



## Microthermometric characteristics of ore forming solutions in Şaphane (Oğuzlar-Çorum) Au mineralization, Turkey

Şaphane (Oğuzlar-Çorum) Au cevherleşmesinin sıvı kapanım özellikleri, Türkiye

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### Abstract

The study area is located in the Çorum province in the North-Central part of Turkey. In the Çorum region various continental blocks are found together. Devecidağ Complex, Artova Ophiolite Complex, Alacahöyük, Bayat, Kızılırmak, Dodurga and Bozkır formations and Dededağ granitoid and quartz veins are exposed in the vicinity of the study area. Extremely altered volcanic rocks, andesite-basalt-trachyte and tuffs, are observed near the mineralization. The silica veins associated with the mineralization crop out in NE-SW direction southeast of Şaphane village. Pyrite, hematite, limonite, chalcopyrite, galena and gold are the major ore minerals within the quartz veins. Fluid inclusion studies show that hydrothermal solutions contain several salts such as NaCl, CaCl<sub>2</sub> and MgCl<sub>2</sub>, the salinity values (wt.% NaCl) changed between 8% and 0.5% in quartz, from 7.4 and 1.4% in calcite, and the temperature of the ore forming solutions varied between 161 and 395°C. Microthermometric results indicate that the mineralization in the region is associated with quartz veins and formed under epithermal-mesothermal conditions.

**Keywords:** Çorum, Şaphane, Gold mineralization, Fluid inclusion

### 1 Introduction

The study area is located in the transition zone between the Sakarya continent and the Central Anatolian Crystalline Complex between the Oğuzlar and İskilip districts of Çorum province. In the study area, rocks of the Sakarya Zone, Kırşehir Massif and ophiolitic suture zone are exposed. The Sakarya continent that starts from the Biga peninsula and extends to the Caucasus consists of a complexly deformed, generally metamorphosed, Pre-Jurassic basement and a less deformed, non-metamorphic Jurassic-Tertiary cover. Pre-Tertiary units observed around the study area are İzmir-Ankara-Erzincan suture zone ophiolites that have a sliced structure. These ophiolites and metamorphics separated from the Sakarya zone and a magmatic rock assemblage that intrude the both units are defined as the Kırşehir block [1-3].

The major geologic events in the region mostly occurred during the closure of the Neotethys ocean, and the mineral deposits in Turkey were also formed in association with the

### Öz

İnceleme alanı Orta-İç Karadeniz bölgesinde Türkiye'nin Kuzey-Orta kesiminde Çorum ilinde bulunmaktadır. Çorum ili, farklı kıtasal blokların birleştiği bir bölgedir. Çalışma alanı yakın çevresinde Devecidağ Karışığı, Artova ofiyolitli karışığı, Alacahöyük, Bayat, Kızılırmak, Dodurga ve Bozkır formasyonlarına ait birimler ile Dededağ granitoyitine ait birimler ve kuvars damarları yüzeylenmektedir. Cevherleşmenin yakınında aşırı derecede altere volkanik kayalar, andezit-bazalt-trakit ve tüflerin varlığı belirlenmiştir. Cevherleşmenin ilişkili olduğu silis damarları Şaphane köyünün güneydoğusunda KD-GB uzanımlı olarak yüzeyde mostra vermektedir. Kuvars damarlarında cevher minerali olarak pirit, hematit, limonit, kalkopirit, galenit ve altın gözlenmiştir. Sıvı kapanım incelemelerinde hidrotermal çözeltiler içerisinde NaCl, CaCl<sub>2</sub> ve MgCl<sub>2</sub> gibi tuzların bulunduğu, tuzluluk değerlerinin %NaCl eşdeğeri olarak kuvarslarda %8 ile 0.5 aralığında, kalsitlerde ise %7.4 ile 1.4 aralığında değiştiği, cevher oluşturuvcu çözeltilerin sıcaklığının ise 161 ile 395°C aralığında değiştiği belirlenmiştir. Mikrotermometrik veriler; yöredeki cevherleşmenin, kuvars damarları ile ilişkili epitermal-mezotermal koşullarda oluşmuş bir cevherleşme olduğunu göstermektedir.

