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Review of Late Cretaceous volcanogenic massive sulfide mineralization in the Eastern Pontides, NE Turkey

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Abstract: The production of Cu-Zn from volcanogenic massive sulfide (VMS) deposits in the eastern Pontides began in the early 1900s, with the exploitation of high-grade ores scattered across the district. The district still possesses economically important blind VMS and associated sulfide deposits. Careful descriptive documentation of the typical features of these VMS ores illustrated the geological characteristics that are important in identifying ore localities and can be used to define exploration targets. The eastern Pontide VMS deposits are examples of volcanic-hosted massive sulfide deposits that exhibit many of the characteristics typical of bimodal-felsic-type VMS mineralization. Nearly all known VMS deposits in the region are hosted by the Kızılkaya Formation, which is characterized by Late Cretaceous dacitic/rhyolitic volcanic rocks that are typically located at the top contact of the dacitic/rhyolitic pile or within the lower part of the overlying polymodal sequence containing various proportions of volcanic and sedimentary facies. Most VMS deposits are composed of a mound of high-grade massive sulfides formed above a zone of lower-grade stringer veins and disseminated mineralization. The dominant sulfide minerals in most deposits are pyrite, chalcopyrite, and sphalerite. Au also occurs in some deposits. The hydrothermal ore facies are diagnostic of subaqueous emplacement of the Pontide massive sulfide deposits that were deposited on the Cretaceous ocean floor. The immediate host lithologies associated with VMS mineralization have typically experienced intense and widespread alteration. The trace element geochemical signatures of the host rocks indicated that the Pontide VMS deposits likely formed in an extensional tectonic regime during subduction. Major lineaments and circular structures exerted fundamental controls on the locations of the VMS deposits in the eastern Pontide district. Age determinations indicated that almost all of the deposits in this region formed in a restricted time interval between ca. 91.1 and 82 Ma. The sulfur isotope compositions of the ore-forming fluids were consistent with those of fluids derived from modified seawater.

Key words: Eastern Pontides, volcanogenic massive sulfide, ore facies, metalliferous sediment, vent chimney, tube worm

1. Introduction

The eastern Pontide orogenic belt has long been the focus of considerable attention and has a history of exploration and exploitation of metals and other mineral commodities dating back to at least 500 BC. (Kaptan, 1978; Kartalkanat, 2007). Ore deposit studies and exploration efforts in the eastern Pontides have mostly focused on volcanogenic massive sulfide (VMS) deposits. These deposits have historically been the most important Cu and Zn resources in Turkey, and continue to dominate the production of these metals in the country. Despite the recognition of this area as a potentially significant VMS district, little research has been published in the international scientific literature (Allen et al., 2003). Early studies concluded that all of the sulfide veins belonged to the VMS category, based largely on their Cu-Zn constituents, but definitive evidence of a VMS classification has largely been lacking. The district needs a better descriptive classification of the styles of massive sulfide mineralization, while those exploring for VMS metals need to acquire and manage information. Properly defined data are essential for exploration management and can influence the exploration strategy of individual companies. District-scale data will then become the foundation for the choice of exploration strategies and techniques in the eastern Pontides. This region, as part of an important metallogenic belt, includes numerous and diverse mineral deposit types. Determining and understanding the typical characteristics of VMS-style mineralization will also be useful in distinguishing other mineral deposit types in the region that are potentially economically significant and in determining important target areas. A paucity of the detailed descriptions of the individual VMS deposits and the genetic processes critical to their formation currently limits the ability to develop precise criteria for their definition and formulate well-constrained geologic and exploration models. Therefore,

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the comprehensive data discussed in this paper provided a basis for understanding the background of global VMS deposits and will be relevant to those exploring for VMS deposits elsewhere in the world. This paper first outlined the general characteristics of the eastern Pontide VMS deposits and then examined some of their attributes in detail. Most of the information in this paper was based on the voluminous geological and geochemical literature.

2. Historical perspective

Eastern Pontide VMS deposits have been exploited for more than 2000 years and have been exploration targets for most of the 20th century. The area is currently the subject of increasing interest for base and precious metal exploration. Numerous ancient and modern exploration shafts and adits have been opened by different companies in the region. A number of ancient wooden tools used for ore processing have been discovered in these shafts and adits (Kaptan 1977, 1978; Kartalkanat, 2007). Parts or all of the historical works and the pre-1979 references were listed by Pejatoviç (1979). In terms of exploration activities, 3 important periods can be identified in the belt. The first period of exploration activities covered the period until the First World War. In the first period, the exploration, which featured reconnaissance geological mapping, was largely guided by German and Russian researchers. A limited number of reports on the origin of massive sulfide ores were first published in the early 1900s. The first geologist to outline the basic geological and economic characteristics of these deposits was Kossmat (1910). In this period, minor exploration by Russian scientists occurred at the Murgul and Lahanos deposits. The second period of exploration activity started with the establishment of the General Directorate of Mineral Research and Exploration (MTA) in 1935. Much of the prospecting was conducted by the MTA. Based on regional prospecting studies, the existence and potential of a number of deposits and prospects were revealed by the MTA during this period. More comprehensive reports on these deposits were prepared during and after the Second World War (Kovenko, 1941, 1943, 1944; Eregan, 1946; Schneiderhöhn, 1955; Kieft, 1956; Schultze-Westrum, 1961; Kraeff, 1963). In particular, in the context of the Turkish-Yugoslav joint project initiated in 1967, much more detailed data were produced on the VMS and associated sulfide deposits in the region. The existence of abundant massive sulfide mineralization, as well as the reserves and grades of these deposits, was determined (Pejatoviç, 1971, 1979). A summary of the models and discussions was published by Pejatoviç (1979). In this period, various hypotheses were proposed for the origins and settings of massive sulfide mineralization, many of which are not valid today. Additional interest and activity in this belt have grown over the last 30 years as a result of revolutionary changes in the models of the genesis of these deposits. During the last period, regional exploration techniques, such as airborne electromagnetic (EM) surveys, ground EM surveys, regional geochemical sampling, regional geological mapping, and drilling, have been used to discover VMS deposits. Drilling of anomalies and alterations has resulted in the discovery of some economically significant deposits.

More work is required to document the VMS setting of the eastern Pontides. The wide distribution of alteration in the belt provides support for the application of further exploration, emphasizing the possibility of additional undiscovered deposits. Since the area where the underground exploration activity has reached depths of approximately 400–500 m and still possesses economically important blind VMS deposits, knowledge of the geology and ore potential at deeper levels of the belt is essential for defining new exploration strategies.

3. Distribution and age of the deposits

VMS deposits are found throughout the eastern Black Sea coastline. This region is known as the eastern Pontide belt. The eastern Pontide belt comprises an ~600 km long by ~150 km wide belt of the Jurassic to Miocene volcanic and sedimentary rocks along the Black Sea coast of northeastern Turkey. The belt is generally divided into 2 parts, each denoting a different lithological environment, as the Northern Zone and the Southern Zone (e.g., Özsayar et al., 1981; Bektaş et al., 1995; Okay and Şahintürk, 1997; Konak et al., 2001; Eyuboglu et al., 2007; Liu et al., 2018). While the Northern Zone is mostly dominated by Late Cretaceous and Middle Eocene volcanic and volcaniclastic rocks, the Southern Zone features exposures of mainly pre-Late Cretaceous ophiolitic and sedimentary and subordinate magmatic rocks (Okay and Şahintürk, 1997). All known VMS deposits and prospects in the eastern Pontides occur within the Late Cretaceous volcanic belt and are confined to the northern half of the belt. Numerous VMS deposits and prospects, together with vein-type base and precious metal deposits, have been documented in the belt (e.g., Pejatoviç, 1979). Noneconomic pyrite mineralization is abundant in the belt, mostly in the Late Cretaceous volcanic rocks. Massive sulfide ores are clustered into 3 major geographic districts, as the Giresun, Trabzon-Rize, and Artvin districts. Figure 1 shows the distribution of the VMS mines and prospects. Well-known examples of the Pontide deposits include the Murgul, Çayeli, and Lahanos mines. By far, the greatest tonnage of VMS metal deposits is in the Artvin district (Murgul mine), followed by the Trabzon-Rize district (Çayeli mine) and the Giresun district (Lahanos mine). These deposits have a number of characteristics in common with analogs in Japan and the Urals (Özgür, 1993; Revan, 2010; Maslennikov et al., 2013).

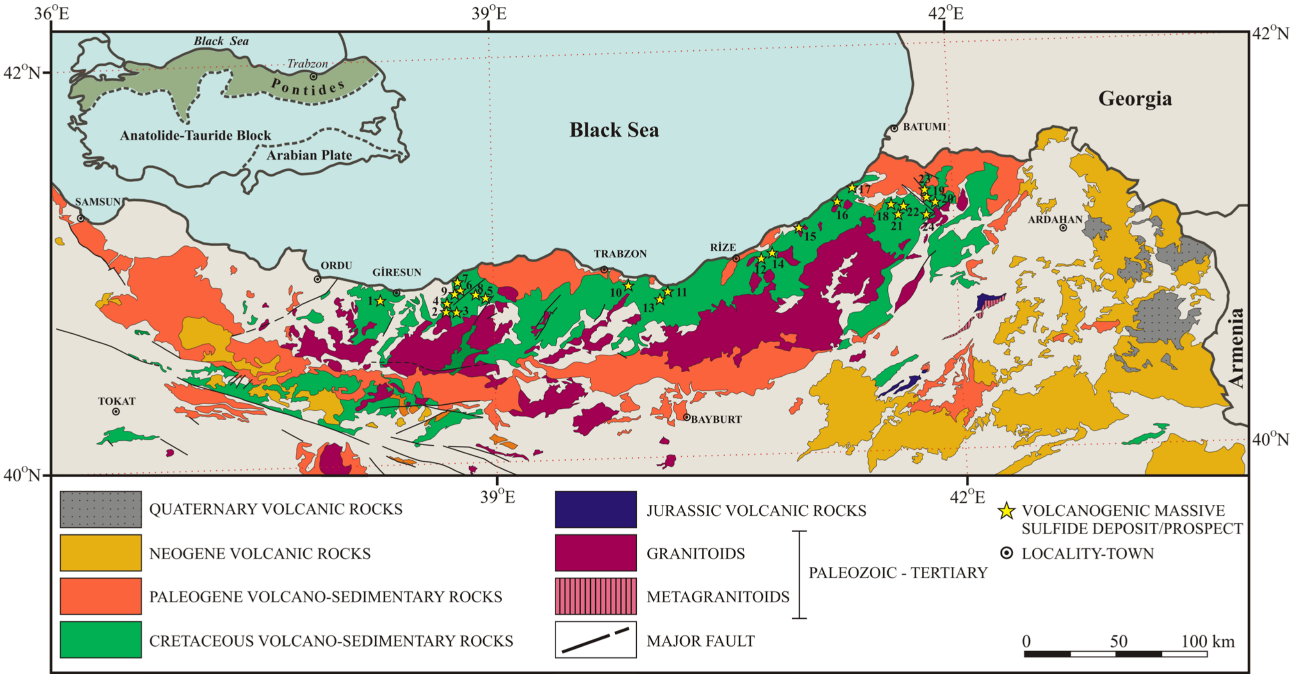

Figure 1. Simplified geological map of the eastern Black Sea region, NE Turkey, showing the regional locations of significant volcanogenic massive sulfide deposits and prospects (modified from MTA, 2013). The upper inset shows the major tectonic units of Anatolia (simplified from Ketin, 1966). Individual deposits are listed in Table 2.

The VMS deposits in the belt are thought to occur in a single stratigraphic horizon. However, some researchers have suggested that the VMS deposits and prospects occur within 2 or more different stratigraphic horizons (Akıncı, 1985; Eyuboglu et al., 2014; Çiftçi, 2019). A descriptive classification of the deposits and their absolute age data will eliminate this uncertainty. The volcanosedimentary horizons hosting the VMS deposits are Late Cretaceous in age, based on the foraminifera faunal assemblages. Fossils identified in the calcareous mudstones/limestones from the host lithologies (JICA, 2003; Revan, 2010; Alan et al., 2016; Kandemir et al., 2019) are indicative of sedimentation during the Turonian to Maastrichtian (between 93.9 and 66 Ma), which was interpreted to be the age range of the sulfide ore occurrences. However, radiometric dating of the felsic volcanic rocks hosting the VMS deposits (^{40}Ar/^{39}Ar, K-Ar, and zircon U-Pb) and of ore minerals (Pb -Pb in galena) implied that almost all of the deposits formed in a restricted time interval between ca. 91.1 and 82 Ma (Çifti, 2004; JICA, 2005; Eyuboglu et al., 2014; Aydın et al., 2016; Revan et al., 2017; Kandemir et al., 2019), as shown in Table 1.

4. Geological setting, stratigraphy and structure

The eastern Pontide volcanic belt is located in the northeastern part of the Anatolian Peninsula, which is part of the Alpine-Himalayan orogenic belt. Ketin (1966) divided the Anatolian Peninsula into 4 east-west-trending tectonic belts, aligned from north to south, as the Pontides, Anatolides, Taurides, and Border Folds (Figure 1). Each tectonic belt has characteristic sedimentary, volcanic, plutonic, and metamorphic patterns that are related to its orogenic development. The Pontides, located north of the northern branch of the Neo-Tethys Ocean, were subdivided into the Sakarya and Rhodope-Pontide sectors by Şengör and Yılmaz (1981) and into the Strandja, İstanbul, and Sakarya zones by Okay and Tüysüz (1999). The Pontides extend as a morphological entity from the Bulgarian Rhodope Mountains in the west to the Caucasus in the east. Geographically, the eastern Pontides, which form the eastern extension of the Sakarya terrane (Okay and Şahintürk, 1997), extend from Samsun in the west to the Lesser Caucasus in the east. This region is bordered in the south by the Ankara-Erzincan Neo-Tethyan suture.

The eastern Pontide belt represents a major fossil submarine arc that formed during the Late Cretaceous period (Stajanow, 1973; Peccerillo and Taylor, 1975; Akın, 1979; Pejatoviç, 1979; Şengör and Yılmaz, 1981, Manetti et al., 1983; Şengör et al., 1985; Robinson et al., 1995; Okay and Şahintürk, 1997; Yılmaz et al., 2000; Kandemir et al., 2019). The geological evolution of the eastern Pontides is genetically related to igneous activity as a result of the subduction of the northern Neo-Tethys lithosphere under the Eurasian margin. The direction and timing of the subduction are still vigorously debated. Many workers believe that the geological evolution of the eastern Pontides

Table 1. Radiometric age data on ores and host rocks from some eastern Pontide VMS deposits.

No.	Location	Rock type	Method	Dating minerals	Age (Ma)	Reference
1	Murgul mine	Sulfide ore from massive ore	Pb-Pb	Galena	89.0	Çiftçi (2004)
2	Lahanos mine	Sulfide ore from massive ore	Pb-Pb	Galena	89.0	[2]
3	Köprübaşı mine	Sulfide ore from massive ore	Pb-Pb	Galena	89.0	[2]
5	Çayeli southeast	Dacite -Tirebolu Fm	^{40}Ar/^{39}Ar	Dacite groundmass	83.2 ± 1.0	Alan et al. (2019)
4	Murgul south	Dacite – Kızılkaya Fm	^{40}Ar/^{39}Ar	Dacite groundmass	88.8 ± 0.9	Kandemir et al. (2019)
6	Tunca prospect	Dacite - Kızılkaya Fm	K-Ar	Sericite	82.0 ± 1.8	JICA (2005)
7	Tunca prospect	Dacite - Kızılkaya Fm	K-Ar	Sericite	83.1 ± 2.1	[2]
8	Tunca prospect	Dacite - Kızılkaya Fm	U-Pb (LA-ICP-MS)	Zircon	88.1 ± 1.2	Revan et al. (2017)
9	İsraildere prospect	Dacite/Rhyolite -Kızılkaya Fm	U-Pb (SHRIMP)	Zircon	91.1 ± 1.3	Eyuboglu et al. (2014)
10	Köprübaşı mine	Dacite/Rhyolite -Tirebolu Fm	U-Pb (SHRIMP)	Zircon	82.6 ± 1.0	[2]
11	Köprübaşı mine	Dacite/Rhyolite-Tirebolu Fm	U-Pb (SHRIMP)	Zircon	86.6 ± 0.8	[2]
12	Çanakçı prospect	Quartz porphyry – Kızılkaya Fm	U-Pb (SHRIMP)	Zircon	88.6 ± 1.4	Aydın et al. (2016)
13	Çanakçı prospect	Dacite/Rhyolite – Kızılkaya Fm	U-Pb (SHRIMP)	Zircon	85.0 ± 1.2	[2]
14	Artvin	Rhyolite – Kızılkaya Fm	U-Pb (SHRIMP)	Zircon	86.5 ± 0.7	[2]

is genetically related to magmatic events as a result of the northward subduction of the Neo-Tethys Ocean during the Late Mesozoic (e.g., Şengör et al., 1980; Ustaömer and Robertson, 1995; Okay and Şahintürk, 1997; Yılmaz et al., 1997; Rice et al., 2009; Dilek et al., 2010; Kandemir et al., 2019; Aydın et al., 2020). Models supporting northward subduction in the eastern Pontide orogenic belt suggested that the VMS deposits were generated in back-arc basins during the Late Mesozoic. However, some others favored the southward subduction of the Tethys Ocean in the Paleozoic, Mesozoic, and Cenozoic (Dewey et al., 1973; Bektaş et al., 1999; Eyuboglu, 2010; Eyuboglu et al., 2012, 2014, 2017; Liu et al., 2018). Models that involve southward subduction in the eastern Pontide orogenic belt correlated the VMS deposits to the intr-aarc or near arc region.

