RARE EARTH ELEMENT GEOCHEMISTRY AND FLUID INCLUSION STUDY OF AKÇAKENT FLUORITE VEINS IN CENTRAL ANATOLIAN MASSIF OF TURKEY

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الخلاصة :

تتكون عروق الفلوريت في شقوق وصدوع الصخور الطباشيرية الأسوانية والجوفية في وسط تركيا. أظهرت المعلومات الجيولوجية وكيمياء العناصر الأرضية النادرة ومحتوى السوائل أن الفلوريت ذات أصل مائي حراري تبلور في المدى الحراري ١٤٠ – ١٨٠ درجة مئوية من خليط رسوبي وسوائل جوية. وترسبات الفلوريت هذه متشابهة تكّونت تحت ظروف متماثلة.

ABSTRACT

Fluorite veins of Akçakent (Central Turkey) occur in the fractures and fissures of the Upper Cretaceous–Paleocene syenites, and gabbros. Their geological setting, rare earth element geochemistry, and fluid inclusion data show that the fluorite is of hydrothermal origin, and has crystallized within a 140–180°C temperature range, probably from a mixture of magmatic and meteoric fluids. The fluorite deposition in the various veins was coeval and occurred under homogenous conditions.

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1. INTRODUCTION

The subject of this article is related to the fluorite veins, located around Karagüney Tepe, Kumlu Tepe, and Değirmendere, which are about 25 km towards the north of Akçakent in the Kırşehir province (Figure 1).

The Akçakent fluorite mineralizations occur in the fracture zones of Upper Cretaceous–Paleocene syenitic rocks and at the contacts between the syenite and gabbro. According to an earlier study on these mineralizations [1], the homogenization temperatures of fluid inclusions of the fluorite veins were found to be 130°–150°C. A second study on mineralization in the Central Anatolian Massif is related to the fluorite occurrence located near Kaman (Kırşehir) town. Thermo-optic analysis and rare earth geochemistry studies at Bayındır, İsahocalı, Yeniyapan, and Alişar villages of Kaman have been carried out in more detail [2–4]. In these investigations, the fluorite occurrences were determined to have formed under epithermal and mesothermal conditions. Mineralizations in different regions were compared in these studies and it was found that the fluorite belonging to the Alişar region seemed to have different REE (rare earth element) contents.

In the present study, fluid inclusion analyses as well as REE geochemistry of the Akçakent fluorite occurrences within the syenite have been carried out and the results are interpreted to determine the nature of the mineralizing fluids and the environmental conditions of fluorite deposition.

