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SEDE BOGOTÁ
FACULTAD DE CIENCIAS
DEPARTAMENTO DE GEOCIENCIAS
RESEARCH GROUP IN GEOPHYSICS

ORE DEPOSITS

Occurrence of Cr-bearing beryl in stream sediment from Eskişehir, NW Turkey

Hülya Erkoyun and Selahattin Kadir *
Eskişehir Osmangazi University, Deparment of Geological Engineering, TR−26480 Eskişehir, Turkey
herkoyun@ogu.edu.tr skadir.euroclay@gmail.com
*corresponding author

ABSTRACT

Beryl crystals are found within stream sediments transecting schists in the northeast of Eskişehir, western Anatolia. This paper studied the Eskişehir beryl crystals with optical microscopy, scanning electron microscopy (SEM-EDX), infrared spectroscopy (IR) and geochemical analyses. Beryl is accompanied by garnet, glaucophane, quartz, epidote, muscovite and chlorite in the stream sediments. The crystals are euhedral emerald (green gem beryl) and light bluish-green aquamarine, with ideal sharp IR bands. Wet chemical analysis of Eskişehir beryl yielded 61.28% SiO_2, 15.13% Al_2O_3, 12.34% BeO, 0.18% Cr_2O_3, 1.49% MgO, 1.69% Na_2O, 0.98% Fe_2O_3, and 0.008% V_2O_3, resulting in the formula $(Al_{1.75}Cr_{0.01}Mg_{0.22}Fe_{0.08})(Be_{2.90}Si_{6.00})(Na_{0.32})O_{18}$. Large Ion Lithophile Elements (LILE) (barium, strontium), some transition metals (cobalt, except nickel) and High Field Strength Elements (HFSE) (niobium, zirconium, and yttrium) in stream sediments that are associated with beryl exhibited low content about metamorphic rocks. Beryl formation appears to be controlled by upthrust faults and fractures that juxtaposed them with Cr-bearing ophiolitic units and a regime of metasomatic reactions. Such beryl crystals have also been found in detrital sediments that are derived from the schists.

Keywords: Beryl, Kaymaz, schist, SEM-EDX, IR.

Presencia de berilios relacionados con Cromo en corrientes sedimentarias de Eskisehir, noroeste de Turquía

RESUMEN

Cristales de berilio fueron encontrados en sedimentos de corrientes que atraviesan en esquistos en el noreste de Eskisehir, al oeste de Anatolia. En este artículo se presentan resultados sobre el estudio de los cristales de berilio de Eskisehir con microscopio electrónico de barrido (SEM-EDX, del inglés Scanning Electron Microscopy), espectroscopia infrarroja y análisis geoquímicos. El berilio estaba acompañado de granate, glaucofana, cuarzo, epidota, moscovita, y clorito en las corrientes sedmientarias. Los cristales son esmeraldas de formas definidas (gema verde de berilio) y aguamarinas color verde celeste, con bandas de espectroscopia infrarroja de buena nitidez. El análisis químico húmedo del berilio de Eskisehir mostró 61.28 % de SiO_2, 15.13 % de Al_2O_3, 12.34 % de BeO, 0.18 % de Cr_2O_3, 1.49 % de MgO, 1.69 % de Na_2O, 0.98 % de Fe_2O_3, y 0.008% de V_2O_3, lo que resulta en la formula $(Al_{1.75}Cr_{0.01}Mg_{0.22}Fe_{0.08})(Be_{2.90}Si_{6.00})(Na_{0.32})O_{18}$. Los elementos litófilos de ion grande (bario, estroncio), algunos metales de transición (cobalto, excepto níquel) y los elementos de gran campo de fuerza (niobio, circonio e itrio) en las corrientes de sedimentos que están con berilio mostraron un bajo contenido sobre las rocas metamórficas. Las formaciones de berilio aparecen controladas por fallas de cabalgamiento y fracturas que se yuxtaponen con las unidades ofiolíticas relacionadas con cromo y un régimen de reacciones metasomáticas. Estos cristales de berilio se han encontrado también en sedimentos detríticos que se derivan de los esquistos.

Palabras clave: Berilio, Kaymaz, esquistos, microscopio electrónico de barrido, espectroscopia infrarroja.

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Introduction

The study area is in the village of Halilbağı, approximately 72 km northeast of the Eskişehir, western Anatolia (Fig.1). The area was previously explored to understand its structural geology and stratigraphy (Erentöz, 1975; Bingöl, 1976, Kulaksız, 1981; Gözler et al., 1996). Groat et al. (2008) and Arif et al. (2010) has classified the genetic types of beryl deposits. Worldwide, beryl deposits occur 1) in association with granitic pegmatite and hydrothermal veins in mafic-ultramafic rocks, with or without schist in contact zones (Kazmi and Snee, 1989; Sinkankas, 1994; Dereppe et al., 2000; Schwarz and Giuliani, 2001; Sabot, 2002). Emerald deposits in Poona (Australia) occur in quartz and pegmatite veins related to metasomatic reactions between quartz-muscovite or quartz-topaz-greisens and ultramafic units (Groat et al., 2008); 2) in schist-type deposits that are controlled by thrust faults and shear zones, with or without pegmatites (Sinkankas, 1994; Schwarz and Giuliani, 2001; Zwaan, 2006). The emeralds from Santa Terezinha (Brazil) formed in metasomatized mica schist related to hydrothermal fluids along thrust fault associated with pegmatite veins (Giuliani et al., 1997a,b); 3) related to black shale with veins and breccias controlled by thrusts and faults (Beus, 1979; Dereppe et al., 2000; Schwarz and Giuliani, 2001). The Colombian (Cordillera Basin) emerald is hosted in the Lower Cretaceous sediments (sandstone, limestones, black shales and evaporates) associated with stratiform breccias and mobilized black shales. Firstly, calcite, pyrite and muscovite filling veins related to hydrothermal fluids developed along faults. Secondly, extensional faulting and folding resulted in the formation of emeralds in voids accompanied by fluorite, dolomite, and quartz as breccia filling of defects (Giuliani et al., 2000; Pignatelli et al., 2015). 4) about oceanic suture zones (Dereppe et al., 2000). The emerald occurrences in Panjshir Valley (Afghanistan) associated with continental suture zone within intrusion of tourmaline-bearing leucogranite into serpentinite units that result of phlogopite bands containing jewels (Sabot et al., 2000); 5) in carbonate rocks (Sabot, 2002). The Swat Valley (Pakistan) emeralds occur as veins and stockworks within fractured quartz-bearing magnesite rocks and chromium-rich tourmaline in limonitized shear zones (Schwarz and Giuliani, 2002); 6) in granitic cupolas (Dereppe et al., 2000). The emeralds from Nigeria formed in pegmatite having contact with alkaline granite bedrock where the chromium is originated from basement schists or younger volcanic units (Schwarz et al., 1996); and 7) rarely, in alluvial-fluvial placer deposits (Dill, 2010). The gem deposits (beryl, chrysoberyl, amethyst, corundum, etc.) of the Ratnapura (Sri Lanka) developed by transportation from gem-bearing source rocks and deposition in old stream terraces and flood plains such as well-rounded gravel or lenses of sand (Dissanayake et al., 2000).

