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Age and source of the Küre/Ödemiş arsenopyrite-gold mineralization (Menderes Massif, Turkey) determined by Re-Os-He isotopes

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Abstract

The Menderes Massif (MM) is considered to be one of the principal regions hosting vein-type quartz-arsenopyrite orogenic gold deposits and occurrences in Turkey. Gold mineralizations in the MM can be grouped into: (i) schistosity-conformable E-trending veins and (ii) shear-controlled NW-trending veins. Arsenopyrite is one of the major gold-bearing minerals in these deposits or occurrences. Rhenium–Osmium isotopic dating of two types of arsenopyrite from the schistosity-conformable and vein-type Küre (Ödemiş) gold deposit has yielded two groups of model ages (maximum ages) at 557-574 Ma and 246-250 Ma, respectively. The data suggested that the quartz-arsenopyrite gold deposit formed in the Neoproterozoic and Early Triassic, with the former and the latter corresponding to Pan-African compressional orogenesis and Palotethys rifting, respectively. Fluid inclusions in Küre arsenopyrite have $^3\text{He}/^4\text{He}$ ratios of $\sim 0.08\text{--}0.09$ Ra ($\text{Ra}=1.39\times 10^{-6}$, the $^3\text{He}/^4\text{He}$ ratio of air) being within the range of middle to upper crustal values. A minor helium contribution of mantle fluids to the Küre gold deposit is possible because the ^4He concentrations in arsenopyrite are enriched 170 to 9520 times relative to argon and typical atmospheric values, indicating that contribution of atmospheric He to the mineralizing fluids is negligible, and $0.08\text{--}0.09$ Ra is slightly above typical crustal $^3\text{He}/^4\text{He}$ ratios. Arsenopyrite yields relatively non-radiogenic initial Os isotopic compositions, also indicating possible contribution from mantle fluids.

Carbonic fluid inclusion type-2 ($\text{H}_2\text{O}-\text{CO}_2-\text{NaCl} \pm \text{CH}_4$) in quartz of NW-trending veins at Küre are gas-liquid-hydrate-crystal-rich and their homogenization temperatures (T_h) range from 244 to 387 °C. Salinity values range from 0.2 to 5.7 wt.% NaCl equiv. The homogenization temperatures (T_h) of aqueous fluid inclusions type 1 ($\text{H}_2\text{O}-\text{NaCl}$) in quartz from NW-trending veins at Küre vary between 237 and 358 °C whereas salinity values range from 1.7 to 7.7 wt.% NaCl equiv. Quantitative EPMA spot analyses on arsenopyrite minerals have shown that As concentrations in EW-trending and NW-trending veins range from 32.5 to 33.8% and 32.3-33.8%, respectively. Based on a phase diagram for the Fe–As–S system along with the arsenopyrite geothermometer, the ranges of temperature and corresponding $\log f \text{S}_2$, at which arsenopyrite is in equilibrium with pyrite are between 380 and 480 °C, and -7.4 and -4.3 for Apy-1, respectively. These values are between 390 and 475 °C, and -7.0 and -4.5 for Apy-2, respectively.

Key words: Re–Os geochronology; noble gas isotopes; orogenic gold-arsenopyrite Küre; Menderes Massif; Turkey

1. Introduction

Orogenic gold deposits are estimated to have supplied about 30 percent of world production of gold (Frimmel, 2008; Bierlein et al., 2009). These deposits are formed within active continental margins in orogenic belts where major tectonic boundaries juxtapose metamorphosed volcanic-plutonic and sedimentary terranes (Bierlein et al., 2006; Goldfarb et al., 2001; Groves et al., 2005). They have variations in isotopic composition, mineral assemblage, and metal enrichments (Goldfarb and Groves, 2015; Groves et al., 1998; Spence-Jones et al., 2018). Gold deposits in metamorphic belts are generally accepted as the dominant style and are represented by orogenic gold deposits, as defined by Groves et al. (1998) (Phillips and Powell, 1993; Robert and Poulsen, 1997; Sillitoe and Thompson, 1998; Poulsen et al., 2000;

Kerrich and Cassidy, 1994; Goldfarb et al., 2001; Bierlein et al. 2004). Country rocks are most commonly regionally metamorphosed into belts with extensive greenschist through lower-amphibolite facies rocks (Groves et al., 2003). Such ore deposition has been considered to most typically occur in rocks of favorable rheology close to the brittle–ductile transition within a late-orogenic tectonic setting characterized by regional uplift (Goldfarb et al., 1986; Groves et al., 1987; Phillips et al., 1996; White et al., 2015) and changing far-field stresses (Goldfarb et al., 2007; Goldfarb and Groves, 2015).

Gold is commonly associated with arsenopyrite minerals within numerous quartz-arsenopyrite vein systems in several locations throughout the MM, e.g Koçarlı (MTA, 1970, 1979; Eurogold Company, 1992), Zeytinlik-Elmacı-Kemer-Yılanlıkaya (Çağatay, 1979; Akiska et al., 2008), Emirli (Akçay et al., 2006), Küre (MTA, 1979), Çavuşlar, Dervişli, Güneyköy (MTA, 1979; Ege Madencilik Company, 2011) and Cemalçavuş (Yılmaz et al., 2015; Fig. 1). Many researchers have highlighted the exploration potential of the MM including mineralizations of Au, Sb, As, Hg and have largely dealt with geology and mineralogy (e.g., İleri and Köksoy, 1977; Özocak, 1977; Çağatay and Eyyüboğlu, 1979; Larson and Erler, 1993; Gökçe and Spiro, 1995; Akiska et al., 2008; Yiğit, 2006, 2009). However, very few studies have been carried out in sufficient detail (e.g., Özgür et al., 1997; Özgür, 2003; Akçay et al., 2006 in the Emirli Sb-As-Au and Halıköy Hg-Sb deposits). Uskut (1977) reported that the major ore mineral of the Küre deposit was arsenopyrite with minor pyrite and suggested that this ore deposit was formed under pneumatolytic temperature conditions. He also suggested that sulfur isotope values indicated a magmatic origin of the MM Küre deposit, with a probable genetic connection to Miocene granodiorite of calcalkaline magmatic affinity. MTA (1979) reported that the Küre deposit was hydrothermal origin and consisted of small and discontinuous veins/veinlets with common ore grades of 1 to 8 g/t and a small reserve of 230 kg Au. Çağatay and Eyyüboğlu (1979) proposed that the epigenetic hydrothermal gold-

arsenopyrite veins, which were located in the vicinity of Ödemiş, were formed by metamorphism and elemental remobilization, e.g. Au and As. Yiğit (2006, 2009), have stated that the origin of the arsenopyrite-rich gold-quartz veins in the MM is debated since they are thought to be remobilized and overprinted by later orogenic events, e.g., Küre prospect.

The purpose of this study is to evaluate the relationship between juvenile crust generation and arsenopyrite-gold deposition at the Küre (Ödemiş) deposit by constraining the timing of a major gold mineralizing events, age comparisons with regional magmatic events as well as new isotopic constraints on the source of metal (Os) and fluid (He) components of the ore system.

Because of the siderophile and chalcophile nature of Re and Os they can partition into ore metals and sulfides from magmas and hydrothermal fluids (e.g., Shirey and Walker, 1998). This has allowed the successful implementation of the Re-Os isotopic system to a number of different ore deposit types and minerals. Using the Re-Os system directly on sulfide and/or ore-bearing minerals, there is no need to infer the sources from the silicates, which may exhibit a more complex history (e.g., Barra et al., 2003). Large differences in $^{187}\text{Os}/^{188}\text{Os}$ ratios of the average upper continental crust (≥ 1.26 ; Esser and Turekian, 1993) compared to the chondritic ratio of the mantle (≈ 0.13 ; Meisel et al., 2001) can be used to readily differentiate between various reservoirs of osmium and, by inference, the sulfide minerals, which contain the osmium.

The conventional behavior of helium and the variation in isotopic composition within the crust ($^3\text{He}/^4\text{He} = 0.02 \text{ Ra}$ on average, where $\text{Ra} = 1.39 \times 10^{-6}$ is the $^3\text{He}/^4\text{He}$ ratio of air), helium in the mantle ($^3\text{He}/^4\text{He} = 6\text{--}30 \text{ Ra}$) and the atmosphere ($^3\text{He}/^4\text{He} = 1 \text{ Ra}$) makes it an important tool for the identification of the sources of the fluids introduced during mineralization as well as interactions between these fluids and the country rocks (Ozima and Podosek, 2002; Levresse et al., 2004). Therefore, $^3\text{He}/^4\text{He}$ ratios showing excesses of ^3He relative to typical crustal fluids may strongly suggest the contribution of mantle volatiles to fluids trapped in the analyzed minerals (Levresse et al., 2004). For instance, helium isotope analyses of sulfides and gangue

minerals in the giant Imiter epithermal silver deposit (Morocco) yielded $^3\text{He}/^4\text{He}$ ratios ranging from 0.76 to 2.64Ra. These data suggested a mantle origin for the fluids associated with the epithermal silver event (Levresse et al., 2004). Similarly, noble gas isotopic analyses of scheelite showed that the ore-forming fluid of the Daping mine (Yunnan/China) was a mixture of mantle-derived fluids and crustal fluids, since $^3\text{He}/^4\text{He}$ ratios were 0.706–1.018 Ra, with an average of 0.898 Ra (Sun et al., 2009).

2. Geological setting of the Menderes Massif

The MM consists predominantly of a Late Neoproterozoic–Early Cambrian basement, which is unconformably overlain by Paleozoic–early Cenozoic cover series (Figs. 1A, B; Candan et al., 2011; Koralay et al., 2012). The high-grade metaclastic sequence unit occurring at the lower levels of the sequence form the oldest unit of the basement. This sequence can be divided into two subunits; locally migmatized paragneisses and conformably overlying schist unit (Dora et al., 2001; Candan et al., 2011c; Koralay et al., 2012). Relic mineral assemblages observed in the basement rocks reveal a complex polyphase metamorphic evolution under granulite-eclogite- and amphibolite-facies conditions. Geochronological data indicated that the depositional age of the protoliths of the paragneiss-schist sequence was confined to 600–590 Ma, i.e., Ediacaran (Koralay et al., 2012). Zlatkin et al (2013) suggested this age interval was younger at 570–550 Ma.

Geological and geochronological data reveal the presence of three periods of magmatic activities: These are (i) Neoproterozoic–Cambrian, (ii) Triassic and (iii) Miocene.

(i) Neoproterozoic–Cambrian magmatic activities: These activities are the most extensive and most complex magmatic activities influencing the basement rocks in the MM. Magmatic activities in this period, from older to younger, consist of orthopyroxene-bearing orthogneisses (charnockites), metagabbros-metanorites, anatectic granites and orthogneisses. Several

different types of orthogneisses (granitoids) intruding the metaclastic sequence have been distinguished based on the mineralogical compositions and textural properties; metagranite, biotite orthogneiss, leucocratic tourmaline orthogneiss and amphibole orthogneiss (Bozkurt et al., 2006; Candan et al., 2011; Koralay et al., 2011, 2012). The orthogneisses, which are interpreted as syn- to post-intrusions, are related to the Late Neoproterozoic amalgamation of Gondwana (Hetzl and Reischmann, 1996; Candan et al., 2011; Koralay et al., 2011, 2012).

(ii) Triassic magmatic activities: The second most extensive magmatism observed in the MM is Triassic leucocratic orthogneisses cut into the Precambrian basement rocks and Permian Carboniferous cover units with intrusive contacts (Akkök, 1983; Candan, 1994, Koralay et al., 2011). If the amphibolite, which are located at the base of the Mesozoic platform (Güngör and Erdoğan, 2002) and characterizes a possible Triassic basaltic volcanism excluded, the Triassic magmatism is dominantly represented by leucocratic orthogneisses in the MM. Triassic magmatism is not limited only to the MM but is also observed in all units belonging to the Anatolides, and is associated with a regional tectonic event.

(iii) Miocene magmatic activities: The Miocene magmatic activities in the MM are represented mainly by granitoid intrusions and volcanism (Ersoy et al. 2011, references therein). They are most commonly observed in the northern and central submassifs. Granitoid intrusions such as Alaçamdağ, Koyunoba and Salihli granites accompany to low-angle normal faults that occurred during the exhumation of the MM (Erkül & Erkül, 2012, references therein).

Recent findings indicate that the main metamorphic events, shaping the Precambrian basement of the MM, are related to the Kuunga orogeny (Koralay, 2015; Candan et al., 2016), whereas Alpine metamorphism leads to limited retrograde events in this basement rocks (Candan et al. 2011). Relict mineral assemblages characterizing granulite (730-760 °C and 6 Kbar), eclogite and amphibolite facies conditions were identified in the Precambrian basement of the MM (Candan and Dora, 1998; Candan et al., 2011). The remnants of high-pressure

metamorphism are characterized by eclogites and eclogitic metagabbros yielding 644 °C and minimum of 15 Kbar P-T conditions corresponding to a burial depth of about 50 km (Candan et al. 2016). Barrovian-type medium-pressure metamorphism resulting in the development of anatectic granites and migmatization has caused the retrograde metamorphism (628°C and 7 Kbar) of granulites and eclogites. Both core and cover series of the MM were affected by the regional metamorphism of Alpine age. Metasediments associated with the cover series of the MM contain pervasive amphibolite-facies metamorphism peaking at ca. 625–670 °C and 7–9 Kbar.

3. Metallogenic features of the Menderes Massif

3. 1. Regional gold feature

Within the Menderes Massif and apart from our study area, several gold-arsenopyrite deposits or occurrences (Table 1) have been reported (e.g., Çağatay and Eyyüboğlu, 1979; MTA, 1970, 1979; Eurogold Company, 1992; Akiska et al., 2008; Sönmez, 2013; Yılmaz et al., 2015; Fig. 1). Yiğit (2006, 2009) suggested that the exact origins of the orogenic gold deposits in the MM are obscured due to remobilization during later Alpine orogenic events, causing epithermal signatures in some deposits, such as Küre and Emirli mineralizations. At least two different events affected orogenic gold deposits in the MM: a low temperature remobilization during Cenozoic metamorphism associated with core complex formation as well as epithermal mineralization related to active and extinct geothermal systems formed during an extensional tectonic regime in the Neogene-Quaternary (Yiğit, 2006). Yılmaz et al. (2015) recently discovered an uneconomic orogenic gold deposit at Cemalçavuş and presented a detailed description of mineralization. According to the authors, two styles of mineralizations exhibit the following characteristics: (i) schistosity-conformable quartz–pyrite–arsenopyrite veinlets or breccias and disseminations with vug-infill, euhedral- and comb-quartz textures

representing deeper levels of an epithermal system; and (ii) minor epithermal quartz veinlets (max. 20 cm wide) with Mn-oxide stains and crustiform, carbonate replacement and vug-in-fill textures cutting schistosity planes. Dark gray, schistosity conformable, pyrite–arsenopyrite–Au–Ag or rare pyrite–arsenopyrite with minor galena-sphalerite-stibnite-rich quartz-vein breccias or veins (i.e., first mineralization style) of up to 3 m in thickness with 400 m strike length were found. They suggested that these multi-level mineralizations appeared to have been controlled by the schistosity or shear planes of the schists and occurred mainly as fracture fillings, crackle breccias and disseminations.

