opening of the Black Sea basin in the north during the final stage of subduction,

before the accretion of the Anatolide-Tauride-South Armenian block (Karslı et al., 2010, 2012a; Rolland et al., 2012; Stephenson and Schellart, 2010).

Extensional tectonic settings and crustal thinning are generally thought to be unsuitable environments for the formation of giant porphyry deposits (e.g. Cook et al., 2005; Sillitoe, 2010). However extensional tectonics during subduction is interpreted to be a favourable environment for migration into upper crustal levels of highly oxidized, mantle-derived magmas, which are commonly linked to the formation of copper-gold mineralization (e.g. Candela and Bouton, 1990; Vigneresse, 2007). Therefore, we used the V/Sc ratio of the rocks investigated in this study to evaluate the oxidation states of magmas from the Elbeyli and Emeksen prospects (Kamvong et al., 2014; Lee et al., 2005) (**Fig 14**). The MgO versus V/Sc diagram, modified after Lee et al. (2005), was originally used to estimate the primary fO_2 during mantle melting for adakites in the Truong Son and Loei fold belts of Thailand and Laos (Kamvong, et al., 2014). In this study, we use it to estimate the oxidization states of ore-bearing high-K calc-alkaline to shoshonitic rocks of the Elbeyli and Emeksen prospects. According to the MgO vs. V/Sc plot (**Fig 14**), the Elbeyli samples cluster at model $\Delta \log fO_2$ values between the FMQ (fayalite-magnetite-quartz buffer) around +1 and > +3. The Emeksen granitic samples cluster between the FMQ and a FMQ+3, and gabbroic samples of the Emeksen prospect lie around a FMQ -1. By contrast, the V/Sc values of the non-mineralized Eocene adakitic intrusions of the Eastern Pontides (Karslı et al., 2011) vary between a FMQ -1 to a FMQ+1. This indicates that the Elbeyli and Emeksen magmatic rocks were derived from more oxidized magmas than the barren Eocene adakitic intrusions of the Eastern Pontides. In addition, the Elbeyli samples correspond to more oxidizing conditions in comparison to the

Emeksen samples, which is also expressed by the high-sulfidation mineral association, including enargite with euhedral pyrite, at the Elbeyli prospect.

Molybdenum-bearing environments, such as at the Elbeyli and Emeksen prospects, are generally associated with less oxidized magmas (e.g. Bao et al., 2014; Candela and Bouton, 1990; Oyarzun et al., 2001, 2002), because molybdenum has an incompatible behavior under high oxidizing conditions (Candela, 1992). Therefore, the widespread occurrence of molybdenum, rather than copper and gold enrichments in the Emeksen and Elbeyli prospects cannot be explained only by highly oxidized magmas. Enargite and euhedral pyrite replaced by tennantite and tetrahedrite along rims and fractures at the Elbeyli prospect reveal decreasing sulfur and oxygen fugacities during hydrothermal fluid evolution, which is a favorable environment for molybdenum precipitation, as evidenced by its occurrence along fractures/cracks within euhedral pyrite and enargite. Accordingly, the high-sulfidation mineralization and the associated advanced argillic alteration with zunyite and pyrophyllite, reflect the uppermost level of the hydrothermal system, which developed under these highly oxidizing conditions. Decreasing oxygen fugacity may explain molybdenum precipitation as well as tennantite and tetrahedrite replacements. We conclude that the shoshonitic mantle-derived magma at Elbeyli is the most likely source of the hydrothermal fluids and metals.

Although there is no consensus about the crustal versus mantle origin of molybdenum in porphyry deposits (Richards, 2011), magma mixing and crustal contamination at the Emeksen, Güzelyayla and Ispir-Ulutaş prospects may have played an important role during molybdenum enrichment and hydrothermal evolution

at these prospects. Continuous mafic magma influx from the mid to lower crust most probably supplied heat and volatiles and may have remobilized molybdenum in the upper crustal levels.