There has been no prior research on the chromium-rich beryl $[Be_3Al_2(SiO_3)_6]$ in the schists from the Halilbağı area (which are in tectonic contact with ophiolites), although Prime Ministry Archives (1993) reported that emeralds (a green gem variety of beryl) were discovered and mined in the Sivrihisar area during the Ottoman Empire. Therefore, the beryl crystals in proximal metamorphic rocks prompted the present study, with emphases on geochemistry, the genetic relationship between the beryl and metamorphic rock, and the mineralogy and geochemistry of beryl crystals that occur in sediments derived from the metamorphic rocks.

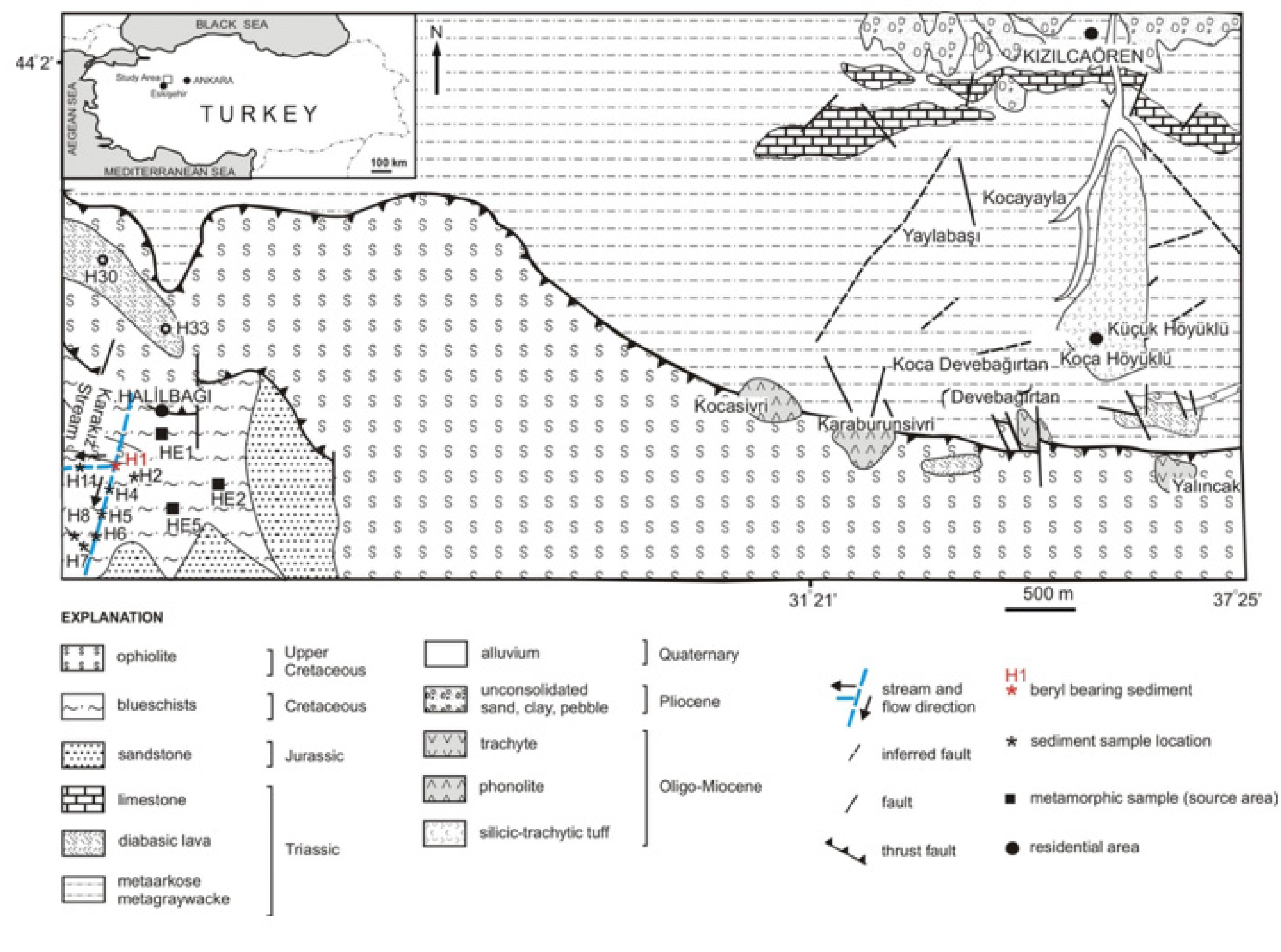

Figure 1. Geological map of the study area (modified from Gültekin et al., 2003; Sarıfakıoğlu et al., 2009).

