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Geochemical patterns of the Akdagmadeni (Yozgat, Central Turkey) fluorite deposits and implications

Ahmet Sasmaz[a,*], Fuat Yavuz[b], Ahmet Sagiroglu[a], Bunyamin Akgul[a]

[a]*Firat Universitesi, Mühendislik Fakültesi, Jeoloji Bölümü, Elazig 23119, Turkey*
[b]*Istanbul Teknik Universitesi, Maden Fakültesi Maslak, Istanbul 80670, Turkey*

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Abstract

Fluorite and fluorite-bearing Pb–Zn–Ag (Cu) deposits are quite common in granitoids and associated skarn formations that are products of Late Cretaceous–Early Paleocene magmatic intrusions into Paleozoic metamorphic rocks of the so called Central Anatolian massif. This study investigates the geochemical features, mainly REE distributions, of fluorites from the Akdagmadeni fluorite and fluorite bearing Pb–Zn–Ag (Cu) deposits. These include the vein type Tad Dere, epidote-skarn hosted Büyükçal Tepe and the skarn and granite hosted Akçakisla deposits. The REE contents of these deposits are 20.6–48.5 ($x = 36.0$), 61.3–149.3 ($x = 113.0$) and 279.2–4222.4 ($x = 1280.0$) ppm for the Tad D., Büyükçal T. and Akçakisla, respectively.

In general, the REE contents are intermediate to high and decrease in abundance with increasing distance from the granitic bodies. The LREE contents are dominantly higher than HREE contents and REE normalized patterns indicate decreasing abundances with increasing atomic number. These indicate that all the fluorites are early stage mineralizations. However, Tb/Ca–Tb/La ratios show distinct differences in the nature of the mineralizing fluids. The high ratios of Akçakisla fluorites are evidence of mineralizing fluids rich in late-stage differentiates from a felsic magma, while intermediate to high ratios of the Büyükçal T. fluorites are products of late-stage differentiates from hydrothermal fluids. Tad D. fluorites were mineralized under hydrothermal conditions. Decreasing ΣREE contents in the order of Akçakisla, Büyükçal T., and Tad D., and Sc/Eu vs Sr distribution (Sr increases with increasing distance from the magmatic rocks) also supports this order of formation. Each of the three types of fluorite deposits plot in well-defined areas in the Sc/Eu vs Sr diagram. Eu and Ce anomalies give a mixed pattern; the Tad D. fluorites have strong negative Eu anomalies indicating low T and low fo_2 mineralizing fluids. Strong positive Eu anomalies for the Akçakisla fluorites are probably due to high fo_2. The Ce anomalies are strongly negative for the Akçakisla, negative for the Büyükçal T. and weakly negative for the Tad D. fluorites. These indicate high fo_2 conditions for the Akçakisla, intermediate for the Büyükçal T. and low for the Tad D. fluorites. Because of distinguishable differences in REE patterns, the fluorite deposits plot in well-defined areas in Sc/Eu vs Sr, $(La/Yb)_n$–$(Eu/Eu^*)_n$, Sr–$(Eu/Eu^*)_n$, Sc–ΣREE, $(Tb/Yb)_n$–$(La/Yb)_n$, Tb/Ca–Tb/La diagrams, and indicate different origins and depositional histories.

The homogenization temperatures (T_H) range from 156 to 185 °C with the corresponding salinities between 12 and 23 wt% NaCl for the Tad Dere ores, 390 to 430 °C with the corresponding salinities 8 and 12 wt% NaCl for the Akçakisla and Büyükçal Tere ores.

Consequently, the field, fluid inclusion data and REE geochemistry indicate that the composition of mineralizing fluids, the locations of ore formations relative to the plutons, the mineralizing mechanisms and the prevailing physicochemical conditions of the depositional environments for the fluorite deposits of Akdagmadeni, were different.

Keywords: Fluorite; REE; Precious metals; Trace elements; Akdagmadeni; Turkey

1. Introduction

Fluorite occurs in various mineral deposits and host rocks and has distinct geochemical patterns indicative of the type of mineral deposit and host rock (Richardson and Holland, 1979; Strong et al., 1984; Ekambaram et al., 1986; Constantopoulos, 1988; Eppinger, 1988; Eppinger and Closs, 1990; Subias and Fernandoz-Nieto, 1995; Hill et al., 2000; Andrade et al., 1999; Bühn et al., 2002; Bosze and Rakovan, 2002; Monecke et al., 2002).

The metamorphic rocks of the Kirsehir Massif (Central Anatolian Massif) were intruded by numerous alkaline granitoids which gave rise to skarn formations and various ore deposits including fluorite deposits in the provinces of Kirsehir, Yozgat, Sivas and Nigde (Fig. 1). The host rocks of

* Corresponding author. Tel.: +424-237-0000; fax: +424-237-2300.
E-mail address: asasmaz@firat.edu.tr (A. Sasmaz).

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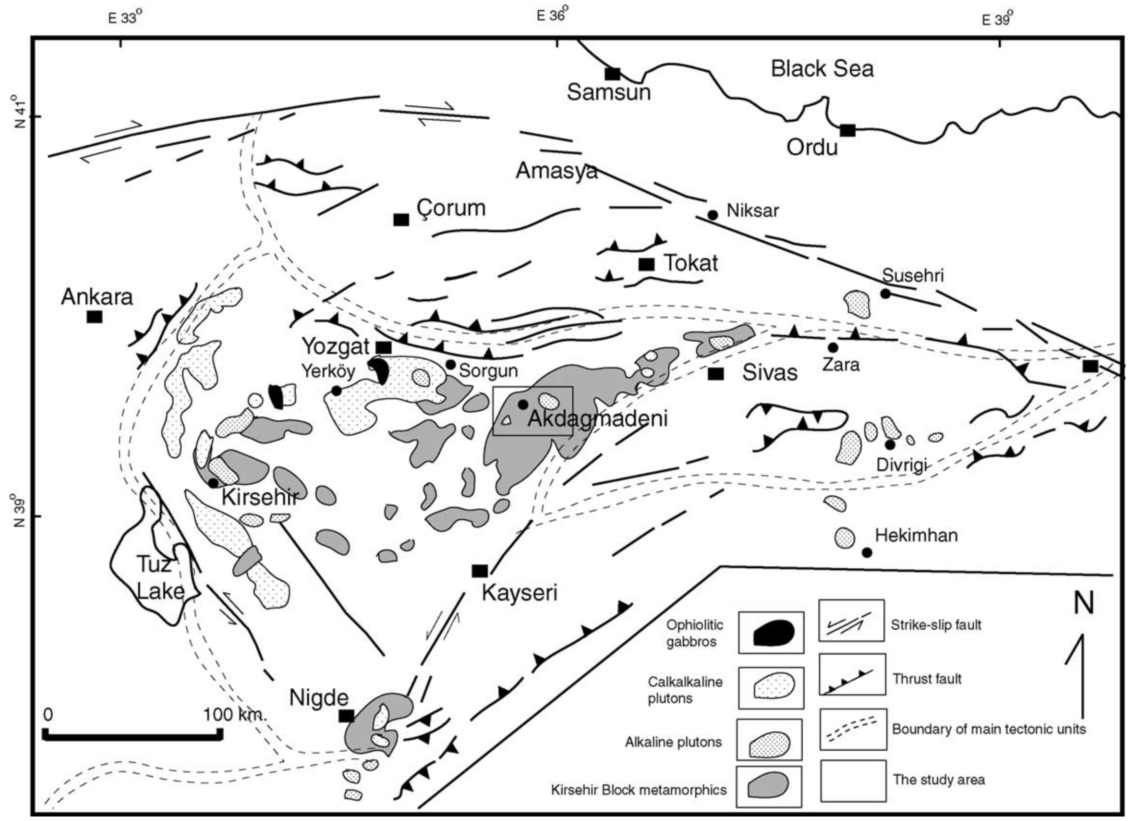

