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Sulfur and Lead Isotopic Compositions of the Akgüney (Ordu) Cu-Pb-Zn Deposit in the Black Sea Region, Turkey

Karadeniz Bölgesinde Akgüney (Ordu) Cu-Pb-Zn Yatağının Kükürt ve Kurşun İzotop Bileşimleri

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ABSTRACT
The Akgüney Cu-Pb-Zn deposit is a vein type hydrothermal Cu-Pb-Zn deposit in the Black Sea Region of Turkey. This deposit is hosted by Upper Cretaceous andesitic rocks. The deposit consists of seven veins with varying thicknesses in the investigated area. The primary mineral paragenesis includes pyrite, galena, chalcopyrite, sphalerite, fahlore, quartz and calcite.
The $\delta^{34}S$ values of sulfide minerals (pyrite, chalcopyrite, sphalerite and galena) range from -0.63 ‰ to 3.02 ‰, with an average of 1.22 ‰. These $\delta^{34}S$ values and the calculated $\delta^{34}S_{H2S}$ values for H_2S dissolved in hydrothermal fluids are suggesting a homogeneous magmatic source.
The galena samples have $^{206}Pb/^{204}Pb$ ratios from 18.533 to 18.745, $^{207}Pb/^{204}Pb$ ratios from 15.633 to 15.657 and $^{208}Pb/^{204}Pb$ ratios from 38.710 to 38.772. These values suggest an orogenic source for lead.

Keywords: *Akgüney deposit, Cu-Pb-Zn, Eastern Black Sea region, lead isotope, sulfur isotope.*

ÖZ
Akgüney Cu-Pb-Zn yatağı, Karadeniz Bölgesi'nde bulunan bir damar tipi hidrotermal Cu-Pb-Zn yatağıdır. Bu yatak, Üst Kretase yaşlı andezitik kayaçlar içinde bulunur. Yatak çeşitli kalınlıklarda yedi damardan oluşur. Birincil mineral parajenezi pirit, galenit, kalkopirit, sfalerit, fahlerz, kuvars ve kalsit içerir.

Sülfürlü minerallerin (pirit, kalkopirit, sfalerit ve galenit) $\delta^{34}S$ değerleri -0.63 ‰ ila 3.02 ‰ arasında değişmekte olup ortalama 1.22 ‰'dır. Hidrotermal çözelti içerisindeki H_2S'in hesaplanan $\delta^{34}S_{H2S}$ değerleri ve sülfürlü minerallerin $\delta^{34}S$ değerleri kükürtün kökeninin homojen bir magmatik kaynak olduğunu düşündürmektedir.

Galenit örnekleri $^{206}Pb/^{204}Pb$ için 18.533-18.745, $^{207}Pb/^{204}Pb$ için 15.633-15.657 ve $^{208}Pb/^{204}Pb$ için 38.710-38.772 değerlerine sahiptir. Bu değerler kurşun için orojenik kökenli bir kaynak önermektedir.

Anahtar Kelimeler: *Akgüney yatağı, Doğu Karadeniz bölgesi, Cu-Pb-Zn, kurşun izotopu, kükürt izotopu.*

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INTRODUCTION

The Eastern Pontide region which is one of the major metallogenic belts in Turkey comprises different stratigraphic units ranging in age from Paleozoic to Cenozoic. The region hosts massive sulfide-skarn and vein type deposits. Furthermore, porphyry Cu-Mo and Mn deposits are found in granitic and volcanic rocks, respectively. Massive sulfide deposits of the region are assumed to be of Kuroko type and they are mainly associated with dacitic rock series.

The Akgüney Cu-Pb-Zn deposit is a typical example of volcanic-hosted vein type deposit and is located in the Akgüney Village of Kabadüz District in Ordu Province (Figure 1).

