

Microthermometric and stable isotopic (O and H) characteristics of fluid inclusions in the porphyry related Çöpler (İliç - Erzincan) gold deposit, central eastern Turkey

Research Article

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Received 04 November 2013; accepted 01 March 2014

Abstract: The Çöpler gold deposit occurs within the stockwork of quartz hosted by the Çöpler granitoid (Eosen) and by surrounding metasediments of Keban metamorphic (Late Paleozoic - Early Mesozoic) and the Munzur limestones (Late Carboniferous - Early Cretaceous).

Native gold accompanied by small amounts of chalcopyrite, pyrite, magnetite, maghemite, hematite, fahlerz, marcasite, bornite, galena, sphalerite, specular hematite, goethite, lepidochrosite and bravoitic pyrite within the stockwork ore veinlets. In addition, epidote (pistazite - zoisite), garnet, scapolite, chlorite, tremolite/actinolite, muscovite and opaque minerals were determined within the veinlets occurred in skarn zones.

The study of fluid inclusions in quartz veinlets showed that the hydrothermal fluids contain CaCl_2 , MgCl_2 and NaCl and the salinities of the two phases (L+V) inclusions range from 1.7 to 20.6% NaCl equivalent. Salinity values up to 44% were determined within the halite bearing three phases inclusions. Their homogenization temperature values have a wide range from 145.0 to 380.0°C, indicative of catathermal/hypothermal to epithermal conditions. The $\delta^{18}\text{O}$ and δD values of the fluid inclusion waters from the Çöpler granitoid correspond to those assigned to Primary Magmatic Water, those from the metasediments of Keban metamorphics fall outside of the Primary Magmatic and are within the Metamorphic Water field. A sample from a quartz vein within the skarn zone hosted by the Munzur limestones has a particularly low δD value.

The results suggest that fluids derived from the granitoids were mixed with those derived from the metasediments of Keban metamorphics and the Munzur limestones and resulting in quartz veinlets in these lithologies and the formation of stockwork ores. In view of the occurrence, the features described and processes envisaged for this study area may be applicable in similar settings.

Keywords: Çöpler (İliç-Erzincan) • gold deposit • fluid inclusion • hydrogen and oxygen isotopes

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1. Introduction

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The Çöpler gold deposit, discovered in the 1990s, is located near the town of İliç in the Erzincan Province in Turkey. Exploration activities started in 1999. Mining

started at the end of 2010 and continues to date (2014). The earliest ore geological investigation in Çöpler area was carried out by [1] and indicated that the iron and copper mineralizations occurred along the contacts between granitoid (diorite) - serpentinite and limestones. The first set of data about the depositional styles, structural and textural characteristics and microscopic features of the copper and manganese occurrences in the area were reported by [2]. No information about the gold enrichment within the area is provided in these studies. Detailed descriptions of geological characteristics of the gold mineralization and grade-tonnage distribution determined from drill cores were given in geological reports of the Anatolian Minerals Mining Company.

The geochemical characteristics of the Çöpler and Kabataş intrusive rocks are given in [3]. They indicate that these granitoid bodies show I-type calc-alkaline affinities, and their normalized trace element patterns show enrichment in large ion lithophile and light rare earth elements, but relative depletions in middle and heavy rare earth elements. These features are described from rocks derived from magma chambers generated in convergent plate margins or back arc basins discussed by [3].

The Çöpler porphyry-skarn Cu-Au deposit is part of Late Cretaceous to Middle Eocene magmatism of the Southeastern Anatolian orogenic belt. Recent investigations of the properties of the main deposits and prospects and their tectonic, magmatic, and geological characteristics are given in [4] who also state that the Eocene porphyry Cu-As occurrences in Eastern Turkey may be broadly comparable to porphyry Cu deposits in Iran.

The investigation of the depositional styles, microscopic and fluid inclusions characteristics of the Çöpler gold deposit forms part of the MSc dissertation [5] of the first author of this paper. The present study concentrates on the microthermometric characteristics of the fluid trapped in fluid inclusions within quartz crystals in the stockwork, and their δD values, and also the $\delta^{18}\text{O}$ values of the quartz and hence the calculated $\delta^{18}\text{O}$ values of the associated water. It aims to clarify the characteristics and identify the sources of the hydrothermal mineralizing fluid, in view of the regional geological setting and provide new information of regional relevance.