Fig. 1. Location map of the investigated area and geographic distribution of the metamorphic and plutonic rocks of Central Anatolia (after Boztug et al., 1997).

the fluorite deposits are generally granitoids and skarns. However, metamorphic and Tertiary sedimentary rock hosted deposits are also present (Seymen, 1984; Tülümen, 1980).

The studied fluorite deposits are located in and around the town of Akdagmadeni, in the Eastern part of the Kirsehir Massif. The Akdagmadeni (Yozgat) fluorite deposits occur in three different areas; the Tad Dere, which is situated 7 km SE, the Büyükçal Tepe, which is located 15 km NE, and the Akçakisla, which is located 20 km SW of Akdagmadeni Township (Fig. 2). The three studied deposits and associated granitoids occur along the axis of the Akdagmadeni Anticline. In addition to these three economic sized

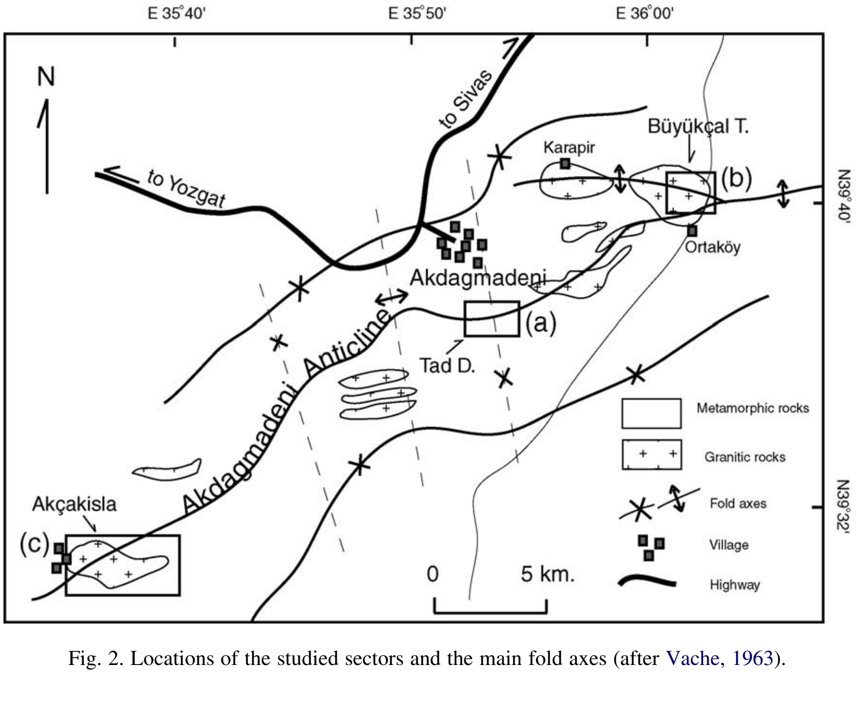

Fig. 2. Locations of the studied sectors and the main fold axes (after Vache, 1963).

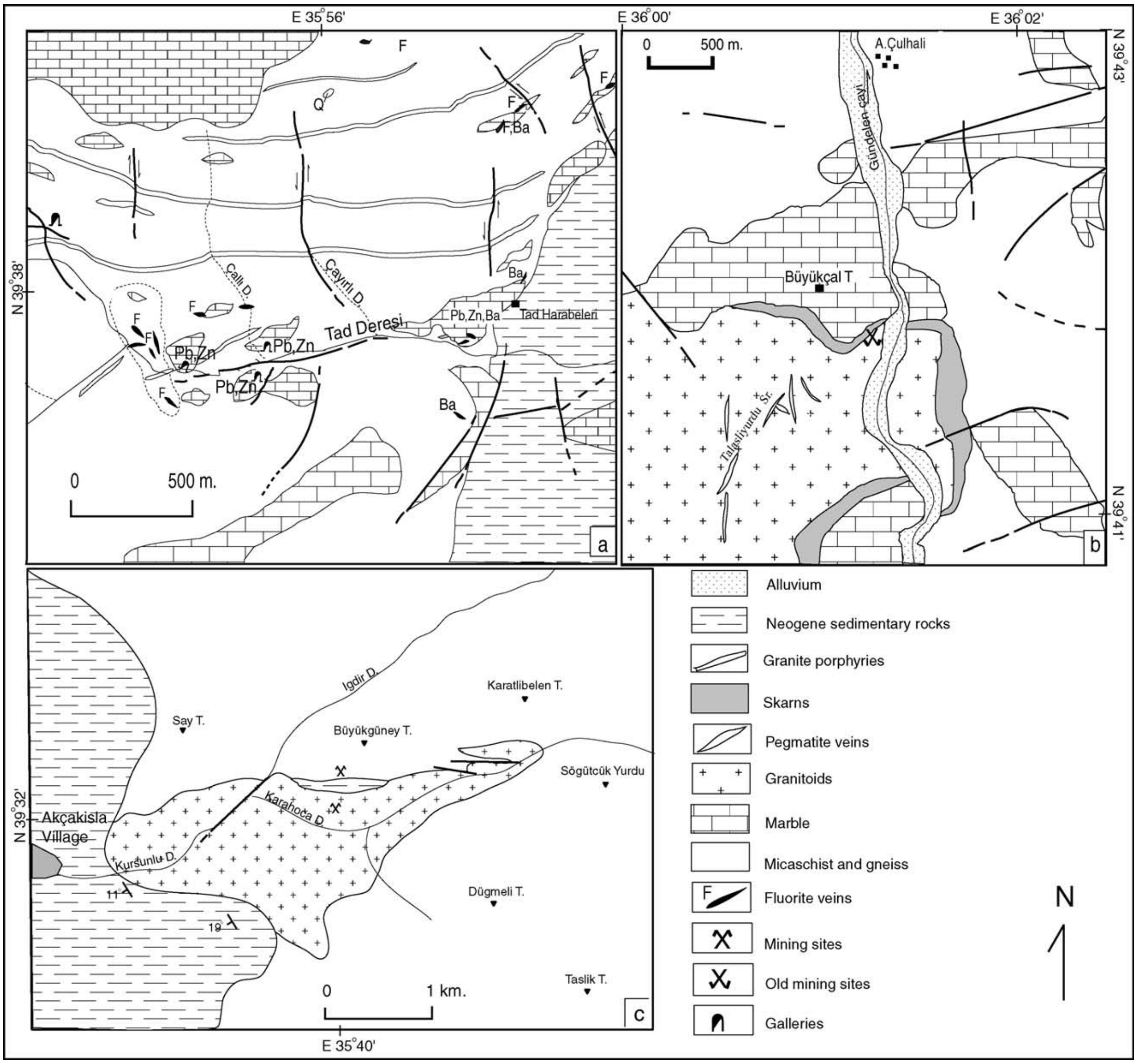

Fig. 3. Geologic map of the (a) Tad Dere (after Sasmaz and Ayaz, 1999), (b) the Büyükçal T., and (c) the Akçakisla (Sagiroglu, 1982) fluorite mineralization deposits.

