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PRELIMINARY APPROACH TO GENESIS OF BERYL GROUP MINERALS IN KAYMAZ, NW SİVRİHİSAR, ESKİŞEHİR

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ABSTRACT.- Kaymaz (Sivrihisar) is located at 80 km east of the Eskişehir. The study area consists of metamorphites, ophiolites, phonolites and pegmatites. Beryl crystals are detected in the sediments which cut the metamorphic units. Optical microscopic determinations show that beryl crystals have 35 µm diameter, green and pale greenish blue colours, hexagonal features, basal cleavages, n_o = 1.584 and n_e = 1.584 refractive indexes, uniaxial (-) and euhedral hexagonal prismatic characters which was supported by scanning images (SEM). Be content of phonolites between 9-31 ppm, of pegmatites between 4-17 ppm and of metamorphic units as 1 ppm were determined. Elements associated with beryllium in phonolites with F (260-440 ppm), Ba (1088-3106 ppm), La (300 ppm), Y (16-19 ppm) content, pegmatite with F (300 ppm), W (10 ppm), Sn (5 ppm) contents and presence of beryl crystals in the sediments cutting the metamorphic units which have tectonic relation with phonolite and pegmatite, seem to imply that formation of the beryl minerals have close releationship with these units.

Key words: Beryl, phonolite, pegmatite, metamorphite, Sivrihisar

INTRODUCTION

The study area, situated in 80 km east of Eskişehir province, northwest of Sivrihisar, is shown on the 1/25.000 scaled Eskişehir İ-26 c4 map sheet (Figure 1).

Regional geology was explored by Romieux (1942), Weingart (1954), Kulaksız (1981), and Gözler et al. (1996). However, there is not any known study related with mineralogy, geochemistry and origin of emerald and accociated minerals originated from Sivrihisar locality famous for gemstones market and recorded at historical times.

If world beryllium occurrences are taken into considerations in general, they seem to form mostly in schists, nepheline syenites, phonolites and pegmatites within ophiolite belts. Based on these informations and carrying the whole parameters, Sivrihisar region seems to be a suitable locality to be considered carefully for this research.

MATERIAL AND METHOD

29 clastic and 29 rock samples were collected along creek valleys cutting metamorphics, ophiolites and pegmatites, complying with the principles of geochemical prospecting. Transparent and opaque minerals collected from clastic samples by using stereomicroscope are classified as groups based on their color and crystal forms. Of transparent minerals, colored minerals considered to be beryl were separated, and refractive indexes of these minerals were determined under polarized light with using 0.002 mm spaced immersion oils, and their optical properties were also determined. In addition, these beryl crystals were analyzed by electron microscope (SEM) (Zeiss Supra 50 VP). Rock samples were petrographically analyzed and their mineral constituents and textures were determined. Trace element analyses of 12 samples were performed for the presence of beryl to be determined with ICP-AES method at ACME laboratory (Canada).

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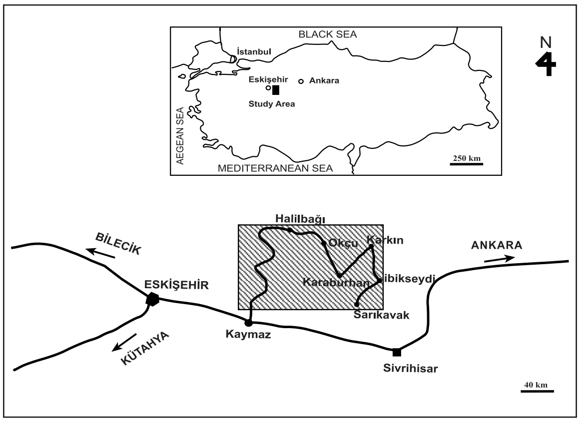

Figure 1- Location map.

GEOLOGICAL SETTING

The study area consists of metamorphics, Karabayır Metaophiolites, Karakaya Granodiorite, Höyüklü formation and Sarıkaya formation (Kulaksız 1981). Metamorphics of Upper Cretaceous aged units forming the basement in the study area include an intercalation of metaquartzite, metapelite, marble, calcschist, metabasite, serpentine schist and metacalcirudite (Okay, 1984; Figure 2). Tectonically overlying Karabayır Metaophiolites contain of metagabbro, metahornblendite, metapyroxenite, metaharzburgite, metaserpentine and metaperidotites. There are also phonolite domes intruding serpentinite along the crack formed by a fault line which have effects up to penetrating depths. K-Ar age of phonolites is given as Middle Miocene (Özgenç, 1982). Karakaya Granodiorite of Upper Cretaceous intruding ophiolites as a pluton bears a pegmatitic vein with quartz, feldspar, tourmaline and pyrite. Höyüklü Formation of Miocene is composed of volcanogenic sandstone, greywacke, tuff, agglomerate and lava flows. Overlying all these units, Sarıkaya Formation of Pliocene begins with volcanic tuff and conglomerate at the bottom and lasts with lacustrine limestone, sandstone, claystone and marl units. This formation overlays locally metaophiolites with angular unconformity (Kulaksız, 1977). The youngest deposits in the study area are Quaternary alluviums (Figure 3).

Emerald and aquamarine were detected by optical analyses on creek sands collected from the valley of Karakız Creek cutting metamorphics to research beryl mineralization. Phonolites were selected as second area within the ophiolites. Pegmatitic vein within granodiorite is considered as third area.

PETROGRAPHIC STUDIES

a- Rock Petrography

Petrographic studies present that metamorphics seem to include garnet-glaucophane schist, epidote-chlorite schist, garnet-lawsonite-glaucophane schist, epidotite, chlorite-lawsonite schist and marbles, Karabayır Metaophiolites contain diabase, serpentinite, ophicalcite and phonolites, and Karakaya Granodiorite seems to bear a pegmatitic vein as well.