2. Geological Background of the study area

The Çöpler area is located in the northeastern margin of the Tauride-Anatolide tectonic units. A simplified

regional geological map of the surrounding area is presented in Figure 1. The Late Paleozoic - Mesozoic Keban metamorphics, form the basement of the region and consist of schists, marbles and limestones. The Late Carboniferous - Early Cretaceous Munzur limestones overlie the Keban metamorphics with a tectonic contact [7-11]. The Munzur limestones consists of a thick succession of deep sea and platform-type carbonate rocks [7-11]. These units were tectonically overlain by the Late Campanian - Early Maastrichtian Divriği ophiolitic melange [11]. These units were intruded by granitoids in Dumluca, Murmana, Çöpler, Kabataş, Bizmişen and Çaltı areas and covered by Cenozoic sedimentary units and Quaternary alluviums [11].

The Keban metamorphics, Munzur limestones, Çöpler granitoid and jasperoid occur in outcrops around the Çöpler gold deposits (Figure 2). The Keban metamorphics consist of low grade metamorphic claystone, sandstone, siltstone and recrystallized limestones. Microscopic investigations of thin sections revealed that microcrystalline quartz and sericite are the dominant minerals showing phyllitic textures and foliation. In addition, skarn minerals such as epidote (pistazite - zoisite), garnet, scapolite, chlorite, tremolite/actinolite and muscovite, occur along the schistosity planes and thin fissures in these rocks, and are assigned to a hydrothermal origin. The secondary biotites and opaque minerals formed in quartz veinlets.

The Late Carboniferous - Early Cretaceous Munzur limestone occurs as massive and laminated beds in extended outcrops, and reaches a thickness of up to 1200 m within the area and consists of massive and laminated levels. It was highly fractured due to intense tectonic activity. The samples collected from the outcrops close to Çöpler granitoid intrusion are highly recrystallized and described as marble. In contrast, the samples taken away from the intrusion show the original characteristics of limestone; micritic matrix, with abundant fossil showing intraclastic/intrabimicritic texture.

The pinkish-gray Çöpler granitoid (Eocene) intruded the Keban metamorphics and Munzur limestones. The emplacement of the granitoids is assumed to have taken place in a back-arc setting [3] or in a postcollisional geotectonic environment [4]. Surrounding the main intrusive body there are discrete elongated apophyses intruded into the older units. This granitoid is heavily altered and fractured at the surface. The outcrop samples have monzonitic, monzodioritic and dioritic composition and show coarse-grained equigranular texture, while samples taken from drill cores have granodioritic composition and show porphyritic texture. This indicates the presence of the porphyry body at depth.

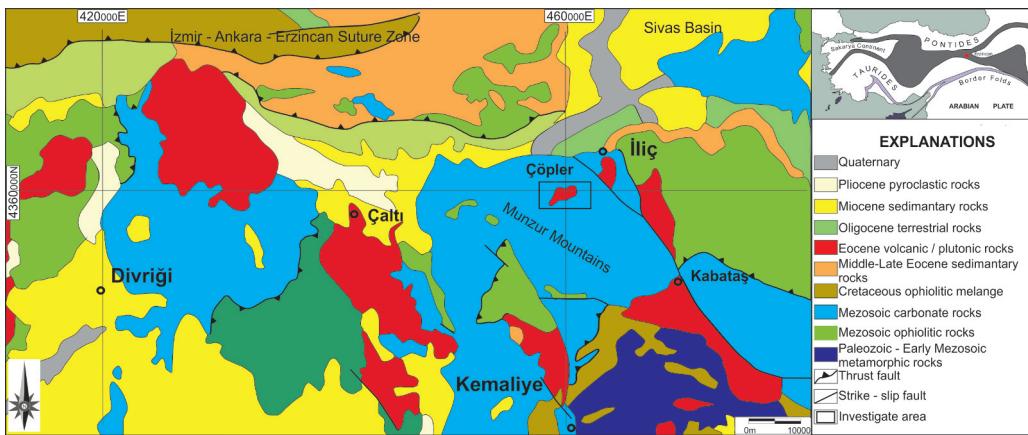


Figure 1. Location and regional geology map of investigation area (Redrawn after [6]).