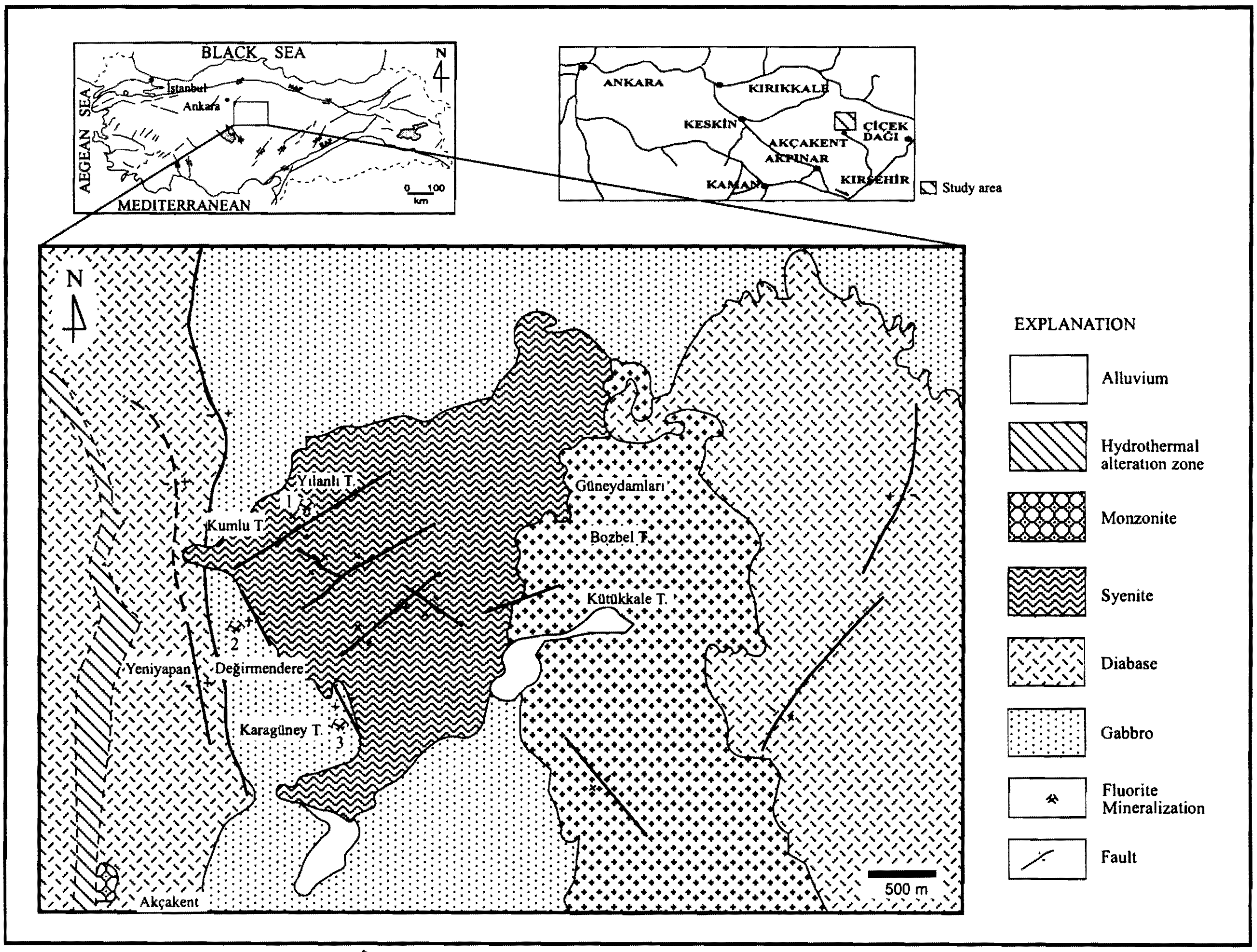

Figure 1. Location and geological map of the study area.

2. METHOD

The rare earth element (REE) analyses of 7 samples were carried out by the Acme Analytical Laboratories Ltd. (Canada). In the analysis, Inductively Coupled Plasma (ICP–MS) method was used. The homogenization temperatures and the salinities of fluid inclusions were determined at the Mining Research and Exploration Directorate (MTA)'s laboratories at Ankara on double polished thin sections, under the microscope, using heating and cooling apparatus capable of working in the temperature range between 640°C and –140°C.

3. GEOLOGY AND MİNERALIZATION

The study area is located in the Central Anatolian Massif where the Upper Cretaceous volcanic rocks are cut by Paleocene plutons [5]. The cover units consist of Eocene, Oligocene, and Neogene sedimentary rocks.

Pre-Mesozoic metamorphic rocks named as "Kaman Group" form the basement of the Central Anatolian Massif [6]. The units named as "ophiolitic series" by Ketin [7], and "ophiolitic mélange" named by Bailey and McCallien [8] and Seymen [9], overlie the basement unit. Both these units were cut by the Upper Cretaceous–Paleocene granitoids and alkali plutons [10]. Relatively younger felsic igneous rocks occur as flows or dykes. The metamorphic and igneous rocks of Lutetian age are covered by sedimentary rocks of upper Paleocene [11]. All these units in the region are unconformably covered by the Oligocene–Pliocene marine and continental deposits, as well as Miocene volcanics [9].

Four different units crop out in the studied area (Figure 1). These are mapped as Karagüney gabbros, Yeniyapan diabases, Yılanlı syenites, and Güneydamları monzonites. Besides these, a 250 m wide and 10 km long hydrothermal alteration zone within the Yeniyapan diabases was distinguished.

Karagüney Gabbro

This rock is typically exposed on Karagüney Tepe, where the gabbros cover large areas in the north and south of the studied area. These gabbros at some places show the cumulate structure, *e.g.* at Karagüney Tepe. The gabbros are cut by syenites and monzonites. They are composed of amphibole and plagioclase as the main constituents and show a granular texture. Some pyroxene relics were locally found in the amphiboles, besides some secondary epidote, calcite, and quartz.

Yeniyapan Diabase

The Yeniyapan diabase is a sub-unit of the Çiçekdağ (Kırşehir) volcanic rocks. The diabase seen mostly in the western and eastern parts of the studied area, is densely fractured. Multiple alteration zones are present along the contact between the Yeniyapan diabase and the Karagüney gabbro, whereas individual zones are too small to be mapped. The alteration comprises silicification, iron-oxidization, and carbonatization. Subophitic and ophitic textures are dominant in the diabases, which are composed of plagioclases and uralitized pyroxenes.

Yılanlı Syenites

The syenites, located in the central part of the studied area, cut the gabbros in the western part and gradually grade into monzonites in the east. These rocks show a hypidiomorphic granular texture and are composed of alkali feldspar, amphibole, and minor pyroxene, biotite, plagioclase, quartz, and opaque minerals. In general, the fractured syenites were intensely hydrothermally altered along the NE–SW and NW–SE trending normal faults. The grain size of fluorite varies from a few microns up to 3 mm. Mafic xenoliths measuring between a few millimeters up to a few centimeters were observed within the Yılanlı syenites. Such xenoliths suggest that the gabbros are the oldest intrusions of the Massif [12]. These xenoliths have recently been shown to be involved in magma mixing process [13].

