Geochemistry and Mineralogy of the Skarns in the Çelebi District, Kırıkkale, Turkey

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Abstract: The Çelebi district is well known for its polymetallic Fe-W and Cu vein ores. These ores are hosted by calcic skarn zones, which are broadly classified as "intrusive around skarn" type. Both exoskarns (pyroxene-garnet) and endoskarns (epidote-pyroxene) occur in the district.

The formation of endoskarns is manifested by complete replacement of plagioclase by epidote and pyroxene; the epidotized granitoids are regarded as incipient and/or early metasomatic products. The abundance of pyroxene in endoskarns tends to increase with plagioclase content and within the groundmass of the granitoids towards exoskarn zones. The increase in pyroxene is also coincident with the formation of anhedral, isotropic brown garnets. The garnet-rich pockets also mark irregular zones and veins of magnetite mineralization. The main magnetite mineralization occurs within the pyroxene-garnet exoskarn as 15 to 20-m-thick pockets and veins within pyroxene-rich zones. The pyroxene crystals are optically zoned and the composition ranges from hedenbergitic (core) to diopsidic (rim).

Elemental compositions vary systematically in relation to skarn zones. A decrease in SiO_2 corresponds to an increase in $FeO_{(T)}$ from granite toward skarn zones. The Çelebi district endoskarns are enriched in CaO, MnO, MgO and $FeO_{(T)}$, yet depleted in SiO_2, TiO_2, Al_2O_3 and K_2O compared to the Çelebi Granitoid. CaO and $FeO_{(T)}$ behave comparably in the endoskarns, suggesting that the iron mineralization is coincident with carbonization of prograde assemblages during retrograde alteration.

Key Words: Çelebi (Kırıkkale), Skarn Zones, Magnetite, Geochemistry of Skarns

Çelebi Bölgesi (Kırıkkale, Türkiye) Skarnlarının Jeokimyası ve Mineralojisi

Özet: Çelebi bölgesi polimetalik Fe-W ve Cu damar tipi yataklarıyla bilinir. Bunlar genel olarak "intrüzif çevresinde gelişen skarnlar" olarak sınıflanan kalsiyumlu skarn zonları içinde bulunurlar. Bölgede hem ekzoskarnlar (piroksen-granat) hem de endoskarnlar (epidot-piroksen) bulunur. Bu çalışma bölgedeki skarnlaşma süreçleri boyunca etkili olan elementlerin kimyasal potansiyellerini sunmanın yanında, skarnların jeokimyalarını, mineralojilerini ve bölgedeki cevherleşmelerin kimyasal kontrollerini araştırmayı amaçlayan bir çalışmadır.

Endoskarnlar, granitik kayaçların çeperlerinde özellikle mermer dokanaklarına yakın kesimlerde, granitoyidlerin renginin yeşilimsi gri tonlarına çalmasıyla karakteristiktir ve plajiyoklazların tamamen epidot ve piroksen tarafından ornatılmasıyla belirgin hale gelirler. Dolayısıyla epidotlaşan granitoyidler erken ya da yeni başlayan metasomatik ürünler olarak değerlendirilmektedir. Endoskarnlar sadece granitlerde gözlenen skarn oluşukları değildir, mermerler arasında bantlar halinde gözlenen gnayslarda ve özellikle şiştozite düzlemlerine paralel ince zonlar halinde skarn zonları da gelişmiştir. Epidotlaşma özellikle zonlu plajiyoklazlarda, zonlanmanın merkezinden itibaren başlar. Önceleri sadece plajiyoklazlar üzerinde gelişme gösterirken mermer dokanağına doğru piroksenlerle birlikte kayacın başka kısımlarında da bulunur. Piroksenlerin miktarı hem ornattıkları plajiyoklazlar üstünde hem de granitik kayacın tamamında (hamur içinde) kireçtaşı dokanaklarına doğru artar. Piroksenlerin artmasıyla birlikte iri magmatik kuvarslar daha ince taneli ve hidrotermal kuvarslar tarafından çepeçevre sarılırken, tek tük kahverengi izotrop ve özşekilsiz granat kristalleri de gözlenir. Granat miktarlarının arttığı kesimler aynı zamanda 2-3 cm kalınlığında çok küçük manyetit ve hematit ceplerinin de ilk kez ortaya çıktığı kesimlere karşılık gelmektedir.

Ekzoskarnlar endoskarnlara göre hem boyut hem de dağılım itibarıyla daha sınırlıdır. Genellikle çok yaygın endoskarn zonları ile göreceli olarak daha küçük mermer mostraları arasına sıkışmış durumdadır. Hakim mineralojisini piroksen ve granat oluşturur. Ekzoskarnlar içindeki epidot, kalsit, tremolit ve kuvars gibi mineraller, piroksen ve granat üzerinde daha ilerlemiş evrelerde etkili olan retrograd olaylarla oluşmuş mineral topluluklarıdır. Çok genel olarak ekzoskarnlar mermerden uzakta piroksen-epidot skarnları, mermere yakın kesimlerde ise piroksen-granat şeklinde belirsiz bir zonlanma içindedir. Ana manyetit cevherleşmesi piroksen-granat zonları içinde 15-20 cm boyutlarında cep ve damarlar halinde bulunur.

Skarn zonlarındaki element bileşimleri her zona göre sistematik değişimler sunar. Çok genel olarak endoskarn zonlarında SiO_2 bakımından bir fakirleşme $FeO_{(T)}$ bakımından bir zenginleşmeye karşılık gelir. Çelebi bölgesindeki endoskarnların oluştukları orijinal kayacın (Çelebi Granitoyidi) bileşimine göre CaO, MnO, MgO, $FeO_{(T)}$ bakımından zenginleştiği, SiO_2, TiO_2, Al_2O_3 ve K_2O bakımından fakirleştiği belirlenmiştir. Ekzoskarnlar ise, kristalize kireçtaşına

göre FeO$_{(T)}$ ve SiO$_2$ bakımından zenginleşirken hem CaO hem de CO$_2$ bakımından hızla fakirleşmektedir. Öte yandan K$_2$O ve Na$_2$O bileşimlerinde bir değişim gözlenmemektedir.