Several gold-bearing quartz-arsenopyrite veins or veinlets of 2-100 cm thick x 2-150 m long grading up to 129 g/t Au were recognized in the basement rocks of the MM located in the vicinity of Karacaören, Arpatarlası, Ören, Akçaabat, Sobucudağ, Karaagaç and Gölcük villages (Fig. 1) south of Koçarlı (Aydın province). The veins having 1 m thickness and 100 m strike length near Ören and Karaagaç returned channel rockchip results up to 39 g/t Au (Eurogold Company, 1992). Arsenopyrite-quartz, irregularly distributed, pocket-like massive arsenopyrite veins or veinlet clusters and disseminated arsenopyrite in schistosity-conformable quartz veins with maximum dimensions of 0.9 x 5m, yielding gold grades ranging from 2 to 20 g/t Au (MTA, 1970; 1979) are commonly hosted by mica schists and amphibolites around the Arıkbaşı, Zeytinlik, Elmacı, Kemer and Yılanlıkaya villages in the central part of the MM (Fig. 1). Magnetite, pyrrhotite, pyrite, scheelite, chalcopyrite, bismuthinite, marcasite, covellite and gold accompany arsenopyrite (Çağatay and Eyyüboğlu, 1979; Akiska et al., 2008). The authors pointed out that mineralizations in the region may have been related to already-metamorphosed basic magmatic rocks, and fluids in successive acidic stages. These primary mineralizations were remobilized during further metamorphism and probable granitic intrusions.

Stibnite mineralization in the Emirli deposit occurs as stratabound lenses in graphite- and mica-schist, and as structurally controlled veins (Akçay et al., 2006). Its mineral paragenesis

consists of quartz, pyrite, arsenopyrite, stibnite, gold, base metal sulfides, marcasite, realgar, orpiment and cinnabar. The authors suggested that the initial fluids were dilute, carbonic and rather hot ($T > 300\text{ }^{\circ}\text{C}$). Pyrite and arsenopyrite precipitation is probably due to cooling of the fluids and to sulfidation and/or decreasing $f\text{O}_2$, caused by interaction with syn-sedimentary sulfides in the country rocks. Arsenopyrite geothermometry indicates an average depositional temperature of $330\text{ }^{\circ}\text{C}$ in the initial quartz vein (Akçay et al., 2006). Fluids forming these deposits are of magmatic and meteoric origin, and the source rocks for ore-forming metals (As, Sb, Hg, Au, Ag, Cu, Pb and Zn) are the mica schists of almandine-amphibolite facies (Özgür et al., 1997; Özgür, 2003).

Fracture-controlled and schistosity-conformable mineralizations occur in the vicinity of Çavuslar, İsmailler, Dervişli, Güneykoy and Balabancı villages on the NE of the MM (Fig. 1) as massive quartz-arsenopyrite veins with maximum dimensions of $1\text{ m} \times 50\text{ m}$, forming in and adjacent to faults within sheared gneisses and schists (Ege Madencilik Company report, 2011). There are several generations of mineralized highly fractured veins, all of which contain mainly quartz, arsenopyrite and pyrite. Gold is irregular in occurrence but occurs in close proximity to sulfides, i.e. arsenopyrite. Some veins, principally within the footwall shear, have undergone brittle to ductile deformation and occur as elongate lens-like bodies along the host structures. Highly fractured veins by shear deformation are the most common, and occur in a wide variety of orientations. Some veins contain breccias, which are occasionally partly or wholly silicified. Minor post-mineralization breccias occur along many vein margins. Arsenopyrite boudin structures occur within strongly sheared mica schists or gneisses. Rockchips from these veins (Balabancı) returned Au, Ag and As values up to 266 g/t , 42.7 g/t and 36.5% , respectively (20 cm thick $\times$ 5 m long). Schistosity-semiconformable quartz-arsenopyrite veins (i.e. 30 cm thick and 5 m long) within the shear zones of mica schists yielded Au values of up to 33.1 g/t from two outcrop rockchip samples at Davutlar (Fig. 1).

232

233 3. 2. *Geology of Küre gold deposit*

234 3. 2. 1. *Geology of Küre area*

235 The study area consists mainly of two tectonic units, which belong to the late
236 Neoproterozoic basement rocks of the MM (Koralay, 2015). Metaclastic rocks (garnet-mica
237 schists) of the Neoproterozoic basement are located in the S-SE and N-NE parts of the study
238 area (Fig. 2). The granulite facies rocks occur as a klippe resting on these metaclastics. The
239 metaclastics hosting the gold-rich arsenopyrite ore consist predominantly of garnet-mica schist
240 and mica schists with minor amphibolite. The mineral composition of schists is quartz,
241 plagioclase, biotite, muscovite, $\pm$ garnet, $\pm$ chlorite, $\pm$ sericite, zircon, apatite and opaque
242 phases. The klippe is consisted of paragneiss/schists intercalations, orthopyroxene orthogneiss,
243 migmatite and metagabbro (Candan, 1995; Koralay, 2015). Koralay (2015) indicated that
244 orthopyroxene orthogneisses shows granodioritic composition. These high temperature rocks
245 are intruded by numerous metagabbro with eclogitic marginal zones (Candan et al., 1994, 2001,
246 2016). They show primary igneous texture and mineralogy in the undeformed cores. The
247 eclogites are overprinted by medium-pressure Barrovian metamorphism and converted to
248 garnet amphibolites (Candan et al., 2016)

249 3. 2. 2. *Küre gold deposit.*

250 The Küre area was selected as the study area because MTA (1979) carried out a detailed
251 exploration on three locations about 1.5 km south of the Küre village (Fig. 2), which included
252 geologic and alteration mapping, trenching, soil sampling and five diamond drill holes. The
253 major arsenopyrite ore mineral commonly occurs as very thin veinlets or disseminations in E-
254 trending schistosity-conformable quartz veins in silicified schist (Plate 1A) lenses and as
255 massive segregations as well as thick veinlets in NW-trending shear zones (Plate 1B). The E-
256 trending quartz veins in silicified schist have a maximum strike-length of 500 m, with

thicknesses ranging from mm to 0.7 m whereas the NW-trending quartz veins range from 0.1 to 2 m at a strike-length over 250 m (Fig. 2). Sericite, chlorite, pyrite and silica alteration halos encompassing the quartz veins have widths ranging from a few cm to 10 m. In the drill holes sections from the quartz veins, arsenopyrite ore appears to have occurred as veinlets and fracture-fillings in multilevel, alternating mineralization and schist zones (averaging 1.5 g/t Au) to depths of 70m. A rare value of up to 15 g/t Au was also detected in an old working.

4. Methodology

4. 1. Petrography and electron microprobe analysis

Analysis of arsenopyrite was carried out on polished and mounted, 1-inch diameter epoxy stubs by JEOL JXA-8230 at Middle East Technical University, Turkey. The areas of interest were identified with the help of reflected light microscopy and were marked and photographed prior to analysis. Working conditions were; the accelerating voltage: 15 kV, the probe current: 40 nA and the spot size: 5 μ m. Native metal standards were used for Ag, Bi, Au, Co, Cu, Mo, Ni, Pb, Sb and Se whereas standards Fe_2O_3 for Fe, HgTe for Te and CdS for Cd were accommodated. The ZAF (Atomic-Number-Absorption-Fluorescence) method was used for matrix correction.

4. 2. Fluid inclusions characterization

4. 2. 1. Microthermometry

For microthermometric analysis, doubly polished thin sections, approximately 100 μ m thick, were prepared. Microthermometric measurements were carried out using a Linkam THMGS-600 heating-freezing stage at the Department of Geological Engineering, Dokuz Eylül University, İzmir, Turkey. The stage is mounted on a DM LM/P Leica microscope with a maximum magnification of 50x and fitted with a video camera and monitor. The heating-freezing stage has a temperature range from -196°C (temperature of liquid nitrogen) to 600

°C. The systems were calibrated by synthetic fluid inclusions (supplied by the Institute of Geosciences, University of Leoben, Austria). The precision of low-temperature phase transitions ($<10\text{ }^{\circ}\text{C}$) is $0.1\text{ }^{\circ}\text{C}$, with a maximum error of $\pm 2\text{ }^{\circ}\text{C}$. Photomicrographs of the fluid inclusions were taken by a PixeLink PL-A662 digital camera prior to microthermometric study in order to record the original vapor/fluid ratio for comparison with those which underwent heating and freezing processes. Salinities of aqueous FIs were estimated using references data of Bodnar (1993) for NaCl-H₂O system. Salinities of CO₂-rich FIs were calculated using the equations of Chen (1979).

4. 2. 2. Noble gases quantification

Noble gas isotope analysis was carried out in the noble gas lab of GFZ German Research Center for Geoscience Potsdam, Germany. Approximately 0.5-1.0 g of 0.5-1 mm arsenopyrite grains were loaded into a screw-type crusher and baked online at 100°C for 24 hours to remove adsorbed atmospheric gases before crushing. Gases in fluid inclusions were released by crushing the mineral grains in a vacuum between hard-metal jaws. The crushing efficiency (i.e., the fraction of fluid inclusions that are opened during the process) is estimated to be between 50 and 100% (Lüders and Niedermann, 2010). The gases released by crushing were exposed to a dry ice-cooled cold trap, two Ti sponge getters and two ZrAl alloy getters (SAES®NP-10), one at room temperature and one at $250\text{ }^{\circ}\text{C}$, for 10 min. each, to remove the active gases. The heavy noble gases (Ar, Kr, and Xe) were then adsorbed to a stainless steel frit in a cryogenic absorber at 50 K (Kelvin), and He and Ne to activated charcoal at 11 K. The gases were released and measured individually (except for Kr and Xe) by sequential heating of the charcoal and steel frit. Two cold NP10 ZrAl getters adjacent to the mass spectrometer source and detectors were employed to minimize the mass spectrometer background; in addition, a liquid N₂-cooled stainless steel frit was included during He and Ne analysis. The analysis of noble gas isotopes (all isotopes of He, Ne, Ar; ^{84}Kr ; $^{128-136}\text{Xe}$) was undertaken in a VG5400 magnetic sector field

mass spectrometer according to procedures described in Niedermann et al. (1997). Helium results are reported in units of Ra, and all error limits correspond to 95% confidence level (2σ). Total analytical blanks were $(3-14) \times 10^{-12}$ cm³ STP (at standard pressure and temperature) for ⁴He, $(1-20) \times 10^{-12}$ cm³ STP for ²⁰Ne, $(5-50) \times 10^{-10}$ cm³ STP for ⁴⁰Ar, $(4-40) \times 10^{-14}$ cm³ STP for ⁸⁴Kr and $(2-6) \times 10^{-14}$ cm³ STP for ¹³²Xe.

4. 2. 3. Re-Os isotopic system

Five arsenopyrite separates from both E and NW veins were selected for this study from the arsenopyrite-bearing quartz veins at the Küre deposit for Re–Os dating. These five samples are OD-13, OD-14 and OD-16 from E and, OD-18 and OD-11 from NW veins. Heavy minerals were separated using routine procedures that involved steel jaw-crusher, steel roller-mill and Wilfley table. Arsenopyrite concentrates were separated from the non-magnetic fraction using heavy liquids, and single arsenopyrites with final hand-picking under a binocular microscope at the Department of Geology Engineering, Dokuz Eylül University, Turkey. The purity was initially between 50 and 80% Apy with the remainder being mainly hydrothermal scorodite (FeAsO₄.2H₂O). Four samples, OD-11, OD-13, OD-16 and OD-18, were re-picked to achieve ca. 99% purity and subsequently analyzed again. Re–Os sample dissolution and preparation were performed at the Re-Os laboratories at the Department of Geoscience, University of Arizona with procedures as reported in Kirk et al. (2014). In brief, approximately 0.5-1.0 g of sulfides were dissolved and homogenized using the Carius tube technique (Shirey and Walker, 1995). Appropriate amounts of Re and Os spike and 16 ml of reversed aqua regia (1HCl:3HNO₃) as well as 2 ml of H₂O₂ were added. Osmium and rhenium were separated and purified using distillation techniques and anion exchange columns respectively. Sulfide samples were analyzed by NTIMS (Negative Thermal Ionization Mass Spectrometry; e.g. Creaser et al., 1991). Blanks during this study were approximately 10 pg (picogram) Re and 0.1 pg Os and data were corrected as such.

332

333 **5. Results**

334 *5.1 Mineralogical features of the Küre mineralization*

335 At least two major episodes of mineralization are observed. These are: (a) schistosity-
336 conformable or layer-like approximately E-trending arsenopyrite vein mineralization and (b)
337 NW- trending lode-type (Phillips and Powell, 1993) that is controlled by shearing (Fig. 2) and
338 that cuts schistosity. The schistosity-conformable-type (a) shows quartz with irregular grain
339 boundaries formed in response to grain boundary migration (GBM) recrystallization (Jessel,
340 1987) in the E-trending quartz-arsenopyrite vein (Fig.3A, C). The lode-type (b) is represented
341 by (i) medium-grained (>1 mm), quartz with undulose extinction (Fig. 3B) associated with
342 arsenopyrite-pyrite-native gold-lillianite (Bi-bearing mineral), (ii) a later network of fine-
343 grained, dark-gray (resulting from fine-grained disseminations of arsenopyrite) arsenopyrite-
344 pyrite-Au veinlets cutting the former veins (Fig. 3B, E) and, (iii) a late-stage replacement by
345 scorodite-orpiment-realgar. The medium-grained quartz also underwent considerable
346 deformation, with undulose extinction (Fig. 3B) and incipient mineralization. Silicification of
347 host rocks is locally pervasive near the veins. Alteration types in E-trending veins are
348 represented by K- and Na-feldspatization (Fig. 3F, G) along with sericitization-chloritization
349 (Fig. 3H, I). Post-mineralization alteration (Fig. 3J) minerals including epidote and rutile
350 overprints previous alterations and mineralizations.

351 In Figure 4, we summarize the paragenetic sequence of mineral deposition. The vein
352 paragenesis is dominated by quartz, sericite and chlorite, with minor calcite. Arsenopyrite is a
353 major sulfide mineral occurring as euhedral (Fig. 5A) and anhedral (Fig. 5B) crystals with
354 variable sizes from 1 mm (associated with coarse Qz1 quartz and Au) to 60 μ m (associated with
355 'Qz2' quartz and Au). Pyrite exhibiting generally euhedral crystals (Fig. 5C) occurs in lesser
356 amounts as compared to the arsenopyrite, which is commonly associated with gold and a

bismuth-bearing mineral called lillianite (Fig. 5D). Gold associated with lillianite ($\text{Pb}_3\text{Bi}_2\text{S}_6$) is frequently visible in grains (tens of μm , up to $300\ \mu\text{m}$) hosted (i) in quartz ($3\text{--}100\ \mu\text{m}$; Fig. 5D), (ii) in arsenopyrite as inclusions ($10\text{--}300\ \mu\text{m}$; Fig. 5E), (iii) in cracks of brecciated arsenopyrites ($6\text{--}80\ \mu\text{m}$; Fig. 5F) and, (iv) in quartz-arsenopyrite-scorodite breccia (Fig. 5G). The late stage mineralization assemblage is represented by rutile, scorodite, orpiment and realgar (Fig. 5H). The quartz-arsenopyrite vein mineralization is encompassed mainly by zones of sericitization and chloritization (Fig. 3E, F). Hydrothermal alteration consists of chloritization, sericitization, carbonatization and silicification that affected all rock types. Chloritization of biotite has resulted in abundant rutile formation, whereas sulfidization coincides with carbonatization. Orpiment usually occurs in association with realgar, in aggregates derived from primary arsenopyrite.

5. 2. Arsenopyrite and associated minerals: from petrography to chemistry

The elemental composition of ore minerals including arsenopyrite, gold, pyrite, lillianite and scorodite (Fig. 6) was determined in polished sections collected from the quartz-arsenopyrite veins of the Küre gold deposit. Back-scattered electron images (Fig. 6) show relationships between Apy-Sco-Au (Fig 6A), Au-Apy (Fig. 6B), Qtz-Au aggregation (Fig. 6C), Apy-Py-Sco (Fig. 6D), Apy (breccia)-Py-Qz (Fig. 6E), Apy (breccia)-Sco (Fig. 6F-G) and Apy-Sco-Py diffusion (Fig. 6H). The visible gold grains occur as solitary grains at boundaries between arsenopyrite and scorodite (Fig. 6A) or in fractures (Fig. 6B) and inclusions in vein quartz (Fig. 6C). The element compositions of arsenopyrite, pyrite, gold, lillianite and scorodite are given in Table 2. Atomic concentrations of As range from 32.33 to 33.83%, whereas corresponding variations for Fe and S are 31.53–33.69% and 31.76–33.44%, respectively (Table 2). Thus, concentrations of Fe and S in arsenopyrites remain relatively uniform compared to those of As. Pyrite contains As values ranging from 0.88 to 1.76 wt. % whereas corresponding

Au concentrations are between 0.01 and 0.05%. This pyrite may be termed gold-bearing arsenian-pyrite (Simon et al., 1999).