The eastern Pontide volcanic belt consists of Mesozoic and Cenozoic rocks overlying a crystalline basement (Figure 2). The crystalline basement rocks are part of the Hercynian orogen, which is represented in this region by Paleozoic metamorphic rocks and intrusive Hercynian granitic rocks (Schultze-Westrum, 1961; Zankl, 1962; Yılmaz, 1976; Moore et al., 1980; Okay and Leven, 1996; Topuz et al., 2004). A volcanosedimentary sequence, ranging in age from Early Jurassic to Eocene, overlies these basement rocks (Okay and Şahintürk, 1997; Yılmaz and Korkmaz, 1999; Kandemir et al., 2019). The entire sequence has been intruded by granitic rocks and various sills and dikes. The lowest exposed stratigraphic unit of the volcanosedimentary sequence, the pre-Late Cretaceous rocks, comprises volcanic and sedimentary units that are widely exposed in the southern part of the belt. The pre-Late Cretaceous rocks are tholeiitic and calc-alkaline in character and most likely related to rifting (Görür et al., 1983; Arslan et al., 1997; Okay and Şahintürk, 1997; Eyuboğlu et al., 2006; Şen, 2007). Cretaceous volcanism was completely submarine, mostly subalkaline and a product of typical volcanic arc formation (Tokel, 1972; Stajanow, 1973; Peccerillo and Taylor, 1975; Pejatoviç, 1979; Şengör and Yılmaz, 1981; Manetti et al., 1983; Eyuboglu et al., 2014; Kandemir et al., 2019). Late Cretaceous arc volcanism initiated in the Early-Middle Turonian and continued uninterrupted until the end of the Early Maastrichtian (Kandemir et al., 2019). The known VMS deposits of the NE Pontides occur only in the Upper Cretaceous volcanic sequences. Güven (1993, 1998) divided the Upper Cretaceous volcanic sequence into 4 formations from the base upward: the Çatak Formation, which is mainly composed of andesitic-basaltic volcanic rocks; the Kızılkaya Formation, which contains predominantly dacitic volcanic rocks with pervasive alteration; the Çağlayan Formation, which is dominated by andesitic-basaltic volcanic rocks; and the Tirebolu Formation, which is mainly composed of rhyolitic/dacitic lavas and associated volcaniclastic rocks. The Eocene rocks, which are the uppermost stratigraphic unit in the volcanosedimentary sequence, consist of andesitic/basaltic volcanic and volcaniclastic rocks. Eocene volcanism was calc-alkaline and most likely related to regional extension (Adamia et al., 1977; Eğin et al., 1979; Kazmin et al., 1986; Çamur et al., 1996). The plutonic rocks of the belt have different ages and compositions. They range in age from Carboniferous to Neogene (Delaloye et al., 1972; Taner, 1977; Kamitani and Akıncı, 1979; Moore et al., 1980; Şen, 1987; Okay and Şahintürk, 1997; Yılmaz et

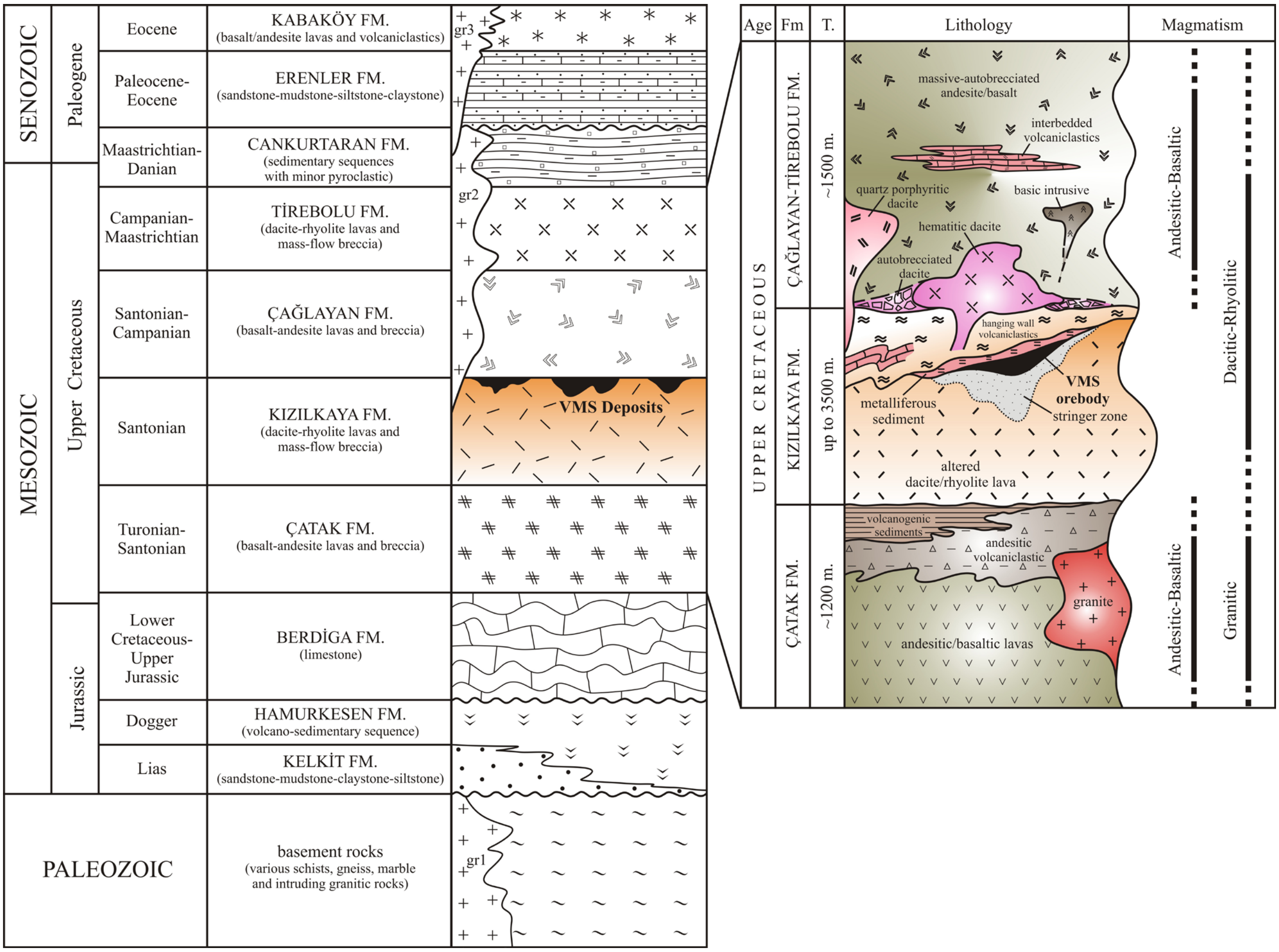

Figure 2. Generalized stratigraphic column for the eastern Pontides, NE Turkey, with the positions of the VMS-type deposits. The stratigraphic range of VMS ores is also shown (compiled from Güven, 1993; Konak et al., 2001; Kurt et al., 2005; Revan, 2010; Alan et al., 2016; Revan et al., 2016; Kandemir et al., 2019).

al., 1997; Kaygusuz, 2000; Arslan et al., 2004; Aydınçakır and Şen, 2013; Delibas et al., 2016; Eyuboglu et al., 2017, 2019; Liu et al., 2018). The plutonic rocks exhibit a broad compositional range and are dominated by tholeiitic and calc-alkaline granitoids and alkaline syenite/monzonites (Yılmaz and Boztuğ, 1996). The emplacement of the plutonic rocks was associated with subduction-related processes and subsequent postcollisional rifting events (Yılmaz and Boztuğ, 1996; Karslı et al., 2004, 2007; Topuz et al., 2005; Boztuğ et al., 2007; Boztuğ and Harlavan, 2008; Aslan et al., 2014; Delibas et al., 2016; Eyuboglu et al., 2017, 2019; Liu et al., 2018).

The lowest exposed stratigraphic unit of the Upper Cretaceous volcanic sequence, the Çatak Formation (~1200 m thick), comprises basaltic-andesitic volcanic rocks with abundant thin units of sedimentary strata composed of alternating sandstone, siltstone, marl, shale, and limestone (JICA, 1998; Revan, 2010; Alan et al., 2016; Kandemir et al., 2019). This formation defines the beginning of the Late Cretaceous arc volcanism and has been intruded by granite and diabase dikes (Figure 2). Some of the mafic lavas have pillow structures indicative of extrusion in a subaqueous environment. The basalts are porphyritic and are commonly vesicular to amygdaloidal, with amygdules composed of siliceous minerals. They contain altered plagioclase and amphibole (JICA, 1998, 2003). The lithological association in the basal section of the formation suggests sudden deepening of the basin in a probable extensional tectonic setting (Kandemir et al., 2019). Foraminifera faunal assemblages within the sediments of the Çatak Formation are Early/Mid-Turonian-Santonian in age (between 93.9 and 83.6 Ma) (Alan et al., 2016). A dated basalt sample yielded an age value of 92.1 ± 1.2 Ma (^{40}Ar/^{39}Ar: Kandemir et al., 2019). The formation unconformably overlies the Jurassic volcanic rocks and Lower Cretaceous neritic limestones (Konak et al., 2001). The Çatak Formation can be correlated with the basic I series of Çekiç et al. (1984).

Nearly all of the known VMS deposits in the eastern Pontides are hosted by the Kızılkaya Formation, which is characterized by Late Cretaceous dacitic/rhyolitic volcanic rocks and is typically located at the top contact of the dacite/rhyolitic pile or within the lower part of the overlying polymodal sequence, containing various proportions of volcanic and sedimentary facies (Revan, 2010; Revan et al., 2014). The Kızılkaya Formation (up to 3500 m in thickness) is mainly composed of dacite lavas, intrusive facies of dacite lavas, dacitic tuff breccias, and pelagic sedimentary intercalations (JICA, 1998, 2003; Kandemir et al., 2019). Dacite lavas range from autobrecciated to less common massive types. These dacite lavas host stringer mineralization and therefore, predate the mineralization. All of the mineralization occurs in silicified zones within dacite lavas and tuff breccias in the Kızılkaya Formation. Due to intense silicification, the original dacitic texture has been destroyed. Dacite lavas are generally aphyric, with plagioclase and quartz phenocrysts rarely observed. Dacitic tuff breccias are exposed in the immediate vicinity of the dacite lavas and consist of rock fragments that are likely derived from the underlying dacite lavas. Dacitic tuff breccias are difficult to differentiate from the autobrecciated portions of the dacite lavas. The Si (±Fe)-rich sedimentary rocks identified in the VMS deposits of the eastern Pontides are metalliferous chemical rocks that represent the proximal sections of the deposits. These siliceous sedimentary rocks are commonly associated with VMS mineralization (Figure 2) and may represent quiescent periods in volcanic activity. The stratigraphic position of the Kızılkaya Formation has been interpreted as Santonian in age (Kandemir et al., 2019). The age of this formation is constrained by planktonic fossils from intercalated sediments within the sequence, and from the units above and below and by radiometric dates from dacites hosting VMS deposits (zircon U-Pb ^{40}Ar/^{39}Ar and K/Ar). The fossils collected from this formation have the Santonian age (83-86 Ma) (Kandemir et al., 2019). Radiometric dating of dacites/rhyolites in the formation indicated a range of 82.0 to 91.1 Ma (JICA, 2005; Eyuboglu et al., 2014; Aydın et al., 2016; Revan et al., 2017; Kandemir et al., 2019). This formation can be correlated with the first dacitic series of Schultze-Westrum (1960).

The Çağlayan Formation (~1000 m thick) is an extensively exposed unit in the field. This formation is a volcanosedimentary sequence of intercalated massive mafic lava flows, volcaniclastic rocks, and calcareous mudstones. Basalt flows, which predominate in the formation, are interlayered with thin calcareous mudstones and volcaniclastic layers. Basalt flows are fine-grained and are commonly vesicular to amygdaloidal, with amygdules composed of calcite, chlorite, and zeolite minerals. Some of the mafic lavas have pillow structures indicative of extrusion in a subaqueous environment. Many calcareous mudstone blocks and lenses are present in the sequence. The calcareous mudstone is a compact rock characterized by a deep red color, and it varies in thickness from several centimeters up to a few tens of meters. The Çağlayan Formation is Late Cretaceous in age, based on foraminifera faunal assemblages (Güven, 1993, 1998; JICA, 2003; Kurt et al., 2005; Alan et al., 2016; Kandemir et al., 2019). Planktonic foraminifera identified in the calcareous mudstone are indicative of sedimentation during the late Santonian to Campanian (between 86.3 and 72.1 Ma). A dacite sample from the overlying unit yielded a zircon U-Pb age of 82.6 ± 1.0 Ma (Eyuboglu et al., 2014), restricting the age of this formation to approximately 82 Ma. A relatively thin (up to a few meters thick) felsic tuff breccia layer, which is poorly exposed, occurs within the formation at some sites and indicates deposition of felsic volcanic rock during basic volcanism. The Çağlayan Formation can be correlated with the upper basic series of Schultze-Westrum (1960) and the basic II series of Çekiç et al. (1984).

The Tirebolu Formation (~500 m thick), which is the uppermost unit of the Upper Cretaceous volcanic sequence, has been interpreted as the latest phase of Late Cretaceous acidic volcanism in the belt. The formation is a volcanosedimentary succession of intercalated felsic volcanic rocks (rhyolite/dacite), and calcareous limestone and volcanic sandstone. The rhyolites/dacites showed columnar jointing in places. The feldspar and quartz phenocrysts are mostly coarse, and the feldspars have commonly been altered to clay minerals. Pyrite is not present in this formation. The Tirebolu Formation is Late Campanian–Early Maastrichtian in age (between 83.6 and 66 Ma), based on the planktonic foraminifera faunal assemblages (JICA, 2003; Alan et al., 2016; Kandemir et al., 2019). A representative dacite sample was dated to 83.2 ± 1.0 Ma (^{40}Ar/^{39}Ar: Alan et al., 2019). The Tirebolu Formation can be correlated with the hematitic dacites (previously termed purple dacite by local geologists) defined by Kahraman et al. (1987) and with the second-phase dacitic series of Güven (1993).

The tectonic history of the Pontide volcanic belt is characteristically complex and has distinctive structural features. The structural style of the Pontides has been defined as a block-faulted tectonic style in several publications (Schultze-Westrum, 1961; Gattinger et al., 1962; Goksu et al., 1974; Bektaş and Çapkınoğlu, 1997). Tectonic activity has commonly occurred along fault planes that trend NE-SW and NW-SW with subsidiary but important faults in the N-S and E-W directions. Step faulting associated with graben and horst structures is commonly recognized in the region (Zankl, 1962; Egin, 1978). The spatial association of the Pontides with faults, especially with conjugate faults oriented NE-SW and NW-SW, has been demonstrated previously (Tugal, 1969; Eğin, 1978). This association has generally been interpreted as an indication of a genetic relationship between the faults and the hypabyssal and volcanic rocks (Doğan, 1980; Bektaş et al., 1999). In contrast to other tectonic belts in Anatolia, major thrusts, nappes, and large-scale folds are not common in the Pontides (Doğan, 1980). Most of the lithologies are folded in a series of NE-SW-trending symmetrical anticlines and synclines. The bedding of the volcanosedimentary rocks along the coastline dips gently to the north. Most of the thrust faults lie almost parallel to the fold axial planes and generally dip toward the southeast. The geometry of the thrusts suggests tectonic transport toward the northwest (Kandemir et al., 2019). Major regional structures exert fundamental controls on the locations of the VMS and associated sulfide deposits in the eastern Pontide orogenic belt (Pejatoviç, 1979; Kurt et al., 2005; Eyuboglu et al., 2014). The Pontide VMS deposits are commonly associated with and even controlled by major lineaments and circular structures in specific stratigraphic horizons (Koprivica, 1976; Hirst and Eğin, 1979; Yıldız, 1983; Revan, 2010). The circular structures form a depression pattern in the district and are commonly cut by NNE- and NNW-striking faults (Figure 3). Control by the faults and fractures has been recognized in many areas, and these features may also control the dacite/rhyolite domes that occur in the footwalls of a number of deposits.

5. Primary geochemistry of the VMS-associated felsic volcanic rocks

In the eastern Pontides, detailed volcanological studies and facies analyses have not been conducted in the successions hosting the VMS deposits. Most of the emphasis in the literature has been on the geochemistry of the VMS-associated felsic volcanic rocks. The host rock succession of the VMS deposits in the eastern Pontide district consists of a submarine association of volcanic and sedimentary rocks. The VMS deposits occur within a felsic-dominated

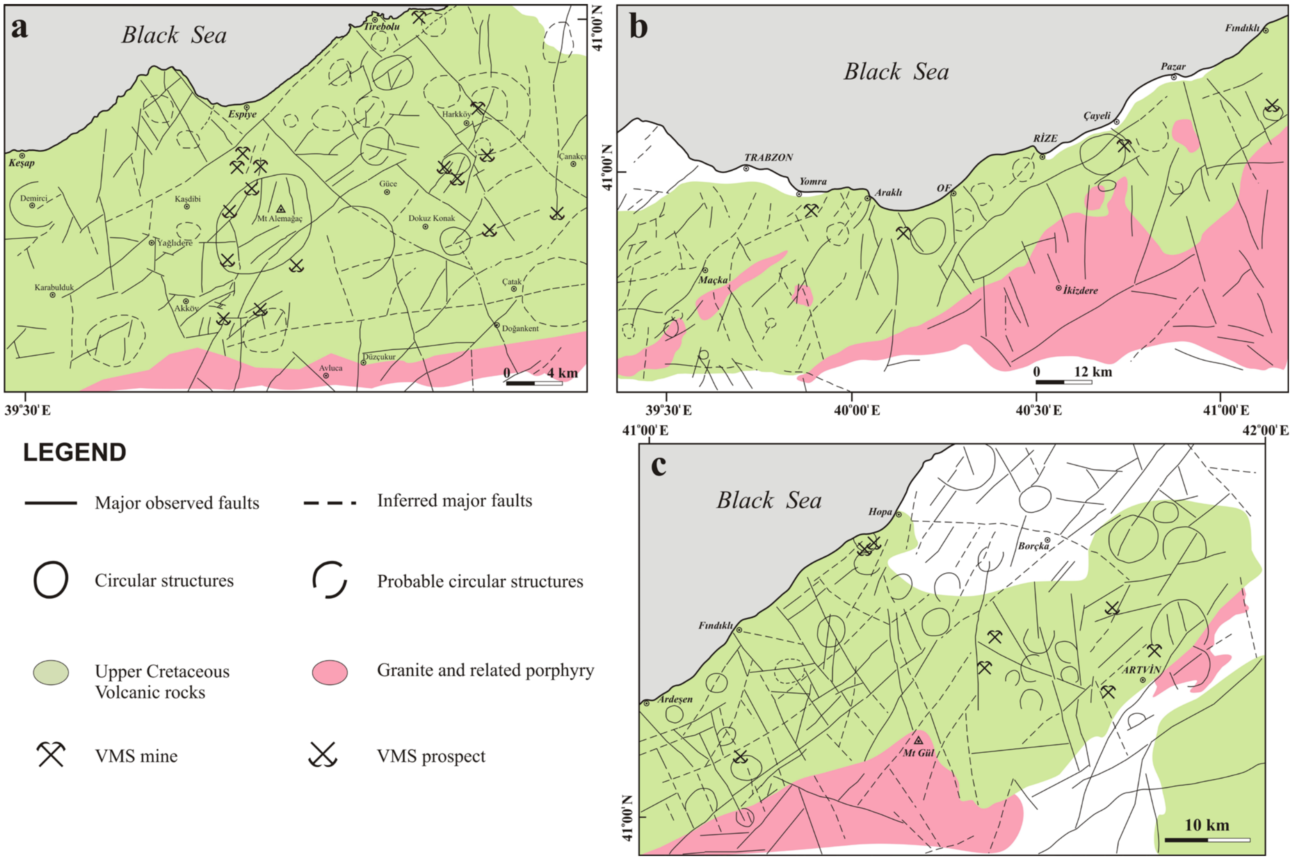

Figure 3. Regional distribution of the VMS-type deposits and prospects in the (a) Giresun, (b) Trabzon-Rize, and (c) Artvin districts of NE Turkey in relation to the host lithologies and tectonic structures. This figure was intended to indicate the spatial correlations among the VMS deposits, tectonic structures, and lithologies. Geological lineaments were mapped using Landsat Thematic Mapper (TM) images. To visualize the structural features, the contrast enhancement method, and spatial filtering (crisp and adaptive filtering) techniques were used.

sequence that is Late Cretaceous in age. The succession of felsic volcanic rocks near the ore horizon consists of dacitic lava flows, tuff breccias, porphyritic dacite intrusions, and related fragmental facies. An extensive dataset of the surrounding rocks is not available for discrimination analyses. In this study, the available major and trace element data reported in the literature were used to classify the Pontide felsic volcanic rocks. All of these data were compiled from a variety of references cited in the text.

The trace and major element compositions of the Late Cretaceous VMS-associated felsic rocks in the eastern Pontides are very consistent with those of rocks with calc-alkaline affinities (Gedik et al., 1992; Arslan et al., 1997; Tüysüz, 2000; Eyuboglu et al., 2014; Revan et al., 2017). Geochemical plots together with petrological data suggested that the compositions of the VMS-associated felsic rocks are commonly dacite, rhyolite, and rhyodacite (Pejatoviç, 1979; Gedik et al., 1992; Tüysüz, 2000; Eyuboglu et al., 2014; Revan et al., 2017). On the $Na_2O + K_2O$ versus SiO_2 plot (Figure 4a) of LeBas et al. (1986), the data points representing the felsic rocks were plotted distinctly within the dacite/rhyolite field. These representative felsic rocks have Zr/TiO_2 (194–1600) and Nb/Y (0.1–0.6) values that suggested rhyodacitic to dacitic rocks with subalkaline affinity (Figure 4b). The data points of the felsic rocks were plotted predominantly within the calc-alkaline field in Figure 4c. The Late Cretaceous felsic volcanic rocks hosting the VMS deposits in the eastern Pontide belt were generally classified as FII type in the scheme of Lesher et al. (1986).