Endoskarnlar içinde CaO ve FeO$_{(T)}$'in ilginç ve zıt davranışlar sunması cevherleşmenin prograd evre skarn topluluklarının retrograd evrede karbonatlaşmasıyla ilgili olduğuna işaret etmektedir.

Anahtar Sözcükler: Çelebi (Kırıkkale), Skarn Zonları, Manyetit, Skarnların Jeokimyası

Introduction

The Çelebi district is one of the main Fe-producing districts in Turkey. The Çelebi district is situated about 3 km northwest of Çelebi (Kırıkkale), and is accessible from the Bala-Kaman highway. Production has come from a series of small isolated skarns, with grades of 50 to 62 % Fe, and variable WO$_3$ (0.93 % to 12 % WO$_3$) (Bayhan 1984), developed along offshoots of the Çelebi Granitoid into marble. Mining occurred from ancient times until the late 1960s. Presently, the skarns in this district are of interest to the Mineral Research and Exploration Directorate of Turkey with the main focus being the geology and ore–reserve estimation of iron and tungsten mineralizations within individual skarn bodies. However, the geochemical controls on mineralization, and skarn-forming processes have not been investigated.

Therefore, this study aims to present the relative setting of the skarn zones with respect to the granitoid, to describe the geochemistry of the skarns and the relative distribution and abundance of elements in relation to iron mineralization. This paper aims to (1) present the relative setting of the skarn zones with respect to the granitoid; (2) describe geochemistry, mineralogy and geochemical controls of mineralization; and (3) shed light on the importance of chemical potential of elements – relative distribution and abundance of elements in relation to iron mineralization – during skarnification in the district.

Geologic Setting

The Çelebi district is located in the northwestern part of the Central Anatolian Crystalline Complex (CACC; Göncüoğlu et al. 1991) in the Fe-W metallogenic skarn zones defined by Kuşcu & Erler (1998). The CACC is an assemblage of metamorphic, ophiolitic, intrusive and extrusive rocks (Figure 1); those rocks exhibiting a metamorphosed platform-type succession have been termed the Central Anatolian Metamorphics (CAM) (Göncüoğlu et al. 1993). Many workers consider CAM to

be basement. CAM comprise three main rocks units consisting of gneisses at the bottom, amphibolite and marble intercalations in the middle and dolomitic marbles with amphibolite lenses at the top of the sequence. Studies concerning the age of the main metamorphic events (Ataman 1972; Erkan & Ataman 1981; Göncüoğlu 1986) suggest a Late Cretaceous (late Campanian-early Maastrichtian) (71-74 Ma). The main metamorphic evolution in the CAM is progressive from medium pressure-medium/high temperature to medium/low pressure-high temperature (Göncüoğlu et al. 1991). Ophiolitic rocks resting on the CAM as nappes are referred to as the Central Anatolian Ophiolites (CAO), and comprise various ultramafic rocks, non-layered gabbro, plagiogranite, diabase, pillow lava, and epi-ophiolitic sediments. The CAO are locally exposed as undeformed/undisturbed slabs, or locally as tectonic units resting on the CAM. The majority of the ophiolites are early Turonian in age (excluding metamorphosed equivalents) and are of supra-subduction type, derived from a supra-subduction zone which developed within the İzmir-Ankara-Erzincan Ocean, during the closure of the northern branch of Neotethyan Ocean (Yalınız et al. 1996). Intrusive rocks in the CACC have been collectively named the Central Anatolian Granitoids (CAG) (Göncüoğlu et al. 1993). These rocks include granite, granodiorite, monzonite, monzodiorite, quartz monzonite and diorite (Göncüoğlu et al. 1991). The Central Anatolian Granitoids (CAG) intrude the metamorphic sequence and gave rise to extensive metasomatic processes between the host marbles and granitoids; the skarns are predominantly restricted to these contact zones. The Central Anatolian Granitoids range from 95 Ma to 75 Ma in age and are members of two broad classes; S- and I-type granitoids, or combinations of the two (hybrid) (see Boztuğ 2000 and references therein). The CAG were generated during and after the southward obduction of the ophiolitic rocks onto the Tauride-Anatolide Platform (TAP) during the Late Cretaceous (Göncüoğlu et al. 1993). The geological evidence indicates that two phases of magmatism

resulted from two successive obductions. The earlier phase resulted in generation of S-type granitoids 95 Ma in age (Göncüoğlu 1986) and was due to the obduction of N-type oceanic crust. The later phase was due to obduction of a supra-subduction zone ophiolitic sequence onto the metamorphic rocks and the previously obducted N-type oceanic crust (i.e., collision of ensimatic arc with the TAP and CACC) (Göncüoğlu et al. 1993).

The Çelebi Granitoid, which caused extensive skarn formation in the district occur as a N-S trending lensoidal body (Figure 1). The Çelebi Granitoid comprises the western-margin the CAG (Figure 1). The granitoid is cut by numerous aplite dikes and contains rounded enclaves of diorite and quartz-diorite in different sizes. The Çelebi Granitoid is not a single, uniform plutonic body, but consists of two different end-members (types): a granitic (more felsic and evolved type), and a dioritic to granodioritic (more mafic or primitive type). These two end-members are poorly mapped since their contacts are obscured by vegetation and soil cover, and are poorly exposed. The primitive component occurs as large (locally > 100 meters in length) and small enclaves (about 10 to 30 cm in diameter) in the felsic rocks, and both are cut by later aplite dikes. The Çelebi Granitoid consists of plagioclase, orthoclase (K-feldspar megacrysts), quartz, hornblende, biotite and clinopyroxene as major constituents, and titanite, zircon and apatite as minor constituents.

The granitoids are classified as subalkaline and calc-alkaline on the basis of the Irvine & Baragar (1971) classification scheme. The primitive suite is gabbroic to granodioritic in composition, whereas the evolved suite is only granitic in composition based on the Cox et al. (1979) diagram (Kuşcu et al. 2000). The molecular A/CNK ratio ($Al_2O_3/CaO+Na_2O+K_2O$) is less than 1.1, and they are metaluminous to mildly peraluminous in nature. The granitoids show I-type characteristics on the basis of the Chappel & White (1974) classification, as evidenced also by the occurrence of hornblende, apatite, titanite, and zircon.

The contact zones with marble are usually concordant, and the calcite crystals therein exhibit plastic deformation textures. Although the exact depth of emplacement is not known, this textural evidence suggests that emplacement took place at relatively great depth, and that these are deep-seated granitoids.