In thin sections of lepidoporphyroblastic-textured garnet glaucophane schist traces of chloritization are present on the edges of subhedral garnets with varying sizes between 0.25 and 0.75 mm (Plate I - Figure 1). Prismatic glaucophane crystals with varying sizes between 0.125 mm and 0.5 mm have significant strong pleochroism. With using immersion oils, refractory index of glaucophane is determined as n_x= 1.642, n_y = 1.656 ve n_z = 1.657 and it implies crossite of glaucophane series. As well as garnet and glaucophane, there are muscovite, epidote, chlorite and quartz.

In lepidoblastic - textured epidote - chlorite schist, there are epidote as elongate crystals in the direction of b axis, clinozoisites with bluish interference colors, and chlorite with no aligned groups of crystals.

In nematoporphyroblastic-textured garnet-lawsonite-glaucophane schist, glaucophane min-

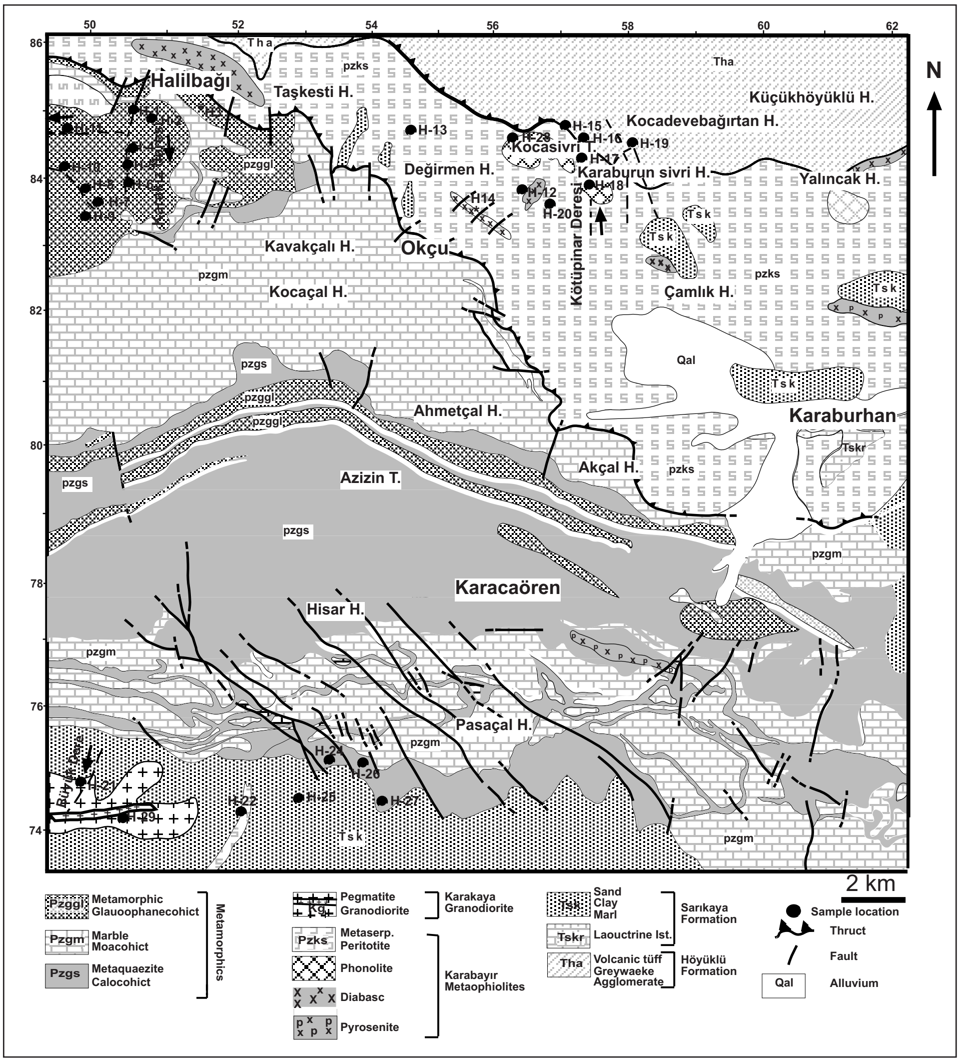

Figure 2- Geological map of the study area (modified from Kulaksız, 1981).

erals have sizes between 0.2 and 0.3 mm. Lawsonite minerals varying sizes between 0.08 and 0.22 mm are short prismatic crystals. There are inclusions in garnet minerals. Epidote minerals are between 0.2 and 0.65 mm, in size.

In nematoblastic-textured epidotite, euhedral albit crystals are found together with epidotes. The size of the calcite mineral inclusions seem to be between 0.15 and 0.3 mm. İn size (Plate I - Figure 2).

In nematoblastic-textured chlorite lawsonite schist, foliated crystals of chlorites surround lawsonite and epidote minerals in bunches. Lawsonite minerals are short prismatic crystals and show parallel extinction. Epidote minerals are 0.13 mm in size and augite minerals are between 0.15 and 0.3 mm in size (Plate I - Figure 3).

In marble sample enclosed in metamorphics, there are very few quartz, sericite, plagioclase and orthoclase besides calcite. Twin glidings and