5. 3. Absolute timing constraints on arsenopyrite.

The Re–Os isotope analytical results for five arsenopyrite separates from samples of the Küre gold deposit are listed in Table 3. The Re concentration in arsenopyrite ranges from 0.279 to 1.041 ppb whereas total Os values vary from 9.6 to 77.2 ppt. The arsenopyrite $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios show narrow ranges from 35 to 435 and 0.4 to 2.4, respectively. We could not obtain a meaningful isochron diagram from E- and NW-trending veins. While it is difficult to evaluate the degree of closed-system behavior in the samples based on the Re–Os data, there were a number of different intrusive and metamorphic events (Table 6) that may have mobilized Re and/or Os to some degree. We can evaluate whether different generations of minerals are represented in the Re–Os data by using an Os-mixing diagram (Fig.7). Both arsenopyrite separates with higher silicate contents and separates that were highly purified by hand-picking and were almost exclusively arsenopyrite, fall along a mixing line as shown in Figure 7. Points A and B in Figure 7 represent the two hypothetical end-members of the mixing line. End-member A is non-radiogenic (low $^{187}\text{Os}/^{188}\text{Os}$ values) and has high Os concentrations and is present in higher proportions in samples OD-13, OD-16/E vein, and impure OD-18/NW veins. End-member B is radiogenic with high $^{187}\text{Os}/^{188}\text{Os}$, lower Os concentrations and is present in higher proportions in samples OD-11/NW, OD-18/NW and OD-14/E veins. Hand-picking in general moved the purified samples towards end-member B and either results from removal of silicates (unlikely as silicates in general have radiogenic $^{187}\text{Os}/^{188}\text{Os}$ values with very low Os concentrations) or from selectively picking the larger arsenopyrite grains and leaving behind small grains or grains that had other phases attached. The fact that both impure and purified separates fall along the mixing line would imply that there are two or more types of arsenopyrite within the separates and that the relative amounts of the different types in the mixture

determines the isotopic composition of the sample. This may explain the poor linearity on the isochron diagrams as well, as mixtures of different generations of arsenopyrite would have different Os and Re concentrations, different time integrated Os isotopic compositions, and possibly different initial Os isotopic ratios.

5. 4. The fluid systems associated to gold events

5. 4. 1. Microthermometric results

The fluid inclusions of the fine-grained quartz in NW-trending quartz-arsenopyrite veins are too small (1-5 μm) to be studied. This is typical for the quartz of orogenic type mineralizations and metamorphic rocks (Crawford and Hollister, 1986; Roedder, 1984; Wilkinson, 2001). The fluid inclusions of the fine- to medium-grained quartz (Fig. 3B, D, E, F, G) in NW-trending quartz-arsenopyrite veins are only fluid inclusions that can be studied. Petrographic studies and inclusion analyses were focused on fluid inclusion assemblages (Goldstein and Reynolds, 1994). Primary fluid inclusions (Bodnar et al., 2014) that occur as isolated individuals, random groups, and planar arrays in inter-granular quartz crystals are not distributed along primary growth zones or along secondary trails (Fig. 8A, B) are inferred to be primary. These classifications were made based on their phases at room temperature using the criteria of Van den Kerkhof and Hein (2001). Secondary inclusions (Bodnar et al., 2014) are also observed and generally follow healed microfractures and grain boundaries (Fig. 8C). Some inclusions showed evidence at room temperature necking down (Roedder, 1984) and partial or total leakage of selective components. Where possible, inclusions suspected of being modified post-entrapment were not measured.

Based on the petrographic and compositional features of primary fluid inclusions at room temperature, three types of inclusions were recognized in the quartz Q₂ (Stage II) in the NW-trending quartz-arsenopyrite veins. Based on microthermometry, the fluid inclusions may be divided into three compositional types and are listed as: Type-1 (two-phase) aqueous fluid

inclusions ($\text{H}_2\text{O}-\text{NaCl}$), Type-2 aqueous-carbonic fluid inclusions ($\text{H}_2\text{O}-\text{CO}_2-\text{NaCl} \pm \text{CH}_4$) and Type-3 vapor inclusions ($\text{CO}_2 \pm \text{CH}_4$) (Fig. 8 A, B). Type-1 and Type-2 shows about equal distribution and are commonly found together in an inclusion cluster in samples. In most cases they are found together with the carbonic and aqueous-carbonic inclusions in an inclusion cluster. Type-3 occurs less commonly.

Results of microthermometric measurements are given in Table 4. Three solid phases were observed in aqueous-carbonic fluid (Type-2) inclusions (1-9 μm) in the quartz of the NW-trending quartz-arsenopyrite vein mineralization during freezing experiments. These were *ice*, *hydrate* and *carbon dioxide* crystals that formed with the freezing of *salt solution*, hydrate and *carbon dioxide gas*, respectively. Due to the very small nature of fluid inclusions ($<10 \mu\text{m}$), hydrate crystals and solid carbon dioxide are unlikely to have been observed, and therefore, measurements were performed based on the critical phase changes. Three phase transformation temperatures were measured (Table 4) during the slow increase of temperature of a completely frozen fluid inclusion (at a speed of $5^\circ\text{C}/\text{min}$ with $\pm 0.3^\circ\text{C}$ error limit). These were (i) the transformation temperature from solid to gaseous carbon dioxide (T_{mCO_2} , measured only in two fluid inclusions), (ii) the final melting temperature (T_{mice}) and (iii) the melting temperature of hydrate crystals. Solid carbon dioxide is suddenly melted at the triple point (Lemmon et al., 2001). Two T_{mCO_2} measurements returned -56.9°C and -63.4°C . Although these temperatures specify that there are other gases mixed with CO_2 gas, critical temperatures (T_{hCO_2}) in these inclusions were measured around 31°C and thus, this value indicates that carbon dioxide gas is the main component (Burrus, 1981). Chemical analyses for gas and liquid in fluid inclusions were not carried out in this study. However, CO_2 , SO_2 , NH_3 , C_2H_6 , C_2H_4 , Ar, C_3H_8 , N_2 , O_2 and H_2 gases are commonly encountered in crustal fluids. All these gases except for NH_3 can be found in fluid inclusions (Diamond, 2003). The final melting temperature of ice crystals (T_{mice}) could not be measured in carbonic inclusions. Even if measured, the salinity values

456 obtained would represent the highest salinity values for those inclusions. Because of the
 457 formation of hydrate crystals ($\text{CO}_2 \cdot 6\text{H}_2\text{O}$) consuming a significant amount of H_2O molecules,
 458 the salt concentration of the remaining fluid is increased (Diamond, 1992). Thus, the salinity
 459 calculation of the liquid solution is made using the values of the measured melting temperature
 460 of the hydrate crystals ($T_{\text{mCO}_2\text{-hydrate}}$): wt.% equivalent NaCl = $15.6192 - 1.1406 T_{\text{mclt}} - 0.035$
 461 $(T_{\text{mclt}})^2 - 0.0007 (T_{\text{mclt}})^3$ (Chen, 1972; Vlahakis et al., 1972). The melting temperature
 462 ($T_{\text{mclt}} = T_{\text{mCO}_2\text{-hydrate}}$) of the hydrate crystals in carbonic inclusions under examination is
 463 between 7.0 and 9.9 °C whereas the calculated salinity values range from 0.2 to 5.7 wt.% equiv.
 464 NaCl (Table 4 and Fig. 9A). These inclusions have always homogenized from the liquid phase
 465 to the gas phase (except for OD-11/6) and the temperature of liquid-vapor homogenization (T_h)
 466 varies from 244 to 387 °C (Table 4, Fig. 9B). Quartz samples of the study area contain aqueous-
 467 carbonic fluid inclusions (Type-2) as well as aqueous fluid inclusions (Type 1 with 3-9 μm in
 468 size) containing liquid and water vapor (Fig. 8A, B). During freezing experiments only one
 469 solid phase formed in the inclusions with the freezing of the salt solution. When the inclusions
 470 were cooled to a very low temperature of -196 °C, no other solid phase formed pointing to the
 471 presence of other gases. The ice-melting temperatures of inclusions in the quartz-arsenopyrite
 472 veins in the study range from -1 and to 4.8°C. By using these values, the salinity of aqueous
 473 solutions was calculated according to the formula: $\text{salinity} = 1.780 - 0.044202\theta^2 + 0.00055703\theta^3$
 474 where $\theta = T_{\text{mice}}$ [°C] (Bodnar, 1993). The salinity values range from 1.7 to 7.7 wt. % NaCl
 475 equiv. These inclusions have been homogenized (T_h) from the liquid phase to the gas phase at
 476 temperatures from 237 to 358 °C (Table 4, Fig. 9B). Although salinity of the Type-1 inclusions
 477 (two-phase) is slightly higher than those of Type-2, they exhibit almost a horizontal distribution
 478 as shown in the homogenization temperature-salinity scatter diagram of the investigated
 479 samples (Fig. 10). In other words, the data points define a straight line almost parallel to the
 480 compositional axis (salinity wt. % NaCl equiv).

5.4.2. Arsenopyrite thermometry

Quantitative EPMA spot analyses on arsenopyrite minerals have shown that As concentrations in EW-trending and NW-trending veins range from 32.53 to 33.76% and 32.33-33.83%, respectively (Table 2). Kretschmar and Scott (1976) carried out subsolidus recrystallization experiments in the Fe-As-S system using dry, eutectic, halide fluxes to speed reaction rates. At 300 °C the composition range of arsenopyrite extends from less than 30% As in equilibrium with pyrite and arsenic to approximately 33.5% As in equilibrium with pyrrhotite and loellingite. Arsenic geo-thermometry for the assemblage arsenopyrite–pyrite–pyrrhotite–loellingite indicated a temperature range between 490° and 570 °C (Kretschmar and Scott, 1976; Sharp et al., 1985). According to these authors, at 700°C arsenopyrite contained approximately 38.5% As irrespective of the assemblage in which it was synthesized and therefore, in the presence of arsenopyrite a temperature calculation may be done depending on the percentage of arsenic. However, no pyrrhotite and loellingite in association with arsenopyrite were recognized in the Küre area. Temperatures of arsenopyrite in Küre gold deposit were calculated at a stability field of pyrite and arsenopyrite at 5 Kbar (Fig. 12)

5.4.3. Noble gas signatures

The concentrations of all five noble gases the He, Ne, Ar, Kr and Xe isotopic compositions of fluid inclusions in two vein quartz and four arsenopyrite samples from the Küre gold deposit are listed in Table 5. The analyzed samples showed evidence of deformation and auriferous quartz-arsenopyrite-pyrite veins, which are encompassed by sericite and chlorite alteration halos. Therefore, we are confident that the extracted fluids were related to mineralization and thus coeval with the unmixed CO₂-type and high temperature aqueous-type fluid inclusions in the quartz hosting the arsenopyrite and gold. The ⁴He contents in quartz are between 0.070 x 10⁻⁸ cm³ STP/g and 0.21 x 10⁻⁸ cm³ STP/g whereas ⁴He values in arsenopyrite range from 8.4 x 10⁻⁸ cm³ STP/g to 68.6 x 10⁻⁸ cm³ STP/g. The ³He/⁴He ratios of fluids extracted from

arsenopyrites (0.08–0.09 Ra) are close to those of crustal origin (<0.1 Ra; Mamyrin et al., 1970 or 0.01–0.05 Ra; Ballentine and Burnard, 2002) and significantly lower than those of typical mantle sources (6–8 Ra; Graham, 2002; Ozima and Podosek, 2002) including subcontinental mantle origin (~6.1 Ra; Gautheron and Moreira, 2002). The $^3\text{He}/^4\text{He}$ ratios of quartz are atmospheric (1 Ra) within error limits. To estimate the contribution of atmospheric He, we use the fractionation factor $F^4\text{He} = (^4\text{He}/^{36}\text{Ar})_{\text{sample}} / (^4\text{He}/^{36}\text{Ar})_{\text{air}}$, with $(^4\text{He}/^{36}\text{Ar})_{\text{air}} = 0.1655$ (e.g. Kendrick et al., 2001). Values of $F^4\text{He}$ in quartz samples are between 2.2 and 3.4 whereas $F^4\text{He}$ values in arsenopyrite range from 170 to 9500 (Table 5). Very high $F^4\text{He}$ values document that the contribution of atmospheric He to the mineralized fluids is negligible, however small values such as for the quartz samples are not indicative because of various fractionation effects that may have taken place. Therefore, the quartz-hosted He cannot be used to infer conclusions about the mineralizing fluids. However, even after applying a correction for air-derived contributions to the He isotopic composition (e.g., Craig et al., 1978), the slightly elevated $^3\text{He}/^4\text{He}$ ratios of the arsenopyrite remain nearly unchanged (Table 5). Therefore, the total He in the Küre fluids in arsenopyrites is essentially unaffected by atmospheric sources.

6. Discussion

6. 1. The Küre deposit: orogenic or epithermal gold deposit

Quartz grains exhibiting irregular grain boundaries (formed in response to grain boundary migration recrystallization in the E-trending quartz-arsenopyrite veins) suggested that mineralization occurred under a high temperature (>400 °C) (boundary migration recrystallization) and a low stress regime (Passchier and Trouw, 2005). However, quartz minerals show typical fabric of dynamic recrystallization in NW-trending quartz-arsenopyrite veins. Relicts of large old quartz grains with undulose extinction and elongate subgrains

transitioning laterally into domains of small, new grains formed by bulging recrystallization under lower temperature (<400 C°) and high-strain shearing conditions.

Gold grains return 86.46-95.36% Au and 3.48-6.23% Ag (Table 2), which is a typical composition of orogenic gold. Groves et al. (1998) suggested that gold in orogenic gold deposits is enriched by orders of magnitudes over Au:Ag ratios are generally >1, which led to their classification as ‘gold only’ or ‘orogenic gold’. This Au:Ag ratio in epithermal deposits (high and low sulfidation) several orders of magnitudes <0.01 and 1). Some of the arsenopyrite exhibits variable and high Au concentrations within a single sample (Table 2). It is considered that Au is not present in the arsenopyrite structure. Such concentrations might result from the presence of submicron-sized (nanosized) particles of gold in arsenopyrite (gold as Au₀; Majzlan et al., 2010). The gold fineness was estimated at 916/1000 from the analysis shown in Table 2. As gold containing > 20% Ag is classified as electrum and <20% Ag is classified as only gold (Robert et al., 2009), the gold in arsenopyrite in the Küre deposit may be identified as ‘only gold’. Lillianite is a bismuth mineral and according to its mineral composition it may take its place in lillianite-gustavite series (Buzatu et al., 2015). In EPMA images, scorodite occurs in brecciated arsenopyrite as fracture-filling (Fig. 6D) or at boundaries between pyrite and arsenopyrite (Fig. 6H).