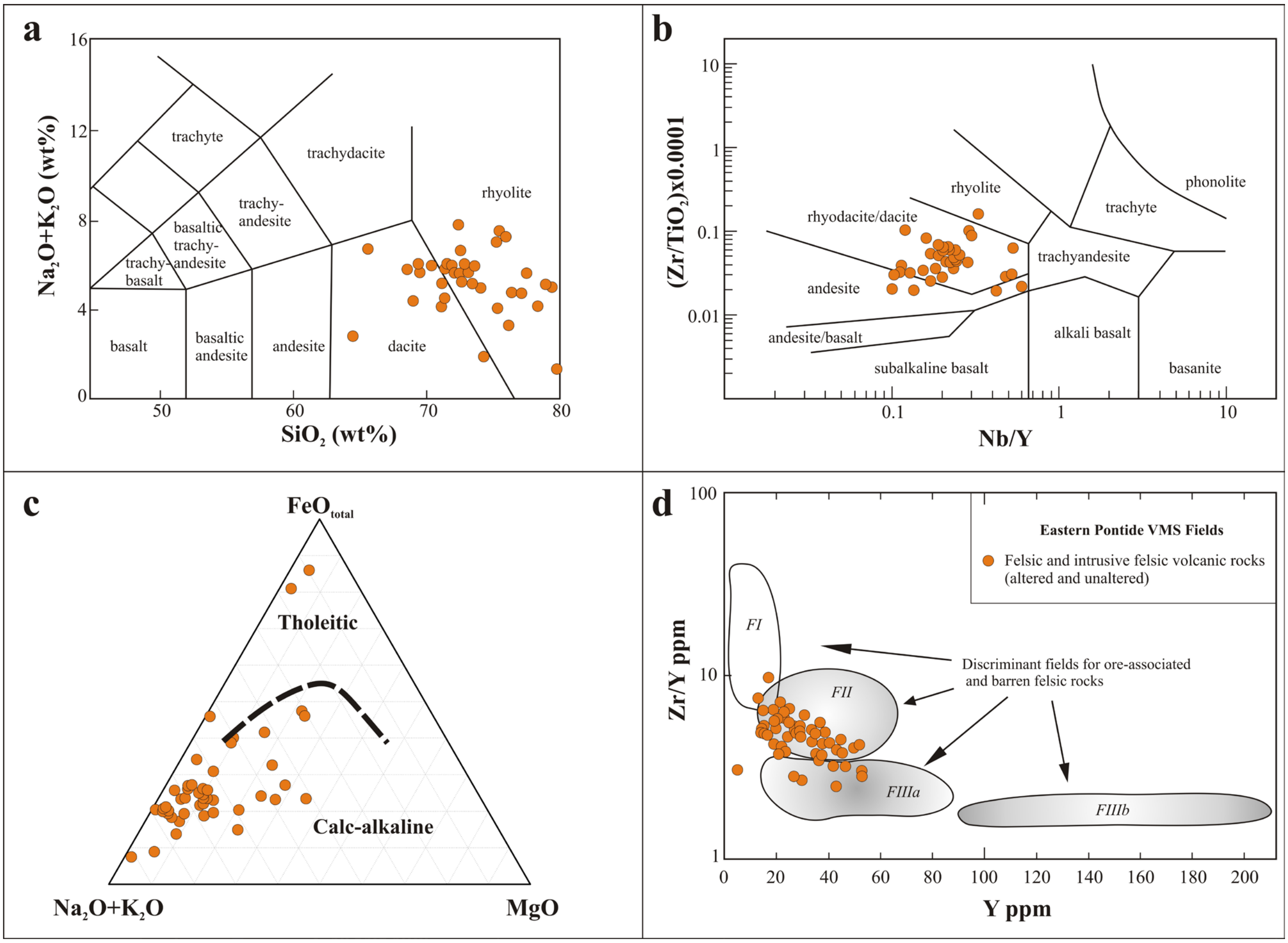

Figure 4. (a) Log (SiO_2) versus $(Na_2O + K_2O)$ plot of LeBas et al. (1986) showing the dacitic/rhyolitic nature of the felsic rocks hosting the eastern Pontide VMS deposits. (b) Log (Nb/Y) versus (Zr/TiO_2) plot of Winchester and Floyd (1977) showing the dacitic/rhyolitic nature of the felsic rocks hosting the eastern Pontide VMS deposits. (c) AFM plot showing the calk-alkaline nature (Irvine and Baragar, 1971) of the felsic volcanic rocks hosting the eastern Pontide VMS deposits. (d) Zr versus Y plot for felsic volcanic rocks hosting the eastern Pontide VMS deposits. Discriminant fields plotted after Lesher et al. (1986). FI, FII, FIIIa, and FIIIb are different felsic volcanic rock groups, with FIIIa and FIIIb being the most prolific, FII moderately prolific, and FI the least prolific (data from Gedik et al., 1992; Arslan et al., 1997; Tüysüz, 2000; JICA, 2003; Eyuboglu et al., 2014).

Zr/Y and rare earth element (REE) data suggested that the felsic volcanic rocks were similar in chemistry to other Phanerozoic felsic rocks related to VMS mineralization (Figure 4d). Many researchers have generally agreed that the geochemical affinities of the VMS-associated felsic volcanic rocks in the eastern Pontides are associated with subduction-related magmatism (Peccerillo and Taylor, 1975; Gedik et al., 1992; Arslan et al., 1997; Eyuboglu et al., 2014; Revan et al., 2017). The trace (Ce and Zr) and major element (P_2O_5 and TiO_2) compositions of the felsic rocks suggested that their origin is most likely linked with a volcanic arc formed on continental crust (Figure 5a). These data were plotted in the volcanic arc field on the Sr/Y versus Y plot of Defant and Drummond (1990) and the Rb versus Y + Nb plot of Pearce et al. (1984) (Figures 5b and 5c). The high field strength element contents (Nb and Y) of these rocks were determined as moderate to low and are characteristic of volcanic arc rocks with I-type affinities (Figure 5d).

6. Metal contents and classification

Pontide-type VMS deposits are important sources of Cu and Zn, and account for more than 50% of the reserves of these elements in Turkey. Economically recoverable metals are confined to the silicified zones in altered footwall dacites/rhyolites and adjacent massive ore lenses. Individual deposits are generally small, and most yield less than 10 Mt of ore. An analysis of the Black Sea region showed that most deposits contained 0.2–2 Mt of ore, while the largest had nearly 73 Mt. The average tonnage and grade of the Pontide-type VMS deposits are listed in Table 2. The Murgul deposit presently being mined in the belt has a higher mean tonnage than the other deposits. Figure 6 shows the Cu-Zn-Pb compositions

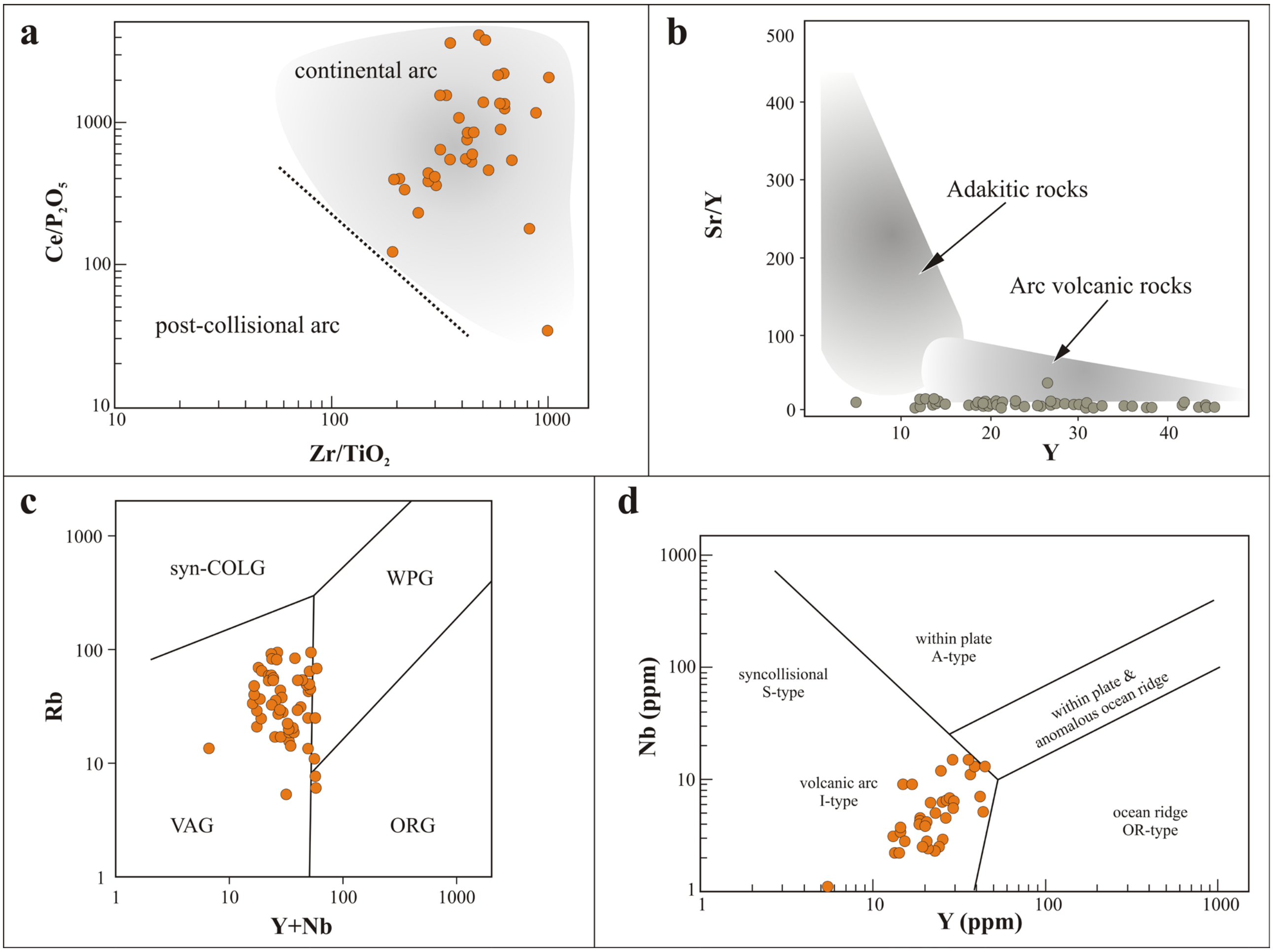

Figure 5. Plots of felsic volcanic rocks hosting the eastern Pontide VMS deposits on tectonic discrimination diagrams. (a) Ce/P_2O_5–Zr/TiO_2 diagram (after Pierce et al., 1984), (b) Sr versus Y diagram (after Defant and Drummond, 1990), (c) Rb versus (Y + Nb) diagram (after Pearce et al., 1984), and (d) Nb versus Y diagram for the felsic volcanic rocks (data from Gedik et al., 1992; Arslan et al., 1997; Tüysüz, 2000; JICA, 2003; Eyuboglu et al., 2014).

Table 2. Grade and tonnage values of the VMS deposits/prospects in the eastern Pontide district, NE Turkey, with ore descriptions, ages, and selected references.

Location	No.*	Deposit/prospect	Ore type	Age	Average metal content					Size	References
					Cu (%)	Zn (%)	Pb (%)	Au (gr/t)	Ag (gr/t)	Mt	
Giresun District	1	Akköy, Bulancak	Massive stratiform and stockwork	Late Cretaceous (ca. 91.3 to 75 Ma)	0.47	2.86	n.a.	n.a.	n.a.	1.9	(1)
	2	Killik			2.50	5.00	0.70	n.a.	73	0.1	(2, 3)
	3	Kızılkaya			0.82	0.83	0.52	n.a.	62–145	10	(3–5)
	4	Lahanos			3.50	2.40	0.30	2.5	100	2.4	(3, 5)
	5	İsraildere			0.41–1.14	1.14–2.33	n.a.	n.a.	n.a.	n.a.	(6, 7)
	6	Ağalık	Stockwork		0.62	2.04	n.a.	n.a.	96	1.4	(3)
	7	Karaerik			0.17–0.20	1.46	<0.01	0.5	2.0	n.a.	(8)
	8	Harkköy			0.96	0.94	0.27	n.a.	n.a.	6.2	(9, 10)
	9	Karılar			0.5–1.1	0.7–2.5	1.0	0.07	50–69	0.1	(8)
Trabzon-Rize District	10	Kanköy	Massive stratiform and stockwork		1.80	0.80	<0.3	up to 7.6	n.a.	2.2	(11, 12)
	11	Kutlular			2.47	1.50	0.04	n.a.	n.a.	1.2	(13, 14)
	12	Çayeli			3.50	4.80	0.29	0.5	41	25	(15)
	13	Kotarakdere	Stockwork		0.66	1.74	0.29	n.a.	n.a.	0.9	(16, 17)
	14	Sırtköy			<0.30	<0.9	n.a.	n.a.	n.a.	n.a.	(18)
	15	Tunca			1.50	0.70	0.15	up to 0.7	up to 37	1.07	(19, 20)
	16	Pesansor			0.01	0.01	<0.01	0.04	<1	n.a.	(21, 22)
Artvin District	17	Peronit	Stockwork		1.03	2.12	0.38	n.a.	n.a.	0.24	(1)
	18	Hahur			1.10	0.10	0.05	n.a.	n.a.	0.23	(1)
	19	Sinkot			0.80	0.06	0.02	0.29	4.6	n.a.	(1, 23)
	20	Seyitler			2.50	<0.60	n.a.	0.3	37	n.a.	(1)
	21	Akarşen	Massive stratiform and stockwork		0.80	4.0	n.a.	1.5	28	1.5	(24, 25)
	22	Murgul			0.9	1.38	0.07	n.a.	n.a.	72.9	(26)
	23	Kuvarshan			1.68	2.51	0.21	n.a.	n.a.	>0.8	(1)
	24	Cerattepe			8.97	0.56	0.22	1.2	27	4.1	(1, 27)

*Numbers refer to the deposit/prospect localities in Figure 1; n.a.: not available or not reported (generally known to be less than 0.1% in the case of Pb). Size refers to probable and proved reserves. References: (1) MTA Mineral Inventory (Unpub. data); (2) Çakır and Çekiç (1982); (3) Demir Export (Unpub. company data); (4) Ronçeviç et al. (1970); (5) Revan (2010); (6) Caner (1970); (7) Kahraman (1981) (8) JICA (1998); (9) Çakır (1979); (10) Çakır and Şarman (1983); (11) NESKO Mining (Unpub. company data); (12) Yılmaz (1988); (13) Turhan and Avenk (1976); (14) Nalbantoğlu and Yılmaz (1992); (15) Çayeli Mineral Inventory (Unpub. company data); (16) Turhan and Akyol (1978); (17) Gümrükçü and Takaoğlu (1976); (18) Turhan (1968); (19) Günalay (1975); (20) Revan et al. (2014); (21) Yılmaz (1978); (22) JICA (2003); (23) Aydın et al. (2019); (24) Güven and Çağlar (1982); (25) Çağlar (1985); (26) Yıldız et al. (2009); (27) Inmet Mining (Unpub. company data).

of the 24 massive sulfide deposits in the eastern Pontide belt. Most deposits are Cu- and Zn-rich relative to the Pb and comparable to the bimodal felsic VMS deposits of the Late Phanerozoic. The Cu grades ranged from 0.1% to 8.9%, averaging approximately 1.5%, and the published Zn grades were generally low, ranging from <0.1% to 5.0%. The Pb content of the most deposits has rarely been determined, so the values are approximate. The mineral assemblages of the stockwork zones are usually very simple, comprising variable and locally significant amounts of pyrite, chalcopyrite, and sphalerite.

Precious metal concentrations vary considerably, with Ag ranging from <1 to 145 ppm and Au ranging from <0.1 to 2.5 ppm. Au is produced as a byproduct of Cu-Zn ores, and there is no current production of Pb.

Over 30 minerals have been observed in the Pontide VMS ore facies associated with mineralization (Table 3). The principal ore mineral in all of the deposits is

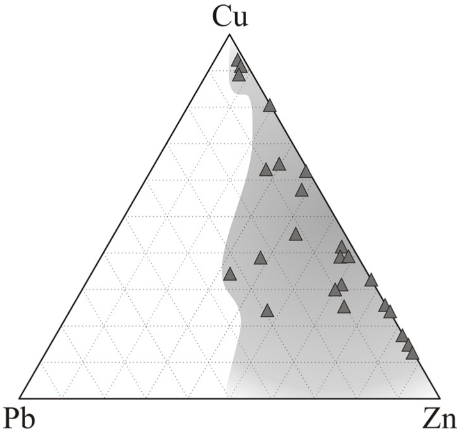

Figure 6. Ternary diagrams of the base metal (Cu-Pb-Zn) contents in the eastern Pontide VMS deposits; also shown in gray are shaded fields for bimodal felsic-type VMS deposits from Barrie and Hannington (1999). The proportion of Pb with respect to Cu and Zn tended to be lowest.

pyrite. Pyrite is accompanied mainly by chalcopyrite, sphalerite, galena, and bornite. The main gangue minerals in deposits are quartz, barite, gypsum, and sulfosalt minerals (Pejatoviç, 1979; Çiftçi, 2000; Revan, 2010; Revan et al., 2014). Several rare minerals, such as kawazulite (Bi_2Te_2Se), hessite (Ag_2Te), pyrrhotite (FeS), cervelleite (Ag_4TeS), stützite ($Ag_{5-x}Te_3$), tellurobismuthite (Bi_2Te_3), aikinite ($CuPbBiS_3$), emplectite ($CuBiS_2$), and wittichenite (Cu_3BiS_3), were also detected (Zaykov et al., 2006; Revan et al., 2014, 2019). Au seems to be particularly common in these deposits. Tellurides and Te-bearing minerals occur in some deposits. Barite and gypsum are prevalent within the upper sections of deposits, where they occur as irregular veins cutting sulfide ores and semi-massive bodies in the immediate footwall and hanging wall. Their geometries are not well defined because of limited exposure. Quartz (or silica in the form of chert or silicified zones) occurs as irregular veins and patches in many of the deposits. The depositional of timing of the silica is assumed to be concurrent with that of the sulfides, but some quartz may have formed later than the ore-stage sulfides. Some siliceous veins and patches of sulfide ores at Lahanos and Tunca have late paragenesis, as indicated by homogenization temperature data (Revan, 2010; Revan et al., 2017).

The classification scheme proposed by Barrie and Hannington (1999) was adopted by Revan et al. (2014), which is based on base and precious metal ratios. The Pontide massive sulfide deposits had the same patterns as bimodal felsic-type deposits when normalized to the primitive mantle (Figure 7). The more than 800 VMS deposits discovered worldwide range in size from 0.2 million tons to giant deposits, with a global average in the 10–20 Mt range (Galley et al., 2007) (Figure 8). At the district scale, the total known resources of ore in the eastern Pontide VMS deposits are in excess of 140 Mt. The largest known Pontide deposit is Murgul, containing approximately 73 Mt of recoverable Cu + Zn, making it a very large VMS deposit. The Çayeli deposit, with 25 Mt, is the second largest Cu-Zn deposit and is classified as a large VMS deposit.