Previous researchers have investigated the geological and mineralogical properties of the deposit (Steinmann and Emerson, 2001; Köse, 1987). Ünal et al. (2009) carried out some geological investigations such as ore petrography, oxygen - hydrogen isotopes and fluid inclusion studies on the Akgüney deposit. According to these authors, the ore-forming fluids contain $CaCl_2$, $MgCl_2$, NaCl and possibly KCl. The salinity values range from 14 to 24 (avr. = 19.0) % NaCl equivalent. The temperature of the fluids were in the range of 276° to 349 °C (avr. 307 °C) at the earlier stages and decreased down to 211°C through later stages of the mineralization. $\delta^{18}O$ – δD isotope data ($\delta^{18}O$ values between + 1.1 and + 4.0‰, δD values between - 94.0 and - 38.0‰) suggest that the ore-forming fluids were mainly meteoric waters and whose oxygen isotopic composition was modified by the interaction with the volcanic host rocks, and they concluded that ore veins were formed by deep circulated meteoric water.

Demir et al. (2015) investigated the mineralogy, mineral chemistry, fluid inclusions and stable isotope characteristics of the Kabadüz ore veins. According to researchers, the homogenization temperatures and salinity of the fluids range from 180 to 436 °C and from 0.4 to 14.7 % NaCl equivalent, respectively. The $\delta^{34}S$ values of sulfides range from 2.14 to 1.47 ‰ while oxygen and hydrogen isotope values range from 7.8-8.5 ‰ and -40-57 ‰, respectively.

This paper reports the sulfur- and lead- isotopes data from galena and accompanying sulfide minerals and deals with the origin of the sulfur and lead deposited in these veins.

GEOLOGICAL BACKGROUND

The investigated area is located in the Pontides orogenic belt. This belt is divided into northern and southern parts according to their geological and tectonic properties (Okay and Şahintürk, 1997; Yılmaz et al., 1997; Okay, 1996). The northern part of the region contains extensive Mesozoic and Cenozoic volcanic rocks while the southern part is characterized by contemporanous sedimentary units or intercalated with volcanic rocks (Eyüboğlu et al., 2014).

Investigated area corresponds to the western part of the Eastern Black Sea Region. Around the Akgüney Cu-Pb-Zn deposits, andesitic rocks crop out. These volcanic rocks were identified as component of Upper Cretaceous Dacitic Series by Akıncı (1985), and named as Upper Cretaceous Mesudiye Formation by Terlemez and Yılmaz (1980).

These rocks occur as interbedded massive lavas and agglomeratic layers. Agglomerates are characterised by tuffaceous matrix whereas massive lavas are lightly brecciated. Additionally, they have dark gray - black colour at the unaltered deeper levels while they are heavily altered at upper levels and show argillization, limonitization and chloritization.

The representative samples of these volcanic rocks were investigated under polarizing microscope, and they were determined to contain quartz, plagioclase, muscovite, biotite and hornblende. Hypo-hyaline porphyritic texture was quite common in samples; in addition, amigdaloidal and pilotaxitic textures were determined in some samples. Chloritization of biotites-hornblendes and sericitization, argillization and silicification of plagioclases are widespread on microscopic scale also. Some samples showed brecciation, and calcite and quartz are determined between brecciated rock fragments.

Positions of fractures indicate that this region is tectonically active and is affected by an N-S trending extensional regime.

ORE GEOLOGY

Mineralizations are formed along fault zones developed in Upper Cretaceous volcanic rocks in the region. Altered quartz veins are numbered D-1, D-2, D-3, D-4, D-5, D-6 and D-7 (Figure 1).

