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P-T-X constraints on the Koru epithermal base-metal (±Au) deposit, Biga Peninsula, NW Turkey

Gülcan Bozkaya ^a, Ömer Bozkaya ^a, David A. Banks ^b, Ahmet Gökçe ^c

^a Department of Geological Engineering, Pamukkale University, 20070 Denizli, Turkey
 ^b School of Earth and Environment, University of Leeds, Woodhouse Lane, Leeds LS2 9JT, United Kingdom
 ^c Department of Geological Engineering, Cumhuriyet University, 58140 Sivas, Turkey

ABSTRACT

The Koru deposit is a typical intermediate sulfidation base-metal (\pm Au) example of volcanic-volcaniclastic hosted mineralization in the Biga Peninsula and north-western Turkey. Ore deposition was controlled by collisional and post–collisional tectonics related to the closure of the Tethys Ocean. Galena, baryte and quartz are main minerals, accompanied by minor amounts of sphalerite, pyrite, chalcopyrite, covellite and marcasite. The homogenization temperature of fluid inclusions indicates two distinct fluid pulses, one at a temperature commensurate with epithermal mineralization and boiling/near boiling conditions at c. 350 °C, the second approximately 150-200 °C lower. Salinity in both instances was from 11.0 to 0.2 wt. % NaCl. The δ D and δ ¹⁸O values of water in equilibrium with early quartz and fluid inclusions, plot close to the magmatic water box indicating the source of the high temperature fluid was magmatic. δ D and δ ¹⁸O values from early and late baryte trend towards the meteoric water line (MWL), but this is not due to mixing with meteoric water and indicates equilibration with alteration assemblages. LA-ICP-MS analyses of fluid inclusions reveal high Cu–Zn–Pb concentrations in the fluids, despite their low salinity, transported as chloride complexes. The range of temperatures within the early quartz and sphalerite samples can be

explained by pressure variations during vein and fracture opening from near lithostatic to hydrostatic pressure.

Keywords: Epithermal, Fluid Inclusion, Koru, Turkey, Base-metals, Gold

1. Introduction

The Turkish segment of the Tethyan Eurasian Metallogenic Belt, which extends from Western Europe through Anatolia to Iran (Fig. 1a, Janković, 1986; Yigit, 2012), is currently being intensively prospected and contains an increasing number of active mines with Turkey becoming a world-class gold-producing country over the last 20 years. The majority of the deposits, in northwest Turkey, are low to intermediate sulfidation (LS-IS) Au + Ag deposits, often with gold as the main resource or in lesser amounts associated with Pb-Zn mineralization. A number of the epithermal Au-Ag (high and low sulfidation/HS-LS), porphyry Au-Cu-Mo and base metal skarn deposits and mineralizations are associated with Tertiary calc-alkaline magmatism in Western Anatolia and the Biga Peninsula (Fig. 1b and Table 1). The epithermal deposits in the Biga Peninsula have the same geological characteristics as other deposits of this style around the globe. Fluid inclusion studies (Unal et al, 2013; Yilmaz et al., 2010, 2013; Orgün et al., 2005; Oyman et al., 2003; Bozkaya and Banks, 2105a,b; Bozkaya et al., 2014, 2016) show that the mineralizing fluids were similar in the Turkish deposits and comparable with deposits of similar style and classification worldwide. Low salinity fluids pre-dominate at deposits where Au is the main resource, however at deposits where base-metal sulfides are the main resource, with lesser amounts of Au and Ag, higher salinity fluids and the low salinity fluids are present.

The Koru deposit can be considered an IS epithermal deposit, hosted by volcanic-volcaniclastic units related to the collisional and post-collisional tectonic regime in Biga Peninsula (Yigit, 2012). There are many studies on the genesis of ore deposition and sources

of fluids in the Biga Peninsula, such as those listed in Table 1. Frequently, a fluid mixing model is inferred for mineralization due to the wide range of salinities and homogenization temperatures of fluid inclusions that are present (Oyman et al., 2003; Orgün et al. 2005; Yilmaz et al. 2010, 2013, Unal et al., 2013). In this study we present an alternative interpretation to meteoric fluid mixing with magmatic fluids that was previously been proposed. Based on the petrography, paragenesis of fluid inclusions, microthermometry and laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) analyses of fluid inclusions, combined with oxygen and hydrogen isotope analyses from quartz, baryte (Bozkaya and Gökçe, 2009; Bozkaya et al., 2016) sulfur isotope data from galena, sphalerite and baryte and propose that all the salinity fluids had a dominantly magmatic origin. A better understanding of the fluid composition and the key physical processes, which led to mineralization in the Koru deposit, can be applied to understand why, in the Biga peninsula, some deposits are dominantly gold deposits and some are dominantly base-metals with minor amounts of gold.

2. Geology and Mineralization

2.1. Regional Geological Setting

The Biga Peninsula which is part of the Tethyan Eurasian Metallogenic Belt represents the westernmost extension of the Sakarya Zone of Pontides, at the intersection of Gondwana (African and Arabian plates) and Laurasia (Eurasian plate) (Jankovic, 1986; Okay et al., 1990; 1991; Yigit, 2012) (Fig. 1a). This area therefore, has a complicated geologic and tectonic history due to the collision of different continental fragments. The peninsula can be tectonically sub-divided into three zones going from the northwest to southeast. These are the Ezine zone (Permian metasedimentary and Permo-Triassic ophiolitic rocks), the Ayvacık-Karabiga zone (eclogite-bearing ophiolitic mélange and Late Triassic limestone blocks) and

the Sakarya zone (Permian metamorphic rocks of the Kazdağ Group and Permo-Triassic metasedimentary and metamagmatic rocks of the Karakaya Complex) (Fig. 1b). Cenozoic volcanic and plutonic rocks cover extensive areas and dominate the geology of the Biga Peninsula. The Late Cretaceous-Tertiary period has been divided into four different subperiods: (1) the Late Cretaceous-Early Eocene (turbiditic sandstones and limestones), (2) Middle Eocene-Oligocene (andesitic lavas and tuffs, granite, granodiorite and limestones), (3) Miocene (granodiorite, rhyolitic and rhyodacitic pyroclastics, andesitic and dacitic lavas, and turbiditic clastics) and (4) Plio-Quaternary (fluvial sediments and lacustrine carbonates). Regional uplift occurred at the end of the Oligocene resulting in the Eocene-Oligocene sequence being deeply eroded. This was followed by extensive late Oligocene to middle Miocene calc-alkaline magmatism. Granodioritic plutons and andesitic-dacitic volcanic rocks developed during the Eocene with Oligocene granite, granodiorite, syenite and early Miocene rhyolite, dacite and calc-alkaline andesites. In the Thrace basin and the Biga Peninsula, Naalkali basalts were emplaced during the late Miocene. The sedimentary, volcano-sedimentary, volcanic and associated plutonic rocks in the Biga Peninsula are all related to the transition from a collisional to an extensional tectonic regime during the period of Cenozoic calcalkaline magmatism from 52 to 18 Ma (Yigit, 2006; 2012) (Fig. 1b).

2.2. Local Geology and Mineralization

The Koru mine is located in the northwest part of the Biga Peninsula, 50 km from Çanakkale (Fig. 2) and had a total reserve of 0.5 Mt at 8 % Pb, 2 % Zn, 300 g/t Ag (Bozkaya, 2001). Mineralization is in veins, stockworks and breccias controlled by a NW trending fault system. Several Pb-Zn deposits in the Koru district are located within a triangular area defined by the villages of Koru, Eskikışla and Karaömerler (Fig. 2) hosted by Oligocene pyroclastic rocks. These are, from NW to SE, Eskikışla, Tahtalıkuyu, İkinci Viraj, Bakır Kuyusu, Derin

Dere, Kuyutaşı Tepe, Sarıoluk and Tesbihdere. The Tahtalıkuyu and Eskikışla deposits were the most active mining areas of the Koru district, therefore, most of the samples in this study were collected from these when mining was active (Fig. 2). All the deposits were exploited by the Çanakkale Mining Company, but none are currently active.

The volcanogenic rocks hosting Pb-Zn deposits consist of agglomerate, lapillistone and tuff with andesite intercalations in the lower parts of the ore bearing sequence, silicified rhyolitic breccias in the middle parts and silicified rhyolitic tuffs in the upper parts (Fig. 2). All rock types were affected by hydrothermal alteration, to a variable degree, which produced quartz + kaolinite and/or illite and/or illite-smectite with small amounts of alunite (Bozkaya et al., 2016). The green color of pyroclastic rocks in the lower parts is mostly related to zeolitization and chloritization resulting from interaction between volcanic glass and seawater (Bozkaya et al., 2007). Silicification increases in the middle and upper parts of the ore bearing sequence, with the main components of the pyroclastic breccias and tuffs formed from intensely silicified rocks (Fig. 2). Tuffs from the upper parts of ore bearing sequence are generally lithic ash tuffs with a large amount of volcanic rock fragments with an argillized and silicified volcanic matrix (Fig. 3a). Silicified vitric ash tuffs contain coarse-grained quartz replacing feldspars with devitrification of the volcanic glass (Fig. 3b,c). Stockwork type veinlets become dominant in the silicified-tuffs and in the upper parts of the succession, whereas massive and/or layered veins oriented WNW-ESE, are most common in the lower parts (Fig. 2). In the Tahtalıkuyu and Eskikışla sectors, the vein-type mineralization in deeper parts and stockwork-type mineralization in upper parts show depositional styles that are comparable with volcanogenic massive sulfide deposits. However, the mineralized fault and stockwork zone cuts the overlying tuffs and in the stockwork-type zones mineralization fills spaces between the agglomerates. In addition the lack of stratiform mineralized lenses and layers indicates that the Koru base metal mineralization is epigenetic, occurring after the

 deposition of the volcano-sedimentary rocks (Bozkaya, 2001; Bozkaya and Gökçe, 2001, 2002, 2009).