7. Ore facies characteristics

The formation of Pontide VMS ores may have varied in style among the deposits, depending on the dominance of different characteristics. The deposits in the eastern Pontide district can be classified into 2 types based on their formational characteristics, as 1) a VMS deposit that is composed of a mound of high-grade massive sulfides formed above a zone of lower-grade stockwork mineralization, and 2) some deposits that are composed of only a stockwork zone that consists of crosscutting sulfide veins and veinlets in a matrix of pervasively altered host rock.

The VMS ores in the eastern Pontide belt consist of 2 parts, as ore facies that formed either on or immediately below the seafloor and ore-bearing sedimentary facies that immediately overlie the stratiform massive sulfide mounds. The ore facies can be subdivided into 4 associated groups, as hydrothermal-metasomatic, seafloor hydrothermal, clastic ore, and biological facies. The ore-bearing sedimentary facies are characterized by relatively thin silica (±Fe)-rich metalliferous beds that occur along the uppermost part of the ore horizon.

The hydrothermal-metasomatic facies are associated with subseafloor processes and include network-disseminated, massive vein, and massive lens facies. The precipitation of sulfide minerals within preexisting volcanosedimentary rocks occurs largely beneath the seafloor, and these ores form an important component of most Pontide VMS deposits (Figure 9). In the Killik deposit, the hydrothermal-metasomatic facies is represented by a stockwork zone and at least 1 massive lens of pyritic ore. The massive pyritic ore lens is nearly tabular and discordant with the enclosing host rocks. The massive pyritic ore has a completely homogeneous texture, shows no evidence of reworking of transported ore, and does not contain any clastic components. This small massive pyritic ore body is approximately 3 m thick and at least 10 m long, and is located approximately 700 m to the north of the main Killik orebody. In the Kızılkaya deposit, network-dissemination and massive vein-type mineralization have large lateral and vertical extents. Massive ore veins found within footwall rocks are up to 50 cm thick. The massive ore veins are discordant with the enclosing host rocks, and the orientations of well-exposed

Table 3. Mineral associations in the ore and ore-bearing facies from the eastern Pontide VMS deposits. The analytical methods used to detect the minerals are indicated.

Mineral	Analytical method					Deposit/prospect							
	TS	PS	MP	XRD	TSp	Çayeli	Kutlular	Lahanos	Killik	Kızılkaya	Murgul	Kanköy	Tunca
Acanthite (Ag_2S)	-	+	+	-	-	-	-	-	-	-	√	-	-
Aikinite ($CuPbBiS_3$)	-	+	+	-	-	-	-	√	-	-	√	-	-
Ankerite ($CaCO_3$)	+	-	-	-	-	-	√	√	-	-	-	-	-
Apatite ($Ca_5(PO4)_3F$	+	+	-	-	-	-	-	√	-	-	-	-	-
Barite ($BaSO_4$)	+	+	-	-	-	√	√	√	√	√	√	√	√
Bornite (Cu_5FeS_4),	-	+	-	-	-	√	√	√	√	√	√	-	√
Cervelleite (Ag_4TeS)	-	+	+	-	-	-	-	-	-	-	√	-	-
Chalcocite (Cu_2S)	-	+	-	-	-	√	-	-	√	-	-	√	-
Chalcopyrite ($FeCuS_2$)	-	+	+	+	-	√	√	√	√	√	√	√	√
Clausthalite (PbSe)	-	+	+	-	-	-	-	-	-	-	√	-	-
Covellite (CuS)	-	+	-	-	-	√	√	-	√	√	√	√	√
Dickite ($Al_2Si_2O_5(OH)_4$)	-	-	-	-	+	-	√	√	-	-	-	-	-
Digenite (Cu_9S_5)	-	+	-	-	-	-	-	-	-	-	√	-	√
Dolomite ($CaMgCO_3$)	-	-	-	+	+	√	√	√	-	-	-	-	-
Electrum (Au, Ag)	-	+	+	-	-	√	-	-	-	√	-	-	-
Emplectite ($CuBiS_2$)	-	+	+	-	-	-	-	√	-	-	-	-	-
Fahlore	-	+	+	-	-	√	-	√	√	√	√	√	√
Ferrihydrite ($Fe_2O_39H_2O$)	-	-	-	-	+	√	√	√	-	-	√	-	-
Galena (PbS)	-	+	-	-	-	√	√	√	√	√	√	√	√
Goethite (FeOOH)	-	+	-	+	-	-	√	√	-	-	-	-	-
Gold (Au)	-	+	+	-	-	√	-	√	-	√	√	√	√
Gypsum ($CaSO_42H_2O$)	-	-	-	-	-	-	-	√	√	√	√	√	-
Halloysite ($Al_2Si_2O_5(OH)_4$)	-	-	-	+	+	√	√	√	-	-	-	-	-
Hematite (Fe_2O_3)	-	+	+	-	-	√	√	√	√	√	-	√	√
Hessite (Ag_2Te)	-	+	+	-	-	-	-	√	-	-	√	-	-
Illite (FeS_2)	-	-	-	+	+	√	√	√	-	-	-	√	-
Kaolinite ($Al_2Si_2O_5(OH)_4$)	-	-	-	+	+	-	-	√	-	-	-	√	-
Kawazulite Bi_2 $(TeSeS)_3$	-	-	+	-	-	-	-	√	-	-	-	-	-
Magnesite ($MgCO_3$)	-	-	-	-	+	-	-	√	-	-	-	√	-
Marcasite (FeS_2)	-	+	-	-	-	√	-	√	√	√	-	-	√
Montmorillonite	-	-	-	+	+	-	-	√	-	-	-	-	-
Pyrite (FeS_2)	-	+	+	-	-	√	√	√	√	√	√	√	√
Pyrrhotite (FeS)	-	+	-	-	-	-	-	-	-	√	-	-	-
Quartz (SiO_2)	+	-	-	-	-	√	√	√	√	√	√	√	√
Rutile (TiO_2)	-	+	+	-	-	-	√	-	-	-	-	-	-
Siderite ($FeCO_3$)	-	-	-	+	+	-	-	√	-	-	√	√	-
Silver-sulfosalt	-	+	-	-	-	-	-	-	√	-	-	-	-
Smectite	-	-	-	-	+	-	√	√	-	-	-	-	-
Sphalerite (ZnS)	-	+	-	-	-	√	√	√	√	√	√	√	√

Table 3. (Continued).

Stützite ($Ag_{5-x}Te_3$)	-	+	+	-	-	-	-	-	-	-	√	-	-
Tellurobismuthite (Bi_2Te_3)	-	+	+	-	-	-	-	√	-	-	-	-	-
Tennantite ($[CuAg]_{12}As_4S_{13}$)	-	+	-	-	-	√	-	√	-	√	√	√	-
Tetrahedrite ($[CuAg]_{12}Sb_4S_{13}$)	-	+	+	-	-	-	-	√	-	-	√	-	√
Tetradymite	-	+	+	-	-	-	-	-	-	-	√	-	-
Wittichenite (Cu_3BiS_3)	-	+	+	-	-	-	-	√	-	-	-	√	-

TS: Thin section, PS: polished section, MP: microprobe, XRD: X-ray diffractometer, TSp: TerraSpec portable mineral analyzer, +: detected, -: not detected, √: present.

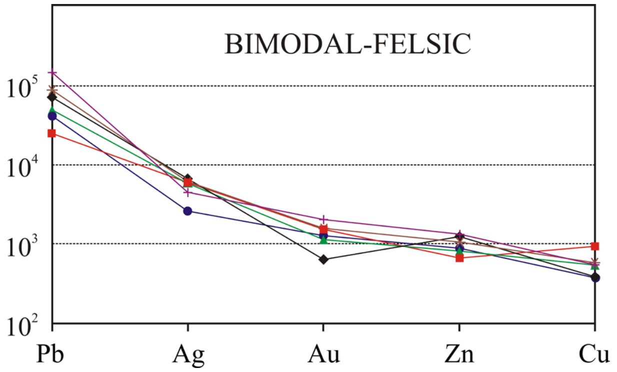

Figure 7. Average primitive mantle-normalized metal values of VMS types by age period and the Pontide VMS deposits. Archean averages: diamonds; early Proterozoic averages: circles; Middle and Late Proterozoic averages: triangles; Early Phanerozoic (Paleozoic) averages: pluses; Late Phanerozoic averages: asterisks; Pontide VMS averages: squares (from Revan et al., 2014).

ore veins are nearly vertical. In the Çayeli deposit, a well-developed stockwork sulfide zone is present beneath the stratiform massive orebody. Massive mineralized veins up to a few 10 cm thick are common, especially close to the massive stratiform orebody. These thicker veins are economically mined. At Lahanos, this facies is represented by a stockwork zone. The stockwork zone developed below the stratiform massive orebody and has limited lateral and vertical extents. Primary textures are commonly well preserved at some distance from the massive orebody due to progressively decreasing alteration intensity. The average thickness of the defined mineralized sulfide veins is several centimeters, with some reaching 15 cm. The Murgul deposit hosts large stockwork mineralization, including massive ore veins and possibly lenses. The thicknesses of these mineralized veins are variable and rarely reach 70–80 cm. The veins commonly contain economically recoverable ore for at least several tens of meters below hanging wall rocks. In the Harkköy and Tunca prospects, the hydrothermal-metasomatic facies are represented by stockwork and possibly massive vein-type mineralization. The thickness of the ore veins is variable and reaches 40 cm in some places.

The term seafloor hydrothermal facies refers to sulfide accumulation on the seafloor and is characterized by hydrothermal vent chimney fragments. All of the fragments of the Paleo-hydrothermal chimneys in the massive sulfide deposits (Çayeli, Killik, Lahanos, Kızılkaya, Kutlular, and Akarşen) are found in clastic sulfide ores (Revan, 2010, Revan et al., 2013, 2014). The mineralized chimney fragments range from a few millimeters to approximately 8 cm in diameter. The well-preserved chimney fragments typically have distinct concentric zones that contain sulfide and sulfate minerals and have distinct mineral abundances. Each concentric zone is characterized by certain dominant minerals. The outer zones are generally enriched in Fe- and Zn-sulfides, whereas the inner zones contain abundant Cu- and minor Fe-sulfides. The axial conduits are commonly filled by barite gangue and pyrite, with minor amounts of Fe- and Zn-sulfides and quartz. Numerous examples of what appear to be chimney wall fragments have porous and laminated textures. Some chimney wall fragments display thin alteration rims, indicative of oxidizing conditions on the seafloor (Revan et al., 2014). Note that the average trace element contents of the vent chimneys have markedly higher metal concentrations (Figure 10a). The chimney fragments are also characteristic of seafloor sulfide accumulations and are evidence of Paleo seafloor hydrothermal vents in the Pontides.

The majority of ores in most of the VMS deposits have apparent clastic textures. Rounded, subhedral, and anhedral sulfide fragments are present in the sulfide matrix. The sizes of individual sulfide fragments vary from the micrometer to centimeter scale. Sulfide fragments are generally composed of pyrite, chalcopyrite, sphalerite, bornite, and galena. The chimney fragments and, to a lesser extent, fossil fauna fragments form the main constituents of the clastic sulfide ores. Rarely, relics of the host facies (volcanic and sedimentary rock fragments) may

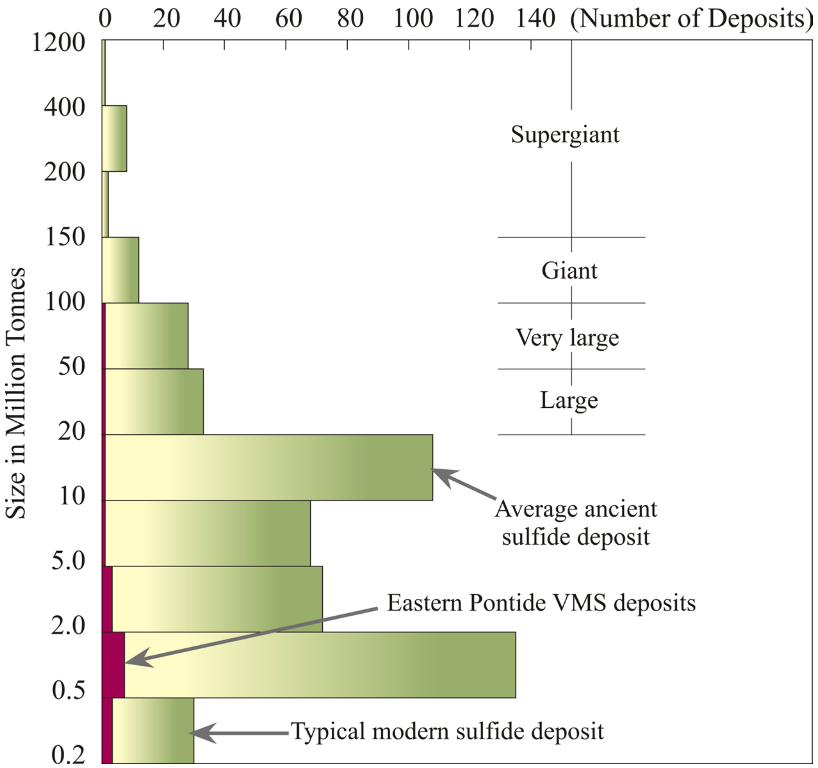

Figure 8. Global size distribution of the VMS deposits. Known examples of the eastern Pontide deposits and prospects are also given for comparison (data from Hannington et al., 2005; Galley et al., 2007).

also contribute to the constituents of clastic sulfide ores. Coarse-grained components predominate close to the vent channels. Due to progressive reworking, the grain size of the ore clasts decreases to sand size during transport, and the deposition of sulfide sandstone, composed mostly of sulfide materials, occurs at a specific distance from the vent channel. The clastic texture (previously termed brecciated ore by local geologists) was interpreted to be the product of redeposition of talus eroded from collapsed/fallen sulfide chimneys and mounds (Revan, 2010). A representative sulfide sandstone sample from stratiform massive ore was characterized by high metal contents (Figure 10b).

The biological facies is characterized by the fossil remnants of vent-related communities. All of the fragments of fossil fauna in the massive sulfide deposits are preserved in the clastic sulfide ores (Revan et al., 2010, 2013). Traces of fauna are well preserved in the Lahanos, Killik, and Çayeli deposits. Fossil fauna from the Kızılkaya, Kutlular, and Kanköy deposits are scarce and not well preserved. The dimensions of the tube worm fossils reach 2.5 cm in diameter and 8 cm in length. The interiors of the tube worm fossils are mainly filled with sulfide minerals (such as pyrite, chalcopyrite, tetrahedrite, sphalerite, and covellite), while very few samples feature external replacement with opaque and gangue minerals (dolomite, barite, serpierite, goethite, jarosite, and gypsum). In some examples, the morphologies of the fossils are completely replaced and preserved, whereas some fossil traces form cavities due to intense and extensive acidic leaching. The tube worm fossils are also evidence of Paleo seafloor sulfide accumulation in the Pontides (Revan et al., 2014).

The ore-bearing sedimentary facies are very special formations, reflecting seafloor alteration within the massive sulfide Paleo-hydrothermal fields (Kalogeropoulos and Scott, 1983; Maslennikov and Ayupova, 2007; Maslennikov et al., 2012; Hollis et al., 2015). The ore-bearing sedimentary rocks of the eastern Pontide VMS deposits occur at the boundary between the footwall and hanging wall rocks and stratigraphically above the massive sulfide ores. The ore-bearing sedimentary rocks generally form layers less than 1.5 m thick above the mineralized horizon and are typically red in color due to their high Fe contents. These silica (±Fe)-rich rocks in the eastern Pontide VMS deposits were first described by Revan et al. (2019) as metalliferous sediments, due to their significant concentrations of metals. They are largely composed of quartz and hematite. While the Si ± Fe content of the sediments directly overlying the stratiform ores is high, an increase in the amount of carbonate is observed in sediments that are not directly overlying the ores. Metalliferous sedimentary rocks have

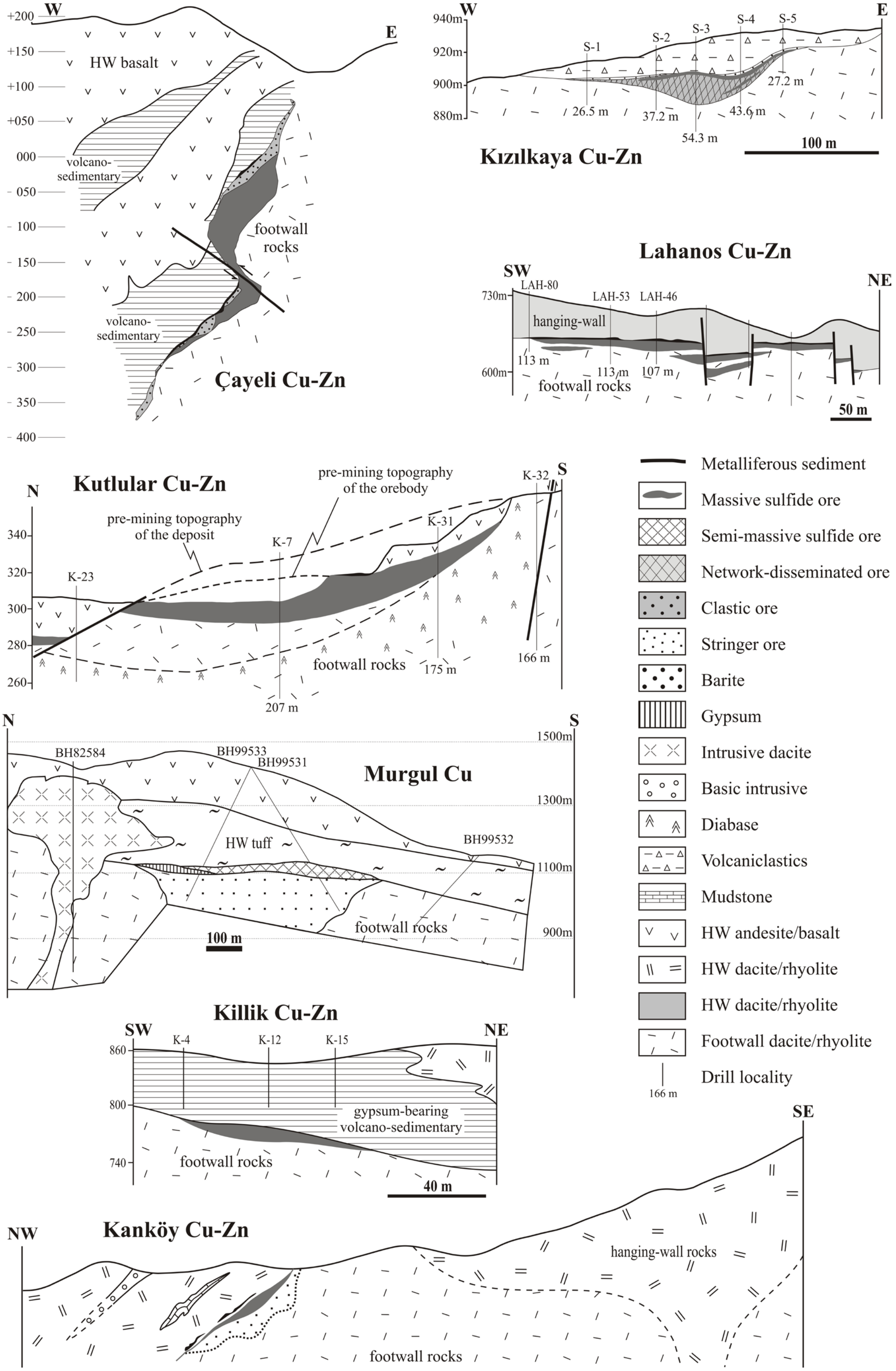

Figure 9. Cross-sections through the eastern Pontide VMS deposits showing the distribution of the main lithologies and stratigraphic units relative to the mineralization (modified from Revan, 2010; Revan et al., 2019). In most deposits, the orebodies were tilted to the NNW.

been identified in detail in the Lahanos, Çayeli, Kanköy, and Kutlular deposits (Revan et al., 2019). In the Lahanos mine, the ore-bearing sedimentary layer directly overlies the massive sulfide orebody. The thickness of this typically red-colored layer ranges from a few centimeters to ~1.5 m. The layer contains ore fragments from the underlying massive ore and rock fragments (hyaloclastic materials) from the immediately overlying hanging wall rocks. A rather hard and silicified layer covers the whole orebody (~300 m in length), but exhibits variable thickness. The ore-bearing sedimentary layer described in the Kanköy deposit does not directly overlie the massive sulfide ore, but is approximately 50 cm above the massive sulfide orebody. No data are available on its thickness and extent. However, observations in some locations indicated that it is at least 20 cm thick. In the Çayeli mine, this facies can be traced discontinuously along the strike for approximately 550 m. Its thickness varies from approximately a few centimeters to ~1 m.