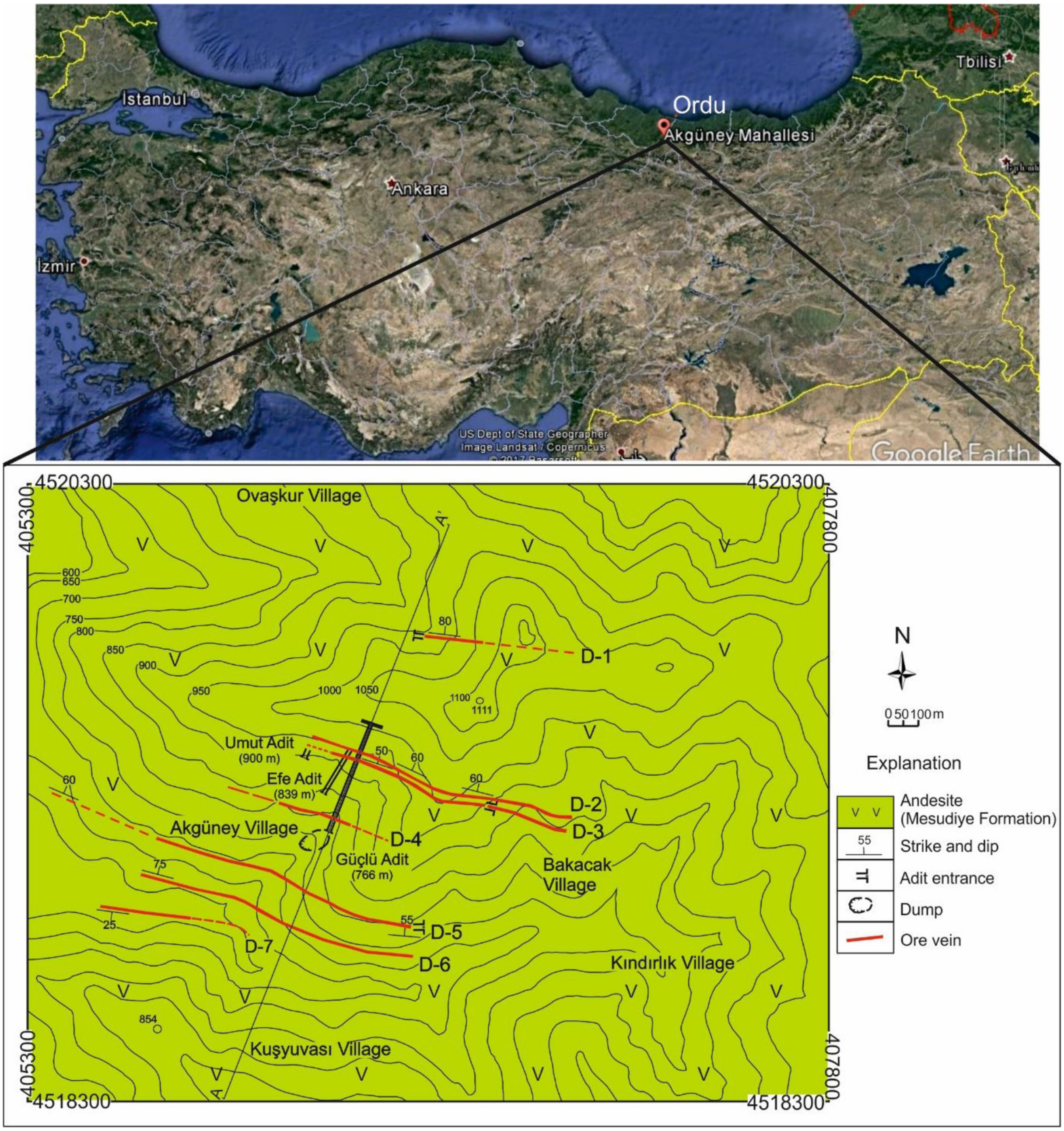


Figure 1. Location and geological map of the Akgüney Cu-Pb-Zn deposits.
Şekil 1. Akgüney Cu-Pb-Zn yatağının yerbulduru ve jeoloji haritası.

Two different types of mineralization were detected in the veins D-2 and D-3 where the mining operation was carried out. Mineralization was characterized by fine-grained and coarse-grained texture within first- and second-type mineralizations, respectively. Whereas the first-type mineralization only contains pyrite, the second-type mineralization contains sphalerite, chalcopyrite, galena, fahlore and limonite together with pyrite. The latter one cuts the first one and they were assumed as early and late stage (1st. and 2nd phase) mineralizations (Figure 2). Additionally, the upper levels of the ore veins are rich in galena and sphalerite, while chalcopyrite and pyrite are enriched in the lower levels.

