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MICROTHERMOMETRIC CHARACTERISTICS OF THE OXIDIZED TYPE W-SKARN, IN SUSURLUK, BALIKESIR, TURKEY

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ABSTRACT.- The Susurluk skarn deposit developed at the contacts of the Çataldağ Granitoid and Mesozoic carbonate rocks is represented by endo and exoskarn (proximal zone, distal zone and vein skarn) zones. The endoskarn zone which occurs in a limited area is characterized by clinopyroxene, plagioclase, sphene, orthoclase and quartz minerals. The exoskarn zone is composed mainly of clinopyroxene, vesuvianite, wollastonite and some accessory minerals such as calcite, quartz, plagioclase, orthoclase, scapolite, biotite, muscovite, sphene and chlorite and ore minerals of scheelite, chalcopyrite and bornite. The presence of anhydrous minerals such as garnet and clinopyroxene is indicative of prograde stage, and the absence of hydrous minerals such as epidote, amphibole and biotite indicates that retrograde stage was not developed. Microthermometric data on exoskarn zone reveal that boiling at temperatures of 587°-592°C took place at the first stage of skarnization. Solutions of the first stage in which scheelite mineralization occurred are characterized by homogenization temperatures of 587 to ≥ 600°C and salinity range of 11-16 wt% NaCl equivalent. At the second stage of skarnization, homogenization temperatures and salinities were recorded as 371 to ≥ 600°C and 36 to >70 wt% NaCl equivalent, respectively. High salinity values are attributed to boiling phenomenon. The Te values of fluid inclusions may indicate a solution composition of $CaCl_2+NaCl+KCl+H_2O$ and significant amount of carbonic additions to the system, CO_2 (Te: -66 to -58°C) and CH_4 (Te: -188 to -178°C). The Susurluk skarn deposit which entirely shows shallow skarn system characterized might have been formed at a pressure of around 1 kbar.

Key words: Susurluk skarn deposit, fluid inclusion, W-skarn, boiling, Çataldağ Granitoid.

INTRODUCTION

In many skarn deposits two different types of alteration are developed in association with pluton evolution (intrusion, crystallization and cooling). The first is prograde stage (also known as early stage) which is characterized with anhydrous minerals (e.g. garnet, pyroxene) deposited from high-temperature and high-salinity solutions. The second is retrograde stage which is distinctive with hydrous minerals (e.g. epidote, amphibole, biotite) crystallized from lower-temperature and lower-salinity solutions. The source of solutions operating in these stages is mostly magmatic and meteoric or combination of both (Einaudi et al., 1981; Einaudi and Burt, 1982; Meinert, 1992).

Homogenization temperature (Th), first melting temperature (Te) and last ice melting temperature (Tm-ice) data from fluid inclusion works are quite useful for reliable assessment of skarn formation conditions as well as nature and salinity (wt % NaCl equivalent) of the solutions. Studies particularly on Sn and W skarns indicate that salinity and temperature are systematically decreased in distal parts of the pluton from prograde to retrograde stage (from proximal to distal zones) (Higgins, 1980; Mathieson and Clarck, 1984; Kwak, 1986; Layne and Spooner, 1991; Larsen, 1991; Fu et al., 1993; Singoyi and Zaw, 2001; Timon et al., 2007).

In this study, fluid inclusion measurements were carried out on samples collected from the

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Susurluk (Serçeören village-Susurluk-Balıkesir) skarn deposit (Figure 1) and skarn development was discussed by basing on the available fluid inclusion data pointing to the nature of the skarn-forming solutions (temperature, salinity and composition). Previous works in the region are geological studies, (Ergül et al., 1980; Ergül et al., 1986; Akyüz 1995) industrial raw material (wollastonite) surveys (Erdinç 1978; Çakır and Genç 1983) and petrographic investigation of the skarn zone (Erdağ, 1976; Arık, 1995; Orhan and Mutlu 2009). Skarn mineralization in the area was first studied by Erdağ (1976) who proposed that diopside, garnet, vesuvianite and wollastonite at the contact between granitoid and marbles form a typical contact metasomatic occurrence. The same worker stated a mineral assemblage consisting of forsterite, quartz, tremolite, scapolite, biotite, calcite and plagioclase and trace amount of ore minerals such as molibdenite, scheelite, bornite and specularite also occur in the skarn zone. According to Arık (1995) epidote also develops in the skarn zone, and host rock is in dolomitic composition. Although mineralogical and petrographic characterizeds of the skarn zone at Susurluk have been determined previously, nature of skarn-forming solutions and skarn formation processes have not been investigated. Orhan and Mutlu (2009) described skarn zones on the basis of mineral abundances and their textural properties and proposed that exoskarn zone has a calcic character and only the products of prograde stage (e.g. garnet, pyroxene) were formed related with the intrusion and crystallization of the Çataldağ Granitoid. Orhan and Mutlu (2009) also state that intrusion and continuous crystallization of Çataldağ Granitoid into shallow depths prevented development of retrograde stage products (e.g. epidote, amphibole, biotite). The same authors investigated chemical composition of garnets and pyroxenes from various mineral zones and concluded that mineralization at Susurluk is of oxidized W skarn character and ore minerals (W and Cu) were formed at different stages of magma crystallization.

In this study, based on previously described mineral zones (Orhan and Mutlu 2009), fluid inclusion studies were conducted on pyroxene, wollastonite, vesuvianite and quartz from a number of skarn zones in Susurluk deposit. Homogenization temperature (Th), inclusion salinity (wt% NaCl equivalent) and possible solution compositions are compared with those from similar W-skarn deposits and skarn formation conditions and processes are discussed.

GEOLOGY OF THE STUDY AREA

Palaeozoic Fazlıkonağı Formation, Mesozoic limestone and marbles, and the Oligocene-Miocene Çataldağ Granitoid are the main rock units in the study area (Figure 1). The Fazlıkonağı Formation forms the basement and is composed of schists and intercalated marble bands and lenses (Ergül et al., 1980, 1986; Akyüz, 1995). Petrography reveals that schists are made up of amphiboleschist, micaschist, quartz-micaschist and talcschist. According to Akyüz (1995), metamorphism occurred at pressures of 4-6 kilobars and temperatures around 550-650°C.