**Anahtar Kelimeler:** Çorum, Şaphane, Altın cevherleşmesi, Sıvı kapanım

collision and magmatism that occurred during this convergence process [4-6]. Turkey hosts a wide range of mineral deposits and, due to the recent mineral exploration works, the Çorum province has become one of the remarkable mining regions in Turkey. There are several Cu-Pb-Zn-Mo-Sb mineralizations around the study area (Soğucak (İskilip-Çorum) Cu-Pb, [7]; Gökçedoğan (Kargı-Çorum) Cu-Zn, [8-9]; Bakırçay (Merzifon-Amasya) Porphyry Cu-Mo, Gümüşhacıköy (Amasya) Pb-Ag-Cu-Zn, [10-11]; Turhal (Tokat) Sb, [12-13] and Başnayayla (Yozgat) Porfiri Cu-Mo, [14]). In this study, the distribution and mineralogical-petrographic characteristics of the lithostratigraphic units outcrop around the Şaphane mineralization and the source and formation conditions of the ore-forming fluids are investigated. The data presented in this paper will provide information on the formation, the regional geological setting and an approach to exploration of such deposits in surrounding areas.

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## 2 Geological setting

The Şaphane Au mineralization is located in the central Pontides. In the study area, Devecidağ Complex (Triassic), Artova Ophiolite Complex (Late Cretaceous) and Eocene-Quaternary sedimentary and magmatic rocks are exposed. Cover units in the region start with Eocene Alacahöyük and Bayat formations and continue with Miocene Kızılırmak, Dodurga and Bozkır formations and end with Quaternary alluvium deposits.

The Permo-Triassic Devecidağ Complex is represented by metamorphic schists and meta-volcaniclastic rocks with limestone blocks [15]. The Artova Ophiolite Complex is composed of Upper Cretaceous ophiolitic rocks consisting of serpentinite, peridotite, gabbro, diabase, pillow lava, chert, flysch and blocks of metamorphic rocks. These units are a part of the complex of continental and oceanic crust units that comprise the İzmir-Ankara-Erzincan suture zone [16-17]. The Early Eocene (Ypresian) Alacahöyük formation consists of conglomerate, sandstone, siltstone, shale, marl, mudstone, limestone and sandy limestone [18-19]. The Middle Eocene (Lutetian) Bayat formation, which is widely observed in the region, is composed of conglomerates and shallow marine sediments at the bottom and continues to the top with volcanic-volcanoclastic layers [15, 18]. Bayat volcanics consisting of lava and pyroclastics and the units of sedimentary Çatkara member are widely observed in the

vicinity of study area. Although the Bayat volcanics occur in different stages, andesite-basalt-basaltic trachyandesite-trachyandesite and trachyandesite-trachyte type rocks are the major types observed in the study area. In addition, there are several silicified zones within these volcanic rocks [20-21]. The Miocene Kızılırmak formation consists of conglomerate, sandstone, siltstone and claystone layers and it unconformably overlies the older units. The Dodurga formation is composed of clay, marl, siltstone and sandstone and conformably sets above the Kızılırmak formation. The Upper Miocene Bozkır formation consists of gypsum, oolitic limestone, claystone, sandstone, marl and salt and is in lateral and vertical transition with the Kızılırmak formation [18, 22]. Quaternary deposits are composed of recent sediments such as alluvium and talus.

The Dededağ granitoid consists of gabbro, diorite, granite-porphry, and aplite, and granite-porphry and diorite-porphry type rocks are widely observed in the study area. Quartz veins in the region can reach up to 4-meter thick and cut the Bayat volcanics, Çatkara member and diorite porphyry.

Among these units, volcanic units of the Bayat formation, sedimentary units of the Kızılırmak formation and quartz diorite are extensively exposed in the study area (Figure 1).