6. Conclusions

The host rocks of the Elbeyli, Emeksen, Güzelyayla and Ispir-Ulutaş prospects share many affinities with other I-type subduction-related Upper Cretaceous granitoids in the Eastern Pontides. New U-Pb ages of zircon grains from the intrusive host rocks show that porphyry-type mineralizations were formed between about 133 to 76 Ma (**Fig 2**). Three independent porphyry mineralization events were identified from east to west: (i) at ca. 133-130 Ma at the Ispir-Ulutaş prospect, (ii) ca. 82-77 Ma at the Güzelyayla and Emeksen prospects, and (iii) ca. 77-76 Ma at the Elbeyli prospect. Recognition of these three porphyry events allowed us to constrain the geodynamic evolution of the Eastern Pontides during the Cretaceous, starting with (i) 133-130 Ma-old calc-alkaline magmatic host rocks of the Ispir-Ulutaş prospect emplaced during the main Early Cretaceous subduction stage of the northern branch of the Neotethys Ocean, (ii) calc-alkaline, high-K calc-alkaline to shoshonitic magmatic host rocks of the Güzelyayla and Emeksen prospects attributed to a transitional compressional to extensional setting at ca. 100-77 Ma, and (iii) magmatic host rocks of the Elbeyli prospect attributed to an extensional tectonic stage at ca. 77-66 Ma. (**Fig 2**). Based on the east to west compositional and age trend of the magmatic host rocks and the abundant Lower Cretaceous calc-alkaline granitoids in the eastern part of the belt, we conclude that subduction started in the east and progressively progressed to the west. Extensional tectonics was contemporaneous with subduction and shaped the entire belt during the Late Cretaceous. Therefore, Early Cretaceous

subduction-related calc-alkaline magmatism is a good fertility indicator for evolved porphyry Cu-Mo systems in the eastern part of the belt. On the other hand, although extensional and transitional tectonic settings during subduction are considered as unsuitable environments for the formation of giant porphyry deposits, highly-oxidized mantle derived shoshonitic magmas, modified during crustal contamination and magma mixing/mingling processes, could have played an important role in the formation of small Cu-Mo±Au-bearing porphyry-type systems, especially in the western part of the Eastern Pontides.

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Figure Captions

Figure 1: Simplified regional geological map of the Eastern Pontides and location of the Elbeyli Mo±Cu, Emeksen Mo, Güzelyayla Cu-Mo and Ulutaş Cu-Mo prospects (modified after MTA, 2002). The inset shows the major tectonic units of Anatolia (simplified after Okay and Tüysüz, 1999).

Figure 2: Time (Ma) vs. tectonic regime/magmatism diagram summarizing the geodynamic evolution of the Eastern Pontides during Paleo-Tethyan and Neo-Tethyan evolution and the setting of the different types of ore deposits (Porphyry-, VMS- and epithermal-type). (Compilation of existing geochronological and geochemical data of the Eastern Pontides from: Altherr et al., 2008; Arslan and

Aslan, 2006; Dokuz et al., 2010; Eyüboğlu et al., 2014; Karslı et al., 2010; 2011; 2012a; Kaygusuz and Şen, 2011; Kaygusuz et al., 2009; Okay, 2008; Okay and Şahintürk, 1997; Okay and Tüysüz, 1999; Şengör et al., 1980; Topuz et al., 2010; 2011). Alternate geodynamic models for the Eastern Pontides are shown in red color (Eyüboğlu, 2010; Hässig et al., 2013).

Figure 3: Geochemical classification and discrimination diagrams. **a** –Geochemical classification of host rocks based on Nb/Y vs. Zr/TiO₂ (Winchester and Floyd, 1977). **b** – SiO₂ (wt.%) vs. Na₂O+K₂O (wt.%) alkaline, sub-alkaline classification diagram. **c** - AFM plot of Irvine and Baragar (1971), A: Na₂O+K₂O (wt.%); F: FeO_t (wt.%) ; M: MgO (wt.%). **d** - SiO₂ (wt.%) vs. K₂O (wt.%) for the magmatic host rocks at Elbeyli, Emeksen, Guzelyayla and Ispir-Ulutaş (tholeiitic, calc-alkaline, high-K calc-alkaline and shoshonitic compositional fields from Peccerillo and Taylor, 1975). Geochemical data for Güzelyayla and Ulutaş are from Yalçınalp (1992) and Taylor and Frey (1980), respectively.