Mesozoic carbonates which are represented by crystallized limestone and marbles are characterized with white-beige colored, coarsely crystalline and laminated structure. The Susurluk skarn deposit was formed at north of the Serçeören village along the contact zone between the Çataldağ Granitoid and the above mentioned carbonate units (Figure 1). The Çataldağ Granitoid is one of post-tectonic intrusions in northwest Anatolia which were formed as a result of Alpine orogeny (Erdağ, 1976; Ergül et al., 1980, 1986; Akyüz, 1995; Ercan et al., 1990). It shows peraluminous / metaluminous composition and calc-alkaline affinity and hololeucocrate and leucocrate character. The granitoid which covers an area of about 450 km^2 at east of Susurluk is composed of a series of dike and sills. The mineral assemblage of muscovite + margarite + biotite (siderofillite) + andalusite at

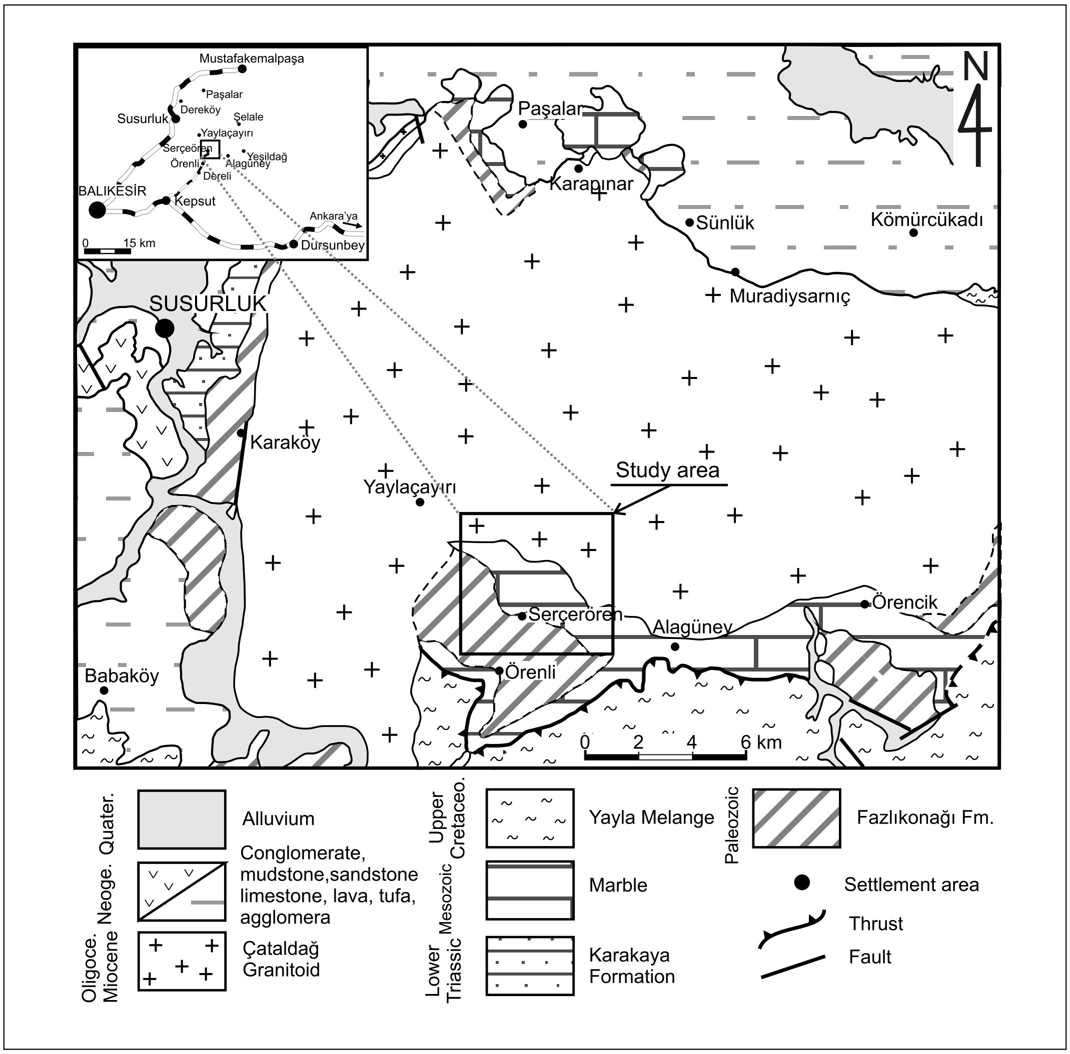

Figure 1- Location and general geology maps of study area (after Ergül et al., 1986).

the contact between the Çataldağ Granitoid and schists might indicate that the granitoid was formed at pressures less than 3.5 kilobars and temperatures around 550-650°C (Akyüz, 1995). The cooling age of intrusion is found as 21.2-25.9 Ma by K-Ar method (Boztuğ et al., 2009) and 20.9 Ma by Rb-Sr isochron method (Mutlu and Orhan, 2009).

The granitoid has a holocrystalline texture at the core changing to porphyric texture to the margins. It shows significant schistosity towards the contacts. Toward the skarn zone cataclasis is evident and feldspars and biotites are coarsened. The changes in textural properties are also accompanied by mineralogical variations. The core of pluton is composed of quartz, plagioclase, K-feldspar, hornblende and biotite ± pyroxene ± apatite ± sphene ± tourmaline ± opaque minerals. Biotite, that is replaced by hornblende, becomes a major mineral in the margins of the facies in porphyritic texture. Some biotite granite samples from the margins contain secondary muscovite. Mineral abundance and geochemical classifications indicate that the granitoid is represented by granitic and granodioritic compositions (Erdağ, 1976; Ergül et al., 1986; Akyüz, 1995; Orhan, 2008; Boztuğ et al., 2009) which may locally change to syenogranite (Arık, 1995; Ergül et al., 1980; Ercan et al., 1990). Towards the skarn contact, it displays notable changes in mineralogy. The quartz abundance is significantly decreased while K-feldspar content varies over a wider range and some secondary minerals such as epidote, pyroxene and calcite and chloritization and sericitization become prominent. In skarn zone and some of veins cutting the granitoid apatites are coarsened and calcite precipitations are developed.

MATERIAL AND METHOD

For fluid inclusion measurements polished thin sections of 80-150 μm were prepared from samples collected from different zones of the Susurluk skarn deposit. Fluid inclusions measurements were carried out with Linkham THMG-600 heating-freezing apparatus (at temperatures between -196 and +600°C). Liquid nitrogen and a thermal resistor were used for cooling and heating, respectively. First melting (Te-eutectic temperature) and final melting of ice (Tm-ice) temperatures of inclusions were measured during cooling while homogenization temperatures (Th) were measured during the heating stage. Calibration of the heating-freezing apparatus was done by measuring melting points of pure CO_2 inclusions hosted by quartz. Measurements yielded a precision of ±0.2°C for melting temperatures and ±0.4°C for homogenization temperatures.

