Turkish Journal of Earth Sciences (Turkish J. Earth Sci.), Vol. 18, 2009, pp. 127–137. *Copyright ©TÜBİTAK*
doi:10.3906/yer-0806-5 First published online 10 July 2008

Lead and Sulfur Isotope Studies of the Koru (Çanakkale, Turkey) Lead-Zinc Deposits

GÜLCAN BOZKAYA & AHMET GÖKCE

Cumhuriyet University, Department of Geological Engineering, TR–58140 Sivas, Turkey
(E-mail: gbozkaya@cumhuriyet.edu.tr)

Received 01 April 2007; revised typescript received 13 November 2007; accepted 31 January 2008

Scientific editing by Nilgün GÜLEÇ & Durmuş BOZTUĞ

Abstract: Koru (Çanakkale) barite-bearing lead-zinc deposits are typical examples of the lead-zinc deposits occurring in the Tertiary volcanic rocks which crop out in the Biga Peninsula. Volcanic rocks around the investigated deposits are distinguished as Eocene Akçaalan andesite, Oligocene Adadağı pyroclastics, Miocene Dededağ dacite and Plio–Quaternary Karaömerler basalt.

The investigated deposits are hosted by Adadağı pyroclastics and show two different mineralization styles such as stockwork ore veinlets in the upper parts and ore veins along the fault zones in WNW–ESE direction, in the lower parts. Sphalerite, galena, pyrite, chalcopyrite, quartz, barite and calcite are the main minerals and they are accompanied by small amounts of fahlore (tennantite), marcasite, covellite and bornite.

Sulfur isotope studies show that the $\delta^{34}S$ values of sphalerite, galena and barite change in the range of –1.9 to –0.1 (average –1.2) $^{o}/_{oo\ VCDT}$, –5.2 to –3.0 (average –3.9) $^{o}/_{oo\ VCDT}$ and +14.9 to +17.3 (average +16.5) $^{o}/_{oo\ VCDT}$, respectively. There are two different ranges of $\delta^{34}S$ values of H_2S in equilibrium with barite (+5.5 to +7.9 $^{o}/_{oo}$) and sulfide minerals (–2.1 to –0.5 $^{o}/_{oo}$), indicating that the sulfur in sulfide minerals and barite derived from different sources. The similarity of the $\delta^{34}S$ values of barite to those of precipitated sulfate minerals in sediments or $SO_4^{=}$ ions dissolved in sea water of Late Tertiary suggests that the sulfur in barite was derived from the precipitated sulfate minerals or $SO_4^{=}$ ions dissolved in pore water in surrounding volcano-sedimentary units. On the other hand, proximity of the $\delta^{34}S$ values of sphalerite, galena and H_2S (in equilibrium with these two minerals) to 0 ‰ points to a genetic relation of the sulfur with the volcanic components of the surrounding volcano-sedimentary units.

Lead isotope data are close to those of a model orogenic reservoir and are very different from a mantle-related reservoir. Calculated Pb-isotope model ages for these deposits (from 70 to 1 Ma) are in accordance with the possible geological age of the mineralization (post Oligocene) and indicate that the lead in galena was derived from the surrounding Eocene–Quaternary volcanic and volcano-sedimentary units.

These data, along with the results of previous studies related to trace element and REE abundances and O- and H-isotope compositions, suggest that the Pb, Zn, Cu and S in sulfide minerals were leached from the volcanic components of the volcano-sedimentary units, while the Ba and S in barite were leached from the precipitated sulfate minerals or $SO_4^{=}$ ions dissolved in pore water in surrounding volcano-sedimentary units by deep circulation of meteoric water.

Key Words: Koru, Çanakkale, lead, zinc, sulfur, isotope

Koru Kurşun-Çinko Yatağında (Çanakkale, Türkiye) Kükürt ve Kurşun İzotopları Jeokimyası İncelemeleri

Özet: Koru (Çanakkale) kurşun-çinko yatakları Biga Yarımadası'ndaki Tersiyer yaşlı volkanik kayaçlar içinde gözlenenen kurşun-çinko yataklarının tipik örneklerinden birisidir. Yatakların yakın çevresinde yüzeyleyen volkanik kayaçlar; Eosen yaşlı Akçaalan andeziti, Oligosen yaşlı Adadağı piroklastikleri, Miyosen yaşlı Dededağ dasiti ve Pliyo–Kuvaterner yaşlı Karaömerler bazaltı şeklinde ayrılmışlardır.

İnceleme alanı içindeki cevherleşmeler, Adadağı piroklastikleri içinde BKB–DGD konumlu fay hattı boyunca damar tipi ve üst seviyelerdeki ileri derecede breşleşmiş kesimlerde stokvork tipi oluşumlar şeklindedir. Cevherleşmelerde galenit, sfalerit ve barit hakim mineraller olup, pirit, kalkopirit, fahlerz (tennantit), markazit, kalkosin, kovellin, bornit, tenörit ve kuvars az miktarlarda bileşime katılmaktadır.

Kükürt izotop jeokimyası incelemeleri, $\delta^{34}S$ değerlerinin baritlerde $^{o}/_{oo}$ +14.9 ile +17.3 aralığında (ortalama $^{o}/_{oo}$ +16.5), sfaleritlerde $^{o}/_{oo}$ –1.9 ile –0.1 aralığında (ortalama $^{o}/_{oo}$ –1.2), galenitlerde ise $^{o}/_{oo}$ –5.2 ile –3.0 aralığında (ortalama $^{o}/_{oo}$ –3.9) değiştiğini göstermektedir. Barit ve sülfür mineralleri ile denge halindeki H_2S'in izotopsal bileşiminin farklı olması (sırasıyla, $^{o}/_{oo}$ +5.5 ile +7.9 ve $^{o}/_{oo}$ –2.1 ile –0.5), galenit ve sfaleritleri oluşturan çözeltilerdeki kükürtün kökeninin baritlerdekinden farklı olduğunu göstermektedir. Baritlerin $\delta^{34}S$ değerleri, literatürde Tersiyer sonrası deniz suyundaki sülfat ve sedimanlar içinde çökelmiş sülfatlı mineraller için belirlenmiş kükürt izotopları bileşimi ile uyumlu olup, kükürtün bölgede bulunan bu yaşlardaki kayaçlar içinde çökelmiş sülfatlı minerallerden veya bu kayaçların gözeneklerinde hapsolmuş deniz suyu içinde çözülü sülfattan kaynaklandığını işaret etmektedir. Galenit ve sfaleritlerin bileşimindeki kükürtün ise ‰ 0 (sıfır)'a yakın olması nedeniyle bölgedeki volkano-sedimanter kayaçların volkanik bileşenleri ile ilişkili olduğu kabul edilmiştir.