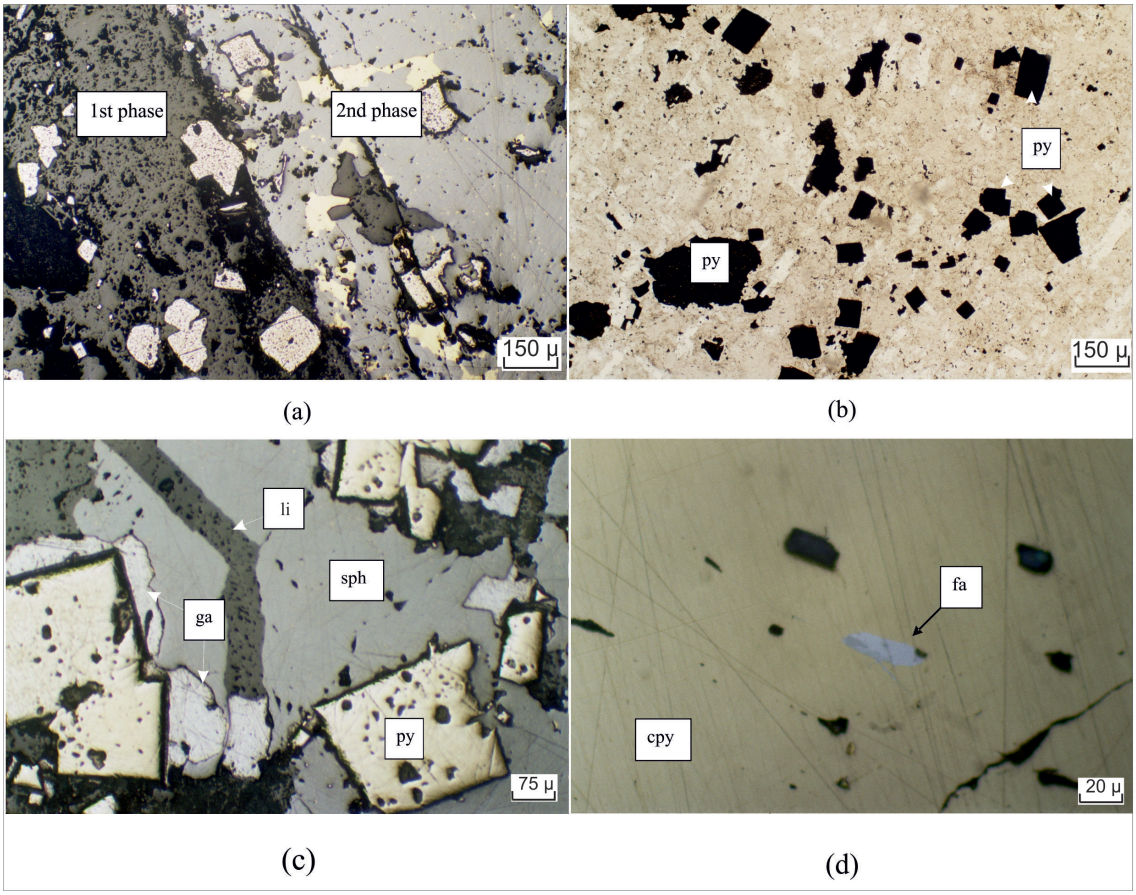


Figure 2. Photo-micrographs of the ore samples: a: views of 1st- and 2nd- type ores, b: the first-type mineralization only contains pyrite (py), c: pyrite (py), sphalerite (sph), galena (ga) and limonitic (li) filling, d: fahlor (fa) inclusion in chalcopyrite (cpy).

Şekil 2. Cevher örneklerinin mikrofotoğrafları: a: 1. ve 2. tip cevherleşmelerin görüntüsü, b: sadece pirit (py) içeren birinci tip cevherleşme, c: pirit (py), sfalerit (sph), galen (ga) ve limonitik (li) dolgu, d: kalkopirit (cpy) içindeki fahlerz (fa) kapanımları.