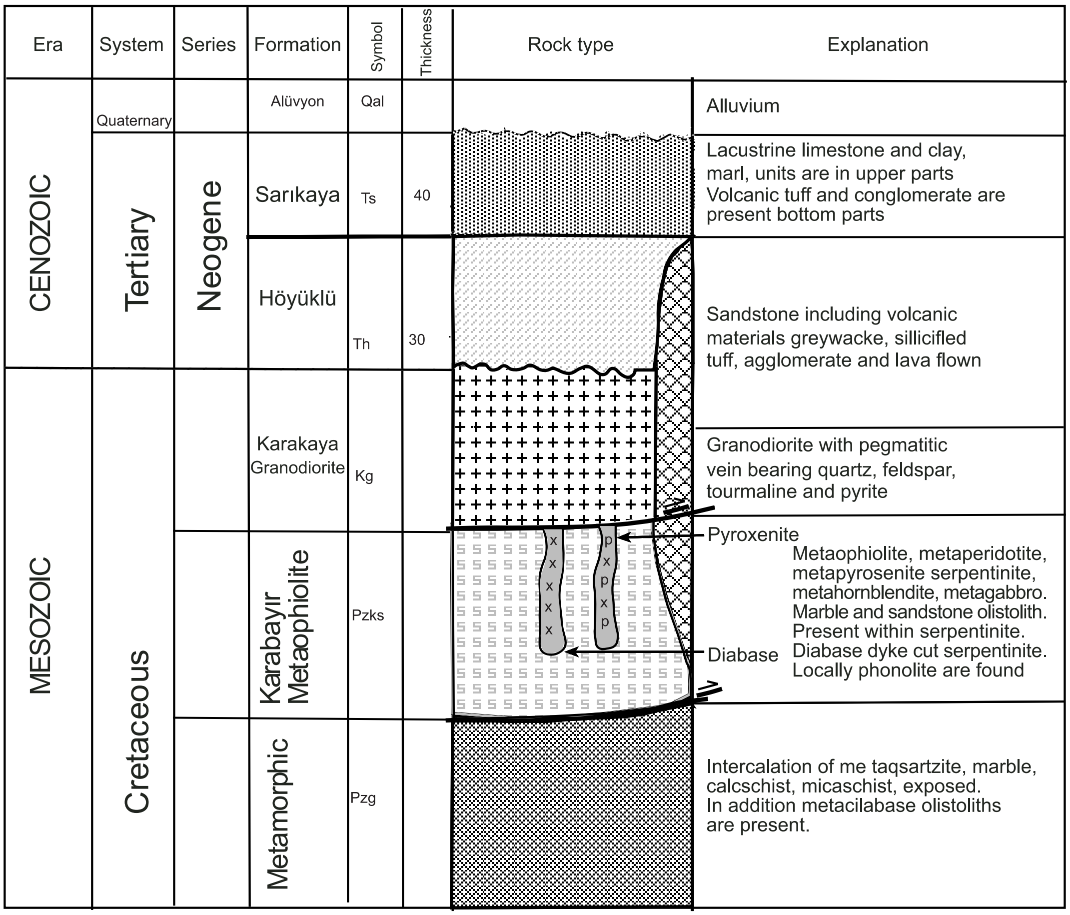

Figure 3- Generalized vertical section of the study area (modified from Kulaksız, 1981; Okay, 1984)

bendings on these twin lamellas are observed in calcite crystals. They show symmetrical extinctions according to the traces of cleavages. Quartz minerals are of anhedral rounded grains and sericite minerals are flakelike assemblages. Few plagioclase and orthoclases of Carlsbad twinning are observed.

Ophitic-textured diabase dyke within Karabayır metaophiolites contain of oligoclase, diopsite, actinolite and zeolite minerals. Diopsites performing uralitization were converted to partial or completely acicular actinolites. Zeolite mineral, defined as natrolite, are found as acicular-fibrous aggregates. In serpentinite, there are antigorite bearing olivine remnants, and fibrous chrysotiles. In the porphyritic-textured phonolite sample (H18), there are euhedral phenocrysts of sanidine varying between 0.2 and 0.7 mm size, hornblende with 0.015 mm. size and leucite minerals. Its groundmass consists of volcanic glass and rock fragments (Plate I - Figure 4). Phonolite sample numbered H28 showing typically trachytic texture contains nepheline and apatite minerals (Plate I - Figure 5). Sieve-textured ophicalcite include twin lamellar calcite, fibrous chrysotile and subparallel aligned antigorite crystals.

Pegmatite sample enclosed in Karakaya granodiorite consists of orthoclase, biotite and quartz minerals. Some of orthoclase minerals show Carlsbad twinnings, some have a combination of Carlsbad and Baveno twinnings (Plate I - Figure 6). Chloritization of biotites ranging sizes from 1 to 4.75 mm are seen from the edges. Quartz grains are between 0.25 and 0.5 mm in size.

b- Beryl Mineralogy

Beryl, with displaying dark green color is defined as emerald, and displaying bluish green to blue coloration, called as aquamarine, and is beryllium aluminosilicate in reality, carrying a formula as $Be_3Al_2Si_6O_{18}$.

25 green and light-green colored beryl grains owning the largest size as 35 μm, numbered as H1 from Karakız Creek cutting metamorphics, were defined as emerald and aquamarine based on the analyses (Plate II - Figure 1).

Views of green crystals (grains) on a stereomicroscope imply that they are crystallized in hexagonal systems (Plate I - Figure 2).

With using immersion oils having 0.002 different values, refractory indexes of the grains were found as n_o=1.568, n_e=1.584 using (Plate II Figure 3).

Beryl minerals, in optical studies, determined as uniaxial (-) and existed as hexagonal prismatic euhedral crystals were defined as emerald when green, and as aquamarine when light bluish green varieties at polarized light in immersion oils. (Plate II - Figure 4). Basal cleavage (0001) is significant (Plate II - Figure 5).

Beryl crystals determined on stereomicroscope were analyzed by SEM (Plate III - Figs 1 and 2) as well. Beryl crystals are euhedral hezagonal prismatic in general. 0001 planar sections of these crystals are six cornered and locally circular. Prismatic beryl crystals showing circular and elipsoidal 0001 planar sections were probably derived from partial abrasion of hexagonal prismatic crystals resulting from probable transportation within detrital sediments.

GEOCHEMICAL ANALYSES

12 samples were taken so as to determine if beryl is existed by performing chemical analyses, in the probable emerald promising areas. Of these samples, 6 samples were taken from Karakız Creek cutting metamorphics (H1-H6), one sample was taken from Kötüpınar Creek cutting phonolites (H18) and one sample was taken from Büyük Creek clastics cutting pegmatites (H29). Rock samples were analyzed as metamorphics (H1), phonolites (H18 and H28), and pegmatites (H29). To compare sediments and rock samples and if there is possibility of any rock types to bear beryllium mineralizations, both rock and sediment samples were analyzed.