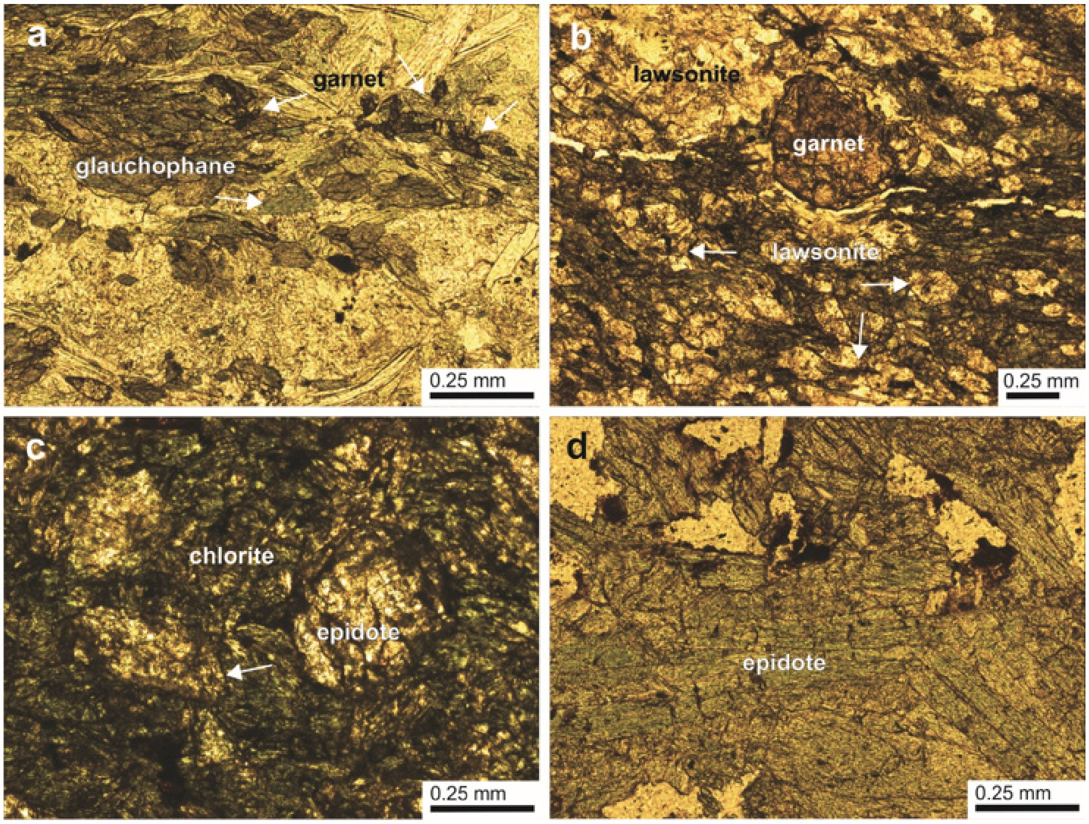

Figure 2. Photomicrographs showing views of a) garnet-glaucophane schist (plane-polarised light) (H1); b) garnet-lawsonite schist (plane-polarised light) (H6); c) epidote-chlorite schist (plane-polarised light) (H2); d) epidotite (plane-polarised light) (H7).

Geological setting

The basement of the study area consists of Triassic phyllites, phyllitic schists and partially metamorphosed clastic rocks (metaarkose, metagraywacke) (Kahya and Kuşcu, 2014)(Fig. 1). Triassic metasediments are overlain unconformably by Jurassic conglomerates and sandstones and Cretaceous Sivrihisar Massif blueschists (garnet-glaucophane schist, lawsonite-glaucophane schist, epidote-chlorite schist, epidotite, and chlorite-lawsonite schist) (Davis and Whitney, 2006). The blueschist facies comprise of sodic amphibole + garnet + phengite + lawsonite and/or epidote ± omphacite ± quartz characterizing a broad range of pressure-temperature conditions (12-16 kbar, 380-500 °C) (Okay, 2002). These units are tectonically overlain by Upper Cretaceous ophiolitic rocks (harzburgites, dunites, wehrlites, pyroxenites, gabbros, and serpentinites). These units are overlain by the Oligo-Miocene rocks comprising silicified and altered trachytic tuffs as well as fresh intrusive alkaline trachytes and phonolites. $^{40}Ar/^{39}Ar$ geochronological analyses of sanidine crystals from the phonolites have yielded an age of 25 Ma (Late Oligocene-Early Miocene) for the alkaline volcanic rocks (Sarıfakıoğlu et al., 2009). Temel (2001) concluded that the alkali basaltic and trachytic rocks of the Sivrihisar (Eskişehir) area are products of post-collisional Miocene alkaline volcanism in an extensional tectonic regime. Pliocene and Quaternary sediments overlie these units.

Structural features indicate that the study area is affected by major and minor E-W- and N-S-trending faults that have been under the tectonic influence of the North Anatolian Fault zone (Şengör, 1979; Şengör and Yılmaz, 1981; Gültekin et al., 2003).

Materials and methods

Twenty-nine sediment samples and twenty-nine rock samples were collected along creek valleys that transect the metamorphites, phonolites, trachytes, and pegmatites (outside the study area) in compliance with the principles of geochemical prospecting. Transparent and opaque minerals were separated from sediment samples using a stereomicroscope (Nikon SMZ-1B), and these minerals were grouped based on color and crystal form. Transparent, colored minerals considered to be beryl were separated, and the refractive indices (r.i.) of these minerals were determined under polarized light using 0.002 r.i.-spaced immersion oils; other optical properties were also measured.