Güneydamları Monzonite

These rocks outcrop typically around the Güneydamları area. They show similar properties to those of the Yılanlı syenites, and are composed of amphibole, orthoclase, plagioclase, biotite, and rarer minor pyroxenes. Accessory minerals include quartz, epidote, calcite, and opaque minerals.

In the fractured and fissured zones of the monzonites, fluorite enrichments exist, as seen in the syenites. However, monzonites do not include any magma mixing xenoliths that are observed in the syenites. The Güneydamları monzonites cross cut diabases in the eastern part of the studied area.

Hydrothermal Alteration

Hydrothermal alteration zones have developed along the fractures in the diabases and syenites. The alterations observed are mostly hematitization and carbonatization in the diabases and silicification in the syenites.

4. GEOLOGICAL ATTRIBUTES OF THE MINERALIZATION

The Akçakent fluorite occurs in the fractures and fissures of the syenites, and in the contact between the syenite and gabbro. The fluorite generally occurs as asymmetric vein fillings, with local lensoid bodies. Quartz is always associated with fluorite in the veins. Calcite also occurs in some veins. Purple, green, dirty yellow, and yellowish white colored fluorite crystals are present in the veins. The age of the intrusive igneous rocks, hosting the mineralization, is of Upper Cretaceous–Paleocene [7, 9]. Yaman [1] gave the lower age limit of these fluorite as the end of Paleocene, based on Ketin's [17] and Seymen's [9] age determination of plutons as Paleocene. Considering their host rocks and age relations, the İsahocalı, Bayındır, Yeniyapan, and Alişar fluorite mineralizations of the Kaman region, are similar to the Akçakent fluorite veins [3, 4]. On the other hand, the Pöhrenk fluorite occurrences of Kırşehir region, situated in the fractures and fissures of the Middle Eocene–Pliocene aged limestone and marls, do not match these occurrences [14]. The fluorite mineralizations in the Central Anatolian Massif range in age from upper Cretaceous to Pliocene.

5. RARE EARTH ELEMENT GEOCHEMISTRY OF AKÇAKENT FLUORITE VEINS

REE analyses of seven different samples taken from various veins have been conducted and the received data as contents are given in Table 1. Plot of log Y *versus* log Yb is shown in Figure 2. All the samples from the Akçakent veins plot in the A-type field. Assuming Tümenbayar's [15] criteria, this A-type field stands for epithermal conditions. Tb/Ca ratios of the fluorites are used as the environmental guides with high Tb/Ca indicating a pegmatitic origin and low Tb/Ca indicating a sedimentary origin of the fluorite [16–19]. In the diagrams that plot Tb/La *versus* Tb/Ca ratios [16, 17], the Akçakent fluorites fall in the form of hydrothermal origin (Figure 3). The relatively narrow range of REE contents implies that the solutions suffered only limited changes in these elements' contents during the formation of the fluorite.

Table 1. REE Contents of the Akçakent Fluorites.

Sample no.	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Total REE
YA8y	28.8	16.0	31.6	5.7	11.4	3.1	0.9	2.3	0.5	2.9	0.3	1.7	0.2	1.6	0.3	107.3
YA10y	22.7	13.1	28.2	4.9	9.7	2.5	0.8	2.1	0.4	2.4	0.3	1.4	0.3	1.4	0.2	90.4
YA68y	31.6	14.3	32.9	5.6	11.8	3.1	1.0	2.6	0.5	3.1	0.3	1.9	0.3	1.8	0.3	111.1
YA70ym	23.4	12.3	31.8	3.5	10.2	2.6	0.8	2.2	0.5	2.6	0.6	1.5	<0.2	1.4	0.2	93.6
YA70mm	13.2	5.1	12.3	2.1	4.2	1.4	0.4	1.2	0.2	1.6	0.4	0.9	0.2	0.9	<0.2	44.1
YA73y	52.8	3.5	8.8	1.8	3.2	1.2	0.4	1.7	0.4	2.7	0.7	1.8	0.2	1.6	0.2	81.0
YA73m	75.1	8.9	18.1	1.9	6.4	2.1	0.7	3.2	0.8	4.9	1.1	3.2	0.3	3.2	0.5	130.4
Average	35.4	10.5	23.4	3.6	8.1	2.3	0.7	2.19	0.47	2.9	0.5	1.8	0.25*	1.7	0.28*	
Max	75.1	16.0	32.9	5.7	11.8	3.1	1.0	3.2	0.8	4.9	0.3	3.2	0.3	3.2	0.5	
Min	13.2	3.5	8.8	1.8	3.2	1.2	0.4	1.2	0.2	1.6	1.1	0.9	<0.2	0.9	<0.2	

* Average values are calculated without < values.