deposits, many small size fluorite occurrences are also present in the Akdagmadeni area (Fig. 3). Previous studies in this area have been the subject of considerable geological, petrographical, and mineralogical research (Uçurum et al., 1997; Sagiroglu, 1982, 1984; Sasmaz and Ayaz, 1999).

This study deals with granitoid, skarn and metamorphic-hosted fluorite deposits of the Akdagmadeni area and its aim is to investigate geochemical features of the fluorite deposits and the effects of host rocks on these geochemical features. These features are correlated with known geochemical patterns of the fluorite deposits.

The emphasis is on the REE geochemistry that plays an important role in defining the physico-chemical conditions during fluorite deposition. Twenty-five representative samples were collected from the outcrops and analyzed for major-oxide trace elements by ICP-ES and REE by ICP-MS techniques at a commercial laboratory in Canada.

2. Geology

The studied area is mainly composed of Palaeozoic Akdag metamorphic rocks, Cenomanien granitoids, and Neogene sedimentary rocks (Fig. 3). Skarn formations are ubiquitous along the granitoid and metamorphic contacts. The metamorphic rocks, which are extensions of the so called the Kirsehir Massif, are composed of amphibolite, gneiss, quartz mica schist, calcschist, and marble. These rocks were metamorphosed under medium to upper amphibolite facies conditions; 5 kbar and less than 620 °C (Sagiroglu, 1982).

The granitoids outcrop mainly as two plutons in the Ortaköy and Karapir areas. Numerous apophyses in different sizes are scattered in the metamorphic rocks (Fig. 2). Granitoids include granite, quartz monzonite, quartz syenite, and syenite, and intrude metamorphic rocks (Fig. 3). The age of granitoids is interpreted as Upper Cretaceous and Eocene by Tülümen (1980) and Sagiroglu (1982), and Cenomanien by Göncüoglu (1986). In the Tad Dere region, fluorite veins occupy E–W strike-slip fault zones (Fig. 3a). The associated vein type sulphide bodies are composed of galena, sphalerite, pyrite, chalcopyrite and fahlore group of minerals. Skarn formations are absent in the Tad D. region. In the Büyükçal T. region, epidote-exoskarn formations occupy large areas and fluorite occurs as massive bodies or disseminated in the epidote skarn zones (Fig. 3b). In addition to fluorite, scheelite is present in this area while sulphides are absent. The Akçakisla pluton occupies an area of 5–6 km^2 and it is characterized as an alkaline granitoid (Figs. 2 and 3c). The fluorite concentrations occur in garnet-epidote skarns along the contact as massive lumps, and in the endo-skarns as fracture fillings. In this area, exo-skarns also contain rich concentrations of sphalerite, chalcopyrite, galena and pyrite. All the plutonic and subvolcanic rocks cut the Palaeozoic metamorphic series, which are dominated by gneiss, amphibolite, micaschist and marble. The skarn formations are widespread along the contacts of granitoid and metamorphic rocks. The Neogene sedimentary cover occupies large areas in the Tad Dere region and also SW of the Akçakisla pluton (Figs. 2 and 3c).

3. The REE geochemistry

Representative samples of the Tad D., Büyükçal T. and Akçakisla fluorite bodies were collected and crushed. Fluorites were separated by hand picking under a binocular microscope. Separated fractions were treated with 10% HCl and rinsed with distilled water. After drying at 25–30 °C, the concentrates were grounded. Twelve fluorite samples from the Tad Dere, eight from the Büyükçal Tepe and four from the Akçakisla were analyzed for major-oxide, trace-, and rare-earth elements by the ACME Analytical Lab (Canada). Major-oxide, fluoride and trace element contents were analyzed by ICP-ES (Table 1), while the REE contents (Table 2) were determined by ICP-MS. The Tad D. fluorites contain 35.7–41.5 wt% F, 54.8–58.6 wt% Ca, minor amounts of Fe, Al, Ba, K, and Na, and have intermediate REE contents, ranging from 20.6 to 48.5 ppm (average 36.0 ppm). On the other hand, fluorites from the Büyükçal Tepe contain 27.8–31.9 wt% F, 35–45 wt% Ca, and have higher REE values of 61.3–149.3 ppm (average 113 ppm). The Akçakisla fluorites have15.01–23.83% F, 25.25–41.81% Ca and their REE contents vary significantly: Three samples have similar total REE values: AK01; 287.1; AK02: 279.2 and AK04: 335.4 ppm, while sample AK03 has 4221 ppm REE. The high REE content was probably caused by the presence of an undetected REE phase. Major-element distributions show positive correlations in Si vs Al and negative correlations between Ca and F. Similar distributions are also observed in fluorites from the Çelikhan (Malatya) region, Eastern Turkey (Sasmaz et al., 1999). Such correlations indicate that the prevailing physico-chemical conditions during fluorite deposition prevented REE from entering the fluorite structure. The chondrite-normalized REE patterns of the studied fluorites exhibit trends similar to the normalized REE patterns of international magmatic standard rock samples and display a decrease from LREE towards HREE (Fig. 4a and b). Fleischer (1969) concludes that fluorites in pegmatitic hosts have higher HREE contents while these from alkalic rocks have higher LREE. In the studied fluorites, LREE contents are substantially higher than HREE and therefore an alkalic magmatic source is likely. High LREE contents also indicate early phases of mineralization (Möller et al., 1976; Ekambaram et al., 1986; Constantopoulos, 1988; Hill et al., 2000).