6.2. Fluid sources: mantle versus crustal contribution

Figure 10 shows that mixing occurs between two different fluids. According to Wilkinson (2001) and Dubessy et al. (2003), this mixing can be defined as an isothermal mixing. The temperature of the fluid was imposed by the host rock where mixing processes took place. The fluid does not disturb the temperature of the host rock if the mixing was isothermal. This corresponds to small fluid–rock ratio and/or fluid flow, a case typical of metamorphism or deep fluid circulation. In Isothermal mixing, the fluid is trapped at the temperature of the rock at the place where mixing occurs. Therefore, the trapping temperature does not depend on the

proportions of each fluid end-member involved in the mixing process. The homogenization temperature is independent of the temperature of the fluid end members and shows only slight variation with salinity, resulting from the variations of the V-X (volume-composition) properties, because the molar volume is only a function of the compositions under fixed pressure and temperature. The data points define a straight line almost parallel to the composition axis ($T_{m_{ice}}$) for each calculated pressure (Dubessy et al, 2003). Fluid inclusions commonly encountered in Archean lode-gold deposits consist of mixed H_2O - CO_2 - $NaCl$ - CH_4 fluids that in many cases are believed to be the product of intermittent phase immiscibility (Hollinger-McIntyre gold deposit: Spooner et al., 1987; Sigma gold mine: Robert and Kelly, 1987; Pamour: Walsh et al., 1988). These inclusions are trapped on or near the solvus and their total homogenization and trapping temperatures are equal. Therefore, no extrapolation to higher temperatures via an independent geothermometer is required.

A predictive thermodynamic model based on the Helmholtz free energy equation of state of CO_2 - H_2O fluid is proposed to calculate the molar volume or density of CO_2 - H_2O - $NaCl$ fluid mixture (Mao et al. 2015). In addition, the parameters developed by Driesner (2007) in the PVTX (P: pressure, V: volume, T: temperatures, X: composition) model of H_2O - $NaCl$ fluid system are refitted by the IAPWS-95 formulation. Comparisons with experimental data available show that the model can reproduce the single- phase PVTX properties of H_2O - $NaCl$ and CO_2 - H_2O - $NaCl$ fluid mixtures of all compositions from 273 to 1273 K and from 0 to 5000 bar, within or close to experimental uncertainty in most cases (Mao et al. 2015).

Mixing of two different fluids would result in distinct inclusion populations showing widely variable temperatures of total homogenization and salinities (Xavier and Foster, 1999).

The fluid properties were calculated with the software package FLUIDS (Bakker, 2003) and additional software from <http://fluids.unileoben.ac.at/Computer.html>. The software AqSo DH was used for calculating density, molar volume of H_2O - $NaCl$ inclusions, with the equations

from Driesner and Heinrich (2007), and Driesner (2007). The isochores are calculated using the equation of state according to Haar et al. (1984) for pure H₂O in the temperature-pressure-molar-volume/density space from 0 to 1000 °C and maximum 1500 MPa with Loner HGK software. The software BULK was used for calculating density and molar volume of CO₂ non-aqueous phase CO₂–H₂O–NaCl fluid inclusions with the equation from Duschek et al. (1990). The isochores are calculated using the equation state according to Span and Wagner (1996) for pure CO₂ with the software Loner SpW.

Bulk molar volumes or densities (Bakker and Diamond, 2000) for Type-1 aqueous fluid inclusions (H₂O–NaCl) and Type-2 aqueous-carbonic fluid inclusions (H₂O–CO₂–NaCl) depend on estimation of volume fractions of the fluid phases. Volume fraction of these inclusions were calculated by the traditional method (Roedder, 1984) in this study. Traditional estimation of non-fluorescing inclusions involves measuring area-fractions of the phases projected in the microscope and then making rough corrections for the third dimension. H₂O–NaCl fluid inclusions have molar volumes between 21.65 and 23.06 cm³/mole and show relatively high densities in a close range (0.72–0.86 g/cm³) (mean 0.80; n=14). H₂O–CO₂–NaCl, fluid inclusions have molar volumes between 56.60 and 63.36 cm³/mole and show densities in a close range 0.69–0.77 g/cm³ (mean 0.72; n=21). These density differences of the fluid inclusions contained within the gold-bearing quartz-vein indicate fluid pressure fluctuations (Robert et al., 1995; Wang et al., 2015) during NW vein development. Assuming that the vapor bubble contains mainly CO₂ and that the salinity of the aqueous phase can be neglected. The final clathrate melting temperatures are between +7.5 and +9.9 °C and the estimated salinities range from 0.4 to 7.7 wt. % NaCl equiv. (Table 4). The measured homogenization temperatures of CO₂ (Th_{CO2}) range from 23 to 26 °C. These inclusions are homogenized to liquid or vapor phase, but mostly to liquid phase CO₂.

604 The isochores are calculated using the equation of state according to Span et al. (1996) for
605 pure CO₂ with the software Loner SpW. The pressure estimated from isochores of the carbonic
606 fluid inclusion-H₂O-CO₂-NaCl (density 0.69-0.77 g/cm³, with Th_{CO2} 23 °C to 26 °C) are
607 between 1536.9 to 903.9 bar (Fig. 11). The isochores are calculated using the equation of state
608 according to Haar et al. (1984) for pure H₂O with the software Loner HGK software. The
609 pressure estimated corresponding to maximum temperature of 358 °C is about 377.9 bar and a
610 minimum temperature of 236.6 °C with 104.1 bar. The estimated pressure (P=p.g.h) coincides
611 with minimum depths of ~0.39–1.56 km, which assumes a hydrostatic regime. Significant
612 pressure fluctuations, but relatively constant homogenization temperatures for Type 1 and Type
613 2 fluid inclusions, suggest that cyclic decompression of the hydrothermal fluids, due to seismic
614 activity along the shear zones that host the gold-bearing veins. The fluid inclusions also
615 indicated that, after repeated pressure fluctuation, the system did not compensate its original
616 lithostatic pressure and that one late-stage fluids with different temperatures and salinities
617 mixed under supra-lithostatic to nearly hydrostatic pressure conditions (Montomoli et al.,
618 2001). These authors have hypothesized that a connection with metamorphic fluid reservoirs
619 under hydrostatic pressure corroborated by connected discontinuities is almost a must in
620 explaining the long-lived low pressure at depth and the input of cooler brines. The ability for
621 determining the existence of strong pressure drops from lithostatic to hydrostatic conditions is
622 of great interest for: (i) the exhumation of crustal terranes, (ii) determination of the role of fluids
623 in deformation and heat and mass transfer in drainage zones (Montomoli et al., 2001). Among
624 the main mechanisms of explaining pressure drops are: (a) a drop in fluid pressure due to an
625 increase in porosity, which is resulted from the opening of dilatant fractures (Sibson, 1981) and
626 (b) fluid pressure discharging along a rupture zone as suggested in the fault-valve model (Mac
627 Caig, 1988; Sibson, 1990, 2000; Sibson et al., 1988 in Montomoli et al., 2001). It is proposed
628 that pressure cycling between near-lithostatic and hydrostatic can occur in orogenic terrains in

both extensional and compressional tectonic environments. (Sibson, 1990; 1994 in Montomoli et al., 2001).

Textural features of ore samples and the formation of arsenopyrite at ages likely between 244 and 249 Ma and between 562 and 577 Ma have indicated that the arsenopyrite mineralizations at Küre were affected by the conditions of metamorphism of the MM. In this case the arsenopyrite mineralization may have probably formed at pressures greater than 1 Kbar. Candan et al. (2011) suggested that the Ödemiş-Kiraz metamorphic rocks of the Neo-Proterozoic basement were formed under the conditions of amphibolite facies (Barrovian- type) and medium pressure metamorphism (530-650 °C, 7-8 Kbar, 540-550 Ma). Experimental studies on arsenopyrite syntheses were carried out by Kretschmar and Scott (1976) at 1 Kbar and by Sharp et al. (1985) at 5 Kbar. Therefore, a diagram constructed by Sharp et al. (1985) for 5 pressure is taken into consideration here (Fig. 12). Based on a phase diagram for the Fe–As–S system along with the arsenopyrite geothermometer, the ranges of temperature are between 380 and 480 °C (Apy-1). These values are between 390 and 475 °C for Apy-2.

Klemd et al. (2002) reported that the amphibolite-facies rocks (600 °C at 5) in the Paleoproterozoic greenstone belts in Ghana host orogenic gold deposits. They have also argued that hydrothermal alteration and mineralization appear to have taken place under somewhat lower temperatures <540 °C. This view is also supported by actinolite rims on hornblende and the appearance of secondary chlorite in altered wall-rocks, which is not a texturally primary mineral phase in the unaltered rocks. Klemd et al. (2002) claimed that the fluid flow causing alteration and mineralization occurred under post-peak-metamorphic conditions and, gold mineralization was associated with arsenopyrite–pyrite (with loellingite inclusions) and arsenopyrite–pyrrhotite. Estimates for the temperature–composition from the arsenopyrite–loellingite mineral assemblage indicated that the formation of these minerals occurred at 550–600 °C (Sahoo and Venkatesh, 2015). These authors also emphasized that there might be some

limitations of applicability of these thermometry results. Increase in pressure would cause decrease in the arsenic content of arsenopyrite coexisting with loellingite, thereby increasing the upper stability field of arsenopyrite-pyrite by approximately 14 °C per (Sharp et al., 1985). Arsenopyrite compositions in the $f(S_2)$ buffered assemblage (arsenopyrite + pyrite + pyrrhotite) yielded a temperature range of 375–390 °C at $\log f(S_2) = -9.7$ to -7.5 (Kretschmar and Scott, 1976; Sharp et al., 1985). Although melting of arsenopyrite might have played a significant role in the melting of ore deposits during metamorphism, the tendency for arsenopyrite to melt depended on reactions in the surrounding rock and the evolution of sulfur fugacity (Tomkins et al., 2006). They stated that once pyrite was fully consumed, however, the $f(S_2)$ was not maintained at elevated values anymore. In most mineral deposits, the likelihood that it will melt, or instead be transformed into loellingite + pyrrhotite, depends upon the durability of pyrite. If rocks hosting arsenopyrite ore were able to maintain pyrite to middle-amphibolite-facies conditions (beyond 491°C at 1 or ~560°C at 5 Kbar), arsenopyrite melting would occur (Tomkins et al., 2006) and if not, arsenopyrite melting was improbable. In deposits with disseminated sulfides and moderately abundant Fe-bearing silicates and oxides, arsenopyrite is unlikely to melt because pyrite is more easily converted to pyrrhotite at relatively low temperatures in such rocks, precluding buffering of $f(S_2)$ to the level required for the reaction.

Arsenopyrite has been occasionally encountered in several different types of deposits. Researchers suggested that some of the ore deposits were metamorphosed under middle-upper amphibolite metamorphic facies conditions. Although melting of arsenopyrite can play a role in the melting of ore deposits during metamorphism, the tendency for arsenopyrite to melt is dependent on reactions in the surroundings of the rock and the evolution of sulfur fugacity (Tomkins and Mavrogenes, 2002). They suggested that in most mineral deposits, the arsenopyrite would melt or instead be transformed into loellingite + pyrrhotite, depending upon the durability of pyrite. The destiny of arsenopyrite during metamorphism is controlled by $f(S_2)$,

679 which is supported by sulfur-bearing minerals in the wall rock. For instance, Tomkins et al.
680 (2006) reported that at the Hemlo gold deposit, Ontario/Canada, containing a range of
681 disseminated sulfides, the breakdown of barite promoted conditions of high $f(S_2)$ and melting
682 of arsenopyrite during prograde metamorphism. On the other hand, they concluded that at
683 several massive sulfide deposits including Osborne Lake, Montauban and Geco in Canada, high
684 $f(S_2)$ conditions were instead generated through pyrite breakdown on the pyrite–pyrrhotite
685 buffer, also causing arsenopyrite to melt in favorable parts of the deposits. Contrary to the
686 suggestion by Tomkins et al. (2006), high sulfur consumption lowering the $f(S_2)$ in
687 metamorphic processes has given way to the solid transformation of arsenopyrite ($FeAsS$) to
688 pyrrhotite ($Fe_{(1-x)}S_x$, $x=0-0.2$) and loellingite ($FeAs_2$) instead of melting (Deol et al., 2012). A
689 major increase in $f(S_2)$ may be caused by the reaction of pyrite to pyrrhotite and the $f(S_2)$
690 increases with the temperature rise. The $f(S_2)$ may not have stayed high anymore when the
691 pyrite was consumed. If arsenopyrite-bearing metamorphic rocks could have maintained pyrite
692 under amphibolite-facies conditions (491 °C at 1k bar, 560 °C at 5 Kbar), arsenopyrite would
693 have become molten. Even if the pyrite was not maintained the arsenopyrite could have melted.
694 Mineral deposits in which arsenopyrite can be melted during metamorphism are pyrite-rich
695 massive or disseminated sulfide mineralizations containing minor iron silicates and oxides. The
696 As/S ratio of natural and synthetic arsenopyrite ranges from 0.82 to 1.22 (Cook and Chryssoulis,
697 1990; Oberthür et al., 1997) and these ratios are defined as sulfur-rich. However, those rich in
698 As were also recognized in some other deposits (Kretschmar and Scott, 1976). The As contents
699 of Küre Apy-1 ranging from 32.50 to 33.83 % As (Table 3) and Apy-2 ranging from 32.53 to
700 33.50 are similar and do not show bimodal distribution. Apy-1 and Apy-2 with As/S ratios
701 range from 1.00-1.33 and from 0.97 to 1.03, respectively. Both EPMA results and textural
702 investigations (Fig. 5 and Fig. 10) indicate that the Küre arsenopyrites (Apy-1, Apy-2) under
703 examination are rich in sulfur and do not show geochemical zoning. Diagrams (Fig. 12) using

the chemical compositions of arsenopyrite associated with these specific assemblages has provided reliable estimations of temperatures and $f(S_2)$. As is known, pyrite accompanies the Küre arsenopyrites and, loellingite and pyrrhotite lack in the paragenetic assemblage. In this diagram, according to As compositions falling in arsenopyrite-pyrite field, Apy-1 is represented by 380-480 °C and $\log fS_2$ between -7 and -4.3 whereas Apy-2 is represented by 390-475 °C and $\log fS_2$ between -7 and -4.5.

If arsenopyrite has undergone metamorphism above the medium amphibolite-facies conditions (>520 °C, 2), it would have melted (Tomkins et al., 2004). Metamorphic rocks bear mostly the traces of ductile deformation. The sulfur melts are quite active under these conditions (Tomkins et al., 2004). Nevertheless, suitable sites for exploration of As-bearing melt occurrences may be structurally dilatant areas such as boudin necks, extensional fractures, fold hinges and fault jogs where mobile substances accumulate (Tomkins et al., 2006). A concentration of ore minerals in these areas can exhibit textural evidence regarding the melting of arsenopyrite. Enrichment of a large volume of gold in arsenopyrite fractures can be seen in polished sections from the Küre mineralization (Fig. 5B).

The origin of the heavier *noble gases* can best be assessed from a plot of the elemental abundances of the five noble gases with respect to atmospheric abundances. Figure 13 shows that the arsenopyrite data (except for He, which is out of scale due to the predominant crustal component) plot close to the unfractionated air or dissolved air patterns. In particular, OD-11 and OD-14 Apy may have obtained their heavy noble gases from a high-temperature water or brine phase, in general agreement with the formation temperatures of this mineral (note that the patterns shown for $\geq 100^\circ\text{C}$ air-saturated water do not include effects of salinity). In the other two arsenopyrite and the quartz samples, a low temperature fluid seems to dominate the noble gas pattern, possibly related to the formation of secondary fluid inclusions. This signature is

superimposed by additional fractionation effects of unknown cause, which have enriched the Xe concentrations and, in quartz, those of He and Ne.