Kurşun izotopları jeokimyası sonuçları yöredeki cevherleşmelerde zenginleşen kurşunun manto kökenli malzemeden çok farklı ve orojenez etkisinde kalmış kıtasal kabukla yakın ilişkili olduğunu göstermektedir. Hesaplanan Pb izotopları model yaş değerleri (70–1 Milyon yıl) cevherleşmelerin olası jeolojik yaş aralığı (Oligosen sonrası) ve çevredeki Eosen–Kuvaterner volkanik ve volkano-sedimanter birimlerin yaşı ile uyuşmakta olup, galenit içindeki kurşunun bu birimlerden kaynaklandığını göstermektedir.

Bu çalışmadaki kükürt ve kurşun izotopları sonuçları ve daha önceki eser element ve nadir toprak elementleri ile yayınlanmamış oksijen ve hidrojen izotop verilerine göre; sülfürlü minerallerin yapısındaki Pb, Zn, Cu ve S'ün çevredeki birimlerin volkanik bileşenlerinden, baritlerin bileşimindeki Ba ve S'ün ise çevredeki volkano-sedimanter birimler içinde çökelmiş sülfatlı minerallerden veya kayaçlar içindeki gözeneklerde hapsolmuş deniz suyu içinde çözülü $SO_4^{=}$ iyonlarından bu birimler içinde dolaşan meteorik kökenli yüzey sularınca çözülerek yataklar içinde çökeltildiği sonucuna varılmıştır.

Anahtar Sözcükler: Koru, Çanakkale, kurşun, çinko, kükürt, izotop

Introduction

Pb-Zn-Cu deposits are widespread in the Biga Peninsula. Some of the deposits hosted by metamorphic rocks show pre-metamorphic occurrences and fingerprints of regional metamorphism, while most of them are vein-type deposits hosted by different rock types belonging to Palaeozoic metamorphics, Permo–Triassic clastic and calcareous rocks and Tertiary volcanic rocks. Authors of the present paper have started to study the geological characteristics, formation conditions and the origin of the vein-type deposits to be able to identify the similarity and differences of the deposits occurred in different units with different lithologies and ages.

This paper reports the first set of data on the isotopic composition of sulfur in sulfide and sulfate minerals and lead isotope characteristics of galena within the ore and deals with the origin of the metals and sulfur in Koru Pb-Zn deposits which are the typical examples of the volcanic hosted vein-type deposits.

These deposits are located near the Koru (Lapseki/Çanakkale) village (Figure 1), and were being mined by Çanakkale Mining Company during the period of the years 1999 and 2001 while the field work of this study was carried out.

The main geological characteristics and genesis of the deposits were investigated by various authors (e.g., Gjelsvik 1956; Dinçer 1958; Tolun & Baykal 1960; Alpan 1968; Ünal 1992; Andıç & Kayhan 1997). Although the views of these authors on the depositional styles of these deposits show differences as vein, stockwork, massive or stratiform, their views on the genesis are concentrated on hydrothermal processes in relation to the volcanic activity within the surrounding area. In addition, Yanagiya & Sato (1989) identified the alteration zones using Landsat TM images in regional scales. Recently, the authors of the present paper carried out some detailed geological investigations on the deposits, including field and underground geology, depositional styles, ore-host rock relations, ore petrography, trace element geochemistry of surrounding rock units, fluid inclusion and stable- (O, H, S) and lead-isotopes. Some of the results have been presented as papers or abstracts (Bozkaya 2001; Bozkaya & Gökce 2001, 2002, 2003). Trace elements and REEs studies (Bozkaya & Gökce 2002); showed that the lead and zinc enriched in Akçaalan andesite, while copper enriched in Dededağ dacite, and normalized REE profiles of barites resemble that of sea water, while those of galena and sphalerite resemble those of volcanic and volcano-sedimentary rocks within the surrounding area.

Geological Background

The study area is located in northeastern part of the Biga Peninsula, covered by metamorphic, igneous and sedimentary units of Permian to Quaternary period. Tertiary volcanic and volcano-sedimentary units crop out in close vicinity of the Koru Pb-Zn deposits. These units are distinguished as Akçaalan andesite (Middle Eocene), Adadağı pyroclastics (Oligocene?), Dededağı dacite (Miocene) and Karaömerler basalt (Plio–Quaternary), and are overlain by Quaternary alluvium (Figures 1 & 2).

Akçaalan andesite (Taa) includes andesite, basaltic andesite, partly rhyodacite and dacite, and contains pyroclastic equivalents and limestone intercalations in the upper parts. Andesites show hypo-hyaline porphyritic texture and consist of phenocrysts of plagioclase, pyroxene (augite and aegirine-augite), rarely hornblende and biotite within a matrix of volcanic glass and microcrystals. The fossil assemblage within the limestone interlayers (*Gypsina* sp., *Assilina* sp., Rotalidae, Gastropod shells, and algae) confirmed middle Eocene age. This unit