The marbles are interpreted as metamorphosed platform carbonates grading upward into pelagic limestones then to calci-turbidites, and are intercalated with gneiss and amphibolite layers. The marbles are aligned parallel to the contact zones. They usually consist of twinned calcite and occasionally dolomite, and generally show evidence of ductile deformation. Dolomitic marbles are very rare and are usually associated with thin gneiss interlayers. Calcite shows plastic deformation and deformation-induced kinking, and is medium-grained with grain size increasing along the contact zones due to synchronous metasomatism.

Skarns and Skarn Deposits in the Çelebi District

The skarn in the Çelebi district is mostly calcic skarn, rich in garnet-pyroxene-epidote (Kuşcu 2000); whereas olivine and phlogopite skarns are also observed at contacts with dolomitic rocks. The general trends of the skarn zones parallel discordant fracture planes within the marbles. These zones trend both NW-SE and N-S. Exoskarns either appear as narrow skarns with limited distributions, commonly along fracture zones in marbles of the Central Anatolian Metamorphics, or are sandwiched between endoskarn zones and smaller marble outcrops. The exoskarns are broadly classified as "intrusive around skarn type" based on the Burt's (1977) classification scheme, since they are enclosed by the Çelebi Granitoid (Figure 2). Extensive endoskarns form along the margins of the granitoid whereas exoskarns occur either as 1–10-m-wide irregular veins within fracture and joint planes of the marble, or as widespread skarn zones along the contacts of the Çelebi Granitoid and marble in roof pendants. Epidote-pyroxene skarns (with some garnet) and pyroxene-garnet skarns are the main skarn zones in the district.

Endoskarns

The endoskarns can be recognized easily in the field by the change in the colour of granite from grey to green, particularly along the marble-granitoid contacts. Mesoscopically, the alteration of amphibole and biotite to epidote can be observed. In places, fresh granitoid patches occur within the skarnized granitoids. Endoskarn formation began with epidotization, and was coincident with sericitization during metasomatism. Endoskarn zones are represented mainly by epidote-pyroxene skarns
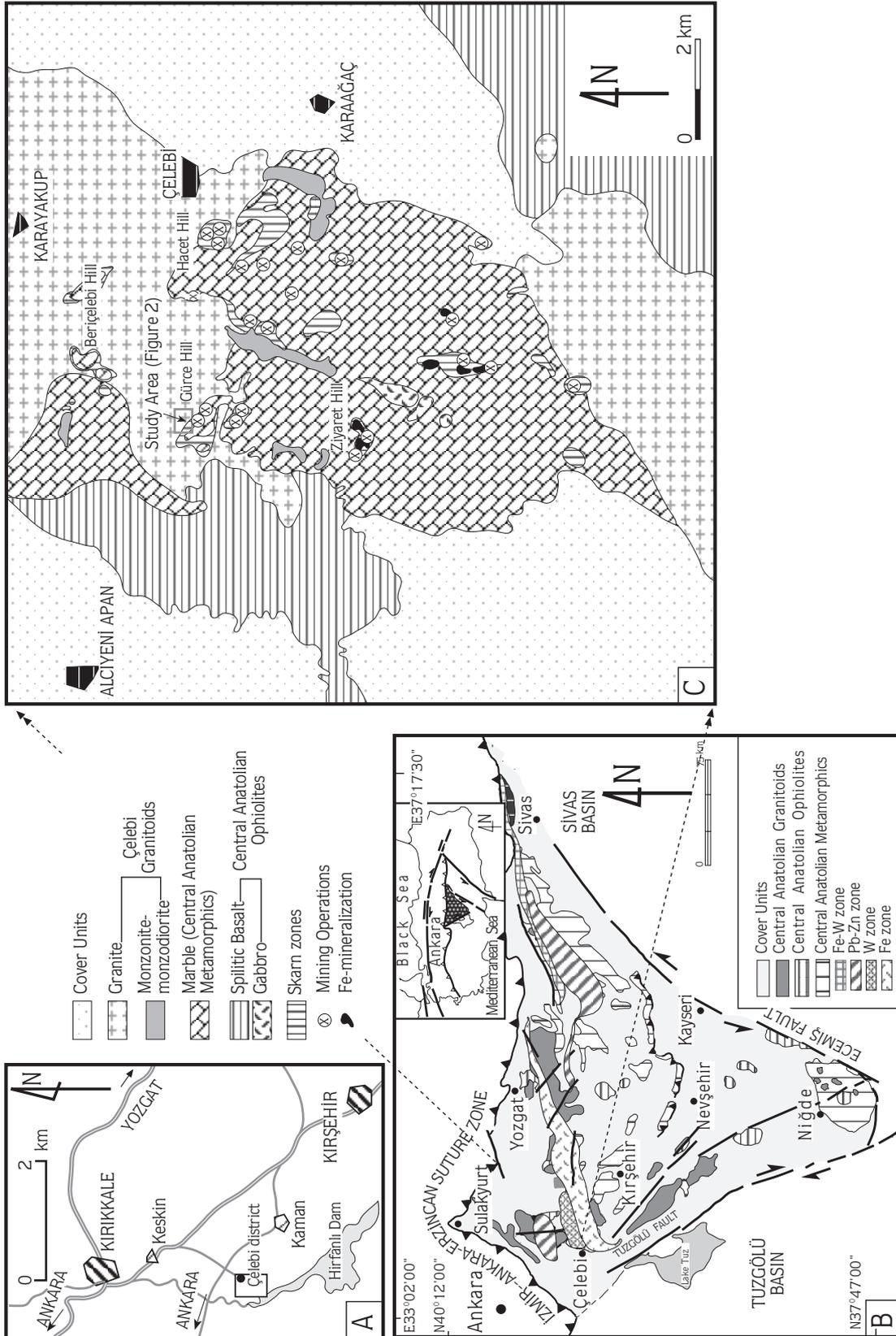
Figure 1. (A) Geographic location map of the Çelebi district. (B) regional geologic map of the CACC. (C) Regional geologic map of the Çelebi district.
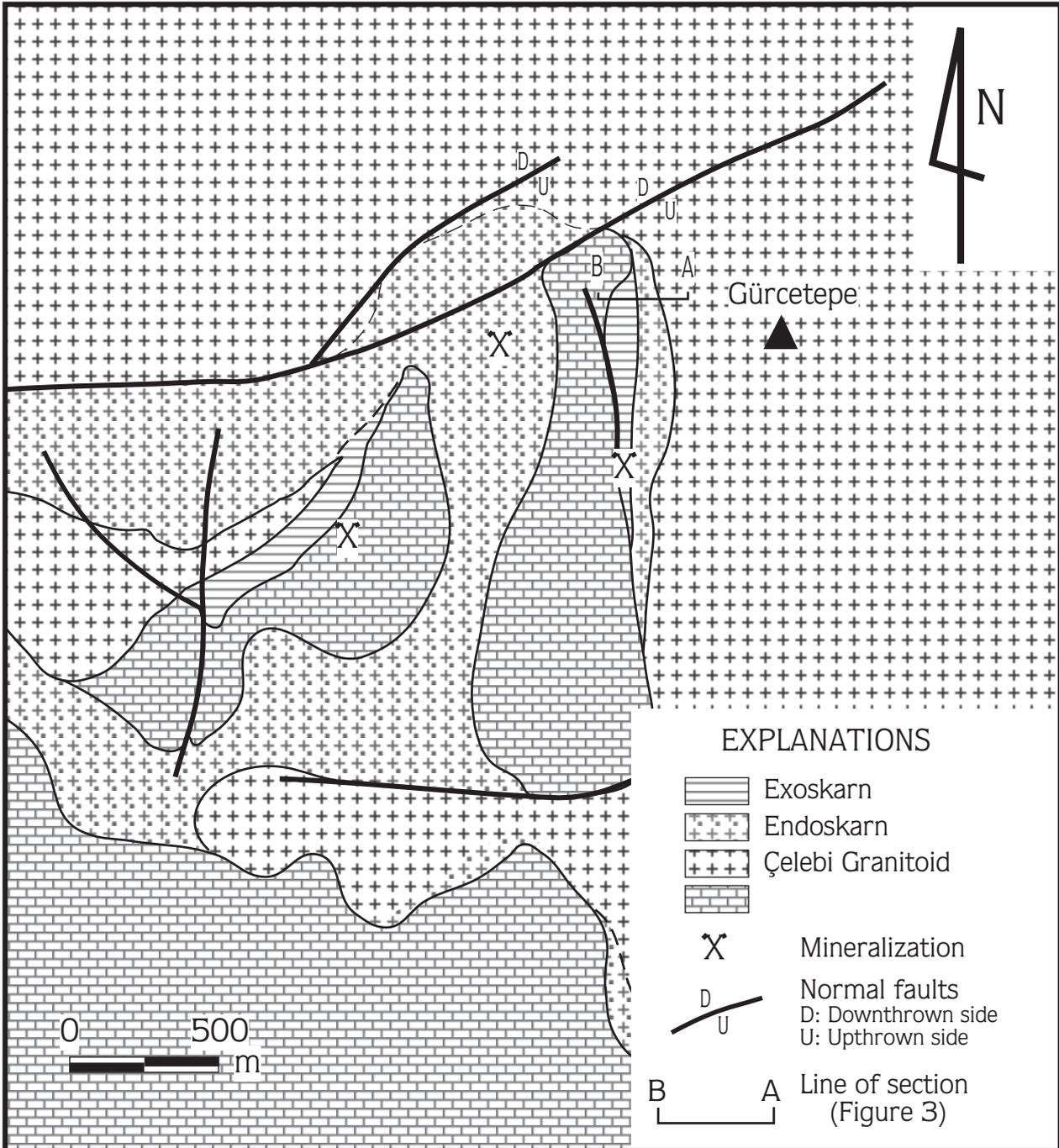
Figure 2. Geologic map of the Çelebi district.

