

## Sulfur isotope study of vent chimneys from Upper Cretaceous volcanogenic massive sulfide deposits of the eastern Pontide metallogenic belt, NE Turkey

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**Abstract:** We obtained sulfur isotope analysis results of sulfide samples from hydrothermal vent chimneys of the eastern Pontide volcanogenic massive sulfide (VMS) deposits. The total range of  $\delta^{34}\text{S}$  values for vent chimneys in the eastern Pontide VMS deposits is  $-2.7$  to  $6.5$  per mil. Sulfide  $\delta^{34}\text{S}$  values show narrow variation in the Lahanos, Killik, and Kutlular deposits, but wider variation in the Kızılkaya and Çayeli deposits. The  $\delta^{34}\text{S}$  values of sulfides in Çayeli chimney samples gave a slightly higher range than the other Pontide chimney samples. In some samples, a rough isotopic zonation pattern was observed throughout chimney zones. Variations in  $\delta^{34}\text{S}$  values of sulfides within chimney walls were probably caused by chemical reactions of reprecipitation and replacement between vent fluids and earlier sulfide minerals in the chimney. Ranges of  $\delta^{34}\text{S}$  values of sulfide minerals are similar for different deposits within the same region. Variations in the  $\delta^{34}\text{S}$  values of the Pontide deposits appear to be geographic rather than stratigraphic. The sulfur isotope values of the deposits have a narrow compositional range, indicative of a fairly specific origin. Although “deep-seated” sulfur may be a potential source in the Pontide district, a significant contribution of seawater sulfate cannot be ruled out. The  $\delta^{34}\text{S}$  values of selected samples from Pontide vent chimneys are within the range of sulfur values obtained from Phanerozoic VMS deposits. The range is similar to, but slightly broader than, the range of values reported for modern vent chimneys and ancient vent chimneys from the Yaman-Kasy deposit.

**Key words:** Eastern Pontide, hydrothermal chimneys, sulfur isotopes, volcanogenic massive sulfide

### 1. Introduction

In the context of volcanogenic massive sulfide (VMS) deposits, seafloor hydrothermal facies refer to seafloor sulfide accumulations on the seafloor and are characterized by vent chimneys and related facies, including biological and sedimentary facies. Hydrothermal vent chimneys can be easily recognized in modern seas due to their unique shape and location; however, it is difficult to detect their presence in ancient deposits due to modifications such as diagenesis followed by deformation and metamorphism (Revan et al., 2014). Relatively well-preserved metal-bearing fossil hydrothermal chimneys are quite rare and limited to a few districts. To date, these unique structures have been documented in VMS districts in the Urals, Cyprus, Japan, and the Pontides (e.g., Qudin and Constantinou, 1984; Herrington et al., 1998; Maslennikov,

1999; Maslennikov et al., 2009; Revan, 2010). Terrains containing VMS deposits have commonly been subjected to greenschist facies or higher-grade metamorphism, and intense deformation and accompanying extensive metamorphism have destroyed many of the primary features of the deposits (e.g., Kalogeropoulos and Scott, 1983; Allen et al., 2002). Unlike in many VMS districts, the primary features of the VMS deposits in the eastern Pontide district have been largely preserved due to the nonmetamorphosed nature of the region (e.g., Çiftçi, 2000; Revan et al., 2012). These VMS ores therefore have well-preserved hydrothermal facies characteristics in terms of components such as chimney fragments, clastic ores, and vent-associated fauna. These features of the eastern Pontide VMS deposits may be useful for global comparison. The vent chimneys reported in this belt (Maslennikov et al.,

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2009; Revan, 2010; Revan et al., 2013, 2014) may thus offer an ideal opportunity for a detailed sulfur isotope study of an ancient seafloor VMS hydrothermal system. Sulfur isotope studies provide valuable information on the source of sulfur and may help explain enigmatic variations of sulfur isotope values in VMS deposits. Isotopic investigation of vent chimneys may therefore provide useful information on the source of fluids responsible for the formation of VMS deposits. To date, the sulfur isotope characteristics of vent chimneys have been studied in modern seafloor hydrothermal systems (e.g., Kerridge et al., 1983; Shanks and Seyfried, 1987; Bluth and Ohmoto, 1988; Janecky and Shanks, 1988; Woodruff and Shanks, 1988; Butler et al., 1998), but the only ancient sulfide chimney  $\delta^{34}\text{S}$  values that have been reported are from the Paleozoic Yaman-Kasy deposit (Maslennikova and Maslennikov, 2007). Although sulfur isotope characteristics of the latter deposit have been studied, no effort has been made to interpret the relevant data (ranging from  $-2.2\%$  to  $2.0\%$ ) and this has not been published in any prominent international journals. In this study, we present and discuss the first results of sulfur isotope analyses of chimney sulfides in the Pontides. Previously published sulfur isotope values for the Pontides originated from the sulfide mound and stockwork zones of VMS deposits (Çağatay and Eastoe, 1995; Gökçe and Spiro, 2000). These values are highly consistent with those obtained in this study. From their study of sulfur isotope characteristics of the Pontide VMS deposits, Gökçe and Spiro (2000) considered the main source of sulfur to be magmatic, but Çağatay and Eastoe (1995) concluded that reduced seawater sulfur was the more likely source. In all VMS districts, as in the Pontides, the source of sulfur remains highly controversial. Despite being extensively studied, problems concerning the genesis and nature of the hydrothermal fluids responsible for the formation of VMS deposits require additional research and discussion. In order to contribute to these discussions concerning sulfur sources, we investigated sulfur isotope compositions of chimneys from five Upper Cretaceous VMS deposits within the eastern part of the Black Sea mountain chain. These deposits were chosen for the following reasons: 1) their general characteristics have already been described; 2) the primary textures and components of massive sulfide orebodies are well-preserved due to the unmetamorphosed nature of the deposits; and 3) the deposits contain relatively well-preserved chimney fragments representing primary sulfide ores that formed on the seafloor. We report on sulfur isotope analyses of 52 sulfide mineral samples from vent chimneys within these deposits. The sulfur isotope data obtained in this study represent a detailed investigation of sulfur isotope distribution in chimney zones and the likely sulfur sources of the studied deposits. These data may therefore be useful in interpreting sulfur sources and in

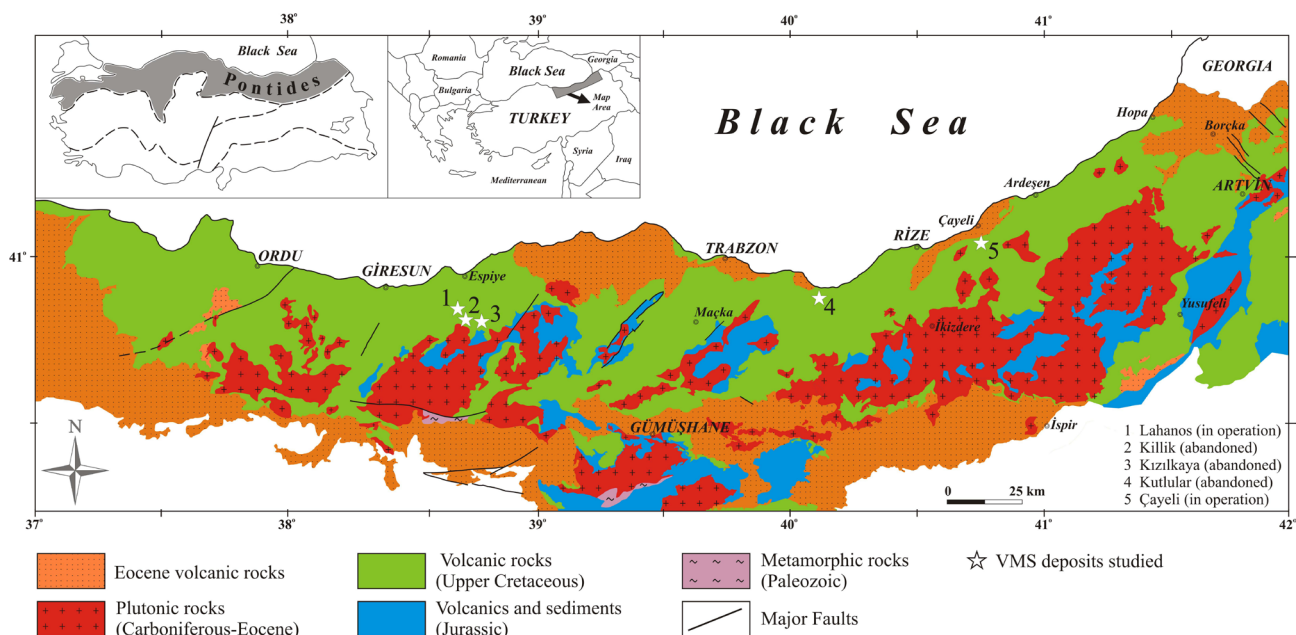
understanding the background to formation of the VMS deposits. No such study of fossil vent chimneys using sulfur isotope geochemistry has yet been attempted in ancient VMS districts.