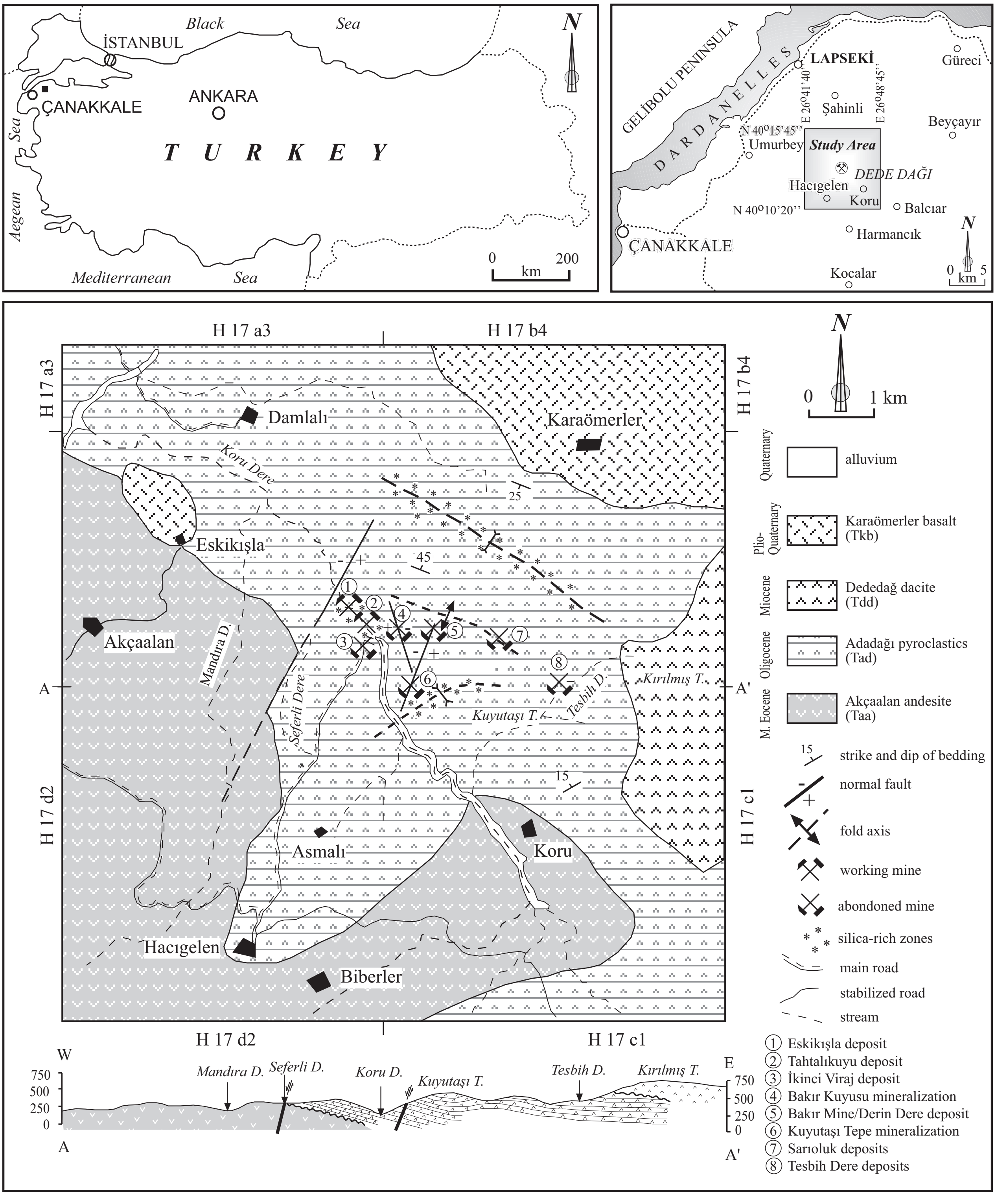

Figure 1. Location and geologic map, and cross section of the study area (Bozkaya 2001).

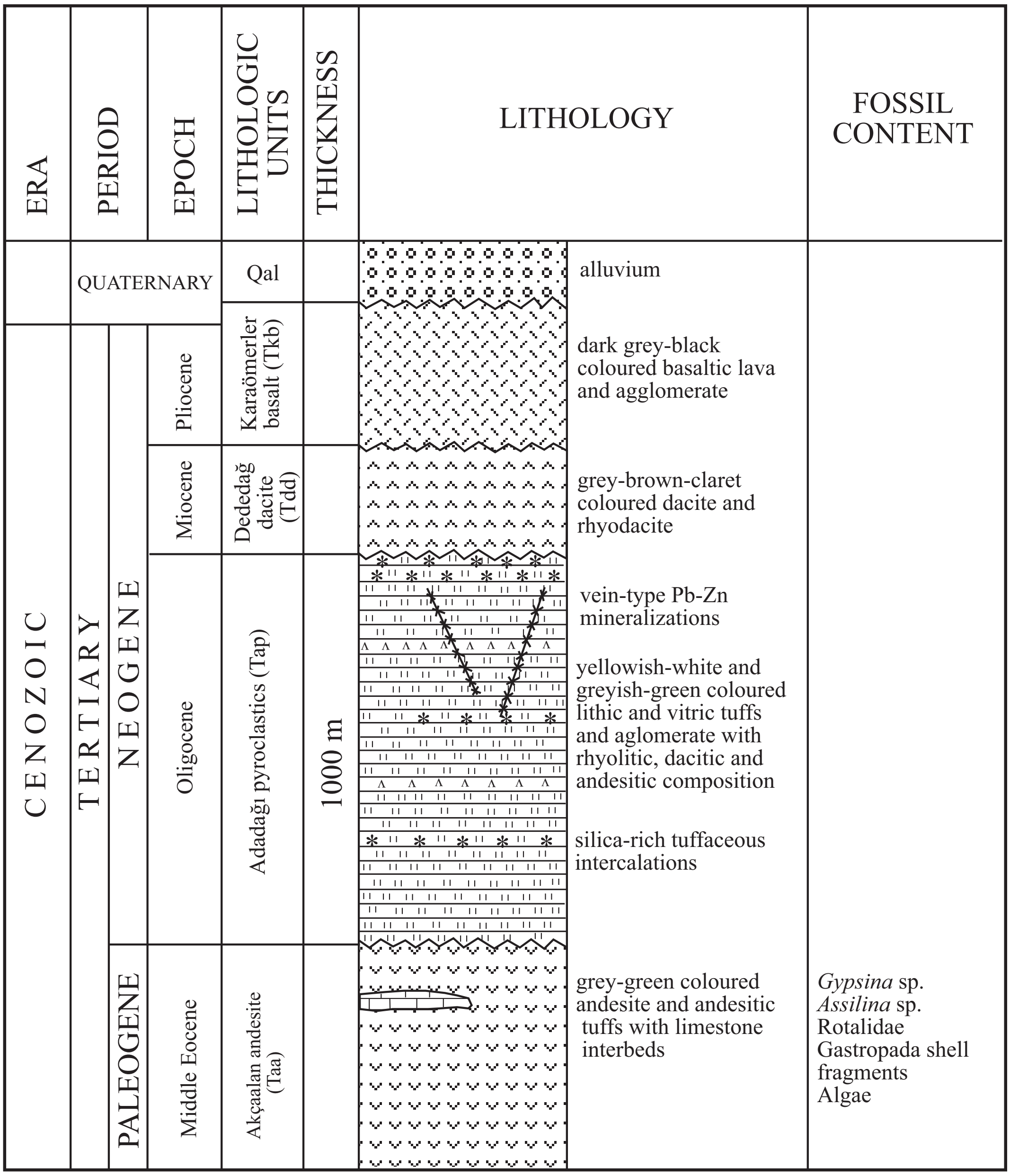

Figure 2. Simplified chronostratigraphic column of the units in the study area.

is separated from the overlying Adadağı pyroclastics by an unconformity and may be assumed as the equivalent of the Balıklıçeşme volcanics described by Ercan *et al.* (1995).