In the mineralized veins, sphalerite, galena, pyrite, chalcopyrite, quartz, baryte and calcite are the main minerals, accompanied by small amounts of tennantite-tetrahedrite, marcasite, covellite, bornite and small amounts of native gold (Fig. 4). Galena and sphalerite generally exhibit anhedral or rarely subhedral crystals. Microscopic studies (Fig. 3d-g) show these minerals were formed in at least two episodes. As seen in Fig. 3d, early-stage sphalerite crystals are cracked and disaggregated by later deformation with a brecciated texture where the fractures were filled by late-stage galena. In another example, the early-stage galena was replaced by later sphalerite and chalcopyrite (Fig. 3e). Chalcopyrite is generally the last sulfide to precipitate and almost all contains inclusions of galena and sphalerite (Fig. 3f). Galena also contains rod-like tennantite-tetrahedrite crystals as late-stage sulfide segregations (Fig. 3g). Baryte and lesser quartz are the main gangue minerals in the deposit, with their crystal sizes increasing with depth. Baryte forms lath-shape euhedral crystals accompanied by quartz and carbonate minerals. Relatively coarse-grained baryte crystals sometimes exhibit a comb texture and are observed to cut the earlier anhedral quartz and calcite crystals (Fig. 3h,i). The two generations of baryte can be distinguished as the early, small irregular crystals are cut by later, large elongate crystals. The large elongate baryte crystals are also observed to cut the anhedral quartz and calcite (Fig. 5).

3. Analytical Methods

3.1. Microthermometry

Microthermometry of the fluid inclusions was carried out using a Linkam THMS 600 heating-cooling stage at the Fluid Inclusion Laboratory of the Department of Geological Engineering Pamukkale University (Turkey). The temperature of phase changes for eutectic

 melting (Te), ice melting (Tm_{ice}) and homogenization (Th) were recorded. Phase transitions below 0 °C are accurate to within \pm 0.2 °C based on calibration with pure CO₂ and H₂O standards, with a similar level of precision. Above 0 °C accuracy was \pm 3 °C based on the melting point of pure solids and precision was \pm 1 °C. The ice-melting temperatures were converted to salinities using the equation of Bodnar (1993), and assuming the fluid composition is represented by the H₂O - NaCl system.

3.2. LA-ICP-MS

The chemical analysis of individual fluid inclusions, or fluid inclusion assemblages, was made by LA-ICP-MS using an Agilent 7500c mass spectrometer, combined with a Geolas ablation system at Leeds University (UK). This system uses a Compex 103 ArF excimer laser producing a wavelength of 193 nm with an energy density between 10 - 15 J cm⁻² at the sample surface. The operating frequency of the laser was typically 5 Hz with spot sizes of 25 µm, occasionally 50 µm, and the main criteria being that the size was greater than that of the inclusions. The ablated material was transported from the ablation cell to an Agilent 7500c ICP-MS using 99.9999 % He flowing at 2 ml min-1 into a cyclone mixer where it was combined with the Ar carrier gas flowing at 1.02 ml min⁻¹. The mixer prolongs the signal from the ablated inclusions and improves precision by increasing the number of cycles of the mass spectrometer through the selected elements and therefore the number of determinations of each element/Na ratio that are made. The instrument was operated in reaction cell mode using 2.5 ml min⁻¹ 99.9999 % H₂ to remove interferences on the main ⁴⁰Ca isotope by ⁴⁰Ar and the main ⁵⁶Fe isotope by ⁵⁶Ar. Element/Na intensity ratios from the mass spectrometer were converted to weight/weight ratios using the NIST glass SRM-610 and the soda lime SRM-1412 as calibration standards. SRM 1412 is used specifically for the calibration of K/Na as it has a K/Na ratio of 0.988 compared to the K/Na ratio for NIST 610

 of 0.0047 which is very different to the values measured from the fluid inclusions. The NIST SRM-610 standard was used to check for instrumental drift, which was found to be insignificant over each day's analysis. Integration of the standard and sample signals used the SILLS software package (Guillong et al., 2008). Full details of the analytical protocols and calibration of the instrument were presented in Allan et al. (2005).

3.3. Hydrogen and oxygen isotopes

The hydrogen and oxygen isotope data of quartz and illite in Koru deposit were reported in Bozkaya et al. (2016). Fluid inclusions from baryte samples were analysed for δD (fluid inclusions) and $\delta^{18}O$. O-isotope analyses were performed using an automatic CO_2 laser-BrF₅ fluorination system with a Micromass Optima mass spectrometer in the Stable Isotopes Laboratories, Royal Holloway University of London (UK). Approximately 1.7 mg of baryte was analysed to obtain $\delta^{18}O$ values that are reported relative to the Vienna Ocean Water Standard (V-SMOW). The analytical precision on standard and sample duplicates was \pm 0.1 ‰. Hydrogen isotope analysis was carried out on fluid inclusions from baryte separates by thermal decrepitation. The extracted water vapor was converted to hydrogen gas, and the δD of each sample was determined. H-isotope analyses were performed with a Micromass Iso Prime mass spectrometer in the Stable Isotope Laboratories, University of Nevada (USA) and are reported as δD ‰ notations versus V-SMOW) with analytical precisions of \pm 1.0 ‰.

4. Results

4.1. Fluid Inclusion Petrography

Fluid inclusions are abundant in quartz, sphalerite and baryte, and those measured were predominantly primary in origin, occurring in growth bands or in fluid inclusion arrays

that were related to the paragenesis of the host minerals. Two types of quartz have been identified: the more prevalent is euhedral quartz (Oz-1) which has numerous euhedral overgrowths that are often delineated by bands of primary fluid inclusions oriented perpendicular to the crystal faces, or contain random individual primary fluid inclusions especially in the inner quartz core (Fig. 5, 6a). Within individual growth bands, the fluid inclusions have variable Liquid (L)/Vapor (V) ratios and often contain V-rich fluid inclusions (Fig. 6b). The primary fluid inclusions in quartz were also found in clusters and have a feather-like structure resulting from their trapping on different quartz faces. These are features commonly observed in epithermal environments (Dong et al., 1995; Moncada et al., 2017) and also in other deposits in the Biga Peninsula (Bozkaya et al., 2014; Bozkaya and Banks, 2015a,b). There are examples of co-existing V-rich, L-V fluid inclusions and fluid inclusions containing semi-prismatic solids, probably trapped during boiling (Fig. 6 e.f). These prismatic crystals are birefringent in crossed polars (possibly illite) and are common in fluid inclusions however, they are very uncommon in the quartz matrix (Moncada and Bodnar, 2012; Moncada et al., 2012). The second type of quartz was observed in places to replace the earlier euhedral quartz, or more commonly to abut these crystals. These smaller anhedral crystals are cleaner in appearance with fewer fluid inclusions. The fluid inclusions are mainly randomly dispersed, but are also present in fluid inclusion arrays (FIA's) that extend to the crystal edge and do not penetrate into the adjacent crystals. All the fluid inclusions are L-V with larger and more consistent L/V ratios than fluid inclusions observed in the first generation of quartz.

Two generations of sphalerite were identified by their texture, but were most easily distinguished by the darker colour of the early sphalerite and the lighter colour of the later sphalerite. The fluid inclusions in the first generation are similar those observed in the euhedral quartz with random L-V fluid inclusions and many that are V-rich in close proximity

to each other (Fig. 6c) which is indicative of boiling. In addition, there are secondary trails of smaller more numerous L-V fluid inclusions cutting the early sphalerite. The second generation of lighter sphalerite also contains primary fluid inclusions of a similar size and with the same L/V ratios as the secondary fluid inclusions in the dark early sphalerite.

There are two generations of baryte, both of which cut the second generation of quartz and are the final phases to precipitate (Fig. 6d). The fluid inclusions in baryte are mainly Lonly but there are some L-V fluid inclusions with small bubbles (Fig. 6e, f). The second generation of baryte contains a large number of small primary fluid inclusions that are L-only and delineate crystallographic growth zones. This baryte also contains pseudosecondary and secondary fluid inclusions that are L-only (Fig. 6g). There are also a small number of L-V fluid inclusions that occur in the same arrays as L-only fluid inclusions (Fig. 6h). As fluid inclusions in baryte frequently stretch or leak (Ulrich and Bodnar, 1988) it is highly likely, given the association with L-only arrays, that the vapor phase may have been artificially produced. Baryte is also observed to replace the earlier euhedral quartz crystals, which then contain the same secondary trails of L-only fluid inclusions as in the baryte (Fig. 6i,j).

4.2. Microthermometry

A summary of the microthermometry data for fluid inclusions in quartz, sphalerite and baryte are presented in Table 2. In quartz and sphalerite the eutectic melting temperature (Te) was observed between -40°C and -50°C. The majority of fluid inclusions homogenize to liquid (Th_{liq}) and comprise the bulk of the measurements. These data are given as the average, minimum and maximum-recorded homogenization temperatures (Th), along with a smaller number of VL fluid inclusions that homogenized to a vapor phase. These values are shown graphically (Fig. 7) as a box and whisker plot where the shaded box represents the 25th to 75th percentile range, the horizontal lines are the 5th and 95th percentile values and individual

points are outliers. The mean and median values (black and white horizontal lines in the shaded box) are in most cases identical and the data is therefore normally distributed. This approach allows a clearer visual appreciation of the data.