The principal objectives of this study are to determine  $\delta^{34}\text{S}$  values of fluids from which sulfide minerals precipitated and to attempt to estimate the sulfur source responsible for the formation of the vent chimneys associated with the Pontide VMS deposits. This paper also provides an overview of previously published sulfur isotopic studies documented in VMS districts.

## 2. Geologic setting and characteristics of the eastern Pontide VMS deposits

The Late Cretaceous VMS deposits of the eastern Black Sea region (NE Turkey) occur within the eastern part of the Pontide tectonic belt (Figure 1). The belt continues northwestward into Bulgaria and eastward into Georgia and is considered to be a relic of a complex volcanic arc system. The basement of the eastern Pontides is composed of Paleozoic metamorphic rocks and Hercynian granitic rocks that intrude into metamorphics (Schultze-Westrum, 1961). A thick volcanosedimentary sequence, ranging in age from Lias to Eocene, unconformably overlies these basement rocks (e.g., Açar, 1977; Robinson et al., 1995; Okay and Şahintürk, 1997; Yılmaz and Korkmaz, 1999). These crystalline basement and overlying volcanic-dominated sequences are intruded by granitoids of different ages (Schultze-Westrum, 1961; Yılmaz, 1972; Çoğulu, 1975; Okay and Şahintürk, 1997). The northern part of the eastern Pontide belt, which contains VMS deposits, is overwhelmingly composed of Late Cretaceous to Eocene volcanic rocks. However, pre-Late Cretaceous rocks are widely exposed in the southern part of the belt. Pre-Late Cretaceous (Early to Middle Jurassic) volcanic rocks are most likely tholeiitic in character and related to rifting (Okay and Şahintürk, 1997). Cretaceous volcanism is completely submarine, mostly subalkaline, and a product of typical arc-related magmatism (e.g., Peccerillo and Taylor, 1975; Gedikoğlu, 1978; Akın, 1979; Eğin et al., 1979; Manetti et al., 1983; Gedik et al., 1992). Eocene volcanism, represented by andesitic volcanics and volcaniclastics, is calc-alkaline and most likely related to regional extension (e.g., Adamia et al., 1977; Eğin et al., 1979; Kazmin et al., 1986; Çamur et al., 1996). The geological evolution of the eastern Pontides is genetically related to magmatic events as a result of the northward subduction of the Neo-Tethyan Ocean during the Cretaceous (e.g., Şengör et al., 1980; Okay and Şahintürk, 1997; Yılmaz et al., 1997).

The Late Cretaceous volcanic rocks are, from the base upward, commonly subdivided into four different formations based on stratigraphic relationships between these formations: 1) the *Çatak* formation, which is

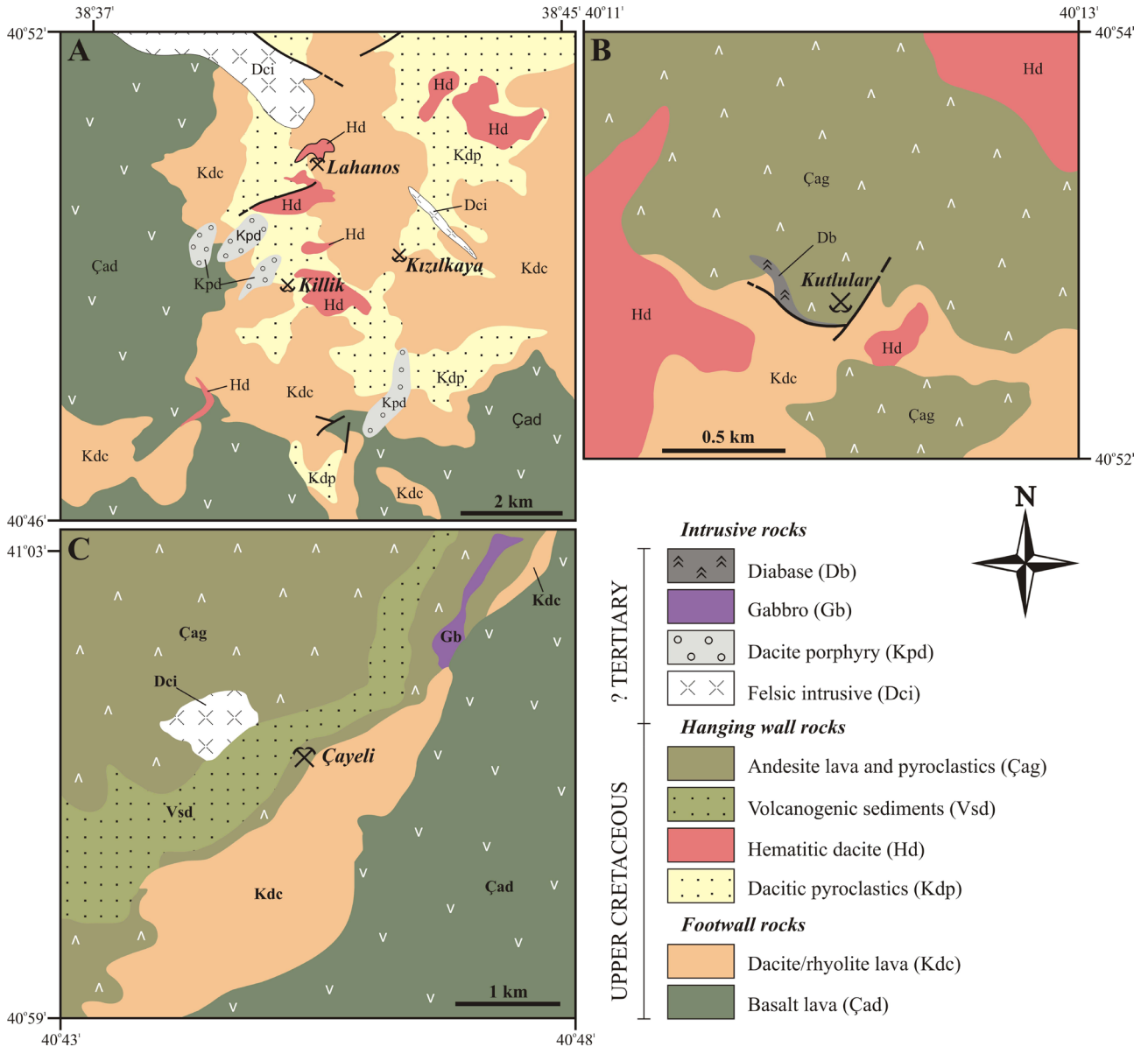


**Figure 1.** Generalized regional geological map of the eastern Pontide belt showing the locations of the studied volcanogenic massive sulfide deposits (simplified from a 1/500,000-scale geological map prepared by the General Directorate of Mineral Research and Exploration of Turkey). The inset shows the Pontide tectonic belt of Anatolia (from Ketin, 1966) and the location of the map area.