SKARN ZONE CHARATERISTICS

Both endo and exoskarn zones occur in the Susurluk skarn deposit. The endoskarn zone with massive and undulated structure is observed at the contact and within the granitoid. In this zone which is represented by clinopyroxene (hedenbergite), plagioclase (labradorite-bytownite), sphene, orthoclase and quartz minerals magmatic texture is well preserved. The exoskarn zone occurs as monomineralic zones or veinlets and lenses and veins within the marbles or irregular bands parallel to the marble layers. The exoskarn zone is composed chiefly of garnet, clinopyroxene, vesuvianite and wollastonite which are accompanied by quartz, plagioclase, orthoclase, scapolite, sphene, biotite, muscovite and chlorite. Scheelite, chalcopyrite and bornite are main the ore minerals in this zone. In proximal zone, zoned garnets are replaced by pyroxene, inclusions of vesuvianite are common within garnets, pores and fractures of garnet are mostly filled by quartz and chloritization and carbonatization are the most common types of alteration. Wollastonite and vesuvianite are observed in distal zones and veins in marbles. Wollastonite usually has a coarse flaky form while vesuvianite with zoned structure appears to replace pyroxene. Towards the contact where marbles are banded pyroxene, vesuvianite, wollastonite, biotite and muscovite are found (Orhan and Mutlu, 2009). Macro and micro textural and mineralogical studies reveal that the Susurluk skarn deposit closely resemble worldwide known W-skarn occurrences (Einaudi et al., 1981; Einaudi and Burt, 1982; Meinert, 1992). The anhydrous minerals (e.g. garnet and pyroxene) in the deposit were formed during the prograde stage which is associated with intrusion and crystallization of the Çataldağ Granitoid while the absence of hydrous minerals (e.g. epidote, amphibole, and biotite) implies that retrograde stage was not occurred during the cooling (Orhan and Mutlu; 2009). When compared to other well known W-skarns (e.g. Kara skarn, Northwestern Tasmania; Singoyi and Zaw; 2001), the exoskarn of the Susurluk skarn deposit is represented by two stages (Figure 2) which are given below:

First stage: Garnet (grossular) + clinopyroxene (hedenbergite) ± vesuvianite ± wollastonite ± quartz ± scapolite ± calcite ± sphene ± scheelite

Second stage: Garnet (grossular-andradite) + clinopyroxene (diopside)+vesuvianite + wollastonite + calcite + chalcopyrite + bornite ± quartz ± plagioclase ± orthoclase ± scapolite ± sphene ± chlorite ± biotite ± muscovite

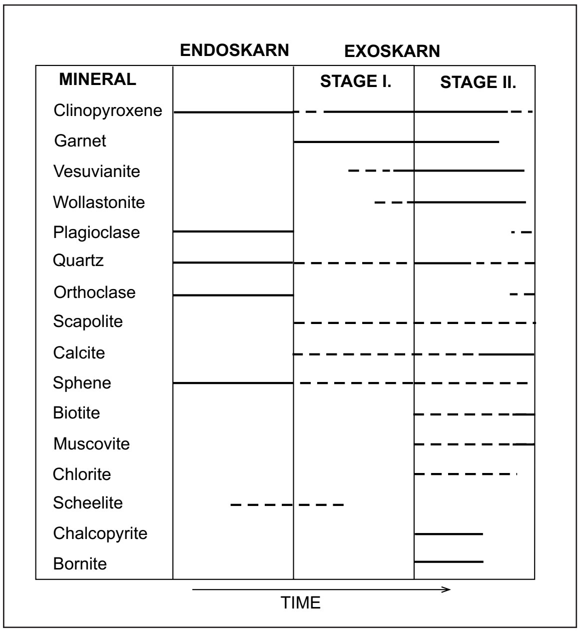

Figure 2- Schematic diagram showing paragenetic relationships of skarn and ore assemblages at Susurluk skarn deposit (after Orhan and Mutlu, 2009).

MICROTHERMOMETRIC MEASUREMENTS

Microthermometric measurements on the Susurluk skarn deposit were conducted on proximal and distal zones of exoskarn and clinopyroxene, quartz, vesuvianite and wollastonite minerals in the vein skarn (Figure 3). Prior to analysis, fluid inclusion types were classified as primary or secondary inclusions according to criteria proposed by Roedder (1984) and Van den Kerkhof and Hein (2001). All the measurements were performed on primary fluid inclusions.

Inclusions are generally irregular-shaped in quartz and vesuvianite, irregular and rectangular or square shaped in clinopyroxene and irregular or tube shaped in wollastonite (Figure 4). The length of inclusions is in the range of 10 to 216 µm. When viewed at room temperature primary inclusions were determined to contain liquid+gas (Type-I) and liquid+gas+soild (Type-II) phases (Figure 4). In Type-II inclusions solid phase is comprised by halite and/or sylvite minerals. In proximal zone of exoskarn clinopyroxene and vesuvianite contain both Type-I and Type-II inclusions while quartz and wollastonite contain only Type-II inclusions. Measurements in distal zone and vein skarn were conducted on clinopyroxene and wollastonite which produced Type-II inclusions.

Homogenization Temperatures and Salinity Values

Homogenization temperatures of Type-I inclusions in clinopyroxene and vesuvianite from the proximal zone were measured as 587°C to ≥ 600°C (n=4) and 438°C to ≥ 600°C (n=2), respectively. Type-I inclusions were generally homogenized into liquid phase and inclusions in one clinopyroxene sample were homogenized to both liquid (592.2°C) and gas (587°C) phases (Table 1).

Homogenization temperatures of Type-II inclusions in skarn minerals of the proximal zone range from 572 to ≥ 600°C (n=15) for clinopyroxene, 369 to 494°C (n=5) for wollastonite, 455 to ≥ 600°C (n=4) for quartz and 403°C (n=1) for vesuvianite (Figure 5). In Type-II inclusions, except for one sample (gas phase sample in wollastonite), homogenization to the liquid phase was observed.

Type-II inclusions in clinopyroxenes and wollastonites of the vein skarn have homogenization temperatures greater than 600°C (Th ≥ 600°C; n=15). Type-II inclusions in clinopyroxenes from distal zone of exoskarn were homogenized to liquid phase at temperatures between 371 and 549°C (n=4) (Figure 5).

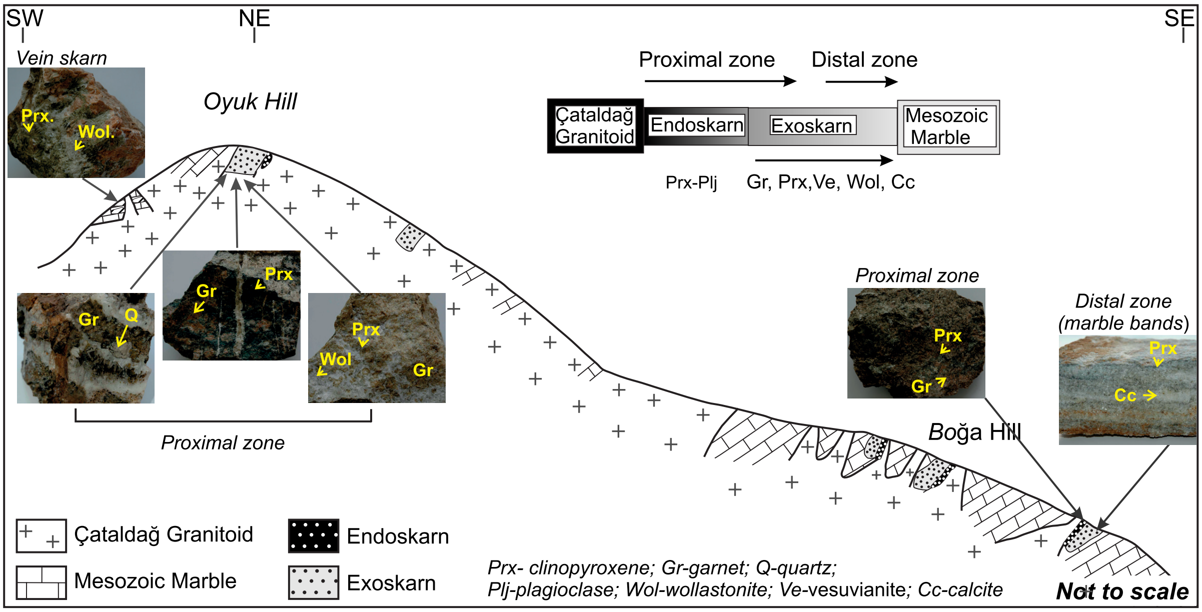

Figure 3- Cross-section showing different skarn zones and locations of samples collected for microthermometric measurements.