The chondrite-normalized REE patterns for the studied samples also show an increase in LREE, distinct negative Eu anomalies for Tad D. samples and detectable Eu positive anomalies for Büyükçal T. and Akçakisla fluorites (Fig. 4a). Eu and Ce anomalies can be useful indicators for the interpretation of fo_2, as well as the fluid temperature (Constantopoulos, 1988; Palmer and Williams-Jones, 1996; Williams-Jones et al., 2000). The strong negative Eu anomaly of Tad D. fluorite indicates low T and low fo_2 which are excepted based on the locations of these deposits relative to the pluton. Akçakisla and Büyükçal T. fluorites have positive Eu anomalies that are very rare according to Strong et al. (1984), Ekambaram et al. (1986), Constantopoulos (1988) and Gilder (1989). On the other hand, all the studied fluorites have negative Ce anomalies that may have resulted from the high fo_2 close to the plutons, and therefore should had high formation temperatures. Sagiroglu (1982, 1984) also claim formation temperatures of 390–430 °C for fluorites in the Akçakisla and epidote skarns. At such high temperatures, Eu is dominantly divalent (Hill et al., 2000) and therefore a strong negative Eu anomaly is expected in fluorites formed at high T conditions. On the other hand, Akçakisla and Büyükçal T. fluorites have positive Eu anomalies which can be explained by the alteration of feldspars (Ekambaram et al., 1986; Hill et al., 2000). In addition, positive Eu anomalies are accepted as probable indicators of precious metal deposition (Eppinger, 1988; Hill et al., 2000). However, neither Büyükçal T. nor Akçakisla display any other evidence of precious metals enrichment. The Tb/La–Tb/Ca ratios of fluorites indicate the degree of fractionation of the ore fluid from which they crystallized. These ratios can be used to classify the fluorites according to their conditions of formation (Möller et al., 1976; Möller and Morteani, 1983). The Tb/La ratios of the Akdagmadeni fluorites are quite low (0.002–0.0199), and show that they are the products of early stage crystallization as explained by Constantopoulos (1988). The Tad D.

Table 1
Major oxide, minor and trace element contents of the studied fluorites

	SiO_2%	Al_2O_3%	Fe_2O_3%	Na_2O%	K_2O%	Ca%	Ba	Sr	Zr	F%	Sc	Th	U	W	Zn	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	ΣREE	Eu/Eu*
TD61	1.61	0.19	3.92	0.09	0.11	52	37	734	23	46.2	0.4	1	13	5	735	9.4	12	6	0.6	0.2	0.18	0.30	0.04	28.7	0.65
TD62	2.3	0.26	2.7	0.12	0.16	50	177	844	48	46.2	0.5	5	12	7	40	19	16	3	0.8	0.4	0.11	0.70	0.11	40.1	0.55
TD63	2.87	0.1	0.8	0.08	0.05	54	10	661	8	48.4	0.2	0.4	8.5	4	50	8	7	5	0.6	0.2	0.15	0.30	0.03	21.3	0.75
TD64	2.09	0.14	1.4	0.09	0.06	49	213	650	18	50.6	0.2	1	9.6	7	75	15	14	5	0.6	0.2	0.09	0.40	0.06	35.4	0.62
TD65	3.08	0.14	1.07	0.06	0.08	49	25	694	64	48.4	0.2	0.4	7.2	3	67	13	13	4	0.6	0.2	0.14	0.30	0.02	31.3	0.48
TD66	2.03	0.13	0.61	0.09	0.07	55	88	682	12	50.6	0.3	0.8	7.8	3	50	16	16	9	0.7	0.2	0.09	0.40	0.06	42.5	0.67
TD67	2.04	0.12	0.79	0.08	0.05	45	49	657	14	44	0.3	0.5	1	3	82	15	17	6	0.8	0.3	0.14	0.60	0.10	39.9	0.52
TD68	5.15	0.15	0.6	0.08	0.05	47	51	689	7	46.2	0.3	0.7	2.9	5	152	16	21	10	0.6	0.2	0.11	0.50	0.07	48.5	0.49
TD69	3.52	0.31	2.4	0.08	0.1	51	8470	757	28	39.6	0.5	1.2	2.2	67	54	14	15	14	0.9	0.4	0.14	0.70	0.10	45.2	0.79
TD70	3.23	0.18	0.93	0.06	0.05	56	120	694	26	46.6	0.3	0.01	1.4	5	70	15	14	6	0.5	0.2	0.06	0.30	0.04	36.1	0.72
TD71	2.52	0.13	0.76	0.09	0.06	54	374	727	23	48.4	0.2	0.3	4.6	4	35	8.8	8	3	0.4	0.15	0.13	0.30	0.04	20.8	0.66
TD72	4.45	0.21	3.47	0.09	0.12	50	148	641	12	44	0.4	4.8	6.7	7	77	18	18	6	0.6	0.3	0.22	0.40	0.08	43.6	0.58
AK01	20.12	5.53	11.33	0.03	1.89	36.66	96	171	26	23.52	6	1.2	60	1649	11,029	82.1	129.4	37.3	6.3	4.83	0.69	2.51	0.35	293	1.8
AK02	12.93	4.82	21.91	0.04	2.63	30.55	179	43	38	20.58	5	1.1	141	691	379	77	121.3	40.1	7.5	2.13	0.93	2.72	0.36	280	1.15
AK03	11.68	4.19	28.2	0.03	1.43	25.25	15	63	20	15.01	4	1.7	102	2380	6573	1340	1772	449.1	89.8	44.5	15.61	58	7.5	4221	1.46
AK04	9.38	3.65	19.45	0.04	0.49	40.92	12	224	0.9	23.83	2	0.02	79	2254	120	93	154	48.9	7.5	1.94	0.77	1.89	0.25	335.4	1.22
BT51	12.4	3.25	6.25	0.05	0.1	42	50	225	22	31.2	0.8	0.8	46	24	3800	23	30	6	0.5	0.2	1.8	1.4	0.2	63.1	1.25
BT52	13.6	2.50	5.43	0.08	0.1	40	280	132	18	31.9	1	1	57	10	820	22	33	11	0.7	0.2	0.1	1.4	0.21	68.7	1.11
BT53	9.8	2.63	4.85	0.05	0.1	45	250	124	26	38.3	0.4	0.4	80	16	1700	64	59	10	0.3	0.4	0.4	1.2	0.18	135.4	1.35
BT54	11.3	2.24	5.23	0.02	0.1	35	50	255	16	28.6	1.5	1.5	62	22	30,000	56	70	3	1.2	0.2	0.2	0.1	0.05	132.8	0.9
BT55	10.5	1.96	4.75	0.04	0.1	42	50	180	25	28.3	1.3	1.3	84	13	82	54	77	15	1.2	0.1	0.1	1.6	0.24	149.3	0.95
BT56	9.6	2.28	6.54	0.08	0.1	42	50	210	17	27.8	1.3	1.3	85	13	81	54	75	15	1.2	0.1	0.1	1.7	0.25	147.7	0.75

