

REE geochemistry and fluid-inclusion studies of fluorite deposits from the Yaylagözü area (Yıldızeli-Sivas) in Central Turkey

Ahmet Sasmaz and Fuat Yavuz

With 11 figures and 2 tables

Abstract: Skarn- and vein-type fluorite deposits in the vicinity of Yaylagözü, Yıldızeli-Sivas, are found within the syenites and their skarn zones that are located in the Central Anatolia Massif. Mining was active on several fluorite mineralizations during the early 1950s, but is presently inactive. The goal of this study, on the basis of REE geochemistry and fluid inclusion investigations, is to explain the genesis and physicochemical conditions of fluorite mineralization hosted by calc-alkaline to alkaline syenites of Upper Cretaceous age.

The rare-earth element content of the Yaylagözü fluorite is quite variable. Fluorites have moderate to high total REE contents ranging from 68 ppm to 5288 ppm, with a mean of 907, compared with the fluorite occurrences elsewhere both in hydrothermal and sedimentary origin. Light rare-earth elements (LREE) are enriched in all the studied fluorite samples. Chondrite-normalized La/Lu ratios range from 13.7 to 364, regardless of color variation in fluorites. This, as well as low Tb/La ratio, is indicative of early crystallization of fluorite from the mineralizing solution. The Tb/La and Tb/Ca ratios of fluorites in the present study indicate that they plot mainly in the “pegmatitic” or “high-hydrothermal” field of the diagram of MÖLLER et al. (1976) with the characteristics of primary crystallization and remobilization trends. Fluid inclusion microthermometry indicates that the fluorite in most of the veins was formed from the fluids at temperatures between 161 ° and 243 °C. Primary fluid inclusions for samples plotting into the “pegmatitic” field of the MÖLLER et al. diagram (1976) has the highest homogenization temperatures.

Key words: Fluorite, fluid inclusion, REE, skarn, syenite, vein, Central Anatolia, Yaylagözü.

1. Introduction

Fluorite of varied color and habit occurs in a wide range of ore deposits, from low-temperature and moderate salinity epithermal veins and replacements to high-temperature and high-salinity magmatic deposits such as greisens, skarns, porphyries, and pegmatite systems (KESLER 1977, RICHARDSON & HOLLAND 1979, GOLDRING & GREENWOOD 1990, GALINDO et al. 1994, SUBIAS & FERNÁNDEZ-NIETO 1995, HILL et al. 2000, WILLIAMS-JONES et al. 2000, CONIGLIO et al. 2000, BÜHN et al. 2002, GAGNON et al. 2003).

Calc-alkaline to alkaline magmatism gave rise to numerous polymetallic ore deposits associated with fluorite in Central Turkey (TÜLÜMEN 1980, SAGIROGLU 1982, SASMAZ 1999). The study area comprises metamorphic rocks of the Central Anatolian Massif with numerous

calc-alkaline to alkaline intrusive bodies. At the contacts of the metamorphic and magmatic rocks, various base-metal sulphide deposits (Pb, Zn, Fe, and Cu) were formed. Fluorite was deposited either as a single phase or as an accessory phase in most of the base-metal sulphide deposits. Many fluorite deposits occur near Kırşehir, Yozgat, and Sivas in the Central Anatolian Massif, which also is known as the Kırşehir Massif (KOÇ et al. 2003, SASMAZ et al. 2005). The Yaylagözü fluorite deposits occur as vein- and skarn-type mineralizations (Fig. 1). Some of these veins were explored by ZESCHKE (1953), but were not subjected to detailed geochemical and fluid-inclusion research. In this study, we report REE and fluid-inclusion data in order to understand the physicochemical environment of the fluids that formed the Yaylagözü fluorite deposit.

2. Regional and local geology

In previous studies (GÖRÜR et al. 1984, POISSON 1986, ALPASLAN & BOZTUĞ 1997) the metamorphic and magmatic rock assemblages outcropping between the eastern parts of Ankara, the Kırşehir-Niğde, and the Sivas-Yozgat areas have been referred to as the Kırşehir Block. The metamorphic rocks of the Kırşehir Block are described either as the Kaman Group (SEYEMEN 1984) or the Kırşehir Metasedimentary Group (TOLLUOĞLU 1986), or the Yıldızeli Metasedimentary Group (ALPASLAN 1993). The Yıldızeli Metasedimentary Group is subdivided into four units: the Aşılık metamorphics, the Fındıcak metamorphics, the Pelitkaya quartzite, and the Kadıköy metacarbonate (ALPASLAN & BOZTUĞ 1997). These metamorphic rocks were intruded by granitic and syenitic, calc-alkaline to alkaline intrusive bodies (Fig. 1).

The Paleozoic basement, which is comprised of metamorphic and intruded magmatic rocks, is covered by Paleocene sedimentary rocks. In the study area, the Yıldızeli metamorphic rocks and the Upper Cretaceous Davulalan syenites are widespread (Fig. 2). Metamorphic

rocks, exposed in the vicinity of Yıldızeli region, start at the basement with pelitic schists and migmatites. This sequence consists of quartzite, quartz schist, and marble at the top (ALPASLAN 1993). The thickness of metamorphic rocks around the Yıldızeli area reaches approximately 30 m. The metamorphic rocks of the study area are mainly characterized by mica schist, calc-silicate, and marble. Radiometric K/Ar studies yielded ages of metamorphism of the Fındıcak metamorphic rocks of Yıldızeli Metasedimentary Group between Santonian and Maastrichtian (ALPASLAN et al. 1996).

The magmatic rocks in the vicinity of Kiremitli and Yücebaba villages are of granitic composition and change to syenitic composition towards the Yaylagözü and Yuvalıçayır villages (Fig. 2). Based on the major- and trace-element studies on the Yıldızeli magmatic rocks, ALPASLAN & BOZTUĞ (1997) have suggested that the granitic rocks originated from anatexis of the thickened crust during Anatolide-Pontide collision along the northward subduction zone of the northern branch of the Neo-Tethys, whereas syenitic rocks were produced by partial melting of upper mantle material as a result of crustal attenuation during the tensional regime, immedia-