As shown in Figure 4, the Y/Ho diagram [20] divides the depositional environments of fluorite into igneous, seawater, hydrothermal, and sedimentary fields. All Akçakent samples fall into the hydrothermal range, with the Y/Ho ratio above the chondrite values. If mixing of hydrothermal solutions were not encountered, the Y/Ho ratios would be constant [21]. If the associated rock alteration product and surficial waters were mixed into the composition of the solution, then Y and REE contents may have changed [20]. In addition, it is known that changes in temperature of the environment, pressure, pH, and oxygen fugacity values may affect the degree of fractionation of Y and Ho [22–25]. A broad linear relation between these two elements is recognized for the Akçakent fluorite (Figure 5). Such distribution of Y and Ho implies that addition of associated rock alteration product and surficial water to the hydrothermal solutions might have taken place, before the deposition of fluorite.

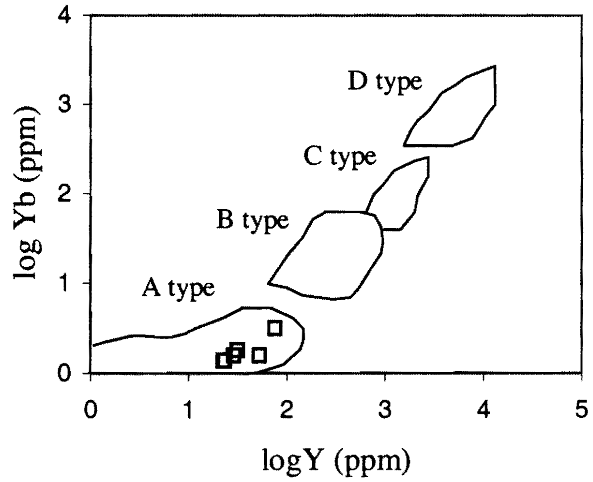

Figure 2. Log Y versus *log Yb diagram of the Akçakent fluorites (open squares).*
A Type: Epithermal fluorites; B Type: Hydrothermal fluorites;
C Type: Pegmatitic fluorites; and D Type: Magmatic fluorites. The field are drawn after Tümenbayar, 1996 [15].

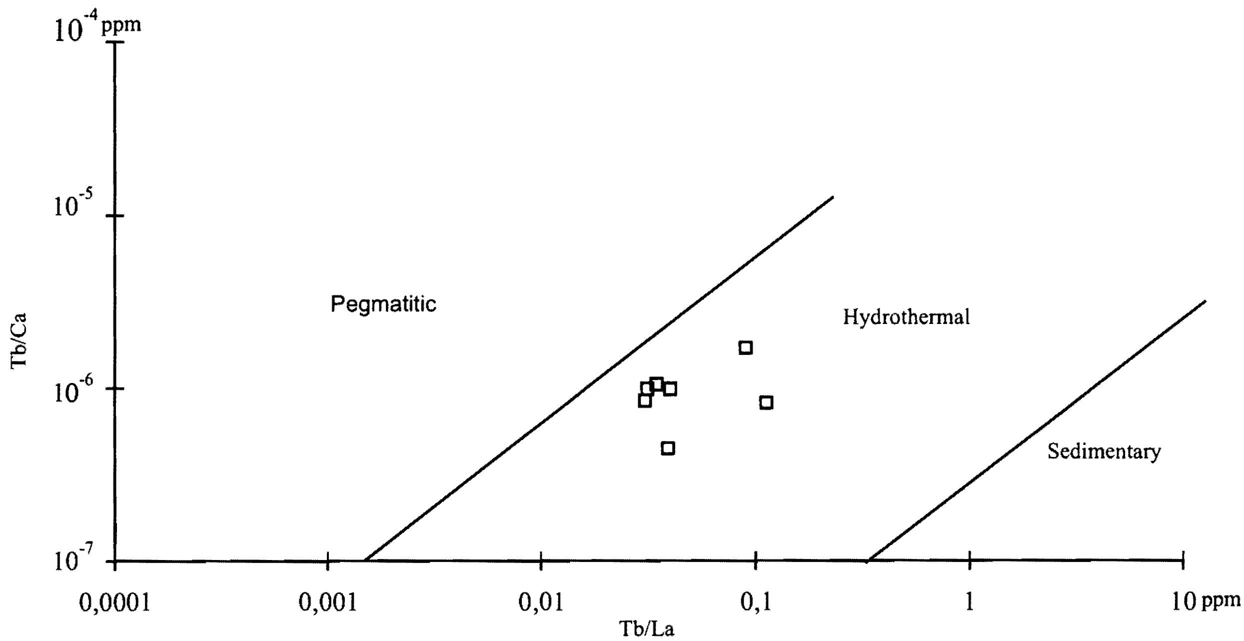

Figure 3. Tb/La versus *Tb/Ca diagram of the Akçakent fluorites (open squares).*
The fields are drawn after Schneider et al. *1975 [16]; Möller* et al. *1976 [17].*