The homogenization temperature data for the fluid inclusions in quartz, sphalerite and barite are given in Fig. 8. In Qz-1 Th_{liq} values are between 249 °C and 354 °C, in Qz-2 between 166 °C and 251 °C and Th_{vap} homogenization for vapor-rich inclusions associated with Qz-1 are between 315 °C and 354 °C (Figs. 7, 8). In Sp-1 Th_{liq} values are between 248 °C and 341 °C, although there were some V-rich fluid inclusions where homogenization could not be observed due to the darkness of the sphalerite. In Sph-2 Th_{liq} was between 134 °C and 228 °C. Th_{lia} values for fluid inclusions in Brt-1 were between 70 °C and 217 °C, but the large range and the petrography of the L-V fluid inclusions makes us treat these values with caution. In Brt-2 the vast majority of fluid inclusions are L-only and Th could not be measured. The Tm_{ice} values for L-V fluid inclusions in Qz-1 are between -0.9 °C and -5.1 °C (1.6 to 8 equiv wt.% NaCl), Qz-2 between -0.6 °C and -5.6 °C (1.1 to 8.7 equiv. wt.% NaCl) but could not be observed in V-rich fluid inclusions (Fig. 9). In Sp-1 Tm_{ice} are between -1.8 °C and -5.5 °C (3.1 to 8.7 equiv. wt.% NaCl) and in Sph-2 between -0.1 °C and -7.5 °C (0.2 to 11.1 equiv. wt.% NaCl). In Brt-1 Tm_{ice} are between -0.3 °C and -3.4 °C (0.5 to 5.5 equiv. wt.% NaCl) and where fluid inclusions in Brt-2 had a vapor phase (although they occur amongst fluid inclusions which only had liquid and the vapor was likely an artefact) the salinity of the fluid inclusions covered a similar range. The salinities of the fluid inclusions in the different minerals essentially covers the same range, however the highest salinities are recorded in sphalerite hosted inclusions.

4.3. LA-ICP-MS

The element/Na weight ratios for fluid inclusions, ablated in quartz, baryte and sphalerite, are presented in Fig. 10 and Table 3 together with the standard deviation and where appropriate the concentration of the elements calculated using salinity from microthermometry measurements. Table 3 contains two columns for K/Na ratios (K^* and K) as the data have been separated into high (K^* /Na) and low (K^* /Na) ratios that are statistically different. The K^* /Na ratios are from inclusions where we have observed or suspect the presence of illite (Fig. 6e) in the inclusions which would increase the ablation signal for K adding to the K signal from the fluid phase. In quartz, the primary L-V or V-rich fluid inclusions, where we do not see any solid phase in the fluid inclusion, have lower K^* /Na ratios. However, there appears not to be a significant difference in the ratios of other elements/Na that were determined, between fluid inclusions that contain a solid and those that do not. The data are shown in Fig. 10 which illustrates the similarities of the trace element ratios.

4.4. Hydrogen and Oxygen Isotopes

The measured δ^{18} O values for baryte (Brt-1) and quartz crystals (Qz-1), the calculated δ^{18} O values for fluid inclusion water in equilibrium with baryte and quartz, together with δD values for the fluid inclusions are given in Fig. 11 and Table 4. Baryte crystals have measured δ^{18} O values ranging from +7.4 to +14.5 ‰, and 14.2 ‰ for quartz. The calculated δ^{18} O values for water in equilibrium with baryte and quartz was determined using the equation of Sharp and Kirschner (1994) and the average homogenization temperatures from fluid-inclusion studies. The calculated δ^{18} O_(V-SMOW) values are between -13.5 to -6.4 ‰ and the $\delta D_{(V-SMOW)}$ values for inclusion waters are between -88 and -62 ‰.

5. Discussion

5.1. Pressure Temperature Conditions of Mineralization

Constraining the P-T conditions during mineralization can be difficult as the measured homogenization temperatures of fluid inclusions are only minimum temperatures unless there is some way to constrain the pressure. When textural evidence from fluid inclusions for boiling exists, this fixes the position on the liquid vapor curve for the appropriate salinity. However, this requires the co-existence of fluid inclusions that homogenise to both liquid and vapor at the same temperature, but the vapor from boiling may not always be trapped. In the earliest generations of quartz at Koru, the Th_{liq} of fluid inclusions in the growth bands of euhedral quartz (Qz-1) cover a large range of temperatures from c. 260 °C to 360 °C, whereas the Th_{vap} covers a narrower range from c. 320 °C to 360 °C. Petrographically, the two types of inclusions can be shown to have co-existed. A similar range of Th_{liq} and Th_{vap} temperatures were recorded for fluid inclusions in the first generation of sphalerite (Sph-1). These higher homogenization temperature fluid inclusions are clearly primary occurring in, and terminating at the boundaries of the growth zones. The presence in both quartz and sphalerite of L-V and V-rich fluid inclusions in close association and which homogenise over the same temperature range is indicative of boiling. Variable L/V ratios are also commonly observed (see Figs. 5, 6) in fluid inclusion arrays in both quartz and sphalerite, which are also indicative of boiling. The morphology of the Qz-1 overgrowths (Fig. 5a) is indicative of near equilibrium quartz deposition by a fluid saturated with respect to silica (Bozkaya and Banks, 2015b) which is consistent with adiabatic cooling.

In Fig. 12, the data of Haas (1971), for the effect of salinity on the temperature-depth relationships of a fluid along the boiling curve at hydrostatic pressure, has been used to construct the P-T-depth association of water of different salinities. Using this data and the evidence of fluid boiling in the earliest quartz allows the pressure and depth of mineralization

to be constrained by the boiling assemblages of L/V and V-rich fluid inclusions that homogenize over the same narrow temperature range c. 310 °C to 350 °C. For a lithostatically pressured system this equates to between c. 600 m to 700 m depth. If the fluid system was hydrostatically pressured, then depth would be approximately 1700 m. The depth of trapping should lie between the depth defined by hydrostatic or lithostatic confining pressures. The lower pressure limit is likely to be above hydrostatic pressure, as this would require unconstrained fluid connectivity to the surface over a depth of 1700 m, which is unlikely as additional pressure from some lithostatic load would be present.

Trapping of liquid and vapor fluid inclusions from the same generation of fluid (in growth zones of FIA's and clusters of fluid inclusions) should occur within a narrow temperature range, largely dictated by the experimental error. For fluid inclusions within the same FIA or growth band to exhibit a large range in homogenization temperature, as occurs here, necessitates a process that can produce a range of homogenization temperatures when trapping fluid inclusions from the same fluid at the same time. The pressure at the temperature of boiling can be constrained (Fig. 12) at ~140 bars for the upper Th values of c. 340 °C for the primary L-V and V-L fluid inclusions in both quartz and sphalerite. The pressure for the lower homogenization temperature values of primary L-V fluid inclusions in Qz-1 and sphalerite is ~50 bars at c. 265 °C. Petrographically, there is evidence that boiling and associated cooling was episodic, with clusters of fluid inclusions observed on growth surfaces of Qz-1 and the growth bands observed in Qz-1 (Fig. 6). Evidence of boiling, is also indicated by bands of chalcedony associated with euhedral quartz. However, the majority of fluid inclusions in the quartz overgrowths do not contain FIA's that indicate extensive boiling with V-L fluid inclusions being largely absent. Rather the variable L/V ratios within FIA's represent trapping of fluid inclusions as the hydrothermal fluid cooled when the pressure decreased from lithostatic to near hydrostatic. The lack of extensive boiling during the

close to that of the L-V curve. In this instance, as the pressure drop did not put the fluid significantly into the vapor field, there would not be a large number of V-L or V fluid inclusions produced. The range of homogenization temperatures can be explained as the earliest fluid to fill the open space of any vein will suffer the greatest pressure drop and therefore the greatest temperature drop. As the pressure in the open space increases, as more fluid enters the fracture and minerals are deposited, so the drop in temperature would decrease. This would be recorded in fluid inclusions trapped over a variable range of pressures and homogenization temperatures. Therefore, when the fluid inclusions are trapped during the precipitation of quartz in the vein, (from early to late) is related to the homogenization temperature. Thus, we suggest that the growth of Qz-1 and sphalerite occurred during periods when the pressure varied from close to lithostatic to close to hydrostatic with the maximum amount of quartz growth at the lower pressures when there was open space in the vein systems.

There are several examples of planes or trails of fluid inclusions that appear to be completely empty (effectively full of vapor of an unknown density with no observable liquid phase) in both sphalerite Sph-1) and in the cores of the euhedral quartz (Qz-1). The fluid inclusions have a negative crystal shape (Fig. 6) which is distinctly different to the shapes of other fluid inclusions that are V-rich, but also contain a very small observable quantity of liquid. Thus we suggest these are the same as the low density vapor (effectively empty) fluid inclusions recorded at the Arapuçandere deposit in the Biga peninsula (Bozkaya and Banks, 2015b) and elsewhere (Sillitoe and Hedenquist, 2003; Moncada, et al., 2012; Shimizu, 2014) that were generated by flashing. Flashing is a process which only occurs if the pressure decreases rapidly (almost instantaneously) to lower than the hydrostatic pressure. The liquid in the system does not have time to boil in the conventional manner but is instead

instantaneously converted into vapor and trapped in fluid inclusions where the vapor pressure is very low (effectively empty). Such fluid inclusions are usually preserved as secondary inclusions in pre-existing minerals due to the low Si concentration that would be present in the very low density vapor. Trapping of flashed vapor will only occur if the vein system had a finite volume and was not open to the surface. In this scenario, when the rock fractures due an instantaneous event, almost certainly a tectonic event, the pressure can decrease well below hydrostatic (Sibson, et al., 1988; Weatherley and Henley, 2013; Wilkinson and Johnson, 1996). If however, the vein opening was in response to supra-hydrostatic fluid pressure exceeding the confining strength of the rock then the volume of fluid flooding into the open space would not have allowed the pressure in the veins to drop quickly or low enough to produce flashing as the more rapid influx of fluid would have limited the pressure decrease.

The later generation of fluid inclusions, with lower homogenization temperatures, are present in the second generation of quartz and sphalerite and possibly the first generation of baryte. Fluid inclusions were located in Qz-2 (one sample Th_{liq} c. 230-250 °C, others Th_{liq} c. 170-210 °C), Sph-2 (Th_{liq} c. 130-165 °C), Bt-1 (Th_{liq} c. 120-165 °C, one sample as low as Th_{liq} c. 70 °C) and finally Bt-2 in which only liquid fluid inclusions are present and is therefore likely to have been trapped at less than c.60 °C (as a general rule if fluids were trapped at above c.60 °C they should nucleate a vapor bubble on cooling to room temperature). The samples were obtained from present day depths of 40 to 70 m, but the fluid inclusion homogenization temperatures would indicate they were trapped at slightly greater depths. The liquid fluid inclusions in the late barite (Bt-2) would be consistent with fluids derived from the surface. The salinity of these fluid inclusions covers approximately the same range as was recorded in the fluid inclusions trapped in the first generations of quartz and sphalerite (Fig. 9) and therefore these later fluids could simply be cooler fluids from the hydrothermal system expelled upwards and trapped at the same depth as the hotter early fluid inclusions. However,

there are a number of fluid inclusions with significantly lower salinities and it is possible that during this latest stage of mineralization there was mixing with cooler surface derived fluids that would fit with final deposition of Bt-2 at less than c.60°C.