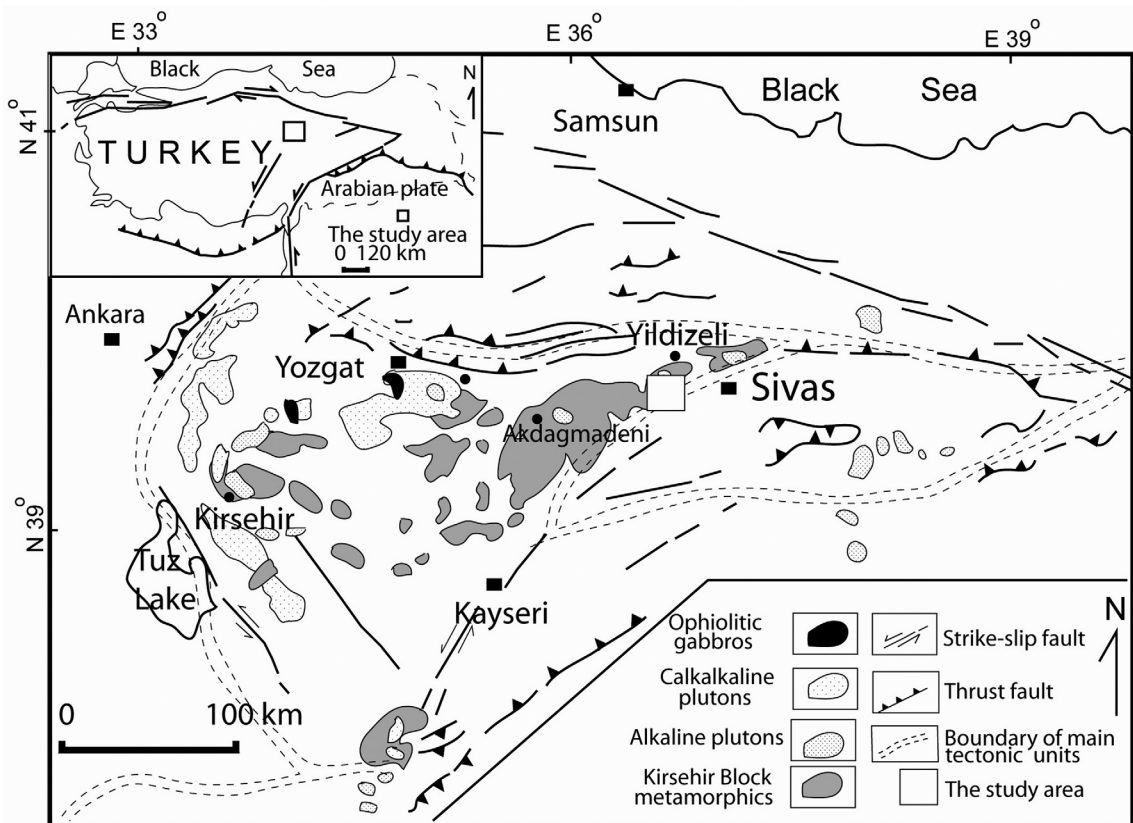


Fig. 1. Location map and the simplified geographical setting of plutonic and metamorphic rocks in Central Anatolia (after ALPASLAN & BOZTUĞ 1997).

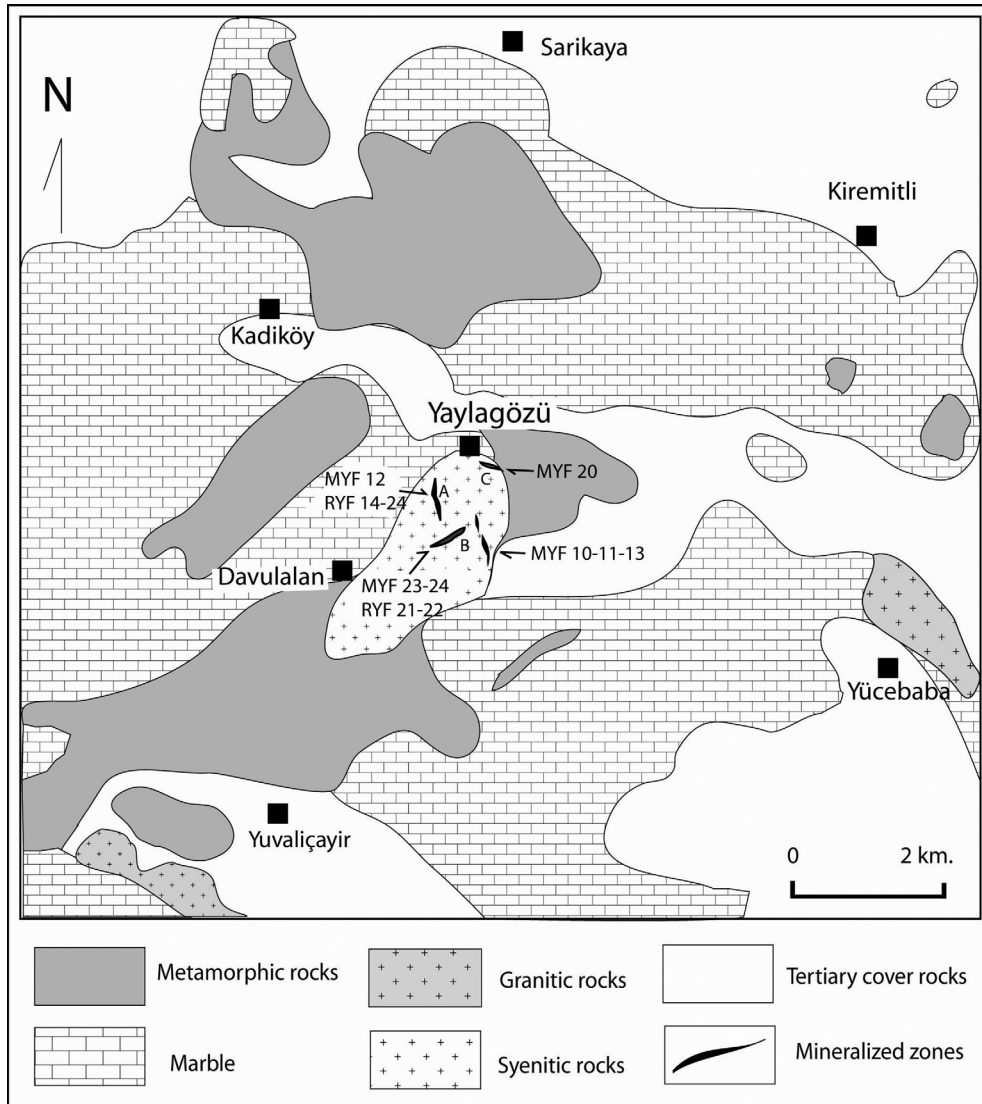


Fig. 2. Simplified geological map of the Yaylagözü and its vicinity (modified from ALPASLAN et al. 1996).

tely after crustal thickening. Fresh samples of magmatic rocks are generally grey to pink in colour and medium- to coarse-grained with a porphyritic texture. They contain quartz, alkali feldspar and plagioclase with subordinate amounts of biotite and amphibole. Intensive skarn zones exist at the contacts of magmatic rocks and marbles. The characteristic skarn minerals, represented by garnet, pyroxene, scapolite, and epidote, are widespread in the endoskarn zone together with fluorite mineralization. The Yaylagözü fluorite deposit occurs as different outcrops north of the Davulalan syenite (ALPASLAN & BOZTUĞ 1997) and south to southwest of the Yaylagözü village (see A, B and C fluorite occurrences in Fig. 2). The studied area hosts an extended fluorite mineralization. The fluorite veins in the syenite are as much as 1

meter thick, predominantly extending in NW-SE striking fractures.

3. Discussion

3.1. Fluid Inclusion Petrography and Microthermometry

Fluid-inclusion studies were performed on doubly-polished fluorite samples taken from the mineralization area. Microthermometric determinations were carried out using a Nikon Labophot-pol microscope mounted with a Linkam THMS-600 and TMS-92 freezing-heating stage at the Department of Geology, Cumhuriyet Univer-

sity, Sivas. The heating rate during the phase transitions was controlled manually in the range of 0.1 to 5.0 °C min⁻¹. Repeated measurements indicated that the reproducibility of the temperature determinations was better

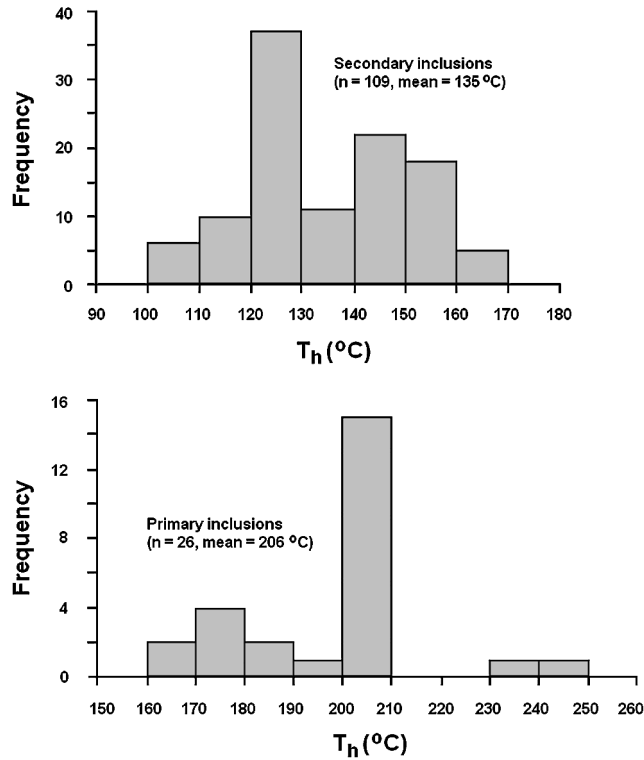


Fig. 3. Histograms showing the homogenization temperatures of primary and secondary inclusions in the Yaylagözü fluorites.

than ± 0.5 °C. The majority of the fluid inclusions range in size from 10 to 50 μm .