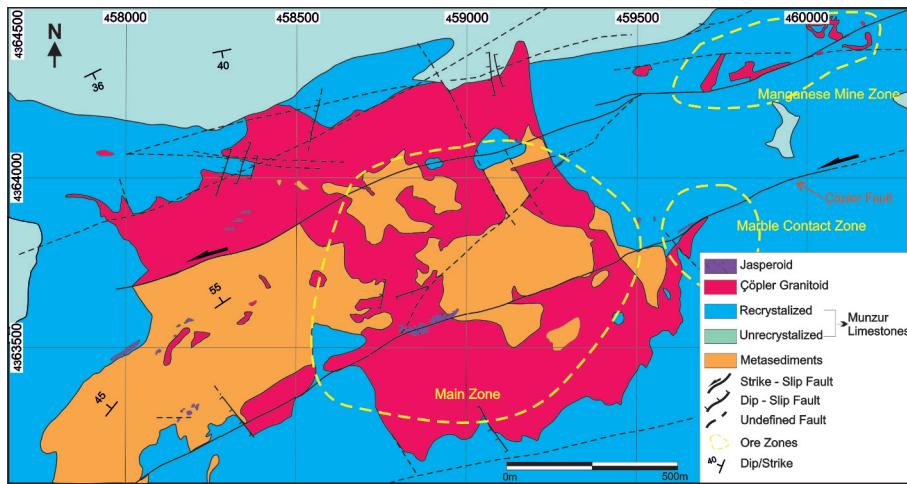


Figure 2. Geology map of the Çöpler gold deposit area (modified after the unpublished geology map prepared by Anatolian Minerals Mining Company).

Very narrow skarn zones were developed along the contact between Çöpler granitoid and metasediments of Keban metamorphics and Munzur limestones. The samples taken from these zones contain epidote (pistazite - zoisite), garnet, scapolite, tremolite/actinolite, muscovite, chlorite and opaque minerals.

Geochronological information in the form of $^{40}\text{Ar}/^{39}\text{Ar}$ radiometric ages from both the igneous and metamorphic complexes indicate ages of about 43-44 Ma which agree with the Eocene age concluded from stratigraphic

studies [4]. The details of the geochronological investigation are as follows: Igneous biotite from two samples of the magmatic complex yielded $^{40}\text{Ar}/^{39}\text{Ar}$ plateau ages of 43.75 ± 0.26 Ma and 44.19 ± 0.23 , whereas igneous hornblende from a third sample yielded a plateau age of 44.13 ± 0.38 . These ages closely overlap with $^{40}\text{Ar}/^{39}\text{Ar}$ ages of hydrothermal sericite (44.44 ± 0.28 Ma) and biotite (43.84 ± 0.26 Ma), and Re-Os ages from two molybdenite samples (44.6 ± 0.2 and 43.9 ± 0.2 Ma) suggesting a short-lived (~ 1 my) magmatic and

hydrothermal history at Çöpler [4].

3. Ore Geology and Mineralogy

Areas of gold enrichment were observed at the apex of the Çöpler granitoid, in the surrounding metasediments of Keban metamorphics and also in the Munzur limestone. The enrichments in stockwork veinlets of quartz are the dominant features in all three types of host rocks. Therefore stockwork mineralization is regarded as the dominant type with less prominent occurrences of disseminated, vein and contact controlled ores.

The host rocks are intensively fractured and altered. The alteration zones are characterized by silicification, sericitization, sulphidation and K-feldspar formation. The borders between the alteration zones are not prominent because of intensive tectonic disturbance. Calcite, chalcedony and quartz are widespread within the stockwork quartz veinlets, and little amount of sulfide disseminations are included. Colloform textures are also common. Structure related features include: 1) jasperoid bodies that occur along the east-west lineaments developed parallel to the Çöpler Fault, identified at nearly 500 m south of the Çöpler Village. 2) manganese mineralization occurring along a fault zone, sub-parallel to the Çöpler Fault, approximately one kilometer northeast of Çöpler Village (Figure 2).