The Küre mineralization has taken place in geological environments similar to those of Muruntau gold, Dongping gold and Pingqiu and Jinjing gold deposits (Fig. 14). These three mineralizations are classified as orogenic gold deposits (Goldfarb and Groves, 2015). Mao et al. (2003) agree with the classification of Sillitoe (2002) that the Dongping deposit is similar in features to many deeper orogenic and intrusion-related gold deposits. Furthermore, ore-forming fluids are a mixture of crustal- and mantle-derived solutions. The Muruntau gold mineralization was formed as a result of interaction between relatively lesser ore-bearing, mantle-derived fluids and predominating meteoric solutions (Graupner et al., 2006). The ore-forming metal elements of the Pingqiu and Jinjing gold deposits may have been derived primarily from the fluids, which may have been sourced from the metamorphic water, though magmatic water cannot be ruled out (Wang et al. 2019). For the fluid inclusions of the arsenopyrite in Küre, mantle-derived helium ($^4\text{He}_{\text{mantle}}$; Table 2) contributions are ~0.7% to 1.0%, assuming a crustal $^3\text{He}/^4\text{He}$ ratio of 0.014 Ra. However, in crustal environments enriched in Li, $^3\text{He}/^4\text{He}$ ratios are higher and may reach the values measured in arsenopyrite fluid inclusions, therefore, we cannot unequivocally infer an involvement of a mantle source based on the He data. For quartz, such an inference is even less possible, since the nominal $^4\text{He}_{\text{mantle}}$ values shown in Table 2 have uncertainties >100% and are based on the assumption of an unfractionated $^4\text{He}/^{20}\text{Ne}$ ratio of 0.319 in the atmospheric component, which is probably not correct as indicated by the higher-than-atmospheric $^{20}\text{Ne}/^{36}\text{Ar}$ ratio in those samples. Thus, the solutions forming gold-bearing mineralizations in Küre have been dominated by crustal fluids, while a minor contribution from mantle-derived fluids is possible but not certain.

6.3. Timing relation between the gold events

Although the MM has had a complex poly-phase metamorphic history, the age of several episodes have been recently clarified. Most researchers agree on the fact that the MM underwent two main orogenic events, including the Kuunga (late Neoproterozoic/ Oelsner et al., 1997; Candan et al. 2011c, 2016; Koralay, 2015) and Alpine orogenies (Eocene / Şengör et al. 1984; Satır and Friedrichsen, 1986; Dora et al. 2005; Candan et al. 2011b). The Kuunga orogeny is recently recognized for the MM and has been previously used widely as Pan-African orogeny. Considering the timing of geological events occurring between 500-600 Ma was accepted as relating to the Kuunga orogeny in recent studies (Koralay, 2015; Candan et al. 2016). It has been suggested that several phases of metamorphism have affected the MM (Table 6). The granulite, eclogite and upper amphibolite facieses and migmatization of these episodes, which are related to Kuunga orogeny, are late Neoproterozoic. The ages of these types of metamorphism have been a subject of debate for a considerable time. Granulitic relics in paragneisses and orthopyroxene orthogneisses (charnockites) returning crystallization ages of ~590 Ma recorded a first HT-MT metamorphism (Candan, 1995; Candan et al. 2011a; Koralay, 2015, Koralay et al., 2005). U/Pb SHRIMP and LA-ICP-MS zircon and monazite ages from granulitic rocks yielded ages of 582 ± 4 and 578 ± 3 Ma, respectively. The age of ~580 Ma is interpreted as the time of granulite facies metamorphism (M1; Table 6) of the basement rocks in the MM (Koralay, 2015). Numerous gabbroic stocks and dykes intruded into the basement rocks. The crystallization age of the protolith of metagabbros showing continental tholeiitic affinity is 563-558 Ma (Candan et al. 2016). After this widespread basic magmatic activity, a high-temperature overprint (M2; Table 6) causing partial melting, migmatization and anatectic granite generation ends with voluminous granitoid intrusions. The conventional U–Pb zircon age of the anatectic metagranites, which are associated with migmatization and do not exhibit deformation, is 551.5 ± 1.4 Ma (Hetzl et al. 1998). This partial melting and migmatization is followed by prevalent S-type granitoid intrusions, i.e. orthogneisses. All of these authors

777 interpreted these ages, *550-545 Ma, as intrusion ages of the precursors of the orthogneisses*
778 (Hetzel and Reischmann, 1996; Loos and Reischmann, 1999; Gessner et al., 2004; Koralay et
779 al., 2004, 2011, 2012; Candan et al., 2011b). These orthogneisses represent the product of the
780 widespread Kuunga magmatic activity attributed the final amalgamation of East and west
781 Gondwana (Koralay et al. 2011, 2012).

782 The Cambrian eclogite occurrences and Eocene-Oligocene HP-LT metamorphism have
783 been documented for the late Neoproterozoic basement and cover series, respectively
784 (Oberhänsli et al. 1997, 1998; Candan and Dora, 1998; Rimmelé et al. 2003). The well-
785 preserved 563-558 Ma metagabbros were locally converted into eclogitic metagabbros and
786 garnet amphibolites along the shear zones and/or contacts. The rim zircon age of 535 ± 3 Ma
787 obtained from eclogitic metagabbros by LA-ICP-MS show that high-pressure metamorphism
788 (M3, Table 6) is of Early Cambrian (Candan et al., 2016). Therefore, the H-P evolution of the
789 basement of the MM and associated basic intrusions can be interpreted to indicate the latest
790 stages of the final amalgamation of the Gondwana during the late Neoproterozoic–Early
791 Cambrian (Candan et al., 2016). Following the eclogite metamorphism, limited syenite
792 intrusions, i.e. amphibolite orthogneiss, were observed at 520 Ma (Koralay et al., 2014). At the
793 latest stage (M4, Table 6), high-grade basement rocks of the MM were affected by retrograde
794 amphibolite facies metamorphism during the exhumation of the Massif. There is no
795 geochronological study on the age of amphibolite facies overprint.

796 Another metamorphic episode that post-dates Triassic granitic intrusions is characterized by a
797 greenschist facies metamorphism (M5, Table 6; Akkök, 1983). The existence of this greenschist
798 facies metamorphism observed in a limited area is still controversial. In addition, Zlatkin et al.
799 (2013) have obtained a large number of ages in the range of 240-270 Ma in their detailed age
800 determinations of orthogneisses and metasediments from basement and cover series in MM.
801 Researchers have attributed these ages to a thermal phenomenon occurring in Triassic,

indicating lead-loss and partial resetting of the samples. These ages support the observations of Akkök (1983). In central and northern submassifs of the MM (Fig. 1) Triassic leucocratic orthogneisses are intruded into basement schists and Lower Paleozoic schist and phyllites (Akkök, 1983; Koralay et al. 2001, 2011). These leucocratic orthogneisses yielded single zircon Pb-Pb ages of ~227-246 Ma (Reischmann et al. 1991; Dannat and Reischmann, 1997, 1998; Koralay et al. 2001, 2011). The intrusion of these granitoids was attributed to the closure of the Paleotethyan Karakaya basin (Akkök, 1983; Koralay et al. 2001). Triassic magmatism is not only restricted activity to the MM, but is also observed in the Afyon Zone (metarhyolite, 224-243 Ma, zircon U-Pb / Akal et al. 2005a, b; meta-trachyandesite, ~250 Ma / Akal et al. 2012), Lycian nappes (Middle Carnian, fossil evidence/Sayit et al. 2015), Karaburun Peninsula (granitoid: 239 ± 2 Ma, Rb-Sr biotite / Ercan et al. 2000; 239 ± 2 Ma, zircon U-Pb / Akal et al. 2011) and Bornova Flysch Zone (granite, 225-230 Ma, zircon U-Pb / Güngör et al. 2016) of the Anatolides, which is associated with a regional tectonic event. It is considered that these metamagmatics developed in an extensional back arc setting, which can be associated to opening of the northern branch of the Neotethys on the northern margin of Gondwana as a result of southward subduction of the Paleotethys (Göncüoğlu et al. 2003; Okay, 2006; Koralay et al. 2011; Akal et al. 2012).

A major event called ‘main Menderes metamorphism’ (M6, Table 6), which was associated with intense deformation is recorded in the entire massif (Şengör et al. 1984; Candan et al, 2011). The metamorphism conditions of the Barrovian-type event reaches upper amphibolite facies in association with local anatexic melting in the structurally lower parts of the massif and greenschist facies in the upper parts of the cover (Akkök, 1983; Okay, 2001; Candan et al. 2011). Mica ages obtained with the Rb/Sr and Ar/Ar methods from the basement and cover rocks of the MM show identical Alpine ages of 60 to 35 Ma (Şengör et al. 1984; Satır and Friedrichsen, 1986; Bozkurt and Satır, 2000; Lips et al. 2001; (Cenki-Tok et al., 2011). U/Th–

Pb in situ ages on monazite and allanite from metapelites record crustal thickening and nappe stacking associated with the internal imbrication of the Anatolide–Taurides platform during Eocene (Cenki-Tok et al., 2011). This main metamorphism is considered to be the product of latest Paleogene collision and consequent internal imbrication of the Menderes Massif-Taurid block across the Neotethys. The last phase (M7, Table 6) corresponds to greenschist facies retrogression associated with the final exhumation of metamorphic rocks below flat lying extensional shear zones and Miocene granitoid intrusions (Hetzel et al. 1995a; Hetzel et al. 1995b; Lips et al. 2001).

The arsenopyrites likewise give very scattered model ages between 874 Ma and 138 Ma (Table 3). In general, separates from NW veins plot at higher $^{187}\text{Os}/^{188}\text{Os}$ values and lower Os concentrations and trend towards end-member B, whereas E veins trend towards the lower $^{187}\text{Os}/^{188}\text{Os}$ values and higher Os concentrations of end-member A. End-member A may represent arsenopyrite derived from mantle fluids ($^{187}\text{Os}/^{188}\text{Os}$ of 0.12-0.13; sulfides derived from these fluids generally have >50 ppt Os; Esser and Turekian, 1993) or relatively juvenile magmatic intrusions; end-member B may represent another arsenopyrite generation derived from fluids of the upper continental crust (average values of $^{187}\text{Os}/^{188}\text{Os}$ of 1.26 and <50 ppt Os concentrations; Esser and Turekian, 1993; but may trend to much higher or lower values depending on age of the crust and time-integrated Re/Os ratio).

If our assumption of multiple arsenopyrite generations is valid, then the model ages of the samples that are most representative of the end-members in likely two-component mixing are the best estimate of the ages of these two components. These model ages are maximum ages, as it assumes a source from mantle-derived fluids and they are possibly younger as the low Os concentrations are more consistent with fluids derived from crustal rocks (average 50ppt; Esser and Turekian, 1993). Sample OD-16, is the best representative of end-member A and three analyses give model ages (TMa) of 557, 562 and 738 Ma and point to a Precambrian age for

the least radiogenic, highest Os concentration arsenopyrite. The concomitance of the ca. 557-562 Ma ages of two of the OD-16 arsenopyrite samples, which correspond to the age of Kuunga metamorphism (540-580 Ma) is compelling, although admittedly very speculative. The most radiogenic sample OD-11 was additionally hand-picked to ca. 99% purity. The purified separates (OD-11-2 and OD-11-3) had very low Os concentrations (9.6-11.9 ppt) and very high $^{187}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Re}/^{188}\text{Os}$ values that yielded TMa ages of 258 and 316 Ma. The 258 Ma age is noteworthy in its concordance with Triassic intrusions and metamorphism.

It is interesting to note that the mean TMa values for the arsenopyrite of the E and NW veins are very similar to the values of the most representative samples of the two end-members in the mixing diagram. The mean value for all arsenopyrite samples from the NW-trending veins is 254 Ma, similar to model ages of the purified OD-11 samples. The mean value for all arsenopyrite samples from the E-trending veins is 569 Ma and similar to model ages of OD-16 samples.

The simplest interpretation of these results is that the Re–Os system in Küre arsenopyrite has been disturbed subsequent to its primary crystallization. If the time gaps between primary and secondary events are longer, the potential isotopic disturbance is more significant (Stein, 2014). As explained above, Küre arsenopyrite deposit should have been affected by regional metamorphic conditions after their deposition. Orebodies with lenticular shapes, well-developed cataclastic texture of fine-grained arsenopyrite, different metamorphic conditions and extensive deformations may have been the result of different deformations. Stein et al. (1998, 2000) and Mathur et al. (1999) indicated that the Re-Os isotope system in sulfides might be disturbed during metamorphism and/or metasomatism, especially during hydrothermal alteration. Likewise, the mean value of model ages from arsenopyrite of the E-trending veins is 569 Ma, and includes sample OD-16 which occurred along the schistosity plane in intensely silicified mica schist and showed almost no alteration. Likewise, the mean value of model ages

877 from arsenopyrite of the NW-trending veins is 254 Ma. We, therefore, conclude that the Küre
878 deposit might have formed at two stages of ca. 569 Ma and ca. 254 Ma, which are consistent
879 with geologic considerations pointing to the time frame of 246-227 Ma (Triassic magmatic
880 activity of the MM) with more evolved, crustal fluids involved. On the other hand, when we
881 look at the results given in Table 3, and Figure 15, there is a fairly normal distribution to the
882 model ages for both E- and NW-trending vein samples. E-trending vein sample OD-16 gives a
883 model age of 738 Ma, whereas OD-14 returns a model age of 874 Ma. This latter age appears
884 to be in accord with the formation age of the rocks in the region. However, arsenopyrites formed
885 within the meta-sediments of Precambrian age maybe thought to show older age due to
886 influence of metallic remnant minerals (i.e. pyrite) precipitated in primordial sediments. E-
887 trending vein samples such as OD-13 also give model ages (435 and 226 Ma) younger than the
888 ages at 577-562. When we look at the chronology of geological events in Table 6, it is observed
889 that Menderes Massif has not been influenced by any metamorphism and magmatism between
890 Silurian (443-419.2 Ma) and Carboniferous (358-298.9 Ma) time. Therefore, it is thought that
891 the mineralization was not formed during and much older than this time interval. For this
892 reason, these younger ages might have derived from resetting and/or isotopic losses of older
893 ages or mixing with younger components within the sample separates. The distribution of model
894 ages for the NW vein samples are more tightly, but still normally distributed with some
895 separates of sample OD-18 younger (250-138 Ma) and separates of sample OD-11 older (384-
896 258 Ma). The mean age of 254 Ma is compatible with the magmatism and metamorphism of
897 Triassic age and likely partially to completely resetting the Re-Os isotope systematics in the
898 NW veins. When considering textural features, these samples exhibit deformation and alteration
899 indicating a secondary origin. Therefore, they are thought to have formed after metamorphism
900 and/or magmatism that effected the MM. Sample OD-18, has secondary arsenopyrite formation
901 and the isotope system was effected by main high-grade Menderes metamorphism that

developed after Triassic (Eocene) and thus, as a result of isotope losses, younger ages were obtained for the mineralization.

5. Conclusions

The Küre (Ödemiş) mineralization occurs as veins, which are both concordant to schistosity (E-trending vein/Stage I) and vein cutting the schistosity (NW-trending vein/Stage II) in the core schists of the MM. The stage I of mineralization (557-562 Ma) is represented by arsenopyrite, pyrite, gold and lillianite whereas the stage II mineralization (244-249 Ma) are arsenopyrite, pyrite, lillianite and gold. The post ore stage minerals are scorodite, rutil, orpiment and realgar. Alteration minerals (Post ore stage) are identified as chlorite, sericite, K-feldspar, Na-feldspar, rutile, epidote and carbonate. The geochronological data presented here suggest a long period of intermittent magmatic and hydrothermal activity in the vicinity of the Küre deposit. These ages coincide with Kuunga Orogeny (500-600 Ma) with associated acidic activity and Triassic magmatic activity (246-227 Ma) of the MM.

The $^3\text{He}/^4\text{He}$ ratios of fluids extracted from arsenopyrites (0.08–0.09 Ra) are close to those of a crustal source ($<0.1\text{Ra}$) and much lower than typical mantle values (6-8 Ra). Besides, judging from elemental abundance patterns the contribution of an atmospheric noble gas component dissolved in water to the mineralized fluids is significantly high. Helium of mantle origin is $\sim 0.7\text{-}1.0\%$ at most in fluid inclusions in arsenopyrite, indicating that the fluids of the Küre gold mineralization consisted predominantly of crustal fluids with minor mantle contribution, if any.