All of the investigated fluorite samples contain primary and secondary fluid inclusions using the definition of ROEDDER (1984). Primary fluid inclusions are observed as semi-spherical to spherical in shape, irregularly dispersed along the fracture planes. Both primary and secondary fluid inclusion populations are dominated by three-phases comprising liquid + CO₂ and liquid + vapor (L + LCO₂ + V). Secondary fluid inclusions are characterized by spherical to square shapes that generally developed along two distinct fracture systems and have different morphological and microthermometric properties. The homogenization temperatures (T_h) of 135 fluid inclusions were measured in 8 fluorite samples. In primary fluid inclusions, the homogenization temperatures range from 161 °C to 243 °C with a mean of 206 °C (Fig. 3). Microthermometric measurements on two inclusions gave 238 °C and 243 °C. These two results may represent the relict primary inclusions showing that the Yaylagözü fluorites were formed at temperatures greater than 230 °C. On the other hand, homogenization temperatures in secondary fluid inclusions range from 103 °C to 164 °C with a mean of 135 °C, and the range in an individual sample is less than 20 °C. Fluid inclusions in fluorite do not contain major amounts of chlorine- and sulfate-bearing daughter minerals. The Yaylagözü inclusions, in general, are dominated by fluids that have low salinities. These inclusions, therefore, homogenize at moderate temperatures and their last ice-melting (T_{ice}) values indicate salinities ranging from 3 to 8 equivalent wt % NaCl.

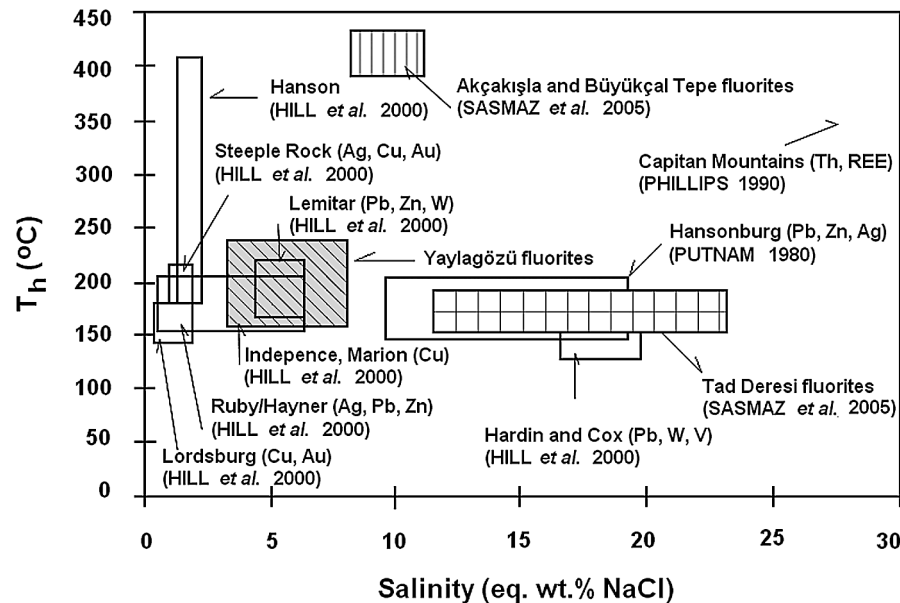


Fig. 4. Homogenization temperature (T_h) versus salinity for primary and secondary fluid inclusions in fluorite from the Yaylagözü area. Fluid inclusion data on other fluorite occurrences have been given for comparison only.

Table 1. Trace and rare-earth element contents of massive fluorite (MYF) and fluorite-rich (RYF) samples in the Yaylagözü area.

Sample No.	MYF-10	MYF-11	MYF-12	MYF-13	MYF-20	MYF-23	MYF-24	RYF-14	RYF-21	RYF-22	RYF-24
Sc	0.8	0.7	0.6	0.8	0.7	1.2	2.3	0.5	6.2	5.8	2.3
Co	1	2.9	3.3	3.4	1.2	3	3.1	1.6	2.6	2.7	1.9
Cu	13	58	158	90	4	8	15	20	3	14	5
Zn	47	90	76	57	128	209	27	30	177	102	113
As	bdl	9	4	13	bdl	3	bdl	2	32	bdl	9
Rb	2.6	7.5	13.5	8.6	1.6	23.9	7.2	11.8	77.3	47.1	595
Sr	299	264	246	308	221	214	235	72	145	262	433
Y	19.5	20.6	29.4	20.9	13.5	25.8	75.4	12.5	153	47.9	50.2
Zr	0.9	2.5	2.4	2.7	1.9	21.5	14.8	10.5	303	92.7	419
Nb	bdl	bdl	2.5	bdl	0.5	4.8	3.6	1.8	106.5	31.5	23.7
Mo	22	48	17	169	2	3	1	2	4	3	2
Cd	0.3	0.5	0.5	0.3	1.1	2.3	bdl	0.2	2.1	1.9	2
Sb	3.2	4.2	5.1	4	1.9	3.7	3.1	1.7	6.2	5.6	5.6
Cs	0.1	0.4	0.4	0.5	0.1	0.7	0.5	0.7	6.1	0.9	13.2
Ba	bdl	bdl	243	bdl	29	232	9	16	168	139	745
La	31.3	40.8	92.3	33.6	19.8	139.6	2282	67.2	360	768	90.5
Ce	47.9	64.1	146.3	54.4	30.1	150.2	2518	101.1	535	890	146.1
Pr	4.18	5.32	12.84	4.71	2.8	9.85	154.5	8.06	46.6	55.7	13.3
Nd	12.1	15.3	36.8	14.2	9.4	25.2	290	22.1	144.9	115.8	42.6
Sm	1.4	1.7	3.8	1.5	1.4	3.4	15.2	2	22.1	9.5	7.1
Eu	0.38	0.44	0.77	0.39	0.25	0.67	2.46	0.41	4.54	1.75	1.46
Gd	1.18	1.33	2.24	1.19	0.99	2.05	4.78	0.95	16.87	6.28	5.3
Tb	0.2	0.24	0.34	0.2	0.13	0.36	1.1	0.18	2.53	0.78	0.91
Dy	1.53	1.69	2.62	1.4	0.9	2.37	7.39	1.28	17.63	4.83	6.12
Ho	0.35	0.43	0.61	0.34	0.21	0.52	1.54	0.26	3.88	0.98	1.34
Er	1.25	1.48	2.18	1.26	0.77	1.89	5.09	0.86	13.78	3.59	4.86
Tm	0.17	0.21	0.35	0.18	0.12	0.31	0.71	0.12	2.22	0.59	0.78
Yb	1.09	1.41	2.47	1.21	0.89	2.3	4.54	0.81	16.02	4.65	5.96
Lu	0.18	0.21	0.41	0.19	0.15	0.38	0.65	0.11	2.58	0.77	0.95
Hf	bdl	bdl	bdl	bdl	bdl	0.7	0.8	bdl	8.7	2.6	8.8
W	bdl	bdl	3	bdl	3	10	16	bdl	41	5	16
Pb	33	153	128	113	117	277	162	8	256	364	493
Bi	7.7	20.1	15.3	8.6	4.1	6.8	25.6	3.7	4.3	5.7	43.6
Th	1	1.5	1.9	3.3	3.7	4.7	105.3	2.3	127.9	48.6	51
U	27	22.4	22.5	41.9	7.4	9.1	39.3	38.6	38	23.6	14.8
® REE	103.2	134.7	304.0	114.8	67.9	339.1	5288	205.4	1188	1863	327
Tb/La	0.00639	0.00588	0.00368	0.00595	0.00657	0.00258	0.000482	0.00268	0.00703	0.001015	0.01006
Tb/Ca	0.00505	0.00667	0.00749	0.00473	0.00267	0.00823	0.0232	0.01294	0.1023	0.01805	0.1396
La/Yb	28.72	28.94	37.4	27.77	22.25	60.7	503	83.0	22.5	165.2	15.18
La/Sm	22.4	24	24.3	22.4	14.14	41.1	150.1	33.6	16.27	80.9	12.75
Y/Ho	55.7	47.9	48.2	61.5	64.3	49.6	49.0	48.1	39.5	48.9	37.5
La/Ho	89.4	94.9	151.3	98.8	94.3	268	1481	258	92.7	784	67.5
Ce/Yb	43.9	45.5	59.2	45.0	33.8	65.3	555	124.8	33.4	191.	24.5
Yb/Ca	0.0275	0.0392	0.0544	0.0286	0.0183	0.0526	0.0957	0.0582	0.647	0.1076	0.914
Eu/Eu*	0.903	0.894	0.807	0.892	0.649	0.776	0.882	0.909	0.719	0.692	0.727
Ce/Ce*	0.981	1.019	0.996	1.013	0.947	0.949	0.994	1.018	0.969	1.008	0.987