Microscopic investigation of thin sections and polished blocks representing the various types of mineralization showed the presence of small amounts of ore minerals: chalcopyrite, pyrite, magnetite, maghemite, hematite, fahlerz, marcasite, bornite, galena, sphalerite, specular hematite, goethite, lepidochrosite, native gold, bravoitic pyrite (Figure 3). There is not much difference in assemblage of ore mineral and their abundances among the different host lithologies, which represent various environments of formation. Quartz and calcite occur as gangue minerals associated with quartz veinlets within the granitoids. In contrast the mineralized samples hosted by skarn zones within the metasediments of Keban metamorphics and also the Munzur limestones near the contact with Çöpler granitoid, contain gangue minerals such as epidote (pistazite - zoisite), garnet, scapolite, chlorite, tremolite/actinolite and muscovite which are typical of skarn.

4. Microthermometry of Fluid Inclusions

Fluid inclusions studies were carried out on quartz crystals. The microthermometric measurements were performed on a Leica DM 2500p microscope mounted with a Linkam THMS - 600 and TMS - 92 freezing - heating stage, at the Geological Engineering Department of Cumhuriyet University.

Fluid inclusions were determined in the quartz crystals from the samples of quartz veinlets hosted by the Çöpler granitoids and the metasediments of Keban metamorphics. The samples from the veinlets occurred in skarn zones within the Munzur limestones rarely contain quartz, and only one sample was investigated.

Both primary and secondary inclusions are common in all veinlet samples. The sizes of inclusions range from 1 to 10 micron and their shapes are very variable. Two phase inclusions (L+V; liquid, 70–80% and vapour, 20–30%) are abundant, and three phases inclusions (L+V+Halite) are rare. Primary inclusions are dispersed within quartz crystals while secondary inclusions occur along the fissures which cut across the quartz crystals. First melting temperature (T_{FM}), last (final) ice melting temperature (T_{m-ICE}) and homogenization temperature (T_H) values were measured within the two phase (L+V) inclusions. A few of salt melting (homogenization into fluid) temperature (T_{m-salt}) values were measured in the three phase (L+V+Halite) inclusions.

The T_{FM} values of all types of inclusions are clustered from -55.0°C to -54.0°C (avg. -55.0°C , $n = 110$). These values are similar to the eutectic temperature of CaCl_2 , MgCl_2 and NaCl bearing water - salt systems [12], and indicate the presence of these salts in hydrothermal fluids. No difference in relation between the microthermometric properties of fluid inclusions having different orientations or location of the respective veinlets. This indicates that the concentration and composition of the dissolved solids in the fluid was the same during the various phases of mineralization.

The T_{m-ICE} values of primary inclusions (without daughter halite crystals), in quartz veinlets in the Çöpler granitoid range from -5.4°C to -2.1°C (avg. -4.4°C , $n = 50$), while those in the metasediments of Keban metamorphics range from -17.5°C to -1.0°C (avg. -6.2°C , $n = 72$) and those in skarn zone within Munzur limestones range from -8.3°C to -6.0°C (avg. -7.3°C , $n = 7$).

The salinity of the fluids were calculated using T_{m-ICE} values and the formula of [13] expressed as $\text{NaCl}\%$ equivalent. The salinity of the inclusions in quartz veinlets in Çöpler granitoid are in the range of 3.6 to 12.1% (avg. 6.9% $n = 50$), those in metasediments of Keban