The samples were analyzed for their mineralogical characteristics by polarized light microscopy (Leitz Laborlux 11 Pol), X-ray powder diffractometry (XRD) (Rigaku-Geigerflex), and scanning electron microscopy (SEM-EDX, JEOL JSM 84A-EDX). XRD analyses were performed at 40 kV and 30 mA with CuKα radiation; slits with divergence 1°, scatter 0.15°, receiving 1° and monochrometer 0.30 mm; and a scanning speed of 1° 2θ/min. Un-oriented mounts of four powdered sediment samples were scanned to determine the mineralogy of bulk samples. Representative beryl crystal samples were prepared for SEM-EDX analyses by adhering each beryl sample onto an aluminum sample holder that had been covered with double-sided tape and coated with a thin film (~ 350 Å) of gold using a Giko ion coater at Eskişehir Osmangazi University.

Infrared spectroscopy was performed using pressed pellets of powdered beryl crystal samples (2 mg of < 2 μm) mixed with 200 mg KBr and a PerkinElmer 100 FT-IR spectrometer; scans were made at 4 cm^{-1} resolution. Data were collected over the range 400-4000 cm^{-1}. Major element analyses and trace element analyses of four metamorphic sediment samples and one metamorphic rock sample were performed using the Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) method at Acme Laboratory Ltd. (Canada) to ascertain their beryllium contents. The detection limits for these analyses were between 0.01 and 0.1 weight percent for major elements, 0.1 and 0.5 ppm for trace elements, and 0.01 and 0.1 ppm for rare earth elements. The detection limit for beryllium was 1 ppm.

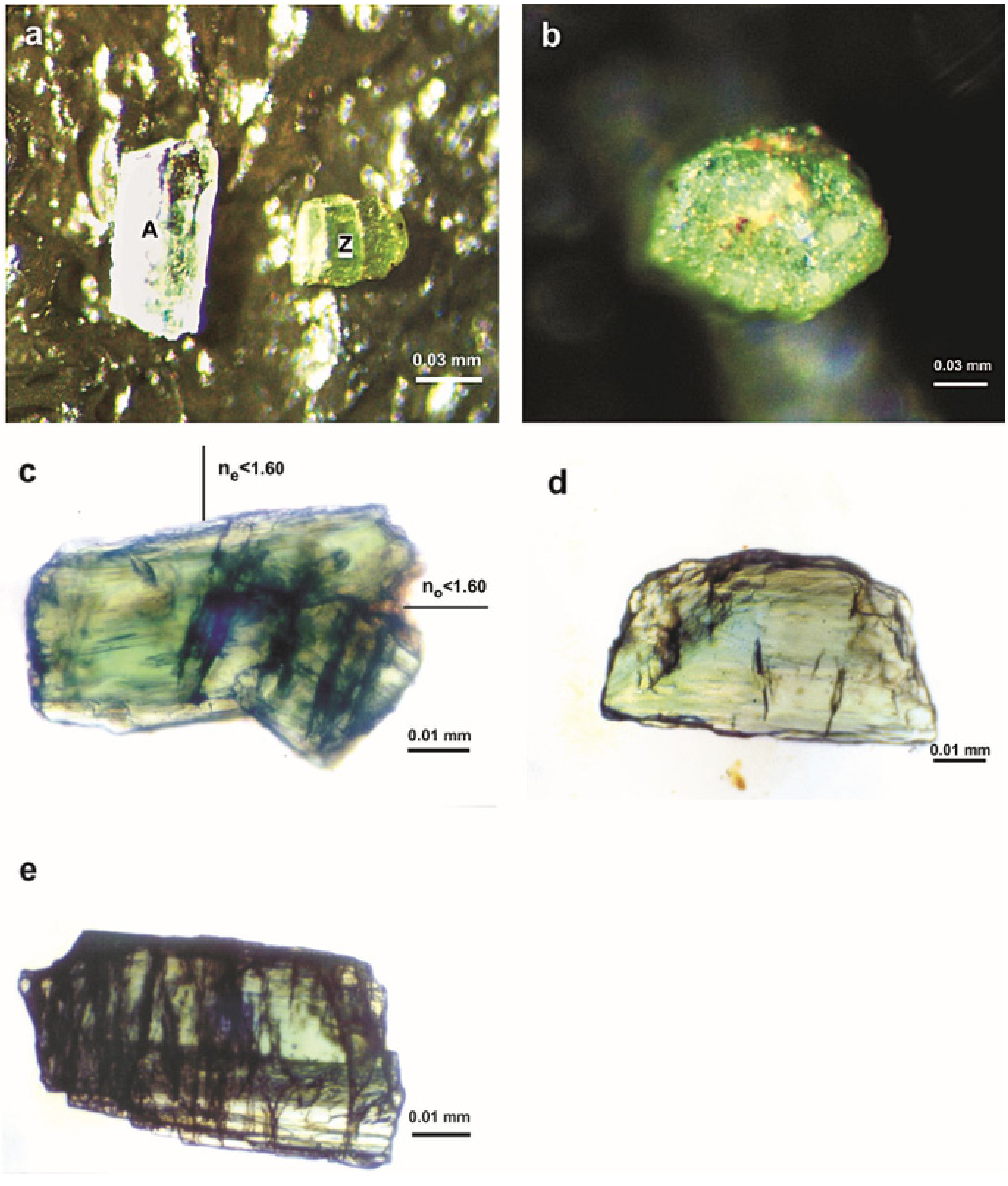

Figure 3. Various views of study-area beryl collected from stream sediments: a) stereomicroscopic view of crystals of aquamarine (A) on the left and emerald (Z) on the right; b) emerald crystal viewed using a stereomicroscope; c) view of a beryl grain in an immersion fluid with an r.i. of 1.60; d) emerald crystal (plane-polarized light); e) basal cleavage (0001) in aquamarine (plane-polarized light).