Salinity values of liquid+gas inclusions (Type-I) were calculated from the last ice melting temperature (Tm-ice) while those of liquid+gas+soild inclusions (Type-II) were computed from melting temperatures of halite and sylvite crystals (Shepherd et al., 1985; Bakker 2003). Results indicate that in proximal zone clinopyroxenes with Type-I inclusions (n=4) have an average salinity of 14.5 wt% NaCl equivalent and the salinity of vesuvianites (n=2) is 11.1 wt % NaCl equivalent (Table 1; Figure 6).

Since some of solid phases did not melt to a temperature of 600°C, all the salinities of Type-II inclusions in proximal zone could not be calculated. From the melting of the halite salinity of one sample in vesuvianite was found as 36 wt% NaCl equivalent, from the melting of halite and sylvite salinities of two samples in wollastonite were computed as 61-61.5 wt% NaCl equivalent and from the melting of sylvite salinities of two samples in quartz were found as 67 and >70 wt% NaCl equiv. Salinities of inclusions in which halite and sylvite did not melt at 600°C were found to be at least 70 wt% NaCl equivalent (Shepherd et al., 1985) (Table 1).

Salinities of clinopyroxenes (n=4) in distal zone are between 51.5 and >70%, salinities of clinopyroxenes in vein skarn are in the range of 58 (n=1) to >70% (n=6) and those of wollastonites (n=3) are from 57 to 66 wt% NaCl equivalent (Table 1).

First Melting (Te), Last Ice Melting (Tm-ice) and Clathrate Melting (Tm-clth) Temperatures

It is a challenging work to determine low-temperature (<0°C) phase transitions (Te and Tm-ice) within the inclusions. Therefore, a total of 33 Te (samples from proximal and distal zones and vein skarn) and 7 Tm-ice (samples from proximal zone) values could be determined in fluid inclusions from the Susurluk skarn deposit (Table 1).

Te values Type-I inclusions in clinopyroxene and vesuvianite from the proximal zone are represented by a narrow temperature range of -68 to

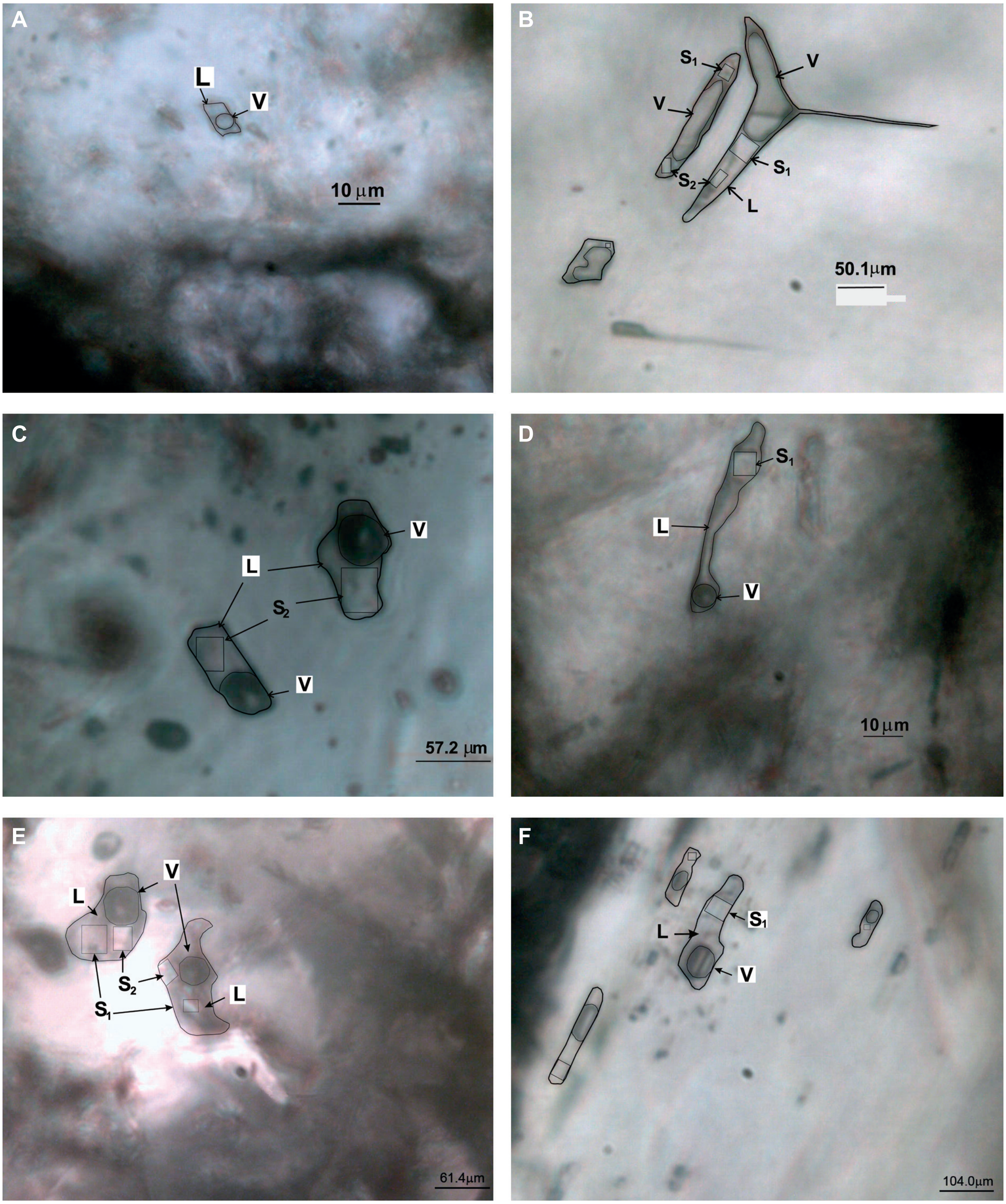

Figure 4- Fluid inclusion photomicrographs of skarn minerals from the Susurluk skarn deposit. (A) Type-I inclusion in clinopyroxene; (B) Type-II inclusion in clinopyroxene from distal zone; from proximal zone (C) Type-II inclusion in quartz; (D) Type-II inclusion in vesuvianite; (E) Type-II inclusion in wollastonite; (F) Type-II inclusion in wollastonite from vein skarn (S1: Halite, S2: Sylvine).