mainly composed of andesitic-basaltic volcanic rocks; 2) the Kızılkaya formation, which contains predominantly dacitic/rhyolitic volcanic rocks with pervasive alteration; 3) the *Çağlayan* formation, which is dominated by basic volcanic rocks; and 4) the Tirebolu formation, which is mainly composed of dacite lavas and related volcanoclastic rocks. Nearly all known VMS deposits in the eastern Pontide belt are hosted by the Kızılkaya formation and are commonly located at the contact between felsic volcanic rocks and an overlying polymodal sequence containing various proportions of volcanic and sedimentary facies (Revan, 2010; Revan et al., 2014). The zircon U-Pb dating of the Kızılkaya formation that hosts VMS deposits has yielded a date of  $91 \pm 1.3$  Ma (Eyuboglu et al., 2014). Volcanic rocks hosting the VMS mineralizations are mainly altered lava flows, lava breccias, and hyaloclastites. The majority of the massive sulfide orebodies are directly overlain by volcanosedimentary units, some of which are either deep marine chert or chemical sedimentary rocks (Revan et al., 2014). Footwall rocks that extend immediately below the stratiform massive sulfides are commonly characterized by the presence of intense silica-sericite-pyrite alteration. The deposits include both seafloor and subseafloor accumulations. Many of the VMS deposits show clear evidence of having formed on the seafloor, with the preservation of fauna and chimney fragments in the sulfide orebodies providing evidence of the seafloor setting of many sulfides (Revan, 2010; Revan et al., 2013). All major VMS deposits in the district relate

to fault-controlled subsidence and circular structures (calderas?) that developed in a volcanic-arc setting. These structurally controlled VMS deposits formed proximal to the rhyolitic/dacitic domes (Revan, 2010; Eyuboglu et al., 2014). Pyrite is the dominant sulfide mineral in the Pontide VMS deposits, followed by chalcopyrite and sphalerite and lesser amounts of galena and bornite. The economic mineralization of deposits is confined to Cu-Zn-rich sulfide lenses, and most of the sulfide ores have apparent fragmental textures.

Regionally, the studied VMS deposits are assumed to occur at one main stratigraphic level. The Lahanos, Kızılkaya, and Killik deposits are located in the western part of the eastern Black Sea region (Figure 2A). Although VMS deposits are distributed throughout the eastern Pontide belt, the region within which these deposits occur is one of the most important VMS fields because it includes the most numerous and typical prospects. In addition to these deposits and prospects, numerous volcanogenic-related alteration zones are present, indicating the possibility of hidden deposits (Revan et al., 2014). The mining area consists mainly of Upper Cretaceous acidic and basic lavas and their autoclastic and resedimented facies. The hanging-wall sequence includes dacitic lavas and related fragmental rocks together with porphyritic dacite intrusives. Stratigraphically, beneath the mineralized horizon, the footwall contains basaltic volcanic and volcanoclastic rocks. Sulfide orebodies of the deposits in this area are directly overlain by a



**Figure 2.** Geological maps of the studied VMS deposits compiled and reinterpreted from Revan (2010) and unpublished reports of the General Directorate of Mineral Research and Exploration of Turkey (Turkish acronym: MTA) and Japan International Cooperation Agency (JICA).

volcanosedimentary sequence with a thickness varying from several centimeters up to ~20 m. The entire sequence has been intruded by hematitic dacites (previously termed “purple dacite” by local geologists). At the Lahanos deposit, mineralization occurs as a single sulfide lens with a small stockwork zone. Varying in thickness from 2 to 10 m, the deposit is up to 350 m long and 250 m wide. The Lahanos mine had original reserves of 2.4 Mt with an average ore grade of 3.5% Cu, 2.4% Zn, and 0.3% Pb. The upper part of the sulfide lens also contains 2.5 g/t Au and 100 g/t Ag. In Lahanos, the Pb-Pb data (Çiftçi, 2004) for sulfide ores

yielded an age of 89 Ma. The Kızilkaya deposit consists of a large stockwork and two small massive sulfide lenses (orebody size not reported). Stockwork and sulfide lenses at Kızilkaya contain about 10 Mt grading 0.8% Cu and 0.8% Zn. A massive sulfide lens at Killik is approximately 150 m long, 60 m wide, and 5–10 m thick. It contained preproduction resources of 0.1 Mt metallic ore at 2.5% Cu, 5.0% Zn, and 0.7% Pb.

The Kutlular deposit is located in the central part of the region (Figure 2B). The deposit is hosted by an approximately 350-m-thick sequence of rhyolitic to

dacitic lavas and associated volcanogenic sediment, which is overlain by andesite and underlain by basalt. A volcanosedimentary sequence (averaging 10 m thickness), comprising interbedded mudstones and tuffs, is the immediate hanging-wall rock. The siliceous mudstones of this sequence directly overlie the sulfide orebody. The stratigraphy is cut by dacites and dolerite dikes. The Kutlular orebody occurs as an approximately 250-m-long lens forming a sulfide mound with an average thickness of 14 m. It is a tabular deposit dipping at 10° to the northwest. This lens contained averages of 2.4% Cu and 0.46% Zn (Turhan and Avenk, 1976). In addition, massive ores have markedly higher average Au and Ag concentrations (6.2 g/t Au, 15 g/t Ag). Total reserves prior to mining were about 1.33 Mt.

The Çayeli deposit is located in the eastern part of the region (Figure 2C). The deposit is at the contact between the altered footwall felsic volcanics and hanging-wall mafic volcanic rocks. The footwall rocks (approximately 600 m thick) consist of felsic and basic lavas and related autoclastic facies. The hanging-wall stratigraphy consists dominantly of andesite lavas and related fragmental rocks. Felsic intrusives crosscut all rock types. Mineralization consists of seafloor massive and subseafloor stockwork sulfides. The orebody has a known strike length of more than 650 m, extends to a depth of at least 560 m, and varies in thickness from a few meters to 80 m (with an average of ~20 m). Development of this mine began in early 1990 and a total of 15 Mt was produced to the end of 2012, at an average grade of 4.03% Cu and 6% Zn. Average Au is 1.2 g/t and Ag values reach up to 150 g/t, plus a lesser amount of lower-grade stockwork sulfides.

The broad geological features and ore facies characteristics of the aforementioned deposits are similar. A generalized stratigraphy of these deposits is depicted schematically in cross-section in Figure 3.

### 3. Sampling and analytic methods

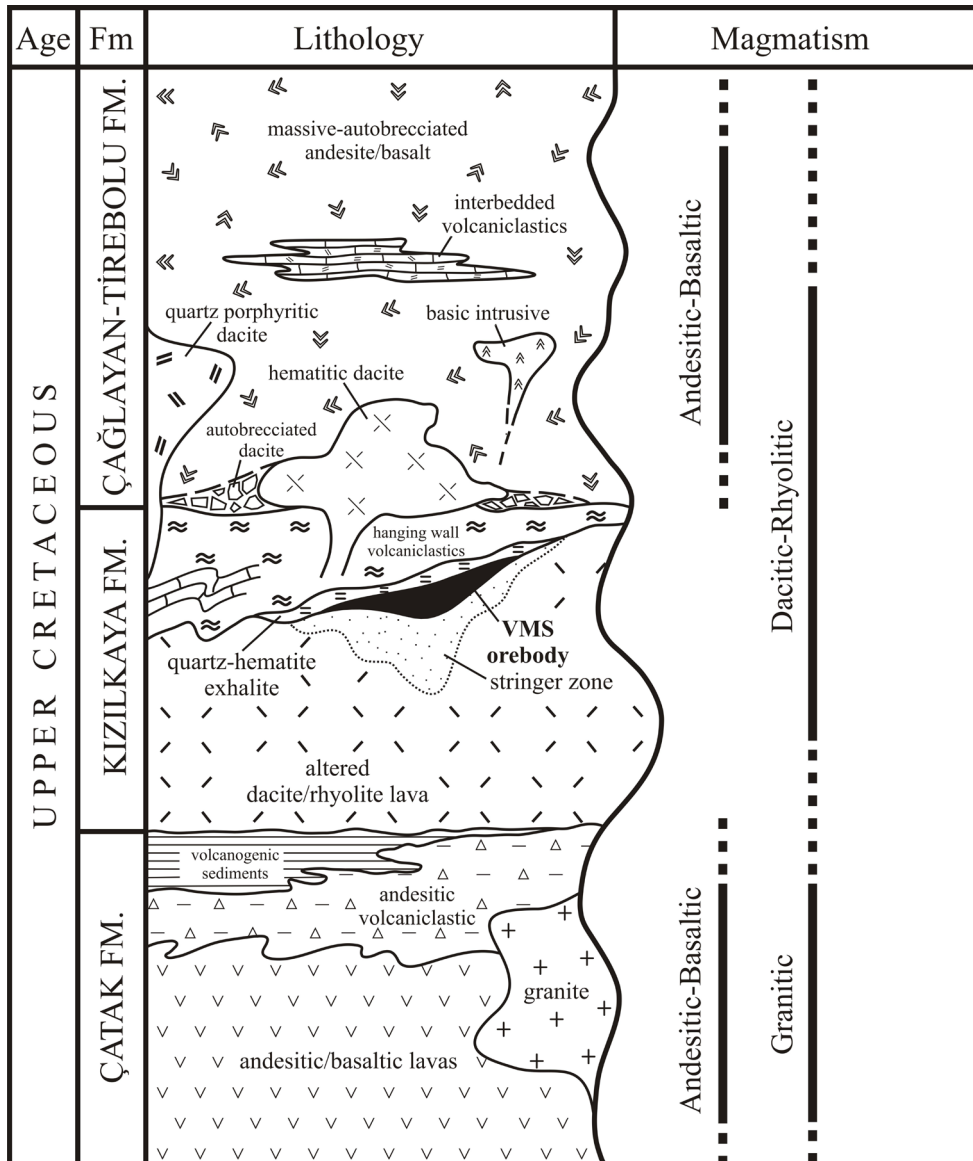
Sulfur isotope studies were undertaken on hydrothermal chimney fragments collected from massive ore bodies in the Çayeli and Lahanos mines and the abandoned Killik, Kutlular, and Kızılkaya deposits. Samples were obtained from material from underground exposures of the Çayeli and Lahanos mines and from mine dump materials at the Killik, Kızılkaya, and Kutlular mines. A total of eight chimney samples were investigated in this study: one sample from the Lahanos mine, one from the Killik mine, one from the Kızılkaya mine, one from the Kutlular mine, and four from the Çayeli mine. Pyrite, chalcopyrite, sphalerite, bornite, and galena were sampled from distinct chimney zones (zones A, B, and C). The samples were hand-picked under a binocular microscope to an estimated purity of >90%. Great care was exercised during sampling