Adadağı pyroclastics (Tap) contain tuffs and agglomerates of trachytic, latitic, dacitic and rhyodacitic composition and lavas with andesitic and dacitic composition. Koru Pb-Zn deposits occurred in these pyroclastics and silicification and kaolinization are developed around the mineralizations. Oligocene age was suggested for this unit because of the stratigraphic position, however no fossil content was identified. This unit may be assumed as the equivalent of the Çan volcanics described by Ercan *et al.* (1995). On the other hand, this unit may be the earlier phase of the following Dededağ dacite unit.

Dededağ dacite (Tdd) consists of dacitic and rarely ryhodacitic lavas with hypo-hyaline porphyritic texture. Matrix is heavily silicified and argillised and phenocrysts of plagioclase, hornblende, biotite, sanidine and quartz are widespread. Although its mineral content and texture are very similar to those of Adadağı pyroclastics, it is identified as a separate unit because of its stratigraphic position. This unit considered as the equivalent of the Behram volcanics described by Ercan *et* al. (1995) and Ezine and Doyran volcanics described by Siyako *et al.* (1989).

Karaömerler basalt (Tkb) cuts the Adadağı pyroclastics and consists of basaltic lavas with hypo-hyaline porphyritic texture. Plagioclase and pyroxene (augite and aegirine-augite) phenocrysts are seen. The age of this unit is assumed as Plio–Quaternary. This unit may be correlated with the Ezine bazalt described by Ercan *et al.* (1995) and Taştepe basalt of Siyako *et al.* (1989) and Okay *et al.* (1990).

All of these units are overlain by unconsolidated detritic materials of alluvium along the drainage net.

Ore Geology

Location of the Known Deposits

Pb-Zn deposits and prospects are known in the locations named as Eskikışla, Tahtalıkuyu, İkinci Viraj, Bakır kuyusu, Derin Dere, Kuyutaşı Tepe, Sarıoluk and Tesbih Dere (Figure 1). The Pb-Zn deposits of Eskikışla and Tahtalıkuyu were the only actively mined ones during the field investigation part of this study, and the investigations were concentrated on these deposits.

Ore Type and Host Rock Relation

The Pb-Zn deposits of Tahtalıkuyu and Eskikışla are the parts of the same deposit mined in two different locations (Figure 1). This deposit is hosted by Adadağı pyroclastics and it is developed as stockwork-type ore at the upper parts while it is formed as vein-type ore at the deeper part (Figure 3). The general direction of the mineralization zone is WNW–ESE.

Stockwork ore occurs as thin veinlets within the porous zones between the rock fragments and pyroclastic materials. The thickness of the veinlets varies from 0.5 to 5 cm. Ore pockets with thickness up to 20 cm are seen within the big caves. Ore veinlets are joined through the lower parts of the stockwork ore and are transformed to vein-type ore. Galena and sphalerite are the visible ore minerals and accompanied by barite and quartz as gangue minerals in macroscopic scales.

Vein-type ore occurred along the fault zones with direction and dip of N60ºW/50ºSW. The thickness of the veins changes from 20 cm to 5 m and it can be followed over 200 m along the direction of the strike. The continuity of the vein to dip side is unknown because of the lack of drilling data, a part about 80 m from surface to 66 m levels has been mined so far. The ore veins were cut and offset by fault of NE–SW direction. Sphalerite, galena, quartz and barite are seen in macroscopic scales. Breccias filling and comb structures are common and the size of the mineral crystals increases in accordance with depth.

Adadağı pyroclastics are heavily altered by hydrothermal fluids, and silicification, kaolinization, alunitization and chloritization are widespread alterations in this unit (Bozkaya *et al.* 2007).

Ore Petrography

The mineral composition of the stockwork and vein-type ores is very simple and similar within the samples collected from the outcrops and mining adits of the Tahtalıkuyu and Eskikışla locations. Sphalerite, galena, pyrite, chalcopyrite, quartz, barite and calcite are the main minerals and they are accompanied by small amounts of fahlore (tennantite), marcasite, covellite and bornite within the polished blocks and thin sections prepared from the representative samples.

Pyrite is widespread in the tuffaceous host rocks as idiomorphic and randomly dispersed crystals. Barite was formed during two different stages and shows two different textures. The first type barites are widespread and are the earliest formed mineral either within the veinlets of stockwork ore or the ore veins. They were mylonitized and replaced by later formed sulfide minerals. The second type barites are scarcely seen as idiomorphic crystals. They were formed later than sulfide minerals. Sphalerite, galena and chalcopyrite occur among the host rock fragments and replace the earlier formed barite crystals. Fahlore occurs in or beside the galena crystals. Quartz and calcite are seen as thin veinlets cutting the earlier formed minerals. Covellite and bornite are seen within the samples collected from the upper levels and occur next to the chalcopyrite crystals.