bdl: below detection limit; detection limits (ppm) are: Eu, Gd, Dy, Ho, Er, Tm, Yb (0.05); Pr (0.02); Tb, Lu (0.01); Hf (0.5); Nd (0.4); Sc, Co, Cu, Rb, Y, Sm, Zr, Nb, Mo, Cd, Sb, Cs, La, W, Pb, Bi, Th, U (0.1); Zn, As, Sr, Ba, Ce (1).

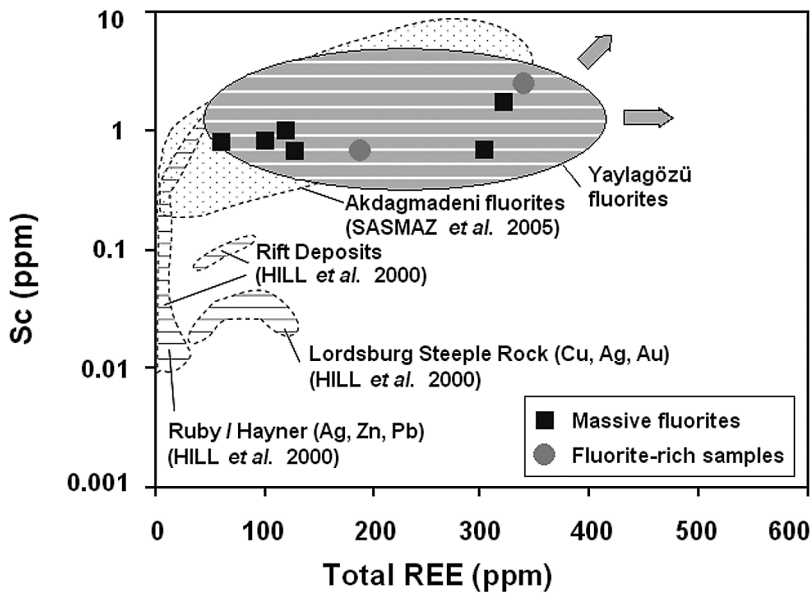
These values are plotted in Fig. 4 and are compared with the data of southwestern New Mexico fluorites (HILL et al. 2000), and with the fluorite deposits of Akdagmadeni (SASMAZ et al. 2005).

3.2. Major, trace, and REE chemistry

In order to determine the geochemical characteristics of fluorites from the Yaylagözü area, 11 massive fluorite

Table 2. Correlation matrix for trace element contents of the Yaylagözü fluorites.

	Bi	Cd	Co	Cs	Cu	Mo	Pb	Rb	Total REE	Sb	Sc	Sr	Th	U	Y	Zn	Zr
Bi	1.00																
Cd	-0.40	1.00															
Co	0.52	0.07	1.00														
Cs	0.30	0.51	0.86	1.00													
Cu	0.20	-0.48	0.57	0.17	1.00												
Mo	-0.14	-0.48	0.37	0.18	0.39	1.00											
Pb	0.11	0.86	0.55	0.83	-0.15	-0.23	1.00										
Rb	-0.04	0.71	0.61	0.85	0.18	-0.09	0.84	1.00									
Total REE	0.73	0.57	0.27	0.27	-0.25	-0.28	0.17	-0.07	1.00								
Sb	0.34	-0.24	0.71	0.49	0.83	0.30	0.14	0.51	-0.32	1.00							
Sc	0.59	0.81	0.26	0.41	-0.42	-0.28	0.34	0.10	0.95	-0.25	1.00						
Sr	-0.07	-0.80	-0.05	-0.25	0.28	0.74	-0.69	-0.41	-0.27	0.27	-0.32	1.00					
Th	0.71	0.80	0.24	0.25	-0.27	-0.26	0.15	-0.10	0.99	-0.23	0.95	-0.26	1.00				
U	0.51	-0.74	0.41	0.17	0.28	0.59	-0.36	-0.26	0.49	0.27	0.39	0.66	0.49	1.00			
Y	0.77	0.15	0.39	0.38	-0.11	-0.27	0.22	0.06	0.98	-0.08	0.93	-0.26	0.97	0.51	1.00		
Zn	-0.52	0.99	-0.01	0.34	-0.27	-0.29	0.73	0.65	-0.43	-0.10	-0.22	-0.62	-0.43	-0.83	-0.42	1.00	
Zr	0.16	0.92	0.38	0.75	-0.40	-0.35	0.85	0.73	0.48	-0.05	0.68	-0.60	0.46	-0.14	0.52	0.51	1.00

**Fig. 5.** Plot of the Yaylagözü fluorites on a Sc versus total REE diagram.

and fluorite-rich samples were taken from the field and analyzed for major-oxide, trace-, and rare-earth elements by a commercial laboratory (ACME Analytical Laboratories Ltd.) in Canada (Table 1). REE concentrations were determined by the ICP-MS method, whereas major-element, trace-element, and F contents were analyzed by the ICP-ES technique. All the analyzed massive fluorite samples are characterized by calcium contents ranging from 36.00 to 48.69 %, and fluorine contents ranging from 25.72 to 43.26 %. Deviations from the ideal calcium and fluorine contents may be caused by the incor-

poration of other mineral phases, such as quartz and calcite, within the bulk samples. Fluorite-rich samples, however, have variable calcium and fluorine contents ranging from 6.52 to 43.22 % and 1.99 to 32.86 %, respectively.

Due to the similarity of size and valence of Ca^{2+} ion and calcium those with the trace elements, fluorite has a tendency to incorporate trace elements in its crystal lattice during crystallization. Fluorite-bearing representative samples were first crushed and then selected under the binocular microscope for geochemical analysis. The

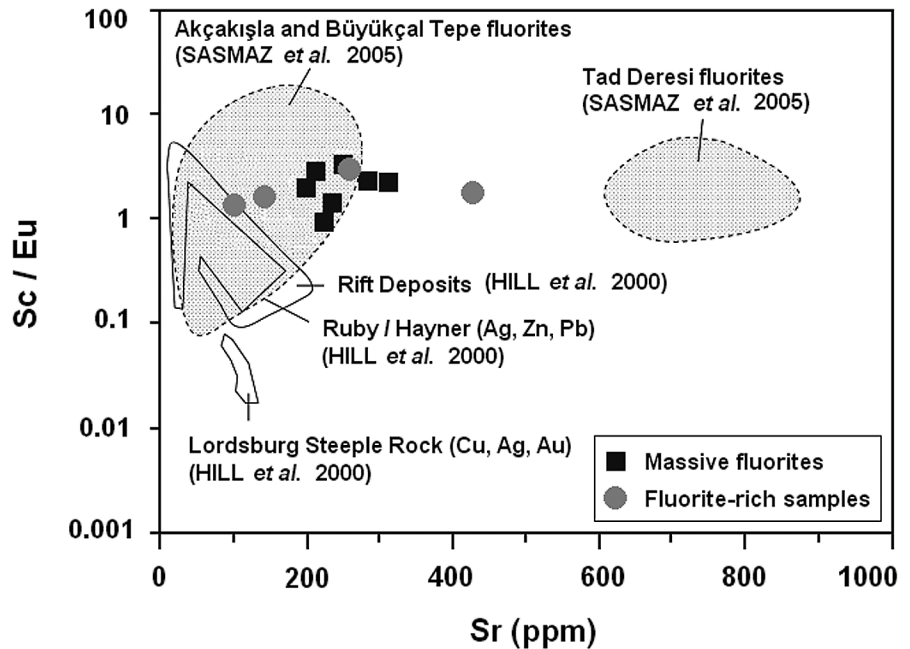


Fig. 6. Plot of the Yaylagözü fluorites on a Sc/Eu versus Sr diagram.