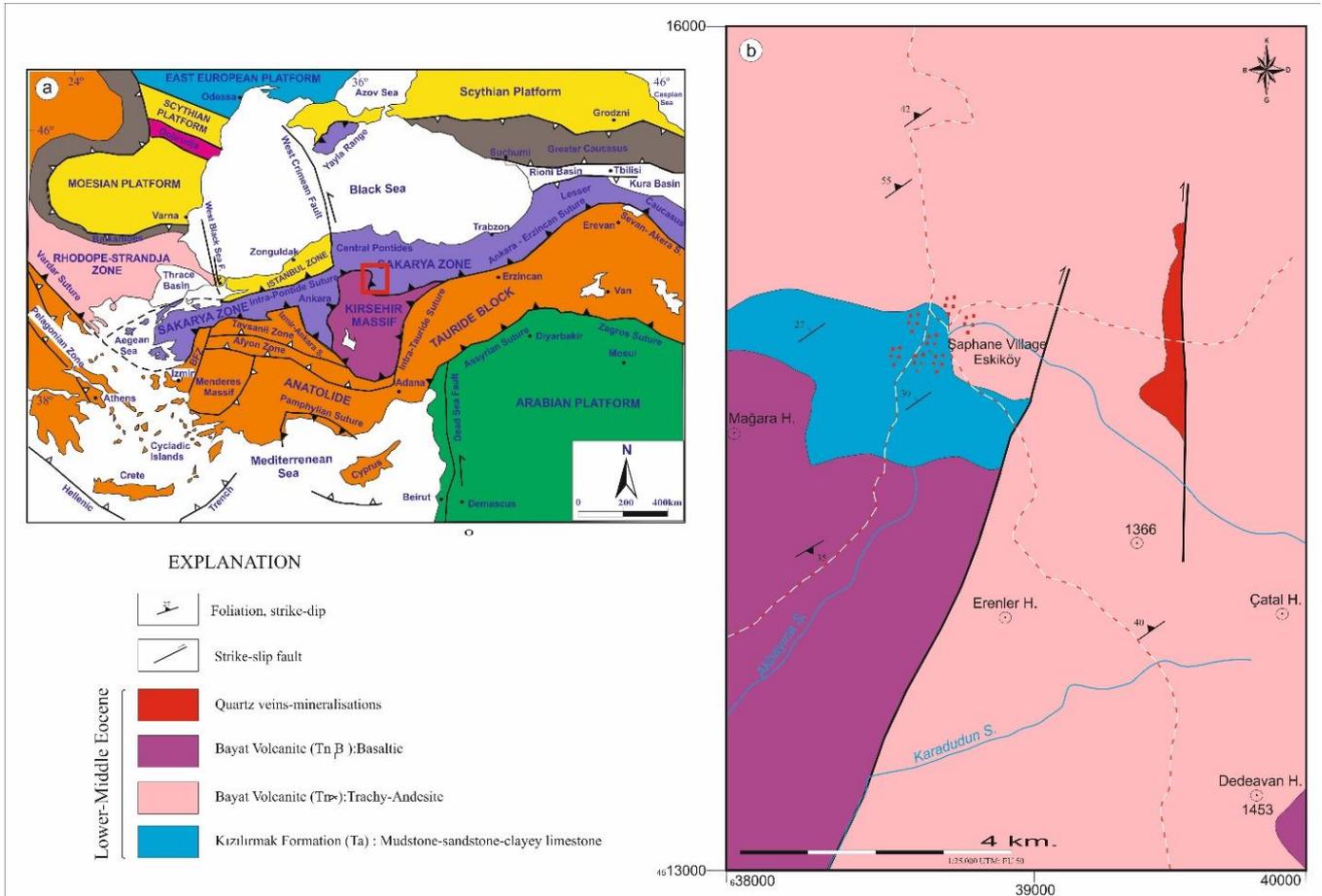


Figure 1. a) Tectonic zones of Turkey from [3], b) Geological map of the study area (modified from [23])

### 3 Material and method

Samples were taken to represent the studied mineralization from rock exposures, silicified zones associated with mineralization, and from drillings (3 boreholes) conducted by the General Directorate of Mineral Research and Exploration (MTA). Thin sections and polished blocks were prepared from the samples and they were examined with polarizing microscope and ore microscopy techniques. In addition, double-polished sections were prepared for microthermometric measurements such as temperature and salinity of the ore-forming solution.