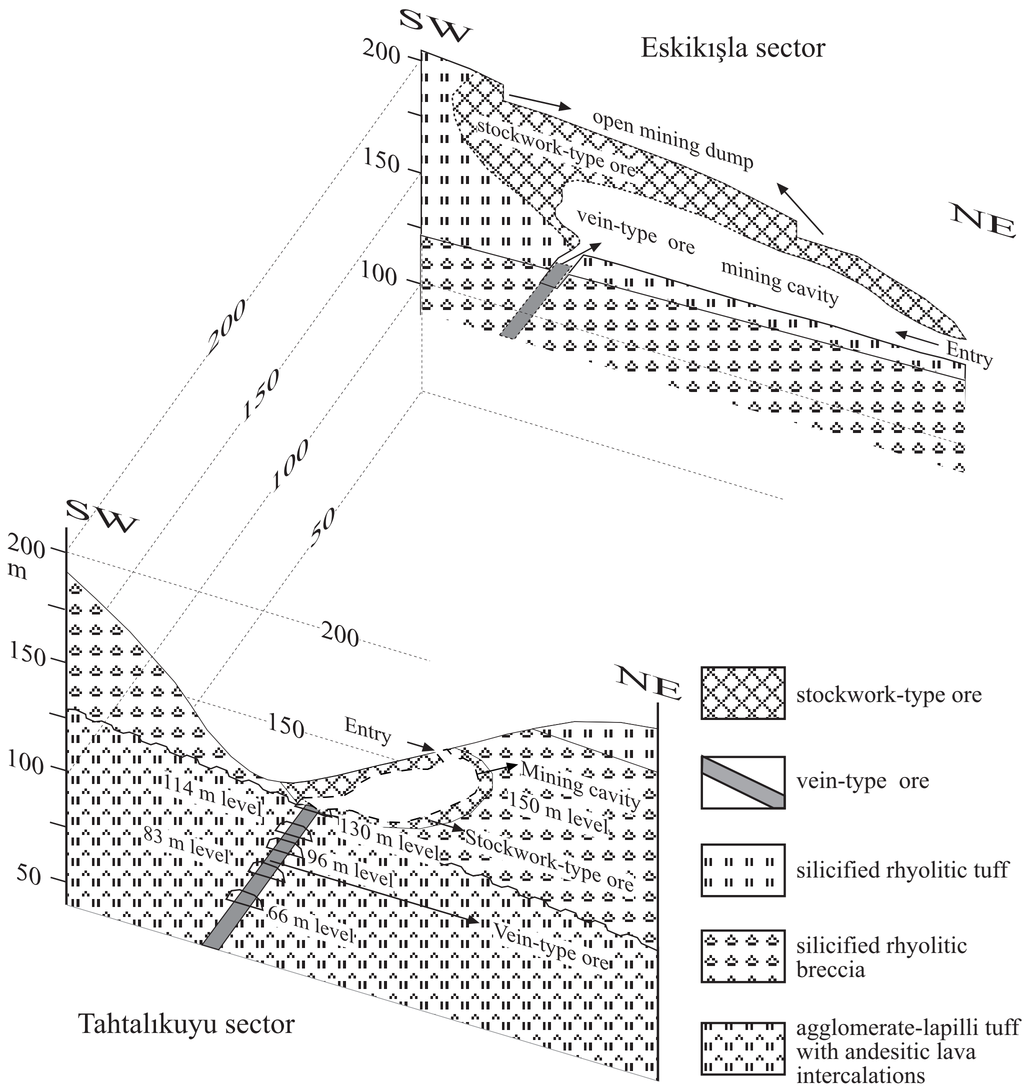

Figure 3. Cross section of the Tahtalıkuyu and Eskikışla sectors.

Sulfur- and Lead Isotope Studies

Analytical Methods

Sulfur-isotope studies were carried out on the galena, sphalerite and barite separates hand-picked from the ore samples representing the various parts of the stockwork and vein-type ores (Table 1). All of the barite samples represent the early phase of barite occurrences.

The sulfur isotope analyses were performed at the Stable Isotope Laboratories of NERC (Keyworth, Nottingham, UK) in the years of 1999 – 2000. Samples of sulfide minerals were prepared for analysis following the method of Robinson & Kusakabe (1975), while the barite samples were prepared following the method of Coleman & Moore (1978). Measurements were performed using a VG SIRA 10 mass spectrometer. The results were reported in the δ notation as per mil (‰) relative to the V-CDT standard (δ^{34}S V-CDT) in Table 1, with an overall analytical reproducibility of ±0.2 ‰.

Lead-isotope analyses were performed on the galena minerals handpicked from the samples collected from the ore veins. Lead isotopic compositions were analyzed in static mode (simultaneous measurement of all isotope ion currents) using Finnigan MAT-261 thermal ionization

Table 1. Sulfur isotope composition of the analysed samples from Koru area.

			δ^{34}S Values		
Sample No	Ore type	Location	Sphalerite	Galena	Barite
EK-6	Vein	(Eskikışla, 130m sublevel)	–1.9	–3.0	–
TK-45	Stockwork	(Tahtalıkuyu, 150m sublevel)	–0.1	–3.4	–
TK-61	Vein	(Tahtalıkuyu, 130m sublevel)	–	–5.2	+17.2
TK-73	Vein	(Tahtalıkuyu, 114m sublevel)	–1.7	–4.0	–
TK-75	Vein	(Tahtalıkuyu, 114m sublevel)	–	–	+17.3
TK-83	Vein	(Tahtalıkuyu, 96m sublevel)	–	–	+14.9

multi-collector mass spectrometer at The Institute for Precambrian Geology and Geochronology, Russia. Lead isotopic ratios presented in Table 2 are corrected for mass fractionation of 0.13% per atomic mass unit calculated from replicate measurements of Pb isotope composition of the US National Institute of Standards (NIST) SRM-982 'equal-atom' Pb isotopic standard. An external reproducibility of lead isotopic ratios of 0.1% for $^{206}Pb/^{204}Pb$, 0.15% for $^{207}Pb/^{204}Pb$, and 0.2% for $^{208}Pb/^{204}Pb$ have been demonstrated at the 2 confidence level through multiple analyses of the US Geological Survey BCR-1 standard. In order to minimize the mass fractionation effects, the measurements of the galena Pb isotope compositions were performed on the constant lead quantities (equal to those measured in NIST SRM-982). This was accomplished through the separation of lead from the galena using ion-exchange columns with a calibrated resin capacity. The NIST standard was run twice with each series of samples. All uncertainties are quoted at the 2 level.

Sulfur Isotope Results and Discussions

Sulfur isotope results show that the $\delta^{34}S_{V\text{-}CDT}$ values of sphalerite, galena and barite change in the range of –1.9 to –0.1 (average –1.2) $^{o}/_{oo}$–5.2 to –3.0 (average –3.9) $^{o}/_{oo}$ and +14.9 to +17.3 (average +16.5) $^{o}/_{oo}$ respectively (Table 1).

The differences between $\delta^{34}S$ values of sphalerite and galena are in accordance with the isotopic fractionation trends between these mineral pairs. The sulfur isotope geothermometric formation temperature of these minerals were calculated as 537 °C for the sample EK-6 (from Eskikışla vein) and as 194 ºC and 286 ºC for the samples TK-45 and TK-73 (from Tahtalıkuyu vein), respectively. The first temperature value is too high for these minerals to crystallize but the latter two values are in accordance with the homogenization temperatures estimated through the fluid inclusion studies (120 to 270 °C; Bozkaya 2001; Bozkaya & Gökçe 2001) for the sulfide mineralization episodes (measured for secondary inclusion in barite and primary inclusion in sphalerite).

Table 2. Lead isotope composition of the analysed samples from Koru area.

