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GEOTHERMOMETRIC STUDIES ON THE ATTEPE IRON DEPOSITS

Ali Rıza ÇOLAKOĞLU* and Gülay SEZERER KURU*

ABSTRACT.- This study was carried out in the Attepe (Yahyalı) iron mineralization zone of Kayseri province. The main mineralization zone is 500 m long and lies approximately in the NNW/SSE direction. The study covers the geothermometric analyses which were carried out on the fluid inclusions of siderite, quartz and barites in relation within the iron mineralization. In this study samples were taken from five different rock groups observed in the field and were evaluated as a, b, c, d, e. Four different fluid inclusion types were determined in the siderite, quartz and barites of these rock groups (type I, type II, type III and type IV fluid inclusions). As a result of these studies three different formation processes were determined within the ore mineralization zone, namely (1) early stage, (2) late stage and (3) final late stage. Homogenization temperatures were 300-350°C in the early stage, 180-270°C in the late stage guartzes of the first group on average have 35 % NaCl and the final stage barites have 3 % NaCl equivalent salinity. According to the macro observations in the mineralization area and the homogenization temperature measurements made in laboratory whatever the origin of the fluids, the deposits were formed in the hydrothermal stage conditions and hypothermal, mesothermal and epithermal stages were active in these hydrothermal stages.

INTRODUCTION

The region within the Attepe iron mine which covers the study area is the second largest iron basin of Turkey. This deposit is described firstly as Faras mine by Lucius in the year 1972. In the region, The first comprehensive studies on ore deposits were started in the year 1967. After this period, studies have been corried out by various researchers and the region were investigated in detail in the terms of regional geology and ore deposits. First geologic studies dealing with the chronostratigraphy were done by Blumenthal (1944) and Abdüsselamoğlu (1958). Most detailed petrographical, geochemical, genetical and ore microscopy studies in the terms of mineralization were done by Küpeli, (1986, 1991 and 1999); Ayhan et al., (1992). Other detailed studies dealing with regional geology

and mineralization are also present (Ayhan and İplikçi, 1980; Metin 1983; Henden et al., 1978; Henden and Önder, 1980; Önder and Şahin, 1979, Şahin and Bakirdağ, 1985; Dağlıoğlu, 1990; Dağlıoğlu and Bançeci, 1992; Dağlıoğlu et al., 1998). This region is very important for steel-iron sector in our country that ore production has been going on since 1969.

Mineralogical, petrographical and geochemical studies have revealed that the iron ores in Attepe and its vicinity were present in three different genetic types (Küpeli, 1986; 1991; Dağlıoğlu et al., 1998). In the region, mineralizations have been seen in the units which are of Mesozoic, Lower-Middle Cambrian, and Lower Cambrian ages (Dağlıoğlu et al., 1998; Küpeli, 1999). These are sedimantary pyrite and hematite occurences (type, I), hydrothermal siderite and hematite occurences (type, II), and karstic iron ores occurences (type, III). Pyrite and hematite occurences (type, I), in the Lower Cambrian aged bituminous shale-phyllite and metaguartzites which are deposited in the sedimentary type are firstly described by (Küpeli, 1986). The argument that the ll'nd. type mineralization in the Lower-Middle Cambrian aged metacarbonates formed as a result of the hydrothermal processes are accepted by the all researchers except Unlu and Stendal (1986). Based on the geochemical data Ünlü and Stendal (1986) suggest a sedimantary model (Küpeli, 1999). The II'nd type mineralization were formed in the Paleocene-Lower Eocene time periods on the other hand the III'rd type mineralization are formed at the beginning of Tertiary epoch, by storage in endokarstic holes in the form of secondary ironhydroxide group of minerals within the framework of terrestrial movements and karstic processes of multiple phases (Küpeli, 1991). The most important mineralizations in the region are classifed as type II and type III ores.

Mineralization have developed in tectonically controlled form and found as veins, lenses and irregularly shaped masses. Pyrite, tetrahedrite, chalcopyrite, marcasite, siderite, barite and little hematite and magnetite are observed as ore minerals in all of these type mineralizations (Küpeli, 1999). In order to determine the conditions of the mineralization process and for the purpose of clarifying the previous observations and conclusions, geothermometric measurements were made on samples of five characters (a, b, c, d, e) in the field studies (fig. 1). In this study siderite, quartz and barite in connection with the mineralization zones are evaluated. The purpose of these geothermometric measurement studies" were the determination of the homogenisation temperatures of these minerals and the determination of the fluid inclusion types developed in connection with the mineralization processes, attempts were also made to obtain new data to support the previous data and to determine the formation processes of the ore deposits.