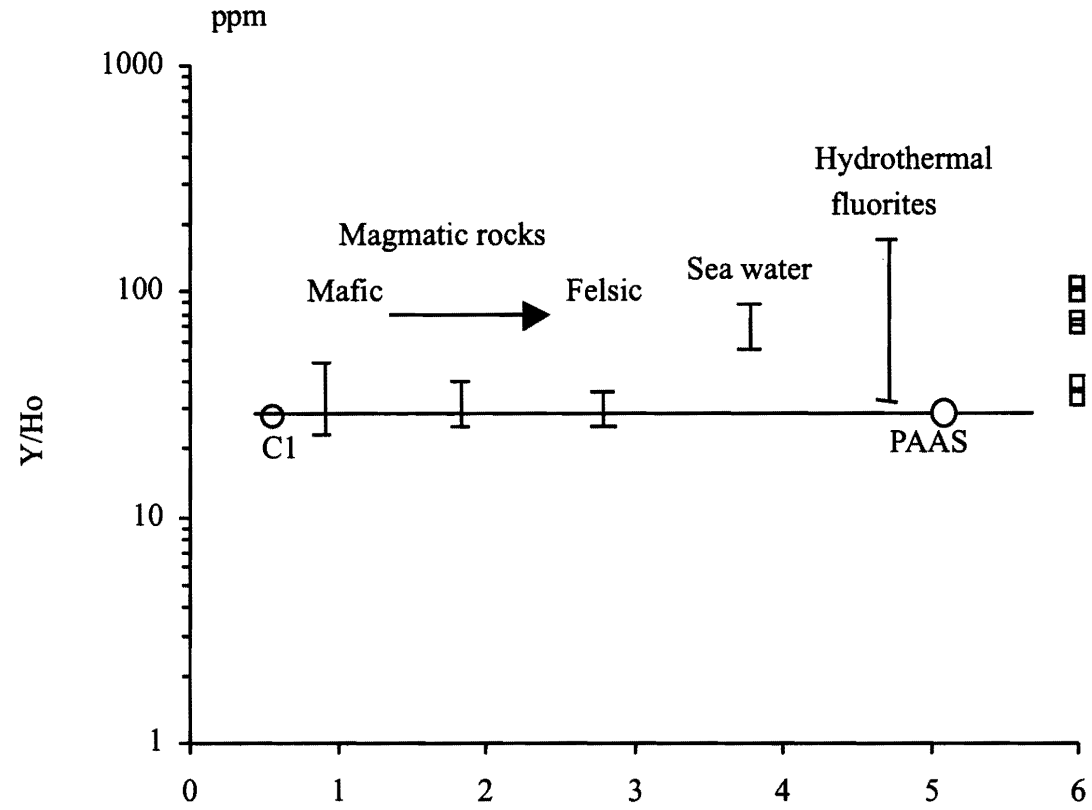

Figure 4. Y/Ho ratios of the Akçakent fluorites (6) compared to those for the igneous rocks (1–3); seawater (4); hydrothermal fluorites (5); c1: Chondrites; PAAS: Post Archean Australian Average Shale. The fields are drawn after Bau and Dulski 1995 [20].

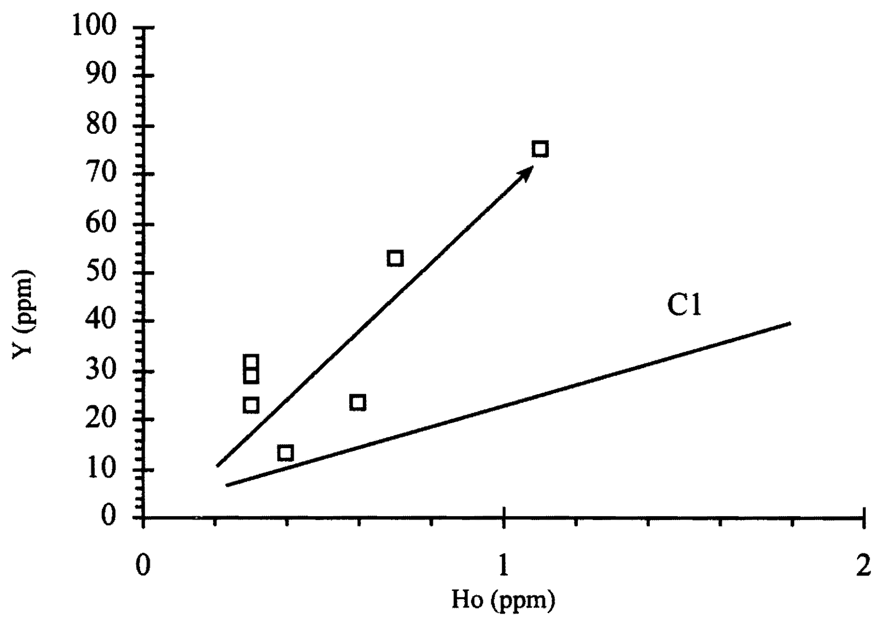

Figure 5. Y versus *Ho diagram of the Akçakent fluorites (open squares) (as explained in the text). The fields are drawn after Bau and Dulski 1995 [20].*

The diagram using La/Ho and Y/Ho gives information about the fluorite deposition (Figure 6). If they are not syngenetic mineralizations, a negative correlation between these ratios would be expected [20, 26]. As seen in Figure 6, the Y/Ho of Akçakent fluorite show almost the same ratios, which are thought to exhibit mostly recrystallization and syngenetic processes. La/Ho ratios seen on the horizontal axis change between 5.00 and 53.00, whereas the Y/Ho values change between 33.00 and 105.33 (Figure 2).