and handling to avoid contamination. Representative samples of about 200 mg taken from polished sections by means of a diamond cutter (diameter of ~1 mm) were pulverized and measured.

Sulfur isotope analyses were conducted by Dr VA Grinenko at the Central Institute of Base and Noble Metals in Moscow. The measurements were carried out on a ThermoFinnigan Delta<sup>plus</sup> stable isotope ratio mass spectrometer. A Flash EA1112 analyzer was used for decay of the samples. Standardization was based on international standards of the International Atomic Energy Agency-IAEA (IAEA-S-1,  $\delta^{34}\text{S}$  value of  $-0.3\text{‰}$  and NBS-123,  $\delta^{34}\text{S}$  value of  $17.1\text{‰}$ ). All sulfur isotope compositions were calculated relative to Canyon Diablo troilite (CDT). The analytical precision for sulfides was  $\pm 0.2\text{‰}$ .

### 4. General characteristics of the Pontide vent chimneys

All paleohydrothermal chimneys in massive sulfide deposits of the eastern Black Sea region are found in clastic sulfide ores, which are dominated by pyrite, sphalerite, and lesser amounts of chalcopyrite. Most of the well-preserved chimney fragments are from the Çayeli, Killik, and Lahanos mines. A smaller number of chimney fragments, which are not well preserved, are from the Kızılkaya and Kutlular mines. Chimney fragments have variable sizes, varying from a few millimeters to few centimeters, with some reaching a diameter of approximately 8 cm. The well-preserved chimney fragments typically have distinct concentric zones with sulfide and sulfate minerals and can be broadly divided into three such concentric zones (Figures 4A and 4B). In the Çayeli-2 sample, unlike all other chimneys, four distinct zones (zones A, B, C, and D) were identified from exterior to interior. The general mineralogical sequence across all chimney zones is similar. Each zone is characterized by predominant sulfide mineral abundance. The outer zone (zone A) contains mainly pyrite and sphalerite, with minor amounts of chalcopyrite. The sulfides within the inner zone (zone B) consist predominantly of chalcopyrite with lesser amounts of pyrite and sphalerite. The axial conduit (zone C) is commonly filled by barite gangue and pyrite, with minor amounts of fahlore, sphalerite, chalcopyrite, galena, and quartz (Revan et al., 2014). Pyrite is the principal sulfide mineral within the chimney zones, followed by sphalerite and chalcopyrite. Zones contain minor concentrations of other minerals including galena, covellite, chalcocite, bornite, tennantite, tetrahedrite, marcasite, and pyrrhotite. Quartz is the principal gangue mineral, followed by barite. Pyrrhotite is only observed in chimney zones from the Kızılkaya sample. Accessory minerals in various zones include gold, electrum, hessite, kawazulite, wittichenite, and tellurobismuthite. The mineralogy of the chimney samples is summarized in Table 1. The trace-element

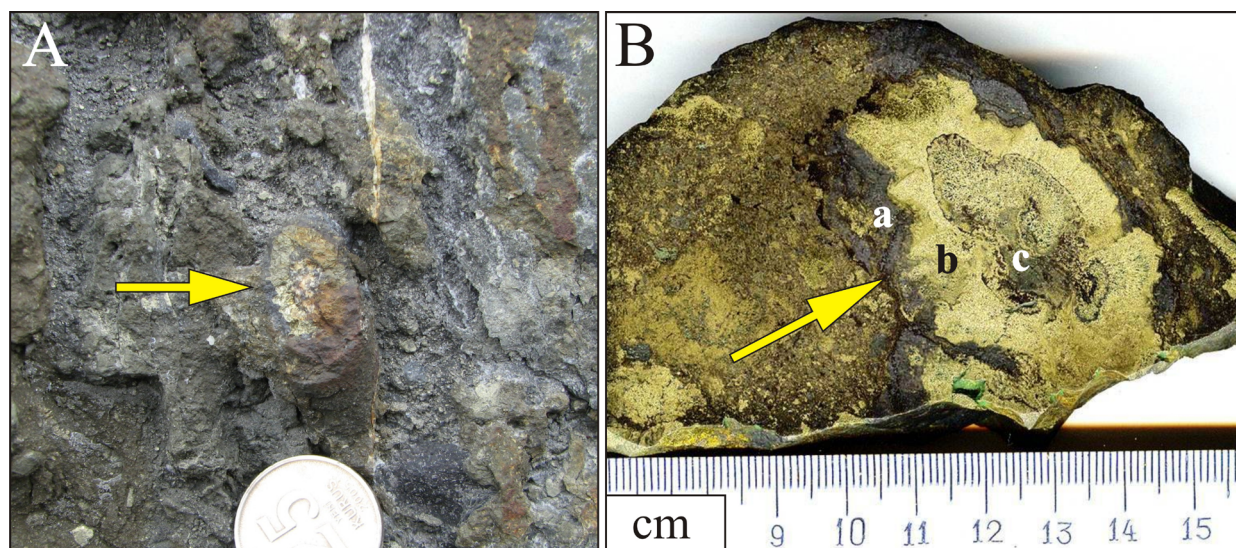


**Figure 3.** Summary stratigraphic column for the VMS-hosting Upper Cretaceous volcanic rocks (modified from Revan, 2015).

geochemistry and mineralogy of the chimneys used in this study was discussed by Revan et al. (2014). The sulfide mineralogy of the Pontide vent chimneys is highly consistent with results obtained from mound and stockwork zones of VMS deposits (e.g., Çiftçi, 2000; Çiftçi et al., 2004; Revan, 2010).

Textures are commonly shared by all chimney samples. Pyrite dominates the mineralogy of the outer zones and appears in many morphologies. Colloform textures are generally prevalent in the outermost chimney walls (Figure 5A). Dendritic-like pyrite and pyrite framboids are also present within the various chimney zones (Figures 5B and 5C). Chalcopyrite and, to a lesser extent, pyrite

dominate the mineralogy of the inner zones (Figure 5D). Chalcopyrite is often replaced by bornite in the outer zone (Figure 5E). Numerous examples of what appear to be chimney wall fragments have porous and laminated textures (Figure 5F). Some chimney fragments display a thin alteration rim, suggestive of oxidizing conditions on the seafloor (Revan et al., 2013, 2014). Sulfide textures and zonation patterns are consistent with the chimney growth model described from the East Pacific Rise at 21°N by Haymon (1983). Chimneys were not classified due to a limited number of findings. Based on the mineral content of chimney zones, the chimneys can be broadly divided into two major types: Zn-rich and Cu-rich



**Figure 4.** Photographs representative of the well-preserved sulfide chimney fragments. (A) The chimney fragment within the clastic sulfide matrix; Killik deposit. See the coin for scale. (B) Mineralogical zonation of the sulfide chimney defined in the Lahanos deposit. Fe- and Zn-sulfide are abundant within the outer zones (a). Fe- and Cu-sulfide are abundant within the inner zones (b). The axial conduits (c) are commonly filled by barite and quartz gangue with various amounts of pyrite, fahlore, sphalerite, chalcopyrite, and galena.