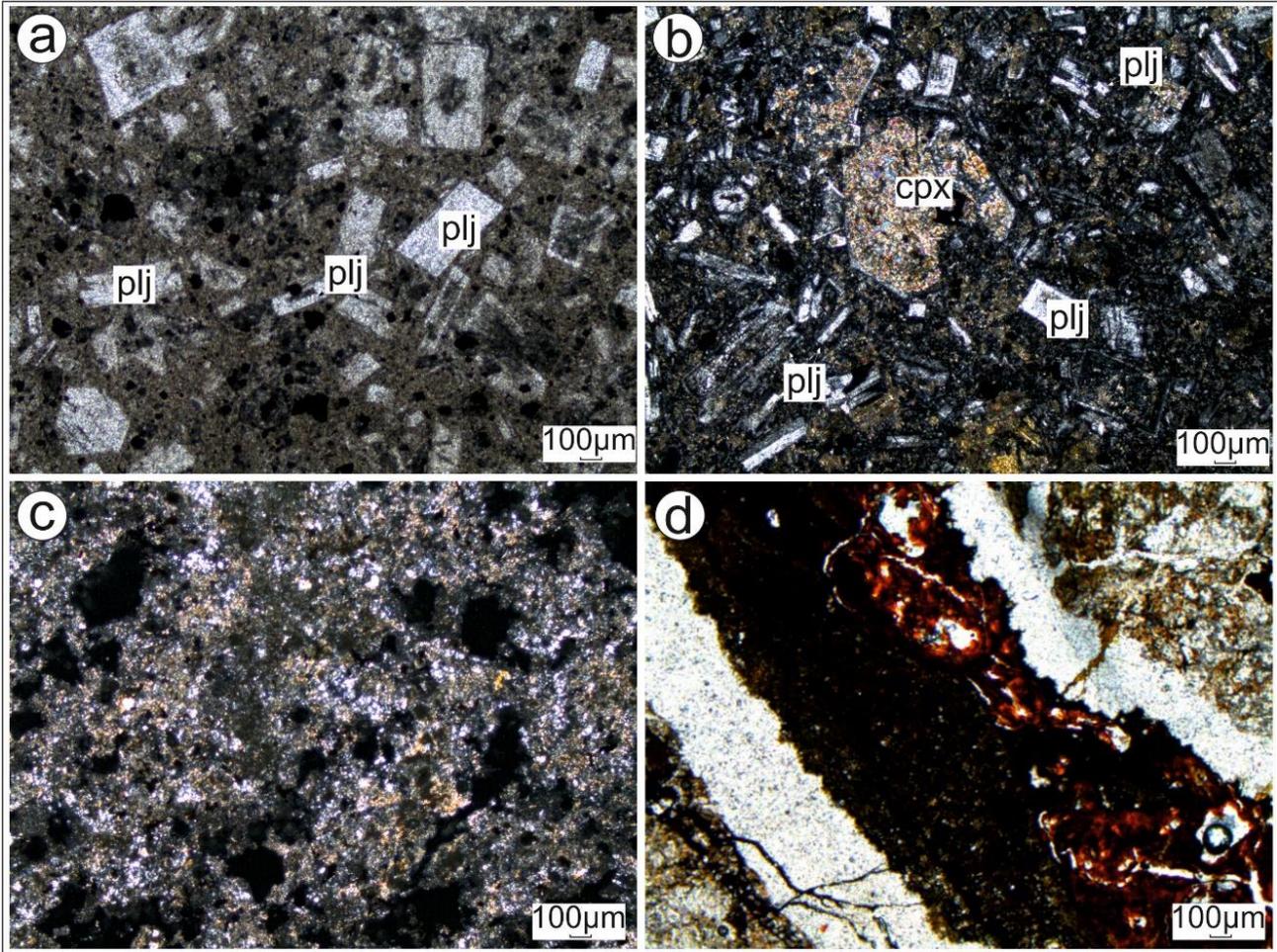
Fluid inclusion studies were carried out at the Fluid Inclusion Laboratory of Department of Geological Engineering of the Pamukkale University. 7 double-polished sections with a thickness of 100  $\mu\text{m}$  were prepared from gangue minerals in the core samples and silicified zones outcropping in the study area. In the double-polished sections, before the microthermometric measurements the fluid inclusion assemblages (FIA) were determined. The measurements were carried out with Linkam THMS-600 and LNP-95 heating-freezing systems attached to an Olympus

Bx51 model polarized microscope. During the microthermometric studies, homogenisation temperature ( $T_H$ ), the first ( $T_{FM}$ ) and the last melting ( $T_{MICE}$ ) temperatures were determined. In the measurements, the accuracy is less than  $\pm 0.5^\circ\text{C}$ .

### 4 Results

#### 4.1 Petrographic characteristics of Şaphane Au mineralization

Results of petrographic examination of rock samples from boreholes and surface exposures in the study area yielded that samples are composed of andesite, altered volcanic rock (basalt?) and crystal tuff. Andesites occur in a hypo-crystalline porphyry texture. The matrix is composed of plagioclase phenocrysts and plagioclase microliths in varying size. They are accompanied by clinopyroxene, biotite and opaque minerals (Figure 2a and b). The spaces in matrix is filled with quartz. Basalts near to the mineralization are extremely altered. The rock is quite silicified, argillized and sericitized and shows altered to opaque minerals (Figure 2c).