SULFUR- AND LEAD-ISOTOPE STUDIES

Sampling and Analytical Methods

Sulfur isotope studies were carried out on the sulfide minerals separated from the representative ore samples collected from the investigated ore veins. Unaltered pyrite, chalcopyrite, galena and sphalerite mineral fragments were liberated by crushing, grinding and sieving (-250 - +125 μm) and hand picked under stereo-microscope. Finally, the mineral separates were powdered and the $\delta^{34}S$ ratios were analysed at the Royal Holloway College of London University using a EA1500 elemental analyser connected to VG/Fisons/Micromass 'Isochrom-EA' system that was operated in the continuous He flow mode (Grassineau et al, 2001). The amount of sample analysed depends of the content of sulfur in the sulfide mineral. Quantity as small as 0.5 mg is used for sulfides with 50 wt% of S (pyrite, marcassite), for sulfides containing about 12 - 13 wt% of S, like galena, the quantity analysed is more than 2 mg. The samples are individually crimped in a tin capsule before being dropped in a furnace at 1030 °C. Under helium atmosphere and with the simultaneous introduction of O_2 in the system, the sample is combusted at 1800 °C by flash combustion. The released gases are then oxidized, and the excess of O_2 is absorbed in copper wires. Carried by He, the resulting gases are then separated in a chromatographic column, their peaks measured, and the SO_2 gas is isolated to be directly measured in the mass spectrometer.

A precision of ± 0.1‰ for $\delta^{34}S$ has been obtained on the sulfide minerals. The results are reported relative to Vienna-Canyon Diablo Triolite (V-CDT). One standard is used to monitor the run at the beginning of the day and regularly during the run. Its role is also to check if the absorption of the excess of O_2 is still complete. In addition, six standards have been used for the correction calibration applied to the raw values obtained for the samples. They cover a range of more than 50 ‰, from – 32 to + 20‰. Three of these standards are international, NBS123, NBS127 and IAEA-S3 and the three other ones are working standards, TB3, CP1 and GRU 9G, that have been measured in other laboratories and by conventional lines. One standard is analysed every five samples to check or eventually modify the calibration, and one blank is run every 10 analyses in order to "flush" the system.

For lead isotope studies, galena samples collected from the investigated ore veins were hand-picked under a binoculer microscope. The Pb isotope compositions were analyzed using a multi-collector mass spectrometer instrument (Finnigan MAT – 261) within the Isotope Geochemistry Laboratory (University of Tubingen). The measured Pb isotope ratios were corrected for mass fractionation of 0.145% per atomic mass unit calculated from replicate measurements of Pb isotope composition in NBS SRM–982 standard. External reproducibility of lead isotope ratios $^{206}Pb/^{204}Pb$ = 0.1%, $^{207}Pb/^{204}Pb$ = 0.15%, $^{208}Pb/^{204}Pb$ = 0.2% has been demonstrated through multiple analyses of standard BCR-1. To minimize the effect of mass fractionation, measurements of the Pb isotope compositions of galena were carried out at constant (and equal to those measured in NIST SRM-982) lead concentrations. This was accomplished through the separation of lead from the galena using ion-exchange columns with a calibrated resin capacity (Krogh's method). SRM Standard was run twice with each series of samples. Lead isotope compositions of the duplicate OC-26 were measured using ^{207}Pb + ^{204}Pb double-spike procedure (Woodhead and Hergt 1997) with uncertainty of 0.03%. All uncertainties are quoted at the 2σ level.

Table 1. Sulfur isotope composition of sulfides in the Akgüney Cu-Pb-Zn deposits.
Çizelge 1. Akgüney Cu-Pb-Zn yatağı kükürt izotopları bileşimi.

Sample No:	Location	Mineral	$\delta^{34}S$ ‰ (VCDT)
OC-01	D-7 vein, surface	Sphalerite	1.67
OC-05	D-3 vein, 843m sublevel	Chalcopyrite	1.77
OC-05	D-3 vein, 843m sublevel	Sphalerite	1.50
OC-05	D-3 vein, 843m sublevel	Galena	-0.25
OC-15	D-3 vein, 843m sublevel	Sphalerite	0.75
OC-15	D-3 vein, 843m sublevel	Galena	-0.63
OC-17	D-4 vein, surface	Sphalerite	1.72
OC-17	D-4 vein, surface	Galena	0.60
OC-23	D-3 vein, 766m sublevel	Pyrite	2.42
OC-23	D-3 vein, 766m sublevel	Chalcopyrite	0.91
OC-25	D-3 vein, 766m sublevel	Pyrite	3.02
OC-25	D-3 vein, 766m sublevel	Chalcopyrite	1.17