One emerald crystal was analyzed for all major and trace elements using both Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) and Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS) methods in the Analytical Services Laboratory of the University of Greenwich (UK). The sample was analyzed by ICP-OES and ICP-MS after dissolution using a lithium metaborate fusion (Jarvis and Jarvis, 1992). These methods are accredited to ISO 17025, by UKAS. In essence, 0.25 g of each sample was mixed with 1.25 g of lithium metaborate flux and fused at 900 °C. The molten bead was poured into weak nitric acid and stirred until dissolved. The resultant solution was made to volume. The analysis of major elements and some trace elements was undertaken using a Thermo ICAP 6500 ICP-OES with calibration via matrix-matched synthetic standards. Certified reference materials and internal QC powders were included within the analytical batch. Analysis of the remaining trace elements and rare earth elements was completed using a Thermo X Series 2 ICP-MS, again with calibration via matrix-matched synthetic standards and the use of CRM s and internal QC powders. Data quality was assessed post analysis via the use of Shewhart charts.

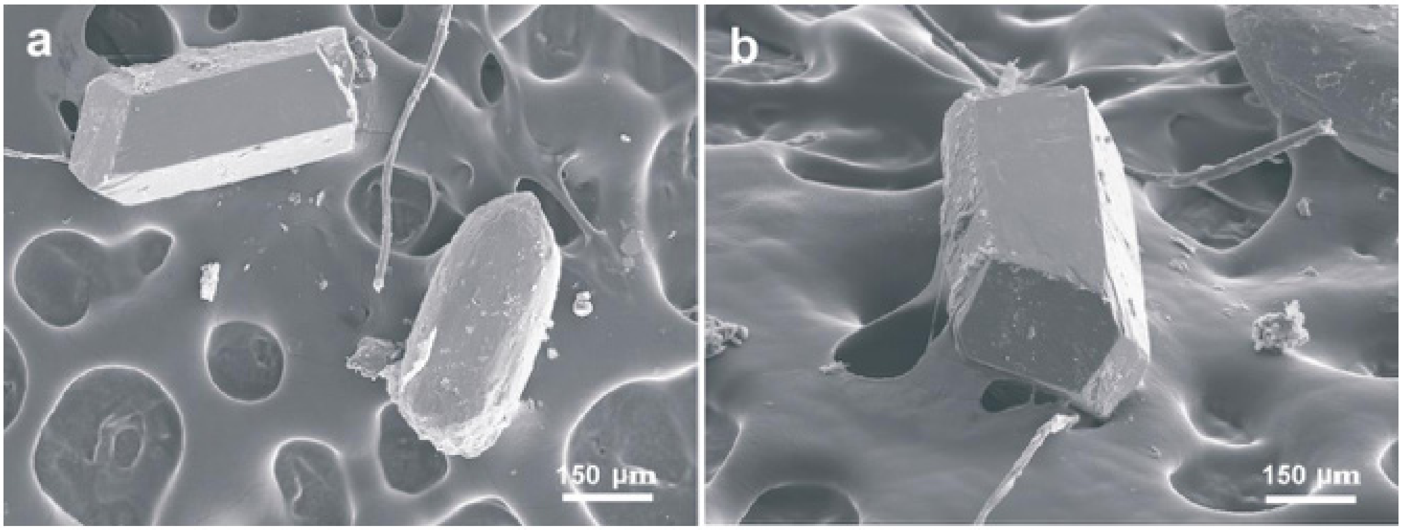

Figure 4. SEM images of a) beryl crystals collected from stream sediments; b) a close-up view of a hexagonal prismatic beryl crystal.

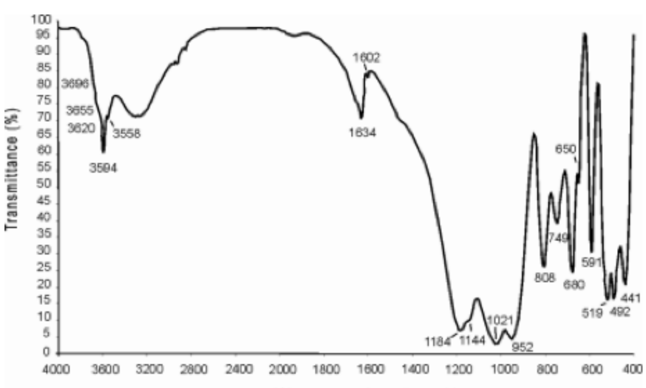

Figure 5. Infrared Spectroscopy spectra for an Eskişehir beryl crystal.

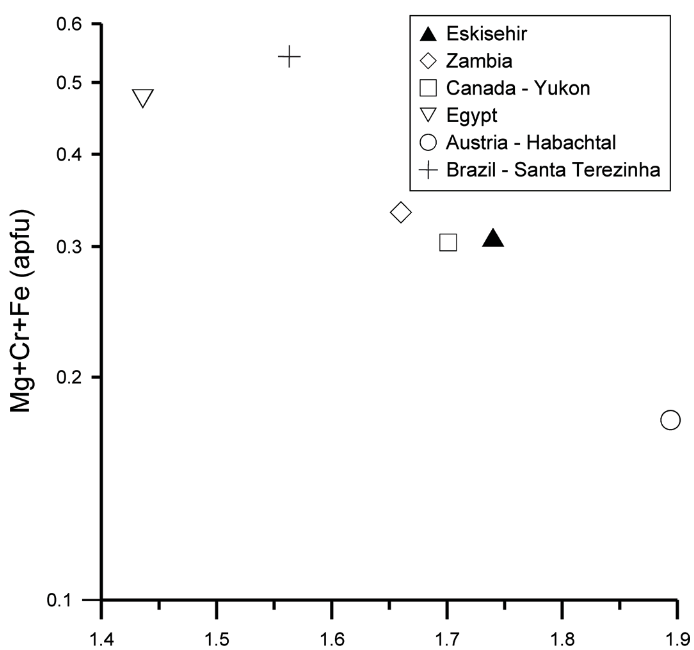

Figure 6. Aluminum versus the sum of Mg+Cr+Fe-site cations of octahedral beryl in atoms per formula unit; from beryl analyses from the literature (Leitmeier, 1937; Abdalla and Mohamed, 1999; Groat et al., 2002; Seifert et al., 2004; Gavrilenko et al., 2006).