Table 2
The REE contents of Akdagmadeni fluorites by ICP-MS techniques

Samp. No	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣNTE
TD.66	14	10	0.84	5	0.72	0.18	1.27	0.09	0.65	0.18	0.59	0.07	0.41	0.05	34.1
TD.67	17	16	1.28	7	1.17	0.26	1.78	0.14	1.02	0.26	0.8	0.11	0.66	0.07	47.6
TD.68	17	21	1.16	6	0.89	0.14	1.43	0.11	0.78	0.19	0.61	0.08	0.48	0.05	49.9
TD.69	15	14	0.94	5	1.16	0.35	1.96	0.14	2	0.24	0.71	0.12	0.66	0.08	42.4
TD.70	14	11	0.7	4	0.53	0.15	1.01	0.06	0.46	0.11	0.43	0.04	0.24	0.03	32.8
BT.06	26.2	36.8	3.4	3.6	0.2	0.1	0.2	0.2	0.5	0.2	0.5	0.1	0.7	0.1	72.8
BT.05	47.8	67.8	4.5	8.7	0.9	0.2	0.4	0.4	0.5	0.3	0.5	0.1	0.9	0.3	133.3
AK01	264	174	96	62	33	69	17	1.5	13	11	11.5	11.3	11.9	11.6	293
AK 02	248	163.5	97	67	39	30	22	1.98	17.5	14	13.1	12.6	12.9	12	280
AK04	300	208	120	82	39	28	20.5	1.63	14.2	10.5	9.9	9.3	9	8.3	4221
AK03	4332	2394	1316	784	473	630	330	3.31	346	287	290	292	276	250	335.4
Chondrites (Boynton, 1984)	0.31	0.74	0.12	0.6	0.19	0.07	0.26	0.47	0.32	0.07	0.21	0.03	0.21	0.03	

fluorites plot in the hydrothermal field, whereas fluorites from the Büyükçal T. plot mainly in the pegmatitic and partly in the hydrothermal fields, while the Akçakisla fluorites plot entirely in the pegmatitic fields (Fig. 5).

The $(Tb/Yb)_n$–$(La/Yb)_n$ ratios indicate the order of crystallization as suggested by Hill et al. (2000). In studied samples (Fig. 6), these two ratios are high and therefore these fluorites crystallized early and are LREE

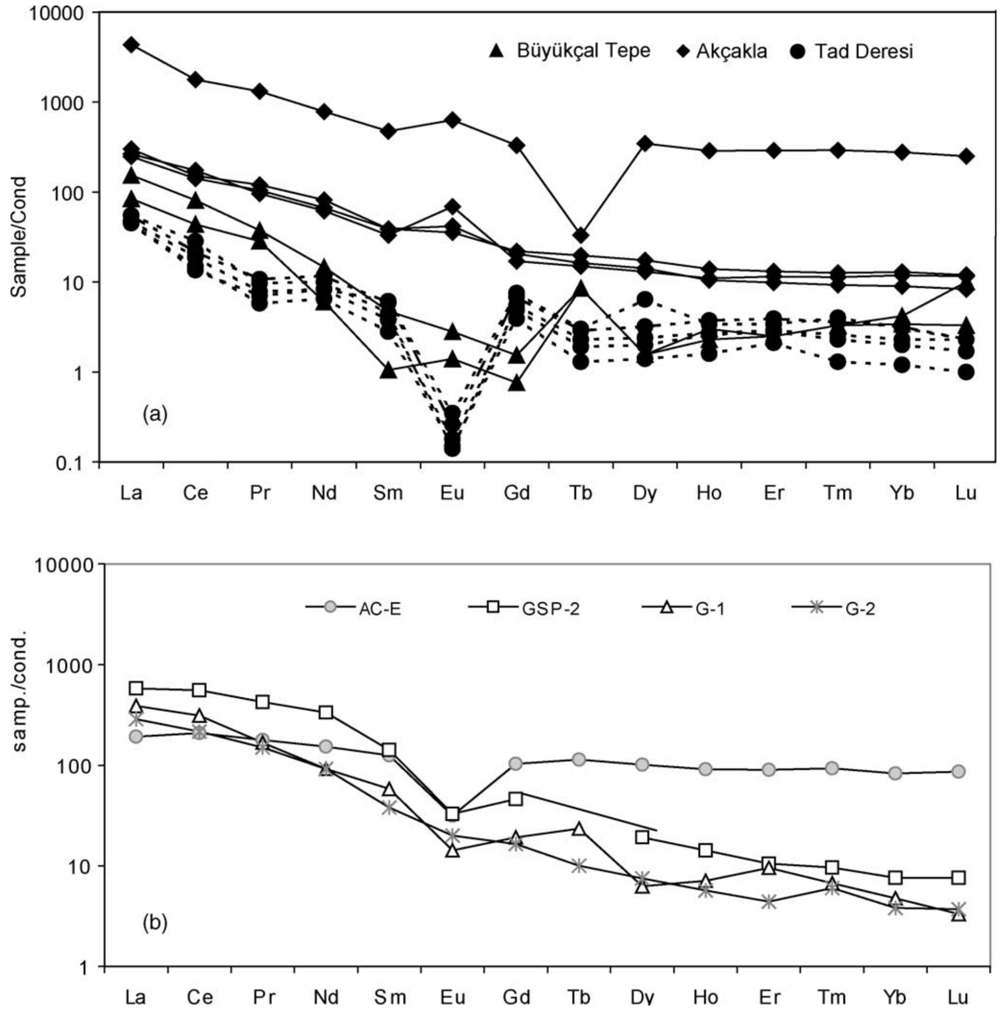

Fig. 4. (a) Chondrite-normalized (Boynton, 1984) REE patterns of the Tad D., the Büyükçal T. and the Akçakisla fluorites. (b) Chondrite-normalized (Boynton, 1984) REE patterns of international standard rock samples: G1, G2, GSP-2 (Flanagan, 1976), AC-E (Navarro et al., 2002). G1, G2, AC-E are granites, GSP-2 is a granodiorite.

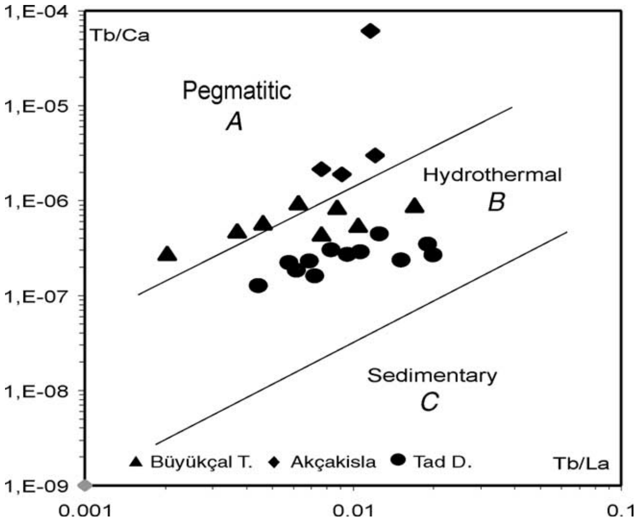

Fig. 5. Plot of Tb/Ca versus Tb/La in fluorites from the Akdagmadeni area. Trend *A* shows primary crystallization, trend *B* represents remobilisation of earlier-formed fluorite, and trend *C* represents the effect of interaction of original hydrothermal F-bearing fluids with limestone wall rocks. Trends are taken from O'Connor et al. (1993)

rich. $(La/Yb)_n-(Eu/Eu^*)_n$ plots of the studied fluorite also indicate LREE enrichment and positive to negative Eu anomalies (Fig. 7). The Sc/Eu vs Sr diagram demonstrates that the studied fluorites plot in three distinct areas and the fluorites of the Tad D. are Sr rich which is expected from its location (Fig. 8). Similarly, the $Sr-(Eu/Eu^*)_n$ diagram indicates that Sr contents increase with increasing distance