in which epidote is the early product. The epidotization is more marked in zoned plagioclases, and its intensity increases rimward. A more intense metasomatism occurred with the complete replacement of plagioclases by epidote and pyroxene as the marble is neared.

Therefore, the epidotized granitoids are regarded as early-stage metasomatic products.

The pyroxene is associated mainly with epidote as replacement of plagioclase. The increase in the abundance of pyroxene is consistent with the rimming of coarser

magmatic fine-grained hydrothermal quartz. Garnet is present as sporadic crystals in endoskarns. They are generally andraditic to granitic with Gro_5And_{95} to $Gro_{60}And_{40}$ (Bayhan 1984), the latter is confined mainly to vein-type skarns close to exoskarn zones. The garnets become more andraditic as Çelebi Granitoid is neared. The abundance of pyroxene tends to increase both in plagioclase crystals and within the groundmass of the granitoids towards the exoskarn zones. The increase in the abundance of pyroxene coincides with the formation of anhedral, isotropic brown garnets in the endoskarns. The only zoned crystals are observed close to the exoskarns. The garnet-rich pockets also mark irregular pockets and veins (2-3 cm in diameter) of magnetite and hematite. The width of the endoskarns ranges from 30 to 300 m. The pyroxene-epidote skarns also occur as veinlets along schistosity planes of the gneisses. These occurrences are referred to as skarnoid that formed by the exchange of elements between unlike lithologies, such as gneiss and marble, and are of minor importance both in distribution and mineralization compared to other skarn zones of the district. The epidote-pyroxene skarns are also zoned from granitoid to marble in terms of epidote-, pyroxene- and garnet-dominant assemblages. Farther within the granite, endoskarns occur only as disseminated veinlets, and are enriched in garnet towards the granite.

Exoskarns

The exoskarn zones typically have N-S and NE-SW orientations and are present in the eastern parts of the district (Figure 2). The dominant minerals are pyroxene and garnet as prograde assemblages, and epidote, tremolite and calcite as retrograde mineral assemblages (Figure 3). The exoskarns are limited in size and distribution relative to the endoskarns (Figure 2). In general skarn and vein trends are conformable to the general trends of the foliation and fracture planes in the marble. The exoskarns occur mainly as pyroxene-garnet skarns. Pyroxene and garnet skarns occur along fractures and veinlets that pinch and swell. In general, the exoskarn shows zoning with pyroxene-epidote assemblages close to the marble front (distal skarns) and with pyroxene-garnet assembalges close to the endoskarn zone (proximal skarn). The skarns that formed along the fracture planes of the marbles are more or less zoned from the centres to the margins of fracture as garnet-

pyroxene-plagioclase. The widths of individual zones range from 3-5 to 30-50 m. Epidote, calcite, tremolite and quartz typically make-up the retrograde assemblages which formed by the alteration of pyroxene and garnet in the advanced stages of skarn formation (Figure 3).