GEOLOGICAL SETTING

The Attepe iron ore deposits are bounded by Geyikdağı unit, considered as otocton by Özgül (1976), in the south, by Aladağ unit in the west, by Kireclivayla melange in the north and by Göksun metamorphics in the east. The oldest rocks of this region within this area are the Sicimindağ formation of Gevikdağı unit. This formation contains Attepe member on the top which is formed by alternating bituminous schist, phyllite and shales and Kandilcikdere member at the bottom composed of schist and phyllite metauartzites (fig. 1). On top of this formation lies the Caltepe formation of Lower-Middle Cambrian age (Dean and Monod, 1970). On top of these formations lies the Seydisehir formation of Upper Cambrian and Ordovician age containing Elmadağı ve Eğrisöğütdalı members and the unit is composed of calcschist, phyllite, limestone with nodules and metasandstones. On top of these formations the Karakızoğlu formation of Mesosoic age are present with an angular discordance. It is composed of schist, phyllite calcschist and recrystallized limestones. The mineralization is observed as lense and vein shaped in all formations older than the Miocene age. The most important mineralization are observed in metacarbonates of Lower-Middle Cambrian age (fig. 1).



Fig. 1- Schematic cross-section view showing the sample types and geological map of the investigation area. (Modifed after Ayhan et all., 1992).

FLUID INCLUSION PETROGRAPHY

Samples are taken from the quarry operated by open-pit method for studies of fluid inclusion. These samples are, (a) siderite veins cutting through grey colored limestones, (b) light brown-dark brown colored siderite transformed into iron-hydroxite group minerals, (c) quartzes found in siderite and partly cutting through it, (d) quartzes in iron-hydroxite zone and (e) less observed barite seen in the mineralization zone.

Fluid inclusions which are classifed into four groups in are further subgrouped into five group samples (fig. 2). According to the composition and fluid inclusions in the samples (a, b, c, d, e) are grouped into four different groups (Roedder, 1984):

Type I. fluid inclusions: two phases (liquid + vapor). Type II. fluid inclusions: three phases (liquid + vapor + solid).

Type III. fluid inclusions: one phases (liquid).

Type IV. fluid inclusins: one phase (vapor)

As a result of the studies similar types of fluid inclusions were differentiated into primary and secondary origins however only the data from the fluid inclusions of primary type were evaluated.

Dimensions of these fluid inclusions of four types are generally within 2-18 microns. They provide different fluid inclusion types with regular and irregular forms morphologies. For example in siderites fluid inclusions of type I and II, in quartzites types I, II, III and IV; and in barites only type I fluid inclusion is observed.



Fig. 2- Fluid inclusion types observed in siderite, quartz and barite in Attepe iron ore deposits.

Geothermometric studies

Geothermometric measurements are made according to the USGS fluid inclusion systems. During the heating and freezing measurements liquid and gaseous nitrogen is used. The instrument is calibrated as $\pm 0,2^{\circ}$ C for temperatures below 0 °C and as $\pm 2,0^{\circ}$ C for higher temperatures. Synthetic fluid inclusions containing CO₂ and liquid phases are used in the calibration. To prevent the spoiling of the primary characteristics of the fluid inclusions by heat cold adhesives (entallan) is used and two sides are polished and 35 micron thick special fluid inclusion sections are produced. Results of geothermometric measurements made on the fluid inclusions of siderite, quartz and barites taken from the mineral phases related to the ore are given in summary form (Table-1).

Sample Type	Туре	Stage	The melting temperature daughter minerals	Dimenson micron e	Salinity Wt % NaCi	Mean	Frequency	Homogeni- zation Temperature Interval	Mean
Second group siderite	Трре І	Stage 1		2-18			12	180-290	236
Second group siderite	Type I	Stage 2		2-18			8	310-370	336
First group quartz	Type I	Stage 1		3-16			16	180-270	214
First group quartz	Type I	Stage 2		3-16			20	300-450	371
First group quartz	Type II	Stage 1	(-23,4/-53,7)*	3-16	31-38	35	18	170-280	235
First group quartz	Type II	Stage 2		3-16	40-45	43	34	300-440	375
Second group quartz	Type I	Stage I		4-18			37	180-350	256
Barite	Type I	Stage I	(-3,1/-4,8)	2-18	2,7-3,2	3	15	170-250	213

Table 1- The properties of fluid inclusion in mineral forming fluid

Siderites

Lenses of siderite are usually of 10-80 cm thickness. In some locations siderites are in the form of crack fills. Siderites are divided into two groupes. First groups of siderite form siderite veins cross cutting to grey colored limestones and schist rocks (a), second group of siderites are of light dark brown colored. These are siderites (b) which show wide scale spreading compared to the first group of siderites and gradually inserted into ironhydroxide group of minerals

First group of siderites (a) have--relatively small crystals (0.1-0.3 mm) and the siderites in this group were not taken into account since sufficient data is not obtained during the geothermometric measurements because

they have very few fluid inclusions. The second group of siderites have larger crystals (0.3 mm to 1 cm) and they contain few amounts of type I fluid inclusions of 6-10 microns dimensions. Homogenization temperatures obtained from the heating experiments made on these fluid inclusions indicate two seperate phases. In the first stage the homogenezation temperatures are in between 180-290°C. In the second stage the homogenezation temperatures are in between 310-370°C (fig. 3). During the freezing experiments as the melting points were not properly observed a clear melting point temperature interval could not be given. For this reason the salinity values of this type fluid inclusions could not be determined.