The ore-bearing sediments have mineralogically similar characteristics. Glass shards, sericitic volcanic rock fragments, corroded crystals (quartz, feldspar, and barite), and opaque minerals (mainly pyrite, chalcopyrite, and hematite) are present within a carbonate, silica, Fe oxide, and Fe hydroxide matrix. Several rare bismuth sulfosalts, such as aikinite ($CuPbBiS_3$), emplectite ($CuBiS_2$), and wittichenite (Cu_3BiS_3), have also been detected in the metalliferous sediments. Flow foliation structure is common. In some samples, the presence of spherules and fossil remains has been noted. The sediments contain Cu, Zn, Pb, Au, Sb, Sr, and Ba in significant proportions. Base metal concentrations are high (Figure 10c), with most samples containing >1000 ppm Cu + Pb + Zn (Revan et al., 2019). These sediments in the Pontide deposits are typically auriferous. They contain anomalous values of up to 10 gr/t Au and 729 gr/t Ag (Revan, 2010). These silica (±Fe)-rich rocks represent the typical products of seafloor hydrothermal systems and can be used as a guide in prospecting for massive sulfide deposits.

Examination of the VMS deposits in the Pontides showed that the primary hydrothermal features of the ore facies are well preserved despite the imprint of later deformational effects. Based on variations in the texture and structures of the VMS deposits in the eastern Black Sea district, a prediction of the ore deposit geometry and facies positions in the system was attempted (Figure 11). The ore facies association suggests that the accumulation processes occurred over the life of the same hydrothermal system.

8. Alteration

Data on the degree, extent, and zoning of hydrothermal alteration associated with the eastern Pontide VMS deposits are quite limited (Figure 12). However, the types of alteration that were determined in some selected deposits provided data that can be important in the determination of the origins of these deposits and in the exploration for new deposits. The hydrothermal alteration in the eastern Pontide VMS deposits is largely confined to footwall rocks. The hanging wall alteration has very low intensity and is limited when compared to the footwall alteration. The original textures in the footwall rocks, especially close to the orebody, have largely been obliterated by intense silicification. The feldspars are almost completely altered. The clay minerals are mainly composed of sericite, kaolinite, illite, smectite, and montmorillonite. Common carbonate minerals are dolomite, siderite, and calcite.

The alteration immediately below the stratiform massive sulfide orebodies generally exhibits lateral zonation. While quartz-sericite-pyrite alteration is mainly developed in the central zones, quartz and sericite are accompanied by chlorite and carbonate in the outer zone. In the outermost portions of some of the deposits, a zeolite-bearing zone (mordenite and laumontite) is observed. Pyrite is less abundant in these outer sections. At Murgul, a quartz-sericite-kaolinite zone hosting mineralization is accompanied by chlorite through the outer zone (JICA, 2004) (Figure 12a). Extensive quartz-sericite-chlorite alteration in the central part of the Lahanos mine and at the adjacent Kızılkaya and Killik mines is accompanied by carbonate minerals in the outer zones (Tüysüz and Er, 1995) (Figure 12b). Tunca is the only deposit that exhibits a well-defined alteration pattern (Revan et al., 2017), where concentric zones are observed (Figure 12c). The hydrothermally altered host rocks mainly consist of the following assemblages: 1) an inner zone of quartz-pyrite-sericite-chlorite ± mixed layer sericite/smectite, 2) a quartz-pyrite-mixed layer sericite/smectite ± chlorite ± smectite zone surrounding the inner zone, and 3) quartz-pyrite-laumontite ± sericite ± chlorite assemblages that are locally concentrated along the outer zones of the field. The most intense mineralization is concentrated in the cores of the zoned alteration pattern. The alteration of the footwall host rock is spatially discontinuous due to the presence of dominant intrusive bodies.

Few studies have been published regarding the alteration style of hanging wall rocks. Widespread recognition of hanging wall alteration has been hampered by its weak and limited development when compared with the more intense footwall alteration. Hanging wall alteration is generally developed immediately above the stratiform massive sulfide orebodies. It is characterized by a large amount of clay alteration and does not contain sulfide. The Çayeli massive sulfide deposit is the only deposit in which the style of the hanging wall alteration has been defined (Çağatay and Boyle, 1980; Çağatay, 1993)

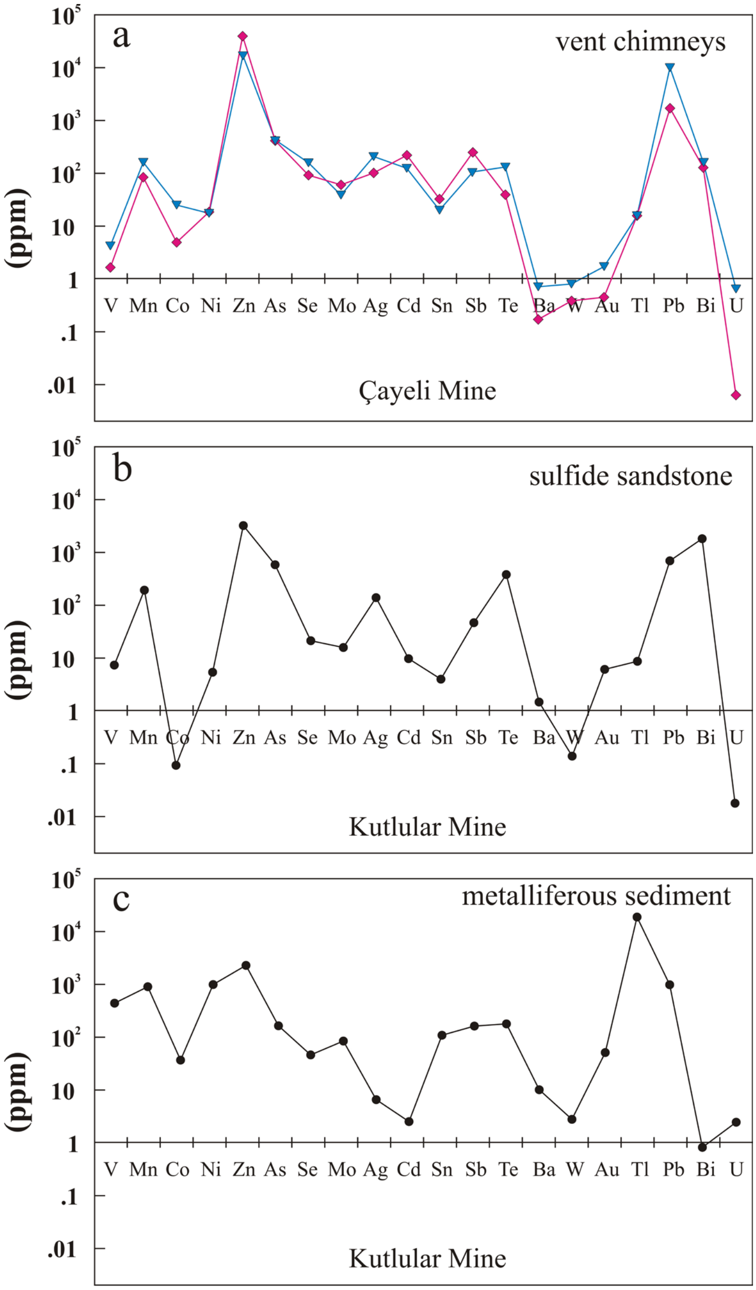

Figure 10. Spider diagram showing the average trace element compositions of the ore and ore-bearing facies from the eastern Pontide VMS deposits. (a) Mineralized chimney fragments from the Çayeli mine. Measurements were conducted on chalcopyrite from the A, B, and C zones of the Çayeli chimneys (b) Sulfide sandstone from the Kutlular mine. Measurements were conducted on chalcopyrite and pyrite. (c) Metalliferous sedimentary rock from the Kutlular mine. Measurements were conducted on chalcopyrite, pyrite, and hematite (data from Revan, 2010; Revan et al., 2014). Values are given in ppm.

(Figure 12d). The clay zones in the hanging wall range up to 200 m in thickness and 2 km in lateral extent. There are 2 principal types of hydrothermal alteration in hanging wall lithologies, as Zone 1 and Zone 2. The montmorillonite + calcite ± chlorite ± kaolinite ± illite zone (Zone 1) occurs at the upper stratigraphic levels in the cover rocks. This zone is approximately 150 m thick and occurs in pumice tuff and basalts. The alteration mineral assemblage in Zone 1 includes smectite with minor amounts of kaolinite, calcite, and chlorite. Feldspars are partly altered, and basalts show propylitic alteration (Mg-rich chlorite and calcite). In the northeastern part of the map area, this zone grades into the zeolite (laumontite-mordenite) zone. Zone 2 is characterized by an assemblage of kaolinite + mixed layer

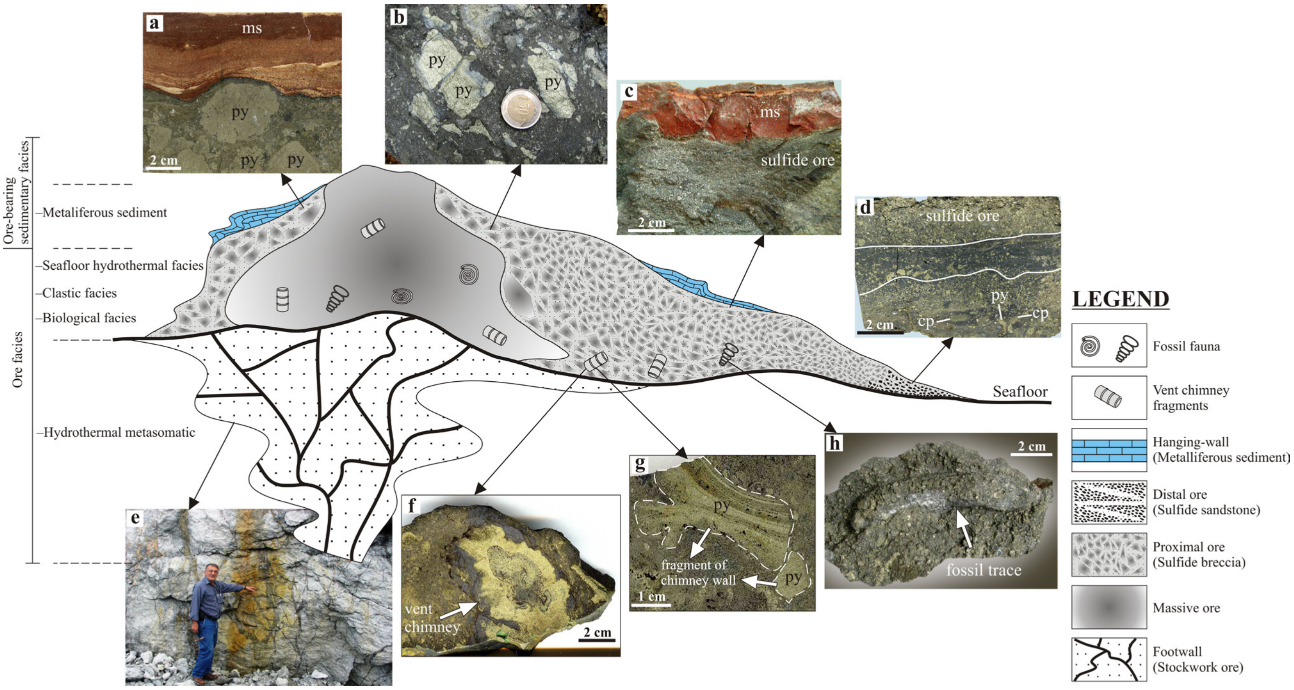

Figure 11. Schematic diagram illustrating the relative position of the ore facies in the eastern Pontide VMS deposits. (a) Fragments of pyrite in the matrix of sulfide ore (proximal ore) with ore-bearing hanging wall siliceous carbonate; Lahanos. (b) Coarse-grained sulfide fragments (proximal ore) up to 3 cm in a clastic sulfide matrix; Killik. See the coin for scale. (c) Sulfide sandstone (distal ore) with ore-bearing hanging wall siliceous carbonate; Kutlular. (d) Graded ore (distal ore) with fragments of pyrite and chalcopyrite in the matrix of the sulfide ore; Kutlular. (e) Stockwork ore in the Murgul mine, representing the hydrothermal metasomatic facies. (f) Example of a zoned vent chimney fragment in a clastic sulfide matrix from the Lahanos mine. (g) Subhedral sulfide (pyrite) fragments of laminated cavernous chimney walls are up to 4 cm in size; Lahanos. (h) Tube worm fossil traces representative of the biological facies and replaced by various sulfide minerals within the clastic sulfide ore from the Killik mine. Parts of this figure were slightly modified and reproduced from Revan et al. (2013). cpy: chalcopyrite, py: pyrite, and ms: metalliferous sediment.

illite-smectite + dolomite ± montmorillonite and occurs in closer proximity to the massive sulfide orebody. Feldspars are largely destroyed, and hematite is present everywhere. This zone has thicknesses of 30 to 60 m and outcrop widths of 20 to 150 m.

The hanging wall alteration is considered to represent ongoing hydrothermal activity after the formation of stratiform sulfide orebodies and deposition of hanging wall lithologies. The zeolite-bearing outer zones suggest that the volcanic rocks in the distal part of the deposits have been affected by deuteric or very low-temperature alterations, which formed mordenite and laumontite.

9. Sulfur isotope geochemistry

Over the past 2 decades, a number of studies have reported on the sulfur isotope compositions of ores from several of the Pontide VMS deposits/prospects considered herein. Previously published sulfur isotope values for the eastern Pontides originated from the stratiform sulfide mound and stockwork zones of the VMS deposits (Gökçe, 1992; Çağatay and Eastoe, 1995; Gökçe and Spiro, 2000; JICA, 2003; Revan, 2010; Fochtman, 2014; Revan et al., 2016, 2017). The sulfur isotope values for sulfide minerals in these deposits showed a total $\delta^{34}S$ range from −2.7‰ to 7.0‰. These values were comparatively uniform at the deposit and district scales (Figure 13). The stockwork zones of the Peronit and Pesansor prospects have $\delta^{34}S$ values between 4.6‰ and 6.8‰ and 5.9‰, respectively (JICA, 2003). Although the sulfur isotope values of both deposits have been studied, no effort has been made to interpret the relevant data. Sulfur isotope investigations at Murgul reveal that the sulfides from both the massive and stockwork ores had similar $\delta^{34}S$ values, ranging from −1.5‰ to 3.4‰ (Gökçe, 1992; JICA, 2003). The S isotope data from the Murgul mine were interpreted by Tüysüz (2000), and indicated that the sulfur was derived from magmatic sources. Fochtman (2014) concluded in his MSc thesis that the fluids that produced Murgul were likely derived from seawater. To evaluate the source of sulfur in the Tunca prospect, a total of 11 samples were analyzed for sulfur isotopes. The sulfur isotope analyses of this study yielded a narrow range from 1.5‰ to 4.1‰ for the stockwork ore (JICA, 2003). These values were considered to represent a reduced seawater sulfate origin, with variable

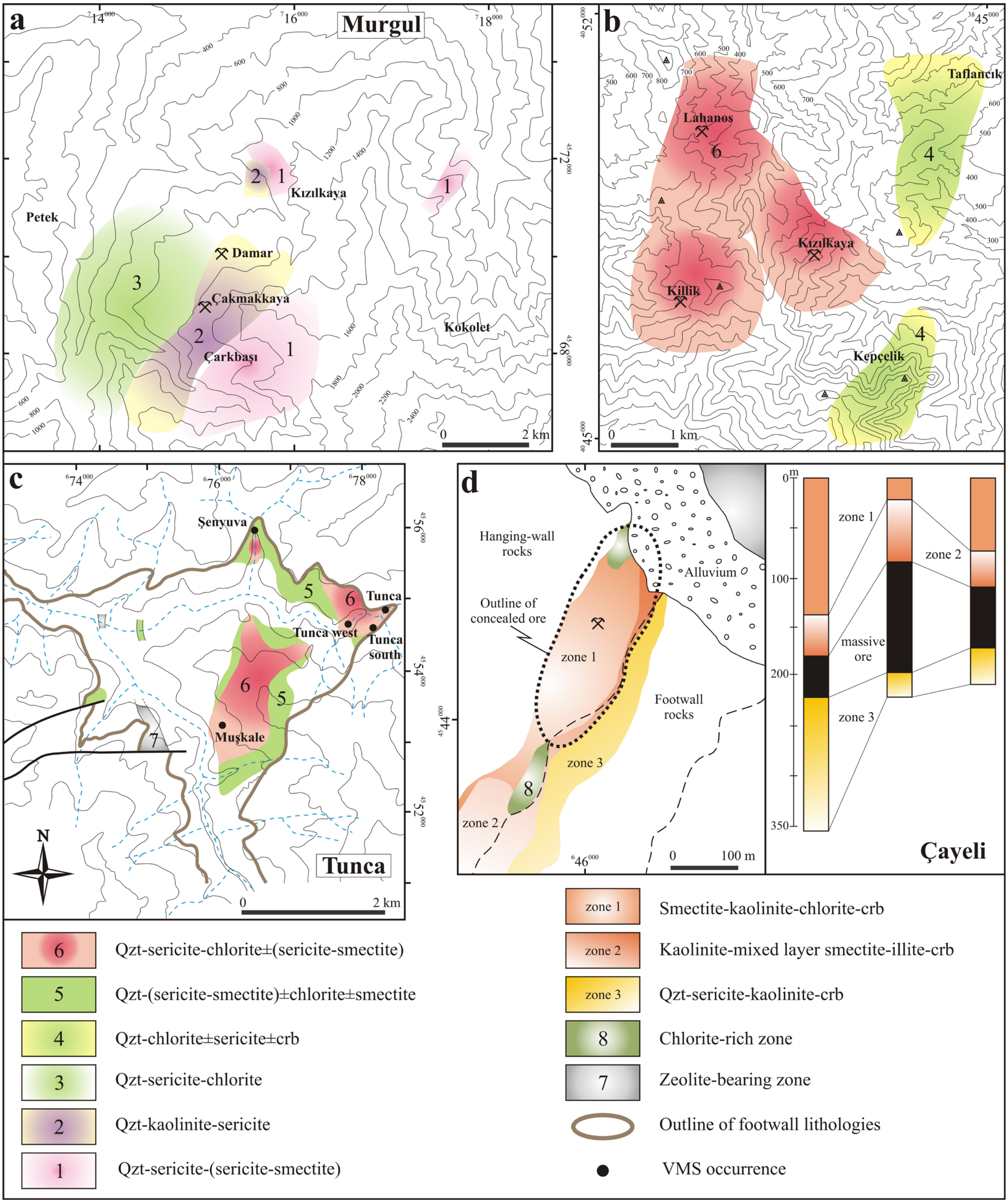

Figure 12. Comparison of the alteration zones in the 4 eastern Pontide VMS deposits. Tunca shows a typical concentric footwall alteration pattern, while the other 3 deposits exhibit irregular or partially conformable alteration patterns.