**Table 1.** Mineralogy of the Pontide vent chimneys.

Chimney sample	Major	Minor	Trace
Lahanos ( <i>n</i> : 2)	Py, Sph, Ccp	Gn, Cv, Cc, Tn, Tt, Mc, Bo, Ba, Qtz	Au, El, Hes, Kwz, Wtc, Te-bi
Killik ( <i>n</i> : 2)		Gln, Cc, Cv	Ss
Kızılkaya ( <i>n</i> : 1)		Gn, Cv, Cc, Tn, Mc, Bo, Po, Ba, Qtz	Au, El
Kutlular ( <i>n</i> : 1)		Ba, Qtz	Au
Çayeli ( <i>n</i> : 4)		Gn, Cv, Cc, Tn, Mc, Bo, Ba, Qtz	Au, El, Hes

Abbreviations: *n*- number of analyzed samples, Au- gold, Ba- barite, Bo- bornite, Cc- chalcocite, Ccp- chalcopyrite, Cv- covellite, El- electrum, Gn- galena, Hes- hessite, Kwz- kawazulite, Mc- marcasite, Py- pyrite, Sph- sphalerite, Te-bi- tellurobismuthite, Tn- tennantite, Tt- tetrahedrite, Po- pyrrothite, Qtz- quartz, Sc- silver-sulfosalt, Wtc- wittichenite. Data from Revan et al. (2014).

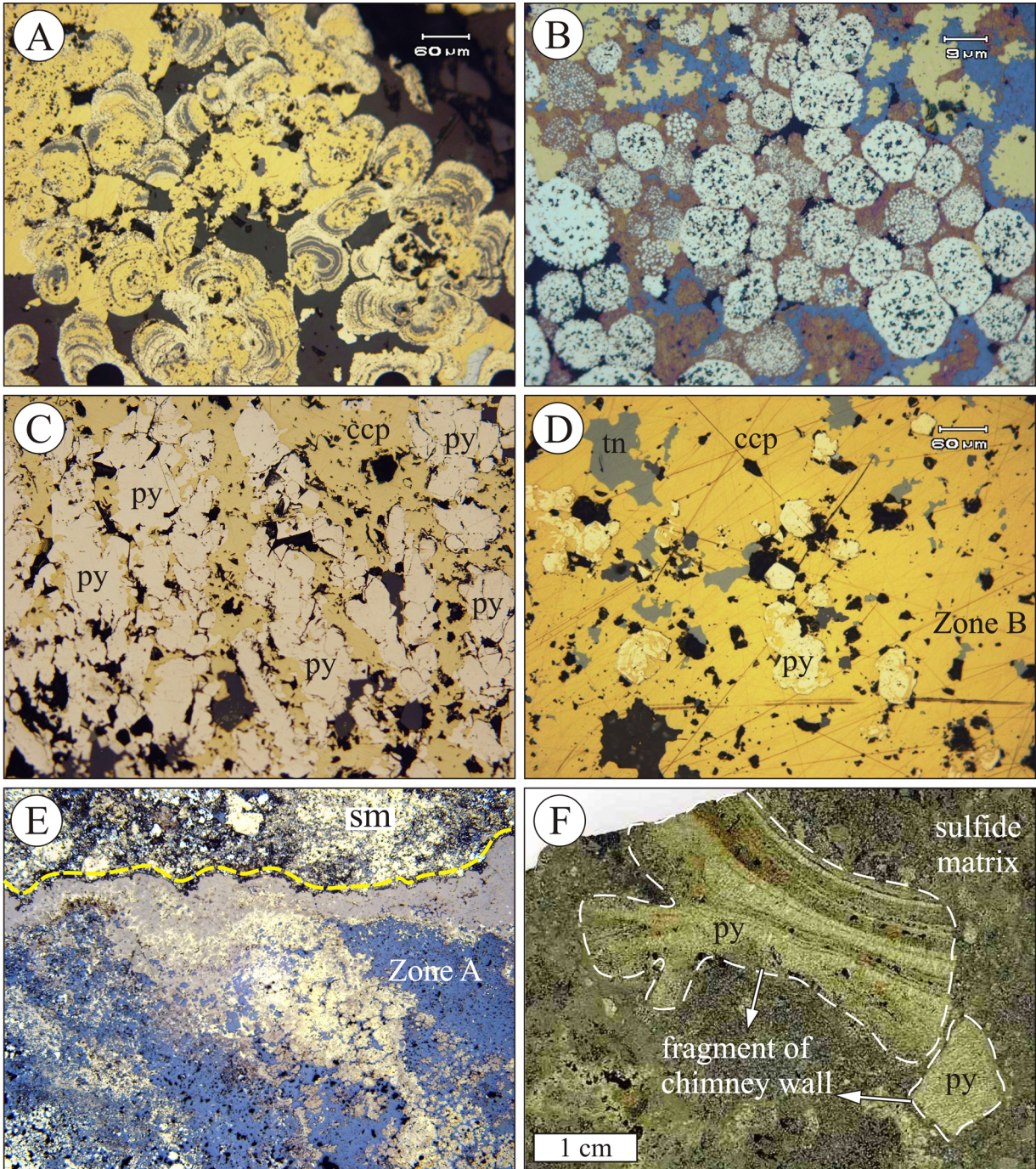
chimneys. The characteristics of chimney fragments in the Pontides are comparable to those defined in Cyprus (Qudin and Constantinou, 1984) and the southern Urals (Herrington et al., 1998; Maslennikov, 2006; Maslennikova and Maslennikov, 2007). They are similar in size, mineral content, textural features, and zoning but differ in age.

### 5. Sulfur isotope data

To evaluate the sulfur source of deposits, a total of 52 mineral separates (10 pyrite, 22 chalcopyrite, 17 sphalerite, 2 bornite, and 1 galena) from eight Pontide chimney samples were analyzed for sulfur isotopes. The results are shown in Table 2 and plotted on a histogram in Figure 6. The range of  $\delta^{34}\text{S}$  values for the vent chimneys is from  $-2.7\text{‰}$  to  $6.5\text{‰}$ , similar to the range of values ( $-2.6\text{‰}$  to  $7.0\text{‰}$ ) reported for massive and stockwork zones of

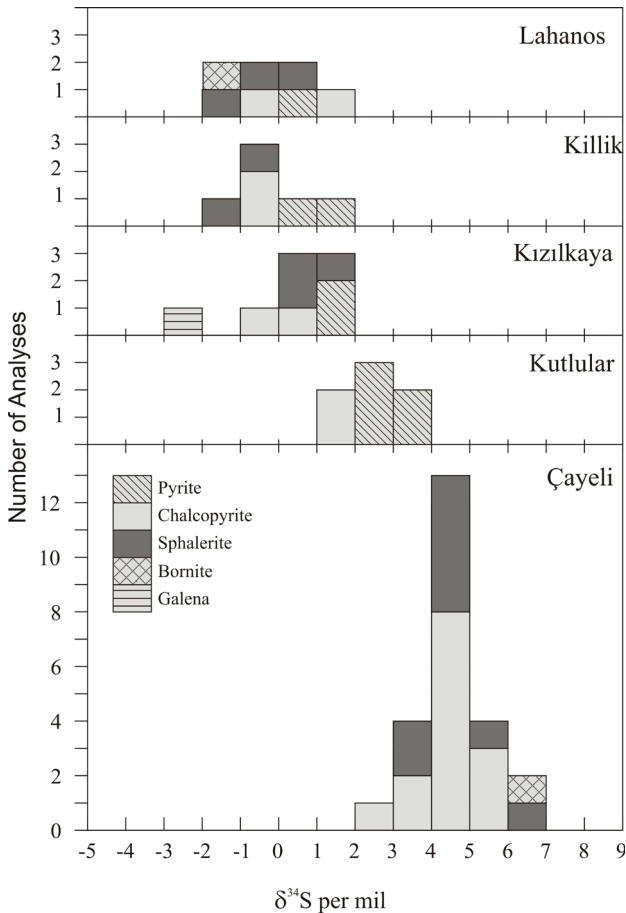
VMS deposits from the eastern Pontide belt (Çağatay and Eastoe, 1995; Gökçe and Spiro, 2000).