Samples taken from Karakız creek (H1- H6) bear 1 ppm Be, creek sands taken from Büyük Creek (H21) cutting pegmatites contain 4 ppm Be (Chart 1). The highest Be value were determined as 9 ppm on creek sands taken from Kötüpınar Creek (H18) cutting phonolites. Related with these sediments, Be content of Karaburunsivri phonolite sample (H18) is 31 ppm, of Kocasivri phonolite (H28) is 19 ppm, of pegmatitic rock (H29) is 17 ppm and metamorphics (H1) bear less than 1 ppm Be. These data show us beryl has probably been derived and enriched from alkaline phonolitic and pegmatitic rocks.

Useful indicators to determine presence of beryl are F, Li, Rb, Cs, Sn, W, and accociated elements are Ba, Sr, B, Sc, Y, and other rare earth elements are U, Th, Nb, Ta, P, Ti, Mo and Mn (Boyle, 1974). Because of Be and Li, Rb, Cs, Sr, Ba, B, Sc, Y, Ti, Th, P, V, Nb, Ta, Cr, W, U, Mn and F are lithophile elements, they are interrelated (Akyol et al., 1985). Of accompanying elements with beryllium, various cations of small radius and often greater valence (U 10-22, Th 4-142, Mo 2-14, W 4-17, Nb 3-182, Sn 2-5 ppm) are called as incompatible elements. Owing to ionic radius and valences, the element Exchange with major ions in silicate minerals seem to be

Table 1- Results of geochemical analyses of the samples taken from the study area

Sample No Type	**H1 Sediment**	**H2 Sediment**	**H3 Sediment**	**H4 Sediment**	**H5 Sediment**	**H6 Sediment**	**H21 Sediment**	**H18 Sediment**	**H1 Schist**	**H28 Phonolite**	**H29 Pegmatite**	**H18 Phonolite**
Mo(ppm)	<2	<2	<2	<2	<2	<2	<2	14	<2	<2	2	<2
Cu(ppm)	34	38	44	56	65	31	14	35	10	3	4	31
Pb(ppm)	11	21	14	11	6	11	58	32	8	189	134	18
Zn(ppm)	51	50	62	78	81	42	32	94	33	308	22	84
Ag(ppm)	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Ni(ppm)	306	192	188	327	247	111	95	107	681	17	5	30
Co(ppm)	31	26	33	40	47	16	9	27	50	<2	<2	27
Mn(ppm)	1590	2596	1595	1718	2663	1014	373	2080	644	1474	294	1033
As(ppm)	<5	<5	<5	<5	<5	<5	25	34	<5	16	14	9
Au(ppm)	<4	<4	<4	<4	<4	<4	<4	<4	<4	4	<4	<4
Th(ppm)	<2	5	4	4	4	5	8	65	<2	142	39	5
Sr(ppm)	137	150	125	143	196	232	131	290	53	976	37	467
Cd(ppm)	<0.4	0.6	0.7	0.5	<0.4	0.5	0.5	0.6	0.5	<0.4	<0.4	<0.4
Sb(ppm)	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Bi(ppm)	7	7	9	8	<5	<5	<5	<5	<5	<5	<5	<5
V(ppm)	103	111	114	148	204	86	21	203	18	99	4	196
La(ppm)	20	17	27	29	33	18	18	165	<2	64	19	21
Cr(ppm)	523	521	278	490	423	219	325	336	619	2	<2	80
Ba(ppm)	96	109	194	210	172	121	275	5008	36	3106	71	1088
W(ppm)	<4	<4	<4	<4	<4	<4	4	8	<4	<4	10	17
Zr(ppm)	7	12	17	24	17	10	21	72	<2	801	35	67
Sn(ppm)	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	5	<2
Y(ppm)	19	22	19	22	30	14	6	32	2	19	4	16
Nb(ppm)	5	7	11	10	11	4	9	22	3	182	25	9
Be(ppm)	1	1	1	1	1	1	4	9	<1	19	17	31
Sc(ppm)	13	16	13	20	27	10	2	14	3	<1	<1	25
F(ppm)	-	-	-	-	-	-	-	-	10	260	300	440
U(ppm)	<10	<10	<10	<10	<10	<10	<10	<10	14	22	<10	15
Ca(%)	6.13	7.69	7.61	3.36	3.77	7.83	3.21	1.22	6.43	1.16	0.27	3.77
Mg(%)	3.34	2.35	2.24	3.88	3.69	1.51	0.61	1.35	9.6	0.13	0.07	2.38
Ti(%)	0.29	0.31	0.43	0.41	0.58	0.21	0.10	0.47	0.01	0.16	0.02	0.53
Al(%)	3.54	3.81	4.25	5.32	5.81	3.48	4.40	7.01	7.35	10.4	6.67	8.26
Na(%)	0.62	0.62	0.62	0.80	1.08	0.53	0.91	1.67	0.72	5.86	2.77	3.35
K(%)	0.28	0.44	0.60	0.74	0.64	0.45	2.83	2.81	0.04	4.55	3.64	1.76
P(%)	0.058	0.054	0.059	0.072	0.094	0.040	0.018	0.078	0.004	0.019	0.002	0.065
Fe(%)	4.17	4.95	4.18	5.88	7.26	3.44	1.34	5.17	3.16	2.59	0.73	5.63

difficult (Krauskopf, 1979). On phonolite samples (H18,H28) values of U as 15-22, of Th as 5-142, of Nb as 9-182, of Mn as 1033-1474, of Sr as 467-976, of La as 21- 64, of Ba as 1088-3106, of Al as 8.26-10.4, of Y as 16-19, and of F, a significant indicator for determining beryl, as 440-260 ppm were determined. On pegmatitic rock sample (H29) higher values of W as 10, of Sn as 5, of F as 300 ppm than other rock samples support that beryllium occurrences on the veins and pyrometasomatic beds own a geochemical affinity between beryllium and W, Sn and F in particular. (Warner et al., 1959).