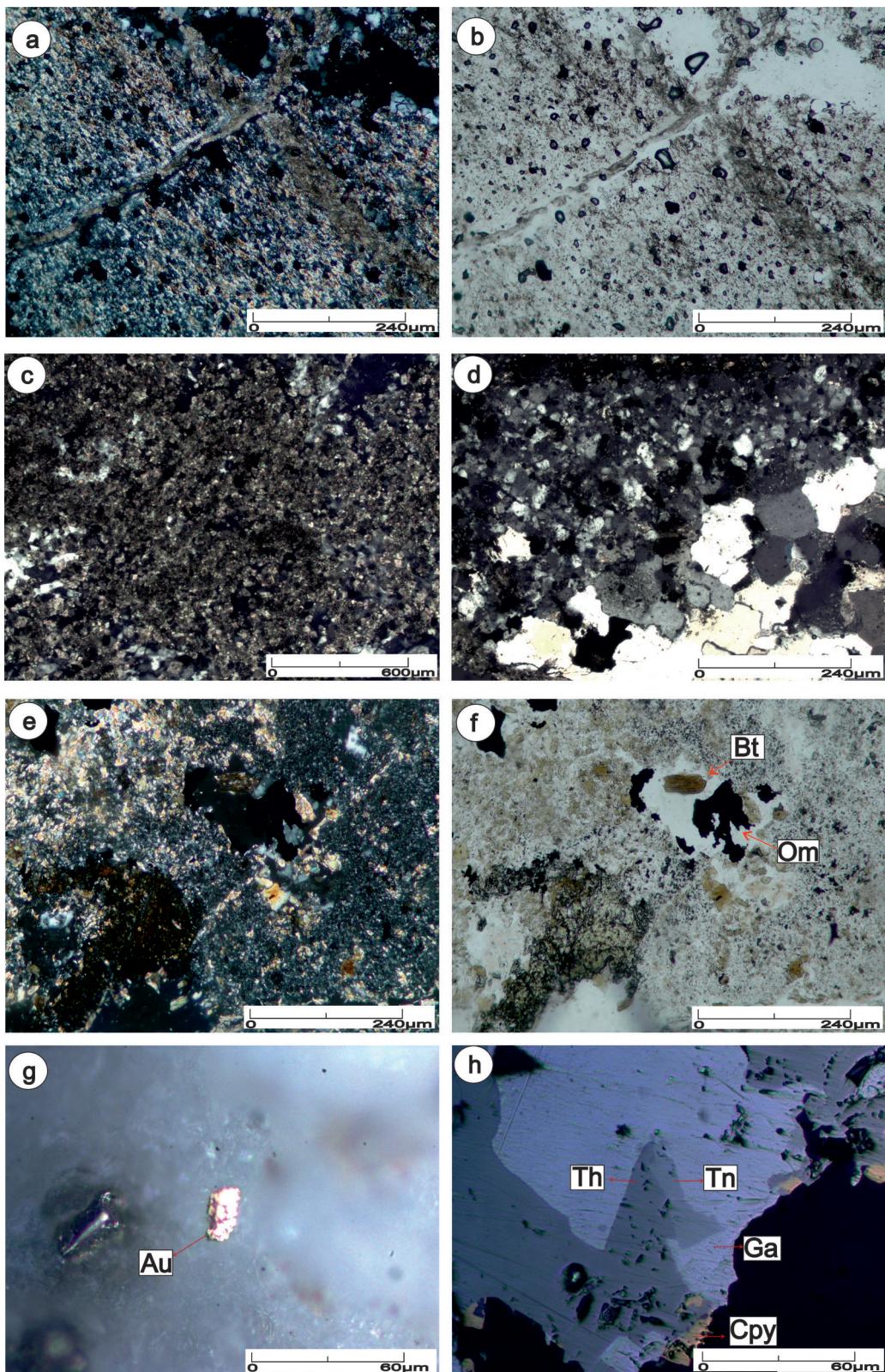


Figure 3. Photomicrographs from the representative ore samples: (a - b) sericitization, (c) carbonization, (d) silicification, (e - f) secondary biotite (Bt) with opac minerals (Om) in quartz veinlets. (g-h) views of ore minerals (Au: Gold, Tn: Tennantite, Th: Tetrahedrite, Ga: Galena, Cpy: Calcopyrite).