Sample No	glaucophane	lawsonite	augite	sphene	garnet	epidote	mica/muscovite	chlorite	quartz
H1					++	+	+	+	+++
H5				+		acc			++++
H6	+	+	+++		+++				
H9		++	+++			+		+	

Table 1. Mineralogical variation in stream sediments of the study area. acc: accessory; +: relative abundance of mineral.

Sediment					Garnet-glaucophane schist	Lawsonite schist	Lawsonite-epidote schist	Peridotite	Pyroxenite
%	H1*	H1S	H2	H4	H1	Δ4-156	Δ3-114	+Y1	+Y12
SiO_2		47.91	53.66	45.67	42.2	45.27	45.62	38.28	21.30
Al_2O_3	6.68	5.88	9.88	7.04	11.91	18.46	14.07	2.26	0.38
Fe_2O_3	5.95	4.18	7.11	6.83	13.12			6.56	6.27
MgO	5.56	3.14	4.92	5.47	8.27	9.20	8.45	37.84	20.60
CaO	8.58	18.75	9.08	16.03	9.22	3.45	3.52	0.36	22.97
Na_2O	0.83	0.58	1.14	0.85	2.87	1.65	1.56	0.08	0.02
K_2O	0.33	0.74	1.08	0.67	0.91	-	-	<0.02	<0.02
TiO_2	0.48	0.51	0.88	0.79	3.23	1.52	2.11	0.01	<0.01
P_2O_5	0.13	0.15	0.18	0.13	0.89	-	0.37	<0.01	0.02
MnO		0.11	0.21	0.26	0.19	3.66	6.52	0.08	0.07
LOI		17.8	11.6	16	6.8	6.38	4.24	13.40	27.00
Sum		99.90	99.89	99.86	99.78			99.70	99.70
ppm									
Ba	96	101	149	96	119	151	190		
Be	**1**				**<1**	**0.5**	**21**		
Cr	**523**	**356**	**360**	**554**	**619**	**196**	**443**	**5515**	**7116**
Sc	13	10	18	15	20				
Co	31				50	80	111	103	101
Cs						2	1.3	<0.1	0.8
Ga								1	1
Hf						3	4.9	<0.5	<0.5
Nb	5	16	33	11	90	4	35	<0.5	<0.5
Rb						41	40	0.6	1
Sn	<2				<2			<1	<1
Sr	137		133	140	490	280	371	204	9
Ta						0.8	5.7	<0.1	<0.1
Th	<2				<2	0.3	4.4	<0.1	<0.1
U	<10				14	0.2	0.9	3	4
V	103				18	228	178	36	76
W	<4				<4			<0.1	0.3
Zr	7		91	80	285	117	210	0.5	2
Y	19		20	20	30	42	26	1	1
Pb	11				8	11	10		
Zn	51				33	98	134		
Ni	306		229	265	681	97	291	2103	1369
Ag	<0.5				<0.5				
Mo	<2				<2		2.2		

Notes: + = Sendir (2004), Δ= Davis and Whitney (2006). H1* = Beryl bearing sediment

Table 2. Chemical compositions of ophiolitic units, metamorphic sediments, and rocks that are associated with beryl in the study area.

	Eskişehir emerald	Zambia emerald [1]	Canada -Yukon emerald [2]	Egypt emerald [3]	Austria - Habachtal emerald [4]	Brazil - Santa Terezinha emerald [5]
%						
SiO_2	61.288	65.24	63.83	64.29	63.54	61.64
Al_2O_3	15.139	15.37	15.34	12.87	17.25	13.70
FeO_{tot}	0.98	0.90	0.46	0.96	0.64	1.08
Cr_2O_3	**0.18**	**0.15**	**0.41**	**0.15**	**0.12**	**0.72**
V_2O_3	**0.008**	-	-	-	-	**0.06**
MgO	**1.49**	**1.86**	**1.69**	**2.28**	**0.84**	**2.77**
CaO	<0.58	-	0.07	0.04	0.78	-
Na_2O	**1.69**	**1.73**	**1.18**	**1.73**	**1.42**	**1.50**
K_2O	<0.29	0.06	-	0.03	0.14	0.02
TiO_2	<0.17	-	-	-	-	-
P_2O_5	<0.12	-	-	-	-	-
MnO	<0.06	-	-	0.02	-	-
BeO	**12.34**	**13.58**	**13.27**	**13.00**	**13.07**	**12.90**
Si^{4+}	5.999	6.001	6.006	6.087	5.920	5.968
Al^{3+}	1.746	1.666	1.701	1.436	1.894	1.563
V^{3+}	-	-	-	-	-	0.005
Cr^{3+}	**0.013**	**0.011**	**0.031**	**0.011**	**0.009**	**0.055**
Be^{2+}	**2.902**	**3.001**	**3.000**	**3.025**	**2.925**	**3.000**
Mg^{2+}	**0.217**	**0.254**	**0.237**	**0.388**	**0.117**	**0.400**
Ca^{2+}	-	-	0.007	0.004	0.078	-
Mn^{2+}	-	-	-	0.002	-	-
Fe^{2+}	**0.079**	**0.069**	**0.036**	**0.076**	**0.050**	**0.087**
Na^{+}	**0.319**	**0.309**	**0.215**	**0.318**	**0.256**	**0.282**
K^{+}	-	-	-	0.004	0.017	0.002

Number of atoms (apfu) were calculated on the basis of 18 oxygen atoms. ICP-OES and ICP-MS methods were conducted.

ppm	
Ba	4
Sc	187
Co	2
Cs	269
Cu	112
Ga	10
Hf	<1
Ni	**68**
Nb	<2
Mo	4
Rb	25
Sr	<4
Ta	<0.3
Th	1
U	<0.5
W	4
Zr	<4
Y	<2
Zn	110

Data sources: [1] = Seifert *et al.* (2004), [2] = Groat *et al.* (2002), [3] = Abdalla and Mohamed (1999), [4] = Leitmeier (1937), [5] = Gavrilenko *et al.* (2006).