On clastics from Karakız Creek cutting metamorphics, the values of Cu, Ni, Co, Mn, Ca, Cr, Mg, Sc, V, and Fe; on a garnet-glaucophane rock sample taken from the surroundings of same creek values of Ni and Cr associated with mafic volcanic and ultramafic rocks; on garnet, glaucophane, epidote and chlorite minerals values of Co, Fe, Ca, and Mg are high. It is noteworthy that the rock sample bear less Cu, Mn, Sc and V than clastic sample does.

On clastics from the creek cutting pegmatite Pb and K got concentrated, and pegmatite sample (H29) enriched in W, Sn and F, and depleted in Sr and Ba. This explains that pegmatite veins bear wolfram, tin and fluorine beds. On sediment sample taken from Kötüpınar Creek cutting Karaburunsivri phonolite, the values of Al, Na, Mo, Zn, As, Th, Sr, La, Ba, K, W, Zr, Y, and Nb seem to be considerably high. On phonolite samples (H18, H28), LFSE elements (Pb, Mn, Na, Th, Sr, Ba, U, K), HFSE (Y, Nb, Zn, Ti, Zr), LREE (La), transition elements (V, Sc), lithophile elements (W, F) and other elements (As, Cu, Fe, Al) got enriched.

Beryl may include alkaline ions like Na and K, and its total alkaline content may rise up to 5-7 %. Beryllium replaces Na, on the contrary, doesn't replace K. Alkaline elements remain within hexagonal channels in the lattice structure of a beryl (Çelik ve Karakaya, 1998), so high-beryllium containing samples bear alkaline elements of considerably enriched values (0.04 - 5.86 %) like Na and K. In fact, Kocasivri and Karaburunsivri phonolitic rock samples enriched in Na, K and Al, and depleted in Ca and Mg show that these rocks carry alkaline character.

It is indicated that there is a slight positive correlation between beryllium and Nb, Mo, Sn, F, Ba, Sr, U, Th and La elements; a negative correlation between beryllium and Sc, P, Ti, Mn, Cr and V, and no correlation between W and Y (Figure 4).

Results of chemical analyses show that a positive correlation between Be and Al may exist except for H1 sample, and Be element enters the lattice structure of Al-bearing minerals (sanidine, leucite, nepheline, hornblende, biotite, orthoclase). Because ionic radii and ionic valences of Be and Al are similar, these elements are isomorphic.

DISCUSSION

It can be referred that beryl minerals were formed due to phonolites and pegmatites in the northwest of Kaymaz (Sivrihisar). Beryllium element's indicating an anomaly on phonolitic and pegmatitic units, and the determination of beryl crystals in sediments cutting metamorphic rocks related with these units seem to exhibit significant geochemical relationship between Be and the rocks. According to Marshall et al. (2003), emerald occurrences are closely related with Cr (+/- V) and Be-bearing solutions in general. The authors state that Cr and V could be derived from local mafic and ultramafic rocks during hydrothermal alteration. At the sample of Kocasivri phonolite (H28), having a high value of V and a negative association, and a higher value of Cr in metamorphic rocks than that of other rocks indicate that chromium transportation is probably resulted from thrusting. Optically determined beryl minerals might have been formed due to an association with schist minerals following the

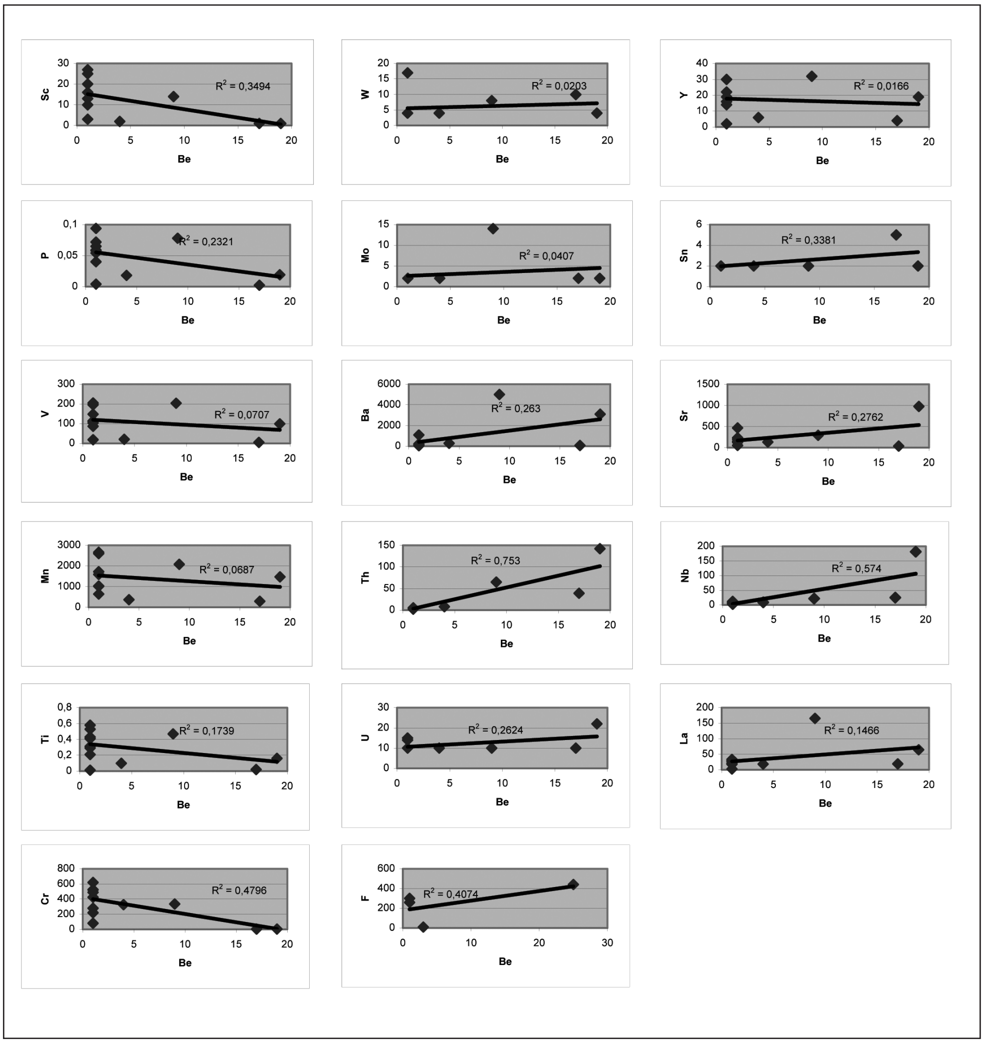

Figure 4- Correlation charts of elements associated with Be.

metamorphism of original rock during a hydrothermal process. Depending with upthrust, alkaline magma derived solutions were filled the fissures and joints of the metamorphic rocks, as result, beryl got deposited as trace amounts.