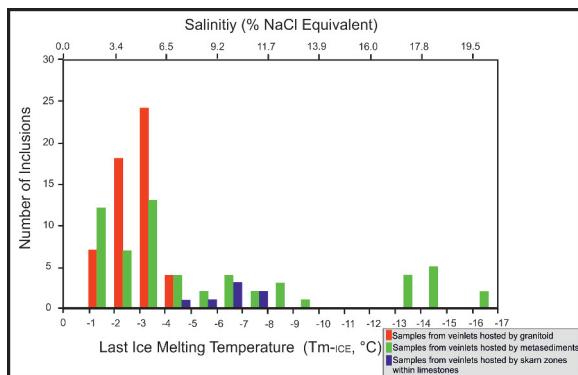


Figure 4. Histogram of the last ice melting temperature values in fluid inclusions in quartz crystals.

metamorphics range from 1.7 to 20.6% (avg. 9.3% $n = 72$) and those in skarn zone within Munzur limestones range from 8.14 to 12.05% (avg. 10.82% $n = 7$) (Figure 4). The average salinity values of the inclusions in quartz veinlets are lowest for the Çöpler granitoids intermediate for the Keban metamorphics and highest for the skarn zone within Munzur limestones.

Salt crystals within the three phase (L+V+Solid salt) inclusions (in samples IC-61 and IC-66; from quartz veinlets hosted by metasediments) melted (homogenised into fluid) within a temperature interval between 315.0°C–380.0°C (avg: 343.5°C, $n = 12$) and suggest salinity values between 39–44% (avg: 40.8, $n = 12$). Similar values (T_{m-salt} values from 103.0°C to 445.0°C and total salinity values up to 71%) were also reported in [14]. Samples IC-61 and IC-66 from the metasediments of Keban metamorphics contain both types of inclusions. The salinity values of these two different types of inclusions indicate that some veinlets record two fluids; either derived from different sources or differentiated from the same fluid. The average salinity values calculated from the T_{m-ICE} and T_{m-salt} measurements in these samples are 5.21% ($n = 12$) and 40.8% ($n = 12$) respectively. It may be estimated an average salinity values about 23.0% if they differentiated from the same fluid.

The TH values for quartz veinlets in Çöpler granitoid are in the range of 176.0°–375.0°C (avg. 263.9°C, $n = 53$) in the metasediments of Keban metamorphics from 145.0° to 375.0°C (avg. 268.0°C, $n = 88$) and for the skarn zone 215.0°C to 299.5°C (avg. 247.0°C; $n = 6$) (Figure 5). There is no significant difference in the range of homogenization temperature (T_H) values of inclusions hosted by these different lithologies. Some

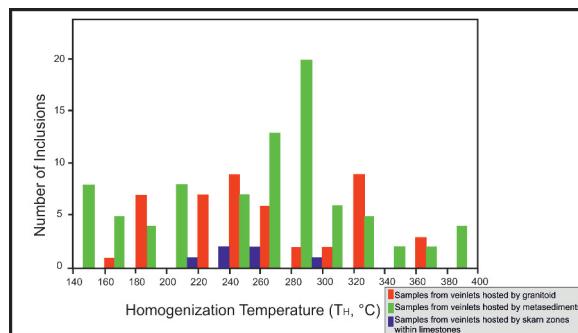


Figure 5. Histogram of the homogenization temperature values in fluid inclusions within quartz crystals.

irregularly shaped fluid inclusions, in quartz veinlets hosted by Çöpler granitoid, whose gas bubbles did not show any movement and not homogenized up to 450.0°C are assumed to be unstable occurrences. These measured T_H values indicate that the trapping of fluids (mineral formation) was started under catathermal/hypothermal condition and continued down to mesothermal and epithermal conditions.

There is little differences in T_H values, in accordance with the vertical and lateral position of the samples. The average values of the shallowest (1150 m of elevation) and the deepest (850 m) samples hosted by Çöpler granitoid are 257.0°C and 284.0°C respectively, and indicate an increase of 27°C in temperature for a 300 m elevation changes. The vertical changes of TH values in metasediments hosted veinlets are very heterogenous and show alternation of temperature values between 166.9°C and 338.7°C in an 120 m interval (from 1163 m to 1042 m) due to the granitoid apophyses intruded into this unit.