Figure 4: SiO₂ (wt. %) vs. major oxides (wt. %) and representative trace elements (ppm) for samples from the Elbeyli and Emeksen prospects.

Figure 5: a - Sr/Y vs. Y (ppm). b - Sr/Y vs. SiO₂ (wt. %). c - La/Yb vs. SiO₂ (wt. %) for samples from Elbeyli, Emeksen and Güzelyayla. The adakite and “volcanic” arc fields are from Castillo et al. (1999), Defant and Drummond (1990) and Richards et al. (2012). Geochemical data for Güzelyayla taken from Yalçınalp (1992).

Figure 6: Primitive mantle-normalized (Sun and McDonough, 1989) multi-element diagrams. Upper crust and lower crust data from Rudnick and Gao (2003). **a** – Elbeyli monzonite samples. **b** – Emeksen porphyritic granite, granite and granodiorite samples. **c** – Emeksen diorite samples. **d** – Güzelyayla dacite porphyry and Ispir-Ulutaş granite porphyry samples. Geochemical data for Güzelyayla and Ulutaş intrusions were taken from Yalçınalp (1992) and Taylor and Frey (1980), respectively.

Figure 7: Chondrite-normalized REE diagrams (Boynton 1984). Upper crust and lower crust data from Rudnick and Gao (2003). **a** - Elbeyli monzonite samples. **b** - Emeksen porphyritic granite, granite and granodiorite samples. **c** – Emeksen diorite samples.

Figure 8: $^{206}\text{Pb}/^{238}\text{U}$ weighted mean ages, concordia plots and cumulative probability density function curves. All reported errors are 2σ . **a** – Elbeyli monzonite sample (OFA-1). **b** – Emeksen porphyry granite sample (GE-1). **c** – Emeksen granodiorite sample (GE-2). **d** – Emeksen granite sample (GE-4).

Figure 9: $^{206}\text{Pb}/^{238}\text{U}$ weighted mean ages, concordia plots and cumulative probability density function curves. All reported errors are 2σ . **a** – Güzelyayla dacite porphyry sample (TMG-1), inset shows xenocrystic cores of zircons. **b** – Ispir-Ulutaş quartz porphyry sample (Ei-1). **c** – Ispir-Ulutaş granite porphyry sample (Ei-3).

Figure 10: **a** – $^{143}\text{Nd}/^{144}\text{Nd}_{(i)}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ plot of samples from the Elbeyli and Emeksen prospects. The composition of present-day CHUR was calculated for a

Late Cretaceous age at 80 Ma. DMM: Depleted MORB and BSE: Bulk silicate earth (BSE) are from Zindler and Hart, (1986). **b** - $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ vs. SiO_2 (wt.%) for Elbeyli and Emeksen samples. **c**- $^{143}\text{Nd}/^{144}\text{Nd}_{(i)}$ vs. SiO_2 (wt.%) for Elbeyli and Emeksen samples. **d**- $^{207}\text{Pb}/^{204}\text{Pb}_{(i)}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}_{(i)}$ plot of samples from the Elbeyli and Emeksen prospects. Upper crust and orogen evolution curves are from Zartman and Doe, (1981). DMM: Depleted MORB is from Zindler and Hart, (1986). The Sr, Nd and Pb isotopic compositions of the Gümüşhane pluton (Topuz et al., 2011), the Köprübaşı pluton (Kaygusuz and Şen, 2011), the Harşit pluton (Karslı et al., 2010), the Pirnalli pluton (Karslı et al., 2012a), the Camiboğazı pluton (Kaygusuz et al., 2014), the Seme quartz diorite (Topuz et al., 2011), and the Sıdağ pluton (Karslı et al., 2012b) are plotted for comparison.