A positive correlation between Be and Na, and also K in phonolitic and pegmatitic rocks shows that beryllium could be present in a crystal lattice structure of some Na and K-bearing minerals like in sanidine, nepheline, hornblende, orthoclase and apatites. Because of trace amounts of beryllium element, beryl minerals can not be observed in thin sections of phonolite and pegmatite rocks and are mostly determined by chemical analysis methods.

Beryllium containing solutions are products of alkaline volcanism together with F in phonolites. Be composing between 9 and 31 ppm, and F between 260 and 440 ppm, and also Be between 4 and 17 ppm, and F as 300 ppm in pegmatites show the presence of a positive correlation between Be and F, and a probable relation as in origin, between them. Where beryllium's having hihger values, F gets high values, fluorine play a reactive role separating F from a solution phase, and beryllium was facilitated to get separate in pneumatolytic and hydrotermal solutions. Be-bearing minerals form due to conditional changes of the solutions like pH, pressure and temperature or due to decaying of complexes like $[BeF_4]^{2-}$, $[BeF_2]^{-}$, $[BeF_2]°$, $[Be(CO_3)F]^{-}$ ve $[Be(CO_3)_2]^{2-}$ when they interact with surrounding rocks (Gökçe, 2000). Either beryllium enters a lattice structure of silicate minerals or enriches in residual solutions during magma crystallization. Which of these happened is dependent upon the fluorine content of magma, hydrostatic pressure, alkalinity of surrounding rocks and other factors. Therefore, Be either is deposited in granitic pegmatites or is carried with fluorine and formed in hydrothermal occurrences and in greisens. Higher F value on Kızılcaören fluoride barite ore formed at the contact of phonolites in the study area shows that they are derived from the same volcanism. Hence, beryl occurrences are associated with phonolites and pegmatites in origin. It is also reported by Preinfalk and Morteani (2002) that similar occurrences derived from anatectic pegmatites in Belmont and Capoeriana (Minas Gerais, Brazil) reacted with Cr-rich ultrabasic rocks in metasomatism, Beryl occurrences in the study area might have been formed as a result of metasomatic reaction between pegmatites and Cr-rich ophiolitic rocks

CONCLUSIONS

1- The presence of beryl as emerald is firstly identified in sediments of Kaymaz locality (NW of Sivrihisar- Eskişehir) in Turkey by mineralogical and geochemical studies.

2- Optical properties of beryl minerals are hexagonal prismatic euhedral crystals, green-colored varieties called emerald, bluish green varieties called aquamarine, basal cleavage, determined light refractory indexes n_o= 1.568, n_e= 1.584, 1st row interference colors and uniaxial (-). On the other hand, beryl crystals on SEM are identified as euhedral hexagonal prismatic forms.

3- For the identification and origin of beryllium, Beryllium shows positive correlations with F, Ba, Sr, U, Th, La, Nb, Sn and, W elements, seem to be considerably important data.

4- Beryl minerals associated with beryllium in geochemistry as volcanogenic hydrothermal products related to phonolites and pegmatites.

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PLATES

PLATE I

Figure 1- Garnet glaucophane schist (H1)
Garnet (gr) indicating chloritization at its environs, and glaucophane (gl).
Single nicole, Obx Ok= 5x10

Figure 2- Epidotite (H7)
Epidote (ep) and calcite
Double nicole, Obx Ok= 10x10

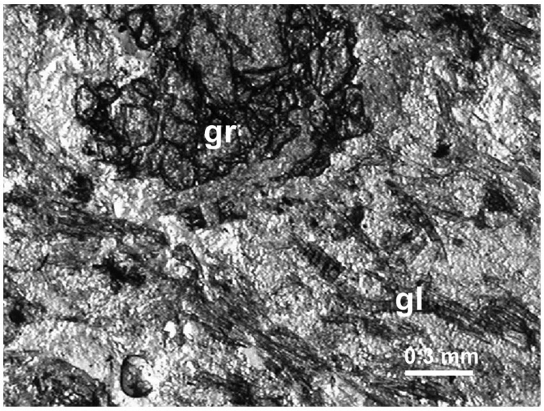
Figure 3- Chlorite lawsonite schist (H9)
Chlorite (kl) with foliated crystals, and short prismatic crystals of lawsonite (lv), Double nicole, Obx Ok= 5x10

Figure 4- Karaburunsivri phonolite (H18)
Hornblende (hnb), sanidine (sa) and leucite (lö)
Double nicole, Obx Ok= 4x10

Figure 5- Kocasivri phonolite (H28)
Hornblende (hnb) and sanidine (sa) minerals
Single nicole, Obx Ok= 4x10

Figure 6- Pegmatite (H29)
Baveno and Carsbad twins on orthoclase are seen.
Double nicole, Obx Ok= 5x10

PLATE - I



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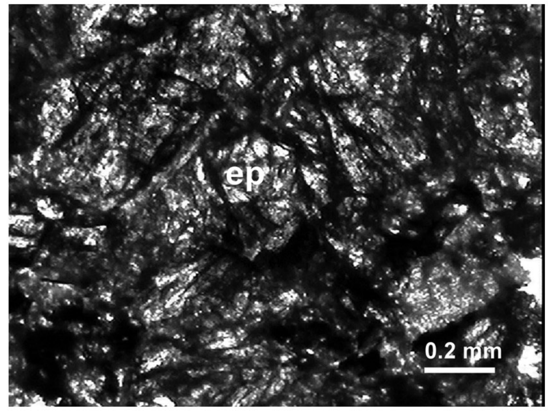