contributions of deep-seated sulfur leached from the host rock during hydrothermal circulation (Revan et al., 2017). From their study of the sulfur isotope characteristics of the Pontide VMS deposits, Gökçe and Spiro (2000) considered the main source of the sulfur to be magmatic, but Çağatay and Eastoe (1995) concluded that reduced

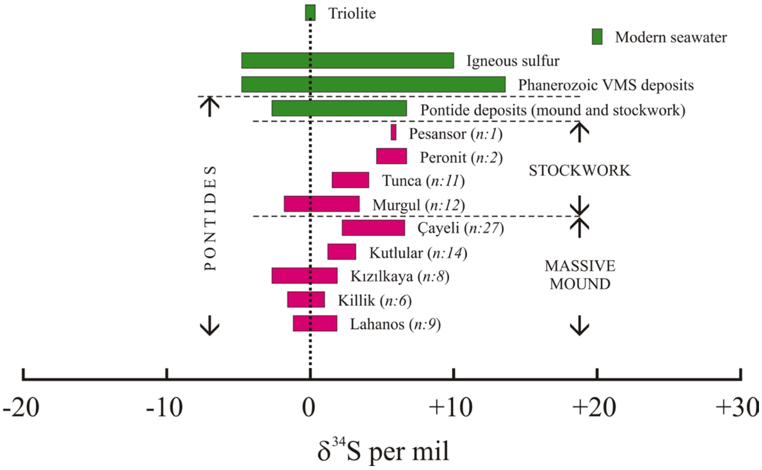

Figure 13. The range of d^{34}S values in the sulfide minerals from the Pontide VMS deposits compared with the analogs. Some geologically important sulfur reservoirs are also given for comparison (data from Gökçe, 1992; Çağatay and Eastoe, 1995; Gökçe and Spiro, 2000; JICA, 2003; Revan et al., 2016, 2017).

seawater sulfur was the more likely source. To contribute to these discussions concerning the sulfur sources, Revan et al. (2016) investigated the sulfur isotope compositions of hydrothermal vent chimneys in 5 VMS deposits. They reported sulfur isotope analytical results for 52 sulfide mineral separates from 8 vent chimneys within these deposits. The δ^{34}S values of the vent chimneys ranged from –2.7‰ to 6.5‰, which were similar to the range of values (–2.6‰ to 7.0‰) reported for the massive and stockwork zones in the VMS deposits in the eastern Pontide belt (Gökçe, 1992; Çağatay and Eastoe, 1995; Gökçe and Spiro, 2000; JICA, 2003). These recent values were considered to represent a reduced seawater sulfate origin with variable contributions of deep-seated sulfur leached from the host rock during hydrothermal circulation (Revan et al., 2016).

10. Discussion

The volcanic sequence hosting the eastern Pontide VMS deposits is bimodal, which was inferred to indicate an extensional geodynamic setting. On a global basis, the tectono-magmatic setting of the rocks hosting the VMS deposits is associated with major crustal extension caused by mafic magma intrusions that were generated by subduction-related processes. In such settings, significant volumes of felsic volcanic rocks are commonly observed in addition to mafic volcanic rocks (Allen et al., 2002; Piercey, 2011). Felsic rocks associated with the eastern Pontide VMS deposits are usually considered to have formed in a subduction-related extensional setting (Eyuboglu et al., 2014; Delibas et al., 2016, 2019; Revan et al., 2017). The trace and major element geochemical signatures of the felsic rocks used in this study suggested that these rocks are strongly associated with a setting characterized by a volcanic arc developed on the continental crust. Rifting of the continental crust can occur behind a volcanic arc developed on a continental margin in response to subduction of oceanic crust and melting of the lithospheric mantle (Barrett and MacLean, 1999). With the progressive opening and deepening of a continental back-arc basin, a marine basin may develop that is floored by a heterogeneous assemblage of mafic to felsic volcanic rocks, pelagic sediments, and volcaniclastic sediments derived from nearby volcanic edifices (Barrett and MacLean, 1999). Felsic volcanic rocks in such settings commonly have 200 to 400 ppm Zr, 20 to 40 ppm Nb, Zr/Y ratios of 4 to 7, and high REE contents (Barrett and MacLean, 1999). These values are highly consistent with the values of felsic rocks associated with the Pontide VMS deposits. There is a close spatial relationship between these felsic volcanic rocks and the Phanerozoic VMS deposits. The Phanerozoic VMS deposits are preferentially associated with FII-type felsic volcanic rocks (Hart et al., 2004). With respect to the VMS-fertile felsic volcanic rocks, the most prolific felsic rocks are FIII-type rocks, while FII-type and FI-type felsic rocks are classified as moderately prolific and least prolific, respectively (Lesher et al., 1986). The preferential association of these geochemically diverse felsic rocks with the VMS deposits can be broadly applied to the Pontide VMS district. Based on the available data and theoretical work in the VMS literature, the Pontide VMS-associated felsic rocks appear to have formed in a similar extensional geodynamic environment. The bimodal felsic-type characteristics of the eastern Pontide deposits support such an extensional tectonic setting related to subduction. Pontide VMS-associated felsic rocks are of FII type in terms of productivity and can be classified as moderately prolific. The lack of large VMS deposits in the eastern Pontide district may have been due to this feature of the deposits.

Due to the complex structure of the VMS deposits forming on the seafloor and at particular geological horizons, a wide variety of ore facies associated with mineralization has formed. The presence of hydrothermal vent chimney fragments, fossil fauna traces, metalliferous sedimentary rocks, and fragmental (or brecciated) ores in the Pontides is clear evidence of formation on the seafloor. Traces of the ore facies are easily recognized in modern seas; however, detecting their traces in Paleo-oceans is difficult due to modifications such as deformation, metamorphism, and structural overprinting (Revan et al., 2014). Researchers studying massive sulfide deposits have argued the origin of various traces encountered in massive ores and have offered various hypotheses. Based on the hydrothermal vent chimneys discovered during deep-sea research and their distinctive locations and shapes, a consensus has emerged that these traces may be similar to traces that were previously encountered in ancient massive sulfide districts. However, the traces found in massive sulfide ores vary significantly, and the shapes and sizes of some traces have been observed to differ from those of vent chimneys (seafloor hydrothermal facies), which has led to the hypothesis that they might be fossil fauna (biological facies) traces. With the discovery of various life forms (vestimentiferan, Polychaetas, etc.) that live on the sulfur emanating from hydrothermal vents from which the vent chimneys form in modern seas, researchers have agreed that these traces may in fact belong to remnants of vent-related communities that thrive under very special ecological conditions. The coexistence of the 2 facies (seafloor hydrothermal and biological facies) is common in both modern and ancient oceans, and when traces of one of the facies are discovered, finding traces of the other facies is possible.

The well-preserved vent chimneys, which are the most important evidence of Late Cretaceous seafloor hydrothermal vents in the Pontides, have distinct concentric zones. Observed concentric patterns in vent chimneys can be a result of a complex combination of physical and chemical factors (e.g., Goldfarb et al., 1983; Haymon, 1983; Qudin and Constantinou, 1984; Butler and Nesbitt, 1999; Maslennikov et al., 2009). Temperature and redox gradients are the most important of many factors that influence the trace element distributions within the chimney zones. Strong physicochemical gradients are responsible for variations in the trace element contents across the chimneys, whereas changes in the fluid temperature during chimney growth cause trace element differentiation over time (Butler and Nesbitt, 1999; Maslennikov et al., 2009). The high levels of U and V found in the outer walls of the chimneys indicate a seawater origin and imply a submarine environment for the formation of the Pontide deposits (Revan et al., 2014). Considering that modern massive sulfides are situated at depths >2500 m near the extension zones (Qudin and Constantinou, 1984), hydrothermal black smoker chimneys likely formed at similar depths. Additionally, all of the known vent chimney-bearing sites (modern and ancient) are located within extensional environments. Haymon (1983) indicated that the presence of high-temperature vent chimneys is important evidence of extensional zones, and at the same time, the mineralogical and chemical zoning observed in these vent chimneys can only be possible in a deep ocean environment. From this, it was concluded that the chimney-bearing VMS deposits in the eastern Pontide district formed in a relatively deep-water environment.

Tube worm fossils are also characteristic of seafloor sulfide accumulations (e.g., Haymon, 1983; Qudin and Constantinou, 1984; Jonasson and Perfit, 1999; Doyle and Allen, 2003) and are evidence of Paleo seafloor hydrothermal vents in the Pontides (Revan et al., 2014). These tubular worm-like fossils can be considered ancestral forms of the unusual vent communities on the modern seafloor (Haymon et al., 1984; Banks, 1986) and have been assigned by several researchers (Kuznetsov and Sobetskii, 1988; Maslennikov, 1991; Little et al., 1997, 2007; Shpanskaya et al., 1999; Revan et al., 2010, 2014) to tube worms based on the following criteria: 1) similar geoecological conditions, 2) consistent associations with chimney fragments in massive orebodies, and 3) similarity to other ancient examples in the Urals, Cyprus, Oman, and Georgia in terms of their shapes and partially their sizes and contents.

One of the most important pieces of evidence regarding the formation on the seafloor is metalliferous siliceous sedimentary rocks. The siliceous sedimentary rocks considered herein are related to the seafloor hydrothermal systems that formed the VMS mineralization. The metalliferous sediments were formed by the mixing of mainly chemical components and, to a lesser degree, detrital components in various proportions, due to the sedimentation processes occurring on the seafloor. The chemical compositions of these rocks reflect the environments in which they formed. The presence of spherules in these rocks is considered a result of hydrothermal fluids vented at the seafloor (e.g., Davidson et al., 2001; Grenne and Slack, 2003; Hollis et al., 2015) or seafloor decay of volcanic glasses (Maslennikov et al., 2012). The high levels of U and V indicate a seawater origin in a submarine environment for the formation of the eastern Pontide metalliferous sedimentary rocks. The volcanic chemistry of the metalliferous rocks in the eastern Pontide VMS deposits showed pronounced negative Ce anomalies in the REE patterns. Distinctive Ce depletions are characteristic of most seawater and marine sediments (e.g., Hogdahl et al., 1968; Parekh et al., 1977; Hole et al., 1984; Neal and Taylor, 1989). Negative Ce anomalies in metalliferous rocks from the Pontides, as in their counterparts worldwide, have been interpreted as a result of interactions with seawater. The geochemical affinity of the metalliferous sedimentary rocks can provide important clues for understanding the tectonic setting in which they were deposited. Zirconium, La, and Sc ratios are the most suitable elements for performing provenance analyses and determining the tectonic setting (Bhatia and Crook, 1986). Provenance-related immobile element compositions of the eastern Pontide metalliferous sediments carry a continental arc provenance signature (Revan et al., 2019).

The presence of sedimentary clastic textures in massive sulfide ores is additional evidence indicating formation on the seafloor. The formation of clastic (or breccia) ores involves a series of processes that include the disintegration, transport, and redeposition of the sulfide mound on the seafloor in response to a variety of factors. Interaction with seawater is the most important of the many factors that influence the formation of the clastic texture (Maslennikov, 1999; Maslennikov et al., 2012). The course of interactions with seawater is a highly complex process. In particular, the presence of alteration rims, which can be observed around several sulfide clasts and indicate seafloor oxidation, might be interpreted as the result of interactions with seawater. A series of other possible mechanisms have been proposed as explanations for the formation of the clastic texture (Clark, 1983; Eldridge et al., 1983; Hashiguchi, 1983; Binney, 1987; Franklin, 1993). Injection of footwall rocks into massive ore may create soft-sediment deformation. Such a process may occur in an unstable seafloor where a voluminous sulfide ore pile accumulates. Hydraulic lifting of ore (the lifting potential of a hydrothermal fluid) can facilitate downslope movement, giving rise to fragmental ores. The growth of the ore pile on the seafloor is another cause of fragmental ores. The oversteepened slopes of the ore piles may slump under their own weight or in response to seismic activity. Changes in volume associated with the dehydration of gypsum or the hydration of anhydrite may cause disintegration. Fluctuation in the temperature of a water-saturated gypsum or anhydrite mass can result in an increase or decrease in volume, causing uplift or subsidence of the ores. Collapse of the sulfide pile in response to the removal of material by a solution at depth within the ore blanket is also an expected process (Eldridge et al., 1983). The syndepositional and postore intrusions of the felsic domes related to mineralization may lead to various deformational and fragmental textures (Hashiguchi, 1983). Forceful hydrothermal eruption by the sudden venting of vein material was also proposed by Clark (1983). At least one or more of the possibilities suggested above for the origin of the clastic ore can be said to have been involved in the formation of the clastic ores that are typically observed in most of the Pontide VMS deposits. The association of felsic domes with mineralization, soft-sediment deformational structures, graded ores, and presence of abundant gypsum and wall rock fragments in the sulfide ore all support many of these possibilities. In summary, it would not be wrong to say that ore precipitation occurred in a highly active and unstable seafloor environment.

The $\delta^{34}S$ isotope values of the sulfide minerals from the VMS deposits in the eastern Pontides had a narrow compositional range, and many of them were clustered around zero. These values in the Pontides were highly-consistent with those of the Phanerozoic VMS deposits. Three broad hypotheses have been proposed for the source of sulfur in the Phanerozoic deposits: 1) a deep-seated (magmatic) source, 2) a biogenic source, and 3) a source involving the inorganic reduction of seawater sulfate. In the literature, although a narrow range of values of $\delta^{34}S$ isotope contents has been interpreted to indicate a deep-seated (magmatic) source, the environment in which the VMS deposits formed is not compatible with this specific origin. Considering that the VMS deposits formed in intermediate and deep marine environments, the possibility that the most likely potential source for the sulfur is seawater sulfate cannot be ruled out. The sulfur isotope values of the sulfur minerals in the VMS deposits were typically clustered around zero or slightly enriched in ^{34}S. Slightly positive $\delta^{34}S$ values are common in many modern and ancient VMS deposits and can be attributed to contributions of sulfur from 2 main sources: rock sulfide and reduced seawater sulfate. Slightly negative values, however, can be attributed to a complex history of precipitation and replacement processes within the hydrothermal structures (chimneys and sulfide mounds) that developed on the seafloor. Furthermore, isotopic fractionation during sulfide replacement reactions at low temperatures leads to negative $\delta^{34}S$ values. Biogenic reduction of seawater sulfate could lead to more negative $\delta^{34}S$ values. In such a case, the $\delta^{34}S$ range value is expected to be much broader. Therefore, biogenic reduction of sulfur could lead to a much broader range of $\delta^{34}S$ values, which cannot account for the observed narrow range in the Pontide deposits. Thus, biogenic reduction is not regarded as a major sulfide-generating process for the Pontide deposits. Some researchers (Revan et al., 2016) have suggested only episodic participation of biogenic reduced sulfide as a source of sulfur in the Pontide deposits. These researchers regarded the presence of framboidal pyrite grains in the sulfide chimneys as traces of the bacteriogenic stage and stated that the precipitation of at least some Fe sulfide was controlled by biological activity. Clearly, sulfate reduction reactions are a highly effective mechanism in seafloor hydrothermal systems. In the context of the VMS deposits, the reduction of sulfate to sulfide can occur at any point in the hydrothermal circulation system, such as in the deep subsurface, in the near-surface groundwater environment, in chimneys, or after exiting chimneys. In summary, although the isotopic signature of the Pontide VMS deposits indicates a deep-seated source, the main source of sulfur was determined as largely seawater sulfate, based on previous studies and theoretical work.

11. Conclusions

The eastern Pontide VMS deposits are examples of volcanic-hosted massive sulfide deposits that exhibit many of the characteristics typical of bimodal felsic-type VMS mineralization. Unlike those in many VMS districts, the VMS ores in the eastern Pontide district have well-preserved hydrothermal facies characteristics in terms of components such as chimney fragments, clastic ores, and vent-associated fauna. The hydrothermal ore facies are diagnostic for subaqueous emplacement of the Pontide massive sulfide deposits, as these facies have unusual mineralogies and are therefore useful exploration guides. Exploration programs designed to discover additional massive sulfide deposits should focus on evaluating the features of the primary hydrothermal ore facies. The sulfide ores are hosted in a thick succession of volcanosedimentary rocks that were deposited on the Cretaceous ocean floor. The stratigraphic footwall for the mineralization comprises hydrothermally altered dacitic/rhyolitic volcanic rocks of the Kızılkaya Formation. The VMS deposits are commonly located at the top contact of the dacitic/rhyolitic pile or within the lower part of the overlying sequence comprising dacite/rhyolite, and esite, basalt, and volcanosedimentary units. The trace element geochemical signatures of the host rocks indicate that the Pontide VMS deposits likely formed in an extensional tectonic regime during subduction. The deposits were formed by submarine hydrothermal systems in isolated basins and controlled by major lineaments and circular structures that served to focus the hydrothermal fluid flow. Age determinations have indicated that almost all of the deposits in this region formed in a restricted time interval between ca. 91.1 and 82 Ma. The $\delta^{34}S$ values of the sulfides from the Pontide deposits were within the range of sulfur values obtained from the Phanerozoic VMS deposits. The sulfur isotope compositions of the ore-forming fluids were consistent with those of the fluids derived from modified seawater.

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References

Adamia SA, Lordkipanidze M, Zakariadze GS (1977). Evolution of an active continental margin as exemplified by Alpine history of the Caucasus. Tectonophysics 70: 183-199.

Akın H (1979). Geologie Magmatismus und Lagerstaettenbildung im ostpontischen Gebirge-Türkei aus der Sicht der Plattentektonik. Geologische Rundschau 68: 253-283.

Akıncı ÖT (1985). Eastern Pontide volcano-sedimentary belt and associated massive sulphide deposits, In: Dixon JE, Robertson AHI, editors. The geological evolution of the eastern Mediterranean: Geological Society London Special Publications 17: 415-428.

Alan İ et al. (2016). Çayeli (Rize)-İspir (Erzurum) arasında kalan alanın jeolojisi. MTA Publ. No. 11859, Ankara.

Alan İ et al. (2019). Tectonostratigraphic characteristics of the area between Çayeli (Rize) and İspir (Erzurum). Bulletin of the Mineral Research and Exploration 158: 1-29.

Allen RL, Weihed P, The Global VMS Research Project Team (2002). Global comparison of volcanic-associated massive sulphide districts. In: Blundel DJ, Neubauer F, von Quadt A (editors). The timing and location of major ore deposits in an evolving orogen. Geological Society London Special Publications 04: 13-37.

Allen RL, Tornos F, Peter J, Çağatay N (2003). Global comparision of volcanic-hosted massive sulphide districts. Unpub. rept. to IGCP, September, 2003, 43 p.

Arslan M, Kolaylı H, Temizel I (2004). Petrographical, geochemical and petrological characteristics of the Güre (Giresun, NE Turkey) Granitoid Bulletin of Earth Sciences Application and Research Centre of Hacettepe University 30: 1-21.

Arslan M, Tuysuz N, Korkmaz S, Kurt H (1997). Geochemistry and petrogenesis of the eastern Pontide volcanic rocks, northeast Turkey. Chemie der Erde 57: 157-187.