REE contents of the Akçakent fluorite normalized to the chondrite values are shown in Figure 7. Ce and Nd show negative anomalies in most samples. In addition, negative anomalies of Ho and Gd in four elements are exhibited. Negative anomalies of Tm are seen in three samples and positive anomalies in four samples. There is no significant difference between the light rare earth elements (LREE) and the heavy rare earth elements (HREE). Non-enrichments of LREE indicate the absence of any noticeable fractionation of REE during the fluorite crystallization. Oxygen fugacity of hydrothermal solutions controls the enrichments of Ce and Eu. Generally, negative Ce and positive Eu anomalies indicate high oxygen fugacities [17–19]. According to this, the very low anomaly of Ce seen in the Akçakent fluorite, together with the absence of any positive Eu anomalies, is an indication of a low oxygen fugacity. A discernable negative anomaly of Nd can be explained by its tendency to remain in the solution during crystallization. In the same way, the behavior of Gd in four samples showing negative anomalies can also be explained by its residence in the solution. Ho shows no anomalies in four samples and negative anomalies in three samples. The negative anomaly of Ho is not expected during crystallization. Since the ionic radius of Ho is close to Ca, it may be concentrated fluorite. This shortage, as seen in the negative anomaly of some of the veins, can be explained as a Ho loss during a possible recrystallization process, as mentioned before.

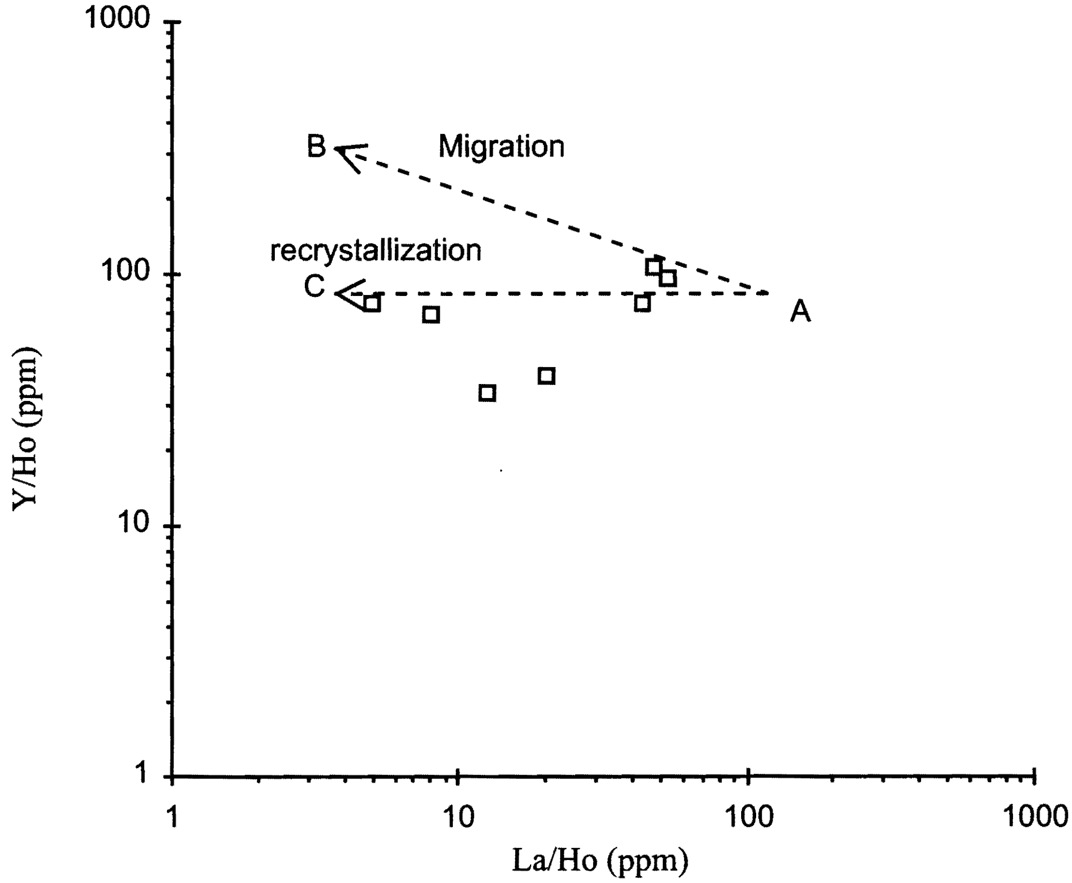

Figure 6. La/Ho versus *Y/Ho diagram of the Akçakent fluorites (open squares). The fields are drawn after Bau and Dulski 1995 [20].*

6. FLUID INCLUSION STUDIES

Fluid inclusion studies were performed on variously colored, medium to coarse, crystallized samples to reveal the formation conditions of the Akçakent fluorite. Some primary and secondary two-phase (fluid–vapor) inclusions were observed in the fluorite crystals (Figure 8). The sizes of such inclusions vary from 2 to 80 μm. Homogenization temperatures of primary inclusions vary from 110° to 280°, whereas homogenization temperatures of secondary inclusions mostly range between 140° and 180°C (Figure 8). On the other hand, Yaman [1], reported that homogenization temperatures for three different veins range as 150°–160°C, 140°–150°C, and 120°–130°C, respectively.