Pyroxene is generally subhedral to euhedral, and hedenbergitic to diopsidic in composition. The euhedral crystals typically occur in distal skarns or along fracture planes in the marbles. Two types of garnets are observed in the exoskarns: smaller, isotropic garnets at the transitions between endoskarn-exoskarn zones, and larger, oscillatory-zoned anisotropic garnets close to the marble fronts. These garnets are mainly grossularitic, ranging from $Gro_{80}And_{20}$ to $Gro_{60}And_{40}$. They also contain pyrope (0-2.11%) and almandine (0-2.61%) (Bayhan 1984). Garnets that predominate at the distal marble front show oscillatory zoning and are accompanied by magnetite mineralization.

Geochemistry of Skarn Zones

Representative samples for each skarn zone, marble and related igneous rocks were analyzed by XRF in the GeoAnalytical Laboratories of Washington State University. The results are given Table 1. In order to understand bulk compositional gradients and metasomatism, the compositions of samples from the endoskarn were compared with granitoid composition, and exoskarns with marble along a line of section (A-B in Figure 2). The results are shown in Figures 4 and 5. Figure 5 was adapted from the Hildreth (1981) diagram, and based on the normalization of components in the endoskarn and exoskarn with respect to components in the original rocks (granitoid and marble, respectively). This diagram enabled the determination of depletion and enrichment in endoskarns and exoskarns relative to original granitoid and marble. The following features are recognized.

The endoskarns are enriched in $FeO_{(T)}$, CaO, MnO and MgO, and are depleted in SiO_2, Al_2O_3, TiO_2, K_2O, Na_2O and P_2O_5 compared to the original granitoid composition (Figures 4 and 5). The SiO_2 content decreases from granitoid to endoskarn since it was used to form calc-silicate assemblages (pyroxene and garnet) in the endoskarns. The decrease is very sharp close to the peripheries of the granitoid (Figure 4). It is negatively correlated with $FeO_{(T)}$, and this situation may be
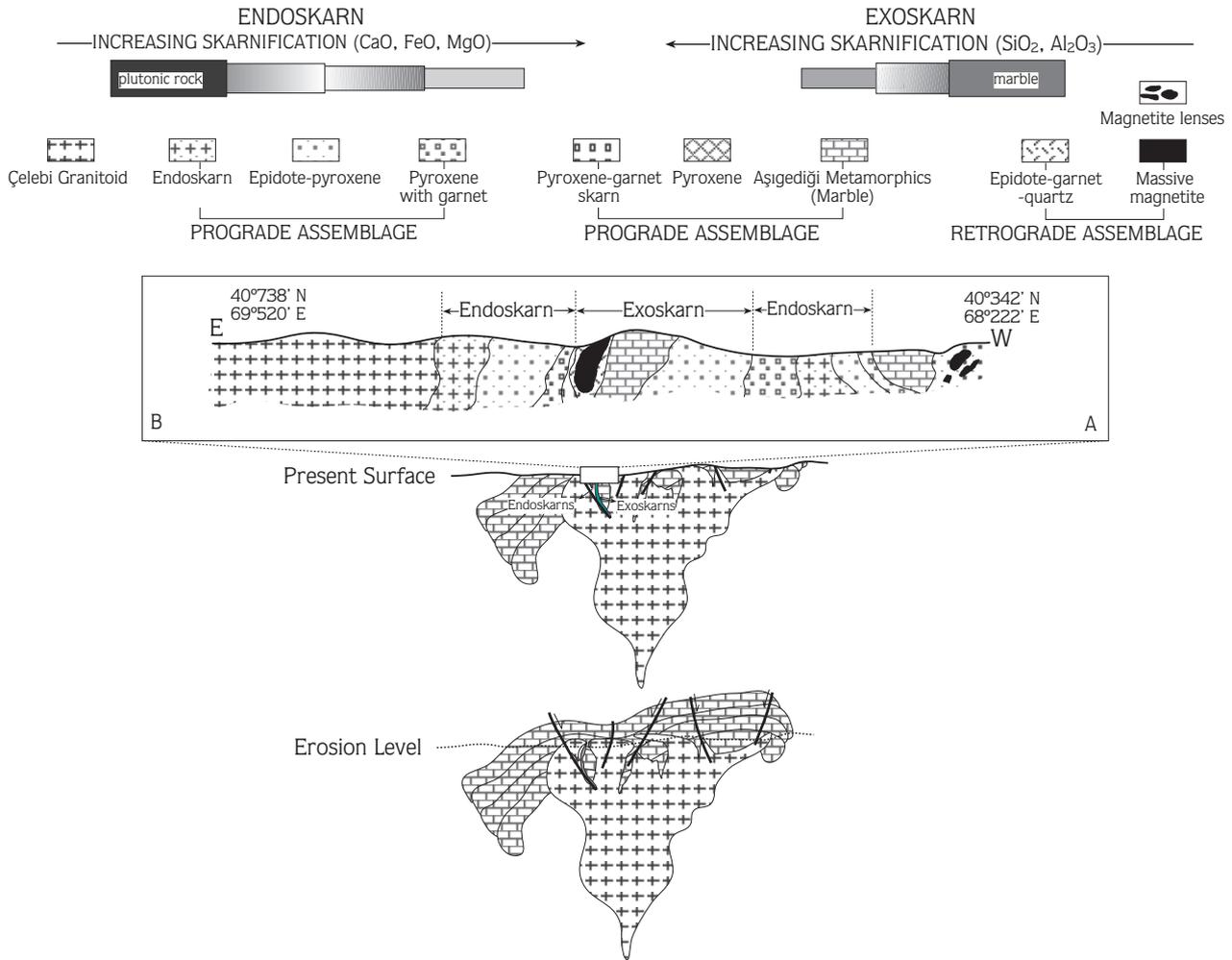
Figure 3. A schematic diagram illustrating the skarn zones. Prograde and retrograde assemblages and relative setting of skarn zones in the Çelebi district.