5.2. Temperature-Salinity Variability

The high homogenization temperatures of primary fluid inclusions (earliest fluids) in quartz and sphalerite have a large range of salinities from c. 2 to 9 equivalent wt.% NaCl. The data does not support any visible correlation between homogenization temperature and salinity. In the lower homogenization temperature fluids (later fluids) there is also no discernible correlation with salinity. However, it was proposed (Cicek and Oyman, 2016) that there was such a correlation, with mixing of the higher temperature high salinity fluid (magmatic fluid) with a lower temperature low salinity fluid (meteoric fluid). This was also suggested for other deposits in the Biga Peninsula (Orgün et al., 2005, Yilmaz, et al, 2010, Çiçek et al., 2012), but this is supposition and has not been corroborated by other evidence (Banks et al. 2017). In the previous section, the homogenization temperature variability was shown to be related to adiabatic cooling of a single hydrothermal fluid as the pressure changed during opening of faults and fractures. This implies that the variation in salinity would not be due to the presence of a second fluid and mixing between two different salinity fluids. It would appear fortuitous that the homogenization temperature decrease caused by fluid mixing would match the decrease caused by adiabatic expansion of the fluid as the pressure decreased from lithostatic to near hydrostatic. Within the individual Qz-1 growth bands (Fig. 6a) fluid inclusions, which are primary, have different L/V ratios and different homogenization temperatures, but with a consistently low salinity. This is likely to have occurred by the process we suggested above, rather than by fluid mixing, which should be homogeneous on the scale of individual growth bands. We do not see individual growth bands in Sph-1, but we can see variable L/V ratios of

fluid inclusions within individual FIA's. Again, on this scale we would expect fluid inclusions with homogeneous L/V ratios from fluid mixing.

Deposits in the Biga Peninsula can either have fluid inclusions with a dominantly high homogenization temperature and low salinity, in the deposits that are gold resources or with similar high homogenization temperatures, but a mixed range of salinities, as we have presented in this study, in deposits that are a base-metal resource with lesser amounts of gold (Table 1). Low salinity fluid inclusions from the Arapuçandere deposit, which is similar to Koru, are interpreted to be derived from magmatic vapors, following a study by Banks et al. (2019). The high homogenization temperature, low salinity fluids have gold and silver concentrations up to 100's of ppm and gold particles can be observed in all of the inclusions. This would not be possible if the fluids were meteoric. We propose that Koru and other deposits in the Biga peninsula, with the same fluid inclusion characteristics, may also contain gold colloids that were transported by a magmatic fluid.

5.3. Fluid Compositions

The low eutectic melting temperatures, between -40 °C and -50 °C, in quartz and sphalerite indicates the fluid inclusions contain a significant amount of cations, such as Ca in addition to NaCl. Most of the fluid inclusions homogenize to liquid and account for the majority of the salinity data. There was no observable CO₂, either at room temperature or during cooling of the L-V or less common V-fluid inclusions. The fluids can therefore be considered as variable salinity chloride fluids that are comparable with other deposits in the Biga Peninsula. In previous studies of two deposits in the Biga Peninsula (Bozkaya et al. 2014: Bozkaya and Banks, 2015b) crush-leach analyses of fluid inclusions were used as an indicator of the source of the fluids, as Cl and Br are predominantly conservative when in solution and are not affected by water-rock-interactions, except when evaporites are involved.

At both Tesbihdere and Arapuçandere the fluid inclusions have very high Cl/Br and Na/Br ratios that are not consistent with either fluids derived from seawater, dissolution of halite or meteoric water. Three quartz samples analyzed in this study, using the method of Banks et al. (2000), have Cl/Br and Na/Br molar ratios for sample TK-83 (49,000 and 60,000) TK-61 (33,000 and 22,000) and TK-75 (18,000 and 21,000) that are similar to those recorded form the Tesbihdere and Arapuçandere deposits. Values in the thousands for Cl/Br and Na/Br have been found in volcanic gases (Pitcairn et al. 2001) and when fluids boil. Chloride preferentially goes into the vapor, relative to Br, while Br remains in the liquid (Germann et al., 2003). Therefore, the high Cl/Br and Na/Br from Koru are consistent with a low salinity vapor derived from a deeper magmatic fluid.

The cation concentrations of the fluids from the Koru deposit were determined in individual fluid inclusions or groups of smaller fluid inclusions in early quartz and sphalerite by LA-ICP-MS. Most of the analyzed fluid inclusions were L-V but some V-fluid inclusions were also ablated. The fluids are dominated by the alkali and alkaline earth elements with Na having the highest concentrations. The element/Na weight ratios are shown in Fig. 10 together with the calculated concentrations in Table 3. It should be noted that in Table 3, the K/Na ratio was used in the calculations of elemental concentrations in the fluid inclusions as the K*/Na ratio has an elevated concentration of K from the presence and ablation of what we interpret to be small crystals of illite.

The K/Na ratios fall into two groups, one where K/Na is greater than 1, the other between c. 0.2 and 0.4. The high ratios (K*/Na) are inconsistent with the homogenization temperatures when used to calculate the temperature from mineral-fluid geothermometers (Verma and Santoyo, 1997). Such high ratios are not uncommon and are often found associated with acid-sulphate alteration zones in high sulfidation hydrothermal systems (Ece et al., 2008). However, this is not the case for the Koru deposit which is a low to intermediate

sulfidation deposit. We surmise that in fluid inclusions where a solid was not visible but had a high K*/Na there would have been a solid present. The most likely mineral is illite, which has been associated with boiling in hydrothermal systems (Moncada et al., 2012). There is no statistical difference (standard t-test) of the individual element/Na ratios of fluid inclusions in quartz, sphalerite or baryte (Fig. 10) which indicates the same fluid was trapped in the different minerals. Although there is a range of salinities, in fluid inclusions trapped in different quartz and sphalerite samples, the element/Na ratios do not have a large range of values within each sample and the average value is similar between samples. The presence of the fluid inclusions with a high K*/Na value fluid, does not imply a different fluid, only that the presence of a K-bearing mineral was responsible for the additional group of K*/Na ratios.

The base metal concentrations of the fluid inclusions are consistent with crustal fluids at these temperatures and salinities (Yardley, 2005). The Cu concentration is between c.150 and 600 ppm, Zn between c.120 and 300 ppm and Pb between c.110 and 300 ppm. In comparison to other higher temperature magmatic fluids the metal contents in these epithermal fluids are much lower as would be expected from their lower temperatures (Audetat et al., 2008; Pudack et al. 2009). The solubility of metal-chloride complexes decreases as temperature is reduced and therefore reduces the amount of metal that can be transported. Other mechanisms of metal precipitation are the increase of pH due to wall-rock interaction, or boiling.

5.4. Isotopic Constraints on the Hydrothermal Fluids

The distribution of measured and calculated isotopic composition of hydrothermal fluids from the Koru mine, which were in equilibrium with quartz (Fig. 11a), is very close to magmatic values (5.5-9.5‰ defined by Ohmoto (1986) and Sheppard (1986). The water in equilibrium with baryte, which was the last mineral to be precipitated, was enriched in

deuterium and had isotopically lighter oxygen thereby plotting close to Eastern Mediterranean Meteoric Water: (EMMW) $\delta^{18}O = -6.12\%$, $\delta D = -37.96\%$ (Gat et al., 1996).

The fluid δ^{18} O values calculated from δ^{18} O $_{Bt}$, are slightly lower than calculated for the δ^{18} O $_{Qz}$ (Fig. 11b). The difference can be interpreted to indicate that baryte and quartz were precipitated at different stages of mineralization. Baryte is often a late-stage mineral in hydrothermal systems. Its solubility increases with increasing salinity between 100 and 250 $^{\circ}$ C, and for solutions that contain more than 1 mol NaCl (Holland and Malinin, 1979). Because baryte is precipitated during cooling and especially during the mixing of late-stage hydrothermal fluids with meteoric water, it occurs principally on the margins and in the late stages of ore deposits (Rye, 2005). In the Koru deposit the petrography indicates baryte was precipitated later than quartz at a lower homogenization temperature.

The $^{34}\mathrm{S}_{V\text{-}CDT}$ values of sphalerite, galena and baryte from the Koru deposit are between -1.9 to -0.1 ‰ (average -1.2 ‰), -5.2 to -3.0 ‰ (average -3.9 ‰) and +14.9 to +17.3 ‰ (average +16.5 ‰), respectively (Bozkaya and Gökçe, 2009). The two different ranges of $\delta^{34}\mathrm{S}$ values for H₂S in equilibrium with baryte and sulfide minerals indicate there were different sources for the sulfur in sulfides and barytes. The heaviest $\delta^{34}\mathrm{S}$ values, from the second generation of baryte, are consistent with SO₄ derived from Eocene seawater. The first generation of baryte has $\delta^{34}\mathrm{S}$ values which are lower than seawater at the time of mineralization and we suggest this was caused by micron sized sulfide inclusions, which are observed in the baryte and could not be removed prior to analysis. These have much more negative $\delta^{34}\mathrm{S}$ and their presence has lowered the measured $\delta^{34}\mathrm{S}$ of baryte from the correct values for a derivation from seawater.