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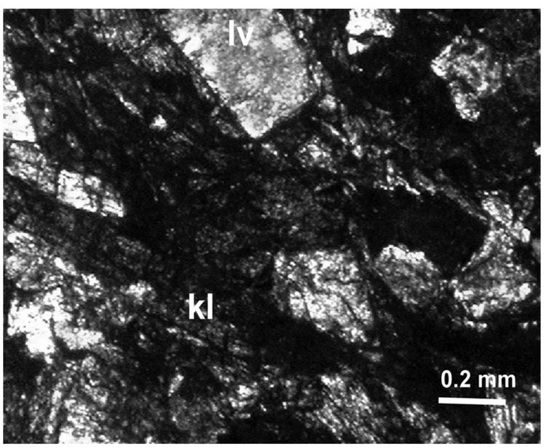

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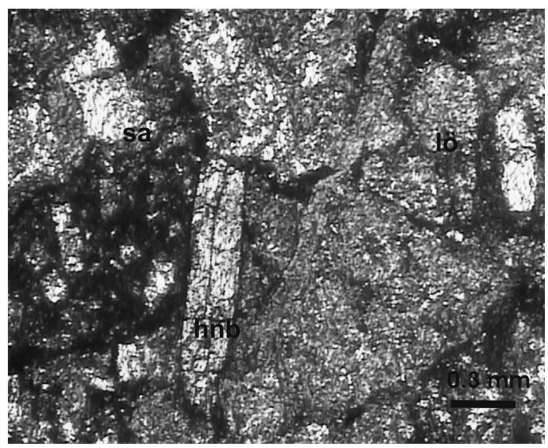

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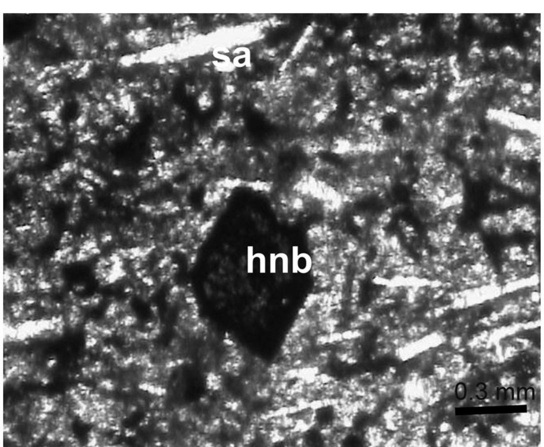

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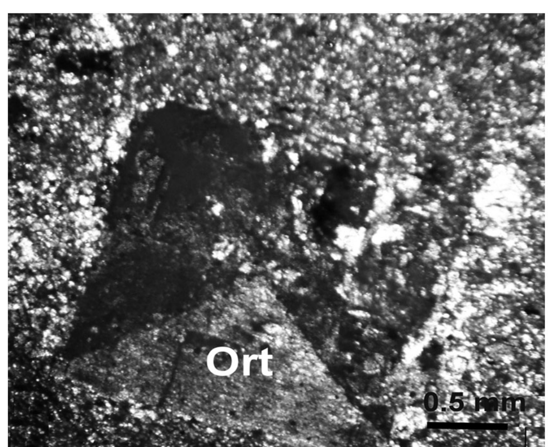

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PLATE II

Figure 1- Stereomicroscobic view of the crystals of aquamarine (A) at the left, emerald (Z) at the right, enlargement = 35X

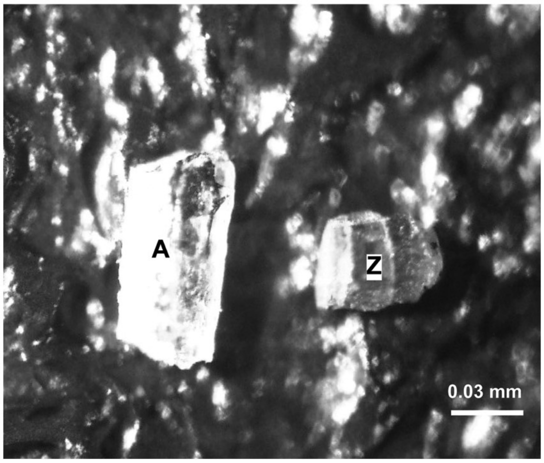
Figure 2- Emerald photo taken by stereomicroskobic view, enlargement = 35x

Figure 3- View of a beryl grain in a 1.60-immersion fluid

Figure 4- Emerald at single nicole, Obx Ok= 5x8

Figure 5- Basal cleavage (0001) on aquamarine is seen. Single nicole, Obx Ok= 5x8

PLATE - II



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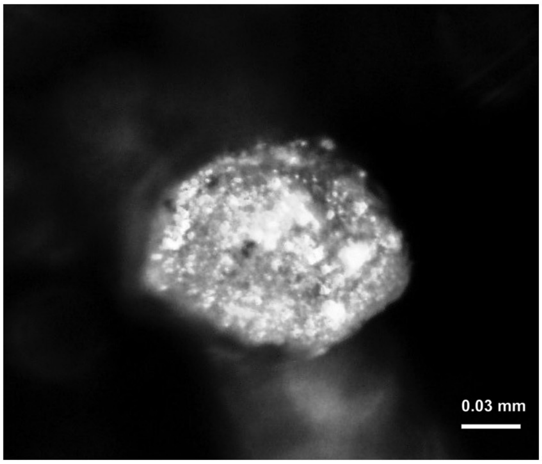