Figure 11: Dy/Yb (**a**), and Zr/Sm (**b**) vs. SiO_2 (wt.%). **c** - $\epsilon\text{Nd}(\text{T})$ vs. Gd/Yb. (**c**), **d** - Th/Yb vs. Ta/Yb diagram after Pearce (1983) and trends from Abratis (1998) (**d**).

Figure 12: **a** - Ba/Nb vs. Nb (ppm), partial melting, fractional crystallization and slab input trends from Kamvong et al., (2014). **b** - Rb/Y vs. Nb/Y, fluid-related and melt-related enrichment trends were taken from Zhao and Zhou, (2007). **c** - La/Sm vs. Sm/Yb, pressure-dependent changes from pyroxene to garnet were taken from Kay and Kay, (1991). **d** - La/Sm vs. SiO_2 (wt.%).

Figure 13: Zr/Sm vs. Nb/Ta. Lines represent primitive mantle values from Sun and McDonough (1989). Rutile eclogite and amphibolite/hornblende eclogite melting fields from Kamvong et al. (2014).

Figure 14: V/Sc vs. MgO (wt.%) for samples from the Elbeyli and Emeksen prospects
Diagram based on Lee et al. (2005) and Kamvong et al. (2014). Data of Eocene adakitic samples from Karslı et al. (2011) are plotted for comparison.

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Table1. Classification of the Elbeyli, Emeksen, Güzelyayla and Ispir-Ulutaş prospects based on their age and geochemical characteristics of the host rocks, ore types and ore geometries.

Prospect Name	Elbeyli (Ordu)	Emeksen (Giresun)	Güzelyayla (Trabzon)	Ispir-Ulutaş (Erzurum)
Principal host rocks	Monzonite Monzodiorite	Granodiorite Granite Porphyritic granite	Dacite Porphyry	Granite Porphyry Quartz Porphyry
Geochemical classifications of host-rock	Shoshonitic, I- type	Shoshonitic to High-K Calc-alkaline, I- type	Calc-alkaline to Adakitic, I- type	Calc-alkaline, I- type
Age of host rocks (mean)	LA-ICP-MS- Zircon U-Pb 77±1 Ma (Monzonite/Monzodiorite) (in this study)	LA-ICP-MS- Zircon U-Pb 78±0.5 Ma (P.granite) 78.5±1 Ma (Granite) 79±0.5 Ma (Granodiorite) (in this study)	LA-ICP-MS- Zircon U-Pb 81.5±1 Ma (Dacite P.) (in this study)	LA_ICP-MS- Zircon U-Pb 133±0.5 Ma (Granite P.) 131.1±1 Ma (Quartz P.) (in this study)
Alteration types	Advanced Argillic Phyllic	Potassic Phyllic Pyrophylic	Potassic Phyllic Pyrophylic	Phyllic Pyrophylic
Orebody	Fracture-controlled NW-oriented quartz veins	NW-, and NS-striking vertical/sub-vertical quartz veins	Stockwork Dissemination	Stockwork NW-striking vertical/sub-vertical quartz veins Dissemination
Ore minerals	Pyrite, Molybdenite, Chalcopyrite, Fahlore, Enargite	Molybdenite Pyrite ±Fahlore ±Sphalerite ±Galena	Chalcopyrite Molybdenite Pyrite Pyrrhotite ±Covellite ±Chalcocite ±Digenite	Chalcopyrite Pyrite Pyrrhotite Sphalerite Molybdenite ±Galena ±Covellite
Reserves/Resource and Grade	No Reserve and Grade Data	No Reserve Data Available 0.08% to 2.87%	186.2 Mt at 0.3%Cu and	73.6 Mt at 0.31% Cu and 0.022 %Mo*

	Available	Mo*	0.002-0.021% Mo*	
References		*MTA, 1984	*Er et al., 1992 Güner and Güç, 1990	*Giles, 1973 Soylu, 1999 Yiğit, 2009