Sample No	$^{206}Pb/^{204}Pb$ (*)	$^{207}Pb/^{204}Pb$ (*)	$^{208}Pb/^{204}Pb$ (*)	Model $^{238}U/^{204}Pb$	Model Age (Ma)
TK-6	18.823	15.69	38.862	9.98	42
TK-45	18.812	15.67	38.811	9.89	7.0
TK-61	18.815	15.679	38.842	9.93	24
TK-65	18.828	15.693	38.893	9.99	44
TK-73	18.839	15.709	38.947	10.1	70
TK-80	18.808	15.669	38.81	9.89	8.0
TK-91	18.806	15.665	38.803	9.87	1.0
TK-133	18.815	15.677	38.849	9.92	20

(*); An external reproducibility of lead isotopic ratios is 0.1% for $^{206}Pb/^{204}Pb$, 0.15% for $^{207}Pb/^{204}Pb$, and 0.2% for $^{208}Pb/^{204}Pb$ at the 2σ confidence level.

The calculated $\delta^{34}S$ values of H_2S dissolved within the mineralizing fluid in equilibrium with sphalerite and galena (precipitated at the above-mentioned temperatures) are in the range of –2.1 to –0.5‰ (Table 3). On the other hand, the calculated $\delta^{34}S$ values of inorganically reduced H_2S from barite range from +5.5 to +7.9‰ for the homogenization temperature values of primary inclusion in barite (Table 4). The dissimilarity of the two groups of $\delta^{34}S$ values of H_2S indicate that the sulfurs in sulfide and sulfate minerals precipitated within the ore were derived from different sources. In addition, the large ranges of temperature and of $\delta^{34}S$ values of H_2S may indicate that sphalerites and galenas within the analysed samples were not formed in equilibrium. Sphalerites started to crystallize at about 286 ºC from a fluid with $\delta^{34}S$ values of H_2S about –2.1‰ at the earlier episode of sulfide formation and the galena crystallized at about 194 ºC from a fluid with $\delta^{34}S$ values of H_2S about –0.5 ‰ at the later episode of sulfide formation.

Unpublished preliminary oxygen and hydrogen isotope data of the authors of the present paper indicate a meteoric water source for the water in mineralizing fluids. This suggests leaching of metals and sulfur from the surrounding rock units by deep circulation of meteoric water. Volcano-sedimentary through the $\delta^{34}S$ values of barite are in accordance with those of precipitated gypsum and anhydrite in sediments or $SO_4^{=}$ ions dissolved in sea water of Late Tertiary (in the range of 17.4 to 22.9 ‰; Claypool *et al.* 1980). It is worth to note here that the results of previous studies of the authors (Bozkaya & Gökce 2002) reveal a REE profile for the barites which resembles that of sea water. In this respect, it may be assumed that the sulfur in barite was derived from the precipitated sulfate minerals or $SO_4^{=}$ ions dissolved in pore water in the surrounding volcano-sedimentary units. On the other hand, the $\delta^{34}S$ values of sphalerite, galena and H_2S in equilibrium with these two minerals are close to 0 ‰. Given the results of previous studies (Bozkaya & Gökce 2002) that (i) the lead and zinc are enriched in Akçaalan andesite, while copper is enriched in Dededağ dacite, and (ii) the REE patterns of galena and sphalerite resemble those of volcanic and volcano-sedimentary rocks within the surrounding area, it appears that both the metals and the sulphur in the sulfide ore minerals might have been leached from the volcanic components of the surrounding volcano-sedimentary units.

Lead Isotope Results and Discussions

The presented lead isotope data in Table 2 for 8 galena samples from various parts of the Koru Pb-Zn deposits

Table 3. Sulfur isotope geothermometric temperature (ºC) and $\delta^{34}S$ values of H_2S in equilibrium with sphalerite and galena.

Sample No	$\delta^{34}S$ values of sphalerite	$\delta^{34}S$ values of galena	Sulfur isotope geothermometric temperature (ºC) (*)	$\delta^{34}S$ values of H_2S in equilubrium with sphalerite and galena (*)
EK-6	–1.9	–3.0	537	–2.1
TK-45	–0.1	–3.4	194	–0.6
TK-61	–	–5.2	–	–
TK-73	–1.7	–4.0	286	–2.0

(*) calculated using the related equation suggested by Ohmoto & Rye (1979)

Table 4. $\delta^{34}S$ values of H_2S in equilibrium with barite.

Sample No	$\delta^{34}S$ values of barite	Homogenization temperature for primary inclusions (ºC)	$\delta^{34}S$ values of H_2S in equilubrium with barite (*)
TK-61	+17.2	68.4	+7.83
TK-75	+17.3	62.1	+7.93
TK-83	+14.9	68.7	+5.53

(*) calculated using the equation suggested by Ohmoto & Rye (1979) are dispersed in narrow ranges from 18.806 to 18.839 ($^{206}Pb/^{204}Pb$), 15.670 to 15.709 ($^{207}Pb/^{204}Pb$) and from 38.810 to 38.947 ($^{208}Pb/^{204}Pb$).

These data plot above the Stacey & Kramers (1975) model curves for average crustal Pb-isotope evolution on $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagrams (Figure 4). On the other hand, lead isotope data are close to those of a model orogen and are very different from a mantle-related reservoir of the Plumbo-tectonics model by Zartman & Haines (1988). These observations suggest that the galena Pb was derived from sources with slightly higher than average crustal $^{238}U/^{204}Pb$ (μ) and $^{232}Th/^{204}Pb$ ratios similar to an orogenic reservoir defined by Zartman & Haines (1988).

Calculated Pb-isotope model ages for these deposits by using ISOPLOT program by Ludwig (1997), range from 70 to 1 Ma. This range indicates that lead in galena was derived from different aged sources and it is in accordance with the ages of the surrounding Eocene – Quaternary volcanic and volcano-sedimentary units where the radioactively produced leads might temporarily rested, and with the possible geological age of the mineralization (post Oligocene).

Summary and Conclusions

Tertiary volcanic and volcano-sedimentary units crop out within the close vicinity of the Koru Pb-Zn deposits. These units are distinguished as Akçaalan andesite (Middle Eocene), Adadağı pyroclastics (Oligocene?), Dededağı dacite (Miocene) and Karaömerler basalt (Plio–Quaternary) which are overlain by Quaternary alluvium.

The Pb-Zn deposits in the investigated area are located in various places, but the Tahtalıkuyu and Eskikışla deposits are the only ones mined. The mineralizations in these mines are parts of the same deposit mined in two different locations. This deposit is hosted by Adadağı pyroclastics and developed as stockwork-type ore at the upper parts and as vein type ore at the deeper part. The general direction of the mineralization zone is WNW–ESE.