Aslan Z, Arslan M, Temizel İ, Kaygusuz A (2014). K-Ar dating, whole-rock and Sr-Nd isotope geochemistry of calc-alkaline volcanic rocks around the Gümüşhane area: Implications for post-collisional volcanism in the eastern Pontides, northeast Turkey. Mineralogy and Petrology 108: 245–267,

Aydın F, Şen C, Dokuz A, Kandemir R, Sarı B (2016). Petrology and origin of the Late Cretaceous volcanism in northeastern Turkey: New evidences on the late Mesozoic geodynamic evolution of the eastern Pontides (in Turkish): İstanbul, Turkey. The Scientific and Technological Research Council of Turkey (TUBITAK). Unpublished Report 112Y365, 142p.

Aydın F, Saka SO, Şen C, Dokuz A, Aiglsperger Tet al. (2020). Temporal, geochemical and geodynamic evolution of the Late Cretaceous subduction zone, NE Turkey: Implications for mantle-crust interaction in an arc setting. Journal of Asian Earth Sciences 192. doi.org/10.1016/j.jseaes.2019.104217.

Aydın Ü, Keskin S, Yurtseven D (2019). Artvin merkez Sümbüllü (Sinkot) köyü AR:201400301 (ER:3312887) no'lu ruhsat sahasının buluculuk talebine esas bakır, altın cevherleşmesine ait maden jeolojisi ve kaynak tahmin raporu (cilt 4). MTA Publ. No. 13838, Ankara. 166 p.

Aydınçakır E, Şen C (2013). Petrogenesis of the post-collisional volcanic rocks from the Borçka (Artvin) area: implications for the evolution of the Eocene magmatism in the Eastern Pontides (NE Turkey). Lithos 172-173: 98-117.

Banks DA (1986). Hydrothermal chimneys and fossil worms from the Tynagh Pb-Zn deposits, Ireland. In: Andrew CJ, Crowe RWA, Finlays S, Pennell WM, Pyne IF (editors). Geology and genesis of Irish deposits: Irish Association for Economic Geology, Dublin, 441-447.

Barret TJ, Maclean WH (1999). Volcanic sequences, lithogeochemistry, and hydrothermal alteration in some bimodal volcanic-associated massive sulfide systems. In: Barrie CT, Hannington MD (editors). Volcanic-associated massive sulfide deposits: Processes and examples in modern and ancient settings. Reviews in Economic Geology 8: 101-131.

Barrie CT, Hannington MD (1999). Classification of volcanic-associated massive sulfide deposits based on host-rock composition. In: Barrie CT, Hannington MD (editors). Volcanic-associated massive sulfide deposits: Processes and examples in modern and ancient settings. Reviews in Economic Geology 8: 1-10.

Bektaş O, Çapkınoğlu Ş (1997). Neptunian dykes and block tectonics in the eastern magmatic arc: findings in relation to the kinematics of the Mesozoic basins. Geosound 30: 451-461.

Bektaş O, Yılmaz C, Taslı K, Akdağ K, Özgür S (1995). Cretaceous rifting of the eastern Pontides carbonate platform (NE Turkey): the formation of the carbonate breccias and turbidites as evidence of a drowned platform. Giarnale di Geologica 57: 233-244.

Bektaş O, Şen C, Atıcı Y, Köprübaşı N (1999). Migration of the upper Cretaceous subduction-related volcanism towards the back-arc basin of the eastern Pontide magmatic arc (NE Turkey). Geological Journal 34: 95-106.

Bhatia MR, Crook KAW (1986). Trace element characteristics of graywackes and tectonic discrimination of sedimentary basins. Contribution to Mineralogy and Petrology 92: 181-192.

Binney WP (1987). A sedimentological investigation of Maclean channel transported sulphide ores, In: Kirkham RV (editor). Buchans Geology, Newfoundland: Geological Survey of Canada Paper 86-24: 107-147.

Boztuğ D, Harlavan Y (2008). K-Ar ages of granitoids unravel the stages of Neo-tethyan convergence in the eastern Pontides and central Anatolia, Turkey. International Journal of Earth Sciences 97: 585-599.

Boztuğ D, Jonckheere R, Wagner GA, Erçin AI, Yeğingil Z (2007). Titanite and zircon fission-track dating resolves successive igneous episodes in the formation of the composite Kaçkar batholith in the Turkish Eastern Pontides: International Journal of Earth Sciences 96 (5): 875-886.

Butler IB, Nesbitt RV (1999). Trace element distribution in the chalcopyrite wall of a black smoker chimney: Insights from laser ablation inductively coupled plasma mass spectrometry (LA ICPMS): Earth and Planetary Science Letters 167: 335-345.

Caner G (1970). İsrail bakırlı pirit yatağı rezerv ve tenörü hakkında rapor. MTA Publ. No. 4567, Ankara.

Clark LA (1983) Genetic implications of fragmental ore texture in Japanese Kuroko deposits. Canadian Institute of Mining and Metallurgy Bulletin 76/849:105-114.

Çağatay MN (1993). Hydrothermal alteration associated with volcanogenic massive sulfide deposits: Examples from Turkey: Economic Geology 88: 606-621.

Çağatay MN, DR Boyle (1980). Geology, geochemistry and hydrothermal alteration of the Madenköy massive-sulfide deposit, eastern Black Sea region, Turkey, In: JD Ridge (editor). IAGOD 5th Symposium Proceedings: E. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart, Germany, p. 653-678.

Çağatay MN, Eastoe CJ (1995). A sulfur isotope study of volcanogenic massive sulfide deposits of the eastern Black Sea province, Turkey. Mineralium Deposita 30: 55-66.

Çağlar O (1985). Artvin-Göktaş-Akarşen Cu-pirit yatağının maden jeolojisi raporu. MTA Publ. No. 2019, Ankara.

Çakır M (1979). Harkköy-1 maden sahasının jeolojik etüd ve sondajları, 1979. MTA Publ. No. 1642, Ankara.

Çakır M, Çekiç Y (1982). Giresun, Espiye, Killik yöresi jeoloji raporu. MTA Publ. No. 1948, Ankara.

Çakır M, Şarman E (1983). Giresun, Tirebolu, Harkköy, Kuskunlu madeni ayrıntılı inceleme raporu. MTA Publ. No. 1853, Ankara.

Çamur MZ, Güven İH, Er M (1996). Geochemical characteristics of the eastern Pontide volcanics, Turkey: An example of multiple volcanic cycles in arc evolution. Turkish Journal of Earth Sciences 5: 123-144.

Çekiç Y, Gümüşel A, Topcu T, Yağcı A, Özdoğan Ket al. (1984). Artvin-F 47/ a1, a2, a3, a4, b1, b2, b3, b4, c3, c4, d1, d3, d4 paftalarının polimetalik masif sülfit cevheri prospeksiyon raporu. MTA Publ. No. 7940, Ankara.

Çiftçi E (2000). Mineralogy, paragenetic sequence, geochemistry and genesis of the gold and silver bearing Upper Cretaceous mineral deposits, Northeastern Turkey. PhD, University of Missouri, Rolla, USA.

Çiftci E (2004). Mineralogy and geochemistry of volcanogenic massive sulfide deposits (VMS) of the eastern Pontides (NE Turkey). 57th Geological Congress of Turkey. Abstracts, pp. 121-122.

Çiftçi E (2019). Volcanogenic massive sulfide (VMS) deposits of Turkey. In: Pirajno F, Ünlü T, Dönmez C, Şahin MB, editors. Mineral Resources of Turkey. Modern Approaches in Solid Earth System 16: 427-495.

Davidson GJ, Stolz AJ, Eggins SM (2001). Geochemical anatomy of silica iron exhalites: evidence for hydrothermal oxyanion cycling in response to vent fluid redox and thermal evolution (Mt. Windsor Subprovince, Australia). Economic Geology 96: 1201-1226.

Defant MJ, Drummond MS (1990). Derivation of some modern arc magmas by melting of young subducted lithosphere. Nature 347: 662–665.

Delaloye M, Çoğulu E, Chessex R (1972). Etude geochronometrique des massifs cristallins de Rize et de Gümüşhane, Pontides orientales (Turquie). C.R. des Seances, SPHN, Geneve 7: 43-52.

Delibaş O, Moritz R, Ulianov A, Chiaradia M, Revan MKet al. (2016). Cretaceous subduction-related magmatism and associated porphyry-type Cu-Mo prospects in the eastern Pontides, Turkey: New constraints from geochronology and geochemistry. Lithos 248-251: 119-137.

Delibaş O, Moritz R, Selby D, Göç D, Revan, MK (2019). Multiple porphyry Cu-Mo events in the eastern Pontides metallogenic belt, Turkey: From Early Cretaceous subduction to Eocene post-collision evolution. Economic Geology 114 (7):1285-1300.

Dewey JF, Pitman WC, Ryan WBF, Bonnin J (1973). Plate Tectonics and the evolution of the Alpine system: Geological Society of America Bulletin 84: 3137-3180.

Dilek Y, Imamverdiyev N, Altunkaynak Ş (2010). Geochemistry and tectonics of Cenozoic volcanism in the Lesser Caucasus (Azerbaijan) and the peri-Arabian region: collision-induced mantle dynamics and its magmatic fingerprint. International Geology Review 52 (4-6): 536-578.

Doğan R (1980). The granitic rocks and related molybdenite mineralization of the Emeksen area, Espiye, NE Turkey: PhD, Durham University, Durham, UK, 334 p.

Doyle MG, Allen RL (2003). Subsea-floor replacement in volcanic-hosted massive sulfide deposits. Ore Geology Reviews 23: 183-222.

Eğin D (1978). Polymetallic sulphide ore deposits and associated volcanic rocks from the Harşit River Area, NE Turkey. PhD, Durham University, Durham, UK, 150 p.

Eğin D, Hirst DM, Phillips R (1979). The petrology and geochemistry of volcanic rocks from the northern Harşit River Area, Pontid volcanic province, northeast Turkey. Journal of Volcanology and Geothermal Research 6: 105-123.

Eldridge SC, Barton Jr PB, Ohmoto H (1983). Mineral textures and their bearing on formation of the Kuroko ore bodies. Economic Geology Monograph 5: 241-281.

Eregan N (1946). Türkiye maden yatakları ile ilgili teknik birlikler arasındaki birlikler. MTA Publ. No. 35, Ankara.

Eyuboglu Y (2010). Late Cretaceous high-K volcanism in the eastern Pontides orogenic belt, and its implications for the geodynamic evolution of NE Turkey. International Geology Review 52 (2-3): 142-186.

Eyuboglu Y, Bektaş O, Seren A, Maden N, Jacoby WRet al. (2006). Three axial extensional deformation and formation of the Liassic rift basins in the Eastern Pontides (NE Turkey). Geologica Carpathica 57 (5): 337-346.

Eyuboglu Y, Bektas O, Pul D (2007). Mid-Cretaceous olistostromal ophiolitic melange developed in the back-arc basin of the eastern Pontide magmatic arc, northeast Turkey. International Geology Review, 49 (12): 1103–1126.

Eyuboglu Y, Santosh M, Yi K, Bektaş O, Kwon S (2012). Discovery of Miocene adakitic dacite from the eastern Pontides belt and revised geodynamic model for the late Cenozoic evolution of eastern Mediterranean region. Lithos 146-147: 218-232.

Eyuboglu Y, Santosh M, Yi K, Tuysuz N, Korkmaz Set al. (2014). The Eastern Black Sea-type volcanogenic massive sulfide deposits: Geochemistry, zircon U-Pb geochronology and an overview of the geodynamics of ore genesis. Ore Geology Reviews 59: 29-54.

Eyuboglu Y, Dudas FO, Thorkelson D, Zhu DC, Liu Zet al. (2017). Eocene granitoids of northern Turkey: Polybaric magmatism in an evolving arc–slab window system. Gondwana Research 50: 311-345.

Eyuboglu Y, Dudas FO, Zhu DC, Liu Z, Chatterjee N (2019). Late Cretaceous I- and A-type magmas in eastern Turkey: Magmatic response to double-sided subduction of Paleo and Neo-Tethyan lithospheres. Lithos 326: 39-70.

Fochtman SN (2014). A stable isotope study on fluid source and temperature of the Murgul deposit. Msc, The university of Georgia, Athens, Georgia, 207 p.

Franklin JM (1993). Volcanic-associated massive sulphide deposits, In: Kirkham RV, Sinclair WD, Thorpe RI, Duke JM, editors. Mineral deposit modeling. Geological Association of Canada Special Paper 40: 315-334.

Galley AG., Hannington MD, Jonasson IR(2007). Volcanogenic massive sulphide deposits, In: Goodfellow WD, editor. Mineral deposits of Canada: A synthesis of major deposit-types, district metallogeny, the evolution of geological provinces, and exploration methods. Geological Association of Canada, Mineral Deposits Division, Spec Publ No. 5: 141-161.

Gattinger TE, Erentoz C, Ketin I (1962). Explanatory text of the geological map of Turkey sheet. 1/500.000 scale. MTA Institute, Ankara.

Gedik A, Ercan T, Korkmaz S, Karataş S (1992). Petrology of the magmatic rocks in the area between Rize, Fındıklı and Çamlıhemşin (eastern Black Sea region) and their distribution in the eastern Pontides. Geological Bulletin of Turkey 35: 15-38 (in Turkish).

Goldfarb MS, Converse DR, Holland HD, Edmond JM (1983). The genesis of hot spring deposits on the East Pacific Rise, 21ºN. Economic Geology Monograph 5: 184-97.

Goksu E, Pamir HN, Erentöz C (1974). Explanatory text of the geological map of Turkey, Samsun sheet, 1/500.000 scale, MTA Institute, Ankara.

Grenne T, Slack JF (2003). Paleozoic and Mezozoic silica-rich seawater: Evidence from hematitic chert (jasper) deposits. Geology 31: 319-322.

Gökçe A (1992). S-isotope studies of Kuroko-type Cu-Zn-Pb massive and stockwork ores in the eastern Black Sea region: Turkish Scientific Institute Project, no. TBAG-915/YBAG-0008, 103 p.

Gökçe A, Spiro B (2000). Sulfur-isotope characteristics of the volcanogenic Cu-Zn-Pb deposits of the eastern Pontide region, Northeastern Turkey. International Geology Review 42/6, 565-576.

Görür N, Tüysüz O, Akyol A, Sakınç M, Yiğitbaş E et al. (1983). Cretaceous red pelagic carbonates of northern Turkey: their place in the opening history of the Black Sea. Eclogae Geologicae Helvetiae 36: 819–838.

Gümrükçü A, Takaoğlu S (1976). Trabzon-Of-Dumlusu (Kotarakdere) yatağının jeolojisi ve rezerv raporu. MTA Publ. No. 5770, 25 p. Ankara.

Günalay ME (1975). Rize İli-Ardeşen ilçesi Tunca köyü civarında bulunan bakırlı kurşun işletme projesi. MTA Publ. No. 5291, 31 p. Ankara.

Güven İH (1993). Geology of the Eastern Pontides: Compilation of the geological maps throughout the region: General Directorate of Mineral Research and Exploration (MTA), Ankara, Turkey, scale 1:250,000, 1 sheet.

Güven İH (1998). Türkiye jeoloji haritaları, 1/100.000 ölçekli açınsama nitelikli Tortum-D31 paftası, no: 60, MTA Publications, Ankara (in Turkish with english abstract).

Güven İH, Çağlar O (1982). Artvin-Murgul-Akarşen Cu-Pb-Zn zuhuruna ilişkin 1/2000 ölçekli jeoloji raporu. MTA Publ. No. 1896, Ankara.

Hannington MD, de Ronde CE, Petersen S (2005). Sea-floor tectonics and submarine hydrothermal systems, In: Hedenquist JW, Thompson JFH, Goldfarb RJ, Richards JP, editors. Economic Geology 100th anniversary volume, 1905–2005: Littleton, Colo., p. 111-141.

Hart TR, Gibson HL, Lesher CM (2004). Trace element geochemistry and petrogenesis of felsic volcanic rocks associated with volcanogenic massive Cu-Zn-Pb sulfide deposits. Economic Geology 99: 1003-1013.

Hashiguchi H (1983). Penecontemporaneous deformation of Kuroko ore at the Kosaka Mine, Akita, Japon. Economic Geology Monograph 5: 167-183.

Haymon RM (1983). Growth history of hydrothermal black smoker. Nature 301: 695-698.

Haymon RM, Koski RA, Sinclair C (1984). Fossils of hydrothermal vent forms discovered in Cretaceous sulfide ores of the Semail ophiolite, Oman. Science 223: 1407-1409.

Hirst DM, D Eğin (1979). Localisation of massive, polymetallic sulphide ores in the northern Harşit river area, Pontid volcanic belt, northeast Turkey. Annales de la Société Géologique de Belgique 102: 465-484.

Hogdahl OT, Melson S, Bowen VT (1968). Neutron activation analysis of lanthanide elements in seawater, In: Gould RF, editor. Trace inorganics in water: Advances in chemistry series 73: 308-325.

Hole MJ, Saunders AD, Marriner GF, Tarney J (1984). Subduction of pelagic sediment: implications for the origin of Ce-anomalous basalts from the Mariana Islands. Geological Society London Special Publications 141: 453-472.

Hollis SP, Cooper MR, Herrington RJ, Roberts S, Earls Get al. (2015). Distribution, mineralogy and geochemistry of silica-iron exhalites and related rocks from the Tyrone Igneous Complex: Implications for VMS mineralization in Northern Ireland. Journal of Geochemical Exploration 159: 148-168.

Irvine TN, Baragar WRA (1971) A guide to the chemical classification of the common volcanic rocks. Canadian Journalof Earth Sciences 8: 523-548.

JICA (1998). Report on the mineral exploration in the Espiye Area, The Republic of Turkey, Summary Report. MTA Publ. No. 10067, Ankara, 104p.

JICA (2003). Report on the mineral exploration in the Hopa Area, The Republic of Turkey, Phase I. MTA Publ. No. 10584, Ankara, 143p.

JICA (2004). Report on the mineral exploration in the Hopa Area, The Republic of Turkey, Phase II: Unpublished report to MTA, Ankara, No. 10646, 117 p.

JICA (2005). Report on the mineral exploration in the Espiye area, The Republic of Turkey, phase II: MTA Publ. No. 10146, Ankara, 114 p.

Jonasson IR, Perfit MR (1999). Unusual forms of amorphous silica from submarine warm springs, Juan De Fuca Ridge, northeastern Pacific ocean. Canadian Mineralogist 37: 27-36.

Kahraman İ (1981). Giresun-Tirebolu-İsraildere Cu-Zn-Pb cevherleşmesi jeoloji raporu. MTA Publ. No. 7710, Ankara.

Kahraman İ, Çağlar O, Şatır F, Çakır M, Yılmaz Tet al. (1987). Rize Fındıklı, Artvin-Arhavi-Yusufeli kuzeyi yörelerinin jeolojisi ve cevherleşmeleri raporu. MTA Publ. No. 8406, Ankara (unpublished).

Kalogeropoulos SI, Scott SD (1983). Mineralogy and geochemistry of tuffaceous exhalites (Tetsusekiei) of the Fukazawa Mine, Hokuroku district, Japan. Economic Geology Monograph5: 412-432.

Kamitani M, Akıncı O (1979). Alpine granitoids and related tungsten-molybdenum deposits in Turkey. Mining Geology 29: 341-350.

Kandemir Ö, Akbayram K, Çobankaya M, Kanar F, Pehlivan Şet al. (2019). From arc evolution to arc-continent collision: Late Cretaceous-middle Eocene geology of the eastern Pontides, northeastern Turkey. The Geological Society of America. doi.org/10.1130/B31913.1

Kaptan E (1977). Murgul madenindeki anayatak kökenli eski devirlere ait yeni buluntu.Bulletin of the Mineral Research and Exploration 89: 90-94.