purity of picked fluorites is estimated to be 95%. In all of the analyzed massive fluorite samples, trace elements were detected at levels ranging from 0.1 to 308 ppm (Table 1). In only a small number of massive fluorite samples, some trace element contents are below the detection limits (e.g., As, Ba, Hf, Nb, and W). However, variable trace element contents exist for Sc (0.6–5.8 ppm, $\mu = 1.61$), Co (1–3.4 ppm, $\mu = 2.57$), Cu (4–158 ppm, $\mu = 45$), Zn (27–209 ppm, $\mu = 92$), As (3–13 ppm, $\mu = 7.25$), Rb (1.6–47.1 ppm, $\mu = 14$), Sr (214–308 ppm, $\mu = 256.1$), Y (13.5–75.4 ppm, $\mu = 31.6$), Zr (0.9–92.7 ppm, $\mu = 17.4$), Nb (0.5–31.5 ppm, $\mu = 8.6$), Mo (1–169 ppm, $\mu = 33.1$), Cd (0.3–2.3 ppm, $\mu = 0.98$), Sb (1.9–5.6 ppm, $\mu = 3.8$), Cs (0.1–0.9 ppm, $\mu = 0.4$), Ba (9–243 ppm, $\mu = 130.4$), Hf (0.7–2.6 ppm, $\mu = 1.4$), W (3–16 ppm, $\mu = 7.4$), Pb (33–364 ppm, $\mu = 168.4$), Bi (4.1–25.6 ppm, $\mu = 11.7$), Th (1–105.3 ppm, $\mu = 21.3$), and U (7.4–41.9 ppm, $\mu = 24.1$) where μ denotes an average content of each trace element. Pearson's product moment correlation matrix of trace element contents of massive fluorites from the Yaylagözü area is given in Table 2. In this table, an absolute correlation coefficient which is greater than 0.70 is displayed in bold character. HILL et al. (2000) compared some trace element contents of fluorite occurrences from southwestern New Mexico in different binary diagrams. A plot of the Yaylagözü massive fluorites in Sc versus Σ REE reveals that most of the samples lie in the region of granitoid-hosted fluorite occurrences from the Akdagmadeni area, Yozgat, Central Turkey (Fig. 5). A similar trend also is observed in the Sc/Eu

versus Sr diagram (Fig. 6). The studied massive fluorites, in terms of strontium contents, overlap considerably within the fields of fluorites from Büyükçal Tepe and Akçakışla, which are found in the Akdagmadeni area, Central Turkey. In this respect, the Yaylagözü fluorites display a chemical similarity with those of the Büyükçal Tepe and Akçakışla fluorite occurrences.

A ratio of La_N/Yb_N can be used to understand the enrichment trends in terms of light and heavy REE contents in fluorite. The Yaylagözü massive fluorites, in general, were more enriched from the point of view of the light REE than the heavy REE, with La_N/Yb_N ratios between 19.4 and 340 with an average of 68. This spectrum also is distinguished on the basis of chondrite-normalized REE patterns (Fig. 7a, b). Some of the studied massive fluorites have slightly negative Eu anomalies ($Eu/Eu^* < 1$; $Eu/Eu^* = Eu_N / \sqrt{Sm_N * Gd_N}$) with a range of 0.65 to 0.90 and having an average of 0.83 (Table 1). These slightly negative Eu anomalies indicate the presence of Eu^{2+} and suggest low oxygen fugacities during fluorite deposition from the solution. Ce anomalies ($Ce/Ce^* = Ce_N / \sqrt{La_N * Pr_N}$), on the other hand, display two distinct characteristics (Table 1). Three massive fluorite samples have positive Ce anomalies ($Ce/Ce^* > 1$) while four of the remaining samples have very slight negative Ce anomalies ($Ce/Ce^* < 1$). CONSTANTOPOULOS (1988) has attributed a similar observation to high oxygen fugacities in the source of the hydrothermal fluids and the resultant oxidation of Ce^{3+} and immobilization of Ce^{4+} .

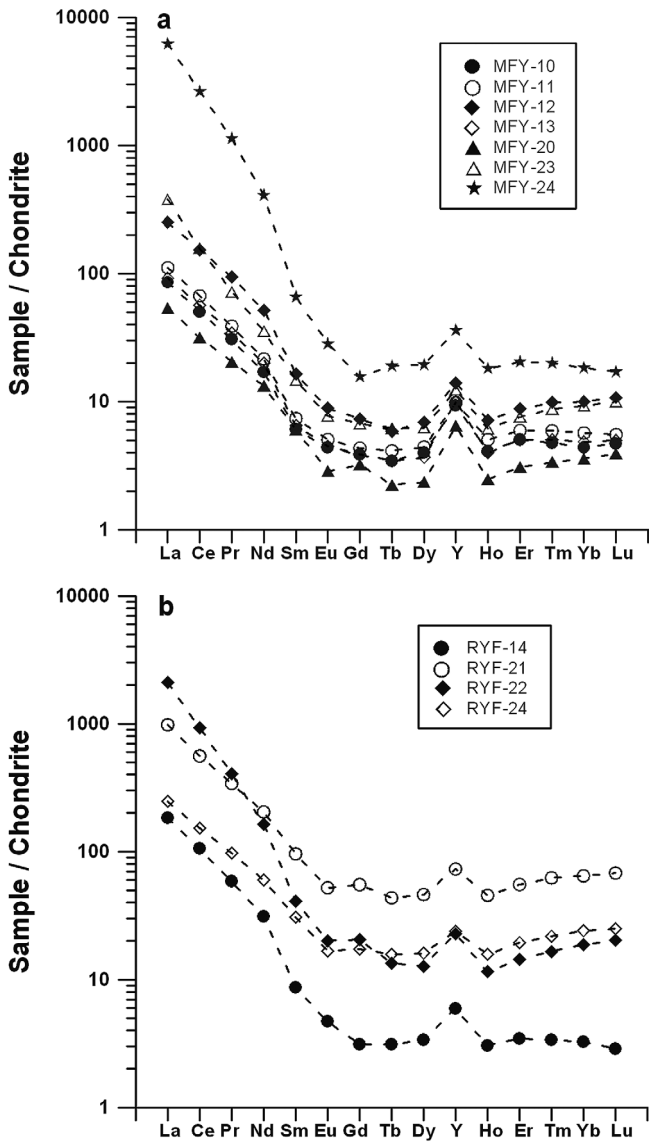


Fig. 7 a, b. Chondrite-normalized REE pattern for the Yaylagözü fluorites.

GAGNON et al. (2003) studied the compositional heterogeneity in fluorite and the genesis of fluorite deposits from Gallinas Mountains (New Mexico), Rock Canyon Creek (British Columbia), South Platte (Colorado) and St. Lawrence (Newfoundland) by LA-ICP-MS analysis. Fluorites from the Gallinas Mountains deposits, which are associated with alkaline magmatism, are characterized by relatively flat to LREE-enriched chondrite-normalized REE patterns showing a lack of Eu anomalies and have slight negative Ce and slight positive Y anomalies. The Yaylagözü massive fluorites and fluorite rich occurrences, which are associated with syenites, display similar chondrite-normalized REE patterns compared to

the Gallinas Mountains fluorites except for marked positive Y anomalies (Fig. 7a, b).