Sphalerite, galena, pyrite, chalcopyrite, quartz, barite and calcite are the main minerals and they are accompanied by small amounts of fahlore (tennantite), marcasite, covellite and bornite.

Sulfur isotopes indicate that the sulfur in sulfide and sulfate minerals precipitated within the ore were derived from different sources. The similarity of the $\delta^{34}S$ values of barite to those of precipitated sulfate minerals in sediments or $SO_4^{=}$ ions dissolved in sea water of Late Tertiary suggests that the sulfur in barite was derived from the precipitated sulfate minerals or $SO_4^{=}$ ions dissolved in pore water in the surrounding volcano-sedimentary units. On the other hand, proximity of the $\delta^{34}S$ values of sphalerite, galena and H_2S (in equilibrium with these two minerals) to 0 ‰ suggests a relationship between the sulfur in these minerals and the volcanic components of the surrounding volcano-sedimentary units.

Lead isotope data are close to those of a model orogenic reservoir and are very different from a mantle-related reservoir of the Plumbo-tectonics model by Zartman & Haines (1988). Calculated Pb-isotope model ages for these deposits (from 70 to 1 Ma) are in accordance with the possible geological age of the mineralization (post Oligocene) and with the age of surrounding Eocene- Quaternary volcanic and volcano-sedimentary units.

The findings from the S-and Pb- isotope data are in conformity with those from the previous studies of the authors (Bozkaya & Gökçe 2002) that (i) the lead and zinc are enriched in Akçaalan andesite, while copper is enriched in Dededağı dacite, and (ii) REE profiles of barites resemble that of sea water, while those of galena and sphalerite are similar to those of volcanic and volcano-sedimentary rocks within the surrounding area. Furthermore, unpublished oxygen and hydrogen isotope data of the authors suggest a meteoric water source for the water in mineralizing fluid.

In the light of these data, it may be concluded that the Pb, Zn, Cu and S in sulfide minerals were leached from the volcanic components of the volcano-sedimentary units, while the Ba and S in barite were leached from the precipitated sulfate minerals or $SO_4^{=}$ ions dissolved in pore water in the surrounding volcano-sedimentary units by deep circulation of meteoric water.

Within the context of the genesis of Pb-Zn mineralizations, a comparison of the Koru deposits with the other deposits from Turkey and worldwide will be the focus of another manuscript in near future.

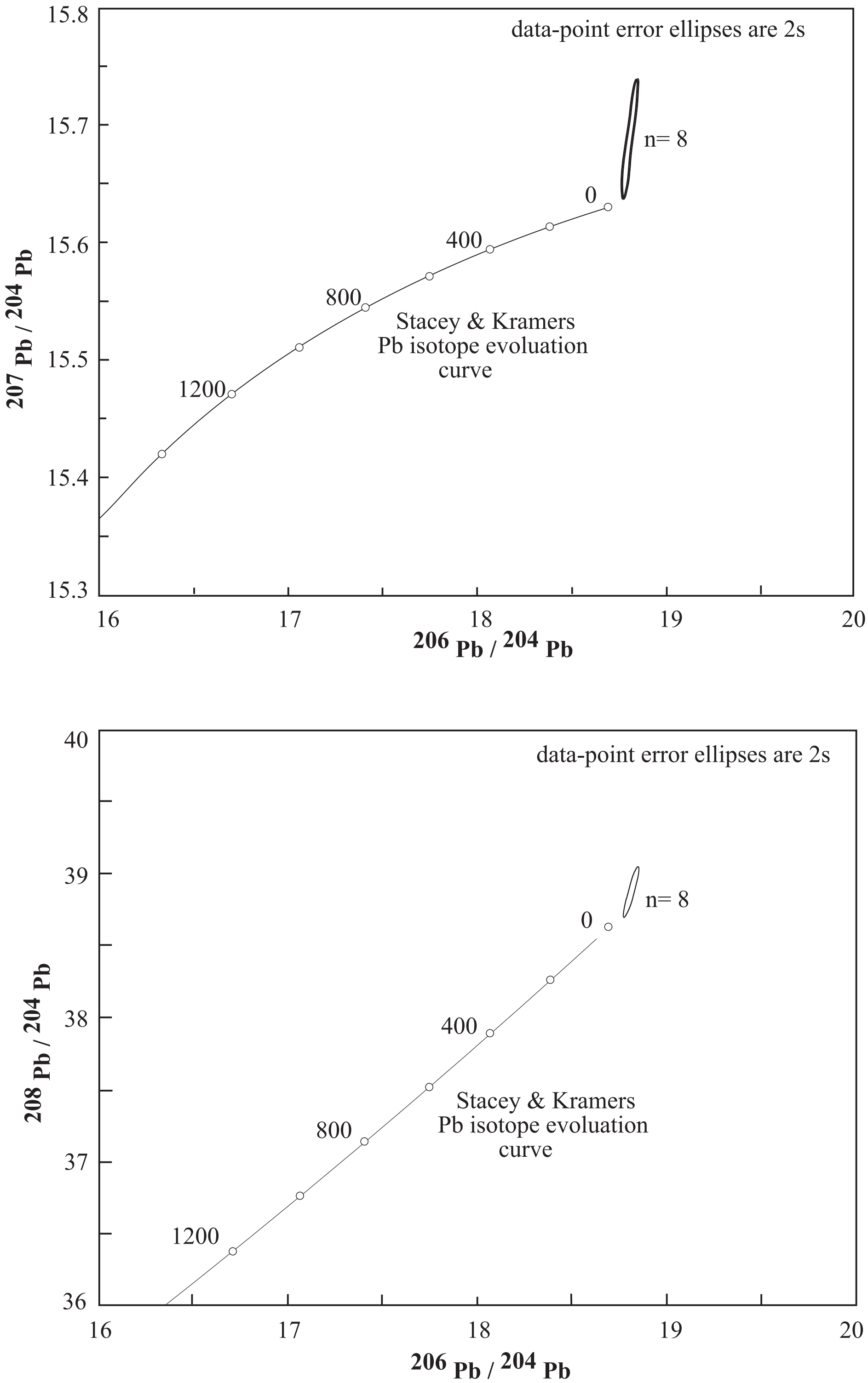

Figure 4. $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ (a) and $^{208}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ (b) diagrams showing lead isotope compositions of galena separates from Koru lead-zinc deposits. Stacey & Kramers (1975) model Pb-isotope evolution curve for average crust are also shown (0, 400, 800, 1200 are ages in million years).