Fig. 3- The homogenization temperatures measured from siderite, quartz and barite in Attepe iron ore deposits.

Quartzes

Quartzes are investigated in two different groups. The first group of guartzes, are the kind of quartzes which are observed together with siderites. They also contain pseudomorphic pyrites transformed into ironhydroxide group of minerals (c). Quartzites are present in the mineral phases related to the above mentioned minerals and are observed in siderites in the form of stockvork and vein type structures. In other words they form the gang mineral within the ore mineral zone. Fluid inclusions of types I., II., III. and IV. are observed in these veins. The dimensions of fluid inclusions vary from 3 to 16 microns. Homogenization temperatures of I'st type fluid inclusions of first group quartzites indicate two different stages. In the first stage the homogenezation temperatures are in between 180-270°C, in the second stage it is in, between 300-450°C (fig. 3). Homogenization temperatures of II'nd type of fluid inclusions of first group of quartzes also indicate to distinct stages. Homogenization temperature of the first stage are in between 170-280°C, in the second stage it is in between 300-440°C (fig. 3). Simultaneous observation of fluid inclusions of types MI and IV in guartzes indicates the occurrence of boiling event. For this reason no pressure correction was applied to the homogenization temperatures measured from the geothermometric measurements.

It is observed that solid phases (daughter crystals) of some of the II'nd type fluid inclusions of first group quartzites did not melt at temperatures higher than 450°C while some of the daughter crystals of the same type of fluid inclusions melted before the disappearance of the fluid inclusion bubble. In the heating tests the daughter crystals of silvine melts at higher temperatures than halite crystals (Roeeder, 1984). Thus it is considered that in this study the crystals which had melted before the disappearance of the bubble is halite and the others, that is those daughter crystals which had not melted at higher temperatures is silvine. The melting temperatures of daughter crystals (for halites) of II'nd type of fluid inclusions varies between 23.4-53.7°C. By consideration of these melting temperatures it is determined that the salinity of this type of fluid inclusion is equivalent to % 31-45 NaCl. From these salinity values the equivalent NaCl for the first stage is % 31-38, and for the second stage % 40-45. For the first group of guartzes geothermomethric measurement result of type I and II fluid inclusion indicate similarities.

The second group of quartzites are those quartzites which are coincident with the ironhydroxide group of minerals and which cross them (d). Among them only the I'st type of fluid inclusions is observed. The dimensions of this type of fluid inclusions vary from 4 to 18 microns and show high inconsistency. The presence of high inconsistency behaviour of fluid inclusions makes the performance of the freezing tests on fluid inclusions difficult. The homogenization temperatures obtained from the heating tests of I'st type of fluid inclusions of second group of, quartzites are dispersed between 180-350°C and the most frequently observed homogenization temperatures are 220-320°C (Refer to fig.3).

Barites

Barites are encountered stratigraphically in the upper levels of the all the iron ore outcrops in the Mansurlu region. Due to the removal of cover layers of barites are rarely encountered in the ore zones. The presence of barites in stratigraphic order necessitates the geothermometric studies in the barites. Barites have larger crystals and are more transparent as compared to other minerals. Among the barites type I fluid inclusions of 2-18 micron dimensions and generally with regular dimensions are encountered. As a result of the geothermometric measurement studies homogenization temperatures varying from 170 to 250°C are determined (Refer to fig. 3). As a result of freezing tests equivalent salinity values of % 2,5-2,7 NaCl are determined. The considerably low homogenization temperature values of barites indicate that they are formed in a rather late epoch. It is known that the barites characterize the medium and the low temperature minerals in the hydrothermal siderite veins (Mondadori, 1990).

THE ORE AND GANGUE MINERALOGY AND PARAGENESIS

Within the study area siderite, hematite and pyrite are observed as the most frequent ore minerals while barites are scarcely observed. Gangue minerals are seen generally as quartz and calcite. Among these minerals siderites, quartzites and barites are used in the fluid inclusion measurements. While the measurements made from the first group of quartzite inclusions of types I and II (c) indicate a two phased temperature interval, the fluid inclusions of second group of quartzites (type I) give a single phase interval. In the second group of siderites a temperature phase similar to the first group quartzites had developed (Refer to fig. 3). Based on the fluid inclusion results three distirict formation processes were determined in the region. These are, (1) early phase formations (first group of quartzites of having type I. and II. fluid inclusions, second groupe of quartzites having I'st type of fluid inclusions and second group of siderites having I'st. type of fluid inclusions), (2) late phase formations (first group of quartzites having I'st and IInd. type of fluid inclusions, and second group of siderites having Ist type of fluid inclusions) and (3) final late stage formations (barites of type I fluid inclusions) (fig.4).