Table 1- The microthermometric data of Susurluk skarn deposit.

Skarn Zone	*Host mineral*	*Inclusion Type*	*Te (°C)*	*Tm-ice (°C)*	*Tm-clth (°C)*	*Tm-solid (°C)*	*Th (°C)*	*Th-phase*	*Salinity (equivalent wt %NaCl)*
PROXIMAL ZONE	**Quartz**	II	n.d.	n.d.	-	432.6 (S)	454.6	**V→L**	67
		II	n.d.	n.d.	-	463 (S)	≥600	-	>70
		II	n.d.	n.d.	-	489.5 (S)	489.5	**S→L**	>70
		II	n.d.	n.d.	-	545 (S)	545	**S→L**	>70
	Clinopyroxene	I	-58.2	-10.7	-	-	587	**V**	13.98
		I	-60.2	-10.7	-	-	≥600	-	13.98
		I	-58.8	-12.9	-	-	592.2	**L**	16
		I	n.d.	-10.9	-	-	≥600	-	14
		II	-180.4	n.d.	-	536.6 (H) 483.9 (S)	≥600	-	>70
		II	-69.5		9.0	522.2 (S)	≥600	-	>70
		II	-67.2		9.0	520.9 (S)	≥600	**-**	>70
		II	-65.4		10.7	n.d.	≥600	**-**	-
		II	-69.4		6.1	517.7 (S)	≥600	**-**	>70
		II	-69.9		10.0	504.5 (H) 488.2 (S)	≥600	-	>70
		II	-69.2		8.3	488.8 (S)	572.2	**V→L**	>70
		II	-48.8	-14.4	-	> 600 (H)	≥600	-	>70
		II	-188.1		19.8	n.o (H, S)	≥600	-	-
		II	-176.5	n.d		n.o (H)	≥600	-	-
		II	-176.4	n.d		n.o (H)	≥600	-	-
	Wollastonite	II	-67.4		10.8	373.5 (H) 368.5 (S)	439	**V→L**	61
		II	-69		11	365.8 (H) 365.7 (S)	369.1	**V→L**	61.5
		II	-81.4		10.5	n.d (H, S)	439.6	**L(?)**	n.d
		II	-62		11.2	424.1 (H) 477.3 (S)	494	**V→L**	>70
		II	-61.6		11.6	381.8 (H) 409.1 (S)	434.6	**V→L**	>70
	Vesu-vianite	I	-	-7.7	-	-	≥600	-	10.49
		I	-68.1	-8.2	-	-	437.6	**L**	11.71
		II	-136	-	-	285.4 (H)	403.1	**V→L**	36

Table 1- continued

Skarn Zone	*Host mineral*	*Inclusion Type*	*Te (°C)*	*Tm-ice (°C)*	*Tm-clth (°C)*	*Tm-solid (°C)*	*Th (°C)*	*Th-phase*	*Salinity (equivalent wt %NaCl)*
D I S T A L	**Clinopyroxene**	II	-126.1	n.d.	-	270.8 (S)	370.8	**V→L**	51.5
		II	-118.6	n.d.	-	379.2 (S) 375.9 (H)	532.3	**V→L**	61
		II	n.d.	n.d.	-	548.9 (S)	548.9	**S→L**	>70
		II	n.d.	n.d.	-	275 (S)	502.9	**V→L**	52
V E I N	**Clinopyroxene**	II	-181.7	-	15.8	525.7 (H)	≥ 600	-	58
		II	-182.5	-	16.3	n.o (H).	≥ 600	-	-
		II	-189.2	-	-	n.o (H)	≥ 600	-	-
		II	-130	n.d.	-	n.o. (S)	≥ 600	-	-
		II	-56.1		12.8	567.9 (S)	≥ 600	-	>70
		II	-55.4	.	9.6	n.o. (S)	≥ 600	-	-
		II	-55.5	n.d.	19.4	n.o. (S)	≥ 600	-	-
	Wollas-tonite	II	-188	n.d.	-	509.8 (H)	≥ 600	-	57
		II	-188.9	n.d.	-	591.1 (H)	≥ 600	-	66
		II	-183	n.d.	-	592 (H)	≥ 600	-	66

Definitions: **Te:** Eutectic temperature; **Tm-ice:** Final ice melting temperature; **Tm-clth:** Clathrate melting temperature; **Tm-solid**: Solid phase melting temperature; **Th:** Homogenization temperature; **n.d:** Not-determined, **n.o.:** Not-occured, **S:** Sylvine; **H:**Halite; **V**: Vapour; **L**:Liquid; **V→L:** Homogenisation occured by disappearance of vapour to liquid phase; **S→L:** Homogenisation occured by disappearance of solid to liquid phase.

-58°C (n=4) while Te values Type-II inclusions in wollastonite, vesuvianite and clinopyroxene from the same zone (n=17) vary over a wider range (-188 to -58°C) (Table 1; Figure 7). Te values from the proximal zone are mainly clustered in two distinct fields. 14 inclusions within the first field have temperatures of -66 to -58°C while 4 inclusions within the second field are represented by a temperature range of -188 to -178°C (Figure 7).

Only two Type-II inclusions in clinopyroxenes from the distal zone yielded Te values from -126.1°C to -118.6°C. In contrast, Te values of all samples in vein skarns are significantly out of this range changing -188 to -183°C in wollastonite (n=3) and -189 to -181°C (n=3) and -55 to -56°C (n=3) in clinopyroxene (Figure 7).

Last ice melting temperatures (Tm-ice) were mostly determined in Type-I inclusions from the proximal zone which range from -13 to -10°C (n=4) in clinopyroxene and from -8.2 to -7.7°C in vesuvianite (Figure 7). In the same zone, Tm-ice value of a clinopyroxene sample with Type-II inclusion was measured as -14.4°C.