attributable to the formation of iron-rich assemblages during prograde skarn formation. The increase in CaO content may verify this in that formation of calc-silicate assemblages by the addition of CaO from the marble also enhanced the formation of iron-rich assemblages such as andraditic garnets and hedenbergitic pyroxenes. However, it resembles Al_2O_3 in that both show the same enrichments and depletions (Figure 4). Al_2O_3 decreases gradually from granitoid to endoskarns close to the granitoid contact, however, and increases close to the exoskarn zones. This situation could be related to increase in abundance of grossular garnets within the endoskarn zones. TiO_2, which is considered to be an immobile component, and concentrated mainly in titanite in magmatic rocks, is almost constant throughout the

skarn zones with only slight depletion from the granitoid to the endoskarn. Bayhan (1984) reported that TiO_2 was not detected the clinopyroxene and garnet, but was detected in epidote and amphibole. This finding is consistent with TiO_2 enrichment at endoskarn-exoskarn transitions (Figure 4) and within the exoskarns where prograde assemblages were altered somewhat to retrograde assemblages, such a tremolite and epidote. $FeO_{(T)}$ increases gradually from granitoid to endoskarn, suggesting that Fe is derived from the granitoid. According to Figure 5, the total iron oxide content of the endoskarn was enriched about 15% with respect to the original granitoid content. However, products of magnetite mineralization that could also contribute to $FeO_{(T)}$ enrichment in the endoskarns. However, the total

Table 1. Representative geochemical data and average values in the skarn zones (**C**: granitoid; **endo**: endoskarn; **ska**: exoskarn; weight percent for major oxides and ppm for trace elements; **nd:** not detected).

	C1	C2	C5	C6	Evolved Granitoid	Primitive granitoid	endo-7	endo-8	endo-11	C15(ska)	C17(ska)	C20(ska)	C24(ska)	C34(ska)	C38(ska)	Marble
SiO_2	74.41	72.03	73.07	72.92	73.10	61.98	72.45	50.89	36.72	61.51	60.63	40.37	9.82	11.45	38.71	3.19
Al_2O_3	13.60	14.51	13.94	14.36	14.10	16.16	8.36	9.70	7.37	11.27	15.23	6.19	0.50	1.18	1.03	0.13
TiO_2	0.16	0.19	0.20	0.17	0.18	0.54	0.09	0.10	0.07	1.35	0.59	0.28	0.00	0.03	0.00	0.00
$FeO_{(T)}$	0.24	1.88	1.47	0.96	1.13	6.80	8.07	23.45	25.00	3.33	5.34	17.07	86.16	86.48	26.61	0.54
MnO	0.02	0.06	0.05	0.04	0.04	0.12	0.20	0.27	0.66	0.22	0.17	0.78	0.17	0.20	1.02	0.21
CaO	1.45	1.85	1.44	1.49	1.55	5.76	9.46	14.09	28.71	10.65	11.78	32.44	2.71	0.60	32.31	50.50
MgO	0.01	0.18	0.17	0.32	0.17	2.65	0.47	0.44	0.66	4.89	1.88	2.71	0.00	0.00	0.20	4.40
K_2O	5.38	5.21	5.22	5.61	5.35	1.03	0.34	0.71	0.02	3.32	0.44	0.02	0.04	0.03	0.01	0.04
Na_2O	3.40	3.86	3.56	3.18	5.53	2.89	0.02	0.00	0.00	2.43	3.20	0.01	0.00	0.08	0.00	0.00
CO_2	0.09	0.11	0.12	0.09	0.12	0.19	0.06	0.76	0.35	0.42	0.21	0.61	1.02	0.21	0.32	41.06
Total	98.76	99.88	99.24	99.14	101.27	98.12	99.52	100.41	99.56	99.39	99.48	100.48	100.42	100.26	100.21	100.07
Ni	nd	533	726	755	504	95	11	5	3	136	23	2	113	143	0	2
Cr	nd	254	246	214	179	732	10	22	0	244	72	120	4	15	0	9
Sc	nd	101	124	160	96	16	405	541	10	11	11	0	0	11	0	ND
V	nd	16	15	17	15	13	8	13	14	119	79	51	32	26	8	15
Ba	9	13	9	12	11	153	7	6	7	727	81	0	1	0	19	30
Rb	177	190	175	172	178	27	169	106	79	135	16	0	0	0	0	2
Sr	16	26	30	17	22	19	10	5	27	279	398	20	18	34	19	292
Zr	40	27	30	29	126	17	28	21	1	127	156	49	20	23	6	9
Y	7	4	9	3	32	30	0	8	0	22	27	26	7	8	3	nd
Nb	20	0	22	0	10	13	0	1	0	32	13	7	5	6	2	nd
Ga		2		4	2	106	0	0	0	12	18	15	12	8	6	nd
La	15	14	12	12	13	68	20	31	18	37	32	0	9	10	0	nd
Ce	1	2	20	21	11	35	65	840	922	89	67	14	7	20	303	nd
Th	64	34	46	32	44	75	69	796	434	6	7	0	1	11	14	nd