Table 3. The chemical composition of an Eskişehir octahedral emerald in schist compared to another emerald in metamorphic rocks of similar nature.

Results

Petrography and mineralogy

The metamorphic units comprise garnet-glaucophane schist (lepidoporphyroblastic texture), epidote-chlorite schist (lepidoblastic texture), garnet-lawsonite-glaucophane schist and epidotite (nematoblastic texture) (Fig. 2A-D). These units consist of glaucophane, garnet, lawsonite, muscovite, epidote, chlorite, augite, quartz, sphene and zircon. Locally, garnet crystal exhibit chloritization and carbonatization developed in microfracture.

The results of the stereomicroscopic and XRD analyses of stream sediments showed lawsonite, quartz, garnet, augite, glaucophane, muscovite, epidote and sphene. Beryl is associated with garnet, glaucophane, quartz, epidote, muscovite and chlorite in the stream sediment. Sediment samples from the Kaymaz stream, which transects the metamorphic rocks, were defined as emerald and aquamarine by transparency and color, with crystal sizes between 200 µm and 1 mm (e.g., H1 sample) (Fig. 3). The examination of green crystals using a stereomicroscope revealed that the hexagonal morphology (Fig. 3A-B); the refractive indices of these grains were found to be n_o= 1.568 and n_e= 1.584 (Fig. 3C). Based on optical studies of the emeralds (Fig. 3D) and light bluish green aquamarine (Fig. 3E) using polarized light and immersion oils, the analyzed grains were determined to be uniaxial (-), euhedral hexagonal-prismatic crystals. Stereomicroscopically determined beryl crystals were also analyzed by SEM (Fig. 4A-B); these crystals exhibit euhedral hexagonal prismatic forms, with locally corroded crystal edges.

Infrared spectra

Bands at 3594, 1634 and 1602 cm^{-1} correspond to the characteristic stretching vibrations of OH and H_2O molecules in the channel coordinated to Be^{2+} cations in tetrahedral coordination and Al^{3+} cations in octahedral coordination along the c-axis direction of the beryl crystal (Łodziński et al., 2005; Makreski and Jovanovski, 2009) (Fig. 5). 1184, 1144, 952, 749, 519 and 441 cm^{-1} bands are characteristic of the Si-O stretching vibration (Farmer, 1974; Łodziński et al., 2005). Bands at 808, 749, 680 and 650 cm^{-1} correspond to Be-O stretching, and bands at 519 and 492 cm^{-1} correspond to Al-O vibrations (Hofmeister et al., 1987; Viana et al., 2002; Łodziński et al., 2005; Makreski and Jovanovski, 2009).

Geochemistry

Major element and trace element analyses of selected schist, schist sediment, peridotite and pyroxenite samples are given in Table 2. Bulk stream sediment samples from the Karakız stream, which cuts the metamorphic rocks, are composed of high CaO (8.58-18.75%), Fe_2O_3 (4.18-7.11%), moderate MgO (3.14-5.56%), chromium (356-554 ppm), nickel (229-306 ppm), strontium (133-140 ppm), vanadium (103 ppm) and zirconium (7-91 ppm). The metamorphic rocks (garnet-glaucophane schist, lawsonite schist and lawsonite-epidote schist) contain appreciable amounts of Fe_2O_3 (13.12%), MgO (8.27-9.20%), moderate Al_2O_3 (11.91-18.46%), nickel (97-291 ppm), chromium (196-619 ppm), zirconium (117-285 ppm), cobalt (50-111 ppm), zinc (33-134 ppm), vanadium(18-228 ppm) and low beryllium (0.5-21 ppm). Large Ion Lithophile Elements (LILE) (potassium, rubidium, and lead) of the metamorphic rocks are depleted, whereas the metamorphic rocks are enriched with barium (119-190 ppm) and strontium (280-490 ppm). In general, LILE (barium, strontium except for lead, potassium), some transition metals (cobalt, except nickel) and HFSE (niobium, zirconium, yttrium except thorium) elements are relatively low or depleted compared to metamorphic rocks. However, chromium and nickel are enriched in stream sediments about the metamorphic rocks. Ophiolitic rocks (peridotite, pyroxenite) of the area contain 20.6-37.84 wt% MgO, 6.27-6.56 wt% Fe_2O_3, 5515-7116 ppm chromium and 1369-2103 ppm nickel.

Beryl chemistry

A chemical analysis of an Eskişehir beryl crystal is given in Table 3. This study reveals that the Eskişehir beryl has crystal chemistry of emerald compared to the composition of similar occurrences of octahedral beryl in metamorphic units of similar nature (Table 3). The calculated structural formula for this Eskişehir beryl is $(Al_{1.75}Cr_{0.01}Mg_{0.22}Fe_{0.08})(Be_{2.90}Si_{6.00})(Na_{0.32})O_{18}$. The high chromium value compared to vanadium and the ratio of Fe^{2+} to Fe^{3+} indicates that the green coloration of the Eskişehir emeralds is derived from chromium. The atoms per formula unit (apfu) for the emerald crystal were calculated based on 18 oxygen. The small aluminum value (1.746 apfu) in the Eskişehir emerald versus a high total value for the octahedral cations (Mg^{2+}, Cr^{3+}, Fe^{2+}), compared to the compositions of other schist-hosted emeralds, shows that the Eskişehir emerald is poor in aluminum (Al<1.75 apfu), similar to Canada-Yukon emeralds, as reported by Groat et al. (2002). Magnesium (0.217 apfu) and iron (0.08 apfu) cations are substituted for aluminum at the octahedral site of the emeralds structure, thus allowing this to be characterized as an octahedral beryl (Aurisicchio et al., 1988) (Fig. 6). Sodium was assigned to the channel site.