Final ice melting temperatures of most Type-II inclusions in proximal zone and vein skarn are in the range of +6.1 to +19.8°C (n=17) (Figure 7). In none of the inclusions immiscible liquid phase was determined at room temperature (e.g. CO_2 or CH_4). However, these melting values above 0°C (between +6.1 and +19.8°C) are indicative of Clathrate ($CO_2.5.¾H_2O$) formation at low temperatures which, although not detectable at room temperature, may imply the presence of carbo-

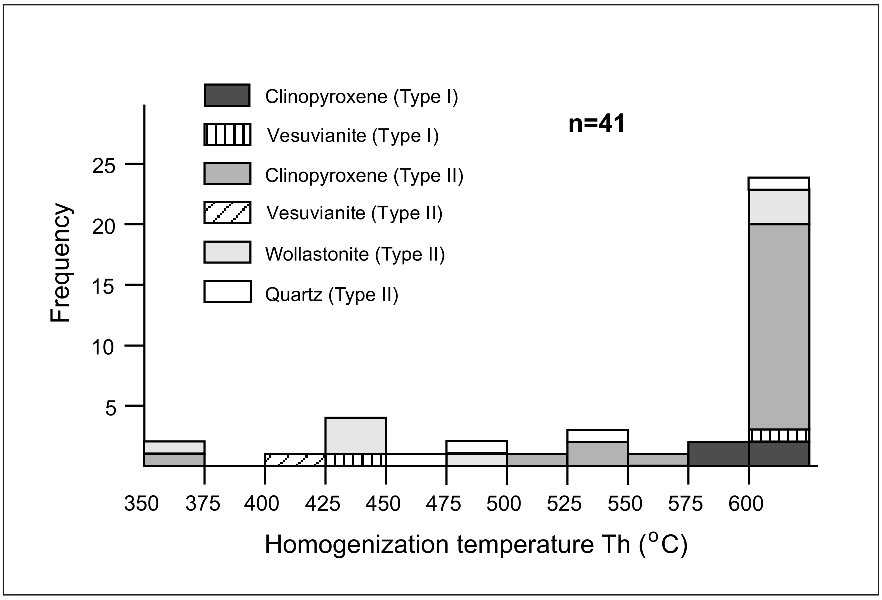

Figure 5- Homogenization temperature vs. frequency histogram of the Type I and Type II inclusions.

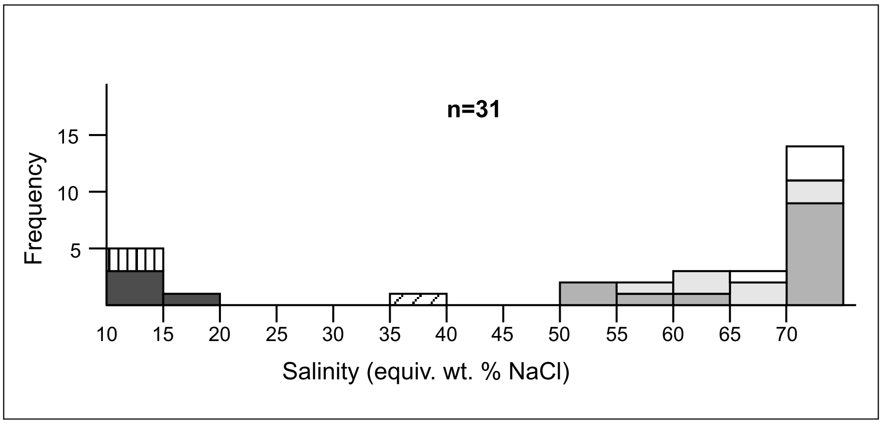

Figure 6- Salinity (equiv. wt. % NaCl) vs. frequency histogram of the fluid inclusions (for symbols see figure 5).

nic compounds (e.g. CO_2 or CH_4) in the solution (Roedder 1984; Shepherd et al., 1985; Van den Kerkhof and Hein 2001).

DISCUSSION AND RESULTS

Skarnization at the contact between Çataldağ Granitoid and Mesozoic carbonate rocks (Figure 1) occurs as proximal zone, distal zone and vein skarn. First ice melting temperatures of Type-I and Type-II inclusions in wollastonite and vesuvianite from these zones are generally clustered in two distinct fields (Figure 7). Te values in the first field (ranging from -66 to -58°C) indicate the presence of CO_2 in the solution system (Tm-CO_2: -56.6°C) and those in the second field (from -188 to -178°C) point to occurrence of CH_4 (Tm-CH_4: -182.5°C) (Roedder, 1984; Sheppard et al.,

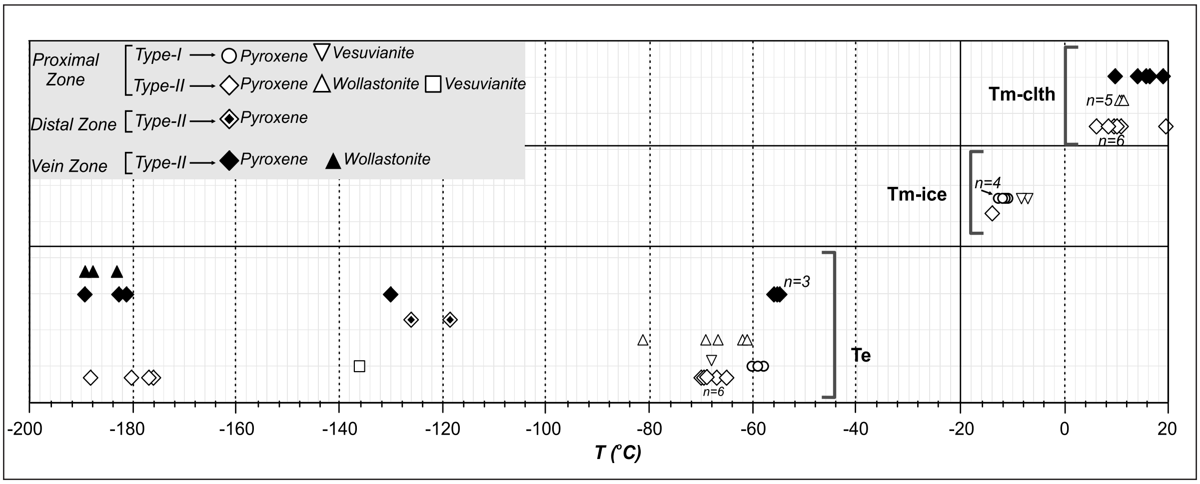

Figure 7- Distributions of the first melting temperatures (Te) of fluid inclusions (for symbols see figure 5).

1985). The fact that last ice melting in these inclusions occurs at temperatures greater than 0°C (between +9 and +19.8°C) (clathrate melting) indicates that significant amount of carbonic phases is also present in the system. Fluid inclusions studies on W-skarns reveal that CO_2 occurrence is associated with W mineralization (Higgins, 1980). It was also stated that that CH_4 is slightly more abundant than CO_2 in reduced systems (Fonteilles et al., 1989). In Susurluk deposit the presence of methane both in proximal zone and distal and vein skarn may be attributed to CH_4 and CH_4+CO_2 development by metamorphism and decomposition of pure marble during the skarnization rather than reduced conditions of the system (Larsen, 1991). A Te value of -48.8°C (Type II) measured on a clinopyroxene from the proximal zone shows that the system contains $CaCl_2$+NaCl+KCl+H_2O (Linke, 1965) which may indicate that carbonate dissolution is operative in skarn formation (Kwak, 1986).