Arsenic content in arsenopyrite obtained from EPMA suggests that the temperatures of arsenopyrite formation in E-vein range from 380 to 480 °C, with a sulfur fugacity between -7.4 and -4.3 at 5 k-bar whereas these temperatures are in the range of 390 to 475 °C at a sulfur fugacity of 7.0 to -4.5, respectively.

The textural relationship indicates that arsenopyrite and pyrite hosted in schists were melted, at least in part, under metamorphic conditions (amphibolite-facies, 625 °C, 7 k-bar, 551-540 Ma) and a melt containing Fe-As-Pb-Au-Ag occurred. Ore minerals (arsenopyrite, pyrite, gold and lillianite) derived from this melt were emplaced in schistosity plains forming E vein. In the following phase, hydrothermal solutions rich in Au and As derived from the remobilization of the E vein have been precipitated in shear-related extensional fractures forming NW vein. During the temperature depression, (250-360 °C) gold constantly crystallized. Precambrian-Cambrian acidic magmatic activity during this period (530-570 Ma) may have played an important role in the melting and crystallization of arsenopyrite. Homogenization temperatures (258-387 °C), salinity (1-6.5 wt.% NaCl equiv.) and the presence of the CO₂+H₂O+NaCl system in the fluid inclusions of the later-stage (Stage-II) quartz.

The Küre mineralization shows great similarities to orogenic gold deposits located in orogenic belts elsewhere in the world. The Re-Os model age and the fluid sources of the mineralization, which are deduced from Re-Os and noble gas isotopes, and the spatial/temporal relationship of the mineralization to metamorphic host rocks suggest that the Küre gold-arsenopyrite mineralization is an orogenic gold deposit and contemporaneous with the evolution of the Menderes Massif.

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FIGURE CAPTIONS

Figure 1. (a) Tectonic map of Turkey showing the major terranes and bounding sutures. The filled triangles indicate the polarity of subduction (Koralay, 2015). Unit abbreviations are as follows: AZ: Afyon Zone; BFZ: Bornova Flysch Zone; BZS: Bitlis-Zagros Suture; CACC: Central Anatolian Crystalline Complex; CM: Cycladic Massif; IPS: Intra-Pontide Suture; IZ: Istanbul Zone; IAES: İzmir-Ankara-Erzincan Suture; LN: Lycian Nappes; MM: Menderes Massif; PS: Pamphylian Suture; RSM: Rhodope-Strandja Massif; SZ: Sakarya Zone. Simplified geological (Candan et al., 2016; Koralay, 2015) and (b) mineralization map (Yilmaz et al., 2015) of the Menderes Massif (main figure) and location of the study area.

Figure 2. Geological map of the Küre area and location of gold-bearing quartz-arsenopyrite veins. Modified from MTA (1970) and Koralay (2015).

Figure 3. Micrographic textures of gold-bearing quartz-arsenopyrite veins in Neo-Proterozoic metamorphic rocks at Küre in thin sections under plain and XPL (cross-polarized light) microscope: A) Polycrystalline quartz with irregular grain boundaries formed in response to grain boundary migration (GBM) recrystallization in the E-trending quartz-arsenopyrite vein; **Apy1: arsenopyrite in E-trending quartz-arsenopyrite vein**. Note the light-grey quartz grain (Qz-1) is bulging into the lighter grain at its left, B) NW-trending quartz-arsenopyrite vein with large quartz crystals displaying undulate extinction (LQzU); incipient fine recrystallized quartz (FRQz) defined by small polygonal quartz grains and subgrains occupying intergrain planes mainly parallel to the grain boundaries and microcracks; **Apy2: arsenopyrite in NW-trending quartz-arsenopyrite vein**, C) Highly serrate quartz (Sqz) boundary, grain boundary migration and subgrain rotation; new grains having similar orientation to the edge of the large quartz grain can be seen adjacent to the sutured grain boundary; the new grains have a similar orientation to the edge of the large quartz grain and these features are clear evidence for dynamic recrystallization in quartz or recrystallization that occurs syntectonically; Ep: epidote, D) Elongated quartz grains (Eqz) with shear planes and dense fractures filled with chlorite-sericite (Chl) minerals; slf: sulfide, E) Cataclastic texture (CT) in quartz-arsenopyrite vein indicating continuous shearing during and after mineralization; Slf: sulfide, F) K-feldspar (Kfs) associated with sulfide (mainly arsenopyrite) in arsenopyrite-quartz vein; Qz-2: quartz,

Slf: sulfide, (G) Albitization, H) Partially sericitized (Ser) vein K-feldspar (Kfs), I) Sericite (Ser)-Chlorite (Chl) alteration and J) Rutile (Rt)-Epidote (Ep)-Chlorite (Chl) alteration overprinting quartz-arsenopyrite vein; Qz-2: quartz, Slf:sulfide, Plj: plagioclase.

Figure 4. Paragenetic sequence in the Küre deposit. Abbreviations: Qz-1 occurring in E-trending, schistosity-conformable quartz-arsenopyrite vein and Qz-2 occurring in E-trending crosscutting quartz-arsenopyrite vein. Apy1 and Apy2 euhedral to anhedral, fine-grained arsenopyrite crystals associated with Qz-1 and Qz-2.

Figure 5. Ore minerals of the Küre deposit in polished sections under reflected light; (A) arsenopyrite (Apy) occurring as euhedral crystals, (B, C) anhedral crystals with variable sizes from 1mm associated with Q₁-Q₂ quartz (Qtz) and Au, (C) euhedral pyrite crystals (Py) superimposed on minute crystals of arsenopyrite (Apy) in a quartz (Qtz) matrix, (D) native gold (Au) and Bi-bearing lillianite (Bi) minerals in quartz, (E) native gold (Au) and Bi-bearing lillianite (Bi) minerals as inclusions in arsenopyrite (Apy) mineral, (F) Au in cracks or in interstitial space of brecciated arsenopyrites, (G) native gold (Au) in scorodite (Sco) with relics of replaced arsenopyrite, (H) replacement of euhedral arsenopyrite (Apy) by scorodite (Sco) in quartz (Qtz) matrix.

Figure 6. Back-scattered electron images showing (A) darker rim of scorodite around arsenopyrite (Apy); a large gold grain (Au) occurring at the boundary between Apy and scorodite, (B) note fine-grained Au along fractures of Apy, (C) occurrence of minute Au grains within Apy, (D) majority of Apy transformed into scorodite matrix, (E) Apy inclusions enclosed by coarse-grained and euhedral pyrite (Py), (F) fractured Apy floating within scorodite matrix, (G) a close up view of (F), (H) replacement of Apy and Py by scorodite; note very irregular contact between Apy and scorodite as well as Apy and Py.

Figure 7. $^{187}\text{Os}/^{188}\text{Os}-1/\text{Os}$ diagram of arsenopyrite samples from E and NW veins.

Figure 8. Microphotograph of fluid inclusion types from gold-bearing quartz-arsenopyrite veins of the Küre deposit, showing (A) microphotograph of doubly-polished thin sections containing different types of fluid inclusions, (B) a close up view of the photomicrograph A where: the two-phase vapor (VCO_2)-liquid- CO_2

(LCO₂-not distinguishable in the picture)-sodium chlorine solution (LNaCl) type inclusion in quartz/Type-1; two-phase vapor (H₂O)-sodium chlorine solution (LNaCl)/Type-2; vapor-CO₂ (VCO₂)/Type-3; (C) Fluid inclusions trails found within dynamically recrystallized fine-grained quartz between larger quartz crystals.

Figure 9. Histograms of salinity (A) and homogenization temperatures (T_h) (B) of primary fluid inclusions in quartz.

Figure 10. Plot of homogenization temperature (T_h) *versus* salinity (wt.% NaCl equiv) for fluid inclusions from arsenopyrite and quartz minerals in the Küre gold deposit (Data from this study).

Figure 11. P-T trapping conditions of type 1 and 2 fluid inclusions in NW-trending quartz-arsenopyrite veins calculated using Loner SpW, Loner HGK (<http://fluids.unileoben.ac.at/computer.html>). Calculated isochores for aqueous fluid inclusions type-1 (H₂O-NaCl) (n=13; Pink-shaded area) and carbonic fluid inclusion type-2 (H₂O-CO₂-NaCl) (n=17; Gray-shaded area). The temperature of arsenopyrite formation, as calculated from mineral chemistry. **Apy-1:** arsenopyrite from E-trending quartz-arsenopyrite vein, **Apy2:** arsenopyrite in NW-trending quartz-arsenopyrite vein.

Figure 12. Phase diagram for the Fe–As–S system along with arsenopyrite geothermometer from Deol et al. (2012), who based their diagram on Barton (1969), Kretschmar and Scott (1976) and Sharp et al. (1985). Arsenic in at % of arsenopyrite for co-existing assemblage of pyrite–pyrrhotite–arsenopyrite; an arsenopyrite–pyrrhotite–loellingite is also plotted. L/As line divides the diagram into upper and lower fields, representing As liquid phase and solid phase. Red and green-shaded areas represents the approximate stability field of arsenopyrite in the Küre deposit.

Figure 13. Element abundance ratios of noble gases, expressed as fractionation factor relative to atmospheric abundance and ³⁶Ar, in fluid inclusions of quartz and arsenopyrite from Küre. Fractionation factor is defined as (ⁱX/³⁶Ar)_{sample}/(ⁱX/³⁶Ar)_{air}, where ⁱX=⁴He, ²⁰Ne, ⁸⁴Kr, ¹³²Xe. Fractionation patterns for

dissolution equilibrium of noble gases in water are given for 0°C and 50°C at 5% salinity according to Smith and Kennedy (1983) and for 100°C, 250°C and 330°C according to Crovetto et al. (1982). Helium Apy data are out of scale because of large crustal contributions.

Figure 14. $^{40}\text{Ar}/^{36}\text{Ar}$ vs. $^3\text{He}/^{36}\text{Ar}$ for Küre (Ödemiş) fluid inclusions in the arsenopyrite host minerals from ore veins. Samples from Küre are presented as red squares and compared with well-studied samples of various types in the world. Data for these deposits are taken from the following studies: Dongping Au from Mao et al. (2003), Red River Au-Cu from Hu et al. (2004), Jiaodong Au from Zhang et al. (2008), Muruntau Au from Graupner et al. (2006), Pingqiu and Jinjing gold deposits from Wang et al. (2019), Carris W-Mo-Sn from Moura et al. (2014), Yaoling-Meiziwo W from Zhai et al. (2012).

Figure 15. The purified separates with very low Os concentrations (~10-12 ppt) and very high $^{187}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Re}/^{188}\text{Os}$ values yielding TMa ages of 258 and 316 Ma.

Plate 1. Plate 1. A) Mineralized sheared mica schist and greenish-gray arsenopyrite mineralization (E-trending vein) conformable to schistosity of sheared, chloritized and slightly silicified mica schist, A) and B) Dark greenish-gray massive arsenopyrite (>50 %)-pyrite vein (NW-trending vein) cutting major schistosity plain.