**Figure 2.** a) and b) General view of andesites (plj: plagioclase, cpx: clinopyroxene, om: opaque mineral); c) General view of altered volcanics; d) iron-oxide solutions within the tuff.

Carbonation and silicification are also common. For tuffs, carbonation, silicification and chloritization are quite common that are accompanied by iron and copper-bearing solutions and hydrothermal secondary veins (Figure 2d).

#### 4.2 Structural and microscopic properties of mineralization

There are several stratiform and vein type Cu-Pb-Zn-Fe mineralizations around the Çorum region. The Şaphane mineralization is considered as a polymetallic type deposit. Silica veins associated with the mineralization are exposed nearly 700 m in NE-SW direction at southeast of the Şaphane village (Figure 3).

Basalt-basaltic trachyandesite-trachyandesite-andesite-pyroclastics and trachyandesite-trachyte-pyroclastics of the Bayat volcanics constitute the major rock units in the region. Quartz veins at the surface have strike of N20-40°E and plunge 10°N. The spaces between the quartz veins in the mineralized zone are comprised by quartz veinlets (stockwork zone) of mm-cm thickness that interrupt themselves and the host rock as well. Kuşçu et al. (2017a and b) reported the presence of clay minerals such as quartz, kaolinite, illite and mica/illite in these ore-bearing quartz veins. Intense alteration and stockwork zone are observed in the vicinity of quartz veins. These alteration zones are associated with NE-SW trending gold-bearing hydrothermal veins [24].



**Figure 3.** Silica veins associated with the mineralization

According to thin section determinations on the quartz vein samples show that they are composed of subhedral-anhedral cryptocrystalline quartz minerals. Cryptocrystalline quartz is widely observed in the matrix of the rock whilst subhedral-anhedral quartzs are found at the margins of the cavities (Figure 4 a). Pyrite, hematite, limonite, chalcopyrite, galena and trace amounts of native gold can be seen in the quartz veins as the ore minerals (Figure 4.b-f). Pyrites are yellow colored, generally fine-grained and observed as euhedral-semihedral crystals. Hematite is observed as bluish gray anhedral-semihedral crystals. Chalcopyrite and galena are observed in the form of anhedral crystals and in small

amounts. Gold occurs in trace amounts and have very small grains.

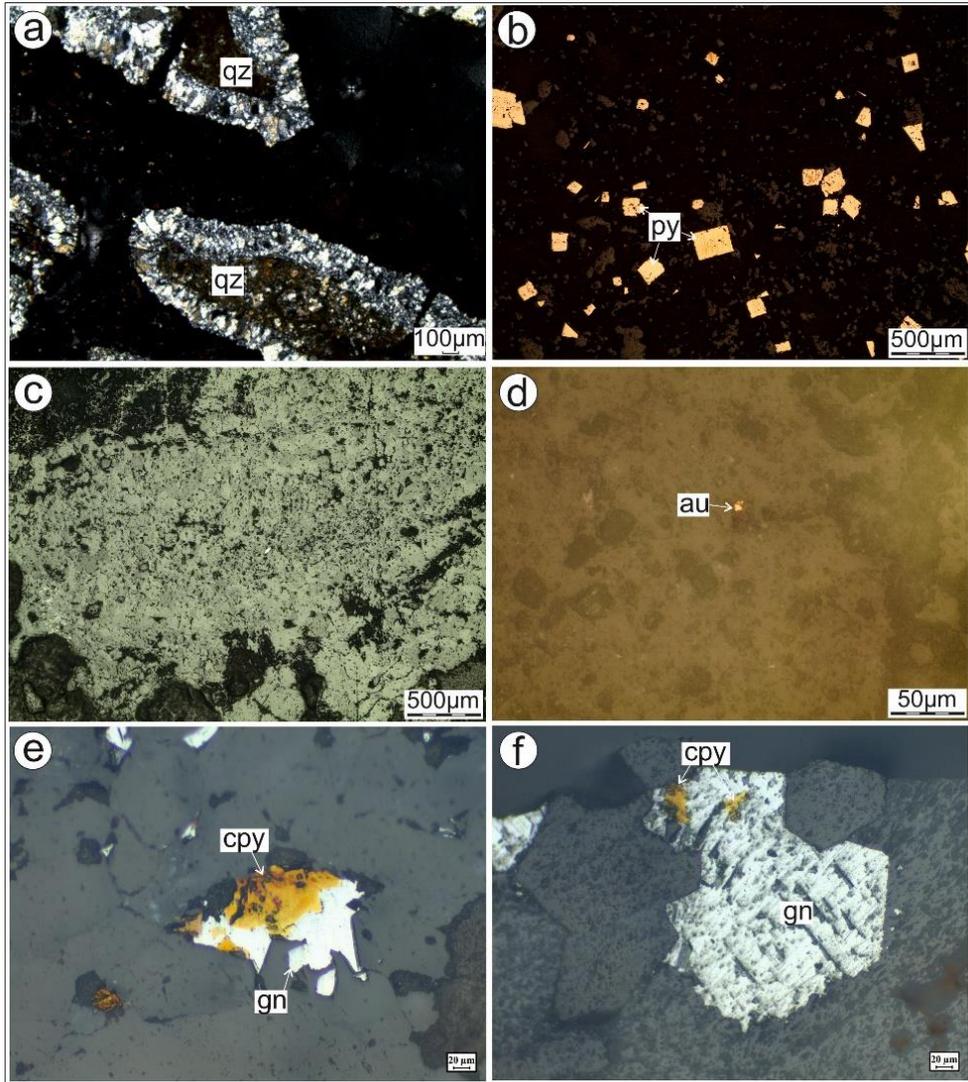
#### 4.3 Microthermometric determinations