The cooling experiment was performed on the same inclusions. The melting temperature were found between 0° and 3°C, and the eutectic temperature as –30°C. These values are consistent with the result of Yaman [1]. This eutectic temperature seems to imply that the fluorite-forming solutions contained NaCl + KCl + $MgCl_2$ + H_2O [27, 28]. The salinity was estimated to be as 4.3–5.9% NaCl equivalent.

Our data show that the hydrothermal solution depositing the fluorite consisted of a mixture of magmatic and meteoric waters.

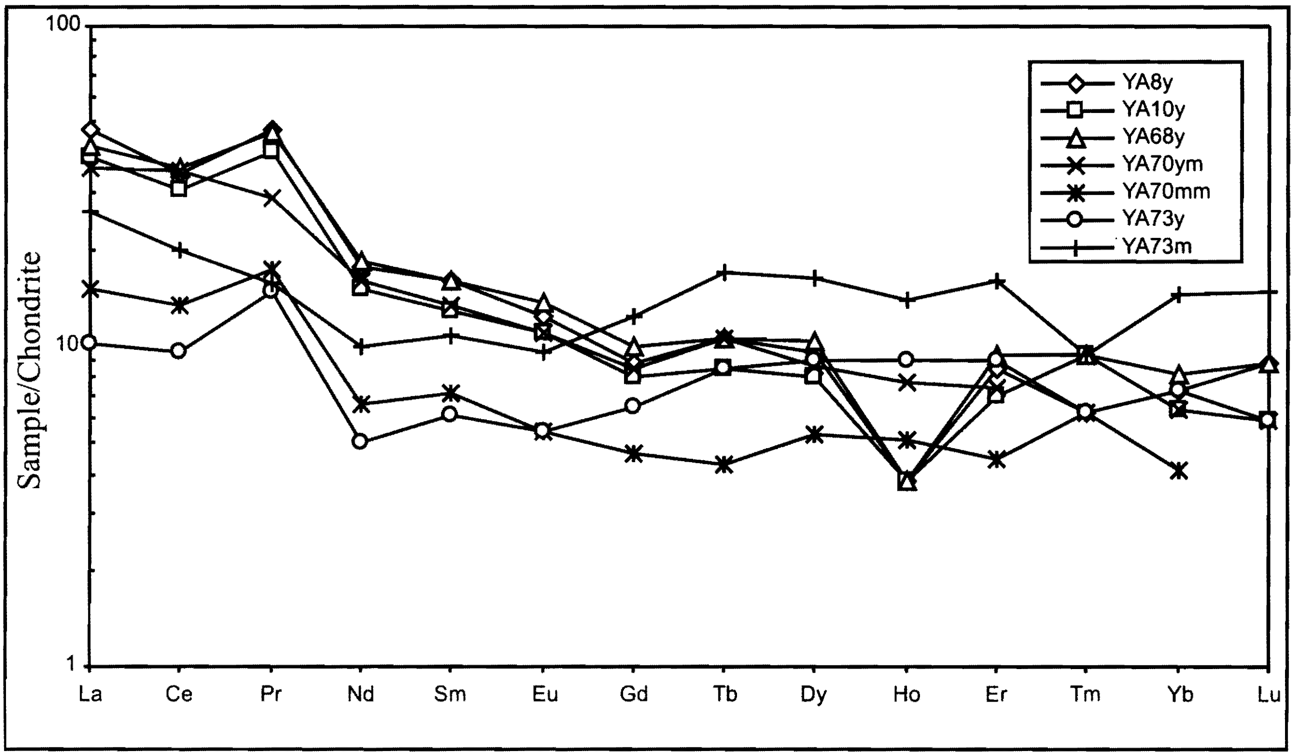

Figure 7. Chondrite-normalized REE patterns of the Akçakent fluorite samples.

7. CONCLUSIONS

This study infers that the Akçakent fluorite were deposited as hydrothermal veins in the fracture and fissure of upper Cretaceous–Paleocene syenites and at the contacts between syenites and gabbros. The REE content of the fluorite veins also indicate its hydrothermal genesis. Relation between the Y and REE contents suggests that there were almost no changes in the contents of these elements in the hydrothermal solutions before fluorite deposition. Despite this, the distribution of Y and Ho shows that there was some mixing of the associated rock components and surficial waters with the hydrothermal solutions before the deposition of the fluorite. Since, in the Akçakent, fluorite does not show any distinctive REE anomalies, there were not significant changes in the environmental conditions during the deposition.