On the salinity value vs. homogenization temperature diagram (Figure 8) solutions are bunched up in distinct fields. Type I inclusions of clinopyroxenes from the proximal zone are represented by a homogenization temperature of ≥ 587°C and an average salinity of 14.5 wt% NaCl equivalent. Type I inclusions in clinopyroxenes are homogenized into both liquid (592.2°C) and gas (587°C) phases at nearly the same temperature (Table 1) indicating boiling occurred in the system. Homogenization temperatures and salinity values of this clinopyroxene and those from the Kara magnetite-scheelite skarn (Northwestern Tasmania; Singoyi and Zaw, 2001) (511 to 616°C Th; 11.9-12.5 wt% NaCl equivalent) are found to be similar. Type I inclusions in clinopyroxenes from the proximal zone plot in the "Primary Magmatic Fluid" and "Metamorphic Fluid" fields (Bodnar, 1999) which represent for the first stage of skarnization. Type I inclusion in vesuvianite from the proximal zone with a homogenization temperature of >437°C and an average salinity of 11.1 wt% NaCl equivalent plots into the "Metamorphic Fluid" field (Figure 8) and these values are nearly similar to those of vesuvianite from stage II of the Kara magnetite-scheelite skarn (Th between 362 and 571°C; salinity between 16.3 and 17.8 wt% NaCl equivalent; Singoyi and Zaw, 2001). Type II inclusions (liquid+gas+(halite± sylvite)) which are commonly observed in proximal and distal zones and vein skarns of the Susurluk deposit have extremely high salinity values (36 to >70 wt%)

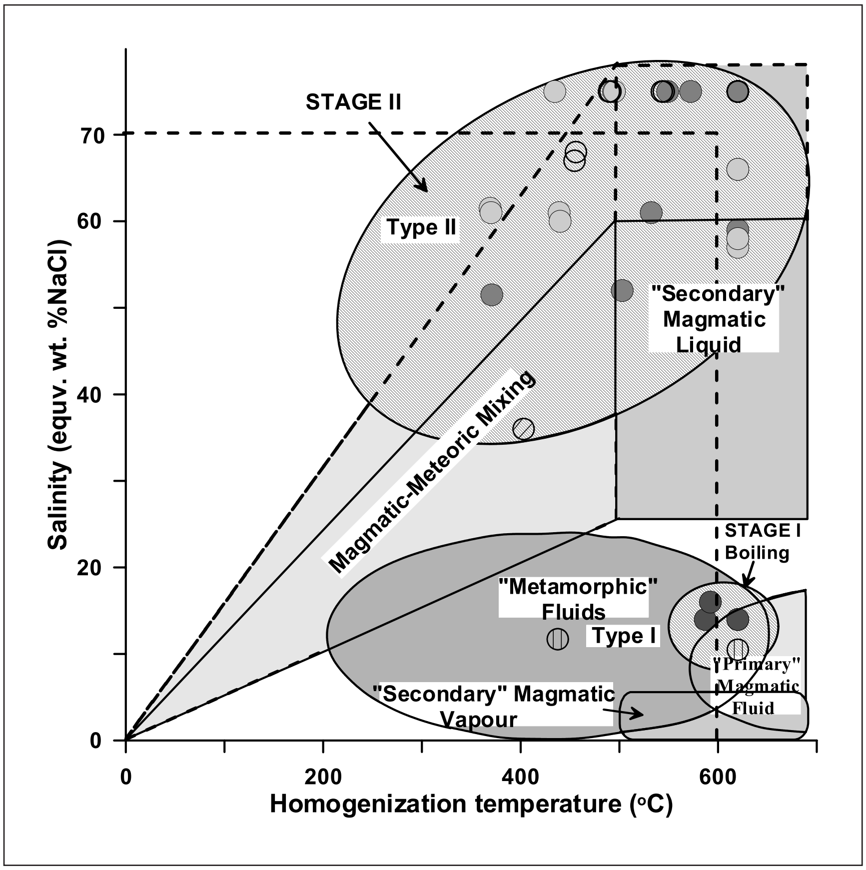

Figure 8- Plot of homogenization temperature vs. salinity values of fluid inclusions from the Susurluk skarn deposit (for symbols see figure 5) (approximate temperature-salinity distributions for hydrothermal solutions of different origins are from Bodnar (1999). Dashed line of "Secondary Magmatic Liquid" and "Magmatic-Meteoric Mixing" belongs to this study).

and plot into the "Secondary Magmatic Fluid" and/or "Magmatic-Meteoric Mixing" fields (Figure 8). In the Susurluk skarn system salinity was found to be increased following the boiling. This behavior of high-salinity magmatic fluid is particularly typical to shallow hydrothermal systems (porphyry copper deposits) (Bodnar, 1999; Wilkinson, 2001) and associated with granitoid crystallization (Kwak, 1986; Bodnar, 1999). Homogenization temperatures and salinity values of Type II inclusions generally decrease from proximal zone to distal zone (Figure 8) which may be indicative of partial mixing of magmatic solutions with cold, dilute meteoric waters (Beane, 1983).

In homogenization temperature vs. salinity value diagram constructed for various types of deposits (Figure 9), Type I and Type II inclusions formed during the first stage of skarnization (587 to ≥ 600 °C and 14-16 wt% NaCl equivalent) are plotted into porphyry and skarn fields above the critical curve. Th-wt% NaCl values of vesuvianite which is associated with anhydrous minerals

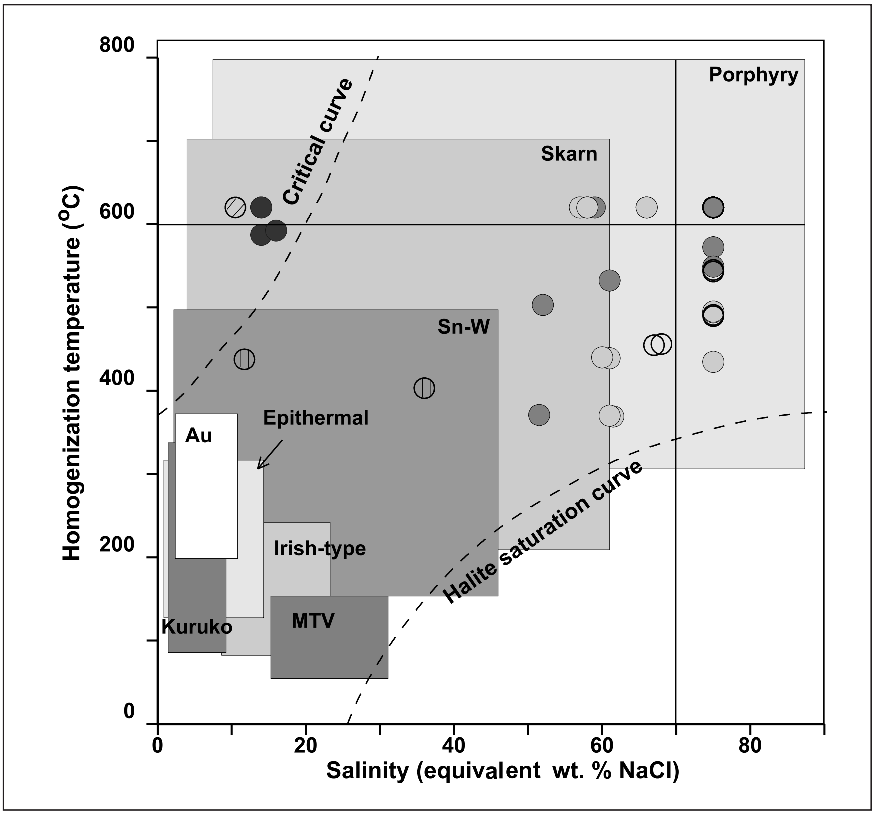

Figure 9- Homogenization temperature vs. salinity (wt. %NaCl) diagram illustrating typical ranges for inclusions from different deposit types (Wilkinson, 2001) (for symbols see figure 5).