Fluid inclusion studies were carried out on quartz and calcite crystals collected from boreholes and quartz veins associated with mineralization. Petrographic determination of fluid inclusions on double-polished sections was made considering the criteria given in Van den Kerkhof and Hein [25] and Goldstein [26]. According to fluid inclusion petrography study, LV-type inclusions containing fluid and gas at room temperature and V-type inclusions containing only fluid were detected in quartz and calcite minerals (Figure 5). Fluid inclusions were categorized as primary, secondary and pseudo-secondary. All measurements were made on primary inclusions. In inclusions containing two-phase gas, the gas-liquid ratio was determined as 60-75% gas and 40-25% liquid. The sizes of the inclusions vary between 5-40  $\mu$  and they are generally circular, ellipsoidal and mostly irregular in shape. During petrographic investigations, it was determined that quartz and calcite were formed in the late phase. The results of measurement are summarized in Table 1.

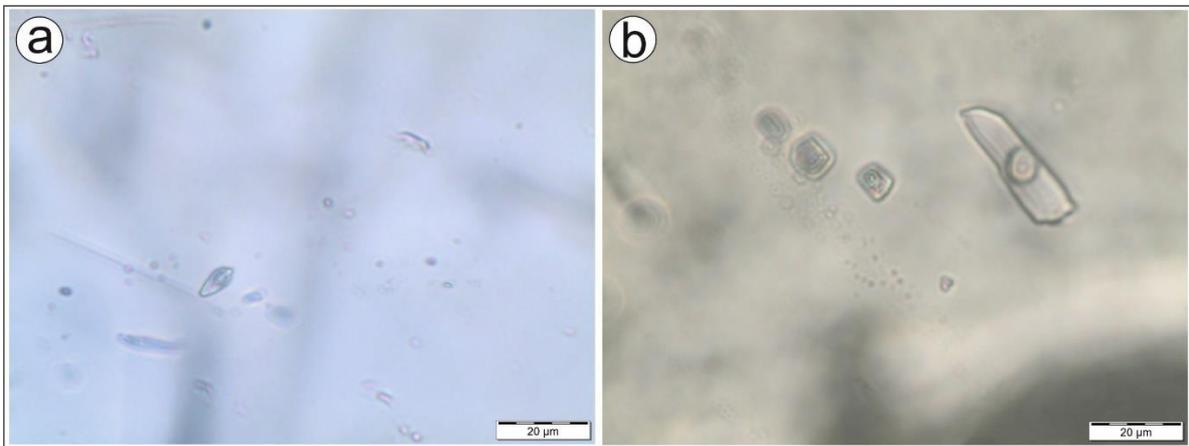
First melting temperature ( $T_{FM}$ ) values ranging from -55.0°C to -43°C were measured in both types of inclusions. Comparison of these measured temperatures with eutectic temperatures of various water-salt systems indicates the presence of NaCl, CaCl<sub>2</sub> and MgCl<sub>2</sub> salts in the solution (eutectic temperatures are -55.0 or -52.0°C for the H<sub>2</sub>O-NaCl-CaCl<sub>2</sub> system, -52.2°C for the H<sub>2</sub>O-MgCl<sub>2</sub>-CaCl<sub>2</sub> system and -49.5°C for the H<sub>2</sub>O-CaCl<sub>2</sub> system; from Shepherd et al. [27]).