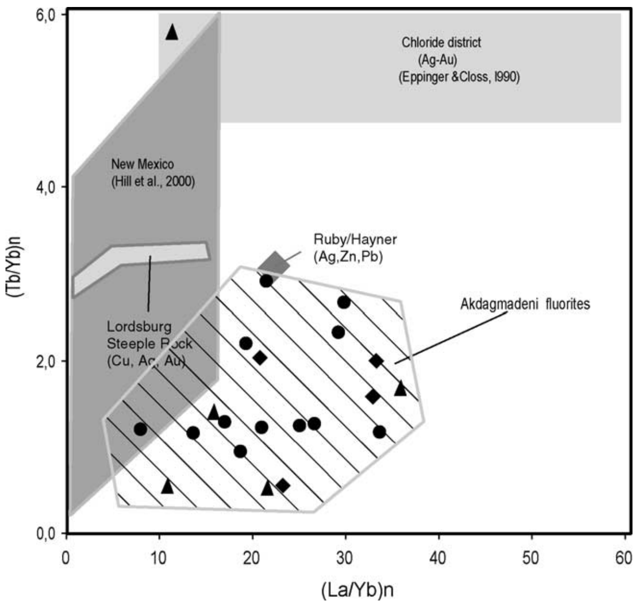

Fig. 6. $(Tb/Yb)_n$ ratio versus $(La/Yb)_n$ ratio of the studied fluorites. All values are normalized to chondritic meteorites, denoted by subscripted 'n'. The range data (Eppinger, 1988) for fluorite associated with precious metals veins in the Chloride district is shown. Fluorite associated with Cu–Ag–Au mineralization in the Lordsburg and Steeple Rock districts clusters within a narrow field. Fluorite from the Ruby Hayner deposits plots on the trend defined by these Au bearing deposits. The studied fluorites are characterized by low Tb/Yb ratios.

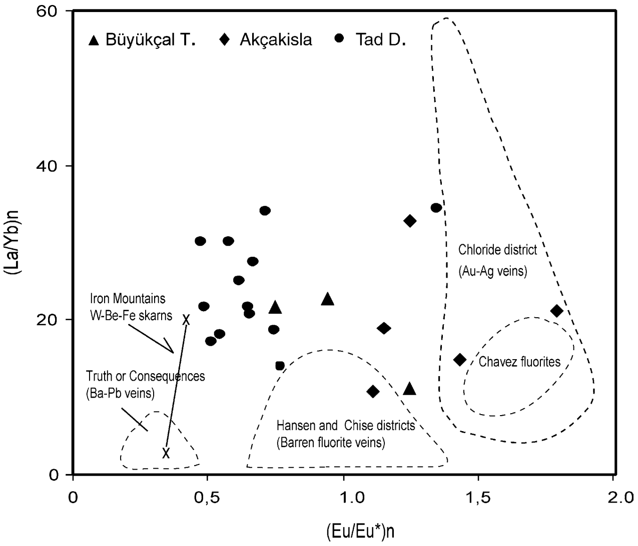

Fig. 7. Chondrite-normalized of $(La/Yb)_n$ versus $(Eu/Eu^*)_n$ diagram showing the distribution of samples.

from the plutonic contact, while Eu anomalies change from negative to positive (Fig. 9). The Sc contents of the Tad D. fluorites are similar to Rift Deposits of New Mexico. Those of the Büyükçal and Akçakisla have slightly higher values (Fig. 10).

4. Fluid inclusion data

Fluid inclusion studies of Uçurum et al. (1997) indicate formation temperatures of 156–185 °C for Tad D. fluorites. The same study also estimates the formation depth at 2–3 km based on 500–800 bars of pressure projected in the *T/P* diagram of Roedder (1984). The salinity range was found as 12–23% NaCl equivalents (Uçurum et al., 1997).

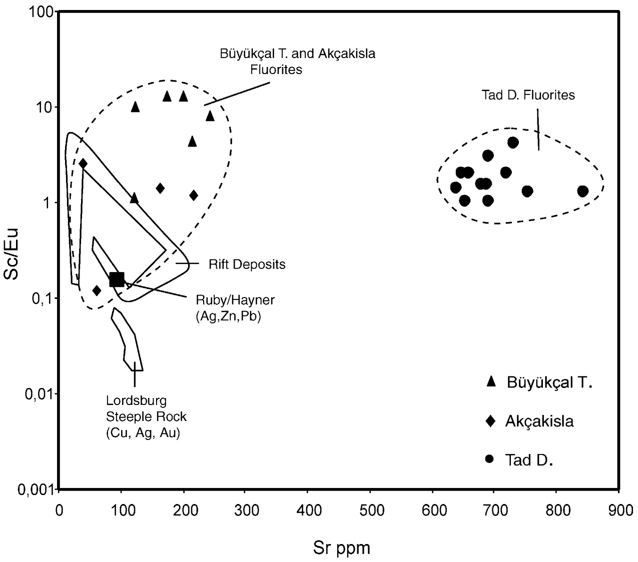

Fig. 8. Sc/Eu ratios versus Sr contents. Note the generally high and very high Sr contents of the Tad Deresi.

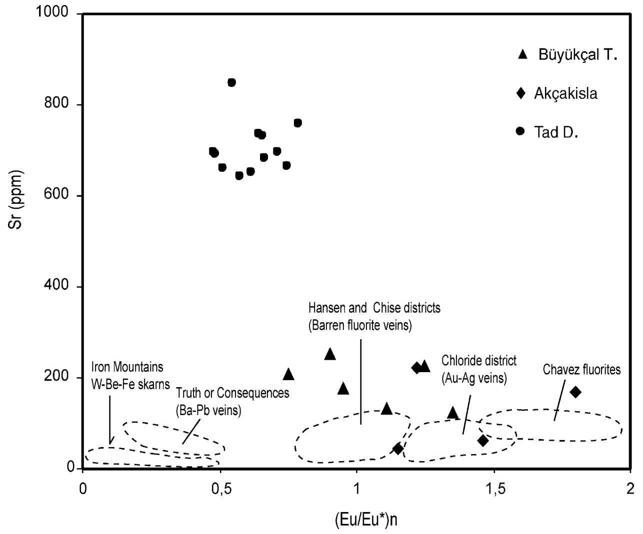

Fig. 9. Sr versus $(Eu/Eu^*)_n$ diagram. Due to their high Sr contents, the studied fluorites differ from the fluorite deposits described in the literature.