Results and Discussion

The $\delta^{34}S$ ‰ (V-CDT) results are reported in Table 1. Pyrite separates have $\delta^{34}S$ values ranging from 2.42 to 3.02 (n = 2, avg.= + 2.72‰); while those for chalcopyrite separates from 0.91 to 1.77‰ (n = 3, avg. = + 1.28‰); those for sphalerite separates from 0.75 to 1.72‰ (n = 4, avg. = + 1.41‰) and that for galena separates from -0.63 to 0.60‰ (n = 3, avg. = - 0.09‰). Frequency distribution of the results indicates an homogenous source for sulfur in minerals with small differences (Figure 3).

Lead isotope data for six galena samples from various locations of the ore veins are presented in Table 2. $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios are dispersed in narrow ranges from 18.533 to 18.745, from 15.633 to 15.657 and from 38.710 to 38.772 respectively. The dispersion of these data on $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagrams plot above the Stacey and Kramers (1975) model curves, which simulate average crustal Pb isotope evolution (Figure 4).

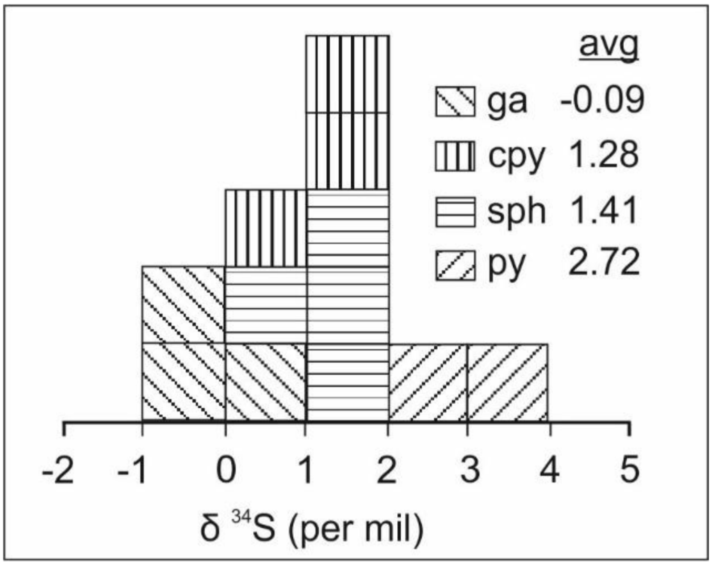
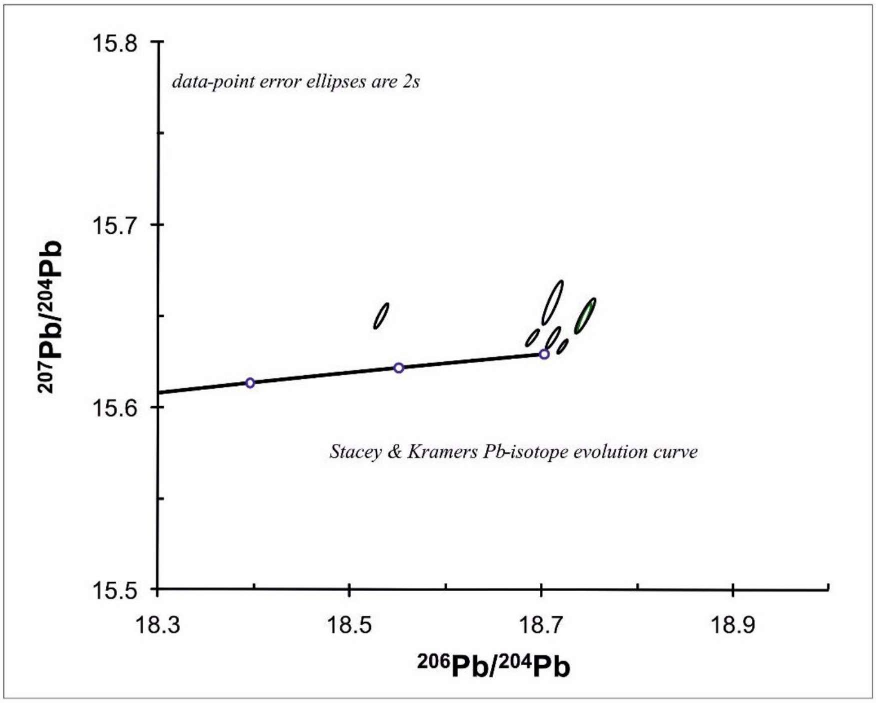