The statistical distribution of the final ice melting temperature ( $T_{mICE}$ ) values measured in fluid inclusions is shown in Figure 6. The final ice melting temperatures measured in quartz crystals vary from -5,2°C to -0,3°C (average -1,5 °C) and those measured in calcite crystals are from -4,7 °C to -0,8°C (average -2,3°C). Using these final ice melting temperatures salinity values were estimated (wt.% NaCl) [28] which vary from 8 to 0,5% (n=57, ave. = 2,5%) for inclusions in quartz crystals and from 7,4 to 1,4% (n=11, ave. = 3,8%) for inclusions in calcite crystals.

The statistical distribution of homogenization temperatures ( $T_H$ ) measured in inclusions trapped within quartz and calcite crystals is shown in Figure 7.  $T_H$  values measured in quartz crystals are from 161 to 395 °C (n = 54, ave. = 238 °C) and those in calcite crystals range from 165 to 312°C (n= 11, ave.= 228 °C). Examination of salinity vs homogenization temperature relation in fluid inclusions reveals that samples have homogenization temperatures of 200 to 260°C and salinity of 1 to 5% (wt.% NaCl)



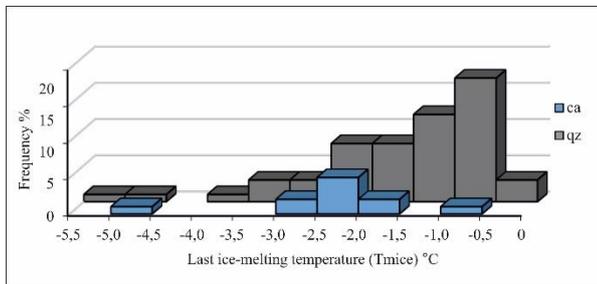
**Figure 4.** a) Quartz filling along the edges (plj: plagioclase, qz: quartz); b) euhedral pyrite crystals (py: pyrite) within quartz veins; c) hematite crystals within quartz veins; d) gold crystal in quartz veins (au: gold); e) and f) anhedral chalcopyrite and galena crystals



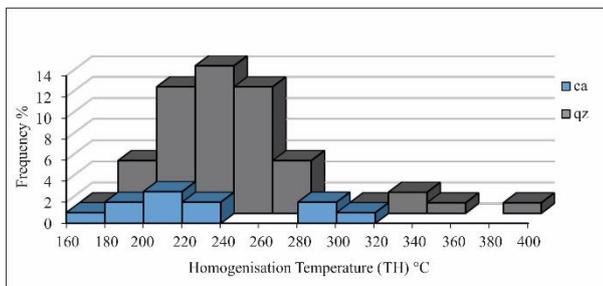
**Figure 5.** Primary inclusion in calcite (a) and quartz (b) crystals

**Table 1.** Results of measurements on fluid inclusions in quartz and calcite crystals from the Çorum-Şaphane mineralization.

Sample No	Mineral	Last ice-melting temperature ( $T_{mICE}$ )		Homogenisation temperature ( $T_H$ )	
		Range	Average	Range	Average
ÇŞK-1	Calcite	-2.5 to -2.0 (2)	-2.3	180 – 312 (2)	246
ÇŞK-2	Quartz	-3.0 to -2.3 (4)	-2.7	202 – 217 (3)	210
ÇŞK-5	Calcite	-4.7 to -2.1 (3)	-3.2	165 – 200 (3)	185
ÇŞK-6	Quartz	-2.4 to -1.0 (8)	-1.8	200 – 355 (7)	265
ÇŞK-7	Calcite	-2.4 to -0.8 (6)	-1.8	215 – 295 (6)	244
ÇŞK-10	Quartz	-3.5 to +0.8 (19)	-1.6	161- 230 (19)	209
ÇŞK-13	Quartz	-7.2 to -0.3 (25)	-1.2	210 – 395 (25)	255



**Figure 6.** Statistical distribution of last ice-melting temperature in the primary fluid inclusions in quartz and calcite crystals.