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TABLE 1

Easting/ Northing	Name	Province	Commodity	Tectonic belt	Host rock	Deposit type	Age of host rock	Main ore minerals; age of mineralization	Orebody and structure	Mineral reserve/resources	Status	Reference
641700E/ 4307800	Değirmenteçi	Manisa	Au, Ag	WAET	Schist, ophiolite	Epithermal (Orogenic)	Neoproterozoic	Gold, arsenopyrite, stibnite, sericite; Tertiary	NE- and NW-trending silicified structures in schists and oribolitic rocks	Rockchip (max): 2.1 g/t Au, >10,000 ppm As, 690 ppm Sb; RC holes: 10 m @ 0.8 g/t Au, 6 m @ 1.33 g/t Au, 2 m @ 1.5 g/t, 4 m @ 2.6 g/t Au	P	Eurogold Company report (1991)
N 674000E/	Cemalcavuş	Uşak	Au, Ag, As	WAET	Schist, gneiss	Epithermal (Orogenic)	Upper Cretaceous Neoproterozoic	ase Gold, silver, arsenopyrite, stibnite, galena, sphalerite; sericite, chlorite; Au/Ar total gas	Shear and schistosity -controlled, fracture filling, crackle breccia, dissemination and dendritic veinlets mineralization within silicified-pyritized mica schist and meiss	Outcrop rockchip: 8 Au values >0.5 g/t with a peak of 3.1 g/t Au, 14 Ag values >10 g/t with a peak of 80 g/t. DDH sections: 1m @ 0.8 g/t Au, 1.3 g/t Ag; 1m @ 0.1 g/t Au, 360 g/t Ag; 1m @ 0.7 g/t Au	P	Eurogold Company report (1992); Ege Madencilik Company report (2011); Yılmaz et al. (2015); Yıldız and Bailey (1978); Larson
N 595800E/	Allahdiyen	Manisa	Sb Au, Ag, As	WAET		orogenic Epithermal L.S.	Neoproterozoic	ase: 28.89 Ma Gold, silver, arsenopyrite, stibnite, cinnabar;	Irregular masses and veins of chalcedony, silicified breccia and micro breccia within ENE-trending low- angle detachment and high-angle normal fault zone or crystalline quartz vein silicified marble	several samples up to 5.36 g/t Au, 20 g/t Ag, 0.22% As, 0.58% Sb; Other workers outcrop rock (max): 7 g/t Au, 35 g/t Ag; old adits for Hg operations	P	Eurogold Comp report (1992) Eurogold Company report (1992); Doga Madencilik Company report (2013); Sönmez and Gümre (2013)
N 660000E/	Devutlar	Uşak	Sb Au, As	WAET		orogenic Mesothermal		Cenozoic age, probably Neogene Gold, arsenopyrite, pyrite	Au-bearing quartz-arsenopyrite veins with maximum thickness of 30 cm and strike length of 5 m	Au, 20 g/t Ag, 0.22% As, 0.58% Sb; Other workers outcrop rock (max): 7 g/t Au, 35 g/t Ag; old adits for Hg operations	P	Eurogold Company report (1992); Doga Madencilik Company report (2013); Sönmez and Gümre (2013)
N 654840E/	Balıbaşı	Uşak	Au, As	WACT	Schist	orogenic Mesothermal	Neoproterozoic	Gold, arsenopyrite, chalcopyrite, pyrite, galena, arsenobismite (?), scorodite, sericite,	Massive to disseminated, fine grained, greenish grey arsenopyrite-bearing crystalline quartz vein in fracture (max: 0.2 m x 5 m) normally cutting mica schist foliation. No alteration halo adjacent to the vein. Free acid grains in arsenopyrite	between 17.5 and 33.1 g/t Au Rockchip outcrop: one sample returning 366 g/t Au, 42.7 g/t Ag, 1255 ppm Bi, 1470 ppm Cu, 36.5% As, 0.19% Sb, 0.26% Pb	P	Eurogold Company report (1992); Doga Madencilik Company report (2013); Sönmez and Gümre (2013)
N 657857E/	Hacıismail	Uşak	Au, As	WACT	Schist, gneiss	orogenic Mesothermal	Neoproterozoic	chlorite; 72.8 ± 6.5 Ma Gold, arsenopyrite, chalcopyrite, pyrite, galena, arsenobismite (?), scorodite, sericite,	Au-bearing quartz-arsenopyrite vein with 50 m strike length and 15 cm width or large pockets (1 m in diameter) of quartz-arsenovirite without extension	Rockchip outcrop: 3 samples Au (max): 1.3% Rockchip outcrop: 3 samples	P	Eurogold Company report (1992); Doga Madencilik Company report (2013); Sönmez and Gümre (2013)
N 657370E/	Çavuşlar	Uşak	Au, As	WACT	Schist	orogenic Mesothermal	Neoproterozoic	and saliniv: 5% NaCl in fluid inclusions Gold, arsenopyrite, chalcopyrite, pyrite, galena, arsenobismite (?), scorodite, sericite,	Au-bearing quartz-arsenopyrite veins with a maximum thickness of 10 cm	Au (max): 1.3% Rockchip outcrop: 3 samples n.d	P	Eurogold Company report (1992); Doga Madencilik Company report (2013); Sönmez and Gümre (2013)
N 660500E/	Dervişli	Uşak	Au, As	WACT	Schist	orogenic Mesothermal	Neoproterozoic	chlorite; Cretaceous (?) Gold, arsenopyrite, pyrite; Cretaceous (?)	Au-bearing quartz-arsenopyrite veins with a maximum thickness of 5 cm	between 25.7 and 192 g/t Au n.d	P	Eurogold Company report (1992); Doga Madencilik Company report (2013); Sönmez and Gümre (2013)
N 633600E/	Derbent	Manisa	Au, As	WACT	Mica schist, graphitic schist,	orogenic Mesothermal	Neoproterozoic	Gold, arsenopyrite, pyrite	EW-trending, Au-bearing stockwork quartz-arsenopyrite veinlet zone	Rockchip outcrop: 1 sample returning 5.8 g/t Au, 9.66 g/t Ag	P	Eurogold Company report (1992); Sönmez and Güngör (2013)
N 590000E/	Bosdağ		Au, As	WACT	Gneiss, marble	orogenic Mesothermal	Neoproterozoic	Gold, arsenopyrite, pyrite	NS-trending crystalline, Au-bearing quartz-arsenopyrite vein over a strike length of 1 km, conformable to or cutting schistosity	Rockchip outcrop: ranging from 1.52 to 21 g/t Au, 0.61% As Rockchip outcrop (max): 86 g/t	P	MTA (1970); Eurogold Company report (1992) Çalıştay and Eyyüpoğlu (1979);
N 4246000	Zeytinlik	İzmir	Au, As	WACT	Gneiss, marble	orogenic Mesothermal	Neoproterozoic	Gold, arsenopyrite, biotite, muscovite, stibnite, chalcopyrite, scorodite, fine pyrite and magnetite in arsenopyrite	NE-trending Au-bearing quartz arsenopyrite veins (max 0.20 m x 2.5m), conformable to or cutting schistosity	Au, >1% As Rockchip outcrop (max): 4.13 g/t	P	Akioğlu (2008) Çalıştay and Eyyüpoğlu (1979);
N 4236680	Yılanlıkale	İzmir	Au, As	WACT	Gneiss, marble	orogenic Mesothermal	Neoproterozoic	Pyrite, pyrrhotite, chalcopyrite occurring in arsenopyrite cracks. No free gold and biotite observed.	Stockwork Au-bearing quartz-arsenopyrite veins/veinlets conformable to or cutting schistosity (up to 0.5 m width) within a NE-trending fault zone over a strike length of 120 m	Au, >1% As 0.057% As, 0.18 g/t Au, 1.1 g/t	P	Akioğlu (2008) Çalıştay and Eyyüpoğlu (1979);
N 4239502	Elmacıoğlu	İzmir	Au, As	WACT	Gneiss, schist	orogenic Mesothermal	Neoproterozoic	Gold, pyrrhotite, pyrite, arsenopyrite, scheelite, chalcopyrite, scorodite, fine pyrite and magnetite in arsenovirite	SSE and N-S, conformable to or cutting schistosity Gold-arsenopyrite mineralizations are concordant with or conformable to or cutting schistosity of the rocks.	Au 1% As, 0.3 g/t Au	P	Akioğlu (2008) Çalıştay and Eyyüpoğlu (1979);
N 596100E/	Kemer	İzmir	Au, As	WACT	Gneiss, schist	orogenic Mesothermal	Neoproterozoic	Gold, pyrite, arsenopyrite, scorodite	The strikes and dips of the mineralizations are measured as N55E /30SE and N80W /76SW NS-trending Au-bearing quartz-arsenopyrite veins, conformable to or cutting schistosity (max: 0.9 m x 5 m)	Au at Au, >0.4% As Rockchip outcrop (max): 5.5 g/t	P	Akioğlu (2008) Eurogold Company report (1992)
N 542600E/	Arikbaşı	İzmir	Au, As	WACT	Gneiss, marble	orogenic Mesothermal	Neoproterozoic	Gold, pyrite, arsenopyrite, scorodite	Mostly thin quartz arsenopyrite veins, conformable to or cutting schistosity plains.	Rockchip outcrop (average): 5.5 g/t Au, >0.4% As Rockchip outcrop (max): 5.5 g/t	P	MTA (1970)
N 4228500	Yusufla	İzmir	Au, As	WACT	Gneiss, marble	orogenic Mesothermal	Neoproterozoic	Gold, pyrite, arsenopyrite	Sh: Ag-Au-Au mineralization in silicified shear and breccia zones in graphite-rich mica schist is closely associated with high angle NW-striking faults and low angle WNW-striking south boundary of Kizilçik Menderes graben; structurally-controlled, crosscutting and unambiguously graphite-schist-hosted ore mineralization	Au 450,000 ton @ 5-7% Sb, DDH cores from 7 drill holes (max): 10.3 g/t Au, 832 g/t Ag, 31% Sb, 6.23% As, 2000 ppm Cu, 1850 ppm Pb, 1400 ppm Zn	P	Erfar and Larson (1992); Larson et al. (1992); Yılmaz et al. (1979); Öztürk et al. (1997)
N 4236500	Emirli	İzmir	Sb, Ag, As	WAET	Mica schist,	Epithermal	Neoproterozoic	Stage I: Gold, arsenopyrite, pyrite, quartz (Th: 321 °C); Stage II: Bismite, gold (max: 10.3 g/t), chalcopyrite, sphalerite, tetrahedrite (Th: 270 °C); Stage III: pyrite, arsenopyrite (Th: 214 °C); Stage IV: realgar, orpiment, marcasite, cinnabar (Th: 158 °C)	with magmatic	Au at 4 g/t Au Outcrop ore grades yielding up to 38.9 g/t Au, 0.51 g/t Ag and Au/Ar ratios ranging up to 78 Outcrop ore grades yielding generally 30 g/t Au with a peak of 128.8 Au Outcrop ore grades yielding max	P	Erfar and Larson (1992); Akçay et al.
N 4217000	Küre	İzmir	Au	WACT	stratite schist Schist/Gneiss	contributions Epithermal	Neoproterozoic	Gold, arsenopyrite, pyrite, scorodite; Th _{max} :	Quartz-arsenopyrite veins with strike lengths of 5 m to	5 g/t Au and 0.5 g/t Au Arsenopyrite outcrops ore returning max 3 g/t Au and <0.5 g/t Au	P	(2006); Yıldı (2009) MTA (1977); Erfar and Larson (1992); Eurogold Company report, (1992); Yılmaz et al. (1979); Öztürk et al. (1997)
N 569000E/	Karacören	Aydın	Au, As	WACT	Gneiss	Mesothermal	Neoproterozoic	210-298 °C Gold, arsenopyrite, pyrite	500 m and widths of up to 2 m Quartz-arsenopyrite veins/veinlets (max length: 150 m, max width 0.6 m), bands and pods cutting gneiss/schist or in some cases parallel to schistosity	containing Au at 4 g/t Au Outcrop ore grades yielding up to 38.9 g/t Au, 0.51 g/t Ag and Au/Ar ratios ranging up to 78 Outcrop ore grades yielding generally 30 g/t Au with a peak of 128.8 Au Outcrop ore grades yielding max	P	MTA (1970); Eurogold Company report, (1992); Yılmaz et al. (1979); Öztürk et al. (1997)
N 567270E/	Karabağ	Aydın	Au, As	WACT	Gneiss	Mesothermal	Neoproterozoic	Gold, arsenopyrite, pyrite	Quartz-arsenopyrite veins/veinlets (max length: 150 m, max width 0.6 m) and pods cutting gneiss/schist or in some cases parallel to schistosity	Au Outcrop ore grades yielding generally 30 g/t Au with a peak of 128.8 Au Outcrop ore grades yielding max	P	Company report, (1992) MTA (1970); Eurogold Company report, (1992); Yılmaz et al. (1979); Öztürk et al. (1997)
N 569800E/	Arpatlarası	Aydın	Au, As	WACT	Gneiss	Mesothermal	Neoproterozoic	Gold, arsenopyrite, pyrite	Quartz-arsenopyrite veins/veinlets (length <50 m, width<0.1 m), bands and pods cutting meiss/schist Quartz-arsenopyrite veins/veinlets (length <30 m, width<0.1 m), bands and pods cutting gneiss/schist or in some cases parallel to schistosity	5 g/t Au and 0.5 g/t Au Arsenopyrite outcrops ore returning max 3 g/t Au and <0.5 g/t Au	P	reort, (1992) MTA (1970); Eurogold Company report, (1992); Yılmaz et al. (1979); Öztürk et al. (1997)
N 561500E/	Sobucudağ	Aydın	Au, As	WACT	Schist	Mesothermal	Neoproterozoic	Gold, arsenopyrite, pyrite	width<0.1 m), bands and pods cutting meiss/schist Quartz-arsenopyrite veins/veinlets (length <30 m, width<0.1 m), bands and pods cutting gneiss/schist or in some cases parallel to schistosity	5 g/t Au and 0.5 g/t Au Arsenopyrite outcrops ore returning max 3 g/t Au and <0.5 g/t Au	P	reort, (1992) MTA (1970); Eurogold Company report, (1992); Yılmaz et al. (1979); Öztürk et al. (1997)
N 569586E/	Akçabaşı	Aydın	Au, As	WACT	Gneiss	Mesothermal	Neoproterozoic	Gold, arsenopyrite, pyrite	width<0.1 m), bands and pods cutting meiss/schist Quartz-arsenopyrite veins/veinlets (max length of 100 m, width of 1 m), bands and pods cutting gneiss/schist or in some cases parallel to schistosity	5 g/t Au and 0.5 g/t Au Arsenopyrite outcrops ore returning max 3 g/t Au and <0.5 g/t Au	P	Company report, (1992) MTA (1970); Eurogold Company report, (1992); Yılmaz et al. (1979); Öztürk et al. (1997)
N 570500E/	Gökçük	Aydın	Au, As	WACT	Gneiss	Mesothermal	Neoproterozoic	Gold, arsenopyrite, pyrite	width<0.1 m), bands and pods cutting meiss/schist Quartz-arsenopyrite veins/veinlets (length <30 m, width<0.1 m), bands and pods cutting gneiss/schist or in some cases parallel to schistosity	5 g/t Au and 0.5 g/t Au Arsenopyrite outcrops ore returning max 3 g/t Au and <0.5 g/t Au	P	Company report, (1992) MTA (1970); Eurogold Company report, (1992); Yılmaz et al. (1979); Öztürk et al. (1997)
N 597300E/	Tatarmemişler	Aydın	Au, As	WACT	Schist	Mesothermal	Neoproterozoic	Gold, arsenopyrite, pyrite	Au-bearing lenses of quartz-arsenopyrite-pyrite veins	5 g/t Au and 0.5 g/t Au Arsenopyrite outcrops ore returning max 3 g/t Au and <0.5 g/t Au	P	Company report, (1992) MTA (1970)
N 693000E/	Sarıköy	Aydın	Au, As	WACT	Schist	Mesothermal	Neoproterozoic	Gold, arsenopyrite, pyrite	Small Au-bearing quartz-arsenopyrite veins	A gold-bearing quartz- arsenopyrite lens with a width of 0.65 m containing 5.4 g/t Au	P	MTA (1970)

WAET: West Anatolian Extensional Tectonism, WACT: West Anatolian Compressional Tectonism, P: Prospect, O. M: Operating Mine

TABLE 2

TABLE 2

Mineral	Sample number	Apy-type/vein trend	As	Fe	S	Zn	Se	Au	Ag	Sb	Cu	Total	As	Fe	S
Unit			Weight %										Atomic %		
Arsenopyrite	OD-11	Apy-1/E	46,27	35,72	20,35	0,28	0,15	n.d	n.d	n.d	0,02	102,79	32,53	33,69	33,44
	OD-11		46,63	35,81	20,41	0,24	0,15	n.d	n.d	0,21	n.d	103,45	32,61	33,59	33,35
	OD-19/1		46,28	33,38	19,16	1,32	0,66	n.d	n.d	0,04	0,01	99,87	33,76	32,23	32,23
	OD-19/1		46,50	33,99	19,50	0,20	0,66	n.d	n.d	0,03	n.d	100,93	33,50	32,44	32,41
	OD-18		45,16	35,32	20,11	1,25	0,60	0,05	n.d	0,01	0,02	102,49	32,83	33,01	32,73
	OD-18		46,63	35,16	19,89	1,41	0,58	n.d	n.d	0,02	0,09	103,78	32,71	33,08	32,60
	OD-18		46,82	35,40	16,96	1,40	0,13	n.d	n.d	0,08	0,10	103,91	32,77	33,24	32,65
	OD-14	Apy-2/NW	45,34	33,33	19,40	2,74	0,57	0,01	n.d	0,02	0,10	101,51	32,57	32,11	32,57
	OD-14		45,76	34,58	19,51	2,40	0,13	0,12	n.d	0,03	0,11	102,55	32,50	34,58	32,39
	OD-14		45,64	34,75	19,49	2,39	0,55	0,01	n.d	n.d	0,09	102,93	32,33	33,02	32,26
	OD-17		46,07	32,88	19,17	n.d	0,50	0,05	0,02	0,06	0,05	100,88	33,39	31,97	32,47
	OD-17		45,89	31,88	19,00	1,74	0,50	n.d	1,32	0,01	n.d	99,11	33,83	31,53	32,74
	OD-14/1		45,53	34,83	19,39	1,65	0,53	n.d	0,01	0,80	0,10	102, 12	33,43	32,87	31,89
	OD-14/1		45,61	35,13	19,39	1,69	0,59	0,07	0,01	n.d	0,07	102,53	33,38	33,04	31,76
	OD-14/1		46,92	34,72	19,68	1,73	0,62	0,04	n.d	0,06	0,03	103,83	33,01	32,76	32,35
Mineral	Sample number		As	Fe	S	Zn	Se	Au	Ag	Sb	Cu	Te	Bi	Total	
Pyrite (FeS ₂)	OD-11	Apy-1/E	1,76	45,82	52,04	0,29	0,02	0,01	0,02	0,03	0,06	n.d	n.d	100,05	
	OD-14	Apy-2/NW	0,93	42,91	50,08	2,90	0,01	0,05	0,01	n.d	0,80	n.d	n.d	96,97	
	OD-14/1	Apy-2/NW	0,88	45,05	51,14	1,76	n.d	n.d	0,01	n.d	0,02	n.d	n.d	98,88	
	OD-14/1	Apy-2/NW	1,35	45,27	51,21	1,67	n.d	0,04	n.d	0,03	0,05	0,02	n.d	99,32	
Mineral	Sample number		As	Fe	S	Zn	Se	Au	Ag	Sb	Cu	Te	Bi	Total	
Gold	OD-11	Apy-1/E	0,01	2,17	0,11	n.d	n.d	94,58	5,56	0,04	0,09	0,04	0,36	102,91	
	OD-11	Apy-1/E	n.d	0,55	0,07	0,31	n.d	95,36	6,23	0,02	n.d	0,07	0,44	103,05	
	OD-14	Apy-2/NW	0,01	0,08	0,10	2,43	n.d	89,33	4,78	0,07	0,12	0,06	0,36	97,32	
	OD-14	Apy-2/NW	0,04	0,50	0,18	1,97	n.d	92,18	4,95	n.d	0,04	0,05	0,30	100,21	
	OD-14	Apy-2/NW	0,03	5,18	0,10	2,00	n.d	86,46	3,48	n.d	0,07	0,02	0,48	97,84	
	OD-14/1	Apy-2/NW	0,04	0,68	0,10	0,92	n.d	91,34	4,71	0,01	0,02	0,09	0,36	98,25	
Mineral	Sample number		As	Fe	S	Zn	Se	Au	Ag	Sb	Cu	Te	Bi	Pb	Total
Lillianite (Pb ₃ Bi ₂ S ₂)	OD 14	Apy-2/NW	n.d	6,30	18,26	n.d	n.d	n.d	0,25	5,15	0,18	n.d	31,64	42,68	104, 49
	OD-17	Apy-2/NW	1,33	0,27	16,09	n.d	n.d	n.d	n.d	2,04	0,10	n.d	69,66	n.d	89,23
Mineral	Sample number		As	Fe	S	O	Total								
Scorodite FeAsO ₄ ·2H ₂ O	OD-17	Apy-2/NW	60,76	13,88	n.d	13,57	88,81								
	OD-19/1	Apy-1/E	73,54	11,98	0,26	14,23	100,00								
	OD-19/1	Apy-1/E	71,89	11,59	0,51	16,01	100,00								
	OD-11	Apy-1/E	71,21	10,04	n.d	13,50	94,75								