Since terbium and lanthanum are strongly fractionated by fluorite, their variations, such as in Tb/La and Tb/Ca, have been used extensively to establish the environment of formation and degree of fractionation of fluorite (MÖLLER et al. 1976). Early-formed fluorite is enriched in La, and thus depleted in Tb contents. The low Tb/La (0.00048 to 0.00657) and relatively high Tb/Ca (0.00267 to 0.02319) ratios of massive fluorites from the Yaylagözü area suggest that they precipitated from fractionated ore-bearing fluids at an early stage of deposition. The REE data of fluorite plot into the mainly “pegmatitic” or “high-hydrothermal” and to a lesser extent into the hydrothermal fields of the Tb/Ca vs. Tb/La diagram (Fig. 8) after MÖLLER et al. (1976). The relative positions of fluorite-rich samples on the Tb/Ca vs. Tb/La diagram are consistent with the primary crystallization environment. However, on the same diagram, it is likely that the positions of some massive fluorite samples towards the “hydrothermal” field may display a remobilization trend or may be referred to as the relative strength of fluoro-complexes. Fluorite samples inclined towards the “hydrothermal” field also show decreasing total REE contents and are characterized by relatively light colors. DILL et al. (1986) observed a similar trend at the Issigau fluorite occurrence and attributed this REE trend to intensive reaction between hydrothermal solutions and the Ca-enriched wall rocks that are composed of basic tuffs prior to fluorite deposition. A similar hypothesis may be applicable to the light-colored Yaylagözü fluorites (Fig. 8) during the circulation of hydrothermal solutions between syenite and the surrounding marble (see Fig. 2).

In general, fluorite samples in the “pegmatitic” field are characterized by high total REE contents. Thus, fluorite from Yaylagözü area seems to be linked by the low salinity fluids. The slight negative Eu anomalies in all studied massive and fluorite-rich samples point to moderate to slightly high temperatures of the fluid prevailing during fluorite deposition. This type of environment, in terms of temperature, is highlighted by the primary fluid-inclusion studies at Yaylagözü fluorites, in which homogenization temperatures range from 161 °C to 243 °C with a mean of 206 °C.

Geochemical studies on the southwestern New Mexico fluorite occurrences revealed that fluorite samples associated with low-salinity precious metals mineralization have $(\text{Tb}/\text{Yb})_n$ ratios between 3.1 and 3.5 and moderate to large $(\text{La}/\text{Yb})_n$ values (HILL et al. 2000). On the other hand, fluorite data from Au-Ag veins hosted by Tertiary intermediate volcanic and volcanoclastic rocks in the Chloride district show high $(\text{Tb}/\text{Yb})_n$ and moderate to

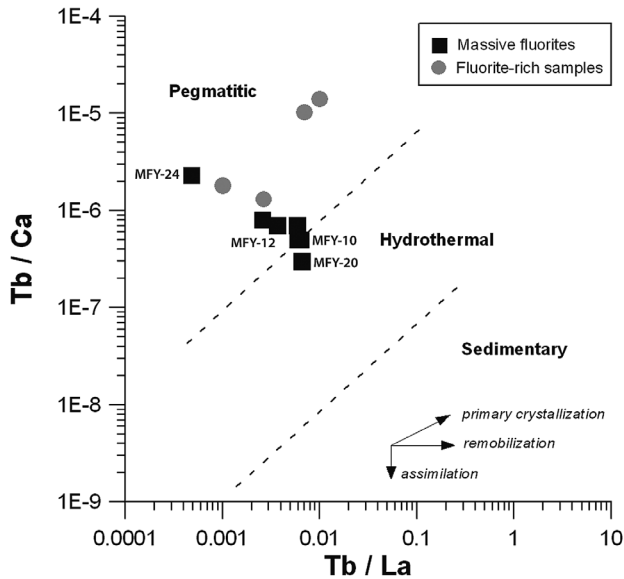


Fig. 8. Plot of the Yaylagözü fluorites on a Tb/Ca versus Tb/La variation diagram (after MÖLLER et al. 1976). Trends are taken from O'CONNOR et al. (1993).

very large $(La/Yb)_n$ values (EPPINGER 1988). Comparing fluorites from New Mexico and the Chloride district, massive fluorites from the Yaylagözü area display relatively low $(Tb/Yb)_n$ ratios with a very large spread of $(La/Yb)_n$ values (Fig. 9). The chemical composition of Yaylagözü fluorite, in terms of $(Tb/Yb)_n$ and $(La/Yb)_n$ ratios, resembles Akdagmadeni fluorite (SASMAZ et al. 2005) except for variable $(La/Yb)_n$ values. Early-crystallized fluorite, in general, has higher light REE concentrations than heavy ones, resulting in high $(La/Yb)_n$ and $(Tb/Yb)_n$ ratios (MÖLLER et al. 1976). Fluorites from the

Yaylagözü are characterized by high $(La/Yb)_n$ and low $(Tb/Yb)_n$ ratios suggesting they became stabilized at relatively low $(Tb/Yb)_n$ values. During the fluorite deposition, the mineralizing fluid at Yaylagözü thus became enriched in La compared to Tb and preferentially substituted for Ca (see Fig. 7–8).

Eu versus Ce anomalies (Eu/Eu^* vs. Ce/Ce^*) of the Yaylagözü fluorites show a transition from the New Mexico Capitan Mountains (Th, REE) to Lordsburg/Steeple Rock (Cu, Ag, Au) fluorites (Fig. 10). The studied fluorite, shows a similar trend those with the Akdagmadeni fluorite deposits (SASMAZ et al. 2005), which are located south west of the Yaylagözü area (Fig. 10). HILL et al. (2000) pointed out that the positive and negative Eu anomalies of fluorite samples may or may not be indicative of precious metal mineralization. The studied fluorites with Ce anomalies around 1 and small negative Eu anomalies are not associated with considerable amounts of precious metal mineralization.

4. Summary and Conclusions

Syenite-hosted fluorite veins, as well as fluorite occurrences in skarn zones, with small amounts of base-metal sulfides are found within the Yaylagözü area (Yıldızeli-Sivas) in Central Anatolia Massif. Some of the fluorite veins were exploited in the past and have been the subject of superficial geologic and petrographic investigations. The fluorite mineralization occurs in three principal ore zones defined as A, B, and C, respectively (see Fig. 2). However numerous minor fluorite occurrences also exist in the study area. The largest ore body is found

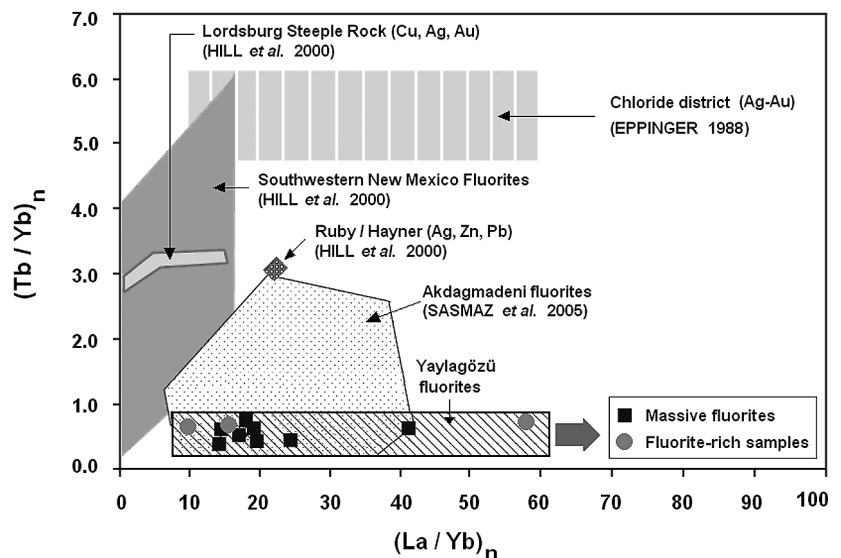


Fig. 9. $(Tb/Yb)_n$ versus $(La/Yb)_n$ ratio for the Yaylagözü fluorites. Chemical compositions of other fluorites are given for comparison only.