Discussion

Beryl rarely occurs in stream sediments of the study area as a result of resistance to alteration processes via short stream transportation distances and accumulates as euhedral to subhedral crystals in alluvial-fluvial placer deposits (Dill, 2010). Similarly, developed occurrences of beryl and other gem crystals in stream sediment by chemical and physical alteration of pegmatite, metamorphic and greywacke type units, were described in the state of Minas Gerais, Brazil (Proctor, 1984); the Ratnapura gem deposit, Sri Lanka (Munasinghe and Dissanayake, 1981; Dissanayake et al., 2000); and Ilakaka River gravels in Madagascar (Pezzotta and Simmons, 2001).

Beryl-bearing sediments of the study area that are derived from metamorphic units consist of garnet-glaucophane schist, lawsonite-glaucophane schist, epidote-chlorite schist, epidotite, and chlorite-lawsonite schist (Kulaksız, 1981) reflecting blueschist facies (Bucher and Frey, 1994; Davis and Whitney, 2006). Green and light bluish-green, hexagonal prismatic beryl crystals occur in stream sediment that transects the metamorphic units, suggesting that the chromium-rich beryl developed within the metamorphic rocks consisting of garnet, glaucophane, epidote, chlorite, feldspar, quartz, lawsonite, muscovite, augite and sphene. Its formation in the metamorphic units was controlled by syn- to post-tectonic deformation due to the upthrust of chromium-rich ophiolitic units, which resulted in metasomatic reactions. Thus, the concentration of magnesium-rich and beryllium-rich fluid favored the crystallization of beryl (Turner et al., 2005; Grundmann and Morteani, 2008; Groat et al., 2008). The host rock of this type of beryl occurrence is similar to beryl (emerald) deposits that are formed via syn- to post-tectonic reactions under low-grade regional metamorphism and within biotite schist tectonically overlain by ophiolite, such as in southern Egypt (Abdalla and Mohamed, 1999) and Habachtal, Austria, (Grundmann and Morteani, 1989) where the source of chromium is believed to be metasomatized ophiolitic rocks (Groat et al., 2008).

The green coloration of the Eskişehir emerald is due to the presence of chromium and, potentially, the ratio of Fe^{2+} to Fe^{3+}, similar to the emeralds of Zambia, Canada, Egypt, Austria and Brazil (Table 3). Aurisicchio et al. (1988) documented substitutions involving Fe^{2+}, Mg^{2+}, Mn^{2+}, Fe^{3+}, Cr^{3+}, V^{5+}, and Sc^{3+}, as well as V^{5+} and Ti^{4+}, for octahedrally coordinated aluminum, as well as lithium for tetrahedrally coordinated beryllium. Additionally, Eskişehir beryl can be classified as chromium-containing beryl according to the Gemological Institute of America (Sinkankas, 1994). The presence of chromium and nickel in the Eskişehir emerald crystals and the small values of barium, strontium, and rubidium suggest that crystallization of this beryl (emerald) crystals was due to a metasomatic-fluid reaction regime controlled by the upthrust of ophiolitic units onto the schists. Eskişehir beryl contains high Na_2O (1.69%) compared to K_2O (<0.29%) and indicates alkali-rich, sodic beryl

(Łodziński et al., 2005). The presence of type-II H_2O molecules narrow 3594 cm^{-1} and strong 1634 cm^{-1} bands corresponds to the presence of alkalis in the structural channels of beryl, similar to that described for beryls of the Sudety Mountains and Macedonian regions (Łodziński et al., 2005; Makreski and Jovanovski, 2009). These stretching bands decrease, and type-II H_2O disappears when the alkali content of the beryl falls (Manier-Glavinaz et al., 1989).

Magnesium is the main constituent of emerald that is derived from metamorphic rocks. The high magnesium contents of the metamorphic units may indicate a genetic relationship to beryl (Schwarz and Giuliani, 2001). The chromium (619 ppm) and nickel (681 ppm) contents in the garnet-glaucophane schist can be explained by the close association with ophiolitic rocks, which contribute chromium and nickel via leaching (Grundmann and Morteani, 2008). Furthermore, LILE (barium, strontium), transition metals (cobalt, except nickel) and HFSE (niobium, zirconium, and yttrium) element values that were low in stream sediments relative to metamorphic rocks suggest that these elements were transported during weathering of primary minerals, similar to what has been reported for LILE values in Sri Lanka (Chandrajith et al., 2000).

The low beryllium content of stream sediment (1 ppm) and rocks (0.46-21.09 ppm) in the study area is similar to that of other beryl-bearing metamorphic rocks and sediments in nature (Grundmann and Morteani, 1989; Grew, 2002). All major oxide (except SiO_2 and CaO) values decrease in stream sediment, possibly during transportation from altered metamorphic units. Beryllium-bearing fluid associated with SiO_2 and Al_2O_3 may indicate thermodynamic conditions (P, T) that are related to the alkalinity of melts and fluids through reactions (Barton and Young, 2002). Thus, beryl is stable under high silica activities and temperature (> 600°C) conditions. By contrast, a decrease of the silica activity of beryl may result in replacement with other beryl crystals, such as chrysoberyl and phenakite, which are absent in the study area.

The occurrence of alluvial gemstones was identified for the first time in the Eskişehir region (Turkey) during this study. This research may be significant for future use in investigations of beryl crystals that are associated with metamorphics and related sediments. Additionally, this study will also help identify the effect of tectonism and metasomatism on the formation of beryl crystals near ophiolite and metamorphic units and the local occurrence of beryls in sediment under short distance transportation from metamorphics.

Conclusions

The Eskişehir green color beryl crystals formed in schists via the upthrust in the Upper Cretaceous of chromium and magnesium-rich metasomatized ophiolites onto metamorphic units. Locally, the contact with ophiolites metamorphic unit is transected by streams, the sediments of which contain micrometric accessory beryl crystals. The euhedral, hexagonal beryl crystals have low refractive index value and between 200 µm and 1 mm sizes. The Eskişehir beryl's chemical composition is characterized by high chromium, iron and magnesium, reduced sodium, cesium and low potassium, vanadium and rubidium.

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