The distinctly negative $\delta^{34}S$ values of galena are lower than for sulfur that had a magmatic source. Sulfides in the country rocks with negative $\delta^{34}S$ values could have been leached by the hydrothermal fluids but there is no evidence of any such sulfides. We suggest

that the negative $\delta^{34}S$ values of the sulfides are due to boiling of the magmatic fluid at depth. Such a process has been shown to produce very negative $\delta^{34}S$ at the surface, such as at White Island, New Zealand (Hedenquist et al. 1993). According to the $\delta^{34}S$ and $\delta^{18}O$ data of the baryte from Koru (Table 5 and 6; Bozkaya and Gökce, 2009), the positive slope of the sulfur and oxygen–isotope data for baryte (Rye 2005) is interpreted to represent mixing of SO_4^{2-} derived from the disproportionation of magmatic SO_2 at depth (magmatic-hydrothermal) with sulfate formed during the oxidation of H_2S near the surface (steam-heated).

In Fig. 11a, the $\delta^{18}O$ and δD for the fluid inclusions are plotted for deposits in the Biga Peninsula; at Arapuçandere (AUD), Balcilar (BA), Tesbihdere- Sahinli (TD-SA) and Ovacik-Narlica (OV-NA). These all lie between the meteoric water line and the magmatic box (Bozkaya and Banks, 2015b, Bozkaya and Gökçe, 2007; Yilmaz, 2002; Yilmaz et al., 2010). Meteoric water at the time of mineralization plots close to the value of present day meteoric water; therefore all the deposits except Ovacik–Narlica have mixing trajectories that would intersect close to meteoric water at c. 20 Ma. Nevertheless, they do not extend to, or would intersect the magmatic box as the δD values are too negative. The data for the deposits of Ovacik and Narlica have $\delta^{18}O_{H_{2O}}$ values that are not close to the magmatic box, and the δD values are approximately 50% too negative when compared to meteoric water at the time of mineralization.

The stable isotope data, δD and $\delta^{18}O$, of illite from Koru plots close to the magmatic water box indicating that the hydrothermal fluids producing these alteration products were predominantly magmatic (Bozkaya et al., 2016). δD and $\delta^{18}O$ from early quartz indicates a magmatic fluid source and the two generations of baryte have values that go towards the MWL and the values for local waters at the time of mineralization. However, these are not indicative of magmatic-meteoric water mixing but are a function of the cooling of the

 magmatic water and equilibration with the alteration products (e.g., Bozkaya et al., 2016). The only evidence of meteoric water comes from the second generation of baryte, which lies on the meteoric water line and has δ^{32} S values that are indicative of Eocene seawater.

The isotopic signatures of fluids can be changed by interaction with igneous rocks, especially at low water/rock ratios (John et al., 2003; Taylor, 1997). Boiling can also affect the original isotopic signature of the hydrothermal fluid as it increases the δ^{18} O and δD values of fluids due to fractionation of ¹⁶O and H into the vapor phase (e.g. Alderton and Fallick, 2000). There is clear evidence that boiling occurred within the vein systems in the Koru deposit. Even although δ^{18} O values have a narrow range, between -8.5 and -1.7 ‰, the δD values cover a large range between -90 and -55 %. Such low δD values can be interpreted to have originated from boiling by either of the two following mechanisms (Imai et al., 1998); 1) a significant degree of vapor from boiling above 225 °C, and 2) a vapor phase separated by boiling at lower temperature (below 160 °C for a fractionation larger than 10 %). In the former case, a large degree of boiling with Rayleigh fractionation is required to significantly modify the δD value of liquid as the hydrogen isotopic fractionation factor between the fluid and H_2O vapor is small. Greater than 50% boiling is required for a 2% of change in $\delta^{18}O$ value, whereas the observed variation in δ^{18} O values of the hydrothermal fluid is from -8.5 to -1.7%, calculated from δ^{18} O value of quartz assuming a temperature of 300°C (Bozkaya et al. 2016). Therefore, boiling alone does not account for the measured isotopic variations of hydrothermal fluids. The lack of evidence for fluid mixing between meteoric and magmatic waters (except in the last stages of baryte precipitation) in the Koru deposit indicates that a simple cooling model is most likely, as also inferred from the fluid inclusion data. The evidence points to magmatic fluids being the more likely significant source of fluids.

6. Conclusions

The geologic characteristics of the Koru deposit; geological setting, alteration style of the host rocks, main textures, mineral assemblages along with the fluid inclusion and stable isotope data, indicate that Koru belongs to the class of intermediate sulfidation type epithermal deposit in the sense of Hedenquist et al. (2000), Sillitoe and Hedenquist (2003), Einaudi et al. (2003) and Sillitoe (2010). The epithermal base-metal (± Au) deposit is characterized by moderate to high temperatures and intermediate to low salinities. The highest temperature inclusions are clearly primary occurring in, and terminating at the boundaries of the growth zones. There is evidence of fluid boiling from the presence in both quartz and sphalerite of closely associated L-V (with variable L/V ratios) and V-rich fluid inclusions that homogenise over the same temperature range in a number of fluid inclusion arrays. In the earliest quartz and sphalerite, the Th range of c. 310 to 350 °C equates to c.1700 m for hydrostatic pressure and c. 600 m to 700 m depth for a fluid system at lithostatic pressure. There is also a large decrease in the homogenization temperatures in FIA's without clear evidence of boiling. In these cases, we suggest the pressure reduction in the veins was more gradual, essentially along or close to the L-liquid vapor curve. We also see evidence of vapor fluid inclusions caused by flashing, by a sudden pressure drop to below hydrostatic pressure. Therefore, we suggest there were a number of scenarios that would have caused a decrease of pressure and hence several physical and chemical changes that led to mineral deposition.

As the temperature decrease is due to pressure variation, stable isotope data that was believed to indicate the presence of a significant amount of meteoric water, can in fact be shown to represent a cooling magmatic fluid in equilibrium with the alteration assemblages. There is no clear evidence for extensive fluid mixing with meteoric water during the main stages of mineralization. Instead, we suggest the lower salinity fluids were magmatic vapor that ascended from deeper in the mineralizing system, to shallower depths to produce a low

 salinity fluid. This was also shown in the comparable Arapuçandere deposit, in the Biga peninsula, where gold particles are present in the low salinity fluid inclusions (Bozkaya and Banks, 2016 Banks et al. 2019). Therefore, in the Biga peninsula base metal deposits may also contain gold, if these contain the low salinity fluids that are associated with transport of gold. The amount of gold will depend on the volume of magmatic vapor that was produced. In either case deposition of the gold or base-metals was controlled by pressure fluctuations and the effect on metal-ligand complexes, pH, temperature and oxidation state.

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TABLE CAPTIONS

Table 1. General characteristics of selected epithermal ore deposits in western and northwestern Turkey.

- Table 2. Summary of the microthermometry data for inclusions from the Koru deposit.
- **Table 3.** LA-ICP-MS analyses of individual fluid inclusions. Average element ratios (wt/wt relative to Na) and concentrations in ppm.

Table 4. Oxygen and hydrogen isotope data and calculated δ^{18} O values for inclusion water in equilibrium with baryte and quartz from Koru samples. Data for quartz is taken from Bozkaya et al. (2016).

FIGURE CAPTIONS

- **Fig. 1.** (a) Location of the Biga Peninsula in relation to the boundaries of the major tectonic plates and Tethyan Eurasian Orogenic Metallogenic Belt (Jingwen et al., 2014), NAF: North Anatolian Fault, EAF: East Anatolian Fault, (b) Simplified regional geological map of the Biga Peninsula (modified from Siyako et al. 1989; Okay et al. 1990) and radiometric ages of volcanic and plutonic rocks and alteration related mineralizations (Ercan et al., 1995; Aldanmaz et al., 2000, Yigit, 2012).
- **Fig. 2.** Geology map of the close surrounding area of the sectors in Koru deposits (Bozkaya, 2001) and cross section of the Tahtalıkuyu and Eskikışla sectors and sample locations.
- **Fig. 3.** Photomicrographs of transmitted (a-b) and reflected-plain polarized (c-f) light images of the representative ore samples from Koru Deposit. (a) Volcanic rock fragments (VRF) and plagioclase (Pg) crystals within the silicified and argillised volcanic matrix of lithic ash tuff

from Adadagi Pyroclastics (KR-123, polarised light), (b-c) Plagioclase and/or sanidine pseudomorphs replaced by coarse-grained of quartz crystals related to intense silicification within the radially devitrified (silicified and argillised) volcanic groundmass (TK-66, gallery of Tahtalıkuyu sector, d-crossed polars, e-polarised light), (d) Brecciated and disaggregated sphalerites (Sph) within the galena (Gln) crytals, and sutured boundary relationships between quartz-rich gangue and galena minerals (TK-82, gallery of Tahtalıkuyu sector, 96 level), (e) Anhedral galena crystals were replaced by sphalerite and chalcopyrite (Cpy) (TK-88, gallery of Tahtalıkuyu sector, 150 level), (f) Chalcopyrites containing sphalerite and galena inclusions (TK-245, gallery of Tahtalıkuyu sector, 83 level), (g) Rod-like tennantite (Tnt) separations within the galena (EK-5, Eskikışla sector), (h-i) Coarse-grained comb texture euhedral baryte crystals (Bt) within the anhedral quartz and calcite (Cal) crystals (TK-43, gallery of Tahtalıkuyu sector, 150 level, a-crossed polars, b-polarised light).