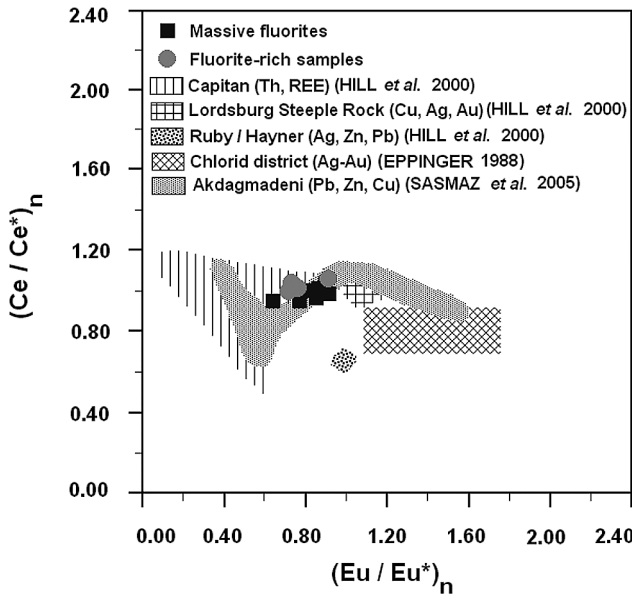


Fig. 10. Comparison of the Yaylagözü fluorites on (Ce/Ce^*) ratio versus (Eu/Eu^*) ratio diagram with the fluorites from New Mexico (USA) and Akdagmadeni (Turkey).

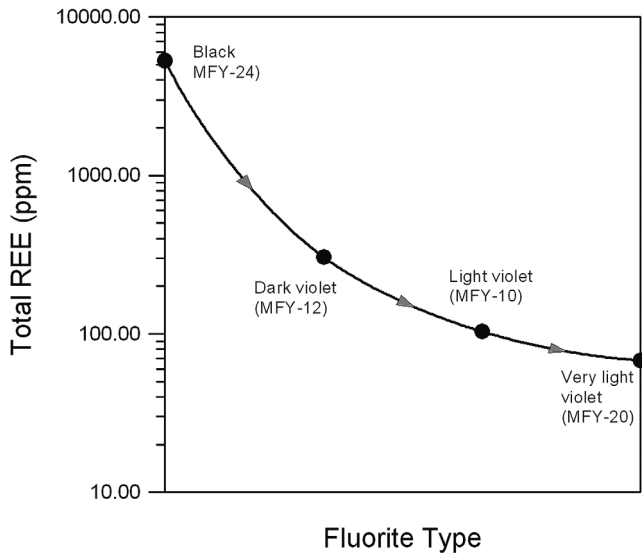


Fig. 11. Variation of total REE contents of dark to light fluorites.

in zone A, which extends up to 50 meters in N-S and 30 meters in E-W directions, with thickness up to 1 meter.

In hand specimens, the colour of studied fluorites ranges from very light violet to nearly black. Colour variation of fluorite may be correlated with its trace element contents. SCHNEIDER *et al.* (1975) have attempted to correlate the various colours of fluorite to its trace- and rare-earth element contents. The total REE contents of the different coloured Yaylagözü fluorites display a negative

enrichment trend from nearly black to very light violet (Fig. 11). However, no clear relationship has been observed regarding the colour type and its specific trace element contents among at the studied samples. PALMER & WILLIAMS-JONES (1996) reported that the yellow and colourless fluorites have higher Yb/La ratios than the blue and violet ones. A similar decreasing trend in terms of Yb/La ratio has also been observed from black to very light violet massive fluorites in the Yaylagözü area.

Fluorites were precipitated from moderate saline solutions (3 to 8 equivalent wt% NaCl) at low and moderate to slightly high temperatures ($T_h = 161^\circ\text{C}$ to $^\circ\text{C}$ 243) and under reducing conditions, as indicated by paragenetic sulfides and slightly negative Eu anomalies. The total REE contents are variable, ranging from 68 ppm to 5288 ppm, and the highest concentration is found in dark massive fluorite. Elemental discrimination diagrams were used in a variety of studies to construe fluorite compositions and draw a conclusion on the depositional environments (SCHNEIDER *et al.* 1975, MÖLLER *et al.* 1976, EPPINGER & CLOSS 1990, HILL *et al.* 2000). Most of the fluorite from Yaylagözü plots within the pegmatitic field on the Tb/Ca ratio *versus* Tb/La diagram after Möller *et al.* (1976) or high-hydrothermal field after DILL *et al.* (1986). The change in Tb/Ca *versus* Tb/La values defined by massive fluorites shows a progressive compositional evolution from relatively high Tb/La and low Tb/Ca to relatively low Tb/La and high Tb/Ca (see Fig. 8). The evolutionary trend in massive fluorites is nearly orthogonal to the primary crystallization trend proposed by MÖLLER *et al.* (1976). Fluorite-rich samples, on the other hand, plot completely in the pegmatitic field and define a compositional trend that approximately parallels the primary crystallization trend of MÖLLER *et al.* (1976).

The Tb/La ratio suggests that fluorite-rich samples were deposited at an early stage of crystallization with a typical primary crystallization trend. The light-coloured fluorite was possibly formed under relatively low temperature conditions (see fluorite sample labeled as MFY-20 in Fig. 8 and Fig. 11). The evidence that supports this idea also is revealed by a remobilization trend on Tb/Ca *versus* Tb/La diagram (Fig. 8). The patterns of massive fluorite from the Yaylagözü area all exhibit negative Eu anomalies. On the basis of this study, the REE patterns of fluorite can be interpreted in terms of typical primary magmatic precipitates due to their moderate to somewhat high light REE contents. The narrow range of Ce anomalies of fluorite may point out that the Yaylagözü massive fluorites formed from the relatively low oxidizing fluids. The slightly negative Eu anomalies may be due to the evolution of mineralizing fluids with gradual drops in f_{O_2} . Such a condition may be achieved by

cooling and equilibration of the hydrothermal fluids within the host alkaline magmatic rocks, especially in syenitic composition and wall rocks. Rare earth element ratio diagrams and patterns of fluorite from the Yaylagözü area show compositional trends that may be indicative of progressive mixing of hydrothermal fluids as well as interaction of hydrothermal fluids with skarn zones.

On the basis of geological and geochemical data from the Yaylagözü fluorites, it is possible to conclude that the Yaylagözü fluorite deposits were deposited from F-bearing hydrothermal fluids circulating within the syenitic intrusive bodies and their skarn zones at the contacts of metamorphic rocks. Our present knowledge indicates that F-rich calc-alkaline to alkaline magmatic rocks in Central Anatolia Massif were probably responsible for the numerous fluorite deposits in the study area, as well as other deposits at the surrounding areas including Akdagmadeni (SASMAZ et al. 2005) and Kaman (KOÇ et al. 2003).

Acknowledgements

The authors acknowledge financial support from the Fırat University Research Foundation (FÜBAP-599). We thank Prof. Dr. AHMET GÖKÇE for his help on the fluid inclusion studies at Cumhuriyet University, Sivas. This paper was significantly improved by Dr. G. C. ULMER. We would like to thank him for his editorial handling of the manuscript and anonymous reviewer for his valuable suggestions and comments.