Acknowledgments

The Research Foundation of Cumhuriyet University supported this study (Project No: M-150). Thanks are due to Baruch Spiro (Natural History Museum, London, UK) for sulfur isotope analyses and to Leonid A. Neymark (U.S. Geological Survey, Denver, Colorado, U.S.A.) for lead isotope analyses. David Lowry (Royal Holloway University of London) and the other anonymous referee are kindly thanked for useful comments.

References

ALPAN, T. 1968. *Geology of Koru-Balcılar (Çanakkale) Village*. Technical Reports of the General Directorate of the Mineral Research and Exploration Institute (MTA) of Turkey, Report no. 6840 [in Turkish, unpublished].

ANDIÇ, T. & KAYHAN, F. 1997. *Report on the General Geochemical Research of the Çanakkale-Lapseki.* Technical Reports of the General Directorate of the Mineral Research and Exploration Institute (MTA) of Turkey, Report no. 10059 [in Turkish, unpublished].

BOZKAYA, G. 2001. *Geology of Koru (Çanakkale) Barite Bearing Lead-Zinc Deposits*. PhD Thesis, Cumhuriyet University [in Turkish with English abstract, unpublished].

BOZKAYA, G. & GÖKCE, A. 2001. Geology, ore petrography and fluid inclusion characteristics of the Koru (Çanakkale) Pb-Zn deposits. *Cumhuriyet University Bulletin of the Faculty of Engineering, Series A, Earth Sciences* 18, 55–70 [in Turkish with English abstract].

BOZKAYA, G. & GÖKCE, A. 2002. Major, trace and rare earth elements geochemistry of the Koru (Çanakkale) lead-zinc deposits. *Geological Bulletin of Turkey* 45, 1–17 [in Turkish with English abstract].

BOZKAYA, G. & GÖKCE, A. 2003. Geology, ore petrography and fluid inclusion studies of the Koru (Çanakkale) Pb-Zn deposits. *Abstract of 56th Geological Congress of Turkey*, 92–93 [in Turkish].

BOZKAYA, Ö., BOZKAYA, G., YALÇIN, H. & GÖKÇE, A. 2007. Diagenetic, hydrothermal and surficial alterations in Eocene pyroclastic rocks in the surrounding of Koru Pb-Zn deposits, Çanakkale, Northwest Anatolia. *13th Clay Symposium*, *12–14 September 2007, Isparta-Turkey, Proceedings*, 80–94 [in Turkish].

CLAYPOOL, G.E., HOLSER, W.T., KAPLAN, I.R., SAKAI, H. & ZAK, I. 1980. The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation. *Chemical Geology* 28, 190–260.

COLEMAN, M.L. & MOORE, N.P. 1978. Direct reduction of sulphate to sulphur dioxide for isotopic analysis. *Analytical Chemistry* 50, 1594–1595.

DINÇER, H. 1958. *Barite Mineralizations in Çanakkale-Lapseki-Umurbey.* Technical Reports of the General Directorate of the Mineral Research and Exploration Institute (MTA) of Turkey, Report no. 2485 [in Turkish, unpublished].

ERCAN, T., SATIR, M., STEINITZ, G., DORA, A., SARIFAKIOĞLU, E., ADIS, C., WALTER, H. & YILDIRIM, T. 1995. Characteristic of Tertiary volcanism in the Biga Peninsula and Gökçeada, Bozcaada and Tavşan islands (NW Anatolia). *Mineral Research and Exploration Institute (MTA) of Turkey Bulletin* 117, 55–86 [in Turkish with English abstract].

GJELSVIK, T. 1956. *Research of Ore Deposits Related Alpine Volcanism in the Biga Peninsula, West of Turkey.* Technical Reports of the General Directorate of the Mineral Research and Exploration Institute (MTA) of Turkey, Report no. 2480 [in Turkish with English abstract].

LUDWIG, K.R. 1997. *ISOPLOT: A Plotting and Regression Program for Radiogenic-isotope Data. Version 2.95 (July 1997 Revision).* USGS Open-File Report 91–445.

OHMOTO, H. & RYE, R.O. 1979. Isotopes of sulfur and carbon. *In*: BARNES, H. (ed), *Geochemistry of Hydrothermal Ore Deposits*. 2nd ed., New York, Rinehart and Winston, 509–567.

OKAY, A.İ., SİYAKO, M. & BÜRKAN, K.A. 1990. Geology and tectonic of the Biga Peninsula. *Turkish Associations of Petroleum Geologists Bulletin* 2, 83–121 [in Turkish with English abstract].

ROBINSON, B.W. & KUSAKABE, N. 1975. Quantitative preparation of sulphur dioxide for 32S/34S analysis from sulphides by combustion with cuprous oxide. *Analytical Chemistry* 47, 1149–1181.

SİYAKO, M, BÜRKAN, K.A. & OKAY, A.İ. 1989. Tertiary Geology and Hydrocarbon Potential of the Biga and Gelibolu Peninsulas. *Turkish Associations of Petroleum Geologist Bulletin* 1, 183–199 [in Turkish with English abstract].

STACEY, J.S. & KRAMERS, J.D. 1975. Approximation of the terrestrial lead isotope evolution by a two-stage model. *Earth and Planetary Science Letters* 26, 207–221.

TOLUN, E. & BAYKAL, F. 1960. *The Report of Çanakkale-Lapseki-Umurbey-Koru Cu-Pb-Zn deposits.* Technical Reports of the General Directorate of the Mineral Research and Exploration Institute (MTA) of Turkey, Report no. 456 [in Turkish, unpublished].

ÜNAL, M. 1992. *Mineralogic and Petrographic Investigation of Koru Village (Lapseki-Çanakkale) Lead–Zinc Deposits*. MSc Thesis, Hacettepe University [in Turkish with English abstract, unpublished].

YANAGIYA, K. & SATO, J. 1989. *Report on the Mineral Exploration in the Çanakkale area Republic of Turkey.* Technical Reports of the General Directorate of the Mineral Research and Exploration Institute (MTA) of Turkey, Report no. 8999. Phase I-II [unpublished].

ZARTMAN, R.E. & HAINES, S.M. 1988. The plumbotectonic model for Pb isotopic systematics among major terrestrial reservoirs – A case for bi-directional transport. *Geochimica et Cosmochimica Acta* 52, 1327–1339.