Plots of the salinity, calculated using the T_{m-ice} values within the two phase L+V inclusion, and temperature values on a cross plot (Figure 6) show that the values of fluid trapped in quartz veinlets in metasediments of Keban metamorphics are spread over a large area, while those in the granitoid body dispersed over a narrower ranges. These different characteristics may be explained as a result of mixing of a fluid of high temperature low salinity derived from Çöpler Granitoid with a fluid of lower temperature and higher salinity within metasediments of Keban Metamorphics (Figure 6).

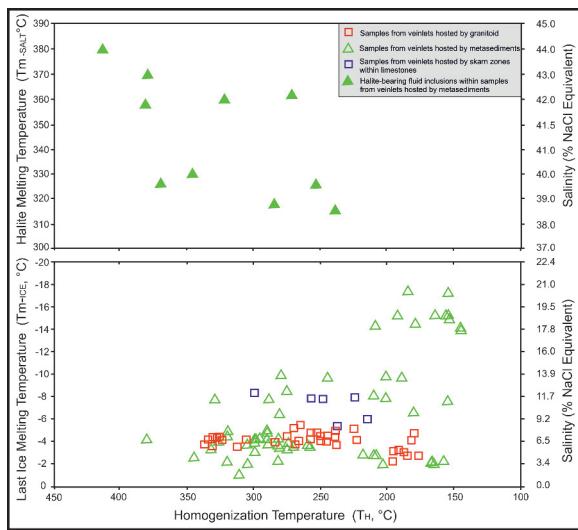


Figure 6. Cross plots of the last ice melting temperature, the salinity and homogenisation temperature values in fluid inclusions within quartz crystals.

5. Oxygen and Hydrogen Isotope

The oxygen and hydrogen isotope analyses were performed at Actlabs in Canada. The determination of $\delta^{18}\text{O}$ in quartz separates followed the method of [15]. Isotopic analyses were performed on a Finnigan MAT Delta, dual inlet, isotope ratio mass spectrometer. The data are reported in the standard delta notation as per mil deviations from V-SMOW. External reproducibility is $\pm 0.19\text{\textperthousand}$ (1σ) based on repeat analyses of our internal white crystal standard (WCS). The value for NBS 28 standard is $9.61 \pm 0.10\text{\textperthousand}$ SMOW (1σ).

Hydrogen isotope analyses were carried out on inclusion fluids extracted from quartz separates by thermal decrepitation. Analyses of the water contents are reproducible to ± 0.2 wt%. The accumulated water representing the total amount of hydrogen in the samples is separated from the other gases by differential freezing techniques. Isotopic analyses were carried out in a dual inlet gas source isotope ratio mass spectrometry Finnigan MAT Delta. Results are reported δD as permil deviation from the SMOW standard. The difference between results of duplicate analyses were smaller than $\pm 3\text{\textperthousand}$. Using the procedure described above NSB-30 biotite standard gave a δD value of $-65\text{\textperthousand}$ SMOW.

The $\delta^{18}\text{O}$ values of water in equilibrium with quartz were calculated using the average T_h values measured in these samples and quartz-water fractionation factors of [16].

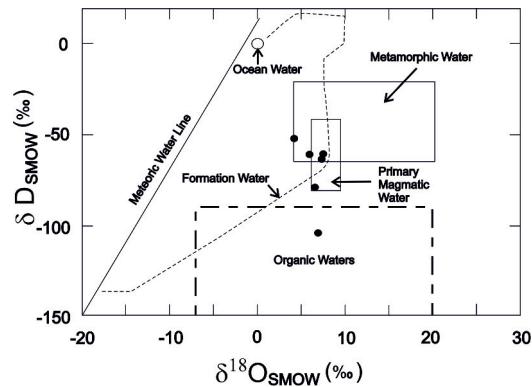


Figure 7. Plots of the hydrogen and oxygen isotope values of the fluid trapped in quartz crystals on the $\delta\text{D}\text{\textperthousand}$ and $\delta^{18}\text{O}$ diagram (diagram was reproduced from [16]).