iron content is low in the granitoid and marble. Therefore, a large amount of iron is considered to have been supplied to these rocks during skarn formation and ore formation. MnO content have geochemical trends to $FeO_{(T)}$ contents. The increase in Mn and Fe in pervasively altered plutonic rocks are attributed to reactions between hydrothermal fluid and melt (Burnham 1979; Urabe 1985). Highest abundances are associated with samples close to exoskarn zones suggesting that the Mn-bearing assemblages, particularly pyroxenes, may confined to these zones. The behaviour of CaO is almsot identical to MnO, particularly in the endoskarn zones (Figure 4), suggesting that both accompanied metasomatic reactions that yielded calc-silicate assemblages. However, it appears that the endoskarn is more enriched in CaO (about 9 %) than MnO (5 %) with respect to the granitoid composition (Figure 5). Since CaO is a component derived mainly from carbonate rocks (marbles in this study), the marble-derived CaO triggered the metasomatism of the granitoid and the formation of calc-silicate assemblages within the granitoid. CaO also has an enrichment trend in the exoskarn zones. Therefore, it is thought that the zonal arrangement of skarns in the Çelebi district is attributable primarily to the geochemical behaviour of CaO. MgO content gradually increases from the granitoid to the endoskarn, with a sharp increase near the exoskarn zones (Figure 4). This trend may suggest that the Mg-bearing assemblages, such as diopsidic pyroxenes, did not form within the endoskarns but formed near the exoskarn zones. K_2O, Na_2O and P_2O_5 all decrease from granitoid to endoskarns, indicating that they were not involved in metasomatic reactions that yielded calc-silicate skarn assemblages. The distribution of these components is considered to be controlled by original plutonic rock
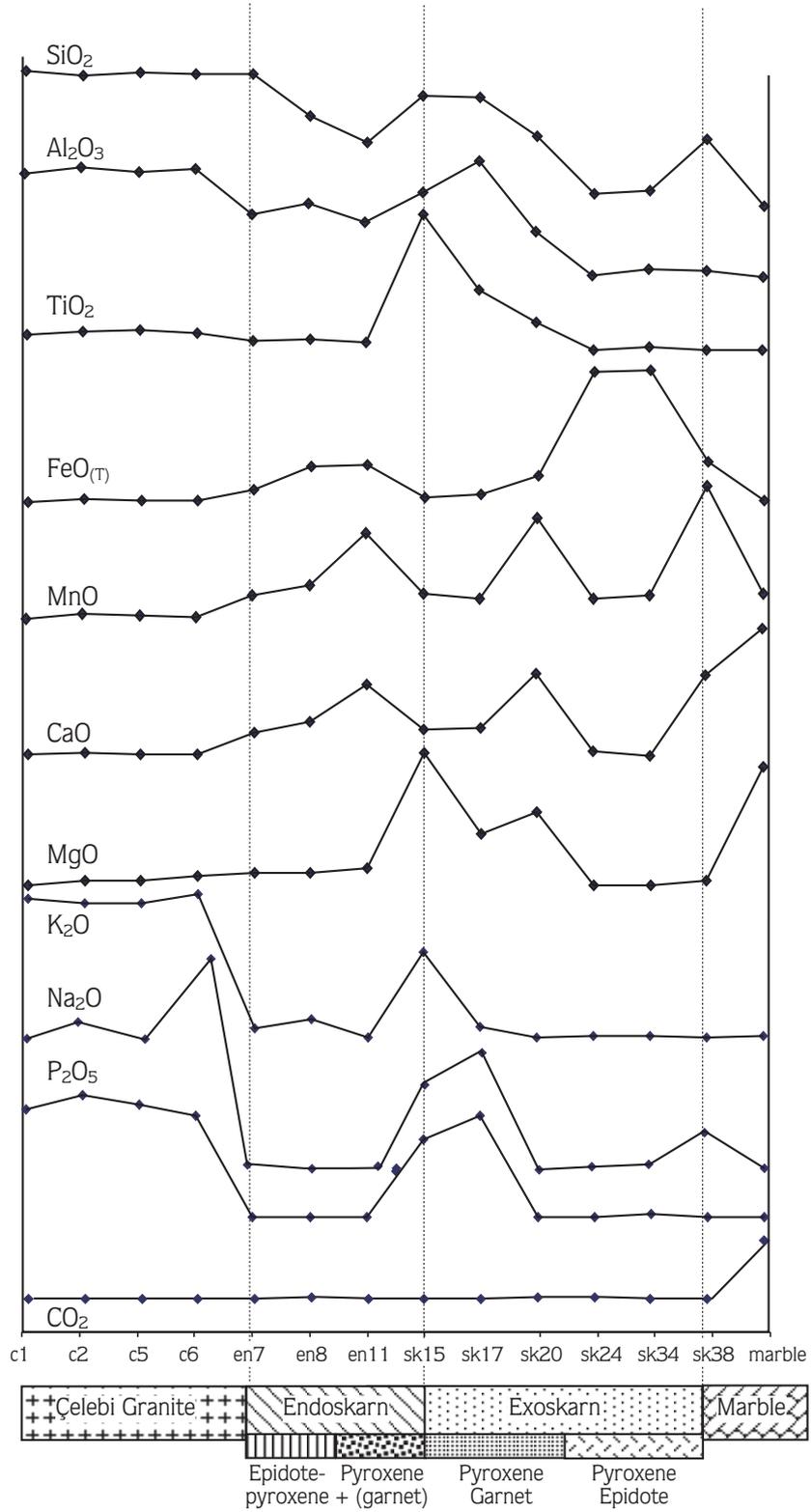
Figure 4. The profiles from granitoid to marble showing the distribution and abundance of elements in skarn zones.

compositions, suggesting that they were leached from the granitoid during hydrothermal alteration. Among these, K_2O is the most depleted component (about 20-23% with respect to the original granitoid), as shown in Figure 5. However, K_2O, Na_2O and P_2O_5 increase near the exoskarn zones, probably indicating that the excess alkalies were derived from hydrolysis of feldspars which coincided with any increase in SiO_2 derived directly from hydrolysis reactions, as suggested by Lentz & Gregorie (1995).