Homogenization temperatures are determined as 300-350°C in the early stage and 180-270°C and 170-250°C in the late and final late stages respectively. The equivalent salinity of the first group of guartzites formed in the early stage is % 43 NaCl while the salinity for late stage is % 35 on the average It is determined that the barites formed in the final late stage, having fluid inclusions of type I have equivalent salinity of % 3 NaCl. The fact that the initially high and later low salinity values can be explained by the possibility that meteoric water mixing into the solutions (fig. 4). In the vein type of deposits after the formation of the first quartzite occures which plaster the crack, a temperature increase in the vein is observed (Akıncı 1976). Most probably, this temperature rise creates a model which is in agreement with the hydrothermal thesis and it probably caused the decreases in the degree of salinity and temperature values in the time in which by the inclusion of meteoric waters (fig. 4).



Fig. 4- The main temperature stages of ore and gangue minerals in Attepe iron deposit.

RESULTS AND DISCUSSION

Attepe iron deposit and the neigh bouring iron mineralization that have been formed in three different genetic types have been reported by the previous studies (Küpeli, 1986; 1991; Dağlıoğlu and et al, 1998). These are sedimentary pyrite and hematite occurances (type, I), hydrothermal siderite and hematite occurances (type, II) and karstic iron ores (type III). The argument that the ores of type II were formed as a result of hydrothermal proceses within the Lower-Middle Cambrian aged metacarbonates are accepted by all investigators except Ünlü and Stendal (1986). In this study in order to support these views, studies of fluid inclusions were performed. By means of the study of geothermometric measurements in the fluid inclusions present in the samples (a, b, c, d, e) taken from the mineralization zone, four different type of fluid inclusions are determined. The dimensions of these fluid inclusions are generally in the range of 2 to 18 microns. As a result, different types of fluid inclusions that have regular and irregular shaped morphologic structure were observed. Since siderites in the first group (a) have small crystals (0.1-0.3 mm) and there were insufficient data due to less fluid inclusions in the geothermometric measuring studies, siderites in these groups were assumed to be negligible (since not considered), only second group of siderites have been evaluated.

Therefore, considering the geothermometric measurement on siderite, quartz and barite content at Attepe iron mineralization, the quartzes with I. and II. type fluid inclusions and the siderites with I. type fluid inclusions represent same type homogenization heat intervals (Table 1).

Based on the geothermometric measurement results three different formation processes were determined for the region. These are: (1) early phase formations (first group of quartzites of having type I. and II. fluid inclusions, second group of quartzites having Ist type of fluid inclusion and second group of siderites having I'st. type of fluid inclusions), (2) late phase formations (first group of quartzites having I'st and II'nd. type of fluid inclusions, and second group of siderites having Ist type of fluid inclusions) and (3) final late stage formations (barites of type I fluid inclusions) (fig. 4).

Homogenization temperatures are determined as 300-350°C for the early stage and 180-270°C and 170-250°C in the late and final late stages respectively. The equivalent salinity of the first groupe of quartzites having type II fluid inclusions, formed in the early stage is %43 NaCl, while the salinity for late stage is on the average %35. It is determined that the barites having type I fluid inclusions formed in the final late stage have equivalent salinity of %3 NaCl. Simultaneous observation of type III and IV fluid inclusions indicates boiling event. For this reason no pressure correction were applied to the homogenization temperatures measured from the geothermometric measurements.

The mineralization in the region took place at homogenization temperatures of 300-350°C (early stage) and 180-270°C (late stage) in acidic and in reductive conditions, in the

solution system of NaCl + KCl + H₂O with high"salinity. The conditions of this formation process matches the mesothermal and hypothermal stages of hydrothermal stage (Lindgren 1933). It is known that waters of magmatic origin as well as the waters of meteoric origin were influential in the conditions of the formation process (Roedder, 1984). With the further decrease of the temperature (170-250°C) and the salinity (approximately %3 NaCl equivalent salinity) of the environment in the final late stage formation of barites are added to the NaCl + H₂O solution system. These formation conditions represent the final periods of epithermal stages of the hydrothermal stages and the mesothermal stages (Lindgren 1933). The decrease of the high temperature and salinity values of the early stage indicate the probable mixing of meteoric waters into the environment in the final late stage.

Finally "hydrothermal thesis" for genetic types of II and III are supported.

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