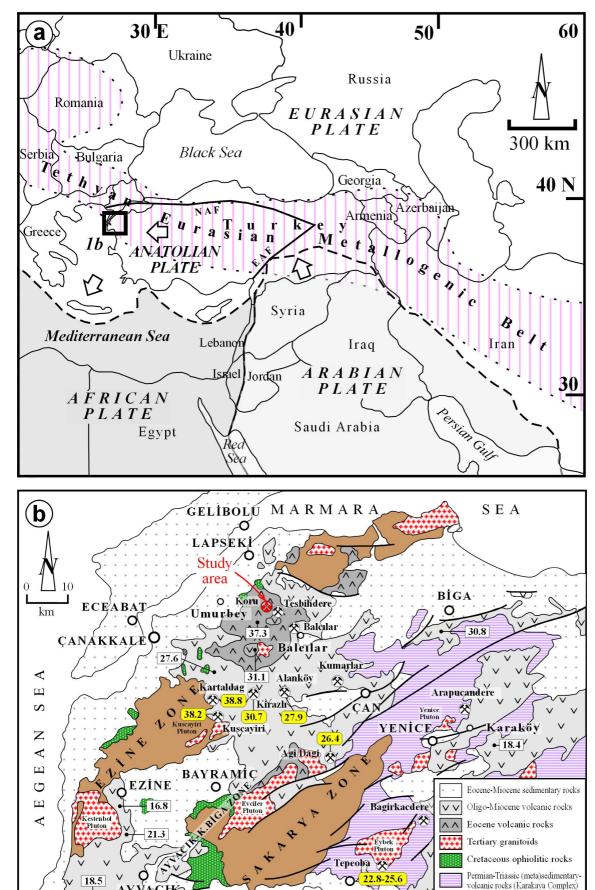
Fig. 4. Paragenetic succession of ore and gangue minerals of Koru deposit.

Fig. 5. Different generations of ore minerals and gangue minerals in comb texture of veins in Koru deposit. Primary fluid inclusion in sphalerite (Sph 2), Liquid rich inclusions in baryte (Ba2), in quartz (Q2) L-V inclusions through to growth zone in baryte (Ba1) L-V inclusions with ore stage.

Fig. 6. Fluid inclusion textures and types. (a) Euhedral overgrowths of quartz delineated by bands of primary inclusions oriented perpendicular to the crystal faces, (b) Variable L/V ratios and often contain V-rich inclusions, (c) The first generation inclusions (L-V) in sphalerites, (d) Coarse-grained baryte observed cutting the second generation of quartz, (e-f) Co-existing V-rich and L-V inclusions and inclusions containing semi-prismatic solids which would appear to have been trapped during boiling, (g) Pseudo secondary and secondary inclusions including L-only, (h) L-V inclusions with same arrays as L-only inclusions, (i-j) L-

only inclusions in baryte replaced the euhedral quartz.

- **Fig. 7.** Homogenization temperatures for the different generations of quartz, sphalerite and baryte. Two distinct temperature ranges are evident.
- **Fig. 8.** Homogenization temperatures of different generation minerals; early and late quartz, sphalerite and baryte from Koru Deposit.
- **Fig. 9.** Homogenization and salinity (equiv. NaCl wt.) of primary and secondary inclusions from different generation minerals from Koru deposit.
- **Fig. 10.** LA-ICP-MS data as wt/wt ratios relative to Na (value 1) from inclusions in the first generation of quartz and sphalerite. K/Na has a bimodal distribution but overall the element ratios are the same in both minerals.
- **Fig. 11.** (a) Distribution of hydrogen- and oxygen-isotopic values from the fluid trapped in quartz and baryte crystals on the δD vs δ¹⁸O diagram (diagram was reproduced from Sheppard, 1986). Illite oxygen isotope data (Bozkaya et al., 2016) is also added for comparison. Fluid compositional areas (BA: Balcılar, AUD: Arapuçandere, OV-NA: Ovacık-Narlıca, TD-SA: Tesbihdere-Şahinli) are given from Bozkaya and Gökçe, 2007 (BA), Bozkaya and Banks, 2015 (AUD), Yilmaz et al., 2010 (TD-SA) and Yilmaz, 2002 (OV-NA). (b) Oxygen isotopic change of waters in equilibrium with quartz and barytes at decreasing temperatures. Illite oxygen isotopic changes (Bozkaya et al., 2016) were also added for comparison.
- Fig. 12. Pressure-Temperature-Depth plot for Koru deposit (drawn from data in Haas, 1971).



EDREMIT

EDREMİT BAY

Paleozoic metamorphic rocks

31.1 Age of magmatic rocks (Ma)

27.9 Age of hydrothermal alterations (Ma)

Figure 1-R1

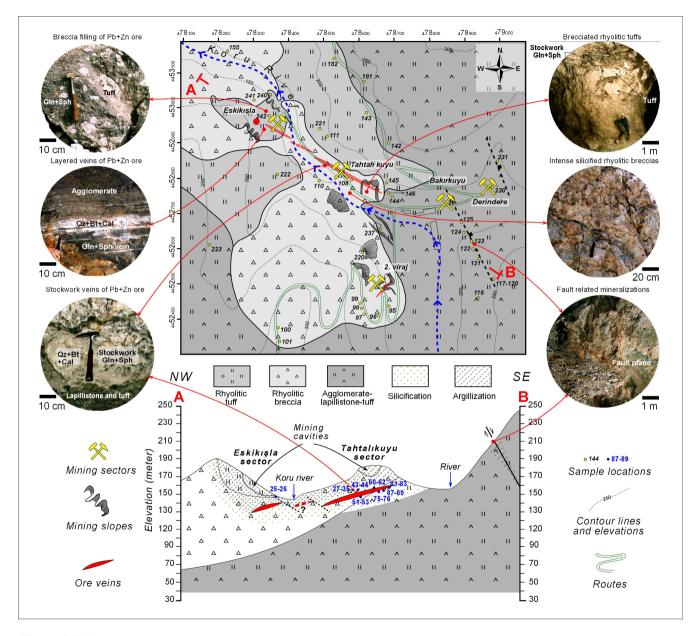


Figure 2-R1

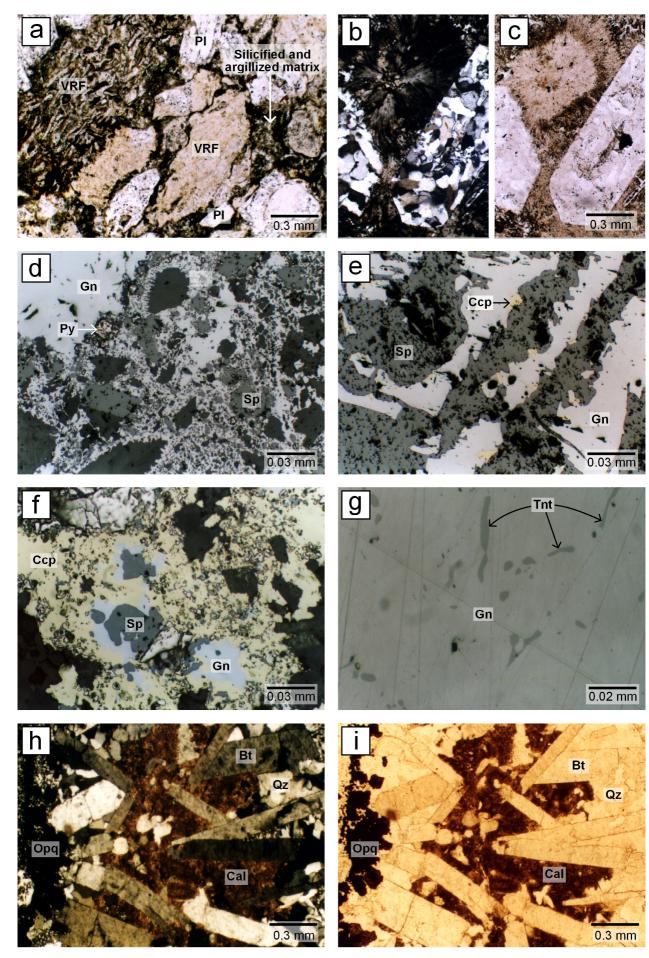


Fig. 3-R2

Mineral	Н	Hydrothermal									
Minicial	Stage-1	Stage-2	Stage-3	Stage-4							
Pyrite	1										
Galena			2								
Sphalerite		1	2								
Chalcopyrite		1	2								
Fahlore											
Bornite											
Marcasite											
Quartz		1									
Baryte			1	2							
Calcite											
Chalcocite											
Covellite											
Tenorite											