Exoskarn is enriched in SiO_2, Al_2O_3, TiO_2, Na_2O, K_2O and $FeO_{(T)}$, and depleted in CaO, MgO and CO_2 contents (Figures 4 and 5) with respect to marble. K_2O and Na_2O remained constant in exoskarns relative to marble. SiO_2 apparently increases from marble to exoskarn. Since SiO_2 is a possible magmatic component, SiO_2 enrichment is attributable to the chemical potential of SiO_2 derived from magmatic rocks in the region. The SiO_2 is enriched 5 to 10% with respect to the original marble composition (Figure 5). Although both $FeO_{(T)}$ and SiO_2 are enriched in exoskarn with respect to marble (Figure 5), $FeO_{(T)}$ and SiO_2 are inversely proportional in exoskarns (Figure 4). This relationship suggests that iron mineralization occurred via replacement of the calc-silicate assemblage during the retrograde skarn-forming stages. Al_2O_3 and TiO_2 behave almost identically, and are enriched in the exoskarns. Figure 5 shows that the exoskarns are considerably enriched in terms of these components. The most striking enrichment in exoskarn is in $FeO_{(T)}$ content (Figures 4 & 5). However, enrichment in $FeO_{(T)}$ content of the exoskarn is confined to pyroxene-epidote zones close to marble. Mno and CaO played similar roles in calc-silicate formation and ore formation. Although depletion of CaO in the marble seems to be insignificant (Figure 5), a sharp decrease in CaO content from marble to exoskarn is coincident with a sharp increase in $FeO_{(T)}$ (Figure 4), suggesting that iron mineralization is accompanied by CaO depletion where retrograde alteration is pervasive. Also noteworthy are the similar CaO and $FeO_{(T)}$ contents of skarns within prograde assemblages near to the endoskarn zones (Figure 4), suggesting that calc-silicate assemblages should be rich in iron close to endoskarns. Both K_2O and Na_2O are enriched with respect to marble (Figure 5), but this is valid only for the transition from endoskarn to exoskarn. The K_2O and Na_2O contents of the rest of the exoskarn are almost constant as shown in Figure 4. The enrichment is related to the metasomatic transfer of alkalies from granitoids to country rocks (Barton et al. 1991). The CO_2 is depleted drastically from marble to the exoskarn, and remains almost constant in exoskarn (Figures 4 and 5), and is accompanied by a pronounced decrease in CaO content. Figure 5 shows that the CO_2 content of marble decreased about 90%; this depletion is apparent at the calc-silicate reaction front where metasomatically induced decarbonation reactions begin along the contact zones between carbonates and granitoids.

Discussions and Conclusions

Geochemical study of the Çelebi skarn zones reveal that the endoskarns are enriched in $FeO_{(T)}$, CaO, MnO and MgO, and are depleted in SiO_2, Al_2O_3, TiO_2, K_2O, Na_2O and
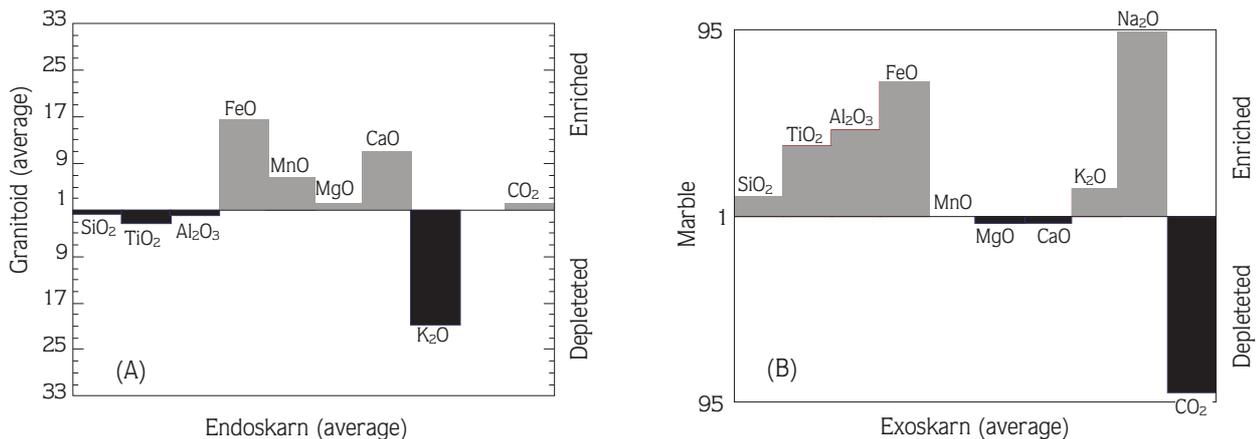
Figure 5. Hildreth (1981) type diagrams showing the relative enrichment and depletion of endoskarn with respect to granitoid **(A)** and of exoskarn with respect to marble **(B)**.

P_2O_5. Accordingly, $FeO_{(T)}$ is introduced from granitoid to marble fronts, and SiO_2, Al_2O_3 and K_2O were transported into the marble. Therefore, the peripheral or fractured granitoids at the marble fronts were metasomatized by Ca and alkalies. However, the steady-state behaviour of K_2O, Na_2O and Al_2O_3 suggest that they did not take part in skarnification as compared to CaO, $FeO_{(T)}$ and SiO_2, in that they remained as almost as they are in the granitoid. This situation is also due to the fact that the alkalies (such as K and Na) are not transported to distal areas during skarnization and are enriched along the margins of the granitoid itself (Burnham 1979) if the intrusive rock assimilates CO_2-rich rocks such as limestone. This behaviour also explains the relative intensity of alkali metasomatism in all skarn-producing granitoids. Figures 4 and 5 suggest that the mineralization of the Çelebi district occurs both in endoskarns and exoskarns and was coincident with the development of calc-silicate assemblages in the endoskarns while they are accompanied by carbonization reactions that took place during retrograde alteration of early prograde skarn assemblages in the exoskarns. Deep-seated emplacement of granitoids into the marbles enhanced the plastic deformation and folding of the marbles such that they parallel the igneous contacts (Figure 3). Therefore, fluids were unable to circulate through fractures in the marbles. However, fluids circulated along the periphery of the granitoids parallel to the carbonate contacts, resulting in inward circulation or influx of Ca-rich fluids into granitoids. This fluid flow initiated the formation of calc-silicate mineral assemblages at the peripheries and along the fracture planes of the granitoids. Consequently, the endoskarns formed particularly along marble-granitoid contact zones and in associated fracture zones.

The formation of endoskarns begins with early metasomatic events triggered by the influx of Ca-rich fluids into the granitoids during the emplacement of the granitoid. It is suggested that the movement of Fe- and SiO_2-rich fluids from the granitoid was coeval with endoskarn formation. CaO and $FeO_{(T)}$ behave similarly in the endoskarns, possibly indicating that the Fe-rich assemblages formed mainly during Ca metasomatism of magmatic minerals in the granitoids (prograde assemblages in the endoskarn). Heating that caused recrystallization of limestones eventually enabled the fluids released from the granitoid to circulate through fractures within the marbles, and gave rise to the formation of silica- and iron-rich minerals as early prograde assemblages within the exoskarns. The main magnetite mineralization occurs within the pyroxene-garnet exoskarns (Figure 3) and resulted from the retrograde alteration of prograde calc-silicate assemblages. In other words, it was accompanied by increase in CaO, inferred to have been associated with carbonization of prograde assemblages during retrograde skarn formation.

Acknowledgements

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