Sagiroglu (1982, 1984) studied fluid inclusions in different mineral assemblages from the Akdagmadeni and Akçakisla regions and correlated the estimates based on fluid inclusion data with the geothermometry and geobarometry findings based on mineral geochemistry. According to Sagiroglu (1982, 1984), fluorites were deposited in the epidote–chlorite–sulphides stage of contact metasomatism and fluid inclusions of this stage (the inclusions in the fluorites as well) had homogenization temperatures (T_H) ranging between 390 and 430 °C, salinity of 8–12 wt% NaCl equivalent and pressure of 500 bars. However, Sagiroglu (1982) also notes that most of his studied samples contained crowded daughter minerals which minimized the apparent pressure of formation. The salinity of the Tad D. varies between 12 and 23 wt% NaCl equivalents, which indicate

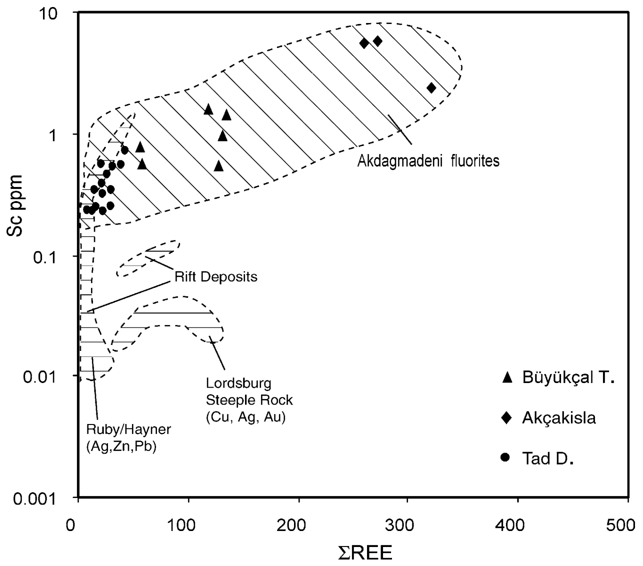

Fig. 10. Sc versus the sum of analysed REE. Pluton-hosted fluorite tends to have the highest total REE abundance while the Tad D. has the lowest.

an inhomogeneous source for hydrothermal fluids. No fluid inclusion data are present for Büyükçal T., but taking into account that these fluorites are hosted by epidote skarns fluid, inclusion data similar to those of Akçakisla can be expected. The fluid inclusion data is correlated with the data of previous workers (Fig. 11) and, as can be seen only the Tad D. fluorites, plot in the area of previous data Pb–Zn–Ag deposits. The associated sulphide mineralization in the Tad D. region is also argentiferous Pb–Zn mineralization.

5. Discussion

The REE patterns of the fluorites from Tad D., Büyükçal T. and Akçakisla are investigated in order to establish characteristic REE patterns for these three different areas. REE geochemistry is a powerful tool in hydrothermal mineralization studies and is widely used in order to understand the genesis of fluorites developed in different geological environments (Grappin et al., 1979; Ronchi et al., 1993, 1995; Sasmaz and Ayaz, 1999; Sasmaz and Çelebi, 1999).

Akçakisla fluorites have total REE contents ranging from 243 to 4200 ppm, those of Büyükçal T. 60–145 ppm and Tad D. 17–46 ppm. Many workers suggest that the total REE contents of fluorites decrease with increasing distance from the magmatic source (Eppinger and Closs, 1990; Ronchi et al., 1995; Hill et al., 2000). This is an expected trend as the granite was apparently the sole source of mineralizing fluids, and the fluids gradually lost heat, pressure and acidity away from the pluton while REE were fractionated. The REE contents of studied ores are in accordance with these conclusions, and the Tad D. fluorites formed far from the plutonic bodies within this context, the fluorites exhibit the features of hydrothermal origin. The Büyükçal T. and the Akçakisla fluorites are associated with epidote-bearing skarns, with formation temperatures estimated between 390 and 430 °C by Sagiroglu (1982, 1984), and have high REE contents. The very high REE contents of the Akçakisla fluorites suggest a pegmatitic source (Fig. 5). The variable REE patterns of fluorites, even within the same deposit, are very common.

The total REE values decrease to 20 ppm in light color fluorites and increase up to 50 ppm in dark fluorites (Ronchi et al., 1995). All of the studied fluorites, except for some of the Tad D. fluorites are dark. The total LREE contents are significantly higher than total HREE contents and may be attributed to an alkali granite source (Hill et al., 2000).

Previous studies on these fluorites showed that the granitoids were the only source for mineralizing fluids. This discrimination is also displayed in chondrite normalized REE patterns (Boynton, 1984) (Fig. 4a). The normalized patterns also exhibit strong negative Eu anomalies for Tad D. fluorites, weak positive Eu anomalies for Büyükçal T. and distinct positive Eu anomalies for Akçakisla fluorites. These indicate low

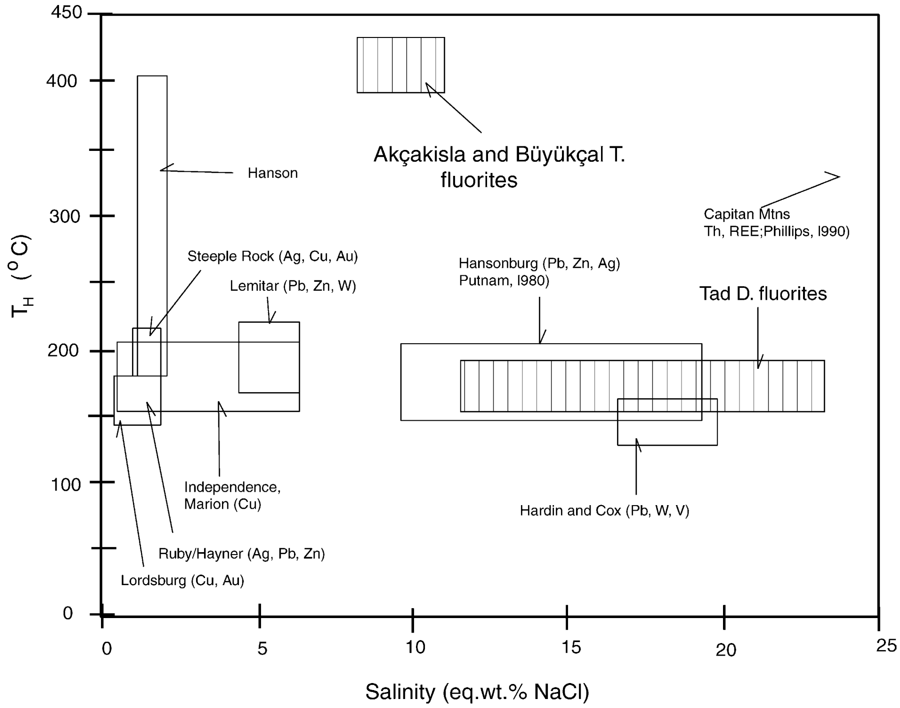

Fig. 11. T_H (°C)—salinity diagram of the studied fluorites compared with fluorite deposits in the Rio Grande Rift and neighbouring areas. The Akçakisla and the Büyükçal T. fluorites plot within a specific area while those of the Tad D. overlap with Hansonburg Pb, Zn, Ag deposits.

temperature–low fo_2 conditions for Tad D., high T and low fo_2 for Büyükçal T., and very high T for Akçakisla fluorites (Constantopoulos, 1988; Palmer and Williams-Jones, 1996; Hill et al., 2000). The following data from previous studies also support these conclusions; Sagiroglu (1982, 1984) estimates temperatures of 390–430 °C for sulphide mineralization and epidote skarn formation for Akçakisla and Karapir. He also states that the Akçakisla ores formed within endoskarn and granite and display evidence of high formation temperatures such as the presence of opaque sphalerite, abundant chalcopyrite and skarn minerals of spinel and olivine.