Fig. 4-R1

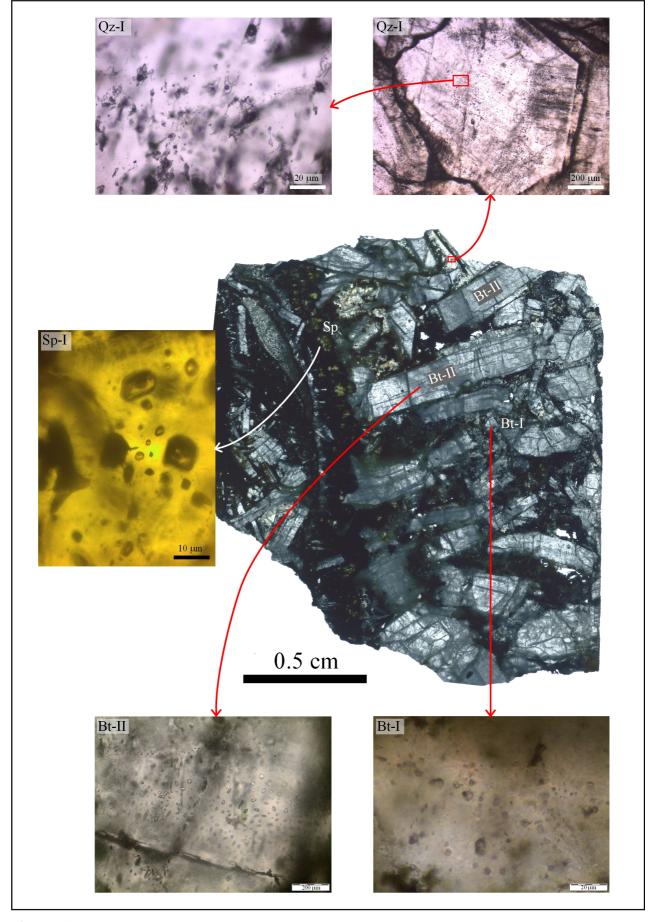


Figure 5-R2

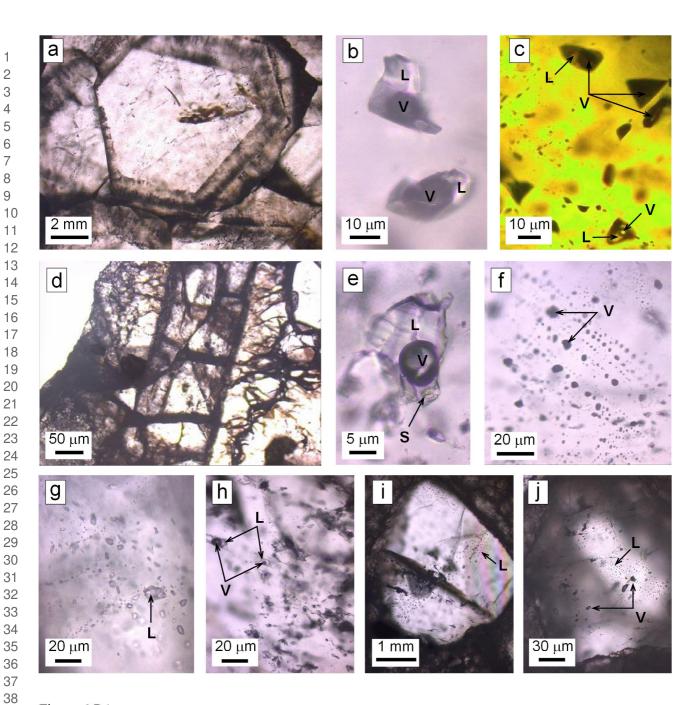


Figure 6-R1

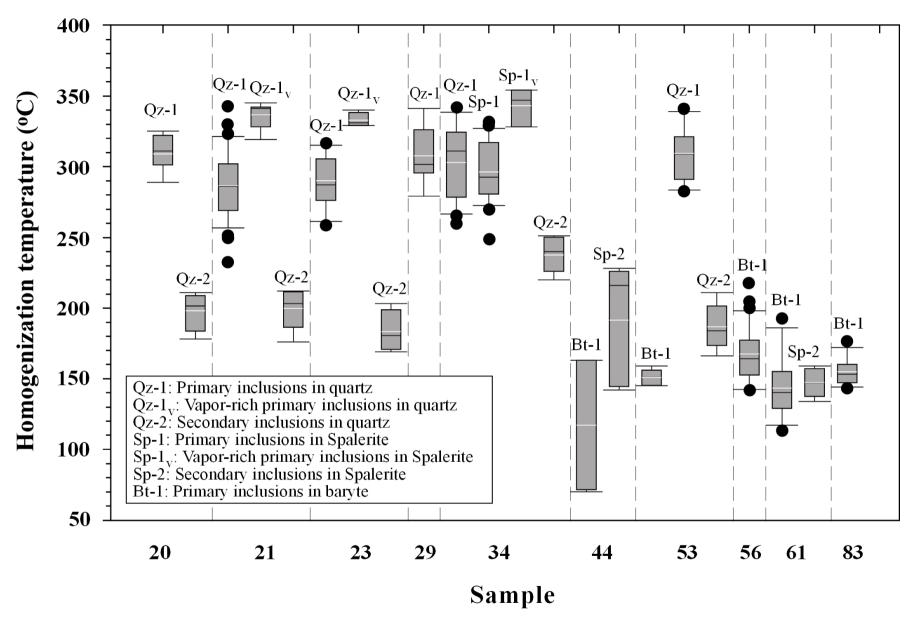


Figure 7-R2

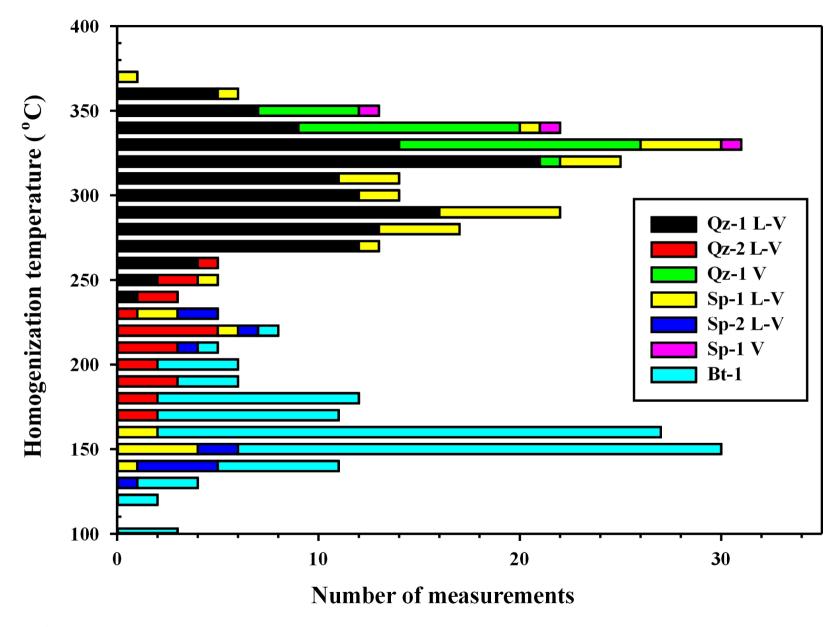


Fig. 8-R2

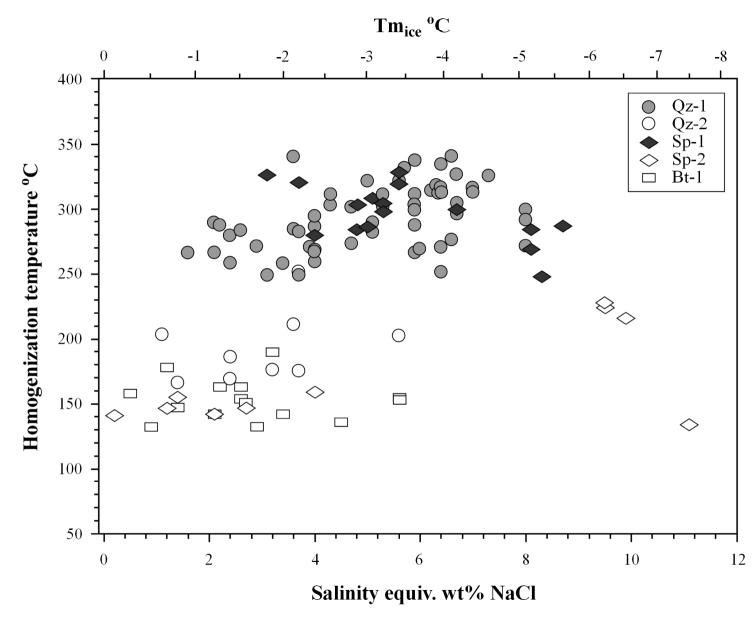


Figure 9-R2

Fig. 10-R3

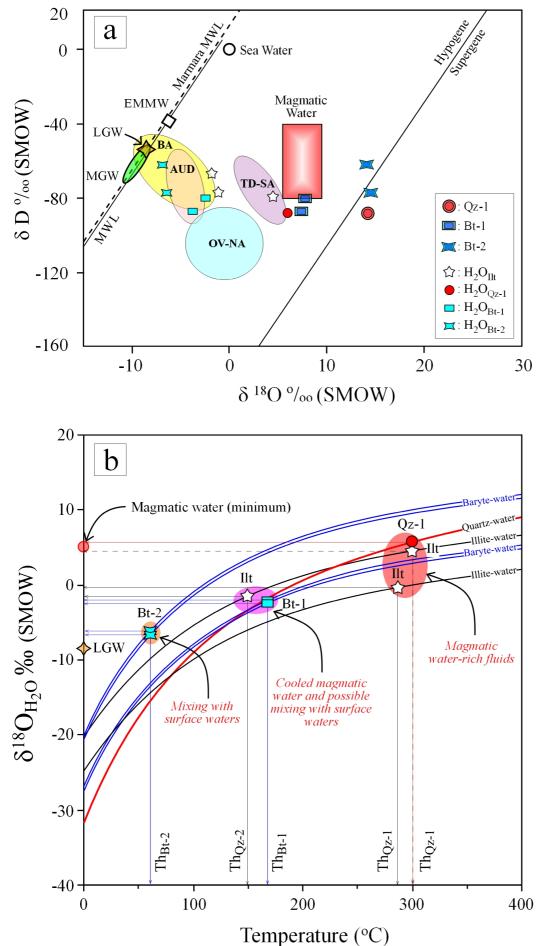


Figure 11-R2

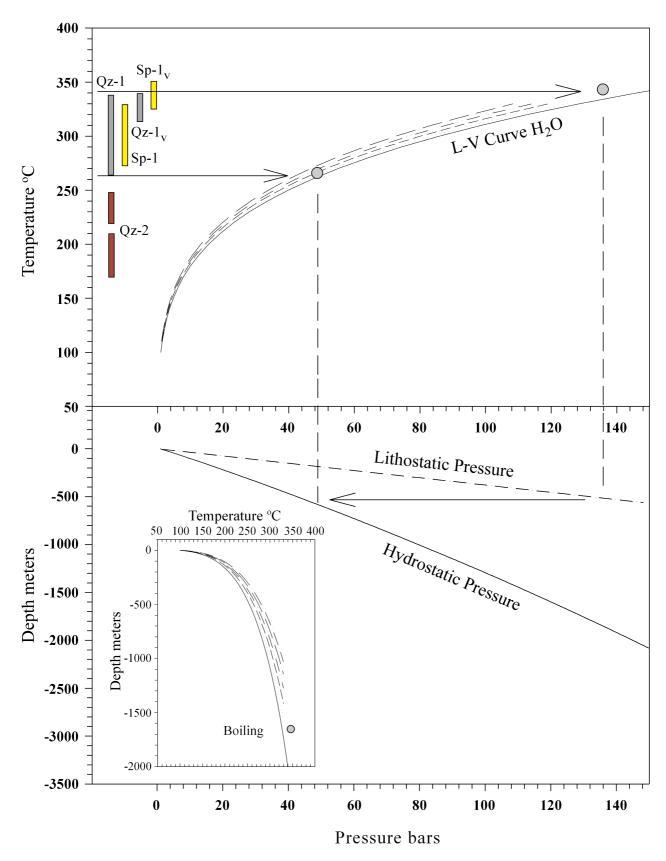


Figure 12-R2

Table 1. General characteristics of selected epithermal ore deposits in western and northwestern Turkey.