indicate Sn-W, skarn and porphyry character (Figure 9). Homogenization temperatures (371 - ≥600ºC) and salinity values (52->70 wt%) of solutions from the second stage of skarnization which developed after the boiling plot predominantly into porphyry and partly into skarn fields. Boiling resulted in a sharp increase in salinity and deposition of some sulfide minerals (e.g. bornite, chalcopyrite) in the skarn zone (Kwak and Tan, 1981).

In W skarns scheelite is less abundant at early stage of skarnization but it increases with increasing of amphibole content (Kwak and Tan, 1981; Singoyi and Zaw, 2001). In the Kara (Northwestern Tasmania) skarn deposit, scheelite was formed during retrograde stage at a temperature range of 360 to 230°C and salinities of 0.2 to 19.8 wt% NaCl equivalent (Singoyi and Zaw, 2001). In the Susurluk skarn deposit, scheelite with trace abundance occurs at early stage of skarn formation at temperature of ≥587°C and salinity of 14-16 wt% while copper minerals (bornite and chalcopyrite) were formed at different periods of prograde stage from solutions with temperatures above 371°C and higher salinities (52 to 70 wt%).

In shallow skarn systems, boiling occurs at early stage of skarnization by hydraulic fracturing and brecciation of rocks by high-temperature solutions due to a major pressure drop from lithostatic to hydrostatic pressure (Kwak, 1986). Early boiling process at Susurluk may indicate that skarnization was formed at shallow depths (less than 4 km) under pressures of about 100 MPa (1 kbar) (Figure 10). Oxidized type W skarns are formed under low pressure conditions while large - reserved W deposits mostly occur under reducing systems (Newberry, 1983). According to Newberry and Einaudi (1981), large- reserved W deposits are formed in systems lacking fracturing and under extremely high temperature and pressure conditions (1.5-3 kbar and 550-650°C). In contrast, Susurluk skarn deposit was developed at high temperature (371- ≥ 600°C) but low pressure conditions (1 kbar).

Although mineralized skarn systems have common characterizeds systems with main skarn minerals (W, Cu, Fe, Pb-Zn, Mo and Sn) may show systematic differences (Einaudi et al., 1981) which include parent rock composition, composition and degree of evolution of fluid, skarn formation depth, metamorphism and metasomatism (Meinert et al., 1980). Einuadi et al. (1981) classify W skarns as "reduced" and "oxidized" types while Kwak and White (1982) categorize them as "W-Sn-F" and "W-Mo-Cu" types. Newberry (1998) divided W-F skarns into Mo-poor and Mo-rich subgroups based on their highly incompatible element contents. Most of mined large-reserved W deposits (e.g. Mactung and Cantung deposits in Canada; Sandong deposit in Korea and Fujigatani deposit in Japan) are of "reduced" type and characterized with garnet composition less than 50% andradite, hedenbergite type pyroxene (Hd_{60-90}) and abundant pyrrhotine and trace pyrite contents (Einaudi et al., 1981). In contrast, "oxidized" type

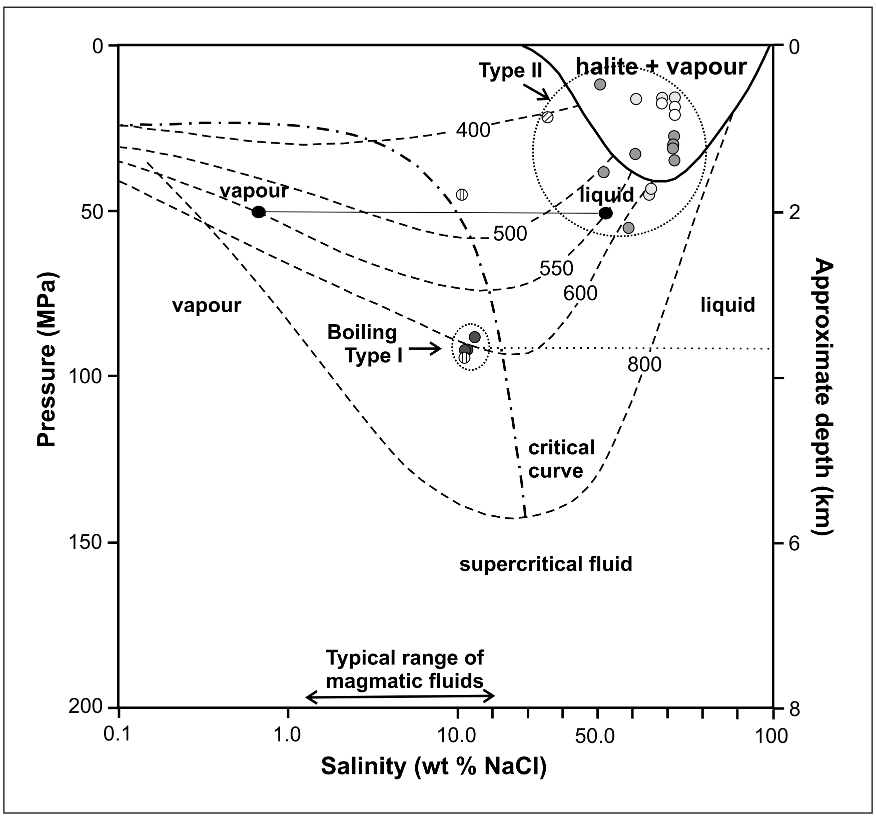

Figure 10- Phase distribution of fluid inclusions under P-T conditions proposed for typical porphyry deposits (Wilkinson, 2001) (for symbols see figure 5).

W skarns mostly contain andraditic garnet (Ad_{80-100}), salic pyroxene (Hd_{20-70}) and abundant pyrite and trace pyrrhotine (Einaudi et al., 1981). Garnets in skarn zones at Susurluk are of dominantly grossular-andradite composition and andradite / grossular ratio of zoned garnets in the exoskarn zone increases from core to rim (Orhan, 2008; Orhan and Mutlu, 2009). High andradite composition of garnets (Eiunadi et al., 1981) and increasing andradite content of zoned garnets from core to rim are suggested to be the indicator of "oxidized" type W skarns (Newberry, 1983). All these findings clearly indicate that scheelite-containing Susurluk skarn is an "oxidized" type W skarn.

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