A positive Eu anomaly is an indicator of precious metal mineralization (Constantopoulos, 1988) and, therefore, the precious metal contents of the Akçakisla sector need to be investigated. All the studied fluorites have weak Ce anomalies, which is an indicator of high fo_2. Total Sc-REE diagram shows (Fig. 10) that all the studied fluorites generally have high total REE and Sc contents, but the Tad D. has the lowest and Akçakisla has the highest Sc values. According to Hill et al. (2000), low salinity precious metal mineralizations contain fluorite with low Sc concentrations. In this respect, Akçakisla fluorites contradict these findings based on Eu anomalies since they contain high amounts of Sc.

All the studied fluorite samples contain very high amounts (up to 844 ppm) of Sr. This is probably due to a high degree of fractionation alkali magmas, which are the source of mineralizing fluids. Because of the very high Sr contents, Sr-related ratios of Akdagmadeni rarely overlap those of other deposits. The Akçakisla and Büyükçal T. fluorites have ratios similar to the Rift and Ruby/Hayner deposits (Hill et al., 2000) located in the Rio Grande rift. The Sr–$(Eu/Eu^*)_n$ ratios of Akdagmadeni fluorites differ from those of the Iron Mountain skarn and Truth Ba–Pb veins (Eppinger and Closs, 1990) in the Rio Grande rift, and partly coincide with the ratios of fluorites in the vicinity of the rift (Figs. 8 and 9). The $(Tb/Yb)_n$ versus $(La/Yb)_n$ ratios characteristically cluster around low $(Tb/Yb)_n$ values (Fig. 6). Exceptionally low values of Tb may be indicative of the contact and contact related fluorites.

These findings, as a whole, indicate that the Tad D. fluorites formed at low temperatures (Uçurum et al., 1997) and low fo_2 during early emplacement of hydrothermal solutions into the fracture zones. On the other hand, fluorites from the Büyükçal T. and the Akçakisla formed from pegmatitic solutions at high temperatures (Sagiroglu, 1982, 1984) and high fo_2 along the contacts of granitoid and metamorphic rocks.

The Tb/La ratios indicate that the Tad D., some of the Büyükçal T., and the Akçakisla fluorites crystallized from the least fractionated fluid. In the other words, they are early crystallized fluorites (Möller et al., 1976; Möller and Morteani, 1983). This is supported by the abundant LREE contents. However, samples from three areas display fractionation trends where Tb/La ratios increases with increasing Tb/Ca values. Based on the relative positions of fluorite on the Tb/La–Tb/Ca diagram (Möller et al., 1976; Möller and Morteani, 1983) (Fig. 5), the Tad D. ores apparently crystallized from primary F-bearing solutions. The chemical compositions of epidote skarn hosted fluorites from the Büyükçal T. represent primary crystallization and remobilization trends.

The $(La/Yb)_n$–$(Eu/Eu^*)_n$ ratios of the studied fluorites do not match those from the Rio Grande rift and neighboring areas (Fig. 7). Only two samples of Akçakisla fluorites plot in the Chloride District field where Au–Ag veins are present. This may be taken as further evidence of the precious metal potential of Akçakisla. This potential is also indicated by the low salinity of mineralizing fluids of Akçakisla (Fig. 11).

Fluorite samples on $(Tb/Yb)_n$ vs $(La/Yb)_n$ diagrams show a positive correlation with moderate to high $(La/Yb)_n$–$(Tb/Yb)_n$ ratios (Möller et al., 1976; Eppinger, 1988; Eppinger and Closs, 1990; Hill et al., 2000)(Fig. 6). This suggests that early crystallized fluorites from the Akdagmadeni area were preferentially enriched in LREE relative to HREE. The moderate to high $(La/Yb)_n$–$(Tb/Yb)_n$ ratios also indicate that fluorites associated with the Akdagmadeni Pb–Zn–Ag metals were deposited from relatively early F-bearing hydrothermal fluids. The homogenisation temperatures (T_H) ranged from 156 to 185 °C with corresponding salinities between 12 and 23 wt% NaCl for the Tad D. ores.

6. Conclusions

The fluorite concentrations of the Akdagmadeni area occur in different modes; (1) veins in metamorphic rocks in the vicinity of alkali granite intrusions, (2) epidote-exoskarn hosted, variously shaped concentrations along metamorphic-intrusive contacts, (3) veins and lumps along the marginal zones of granitic plutons. The studied deposits from the Tad D., Büyükçal T., and Akçakisla areas represent these three different types of mineralization, respectively.

In all three deposits, the source of mineralizing fluids was highly fractionated alkali granitoids as indicated by high Sr contents. The REE diagrams show that all the studied fluorites formed from the least fractionated, early stage fluids. The fluorite minerals are contact related. Total REE contents decrease with increasing distance from the granitic bodies.

The physico-chemical conditions prevailing during mineralization are estimated as:

1. Low T (negative Eu anomaly, fluid inclusion data), low fo_2 (negative Eu anomalies) for Tad D. fluorites.
2. Moderate–High T and high fo_2 (both based on positive Eu anomalies) for Büyükçal T. deposits.
3. Very high T (positive Eu anomalies, fluid inclusion data) and very high fo_2 (distinct positive Eu anomalies) for Akçakisla deposits.
4. In comparison with the other fluorite deposits, Akdagmadeni deposits were formed under higher fo_2 conditions.

These differences are reflected in normalized REE patterns and other REE diagrams. It is possible to categorize the studied deposits as Tad D. deposits (hydrothermal), Büyükçal T. fluorites (hydrothermal-pegmatitic) and Akçakisla deposits (pegmatitic).

Comparisons of the studied samples with other deposits indicate that the Tad D. deposits are similar to fluorite bearing Pb–Zn–Ag (Mexico, Rift Valley Deposits) and Pb–W–V (Hardin and Cox deposits) deposits. In the Tad D. area, fluorite bodies are closely related to argentiferous Pb–Zn ores.

Akçakisla deposits display many aspects (low salinity fluids, positive Eu anomalies, high Sc values, $(La/Yb)_n$–$(Eu/Eu^*)_n$ ratios) indicative of precious metal enrichment.

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