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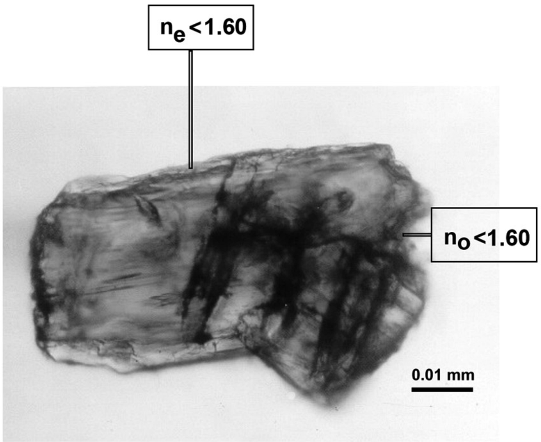

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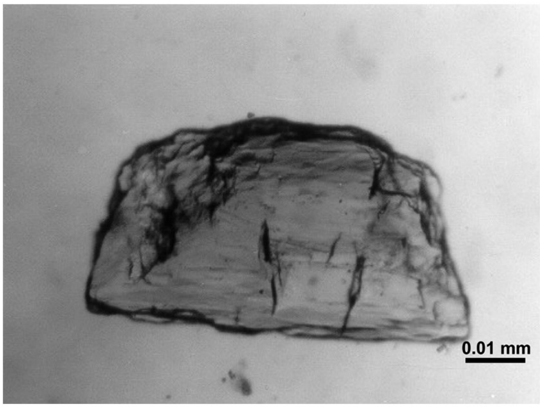

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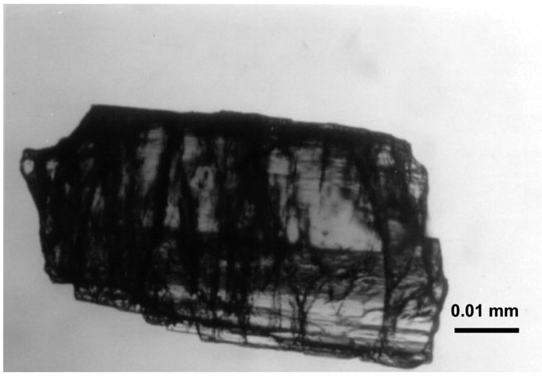

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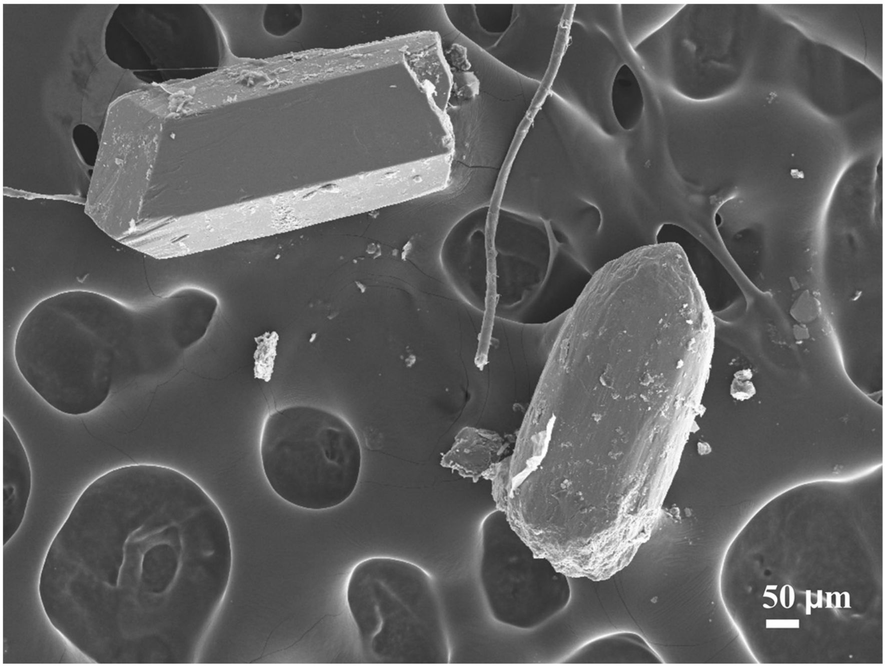
PLATE III

Figure 1- General view of beryl crystals

Figure 2- Surficial view of a hexagonal prismatic beryl crystal (0001)

PLATE - III



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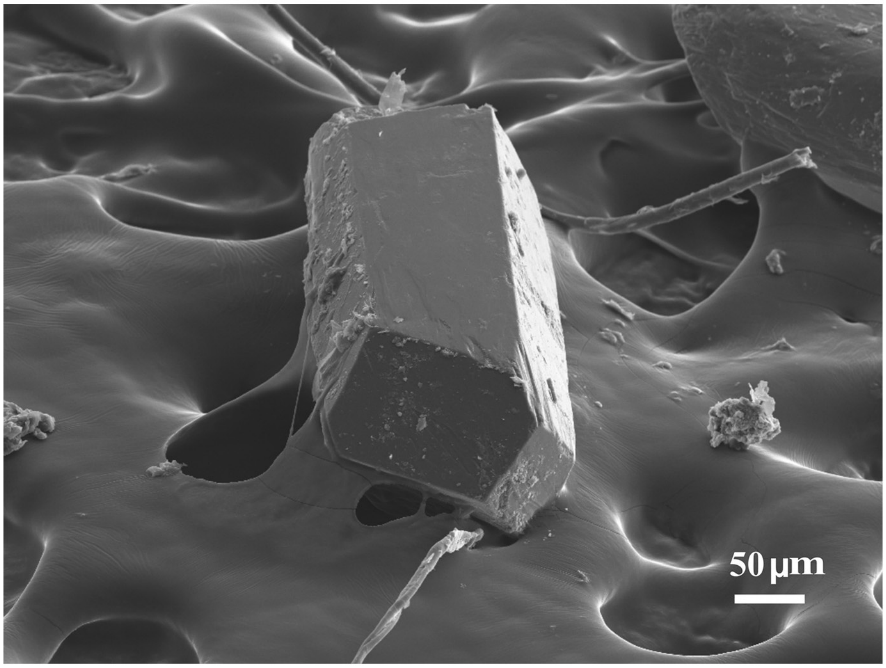

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