Kaptan E (1978). Espiye-Bulancak yöresindeki eski maden ocaklarına ait bulgular. Bulletin of the Mineral Research and Exploration 91: 117-129.

Karslı O, Aydın F, Sadıklar MB (2004). Magma interaction recorded in plagioclase zoning in granitoid systems. Zigana Granitoid, Eastern Pontides, Turkey. Turkish Journal of Earth Sciences 13: 287-305.

Karslı O, Chen B, Aydın F, Şen C (2007). Geochemical and Sr-Nd-Pb isotopic compositions of the Eocene Dölek and Sarıçiçek plutons, Eastern Turkey: Implications for magma interaction in the genesis of high-K calc-alkaline granitoids in a post-collision extensional setting. Lithos 98: 67-96.

Kartalkanat A (2007). The history of mining in Anatolia. Bulletin of the Mineral Research and Exploration 134: 35-39 (in Turkish).

Kaygusuz A (2000). Torul ve çevresinde yüzeyleyen kayaçların petrografik ve jeokimyasal incelenmesi. PhD, Karadeniz Technical University, Trabzon, 250 p.

Kazmin VG, Sbortshikov IM, Ricou LE, Zonenshain LP, Boulin J et al. (1986). Volcanic belts as markers of the Mesozoic-Cenozoic active margin of Eurasia. Tectonophysics 123: 123-152.

Ketin I (1966). Tectonic units of Anatolia. Bulletin of the Mineral Research and Exploration66: 20-34.

Kieft C (1956). Harşit nehri vadisi havzası metalik maden yatakları hakkında bazı mülahazalar. Bulletin of the Mineral Research and Exploration48: 53-62.

Konak N, Hakyemez Y, Bilgiç T, Bilgin ZR, Hepşen N et al. (2001). Kuzeydoğu Pontidlerin jeolojisi. MTA Publ. No. 10489, Ankara (in Turkish).

Koprivica D (1976). Geology, structural features and sulfide and manganese occurrences of the Hopa-Arhavi (Northeast Turkey). Bulletin of the Mineral Research and Exploration87: 1-10.

Kossmat F (1910). Geologische untersuchungen is den Erzdistrikten des Vilayets Trapezunt, Kleinasien. Mitt D Geol Ges, Wien, 214-284.

Kovenko V (1941). Gümüşhane'nin simli kurşun madenleri. MTA Publ. No. 3/24, Ankara.

Kovenko V (1943). Bakırlı pirit madenleri bölgesi, Giresun vilayetinde Espiye ve Görele dolaylarındaki Karaerik, Ağalık, İsrail madenleri. MTA Publ. No. 2/30, Ankara.

Kovenko V (1944). Küre'deki eski bakır yatağı ile yeni keşfedilen Aşıköy yatağının ve karadeniz orta ve doğu kesimleri sahil bölgesinin metalojenisi. MTA Publ. No. 2/32, Ankara.

Kraeff A (1963). Geology and mineral deposits of the Hopa-Murgul region (western part of Artvin, NE Turkey). Bulletin of the Mineral Research and Exploration 60: 30-60.

Kurt İ, Özkan M, Karslı Ş, Çolak T, Topçu T (2005). Doğu Karadeniz bölgesinin jeodinamik ve metalojenik evrimi Keşap (Giresun)-Çarşıbaşı (Trabzon)-Torul (Gümüşhane) arasının jeolojisi. MTA Publ. No. 10875, Ankara.

Kuznetzov AP, Sobetskii VA (1988). Fosil fauna in the sulfide hydrothermal hills from the middle Devonian paleo-ocean of the Ural area. Doklady Akademii Nauk SSSR, 303, 1481 (in Russian).

LeBas MJ, Lemaitre RW, Streckeisen A, Zanettin B (1986). A chemical classification of volcanic-rocks based on the total alkali silica diagram. Journal of Petrology 27 (3): 745-750.

Lesher CM, Goodwin AM, Campbell IH, Gorton MP (1986). Trace-element geochemistry of ore-associated and barren, felsic metavolcanic rocks in the Superior province, Canada. Canadian Journal of Earth Sciences 23: 222-237.

Little CTS, Herrington RJ, Maslennikov VV, Morris NJ, Zaykov VV (1997). Silurian high temperature hydrothermal vent community from the Southern Urals, Russia. Nature 385: 3-6.

Little CTS, Magalashvly AG, Banks DA (2007). Neotethyan late Cretaceous volcanic arc hydrothermal vent fauna. Geology 35: 835-838.

Liu Z, Zhu D, Wang Q, Eyüboğlu Y, Zhao ZD et al. (2018). Transition from low-K to high-K calc-alkaline magmatism at approximately 84 Ma in the Eastern Pontides (NE Turkey): Magmatic response to slab rollback of the Black Sea. Journal of Geophysical Research-Solid Earth 123: 7604-7628.

Manetti P, Peccerillo A, Poli G, Corsini F (1983). Petrochemical constrains on the models of Cretaceous-Eocene tectonic evolution of the eastern Pontic chain (Turkey). Cretaceous Research 4: 159-172.

Maslennikov VV (1991). Lithological control of copper massive sulfide ores (after the example of Sibai and Oktyabrskoye deposits, Ural). Sverdlovsk, UB AS USSR, 139 p (in Russian).

Maslennikov VV (1999). Sedimentogenesis, halmyrolysis, ecology of massive sulfide-bearing paleohydrothermal fields (after example of the Southern Urals). Miass, 348 p (in Russian).

Maslennikov VV, Ayupova NR (2007). Siliceous-ferruginous sediments of the Uzelga massive sulfide bearing field, South Urals. Lithosphera 4, 110-129 (in Russian).

Maslennikov VV, Maslennikova SP, Large RR, Danyushevsky LV (2009). Study of trace element zonation in vent chimneys from the Silurian Yaman-Kasy volcanic-hosted massive sulfide deposits (the southern Urals, Russia) using laser ablation inductively coupled plasma mass spectrometry (LA-ICP MS). Economic Geology 104: 1111-1141.

Maslennikov VV, Ayupova NR, Herrington RJ, Danyushevskiy LV, Large RR (2012). Ferruginous and manganiferous haloes around massive sulphide deposits of the Urals. Ore Geology Reviews 47: 5-41.

Maslennikov VV, Simonov VA, Ankusheva NS, Maslennikova SP, Little CTSet al. (2013). Hydrothermal vent fauna in the Urals VMS deposits: Criteria for occurrence. Ore Genesis, Abstracts of the international conference, Miass, Russia, p. 42-46.

Moore WJ, McKee EH, Akıncı Ö (1980). Chemistry and chronology of plutonic rocks in the Pontide Mountains, northern Turkey: European Copper Deposits, Belgrade, p. 209-216.

MTA (2013). Magmatic rocks of Turkey. 1/250.000 scale. MTA Institute, Ankara.

Nalbantoğlu AK, Yılmaz T (1992) Kutlular maden arama ve geliştirme projesi Kutlular sahası detay jeoloji ve detay jeokimya Etüdü Raporu. MTA Publ. No. 2450, Ankara.

Neal CR, Taylor LA (1989). A negative Ce anomaly in a peridotite xenolith: Evidence for crustal recycling into the mantle or mantle metasomatism? Geochim Cosmochim Acta 53: 1035-1040.

Okay AI, Leven EJ (1996). Stratigraphy and paleontology of the Upper Paleozoic sequence in the Pulur (Bayburt) region, Eastern Pontides: Turkish Journal of Earth Sciences5: 145-155.

Okay AI, Şahintürk Ö (1997). Geology of the eastern Pontides. In: Robinson AG, editor. Regional and petroleum geology of the Black Sea and surrounding regions. American Association of Petroleum Geologist Memoirs 68: 291-311.

Okay AI, Tüysüz O (1999). Tethyan sutures of northern Turkey. In: Durand B, Jolivet L, Horv´ath F, S´eranne M, editors. The mediterranean basins: Tertiary extension within the Alpine orogen. Geological Society London Special Publications 156: 475-515.

Özgür N (1993). Volcanogenic massive sulfide deposits in the East Pontic metallotect, NE Turkey. Resource Geology Special Issue, no: 17, 180-185.

Özsayar T, Pelin S, Gedikoğlu A (1981). Cretaceous in the eastern Pontides. Black Sea Technical University Earth Science Bulletin 1/2: 65-114 (in Turkish with English abstract).

Parekh PP, Moller P, Dulski P, Bausch, WM (1977). Distribution of trace elements between carbonates and non-carbonate phases of limestone. Earth and Planetary Science Letters 34: 39-50.

Pearce JA, Harris NBW, Tindle AG (1984). Trace element discrimination diagram for the tectonic interpretation of granitic rocks. Journal of Petrology25: 956–983.

Peccerillo A, Taylor SR (1975). Geochemistry of upper Cretaceous volcanic rocks from the Pontic chain, Northern Turkey. Bulletin of Volcanology 39/4: 557-569.

Pejatoviç S (1971). Metallogenic zones in the eastern Black Sea-minor Caucasus regions and distinguishing features of their metallogeny. Bulletin of the Mineral Research and Exploration 77: 10-21.

Pejatoviç S (1979). Metallogeny of the Pontide-type massive sulfide deposits. MTA Publ. No. 177, 100 p.

Piercey SJ (2011). The setting, style, and role of magmatism in the formation of volcanogenic massive sulfide deposits. Mineralium Deposita 46: 449-471.

Qudin E, Constantinou G (1984). Black smoker chimney fragments in Cyprus sulphide deposits. Nature 308: 349-353.

Revan MK (2010). Determination of the typical properties of volcanogenic massive sulfide deposits in the eastern black sea region. PhD, Hacettepe University, Ankara, Turkey, 320 p (in Turkish with English abstract).

Revan MK, Ünlü T, Genç Y (2010). Preliminary findings of fossil traces from massive sulfide deposits (Lahanos, Killik, Çayeli) of eastern Black Sea region. Bulletin of the Mineral Research and Exploration140: 75-81.

Revan MK, Genç Y, Maslennikov VV, Ünlü T, Delibaş O et al. (2013). Original findings on the ore-bearing facies of volcanogenic massive sulphide deposits in the eastern Black Sea region (NE Turkey). Bulletin of the Mineral Research and Exploration147: 73-89.

Revan MK, Genç Y, Maslennikov VV, Maslennikova SP, Large RR et al. (2014). Mineralogy and trace-element geochemistry of sulfide minerals in hydrothermal chimneys from the Upper-Cretaceous VMS deposits of the eastern Pontide orogenic belt (NE Turkey). Ore Geology Reviews 63, 129-149.

Revan MK, Maslennikov VV, Genç Y, Delibaş O, Maslennikova SP et al. (2016). Sulfur isotope study of the vent chimneys from the Upper Cretaceous VMS deposits of the eastern Pontide metallogenic belt, NE Turkey. Turkish Journal of Earth Sciences 25: 227-241.

Revan MK, Hisatani K, Miyamoto H, Delibas O, Hanilçi Net al. (2017). Geology, U-Pb geochronology, and stable isotope geochemistry of the Tunca semi-massive sulfide mineralization, NE Turkey: Implications for ore genesis. Ore Geology Reviews 89: 369-389.

Revan MK, Genç Y, Delibaş O, Maslennikov VV, Nuriya RA et al. (2019). Mineralogy and geochemistry of metalliferous sedimentary rocks from the upper Cretaceous VMS deposits of the eastern Pontides (NE Turkey). Turkish Journal of Earth Sciences 28: 299-327.

Rice SP, Robertson AHF, Ustaömer T, İnan N, Taşlı K (2009). Late Cretaceous-early Eocene tectonic development of the Tethyan suture zone in the Erzincan area, Eastern Pontides, Turkey: Geological Magazine 146 (4): 567-590.

Robinson AG, Banks CJ, Rutherford MM, Hirst JPP (1995). Stratigraphic and structural development of the eastern Pontides, Turkey. Journal of the Geological Society 152: 861-872.

Ronçeviç G, Antonoviç A, Arslaner G (1970). 1968-69 yıllarında Kızılkaya bakır kurşun-çinko yatağında yapılan araştırma çalışmaları. MTA Publ. No. 988, Ankara.

Schneiderhöhn H (1955). Die kupfererzlagerstatte Murgul in schawarzmeer Kustengebiet, provinz Çoruh, Nordost Turkei, Erzmetall, VIII, pp. 468-478.

Schultze-Westrum HH (1960). Giresun-Aksudere (Doğu Pontus cevher bölgesi) hinterlandında yapılan prospeksiyon ve jeoloji harita çalışmaları hakkında rapor. MTA Publ. No. 3184, Ankara.

Schultze-Westrum HH (1961). Giresun civarındaki Aksu deresinin jeolojik profili; Kuzeydoğu Anadolu'da, Doğu Pontus cevher ve mineral bölgesinin jeolojisi ve maden yatakları ile ilgili mütalaalar. Bulletin of the Mineral Research and Exploration57: 63-71.

Shpanskaya AYU, Maslennikov VV, Little CTS (1999). Vestimentiferan tubes from the early Silurian and middle Devonian hydrothermal biota of the Uralian paleobasin. Paleontol. Zh. 33: 222-228 (in Russian).

Stajanow R (1973). Pontidlerde Harşit nehri arasında volkanik taşların petrolojisi: Cumhuriyetin 50. yılı Yerbilimleri Kongresi Tebliğler Kitabı, pp. 490-517.

Şen C (1987). Dağbaşı (Trabzon) bölgesinde yüzeyleyen alt bazik (Jura) - granitoyid (üst Kretase) formasyonlarının petrografik-kimyasal özellikleri. MSc, KTÜ Fen Bilimleri Enstitüsü, Trabzon, 80 p.

Şen C (2007). Jurassic volcanism in the Eastern Pontides: is it rift related or subduction related? Turkish Journal of Earth Sciences16: 523–539.

Şengör AMC, Yılmaz Y (1981). Tethyan evolution of Turkey: a plate tectonic approach. Tectonophysics 75: 181-241.

Şengör AMC, Yılmaz Y, Ketin İ (1980). Remnants of a pre-Late Jurassic ocean in Northern Turkey: Fragments of a Permian-Triassic Paleo-Tethys. Geological Society of America Bulletin 91: 599-609.

Şengör AMC, Görür N, Şaroğlu F (1985). Strike slip faulting and related basin formation in zones of tectonic escape: Turkey as a case study. In: Biddle TR, Christie-Blick N, editors. Strike-slip deformation, basin formation and sedimetantion. Societyof Economic Paleontologists and Mineralogists, Special Publication 37: 227-264.

Taner MF (1977). Etude géologique et pétrographique de la région de Güneyce-İkizdere, située au sud de Rize (Pontides Orientales, Turquie). PhD, Geneva, Switzerland, Université de Genève, 180 p.

Tokel S (1972). The stratigraphical and volcanic history of the Gümüşhane area, northeastern Anatolia. PhD, University of London, 265 p.

Topuz G, Altherr R, Kalt A, Satır M, Werner O et al. (2004). Aluminous granulites from the Pulur Complex, NE Turkey: a case of partial melting, efficient melt extraction and crystallisation. Lithos 72: 183-207.

Topuz G, Altherr R, Schwarz WH, Siebel W, Satır M et al. (2005). Post-collisional plutonism with adakite-like signatures: The eocene Saraycık granodiorite (Eastern Pontides, Turkey): Contributions to Mineralogy and Petrology 150 (4): 441-455.

Tugal T (1969). Pyritic sulphide deposits of the Lahanos mine area, eastern Black Sea region, Turkey: PhD, Durham Univesity, Durham, UK.

Turhan K (1968). Sırtköy-Gümüşdere sahasının jeolojik raporu. MTA Publ. No. 4592, 10 p. Ankara.

Turhan K, Avenk T (1976). Trabzon-Sürmene Kutlular yatağı rezerv hesabı. MTA Publ. No. 1417, Ankara.

Turhan K, Akyol H (1978). Trabzon-Of-Dumlusu (Kotarakdere) bakırlı pirit yatağı rezerv raporu. MTA Publ. No. 6245, 25 p. Ankara.

Tüysüz N (2000). Geology, lithogeochemistry and genesis of the Murgul massive sulfide deposit, NE Turkey: Chemie der Erde 60: 231-250.

Tüysüz N, Er M (1995). Chemical and mineralogical changes in the alteration zones at the Lahanos (Espiye) and İsraildere (Tirebolu) massive sulfide mineralizations, Giresun, NE Turkey. Bulletin of Geological Cogress of Turkey 10: 104-113 (in Turkish).

Ustaömer T, Robertson AHF (1995). Paleotethyan tectonic evolution of the north Tethyan margin in the central Pontides, N Turkey. In: Geology of the Black Sea region. Erler A, Ercan T, Bingöl E, Örçen S, editors. Procceedings of the international symposium on the geology of the Black Sea region, Ankara, Turkey, 24-33.

Winchester JA, Floyd PA (1977). Geochemical discrimination of different magma series and their differentiation products using immobile elements. Chemical Geology 20: 325-343.

Yıldız B (1983). The relationships between Cu-Pb-Zn mineralization and certain structures identified on Landsat images in the eastern Black Sea region. Bulletin of the Mineral Research and Exploration 99: 49-56.

Yıldız B, Kurtuluş O, Çiftçi B, Muratlı S (2009). Geology and mineralization of the Murgul Cu mine, Northeastern Turkey. 2th international symposium on the geology of the Black Sea region, Turkey. Abstracts, p. 126-128.

Yılmaz A, Adamia S, Chabukiani A, Chkhotua T, Erdoğan Ket al. (2000). Structural correlation of the southern Transcaucasus (Georgia)-Eastern Pontides (Turkey). In: Bozkurt E, Winchester JA, Piper JDA, editors. Tectonics and magmatism in Turkey and surrounding area. Geological Society London Special Publications173: 171-182.

Yılmaz BS (1988). Trabzon-Yomra-Kayabaşı (Kanköy) ve Kömürcü köyleri yöresindeki Pontid tipi masif sülfit yatağının (Cu-Zn-Pb-Ag-pirit) maden jeolojisi raporu. MTA Publ. No. 8836, 132 p. Ankara.

Yılmaz C, Korkmaz S (1999). Basin development in the eastern Pontides, Jurassic to Cretaceous, NE Turkey. Zentralblatt fur Geologie und Palaontologie. Teil I H10-12, 1485-1494.

Yılmaz S, Boztuğ D (1996). Space and time relations of three plutonic phase in the eastern Pontides, Turkey. International Geology Review 38: 935-956.

Yılmaz T (1978). Rize-Fındıklı Pesansör Mezrası pirit-bakır zuhuru, 1/10000 ölçekli jeoloji raporu. MTA Publ. No. 13186, Ankara, 13 p.

Yılmaz Y (1976). Geology of the Gümüşhane granite (petrography): İstanbul Üniversitesi Fen Fakültesi Mecmuası, Seri B, 39: 157-172.

Yılmaz Y, Tüysüz O, Yiğitbaş E, Genç ŞC, Şengör AMC (1997). Geology and tectonic evolution of the Pontides. In: Robinson AG, editor. Regional and petroluem geology of the Black Sea and surrounding regions. American Association Petroleum Geologist, Memoir 68: 183-226.

Zankl H (1962). Magmatismus und Bauplan des Ostpontischen Gebirges im Querprofil des Harşit-Tales, NE Anatolien: Geologische Rundschau 51: 218-239.

Zaykov VV, Novoselov K, Kotlyarov V (2006). Native gold and tellurides in the Murgul and Çayeli volcanogenic Cu deposits (Turkey). In: NJ Cook, Özgenç İ, Oyman T, editors. Au-Ag-Te-Se deposits. Proceedings of the field workshop of IGCP-486, Dokuz Eylül Univ. Department of Geology, 167-172.