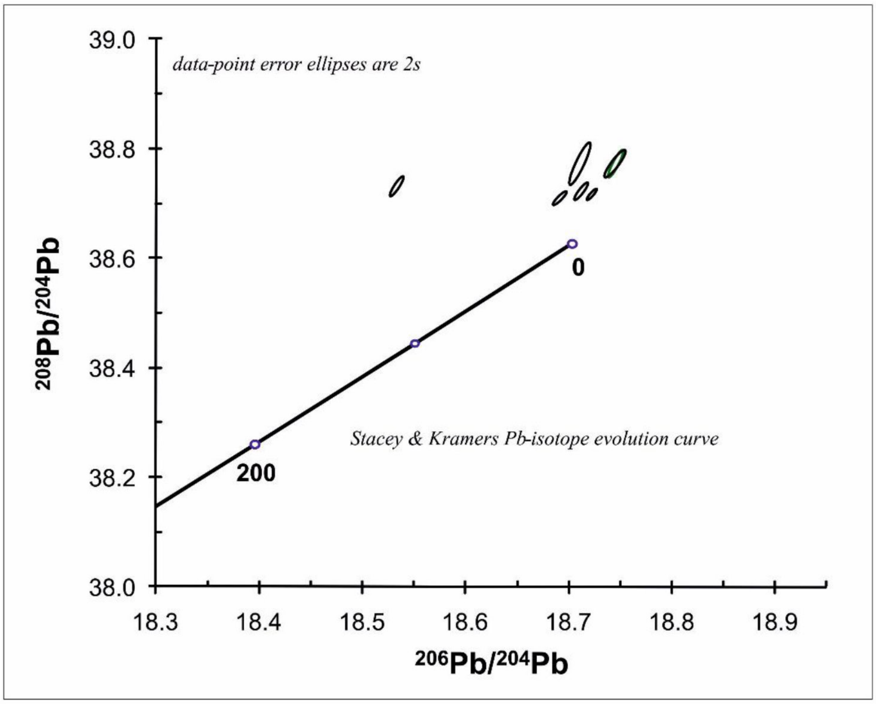
Figure 3. Histogram of sulfur isotope data in the Akgüney Cu-Pb-Zn deposits.
Şekil 3. Akgüney Cu-Pb-Zn yatağı kükürt izotop verilerinin histogramı.

Table 2. Lead isotopic composition of the galena samples from Akgüney Cu-Pb-Zn deposits.
Çizelge 2. Akgüney Cu-Pb-Zn yatağı galenit örneklerinin kurşun izotopları bileşimi.

Sample	206/204	1 SD [%]	207/204	1 SD [%]	208/204	1 SD [%]	Model Age (Ma)	μ
OC-05	18.533	0.015	15.650	0.018	38.731	0.020	174	9.87
OC-07c	18.691	0.014	15.638	0.012	38.710	0.013	29	9.78
OC-15	18.722	0.011	15.633	0.010	38.716	0.010	-5	9.75
OC-17	18.711	0.023	15.657	0.031	38.772	0.041	55	9.86
OC-26	18.745	0.016	15.649	0.020	38.772	0.026	12	9.82
OC-26 (WDH)	18.745	0.023	15.650	0.025	38.772	0.027	14	9.82
OC-27	18.712	0.015	15.638	0.015	38.722	0.016	13	9.78



(a)



(b)

Figure 4. Lead isotopic composition of galena in the Akgüney Cu-Pb-Zn deposits. (a) Diagram of $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ (a) and Diagram of $^{208}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ (b) Model Pb-isotope evolution curve is from Stacey and Kramers (1975).