Deposit	Location	Deposit Style	Ore Mineral Assemblages(*)	Th °C	Th °C Salinity wt.%NaCl		δD ‰	References
Kisladag	Usak	Porphyry	Au, Gn, Sp, Mol	322-483	>35	None	None	Hanilci et al. 2015
Efemcukuru	Izmir	LS-IS	Au, Ag, Ccp, Py, Gn, Rds, Rdn	200-300	0-9	1.3 to 25.3	None	Oyman et al. 2003; Boucher, 2016
Kartaldag	Canakkale	HS	Py, Sp, Cv, Au	245-285	0-1.7	-7.95 to 1.49	None	Unal et al, 2013
Madendag	Canakkale	HS	Py, Sp, Au	235-255	0-0.7	-2.97 to 5.54	None	Unal et al, 2013
Tepeoba	Balikesir	Porphyry	Mo, Au, Py	500-600	>35	5 to 5.4	-69 to -61	Tufan et al, 2018
Soma	Balikesir	Porphyry	Ccp, Py, Au	250-400	20	None	None	Bozkaya et al, 2018
Arapucandere	Canakkale	LS-IS	Py, Ccp, Sp, Au	160-360	0-1.7	-8.5 to -1.7	-90 to -55	Bozkaya et al, 2008
Koru	Canakkale	IM-S	Gn, Sp, Py, Au	135-355	0.2-11	-13.5 to -6.4	-87 to -62	Bozkaya and Gökce, 2001
Tesbihdere/ Sahinli	Canakkale	IM-S	Gn, Sp, Py, Ccp, Au	170-360	0.5-10	None	None	Bozkaya et al, 2014
Balcilar	Canakkale	LS	Gn, Sp, Ccp, Py, Au	115-130	3.8-8.5	-0.23 to -6.95	-50	Bozkaya et al. 2011
Kuscayir	Canakkale	Porphyry HS	Mag, Ilm, Py, Apy, Ccp, Au	270-350 190-370	50 22.33-31.19	None	None	Yilmaz, 2003 Vural, 2006
Sindirgi	Balikesir	LS	Py, Au-Ag, Elc	157-330	0.5-4.8	None	None	Yilmaz et al, 2013
Ovacik	Balikesir	LS	Py, Ccp, Sp, Au, Apy	147-298	0-1.2	-2.9-3.5	-82 to -125	Yilmaz, 2002; Yilmaz et al, 2007
Kisacik	Canakkale	LS	Py, Au, Gth, Lm	190-320	0.16-6.5	None	None	Vural, 2006

^(*) Mineral abbreviations are taken from Whitney and Evans (2010). Au: Native gold, Ag: Native silver, Gn: Galena, Sp: Sphalerite, Py: Pyrite, Ccp: Chalcopyrite, Mol: Molybdenite, Rds: Rhodochrosite, Rdn: Rhodonite, Cv: Covellite, Apy: Arsenopyrite, Elc: Electrum, Mag: Magnetite, Gth: Goethite, Lm: Limonite

Table 2. Summary of the microthermometry data for inclusions from the Koru deposit.

C1-	Т	M:1	T. 9C	Tm ice °C			Salinit	y equiv.	wt% NaCl	Th °C			
Sample	Type	Mineralogy	Te °C	Min	Max	Average	Min	Max	Average	Min	Max	Average	
TK-20	L-V	Quartz-1	< -40	-3.2	-2.6	-3	4.3	5.1	4.9	289	325	309	
	L-V	Quartz-2		-3.4	-2.1	-2.8	3.6	5.6	4.6	178	211	198	
TK-21	L-V	Quartz-1	~-45	-5.1	-1.2	-3	2.1	8	5.0	249	329	287	
	V	Quartz-1								315	342	331	
	L-V	Quartz-2				-1.9			3.2	176	212	200	
TK-23	L-V	Quartz-1	~ -45	-5.1	-0.9	-2.8	1.6	8	4.6	258	316	290	
	V	Quartz-1								329	340	332	
	L-V	Quartz-2		-2.2	-0.6	-1.4	1.1	3.7	2.4	169	203	183	
TK-29	L-V	Quartz-1	~ -50	-3.6	-2.8	-3.2	4.7	5.9	5.3	279	341	308	
TK-34	L-V	Quartz-1	~ -40	-4.2	-1.5	-3.2	2.6	6.7	5.2	259	342	303	
	L-V	Quartz-2				-2.2			3.7	220	251	237	
	L-V	Sphalerite-1	~ -45	-5.6	-1.8	-3.6	3.1	8.7	5.8	248	331	296	
	V	Quartz-1								328	354	343	
TK-44	L-V	Baryte-2		-1.5	-1.3	-1.4	2.2	2.6	2.4	70	163	117	
	L-V	Sphalerite-2		-6.5	-1.2	-4.4	2.1	9.9	6.7	142	228	191	
TK-53	L-V	Quartz-1		-5.1	-2.1	-3.6	3.6	8	5.8	282	340	309	
	L-V	Quartz-2				8			1.4	166	211	186	
TK-56	L-V	Baryte-1		-1.9	-0.7	-1.3	1.2	3.2	2.3	140	217	167	
TK-61	L-V	Baryte-1		-3.4	-0.3	-1.8	0.5	5.6	3.0	113	192	143	
	L-V	Sphalerite-2		-7.5	-0.1	-2.3	0.2	11.1	3.6	134	159	147	
TK-83	L-V	Baryte-1		-3.4	-0.8	-1.9	1.4	5.6	3.2	140	217	167	

Table 3. LA-ICP-MS analyses of individual fluid inclusions: Average element ratios (wt/wt relative to Na) and concentrations in ppm.

Sample	Salinity		Na	Mg	K *	K	Ca	Mn	Fe	Cu	Zn	As	Sr	Ag	Ba	Pb
	Wt% NaCl															
TK-20		Average	1	.337	1.376	.441	.481	.0052	.049	.044	.018	.030	.016	.001	.0067	.034
Quartz		Std Dev		.201	.588	.09	.234	.003	.016	.022	.009	.017	.008	.0006	.002	.019
	4.9	ppm*	7980	2691		3516	3863	41	393	350	144	240	127	8.1	53.2	274
TK-21		Average	1	.246	1.094	.250	.165	.0045	.059	.056	.0112	.032	.002	.002	.0009	.0165
Quartz		Std Dev		.177	.659	.169	.122	.003	.018	.027	.007	.014	.002	.0002	.0008	.013
	5.0	ppm*	10668	2629		2665	1765	48	632	597	126	338	22	2.6	9.7	176
TK-29		Average	1	.382	1.08	.230	.530	.059	.038	.020	.033	.022	.017	.0003	.0104	.013
Quartz		Std Dev		.184	.609	.147	.243	.022	na	na	.019	.014	.013	.0002	.010	na
	5.3	ppm*	8338	3187		1921	4422	494	316	166	278	183	143	2.6	116	112
TK-34		Average	1	.387	1.011	.369	.505					.025	.014	.00035	.010	.006
Sphalerite		Std Dev		.099	.175	.116	.239					.009	.012	.00021		
	5.8	ppm*	9743	3771		3592						239	137	3.4	101	
TK-44		Average	1	.096				.031	.072	.039			.026	.0064		.048
Baryte		Std Dev		.051				.020	.020	na			.011	.017		.013
	2.4	ppm*														
TK-53		Average	1	.124	1.609	.464	.695	.031	.041							
Baryte		Std Dev		.121	.283	.127	.424	.025	.020							
	3.0	ppm*	5013	621		2328	3486	158	204							
TK-60		Average	1	.131	1.274	.310	.675	.035	.079	.049				.0062		
Baryte		Std Dev		.063	.314	.088	.273	.016	na	.016				.004		
	3.0	ppm*	5168	675		1604	3489	179	410	253				32		
TK-61		Average	1	.157	1.217	.278		.561	.020	.039	.025			.0008		.029
Baryte		Std Dev		.121	.365	.168	.250	.014	.033	.022	na			.0006		.022
	3.0	ppm*	5498	862		1521	3087	113	215	139	211			4.2		161
TK-75		Average	1	.118	1.117	.479	.501	.019	.033	.042				.0028		
Baryte		Std Dev		.084	.287	.134	.205	.010	.021	.020				.0023		
	3.0	ppm*	5381	638		2578	2694	100	180	224				15		
TK-83		Average	1	.021	1.160	.439		.0145	.038	.039				.0007		.048
Baryte		Std Dev		.014	.308	.146		.009	.022	.020				.0007		.023
	3.2	ppm*														

^(*) Calculation of concentrations uses the lower values of K/Na. This is not affected by solid inclusions of illites which increase the K concentration (K*/Na values). Where K/Na or Ca/Na ratios were not suitable, usually due to contamination by solid mineral phases, it was not possible to calculate ppm values for the other elements.

Table 4. Oxygen and hydrogen isotope data and calculated δ^{18} O values for inclusion water in equilibrium with baryte and quartz from Koru samples. Data for quartz is taken from Bozkaya et al. (2016).

Sample	Mineral	δ D (‰)	δ ¹⁸ O (‰)	Average Th (°C)	$10^3 \ln \alpha$	Calculated δ ¹⁸ O (‰)
TK-53-1	Quartz	-88	14.2	300	8.2	6.0
TK-61	Baryte-I	-87	7.8	143	11.5	-3.7
TK-75	Baryte-I	n.d.	7.4	167	9.8	-2.4
TK-83	Baryte-I	-80	7.4	167	9.8	-2.4
TK-44	Baryte-II	-62	14.1	60	20.9	-6.8
TK-56	Baryte-II	-77	14.5	60	20.9	-6.4
TK-60	Baryte-II	n.d.	14.0	60	20.9	-6.9