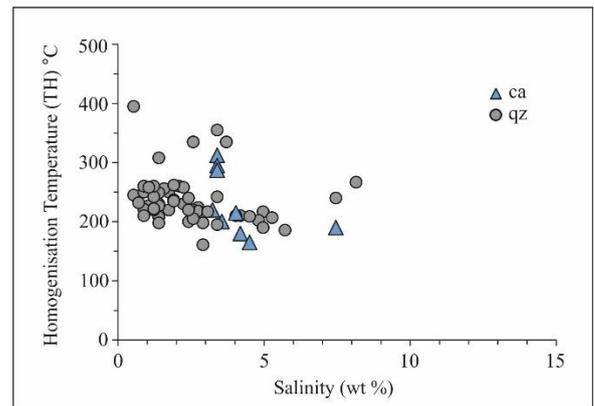


**Figure 7.** Statistical distribution of Homogenisation temperature (TH) in the primary fluid inclusions in quartz and calcite crystals.

Although it is generally accepted that the presence of salts such as  $\text{CaCl}_2$  and  $\text{MgCl}_2$  in the solution indicates that hydrothermal solutions are directly or indirectly related to seawater or circulate within marine deposits, they may also have been affected by ophiolitic rocks that formed on the surrounding ocean floors and came into contact with seawater and Eocene aged volcanosedimentary rocks that were realized in marine environments.

According to the % NaCl salinity values with corresponding  $T_{mICE}$  data, the salinity of calcites does not change much but salinity of quartz varies in a wider range.

However, this interval cannot be explained as a change in the salt composition of the hydrothermal solution.



**Figure 8.** Distribution of salinity-homogenisation temperature measured in fluid inclusions of calcite and quartz crystals

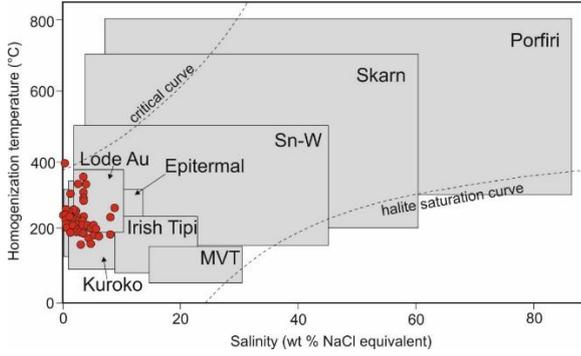
TH values vary in a wide range, and it can be considered that two separate solutions with an average temperatures of 230°C and 330°C are operative in the system. Microthermometric studies show that mineralization occurred under epithermal-mesothermal conditions.

Comparison of homogenisation temperature and salinity values of the Şaphane mineralization with the data from various deposit types in the world yields that the studied deposit can be considered as an epithermal deposit (Figure 9).

## 5 Conclusions

The Şaphane gold mineralization is located in the Çorum province in the Middle-Inner Black Sea region. Devecidağ Complex, Artova Ophiolite Complex, Alacahöyük, Bayat, Kızılırmak, Dodurga and Bozkır formations and Dededağ granitoid and quartz veins crop out in the region. The mineralization is associated with quartz

veins within extremely altered volcanic rocks and these veins trend in NE-SW and are exposed nearly 700 m.



**Figure 9.** Comparison of salinity vs homogenisation temperatures of calcite and quartz crystals with other deposits [29].

From the petrographic studies of the samples taken from the quartz veins, pyrite, hematite, limonite, chalcopryrite, galena and trace amounts of native gold were found as the ore minerals and quartz and calcite are defined as the gangue minerals.

The first melting temperature measurements in the fluid inclusion indicated the presence of salts in the hydrothermal solution such as NaCl, CaCl<sub>2</sub> and MgCl<sub>2</sub>. The salinity values calculated using the last ice melting temperature values vary between 8.0 and 0.5% in quartz and between 7.4 and 1.4% in calcites (wt. %NaCl equivalents). The average homogenization temperatures are 238°C in quartz and 228°C in calcite. In addition, TH values vary in a wide range, and it can be considered that two different solutions with average temperatures of 230 °C and 330 °C are effective in the system.

As a result, it has been determined that the mineralization in Şaphane is associated with quartz veins and formed at epithermal-mesothermal conditions between 161 and 395°C.

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#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Similarity rate (iThenticate):** 6%

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