The analysed and calculated $\delta^{18}\text{O}$ and δD values of all samples are shown in Table 1. The plots of these values on the bivalent $\delta^{18}\text{O}$ and δD diagram are given in Figure 7. The values of the quartz veinlets in the Çöpler granitoid are located in the "magmatic water box" on Figure 7 and indicate the presence of magmatic water in hydrothermal fluids derived from the Çöpler granitoid host. The two values belong to quartz veinlets from the metasediments of the Keban metamorphics are located outside the magmatic water box, within the "metamorphic water box" but may also represent mixtures of formation or metamorphic water in metasediments hosting these samples with magmatic fluids. The single value recorded from a sample from the skarn has a low δD value below the magmatic water box. This result is interpreted as an indication to the fluid being a residual water with light hydrogen as a result of formation of the hydroxyl bearing skarn minerals.

6. Conclusions

The Çöpler (İliç-Erzincan) gold deposit is a porphyry related deposit within the stockwork quartz veinlets hosted by Çöpler granitoid and surrounding metasediments of Keban metamorphics and Munzur limestones.

Native gold is accompanied by small amounts of pyrite, chalcopyrite, galena, fahlerz, marcasite, bornite, bravoitic pyrite and limonite (goethite, lepidocrocite). There is not much difference in the content of ore minerals and their abundance, in accordance with the host lithology and depositional types. Quartz and calcite are the

Table 1. SHydrogen and oxygen isotope results of investigated quartz samples.

Sample No:	$\delta^{18}\text{O}$ values of quartz	average T_H values measured in fluid inclusions (°C)	$10^3 \ln \alpha$ (*)	calculated $\delta^{18}\text{O}$ values of water in equilibrium quartz	δD values of water analysed in with inclusion fluid
IC-11 (a)	16.7	284.33	8.84	7.86	-60
IC-36 (b)	14.2	301.14	8.17	6.03	-61
IC-40 (a)	14.9	326.00	7.27	7.63	-63
IC-68 (a)	13.1	338.00	6.87	6.23	-78
IC-71 (b)	13.6	272.60	9.38	4.22	-52
IC-124 (c)	16.2	247.00	10.59	5.61	-103

$10^3 \ln \alpha$ (*) values were calculated from the $\delta^{18}\text{O}$ results of quartz using the average T_H values measured in fluid inclusions and equations of [15].

(a) samples from veinlets hosted by granitoid

(b) samples from veinlets hosted by metasediments

(c) samples from limestone-granitoid skarn zone.

gangue minerals of the quartz veinlets within the granitoid while the samples hosted by skarn zones within the metasediments and limestones contain skarn minerals such as epidote (pistazite - zoisite), garnet, scapolite, chlorite, tremolite/actinolite and muscovite.

Microthermometric investigations of the fluids trapped in quartz crystals from veinlets indicate the presences of CaCl_2 , MgCl_2 and NaCl in hydrothermal fluids. The salinity and the temperature values show large ranges and indicate the mixing of a hydrothermal fluid of high temperature and low salinity derived from the Çöpler granitoid with a fluid of lower temperature and higher salinity derived from the metasediments of Keban metamorphics and from Munzur limestones

The oxygen and hydrogen isotope composition of the water in hydrothermal fluids indicate the presence of magmatic water trapped in quartz veinlets hosted by granitoid body and mixing of formation or metamorphic water into magmatic water in quartz veinlets hosted by metasediments of Keban metamorphics. A single value with lighter hydrogen isotope composition, belongs a sample from skarn zone, may be explained as a residual water with light hydrogen as a result of formation of hydroxyl bearing skarn minerals.

These results suggest that the Çöpler gold deposit is mainly of porphyry type. The presence of mineralization outside the granitoid body indicate that the impermeable outer zone of Çöpler granitoid was not developed very well and hydrothermal fluids escaped outside of the granitoid body and precipitated some of their metal contents along the fissure zones and schistosity surfaces

within the metasediments of Keban metamorphics and Munzur limestones, in addition to those in the granitoid.

Acknowledgment

This study was supported by The Research Foundation Council of Cumhuriyet University (Projects No: M-416 and M-500). Baruch Spiro (Natural History Museum, London, UK) is gratefully acknowledged for his critical reading of the manuscript and correcting the English.

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