References

- ALPASLAN, M. & BOZTUĞ, D. (1997): The co-existence of the syn-collision and post-collision plutons in the Yıldızeli Area (W-Sivas). – *Turkish J. Earth Sci.* **6**: 1–12.
- ALPASLAN, M. (1993): Yıldızeli yöresi metamorfizmasının petrolojik incelenmesi. – C.Ü. Fen Bil. Ens. Doktora Tezi. 359 s., Sivas (yayınlanmamış).
- ALPASLAN, M., GUEZOU, J. C., BONHOMME, M. & BOZTUĞ, D. (1996): Yıldızeli metasedimanter grubu içindeki Fındıcak metamorfizmasının metamorfizma ve yaşı. – *Türkiye Jeoloji Kurumu Bülteni* **39/1**: 19–29.
- BÜHN, B., RANKIN, A. H., SCHNEIDER, J. & DULSKI, P. (2002): The nature of orthomagmatic carbonatitic fluids precipitating REE, Sr-rich fluorite: fluid-inclusion evidence from the Okorusu fluorite deposit, Namibia. – *Chem. Geol.* **186**: 75–98.
- CONIGLIO, J., XAVIER, R. P., PINOTTI, L. & D'ERAMO, F. (2000): Ore-forming fluids of vein-type fluorite deposits of the Cerro Aspero Batholith, southern Cordoba Province, Argentina. – *Int. Geol. Rev.* **42**: 368–383.
- CONSTANTOPOULOS, J. (1988): Fluid inclusions and rare earth element geochemistry of fluorite from South-Central Idaho. – *Econ. Geol.* **83**: 626–636.
- DILL, H., DULSKI, P. & MÖLLER, P. (1986): Fluorite mineralization and REE patterns in vein-type deposits from the N Bavarian Basement. – *N. Jb. Miner. Abh.* **154**: 141–151.
- EPPINGER, R. G. (1988): Trace element and rare earth element variation in fluorites collected from skarn and epithermal mineral deposits in the Sierra Cuchillo area, south-central New Mexico. – *U. S. Geol. Surv. Open-File Rept.* 88–566, 108 pp.
- EPPINGER, R. G. & CLOSS, L. G. (1990): Variations of trace elements and rare elements in fluorite: a possible tool for exploration. – *Econ. Geol.* **85**: 1896–1907.
- GAGNON, J. E., SAMSON, I. M., FRYER, B. J. & WILLIAMS-JONES, A. E. (2003): Compositional heterogeneity in fluorite and the genesis of fluorite deposits: insights from LA-ICP-MS analysis. – *Can. Miner.* **41**: 365–382.
- GALINDO, C., TORNOS, F., DARBYSHIRE, D. P. F. & CASQUET, C. (1994): The age and origin of the barite-fluorite (Pb-Zn) veins of the Sierra del Guadarrama (Spanish Central System, Spain): a radiogenic (Nd, Sr) and stable isotope study. – *Chem. Geol.* **112**: 351–364.
- GOLDRING, D. C. & GREENWOOD, D. A. (1990): Fluorite mineralization at Beckermeth iron ore mine, Cumbria, north England. – *Trans. Instn. Min. Metall. (Sect. B: Appl. Earth. Sci.)* **99**: B113–B119.
- GÖRÜR, N., OKTAY, F. Y., SEYMEN, I. & ŞENGÖR, A. M. C. (1984): Paleo-tectonic evolution of the Tuz Gölü basin complex, Central Turkey: Sedimentary record of a Neo-Tethys closure. – In: DIXON, J. E. & ROBERTSON, A. H. F. (eds.): *The geological evolution of the eastern Mediterranean*. – *Spec. Publ. Geol. Soc. London* **17**: 455–466.
- HILL, G. T., CAMPBELL, A. R. & KYLE, P. R. (2000): Geochemistry of southwestern New Mexico fluorite occurrences implications for precious metals exploration in fluorite-bearing systems. – *J. Geochem. Expl.* **68**: 1–20.
- KESLER, S. E. (1977): Geochemistry of Manto fluorite deposits, northern Coahuila, Mexico. – *Econ. Geol.* **72**: 204–218.
- KOÇ, Ş., ÖZMEN, Ö. & DOĞAN, A. U. (2003): Geochemistry of fluorite mineralization in Kaman, Kırşehir, Turkey. – *J. Geol. Soc. India* **62**: 305–317.
- MÖLLER, P., PAREKH, P. P. & SCHNEIDER, H.-J. (1976): The application of Tb/Ca-Tb/La abundance ratios to problems of fluorite genesis. – *Miner. Deposita* **11**: 111–116.
- O'CONNOR, P. J., HÖGELSBERGER, H., FEELY, M. & REX, D. C. (1993): Fluid inclusion studies, rare-earth element chemistry and age of hydrothermal fluorite mineralization in western Ireland—a link with continental rifting? – *Trans. Instn. Metall. (Sect. B: Appl. Earth Sci.)* **102**: B141–B148.
- PALMER, D. A. S. & WILLIAMS-JONES, A. E. (1996): Genesis of the carbonatite-hosted fluorite deposit at Amba Dongar, India: Evidence from fluid inclusions, stable isotopes and whole rock-mineral geochemistry. – *Econ. Geol.* **91**: 934–950.
- PHILLIPS, R. S. (1990): Geochemistry of hydrothermal Th-U-REE quartz/fluorite veins from the Capitan Pluton. – Unpubl. M. Sc. Thesis, New Mexico Inst. of Mining and Technology, Socorro, 202 pp.
- POISSON, A. (1986): The Anatolian micro-continent in the Eastern Mediterranean context: The Neo-Tethysian oceanic troughs. – *Sciences de la Terre, Memoire* **47**: 311–328.

- PUTNAM, B., III. (1980): Fluid inclusion and microchemical analysis of the Hansonburg Mississippi Valley – Type ore deposits in central New Mexico. – Unpubl. M. Sc Thesis, New Mexico Inst. of Mining and Technol., Socorro, 156 pp.
- RICHARDSON, C. K. & HOLLAND, H. D. (1979): Fluorite deposition in hydrothermal systems. – *Geochim. et Cosmochim. Acta* **43**: 1327–1335.
- ROEDDER, E. (1984): Fluid inclusions. – *Mineral Soc. Amer. Rev. Mineral.* **12**: 644 p.
- SASMAZ, A. (1999): Başçatak (Akdağmadeni-Yozgat) Pb-Zn skarnlarının mineralojik ve jeokimyasal özellikleri. – *Geosound* **34**: 107–118.
- SASMAZ, A., YAVUZ, F., SAGIROGLU, A. & AKGUL, B. (2005): Geochemical patterns of the Akdagmadeni (Yozgat, Central Turkey) fluorite deposits and implications. – *J. Asian Earth Sci.* **24**: 469–479.
- SAGIROGLU, A. (1982): Contact metasomatism and ore deposits of Akdagmadeni, Yozgat. – Ph. D. Thesis (unpubl.), Univ. of London, 324 pp.
- SEYMEN, I. (1984): Kırşehir metamorfitlelerinin jeolojik evrimi, Kertin Sempozyumu. – Türkiye Jeoloji Kurumu Yayını, 133–148, Ankara.
- SCHNEIDER, H. J., MÖLLER, P. & PAREKH, P. P. (1975): Rare earth element distribution in fluorites and carbonate sediments of the East-Alpine Mid-Triassic sequences in the Nördliche Kalkalpen. – *Miner. Deposita* **10**: 330–344.
- SUBÍAS, I. & FERNÁNDEZ-NIETO, C. (1995): Hydrothermal events in the Valle de Tena (Spanish western Pyrenees) as evidenced by fluid inclusions and trace-element distribution from fluorite deposits. – *Chem. Geol.* **124**: 267–282.
- TOLLUOĞLU, A.Ü. (1986): Orta Anadolu Masifinin güneybatısında (Kırşehir yöresinde) petrografik ve petrotektonik incelemeler. – H.Ü. Fen Bilimleri Ens., Doktora Tezi, Ankara, 237 p.
- TÜLÜMEN, E. (1980): Akdağmadeni yöresindeki petrografik ve metalojenik incelemeler, Doktora Tezi, Karadeniz Teknik Üniversitesi, Yerbilimleri Fakültesi Yayını, Trabzon, 85 s.
- WILLIAMS-JONES, A. E., SAMSON, I. M. & OLIVO, G. R. (2000): The genesis of hydrothermal fluorite-REE deposits in the Gallinas Mountains, New Mexico. – *Econ. Geol.* **95**: 327–342.
- ZESCHKE, G. (1953): Yıldızeli fluoritleri. – MTA Rapor, 233 p., Siyas.

Received: June 13, 2006; accepted: November 28, 2006.

Responsible editor: G. C. Ulmer

Authors' addresses:

AHMET SASMAZ, Fırat Üniversitesi, Jeoloji Mühendisliği Bölümü, 23119 Elazığ, Turkey.

FUAT YAVUZ, İstanbul Teknik Üniversitesi, Jeoloji Mühendisliği Bölümü, 34711 Maslak, İstanbul, Turkey. Corresponding address: Fuat Yavuz, P. K. 90, 34711, Kadıköy, İstanbul, Turkey. E-mail: yavuz@itu.edu.tr