Şekil 4. Akgüney Cu-Pb-Zn yatağında galenitlerin kurşun izotopları bileşimi. (a) 207Pb / 204Pb'a karşı 206Pb / 204Pb diyagramı ve (b) 206Pb / 204Pb'a karşı 208Pb / 204Pb diyagramı. Pb-izotop gelişim eğrisi modeli Stacey ve Kramers'ten (1975).

$\delta^{34}S$ values of twelve sulfide separates range from -0.63 ‰ to 3.02 ‰, with an average of 1.22 ‰. The differences of the $\delta^{34}S$ values of sulfides of the same samples are in accordance with the expected isotopic fractionation trends of these mineral pairs. The $\delta^{34}S$ value of the H_2S dissolved in hydrothermal mineralizing fluids is expected to be between those of sphalerite and galena; very close to 0.0‰. The similarity of the $\delta^{34}S$ values of the sulfides suggest that the sulfur was derived from the same sulfur reservoir. In addition, the proximity of the $\delta^{34}S$ values to 0.0 ‰ and the abundance of the volcanic rocks within the surrounding region encourage to suggest a magmatic sulfur reservoir; either leached from the surrounding volcanic host rocks or derived from a deep seated plutonic intrusion.

The $\delta^{34}S$ value of sulfides in Akgüney deposits are similar to those of vein type deposits in Kabadüz, İnleryaylası and Kurșunlu lead-zinch deposits (Demir et al. 2015; Gökce and Bozkaya, 2006; Gökce, 1990). The $\delta^{34}S$ values are given from-3.7 ‰ to -8.4 ‰ in Kurșunlu, from -3.9 ‰ to 0.4 ‰ in İnler Yaylası and from 2.14 ‰ to -1.47 ‰ in Kabadüz. These authors also suggest a magmatic source for the sulfur in sulfide minerals within the investigated deposits.

Our $\delta^{34}S$ values of sulfides and estimated $\delta^{34}S$ values of H_2S suggest a homogeneous magmatic source, with sulfur produced directly by magmas or by derived from surrounding volcanic rocks.

Six galena have $^{206}Pb/^{204}Pb$ ratios from 18.533 to 18.745, $^{207}Pb/^{204}Pb$ ratios from 15.633 to 15.657 and $^{208}Pb/^{204}Pb$ ratios from 38.710 to 38.772. These values plot on the $^{207}Pb/^{204}Pb$ versues $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ versues $^{206}Pb/^{204}Pb$ diagrams above of average crustal Pb isotope evolution curve. In addition, these isotope ratios mentioned indicate the orogenic origin lead when compared with the values determined for possible sources by Zartman and Haines (1988).

Except two values (175 and - 5 Ma), calculated Pb-isotope model ages of these deposits have range from 55 to 12 Ma. At that rate, it can be said that the mineralization occurs between Eocene and Miocene. The value of - 5 Ma can be assumed as J type lead whereas the value of 175 Ma., may represent the leaching of lead from Jurassic volcanics in the area.

Lead isotope data are close to those of orogene reservoir of distal and proximal characteristics concluded by Zartman and Haines (1988), and possibly very little amounth of lead derived from a mantle releated reservoir may be included.

CONCLUSIONS

The Akgüney Cu-Pb-Zn deposit is a vein typemineralization within the Upper Cretaceous andesites.

The sulfur isotope data (values from -0.63 ‰ to 3.02 ‰, n=12) suggest a magmatic origin for the sulfur in sulfide minerals, while the lead isotope data suggest an orogene reservoir for lead in galenas, and the age of 175 Ma suggests a possible Jurassic source for lead in galena. In the light of these data, it may be conluded that the ore veins were formed by deep circulated meteoric water. The sulfur in sulfide minerals was leached from volcanic rocks widespread within the surrounding area, while the lead was possibly leached from a Jurassic reservoir. Jurassic volcanics and/or massive sulfide enrichments occured in these volcanics are likly to be the source of both components of sulfide minerals.

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