n.d: not detected

As/S
0,97
0,97
1,04
1,03
1,00
1,00
1,00
1,00
1,00
1,00
1,06
1,33
1,04
1,05
1,02

1

TABLE 3

Sample	Vein trend	Type	Total Re	Total Os		187Os		1/Os	Common	
			(ppb)	±	(ppt)	±	(ppt)	±	Os (ppb)	
OD-11	NW	*	0,700	0,007	20,1	0,2429	3,1	0,06	49,79	0,017
OD-13	E	*	0,560	0,008	36,5	0,2893	3,1	0,03	27,43	0,033
OD-14	E	*	0,279	0,007	14,7	0,1647	2,8	0,04	67,98	0,012
OD-16	E	*	0,526	0,007	57,6	0,5034	4,1	0,06	17,36	0,054
OD-16-2	E	*	0,542	0,007	77,2	0,5831	4,4	0,06	12,95	0,073
OD-18	NW	*	0,932	0,008	40,3	0,2876	3,1	0,04	24,84	0,037
OD-18-2	NW	*	1,016	0,008	70,9	1,0441	3,7	0,07	14,10	0,067
OD11-2	NW	**	0,652	0,007	9,6	0,2386	2,3	0,03	104,25	0,007
OD11-3	NW	**	0,606	0,008	11,91	0,1668	1,8	0,02	83,99	0,010
OD-18-3	NW	**	1,041	0,007	20,6	0,3705	2,4	0,09	48,50	0,018
OD-18-4	NW	**	1,035	0,008	18,2	0,2481	1,8	0,04	54,85	0,016
OD-13-2	E	**	0,734	0,008	22,5	0,2260	2,1	0,02	44,48	0,020
OD-16-3	E	**	0,750	0,007	71,9	1,7135	7,0	0,61	13,91	0,065

	*** ¹⁸⁷ Re/ ¹⁸⁸ O s	±	187Os/ ¹⁸⁸ O s	±	rho	Tma (Ma)	Intensity of Apy alteration to
OD-11	196,01	5,23	1,382	0,043	0,714	384	Moderately high
OD-13	79,68	1,44	0,704	0,011	0,516	435	Moderately high
OD-14	110,92	3,91	1,748	0,050	0,565	874	Very high
OD-16	46,63	0,88	0,574	0,012	0,438	577	Minor alteration
OD-16-2	35,29	0,64	0,455	0,008	0,446	562	Minor alteration
OD-18	118,62	1,89	0,621	0,011	0,642	250	Moderately high
OD-18-2	71,72	1,40	0,420	0,011	0,615	246	Moderately high
OD11-2	434,81	27,07	2,421	0,151	0,965	316	Moderately high
OD11-3	284,18	9,26	1,348	0,043	0,868	258	Moderately high
OD-18-3	277,90	9,79	1,001	0,050	0,671	189	Moderately high
OD-18-4	299,02	7,76	0,813	0,028	0,685	138	Moderately high
OD-13-2	171,86	3,86	0,774	0,018	0,783	226	Moderately high
OD-16-3	54,64	1,52	0,798	0,073	0,266	738	Minor alteration

*: 50-80% arsenopyrite concentration, **: pure arsenopyrite, *** Common Os is the non-radiogenic Os component.

Tma model ages were calculated with a ¹⁸⁷Re decay constant (λ) of 1.666E⁻¹¹ (e.g., Shirey and Walker, 1998),

a present day mantle ¹⁸⁷Os/¹⁸⁸Os of 0.1270 and a ¹⁸⁷Re/¹⁸⁸Os value of 0.401 (Pearson et al., 1995).

I/Common
Os
58,96
29,99
83,75
18,68
13,74
26,90
14,88
136,93
99,04
54,93
60,74
49,01
15,40

TABLE 4

Sample	Fluid inclusion types	Size of fluid inclusion μm	Tm-ice $^{\circ}\text{C}$	Tm-first $^{\circ}\text{C}$	Tm-CO ₂ hydrate (clathrate) $^{\circ}\text{C}$	Total homoge- nization Th $^{\circ}\text{C}$	Wt.% NaCl equiv.
OD-18-1-1	Type-2	4,4		-25,0	7,7	336,8	4,9
OD-18-1-2	Type-1	8,0	-3,0			237,1	5,0
OD-18-1-3	Type-2	6,2		-28,0	7,7	280,0	5,7
OD-18-1-4	Type-1	8,1	-2,0	-23,2		340,0	3,4
OD-18-1-5	Type-1	8,1	-2,9	-24,0		254,0	4,8
OD-18-1-6	Type-1	8,2	-2,8	-25,0		271,6	4,7
OD-18-1-7	Type-2				9,8	340,0	0,4
OD-18-1-8	Type-1	7,2	-4,8	-20,0		282,0	7,6
OD-18-1-9	Type-1		-3,6			264,0	5,9
OD-18-1-10	Type-2				9,9	287,0	0,2
OD-18-1-11	Type-2				9,6	322,4	0,8
OD-18-1-12	Type-1	5,8	-4,0			271,0	6,5
OD-11-1	Type-1	5,7	-3,5			258,0	5,7
OD-11-2	Type-1	5,7	-5,0			266,0	6,5
OD-11-3	Type-2	6,4			7,5	284,5	4,8
OD-11-4	Type-2	5,7			9,5	349,0	1,0
OD-11-5	Type-2	6,2		-22,0	9,0	288,0	2,0
OD-11-6	Type-1	5,8	-4,5	-23,0		277,2	7,2
OD-11-7	Type-2	5,2			9,9	294,0	0,2
OD-11-8	Type-1	5,1	-3,3			323,1	5,4
OD-11-9	Type-1	6,1	-4,2			330,0	6,7
OD-11-10	Type-1	6,1	-4,5			326,5	7,7
OD-19-1	Type-2	6,0			8,8	273,0	2,4
OD-19-2	Type-2	5,5			7,5	301,0	4,8
OD-19-3	Type-2	4,0			8,0	330,0	3,9
OD-19-4	Type-2	4,0			8,3	370,0	3,4
OD-19-5	Type-2	6,1			7,5	259,5	4,8
OD-19-6	Type-2	8,4			7,0	259,0	5,7
OD-19-7	Type-2	5,6			9,0	387,0	2,0
OD-19-8	Type-1	4,2	-1,5	-20		274,0	2,6
OD-19-9	Type-1	3,0	-1,0	-20		358,0	1,7
OD-19-10	Type-1	5,5	-4,0			260,2	6,5
OD-19-11	Type-1	6,5	-2,0			236,6	3,4
OD-19-12	Type-2	7,4			9,10	244,1	1,8
OD-19-13	Type-1	6,4	-4,5			340,0	7,2

Tm-ice: final melting temperature of ice crystals of fluid inclusion in quartz, Tm-CO₂:

melting temperature of hydrate crystals, Th $^{\circ}\text{C}$: homogenization temperature of fluid inclusion, Wt.%NaCl equiv.: Weight % NaCl equivalent.

TABLE 5

Sample	^4He	^{20}Ne	^{40}Ar	$^3\text{He}/^4\text{He}$	$^3\text{He}/^4\text{He}$	$^{20}\text{Ne}/^{22}\text{Ne}$	$^{21}\text{Ne}/^{22}\text{Ne}$	$^{40}\text{Ar}/^{36}\text{Ar}$	$^{38}\text{Ar}/^{36}\text{Ar}$	$(^3\text{He}/^4\text{He})_{\text{Cor}}$	$^4\text{He}_{\text{mantle}}$
Weight	$10^{-8} \text{ cm}^3/\text{g}$	$10^{-12} \text{ cm}^3/\text{g}$	$10^{-8} \text{ cm}^3/\text{g}$	10^{-6}	Ra					Ra	%
OD-11 Qtz	0,0704	1521	188,0	1,4	1,0	9,767	0,03006	972,2	0,1878	1,0	13
0.50384 g	± 0.0036	± 82	± 9.4	$^{+1.6}_{-1.4}$	$^{+1.2}_{-1.0}$	± 0.024	± 0.00033	± 4.3	± 0.0011	$^{+3.7}_{-1.0}$	$^{+46}_{-13}$
OD-18 Qtz	0,213	3860	194,8	1,08	0,78	9,756	0,02921	521,7	0,18834	0,47	6
0.50374 g	± 0.011	± 200	± 9.8	± 0.55	± 0.40	± 0.027	± 0.00037	± 3.3	± 0.00090	$^{+0.94}_{-0.47}$	$^{+12}_{-6}$
OD-11 Apy	68,6	9730	726	0,1094	0,0787	9,811	0,02882	302,0	0,1882	0,0745	0,753
1.00204 g	± 3.4	± 490	± 77	± 0.0089	± 0.0064	± 0.025	± 0.00031	± 2.3	± 0.0010	0,0065	± 0.081
OD-14 Apy	59,8	10010	632	0,120	0,0864	9,826	0,02884	309,1	0,1886	0,0814	0,839
0.64848 g	± 3.0	± 500	± 44	± 0.010	± 0.0073	± 0.050	± 0.00049	± 1.5	± 0.0011	0,0072	± 0.091
OD-13 Apy	8,43	58,7	16,25	0,127	0,091	9,633	0,0303	469,1	0,1887	0,091	0,96
0.69982 g	± 0.42	± 3.1	± 0.85	± 0.026	± 0.019	± 0.096	± 0.0015	± 5.0	± 0.0012	0,019	± 0.23
OD-18 Apy	46,2	83,0	19,8	0,110	0,079	9,61	0,0326	684,9	0,1887	0,079	0,81
0.50102 g	± 2.3	± 4.4	± 1.0	± 0.016	± 0.011	± 0.15	± 0.0021	± 9.4	± 0.0014	0,011	± 0.14

Sample	$^{40}\text{Ar}^*$	$^{40}\text{Ar}^*$	F^4He	^{84}Kr	^{132}Xe	^{128}Xe	^{129}Xe	^{130}Xe	^{131}Xe	^{134}Xe	^{136}Xe
Weight	$10^{-8} \text{ cm}^3/\text{g}$	%		$10^{-12} \text{ cm}^3 \text{ STP/g}$	$10^{-12} \text{ cm}^3 \text{ STP/g}$	$^{132}\text{Xe} = 100$					
OD-11 Qtz	130,3	69,3	2,17	91,4	16,6	7,05	98,2	15,08	78,7	38,85	32,90
0.50384 g	± 6.5		± 0.16	± 4.6	± 1.0	± 0.22	± 1.4	± 0.37	± 1.9	± 0.84	± 0.88
OD-18 Qtz	83,3	42,8	3,39	91,7	11,04	7,13	98,1	15,05	78,9	39,17	32,9
0.50374 g	± 4.3		± 0.24	± 4.6	± 0.58	± 0.31	± 1.3	± 0.35	± 1.1	± 0.58	± 1.0
OD-11 Apy	8,3	1,1	170	453	17,77	7,13	98,6	15,19	79,41	38,78	32,75
1.00204 g	± 5.5		± 20	± 24	± 0.90	± 0.23	± 1.0	± 0.27	± 0.73	± 0.53	± 0.56
OD-14 Apy	21,6	3,4	174	429	17,66	7,14	98,6	15,24	79,18	38,95	32,81
0.64848 g	± 3.3		± 15	± 22	± 0.91	± 0.21	± 1.4	± 0.39	± 0.98	± 0.58	± 0.57
OD-13 Apy	5,91	36,4	1450	19,9	2,63	7,12	97,9	15,05	78,6	39,0	32,9
0.69982 g	± 0.33		± 110	± 1.0	± 0.15	± 0.59	± 3.8	± 0.56	± 3.2	± 1.4	± 2.0
OD-18 Apy	11,17	56,4	9520	14,6	2,84	7,10	98,7	15,0	79,2	39,0	32,7
0.50102 g	± 0.58		± 710	± 1.1	± 0.56	± 0.83	± 4.0	± 1.1	± 4.4	± 2.0	± 1.5

Qtz: quartz, Apy: arsenopyrite

Cor: corrected for atmospheric He contribution assuming $(^4\text{He}/^{20}\text{Ne})_{\text{air}} = 0.319$ $^4\text{He}_{\text{mantle}}$: mantle He contribution estimated assuming $(^3\text{He}/^4\text{He})_{\text{crust}} = 0.014 \text{ Ra}$, $(^3\text{He}/^4\text{He})_{\text{mantle}} = 8 \text{ Ra}$ $^{40}\text{Ar}^*$: excess ^{40}Ar $\text{F}^4\text{He} = (^4\text{He}/^{36}\text{Ar})_{\text{sample}} / (^4\text{He}/^{36}\text{Ar})_{\text{air}}$

TABLE 6

Metamorphic phase	Metamorphic grade	Evidence-magmatism	Age	Reference
Magmatism1 M1	Granulite facies	Intrusion of (meta)tonalite Relics within the paragneisses charnockitic orthogneisses	590 Ma ~580 Ma	Koralay (2015) Candan (1995); Candan and Dora (1998); Candan et al. (1994, 2011b); Dora et al. (2001, 2002); Koralay (2015)
Magmatism 2		Intrusion of gabross (metagabbro)	565-560 Ma	Candan et al (2016)
Küre, arsenopyrite-Au mineralization/ore-stage-I/ E-trending vein			577-557 Ma	This study
Magmatism3		Intrusion of granitoids (orthogneisses)	570-530 Ma	Loos & Reischmann (1999); Koralay et al. (2011, 2012)
M2	Amphibolite facies -migmatization	From central and southern submassifs	~550 Ma	Hetzel et al. (1998); Dora et al. (2002); Candan et al. (2011b)
M3-M4	Eclogite facies/amphibolite facies	Relics within the metagabbros and metabasic volcanics	535±3 Ma	Candan and Dora (1998); Oberhänsli et al (1997, 2010); Candan et al. (2011b, 2016)
Küre, arsenopyrite-Au mineralization/ore-stage-II/ NW-trending vein			257-246 Ma	This study
Magmatism 4		Intrusion of leucogranites	246-227 Ma	Koralay et al. (2001)
M5	Greenschist facies	From central submassif	Pre-230 Ma	Akkök (1983), Zlatkin et al. (2013)
M6 (MMM)	Amphibolite facies/ greenschist facies	Rb/Sr and Ar/Ar mica ages	60-35 Ma	Şengör et al. (1984); Satır and Friedrichsen, H., (1986); Bozkurt and Satır (2001); Lips et al. (2001); Cenkitok et al. (2016)
M7	Greenschist facies	Ar/Ar mica and amphibole ages	20-12 Ma	Hetzel et al. (1995 a, b), Zlatkin et al. (2013) Lips et al. (2001)