This conclusion is supported by the absence of any significant fractionation changes between the LREE and HREE contents during the formation of the fluorite veins. The similar Y/Ho and La/Ho ratios of the Akçakent fluorite veins show recrystallization and syngenetic process. The Ce and Eu contents of the fluorite imply that the mineralization took place under low oxygen fugacities.

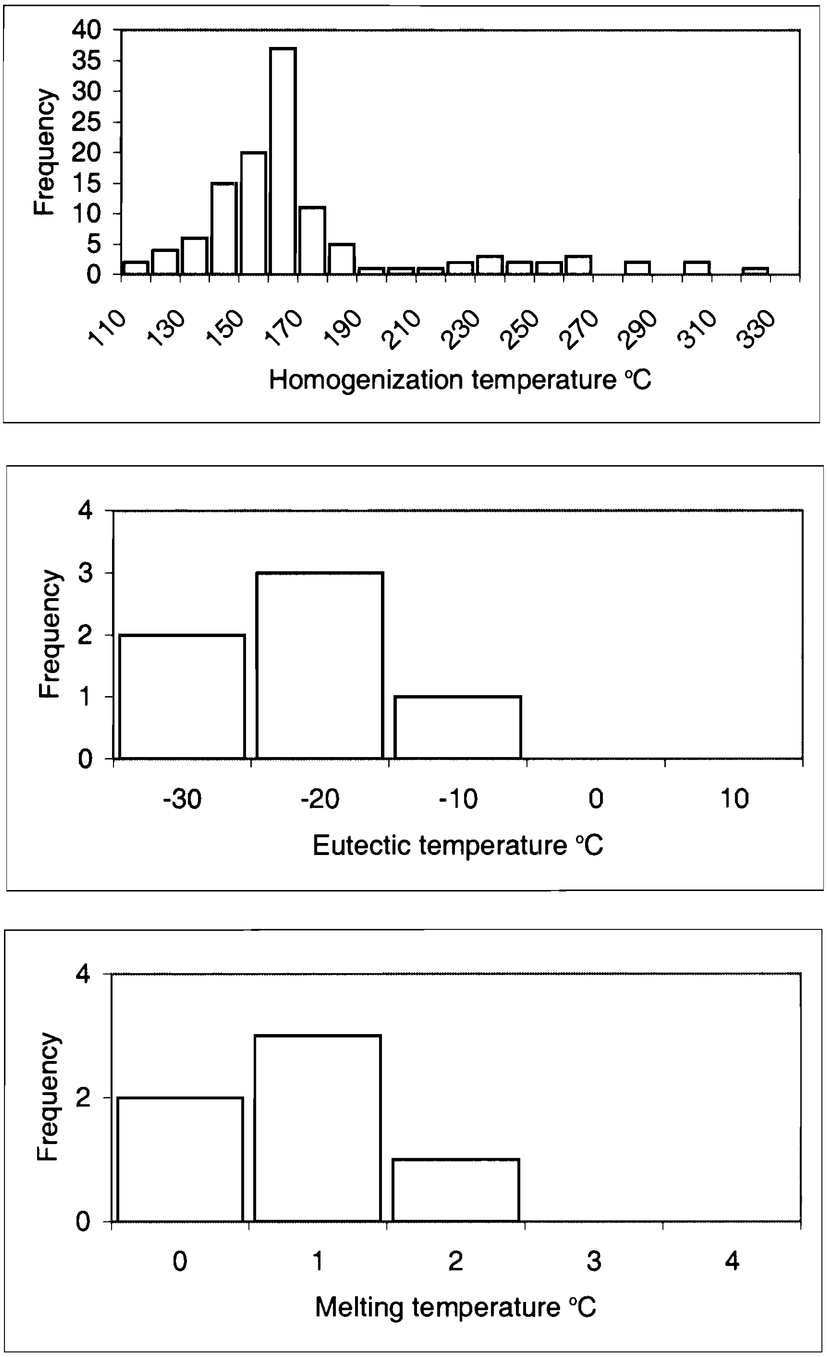

Figure 8. Histograms of primary and secondary fluid inclusions in two phases (liquid + vapor); freezing and heating of the Akçakent fluorites.

The fluid inclusion homogenization temperatures vary between 110° and 280°C, with most values concentrating between 140° and 180°C. The melting temperatures range between 0° and 3°C and eutectic temperatures extend down to –30°C. This eutectic temperature suggest that the composition of the fluorite-forming hydrothermal solution is of NaCl + KCl + $MgCl_2$ + H_2O type. A salinity ranging between 4.3 and 5.9% NaCl equivalent is indicated for the hydrothermal solutions.

The overall results suggest that, the Akçakent fluorite veins were deposited coevally from a hydrothermal solution, probably composed of mixtures of magmatic and meteoric fluids under epithermal temperature conditions. The mineralization process were affected very little by hydration as well as recrystallization.

8. ACKNOWLEDGEMENTS

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