Sulfur isotope analyses for the Pontide deposits yielded  $\delta^{34}\text{S}$  values of 0.4 to 3.2 per mil for pyrite,  $-0.7$  to 5.8 per mil for chalcopyrite,  $-1.6$  to 6.1 per mil for sphalerite, and  $-1.2$  to 6.5 per mil for bornite. A value of  $-2.7$  per mil was obtained from 1 galena separate. Pyrite  $\delta^{34}\text{S}$  values showed a very narrow spread. The  $\delta^{34}\text{S}$  values of sulfides from the Çayeli deposit ranged from 2.2 to 6.5 per mil, with most clustered between 4 and 5 per mil. The range for Lahanos ( $-1.2$  to 1.0 per mil) was similar to that of the Killik values, which ranged from  $-1.6$  to 1.0 per mil. The Kutlular deposit yielded  $\delta^{34}\text{S}$  values between 1.2 and 3.2 per mil, slightly higher than the ranges at Lahanos, Killik, and Kızılkaya. The  $\delta^{34}\text{S}$  values for the Kızılkaya deposit varied between  $-2.7$  and 1.9 per mil. Chimney sulfides



**Figure 5.** Photographs of some chimney textures and of the various chimney zones (from Revan, 2010; Revan et al., 2014). (A) Colloform pyrite, partly replaced by chalcopyrite and sphalerite in the outermost part of the outer wall; Lahanos. (B) Pyrite framboids in the central zone; Kizilkaya. (C) Replacement of dendritic pyrite by chalcopyrite in the middle part of the inner wall; Kutlular. The long side of the photograph represents ~1.2 mm. (D) Euhedral pyrite and tennantite within the chalcopyrite-dominated inner zone; Lahanos. (E) Clastic sulfide matrix in which chimney was found and sphalerite-chalcopyrite-bornite assemblage in the outer wall. The long side of the photograph represents ~1.2 mm. (F) Subhedral, laminated cavernous chimney sulfide (pyrite) fragments up to 4 cm in size (Lahanos). Abbreviations: py- pyrite, ccp- chalcopyrite, Tt- tennantite, sm- sulfide matrix.

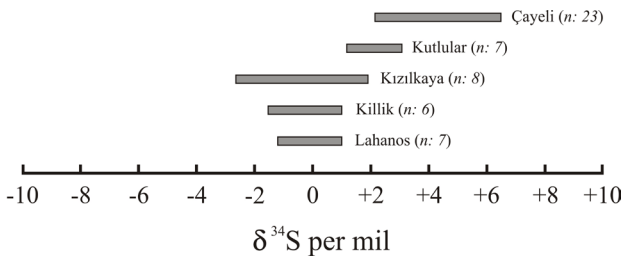




**Figure 6.** Histogram of  $\delta^{34}\text{S}$  compositions of sulfide minerals in the studied vent chimneys. Data from Table 2.

from Çayeli had the highest  $\delta^{34}\text{S}$  values. The sulfur isotope values of chimney sulfides from Kızılkaya varied more than those of other Pontide deposits. The chimneys in Lahanos and Killik tended to have negative  $\delta^{34}\text{S}$  values, with the majority being lighter than zero per mil (Figure 7).

A general trend of decreasing  $\delta^{34}\text{S}$  values from the outer zones to the interior of chimneys was clearly observed at Çayeli (Çayeli-1 and Çayeli-2), Kızılkaya, and Kutlular. The  $\delta^{34}\text{S}$  values of some chimney samples at Çayeli (Çayeli-3



**Figure 7.** Sulfur isotope compositions of sulfide minerals from vent chimneys in the Pontide deposits. Abbreviation: *n* - number of measurements.

and Çayeli-4) showed a small increase from exterior to interior. In the Lahanos and Killik samples, random variations were noted. Among the sulfide minerals, values of chalcopyrite were slightly higher than the rest, whereas the galena sample had the lowest  $\delta^{34}\text{S}$  values. The sulfur isotope composition of pyrite was rather uniform, with  $\delta^{34}\text{S}$  values of 0.4 to 3.2 per mil. Bornite showed a relatively broader range of  $\delta^{34}\text{S}$  (-1.2‰ to 6.5‰), which was slightly broader than the range of chalcopyrite values (-0.7‰ to 5.8‰). Figure 8 shows some of the chimney zones from where sulfide samples were collected and dominant minerals of these zones.

**6. Discussion of sulfur isotope data**

The stable isotope geochemistry of sulfide minerals is an integral part of investigating mineral deposits. When combined with geological data, sulfur isotope data provide significant information not only on the sulfur source, but also on the mechanism of sulfide precipitation. Given that VMS deposits form in moderate to deep marine environments that are characterized by abundant volcanic rocks, potential sources of sulfur for these deposits include sulfur dissolved in seawater, sulfur present within the rock column, and magmatic sulfur (Huston, 1999). Three broad hypotheses have been advanced for the origin of the sulfur in Phanerozoic VMS deposits: 1) partial to complete inorganic reduction of seawater sulfate combined with dissolution of sulfur from country rocks (e.g., Sasaki, 1970; Zierenberg et al., 1984; Solomon et al., 1988); 2) biogenic reduction of seawater sulfate (e.g., Sangster, 1968); and 3) derivation of reduced sulfur from a deep-seated (magmatic) source (e.g., Ishihara and Sasaki, 1978). It is clear that sulfate reduction reactions are a highly effective mechanism in seafloor hydrothermal systems. In the context of VMS deposits, reduction reactions can occur in the deep subsurface, in the near-surface groundwater environment, in chimneys, or after exiting the chimneys. In the deep subsurface environment, only a small amount of sulfate is introduced into the high-temperature portion of the system. The small amount of sulfate that does penetrate to the deep subsurface environment is reduced to sulfide and mixed with sulfide leached from host rocks (Zierenberg et al., 1984). Some sulfate reduction may occur due to sulfate entrainment during upwelling of fluids. Sulfate reduction in the near-surface environment can proceed using ferrous iron in the hydrothermal fluid as the reducing agent (Shanks and Seyfried, 1987). Adiabatic mixing reactions of hydrothermal fluids and seawater sulfate within developing chimneys can only account for  $\delta^{34}\text{S}$  values of up to 4.5 per mil (Janecky and Shanks, 1988). Values of  $\delta^{34}\text{S}$  in excess of 4.5‰ can only be explained by reaction of seawater within the feeder zones immediately underlying the seafloor sulfide deposition. Isotopically

**Table 2.** Sulfur isotopic compositions of vent chimneys from the Pontide deposits.

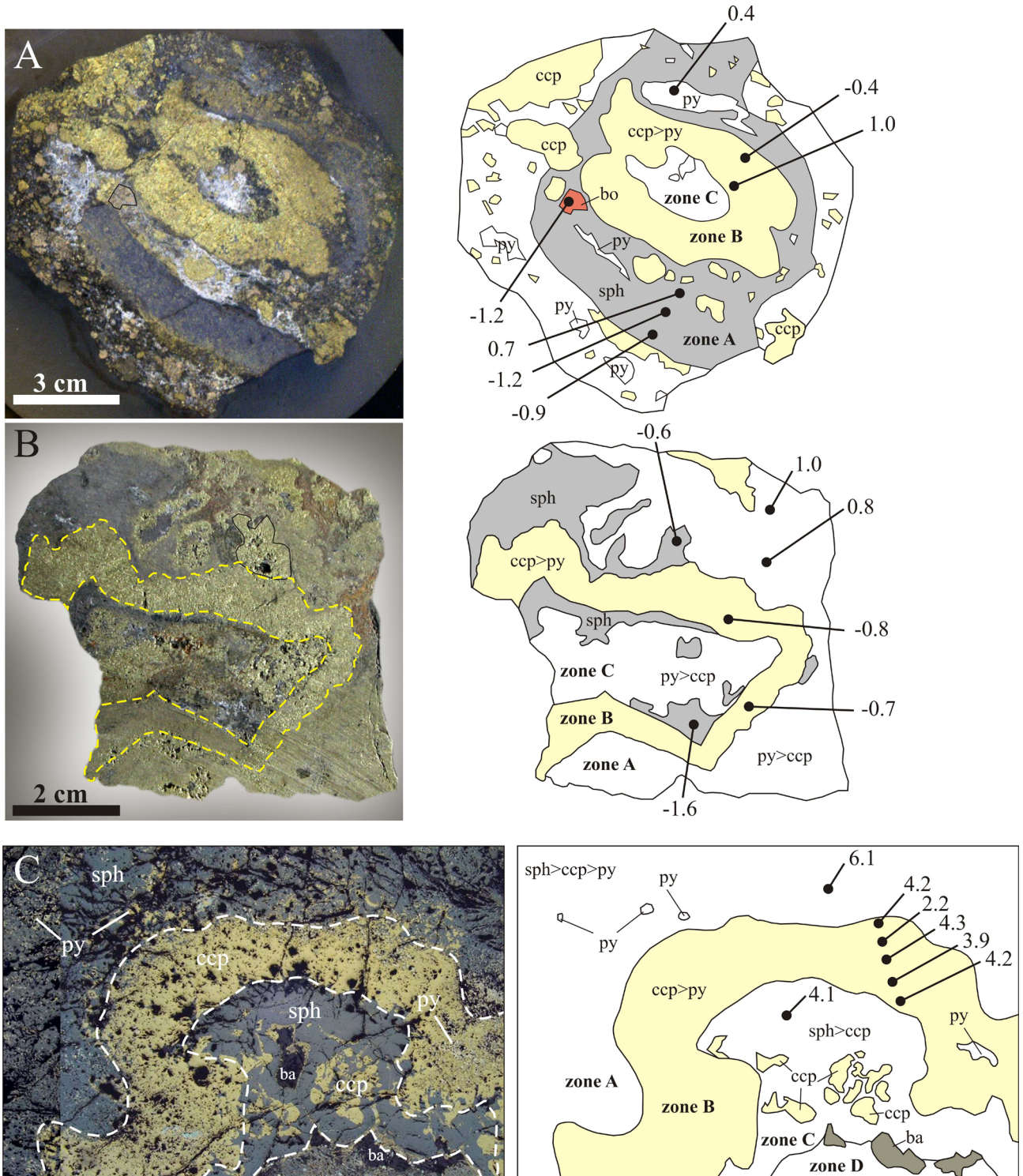
Deposit	Ore type	Zone	$\delta^{34}\text{S}$ per mil				
			Pyrite	Chalcopyrite	Sphalerite	Galena	Bornite
Lahanos	Chimney fragment within the clastic sulfide orebody	A	0.4	-	-0.9/-1.2	-	-
		B	-	-0.3/1.0	-	-	-1.2
		C	-	-	0.7	-	-
Killik		A	1.0/0.8	-	-0.6	-	-
		B	-	-0.7/-0.8	-	-	-
		C	-	-	-1.6	-	-
Kızılkaya		A	1.9/1.7	-	0.7/1.4	-	-
		B	-	-0.3/0.6	-	-	-
		C	-	-	0.6	-2.7	-
Kutlular		A	2.3/ 2.7/3.1/3.2	-	-	-	-
		B	2.3	1.2/1.2	-	-	-
		C	-	-	-	-	-
Çayeli-1	A	-	-	5.3	-	6.5	
	B	-	3.7/4.1/5.4	-	-	-	
	C	-	4.7	-	-	-	
Çayeli-2	A	-	-	6.1	-	-	
	B	-	2.2/3.9/4.2/4.2/4.3	-	-	-	
	C	-	-	4.1	-	-	
Çayeli-3	A	-	-	3.2/4.2/4.4/4.4	-	-	
	B	-	4.0/4.6/5.3/5.8	-	-	-	
	C	-	-	-	-	-	
Çayeli-4	A	-	-	3.9	-	-	
	B	-	4.6	-	-	-	
	C	-	-	4.9	-	-	

Abbreviations: A- outer wall, B- inner wall, C- central zone (conduit).

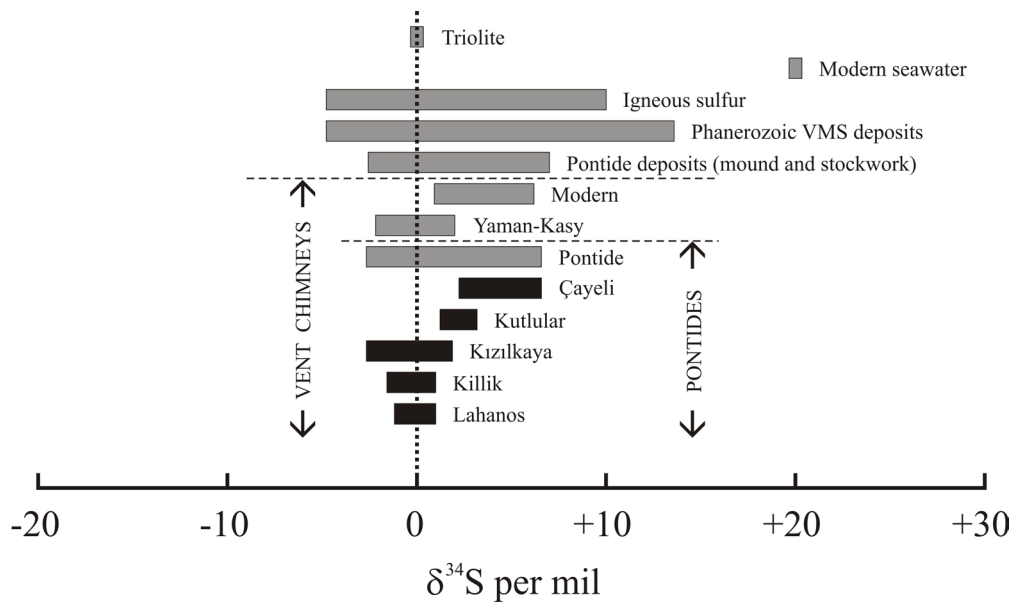
light sulfur is attributable to minimal seawater inputs into the feeder zone and also to minimal seawater reduction by hydrothermal fluid-seawater mixing within the chimneys (Butler et al., 1998). As described, reduction of sulfate to sulfide can occur at any point in the hydrothermal circulation system, and there are differing views about which of the aforementioned environments would more effectively promote sulfate reduction processes.

The sulfur isotope compositions of sulfide minerals from ancient seafloor massive sulfide deposits are interpreted in terms of the same geochemical processes that operate in modern systems. A comparative summary of the isotopic compositions of some major sulfur reservoirs and studied deposits is given in Figure 9, from which it can be noted that the studied deposits have a narrow compositional range, indicative of a fairly specific

origin. In contrast, a wide compositional range would likely indicate multiple origins (Rollinson, 1993). Sulfur isotope values of sulfide minerals in VMS deposits are characteristically clustered around zero per mil or are somewhat enriched in  $^{34}\text{S}$ . Slightly positive  $\delta^{34}\text{S}$  values of sulfides are typical of many modern and ancient massive sulfide deposits because of contributions of sulfur from two main sources, rock sulfide and reduced seawater sulfate (Woodruff and Shanks, 1988). Slightly negative  $\delta^{34}\text{S}$  values of sulfides can be attributed to a complex history of precipitation and replacement reactions within hydrothermal structures (chimneys, mounds) developed on the sea floor. Equilibrium isotopic fractionation during lower temperature sulfide replacement reactions leads to negative  $\delta^{34}\text{S}$  values (Janecky and Shanks, 1988). The deep-seated source hypothesis can account for districts with



**Figure 8.** Horizontal sections of some well-preserved vent chimneys from the (A) Lahanos, (B) Killik, and (C) Çayeli deposits showing mineralogical zonation and the location of sampling points for  $\delta^{34}\text{S}$  analysis. The long side of the photograph (C) represents  $\sim 3.2$  cm. Abbreviations: ccp- chalcopyrite, py- pyrite, sph-sphalerite, bo- bornite, ba- barite.



**Figure 9.** The ranges of  $\delta^{34}\text{S}$  values of chimney sulfide minerals from the Pontides and Urals (Yaman-Kasy) compared with modern analogues. The  $\delta^{34}\text{S}$  values for ancient volcanogenic massive sulfide deposits and some geologically important sulfur reservoirs are also given for comparison (data from Ohmoto and Rye, 1979; Arnold and Sheppard, 1981; Kerridge et al., 1983; Zierenberg et al., 1984; Shank and Seyfried, 1987; Woodruff and Shanks, 1988; Çağatay and Eastoe, 1995; Huston, 1999; Gökçe and Spiro, 2000; Maslennikova and Maslennikov, 2007).

sulfide  $\delta^{34}\text{S}$  values of 0 to 5 per mil. Hence, although “deep-seated” sulfur may be important in some districts, such as in Precambrian terranes, the most important source of sulfur in Phanerozoic deposits is seawater sulfate that was inorganically reduced (Huston, 1999). Biogenic reduction of seawater sulfate could lead to more negative  $\delta^{34}\text{S}$  values; if this is the case, there should be broader overall  $\delta^{34}\text{S}$  ranges (Ohmoto and Rye, 1979). Biogenic fractionation of sulfur isotopes is hence too large to account for the observed narrow range of  $\delta^{34}\text{S}$  values. Observed ranges of  $\delta^{34}\text{S}$  values of Pontide chimneys indicate only episodic participation of biogenic reduced sulfur. Bacteriogenic stages are marked by framboidal pyrite within some chimney walls, suggesting that deposition of some Fe sulfide was controlled by biological activity. The very light sulfur isotope values for some chimneys may also indicate local biogenic processes. However, biogenic reduction is not considered to have been a major sulfide-generating process in the Pontide deposits.

Although the gross sulfur isotope variability of most Phanerozoic VMS deposits can be related to the seawater sulfate evolution curve, many deposits in different districts have large internal variability in  $\delta^{34}\text{S}$  (Huston, 1999). In districts such as Bathurst, New Brunswick and Mt. Windsor, Queensland, the average  $\delta^{34}\text{S}$  value of individual deposits varies according to the stratigraphic position at which the deposit occurs (Lusk, 1972; van Staal, 1992). However,

in some districts, such as the Mt. Read Volcanics, the variation in  $\delta^{34}\text{S}$  appears to be geographic (Huston, 1999). Ranges of  $\delta^{34}\text{S}$  values of sulfide minerals are often similar in different deposits within the same district (Woodruff and Shanks, 1988). The sulfur isotope values of the Pontide deposits are broadly in close proximity. However,  $\delta^{34}\text{S}$  values of sulfides in the Çayeli mine had a higher  $\delta^{34}\text{S}$  range than other deposits. When considered according to the geographic location of deposits, the Lahanos, Killik, and Kızılkaya deposits, which are located in the same area, have a close compositional range. The Kutlular deposit, located farther east, has slightly higher  $\delta^{34}\text{S}$  values, while the easternmost deposit, the Çayeli, exhibits relatively higher values than the others. Considering that these deposits occur in the same stratigraphic horizon, the variation in  $\delta^{34}\text{S}$  values of the Pontide deposits appears to be geographic rather than stratigraphic. Distance to heat source may be an important factor determining isotope ratios in vent chimneys (Shanks and Seyfried, 1987). Çayeli chimneys may have formed distal to the existing heat source that drove convection of metal-precipitating hydrothermal fluids. In such settings, fluid fluxes are lower, leading to less vigorous venting. Such vents result in increased mixing during chimney formation and produce isotopically heavier sulfide minerals by reduction of ambient sulfate. Çayeli chimneys probably represent weak vents, distal to the magmatic heat source; such vents have

a high degree of seawater admixture through very porous chimney walls.

Sulfur isotope values of the chimney zones have no systematic variation throughout the chimney zones; however,  $\delta^{34}\text{S}$  values of the sulfide phases vary slightly from the outer wall to the interior. Rapid deposition of sulfide minerals prevents complete sulfur isotopic equilibrium from taking place (Gregory and Robinson, 1984). Thus, no systematic isotopic shifts across the chimney walls were detected. In some samples, a rough isotopic zonation pattern from exterior to interior was observed. An opposite zonation pattern is also present. This was explained by Bluth and Ohmoto (1988) with a model in which the  $\delta^{34}\text{S}$  value of fluid changes with time during the life of a chimney, as a result of changes in hydrothermal plumbing and water/rock ratios in the footwall rocks beneath the vent system. According to this model, sulfides in all chimney zones inherit the chemical and isotopic characteristics of all stages of hydrothermal activity. In addition, the hydrothermal fluid reacts with already precipitated sulfides in the chimney walls, causing local isotopic variations during chimney growth. Variations in  $\delta^{34}\text{S}$  values of vent fluids and isotopic effects related to replacement reactions have a major role in controlling the sulfur isotopic variations of chimney sulfides (Styrt et al., 1981; Zierenberg et al., 1984; Woodruff and Shanks, 1988). Complex variations in chimney zonation can also occur depending on the developmental stage of the hydrothermal site.

The sulfide chimneys from the Pontides exhibit marked concentric mineral zonation. The chimneys are also characterized by significantly higher metal content within the outer walls of the chimneys, suggesting rapid precipitation in high-gradient conditions (Revan et al., 2014). The observed concentric patterns are the result of interactions of fluids with different isotopic compositions with each other within the chimney wall. Some sulfide minerals within the chimney walls (mainly pyrite) show a dendritic texture, resulting from rapid cooling on the seafloor. The existence of both Cu- and Zn-rich chimneys reflects either temperature differences in the hydrothermal fluids beneath the different chimneys or differences in the stages of chimney evolution (Goldfarb et al., 1983). The colloform textures within the outer zones of some chimneys suggest that some of these, probably the Zn-rich chimneys, are the result of mixing of lower temperature (~250 °C) fluids with ambient seawater. The Zn-rich chimneys thus represent an earlier, lower-temperature stage of chimney development.

## 7. Conclusions

The isotopic signatures of sulfides from the Pontide chimneys reflect multiple episodes of precipitation, dissolution, and reprecipitation over a wide range of conditions. Several factors (e.g., water/rock ratios in the footwall rocks beneath the vent system, permeability and porosity of the chimney walls, changes in hydrothermal activity during the life of the chimney, and replacement of earlier sulfides by later fluids) have influenced isotopic variations within the chimney walls, but chemical reactions between vent fluids and earlier sulfide minerals in the chimneys appear to have had the largest effect. Ranges of  $\delta^{34}\text{S}$  values of Pontide chimneys are similar for different deposits (Lahanos, Killik, and Kızılkaya) within the same region. Variations are largely ascribed to vent sites distal to the magmatic heat source. Çayeli chimneys have the isotopically heaviest sulfides relative to the other deposits and they probably occurred at vent sites distal to the magmatic heat source. The source of sulfur in the Pontide chimneys could be attributed to mixing of fluids with different isotopic compositions. Although the isotopic signature of the studied deposits indicates a deep-seated source, the main source of sulfur is considered to be seawater sulfate based on previous studies and theoretical works. Seawater sulfate can be reduced, thus providing a significant component of source sulfur. In this case, seawater sulfate reduction mechanisms were likely effective. At some deposits, such as those of Çayeli and Kutlular, seawater sulfate reduction reactions were probably highly effective due to their setting near the heat source. Biogenic reduction is not regarded as a major sulfide-generating process; however, the framboidal textures identified in some chimney zones suggest that episodic participation of bacteriogenic-reduced sulfur may have occurred during chimney growth.

The range of  $\delta^{34}\text{S}$  values of the studied deposits is highly consistent with the range of Phanerozoic VMS deposits. The sulfur isotope values for Pontide chimney sulfides, ranging from -2.7‰ to 6.5‰, are considered to represent reduced seawater sulfate origin with a variable contribution of deep-seated sulfur leached from host rock during hydrothermal circulation.

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